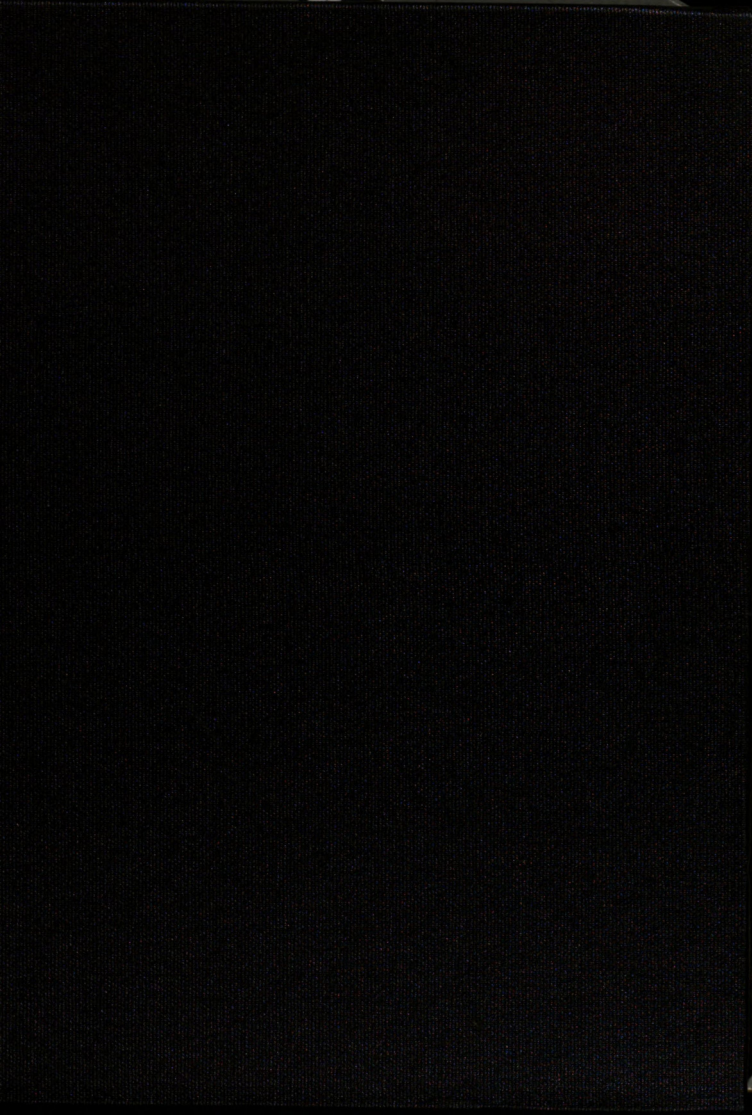




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**CYANIDE AND NITRILE COMPOUNDS WITH APPLICATIONS
IN MATERIALS AND CLUSTER CHEMISTRY**

By

Paul S. Szalay, Jr.

AN ABSTRACT OF A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Chemistry

2001

Professor Kim R. Dunbar

ABSTRACT

CYANIDE AND NITRILE COMPOUNDS WITH APPLICATIONS IN MATERIALS AND CLUSTER CHEMISTRY

By

Paul S. Szalay, Jr.

Novel transition metal cyanide and nitrile compounds are targeted as building blocks for the synthesis of clusters or materials that might exhibit interesting magnetic properties. The reaction of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$ produces $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ the first example of an edge-sharing bioctahedral compound of Mo(II) and only the third example of a structurally characterized metal-metal bonded compound with terminal cyanide ligands. Investigations of the electrochemistry of $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ led to the isolation of the one and two electron oxidation products $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^-$ and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$. A series of transition metal compounds were prepared with the facial capping ligand 1-(hydro)trispyrazolylborate and three acetonitrile or cyanide ligands. The facial arrangement of the dangling cyanides and acetonitrile leaving groups in these compounds were designed to allow for the formation of molecular

cubes. Displacement of the acetonitrile leaving groups by nitrogens of the cyanides could result in closure and formation of heterobimetallic cubic clusters and reactions to this end were investigated. The aromatic molecule, hexazatriphenylene-hexacarbonitrile (HAT-(CN)₆), with trigonally disposed chelating sites was explored as an alternative to cyanide as a linking group for paramagnetic transition metal ions. Convenient chemical reduction routes to [HAT-(CN)₆]^{•-} and [HAT-(CN)₆]²⁻ have been demonstrated. The transition metals Co and Zn can be used as reducing agents, but in these cases complexation of the metal with the reduced HAT-(CN)₆ species occurs to yield the soluble paramagnetic complexes M[HAT-(CN)₆]₂ (M = Co, Zn). Computational and EPR spectroscopic studies indicate [HAT-(CN)₆]²⁻ has a triplet ground state electronic configuration.

To my wife Shelley and my son Carter.

ACKNOWLEDGMENTS

This work would not have been possible without the assistance and support of many people. First and foremost, I have to thank my advisor Professor Kim R. Dunbar. I will always appreciate her patience, support, guidance, and enthusiasm. From her example, I have learned much about professionalism and what it means to be a scientist, teacher, and mentor. My thanks goes out to the members of my guidance committee, Professors Mitch Smith, Rob Maleczka, and Gary Blanchard for the advice they offered during the course of my studies. I would also like to thank Professors Aaron Odom and Joan Broderick for the generous use of their laboratory facilities. My appreciation goes out to Professor Ned Jackson for his assistance in overcoming some of the computational chemistry challenges that arose during my research efforts. I am grateful for the help and advice with EPR spectroscopy provided by Dr. Andrew Ichimura. My thanks go out to Dr. Donald Ward for his X-ray crystallography tutorials and help with some difficult structures. I would like to thank all of the members of the Dunbar group, with whom I had the opportunity to work. Their friendship helped make my time at Michigan State as enjoyable as it was fulfilling. A special thanks goes out to Matt Prater for his knowledge and patience in answering so many of my questions during the early stages of my graduate career and

Jennifer Smith, my partner in the development of some of the work presented in this dissertation. My appreciation goes out to Dr. Rodolphe Clérac for his assistance and advice with my studies of magnetism, Dr. Jitendra Bera for his aid with my computational studies, and Dr. J.R. Galán-Mascarós for many helpful discussions. I would like to thank Bill Scanlon, Pete LeBaron, Randy Hicks, and Jim Ciszewski for the friendship that was so helpful through some of the more difficult times as well as all the discussions of their research, which helped me develop a more broad understanding and appreciation of science. I would also like to acknowledge the support provided by the Department of Chemistry at Michigan State University and the Carl H. Brubaker Endowed Fellowship.

I would like to thank my parents for giving me the freedom to choose my path and the means to pursue my dreams. It is largely through their sacrifices that I was able to reach this point. My appreciation goes out to my brothers and sisters for their love, support, and encouragement.

My thanks go out to my in-laws for the get-away weekends and help taking care of my son when I needed time for my studies. Finally, a special thanks to my wife Shelley for her support, encouragement, boundless patience, and all the sacrifices she made in helping me achieve my goals.

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LIST OF SYMBOLS AND ABBREVIATIONS

Å	Angstrom
Ag/AgCl	silver-silver chloride reference
B.M.	Bohr magneton
br	broad
<i>n</i> -Bu	<i>n</i> -butyl
<i>ca.</i>	about
CH ₃ CN	acetonitrile
cm	centimeter
cm ⁻¹	wavenumber
CN	cyanide
CV	cyclic voltammetry
°C	degree centigrade
δ	parts per million (ppm)
dmpe	dimethylphosphinoethane
dppm	diphenylphosphinomethane
ε	molar extinction coefficient
E _{p,a}	anodic peak potential
E _{p,c}	cathodic peak potential

emu	electromagnetic unit
EPR	electron paramagnetic resonance
ESBO	edge-sharing bioctahedral
esd	estimated standard deviation
Et	ethyl
FAB	Fast Atom Bombardment
g	gram
G	Gauss
h	hour
H.S.	high spin
HAT-(CN) ₆	hexazatriphenylene-hexacarbonitrile
Hz	Hertz
IR	infrared
K	Kelvin
L	liter
L.S.	low spin
λ	wavelength
m	medium
M	moles per liter
Me	methyl

mg	milligram
min.	minute
mL	milliliter
mm	millimeter
mmol	millimole
mult	multiplet
μ	bridging ligand
nm	nanometer
ν	frequency, stretching
NMR	nuclear magnetic resonance
ox	oxidation
red	reduction
r. t.	room temperature
s	singlet (NMR), strong (IR)
sh	shoulder (UV-vis), sharp (IR)
SQUID	Superconducting Quantum Interference Device
T	temperature
Tp	1-(hydro)trispyrazolborate
THF	tetrahydrofuran
UV	ultraviolet

vs

versus, very strong

w

weak

LIST OF PRELIMINARY PRODUCT INVESTIGATIONS

- (1)-----Product of $W_2(O_2CC_6H_5)_4$ and $[Et_4N][CN]$ in THF
- (2)-----Product of $W_2(O_2CC_6H_5)_4$ and $[Et_4N][CN]$ in CH_2Cl_2
- (4)-----Product of $Re_2(O_2CCH_3)_4Cl_2$ and $[n-Bu_4N][CN]$
- (5)-----Product of $Os_2(O_2CCH_3)_4Cl_2$ and $[n-Et_4N][CN]$
- (6)-----Product of $Os_2(O_2CCH_3)_4Cl_2$ and $[n-Bu_4N][CN]$
- (7)-----Product of $Mo_2(O_2CCH_3)_4$ and $(CH_3)_3SiCN$

LIST OF COMPOUNDS

- (3)-----[Et₄N]₂[Re₂(CN)₈]
- (8)-----[*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂]
- (9)-----[Et₄N]₂[Mo₂(CN)₆(dppm)₂]
- (10)-----[*n*-Bu₄N][Mo₂(CN)₆(dppm)₂]
- (11)-----Mo₂(CN)₆(dppm)₂
- (12)-----Ni(en)₂Mo₂(CN)₆(dppm)₂
- (13)-----Na[(Tp)CrCl₃]
- (14)-----K[(Tp)CrCl₃]
- (15)----- (Tp)MoBr₂(THF)
- (16)-----[(Tp)Mn(CH₃CN)₃][PF₆]
- (17)-----[(Tp)Co(CH₃CN)₃][PF₆]
- (18)-----[(Tp)Mo(CH₃CN)₃][PF₆]₂
- (19)-----[(Tp)V(CH₃CN)₃][PF₆]₂
- (20)-----K[(Tp)Cr(CN)₃]
- (5.0)-----*trans*-[Ni(CH₃CN)₂(en)₂][PF₆]₂
- (22)----- (Tp)CrCl₂(CH₃CN)•AgPF₆•2 CH₃CN
- (23)----- (Tp)CrCl₂(CH₃CN)•TiPF₆•2 CH₃CN
- (24)-----V(Tp)₂•1/3CH₃CN•1/6Et₂O
- (25)-----HAT-(CN)₆

- (26)-----HAT-(CN)₆•C₇H₈•CH₃CN
- (27)-----Co(HAT(CN)₄O₂)(H₂O)₄.4H₂O
- (28)-----Mn(HAT(CN)₄O₂)(H₂O)₄.4H₂O
- (29)-----Ni(HAT(CN)₄O₂)(H₂O)₄.4H₂O
- (30)-----{(Cp₂Fe)₃[hat(CN)₆]}•CH₃CN
- (31)-----{[(Cp)₂Co][PF₆]}₃HAT-(CN)₆
- (32)-----{([*n*-Bu₄N][I])₃[I][HAT-(CN)₆]₂}•3C₆H₆
- (33)-----[CoCp₂][HAT-(CN)₆]
- (34)-----[CoCp₂]₂[HAT-(CN)₆]
- (35)-----Co[HAT-(CN)₆]₂
- (36)-----Zn[HAT-(CN)₆]₂

Chapter I
Introduction

A. Transition metal cyanide compounds in solid state and cluster chemistry

The use of transition metal precursors as building blocks for the preparation of extended structures allows for impressive structural diversity and opens up a wealth of potential applications for porous¹, magnetic², and conducting³ solids. Transition metal cyanides constitute a class of compounds that have been significantly involved in the development of this area in recent years.⁴

Cyanide has a rich history in coordination chemistry.^{4,5} Nearly all of the d-block metals are known to form cyano complexes in which cyanide has been observed to adopt numerous different binding modes (Figure 1.1). Homoleptic and mixed ligand cyanide complexes with a wide range of oxidation states and coordination numbers ranging from two to eight are known. The bidentate, linear nature of cyanide gives rise to extended structures with 1D, 2D, and 3D motifs, the exact nature of which depends on the coordination number and arrangement of ligands around the metal centers. The distances spanned by the group defined by M-CN-M', are typically in the range of 5.0-5.6 Å, which is sufficiently long to allow for the formation of cavities in these polymeric structures. Metal cyanide materials with void spaces that trap interstitial solvent molecules are termed clathrates,

these are often referred to as inclusion compounds. Prominent examples (Figure 1.2) of transition metal cyanide clathrates are the Hofmann-type compounds of the general formula $M(NH_3)_2M'(CN)_4$ where M' is square planar and modified Hofmann-type compounds involving replacement of the monodentate ammonia ligands with other ligands or substitution of the square planar metal $M'(CN)_4$ unit with a tetrahedral $M'(CN)_4$ group.⁵

In addition to forming interesting extended structures with inclusion capabilities, the ability of cyanide to communicate magnetic information between paramagnetic metal centers is a topic of much interest.^{4,5} The classic example of this application is the $Fe^{III}[Fe^{II}(CN)_6] \cdot xH_2O$ material called Prussian Blue (PB) (Figure 1.3), which precipitates as a dark blue solid from the condensation reaction of $K_4[Fe(CN)_6]$ and $[Fe(H_2O)_6][NO_3]_3$. The Fe^{III} and Fe^{II} centers form a nearly perfect cubic lattice linked by cyanide wherein Fe^{II} is ligated by the strong field carbon and Fe^{III} is coordinated to the weak field nitrogen end of cyanide. Despite the separation of the paramagnetic Fe^{III} centers by the diamagnetic Fe^{II} centers, PB exhibits ferromagnetic coupling with a Curie temperature (T_c) of 5.5K.

The Prussian Blue (PB) family of compounds has expanded in recent years as researchers pursue high T_c ferromagnetic materials (Table 1.1).⁴ In

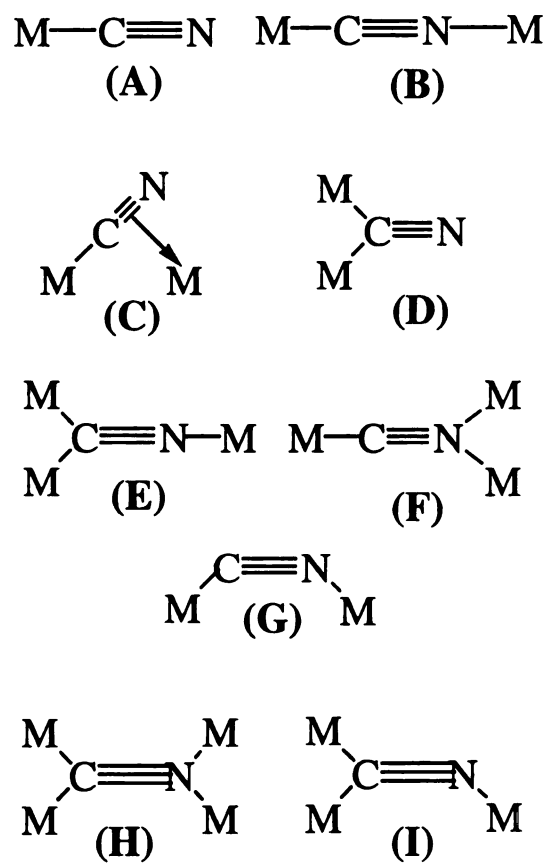
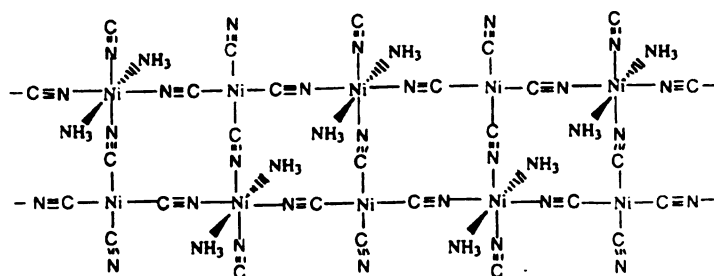
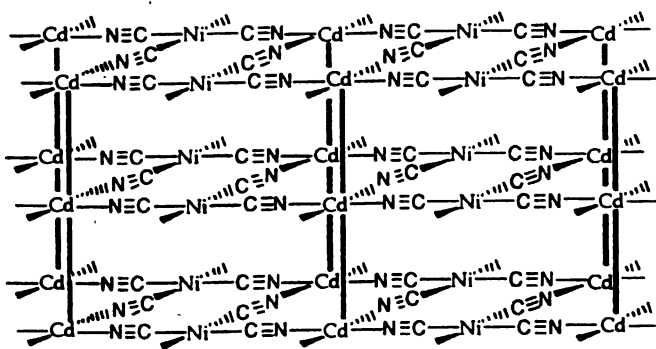


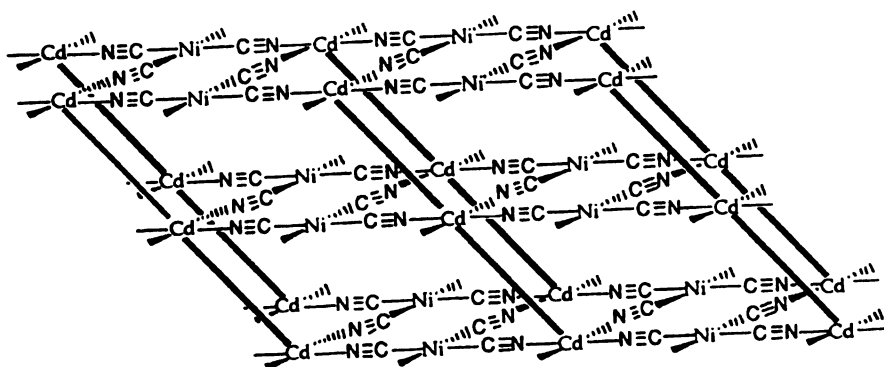
Figure 1.1. Coordination modes of the cyanide ion.



Hofmann 2-D motif with square planar $\text{Ni}^{\text{II}}(\text{CN})_4$ and octahedral $\text{Ni}^{\text{II}}(\text{NH}_3)_2(\text{NC})_2$ units

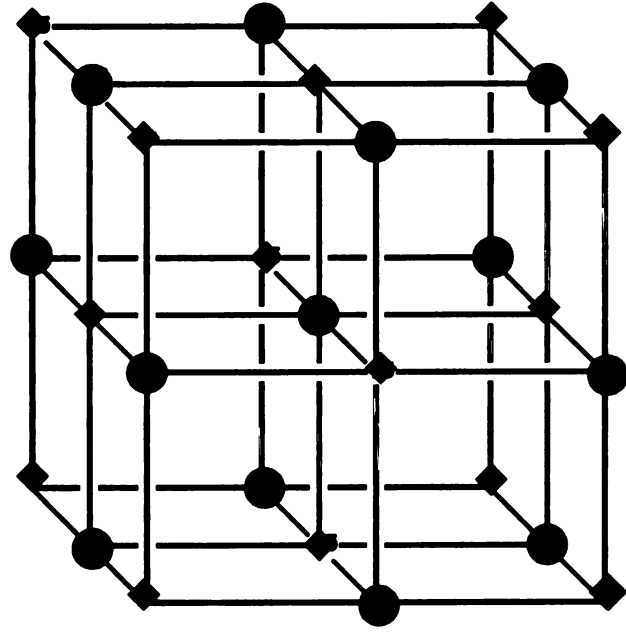


Vertical pillaring of the Hofmann 2-D motif with bidentate amines depicted as solid, bold lines



Slanted pillaring of the Hofmann 2-D motif with bidentate amines depicted as solid, bold lines

Figure 1.2. Representations of Hofmann-type compounds



Face-Centered Cubic Three-Dimensional Solids

- - Fe(II) (C_6 coordination)
- ◆ - Fe(III) (N_6 coordination)

Figure 1.3. Three dimensional cubic structure of an idealized Prussian Blue (PB) compound.
For PB, $M = Fe^{II}$ and $M' = Fe^{III}$. Replacing one or both of the Fe sites in PB with paramagnetic metal ions has given rise to the PB family of compounds.

Table 1.1. Prussian blue and PB analogues with their T_c values.

Compound	T_c (K)	Magnetic Behavior	Ref.
$V^{II}_{0.42}V^{III}_{0.58}[Cr(CN)_6]_{0.86} \cdot 2.8H_2O$	315	ferri	37a
$[Cr_5(CN)_{12}] \cdot 10H_2O$	240	ferri	37b
$[Et_4N]_{0.5}Mn_{1.25}[V(CN)_6] \cdot 2H_2O$	230	ferri	37c
$Cs_{0.75}[Cr_{2.125}(CN)_6] \cdot 5H_2O$	190	ferri	37b
$Cs_2Mn[V(CN)_6]$	125	ferri	37c
$CsMn[Cr(CN)_6]$	90	ferri	37d
$CsNi[Cr(CN)_6] \cdot 12H_2O$	90	ferri	37e
$[(CH_3)_4N]Mn[Cr(CN)_6]$	59	ferri	37d
$Mn^{II}[Mn^{IV}(CN)_6] \cdot 1.14H_2O$	48.7	ferri	37e
$K_2Mn[Mn(CN)_6]$	41	ferri	37e
$CsMn[Mn(CN)_6] \cdot 1/2H_2O$	41	ferri	37e
$Mn_3[Mn(CN)_6]_2 \cdot 12H_2O$	37	ferri	37e
$Ni_3[Fe^{III}(CN)_6]$	23.6	ferro	37f
$Cu_3[Fe^{III}(CN)_6]_2$	20	ferro	37g
$Co^{II}_3[Fe^{III}(CN)_6]_2$	14	ferri	37f
$Mn^{II}_3[Fe^{III}(CN)_6]_2$	9	antiferro	37e
$Fe_4[Fe(CN)_6] \cdot xH_2O$ $x = 14-16$	5.5	ferro	4

these new compounds, one or both of the Fe sites has been replaced with a different paramagnetic metal ion (Figure 1.3). The octahedral coordination of the metals in these cubic PB type structures provides an opportunity to test the principle of orthogonality to regarding which combinations of transition metal ions will lead to the greatest number of unpaired spins. This refers to the fact that unpaired electrons in adjacent metal orbitals of compatible symmetry ($t_{2g} + t_{2g}$ or $e_g + e_g$) couple antiferromagnetically across the cyanide bridge, while those in orthogonal orbitals ($t_{2g} + e_g$) couple ferromagnetically (Figure 1.4). This principle is illustrated in the PB analogue $\text{Ni}^{\text{II}}_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2$.⁹ The t_{2g}^5 electrons of Fe are strictly orthogonal to the e_g^2 electrons of Ni, consequently they are unable to cancel and ferromagnetic coupling is observed.

The orthogonality principle is tremendously useful because it enables the rational design of materials, which if assembled properly, could have extremely large magnetic moments. Two structural motifs increasingly common in metal cyanide chemistry provide an opportunity to apply this principle to rationally designed products in the molecular regime. One of these is molecular squares and the other is molecular cubes.

Molecular squares of four metals bridged by four cyanides have been known since the early 1900's (Figure 1.5).⁶ These are prepared from four

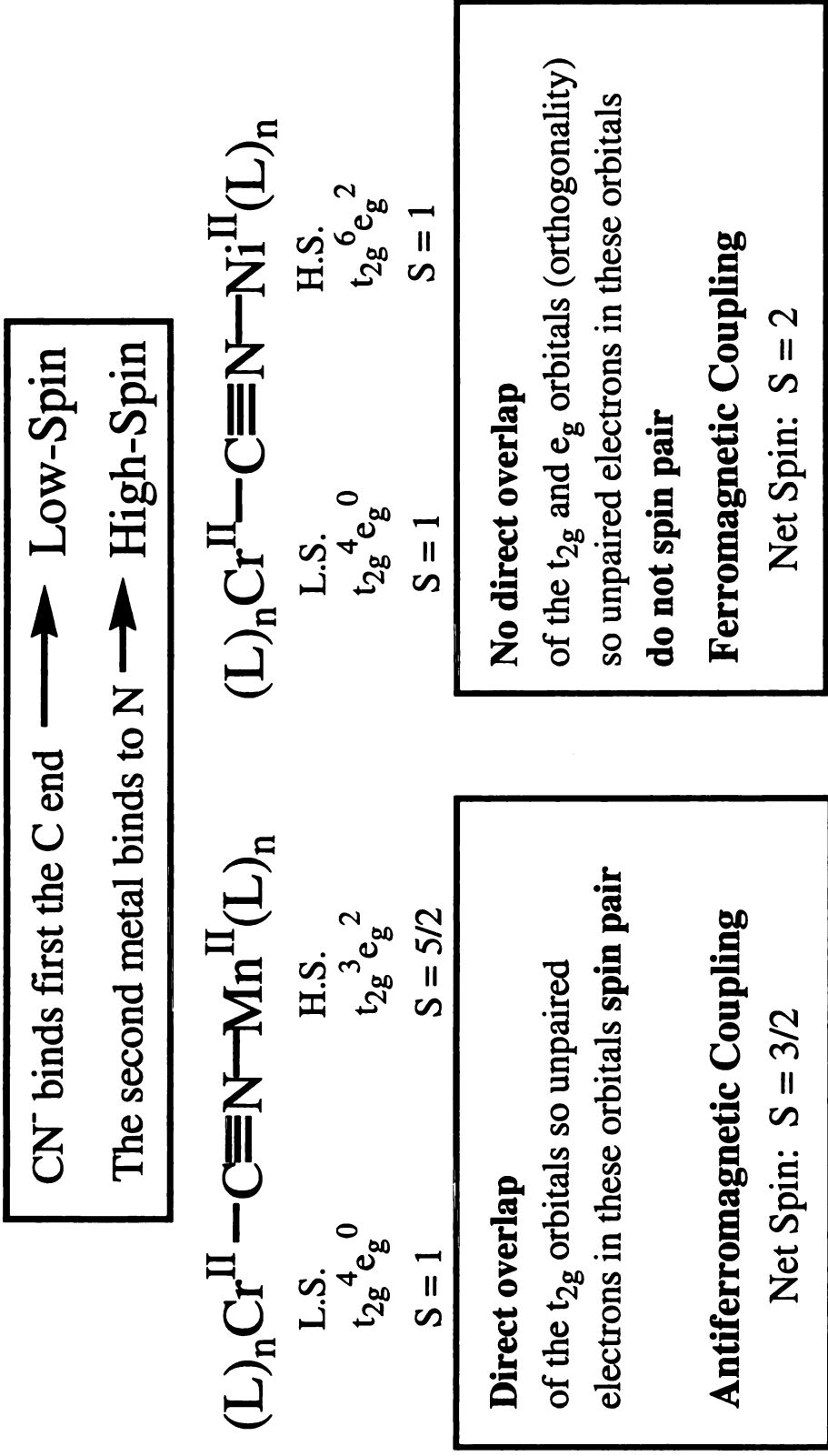


Figure 1.4. Schematic representations of antiferromagnetic and ferromagnetic coupling of open-shell transition metals bridged by cyanide.

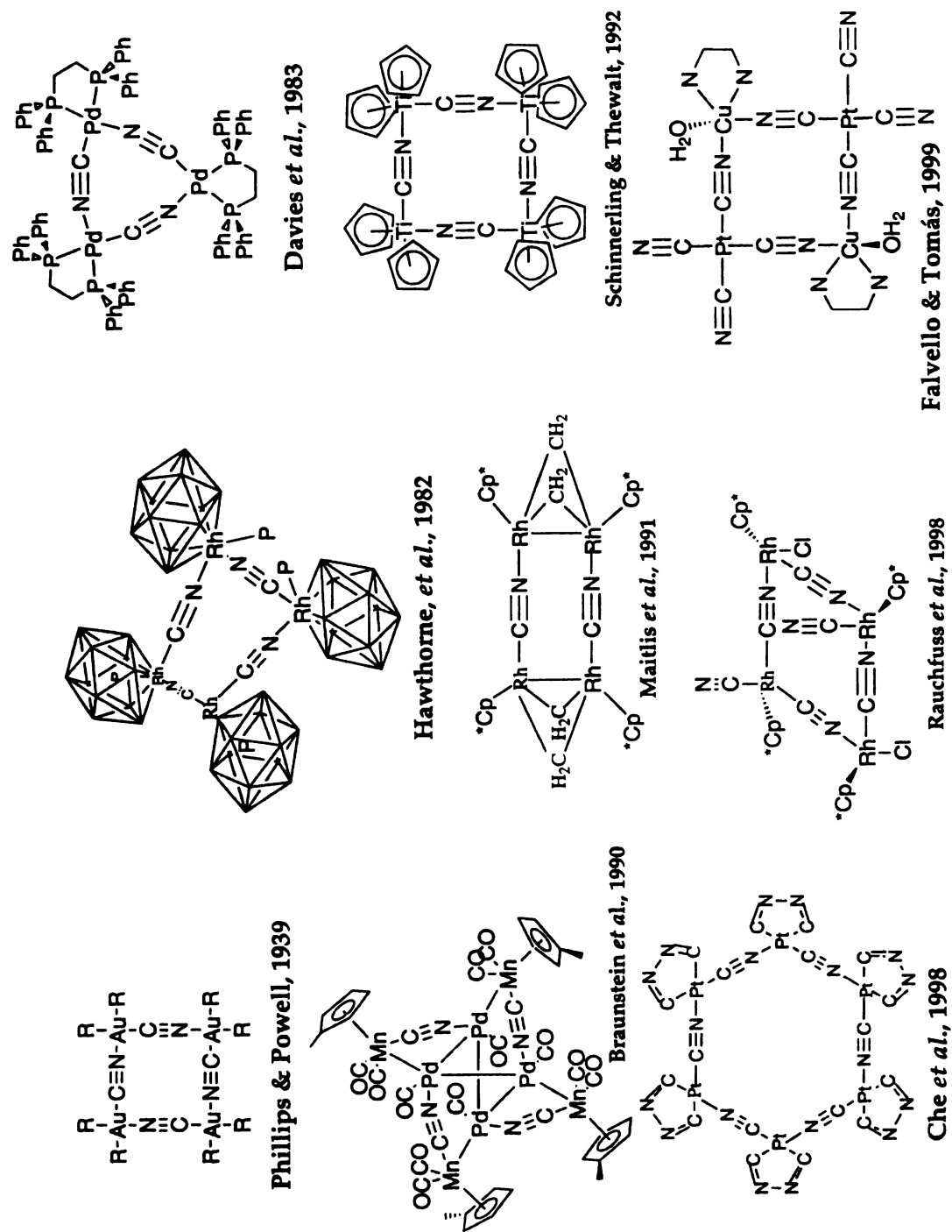


Figure 1.5. Examples of cyclic metal cyanide clusters characterized by X-ray studies

mononuclear precursors with two *cis* chelating ligands (L-L) that leave two *cis* coordination sites open that can be occupied by either cyanide or leaving groups (L).

One outcome of the reaction between precursors of the type $[(L-L)_2M(CN)_2]^n$ and $[(L-L)_2M'(L)_2]^n$ species is loss of L ligands from M' and coordination of the N end of the cyanides to produce a molecular square. Squares for octahedral 3d transition metals have been prepared, but they are less common than square planar 4d and 5d metals.⁶ If the same metal is used for all four corners of the square, antiferromagnetic coupling would ensue and the structure would be diamagnetic. By using the orthogonality principle as a guide in selecting metals for a heterometallic, it should be possible to prepare a heterometallic square with a net magnetic moment. Indeed, this was demonstrated by Oshio in the preparation of the molecular squares $[Fe_2^{II}Cu_2^{II}(\mu-CN)_4(bpy)_6][PF_6]_4 \cdot 2H_2O \cdot 4CHCl_3$ and $[Fe_2^{III}Cu_2^{II}(\mu-CN)_4(bpy)_6][PF_6]_6 \cdot 4CH_3CN \cdot 2CHCl_3$ (Figure 1.6).⁶ⁱ Magnetic susceptibility studies revealed the $Fe_2^{II}Cu_2^{II}$ square based on L.S. Fe^{II} and $S = \frac{1}{2}$ Cu^{II} centers to be a simple paramagnet with noninteracting Cu^{II} centers. The $Fe_2^{III}Cu_2^{II}$ square with two $S = \frac{1}{2}$ Fe^{III} centers in addition to two $S = \frac{1}{2}$ Cu^{II} centers exhibits ferromagnetic coupling between the the open shell Fe and Cu centers which gives rise to a ground state of $S = 2$.⁶ⁱ

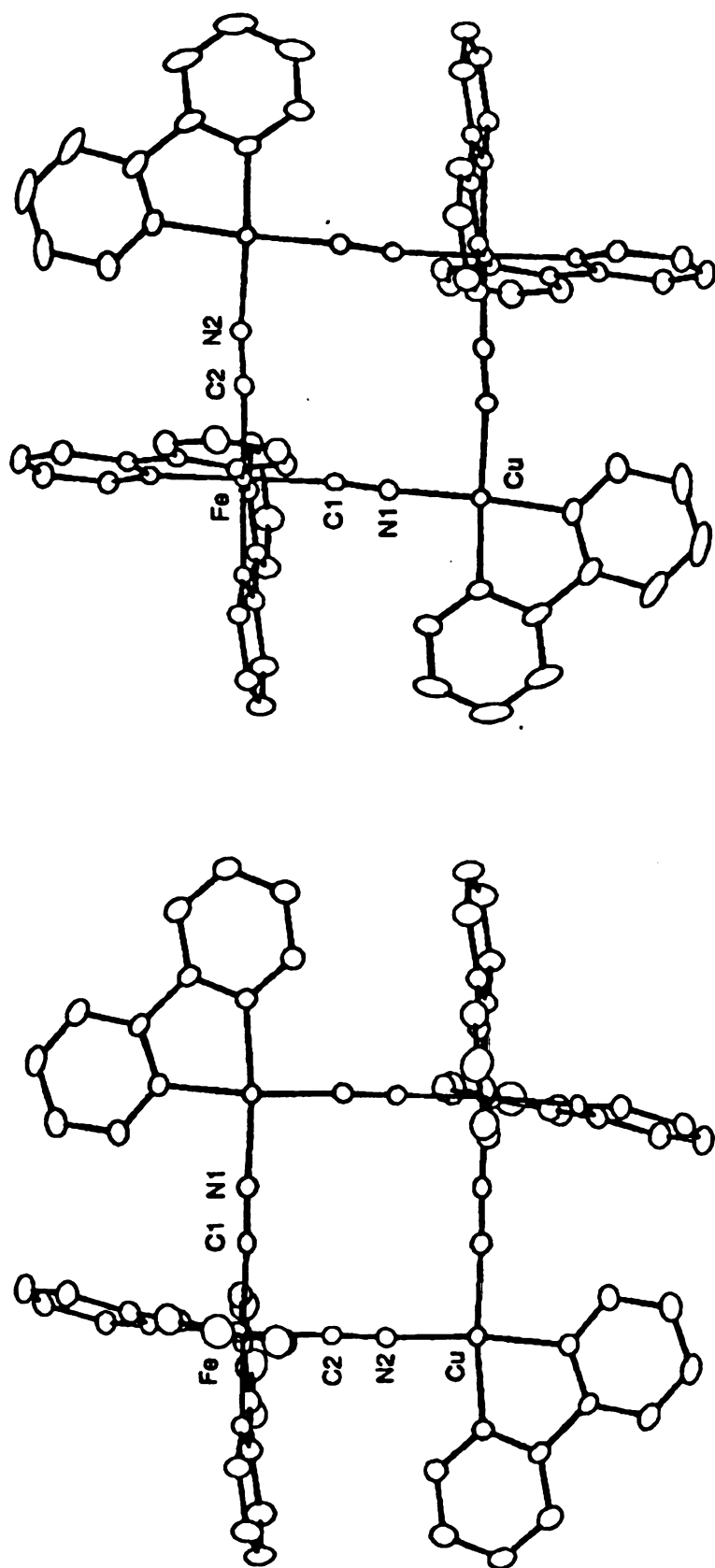


Figure 1.6. Structural representations of the molecular squares $[\text{Fe}_2^{\text{II}}\text{Cu}_2^{\text{II}}(\mu\text{-CN})_4(\text{bpy})_4][\text{PF}_6]_4 \cdot 2\text{H}_2\text{O} \cdot 4\text{CHCl}_3$ (left) and $[\text{Fe}_2^{\text{III}}\text{Cu}_2^{\text{II}}(\mu\text{-CN})_4(\text{bpy})_4][\text{PF}_6]_6 \cdot 4\text{CH}_3\text{CN} \cdot 2\text{CHCl}_3$ (right).⁷

In theory, it is possible to prepare molecules with CN^- bridges that exhibit much higher moments if the structural motif of molecular squares could be extended into a third dimension, i.e. to molecular cubes or boxes. Metal cyanide compounds based on the $\text{M}_8(\text{CN})_{12}$ building block can be thought of as discrete cluster analogues of the cubic cages inherent to the PB-type structure and represent a vehicle for probing the diverse inclusion and magnetochemistry of the PB family of compounds at the molecular level. The level of synthetic control required to achieve the goal of a molecular cube was recently demonstrated in independent work reported by Rauchfuss and Long in the preparation and crystallization of molecular cubes with corners consisting of eight metal atoms with bridging cyanides spanning the edges.^{7,8} The remaining three coordination sites on the metal atoms are occupied by the facial capping ligands Cp^* or triazacyclononane (tacn) respectively.

The research efforts of the Rauchfuss group focused on molecular box preparation for the purposes of exploring the host-guest behavior of these species. The “organometallic box”, $[(\text{Cp})_4(\text{C}_5\text{Me}_4\text{Et})_4\text{Co}_4\text{Rh}_4(\text{CN})_{12}][\text{PF}_6]_4$ (Figure 1.7), was characterized by single crystal X-ray diffraction studies and found to have face diagonal distances of 7.1 and 7.4 Å with an interior volume estimated to be 132 Å³.⁷ The covalent radii of the cube framework

prohibits access to the interior as evidenced by the fact that six CH₃CN molecules are located near the cube faces, but are neither bound to nor inserted into the cube.

The inclusion capabilities of a molecular analogue to PB were demonstrated by the Rauchfuss group with the alkali metal templated assembly of the cyanometallate boxes [Et₄N]₃{M[(Cp*)Rh(CN)₃]₄[Mo(CO)₃]₄} (M = K, Cs) (Figure 1.8).⁹ These molecular boxes form in solution from the reaction of [Et₄N][(Cp*)Rh(CN)₃] and (C₆H₃(CH₃)₃)Mo(CO)₃ in the presence of the respective alkali metal cation. By incorporation of the larger Mo⁰ atom in place of the Co^{III} allows for an expansion of the cube such that alkali metal inclusion is possible. Competition experiments revealed the cube to have a higher affinity for Cs⁺ than K⁺ thereby demonstrating the possibility for selective host-guest chemistry for these cyanometallate cages.

In the aforementioned work from the Rauchfuss group, the selection of metals to use as cube corners was made on the basis of size and inertness to substitution. The diamagnetic Co^{III}, Rh^{III}, and Mo⁰ corners cubes do not confer any magnetic properties on these molecules. Work in our laboratories and in those of Long and coworkers have alternatively focused on extending the rich magnetochemical history of the PB family of

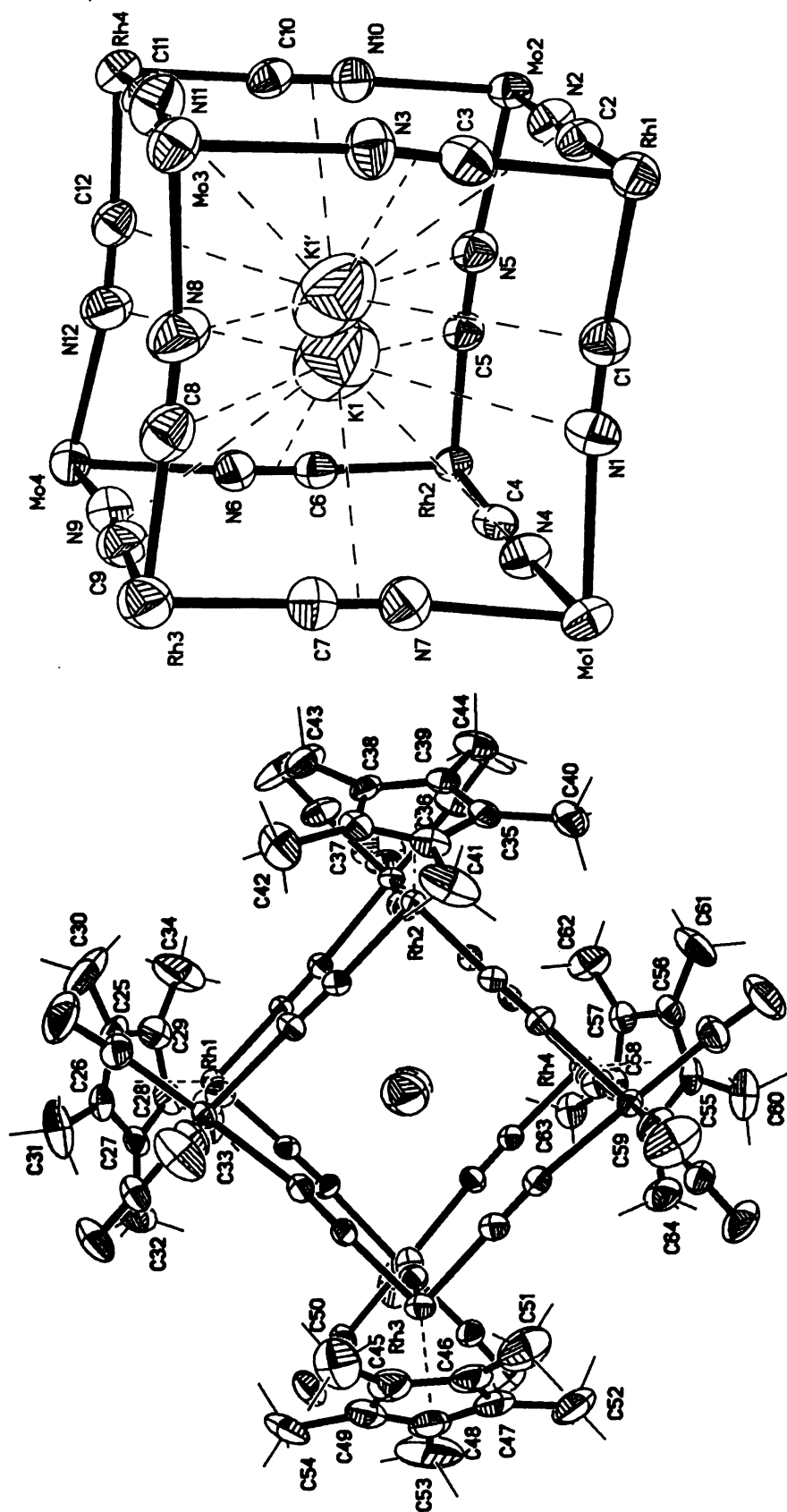


Figure 1.8. Thermal ellipsoid plots of $\text{K}[(\text{Cp}^*)_4(\text{CO})_{12}\text{Rh}_4\text{Mo}_4(\text{CN})_{12}]^9$ (a) full molecule (b) skeletal view emphasizing K^+ occupancy and contacts.

compounds to the molecular level by preparing heterometallic cyanide cubes with paramagnetic transition metals.

Long and coworkers reported the open shell molecular cube, $[(\text{tacn})_8\text{Cr}_4\text{Co}_4(\text{CN})_{12}][\text{CF}_3\text{SO}_3]_{12}\cdot 8\text{H}_2\text{O}$, from the reaction of $[(\text{tacn})\text{Cr}(\text{H}_2\text{O})_3][\text{CF}_3\text{SO}_3]_3$ and $(\text{tacn})\text{Co}(\text{CN})_3$.⁸ The diamagnetic analog, $[(\text{tacn})_8\text{Co}_8(\text{CN})_{12}][\text{CF}_3\text{SO}_3]_{12}$ (Figure 1.9), was structurally characterized by single crystal X-ray diffraction.⁸ X-ray data for the Cr_4Co_4 cube were not reported, but the identity of the cluster was confirmed by electrospray mass spectroscopy. The open-shell Cr^{III} ions are arranged in a tetrahedron sub-set of the cube vertices separated by intervening Co^{III} ions. Magnetic susceptibility measurements revealed a room temperature μ_{eff} value of 7.51 B. M. with $g = 1.97$ which is consistent with four isolated $S = 3/2$ Cr^{III} ions per cube.

Despite the lack of exchange interactions in the $[(\text{tacn})_8\text{Cr}_4\text{Co}_4(\text{CN})_{12}][\text{CF}_3\text{SO}_3]_{12}\cdot 8\text{H}_2\text{O}$ cube, this result demonstrated the opportunity for these types of compounds to contribute to the magnetochemical research area of open-shell nanoscale molecules.¹⁰ This interest stems from the demonstration of a phenomenon similar to superparamagnetism in large spin paramagnetic clusters that exhibit

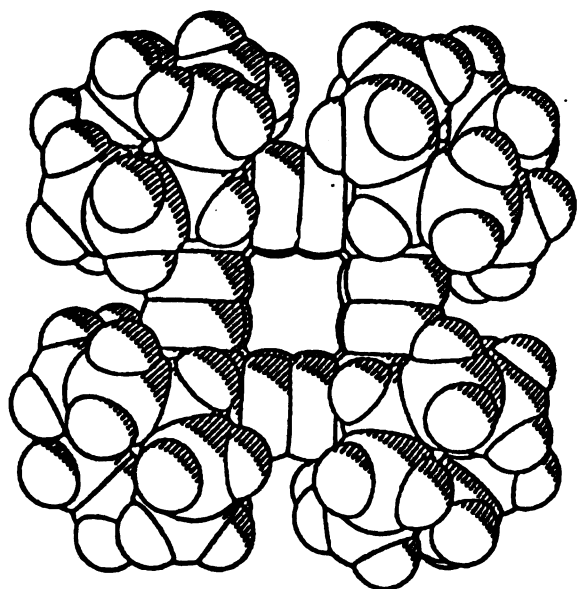
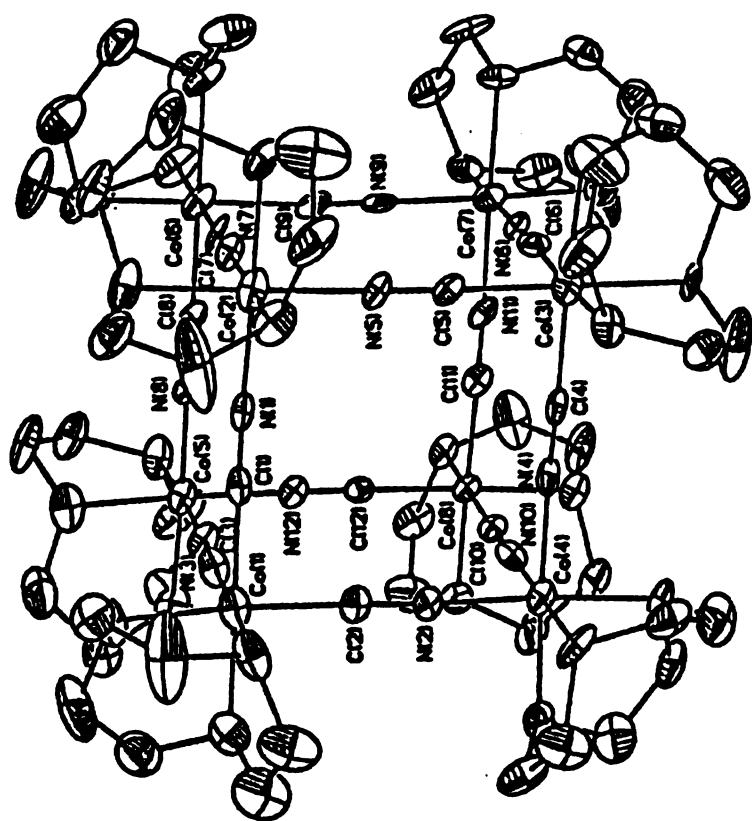
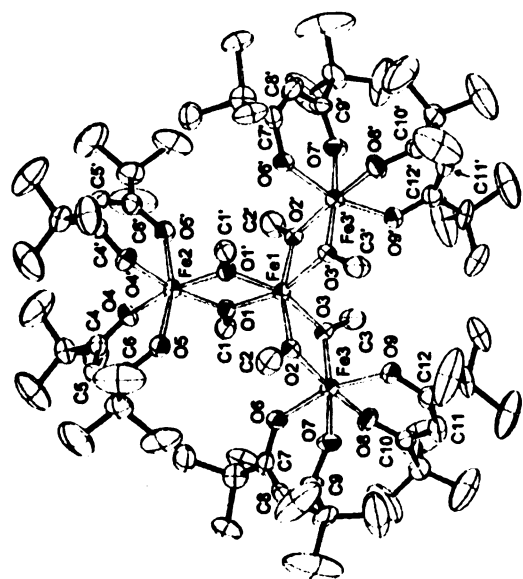


Figure 1.9. Thermal ellipsoid plot of the structure of the molecular cube $[(\text{tacn})_8\text{Co}_8(\text{CN})_{12}][\text{CF}_3\text{SO}_3]_3$ and a space filling diagram.⁸

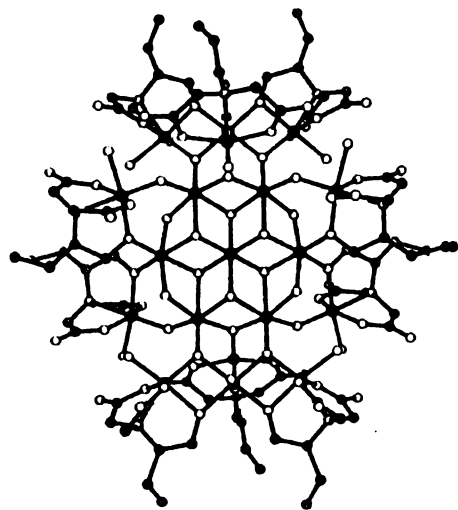
magnetic anisotropy. Several mixed valence clusters Mn clusters with carboxylate bridges constitute one family of compounds with high ground state spin values that have been prepared for the purposes of investigating single molecule magnetic phenomena (Figure 1.10).¹¹ Unfortunately, traditional cluster chemistry such as the Mn carboxylate clusters suffers from the limitation that, *a priori*, reliable prediction of the structure and composition of the resulting products is often not possible. The synthetic control afforded by transition metal cyanide chemistry as demonstrated by Rauchfuss and Long provides a possible answer to this challenge.

Besides the Mn carboxylates, other metal-oxo clusters were discovered to exhibit the slow magnetic relaxation characteristic of single molecule magnetism (Figure 1.10).¹² This slow relaxation is a consequence of an energy barrier for magnetic moment reversal that arises from a ground state with a combination of high spin, S , and negative axial magnetic anisotropy, $D < 0$. A diagram of this double-well potential energy barrier for $[\text{VO}_2(\text{O}_2\text{CEt})_7(\text{bpy})_2]^+$ ($S = 3$) is depicted in Figure 1.11. In this instance, the barrier for reversal of the magnetization direction from $m_s = 3$ to $m_s = -3$ is $|9D|$.

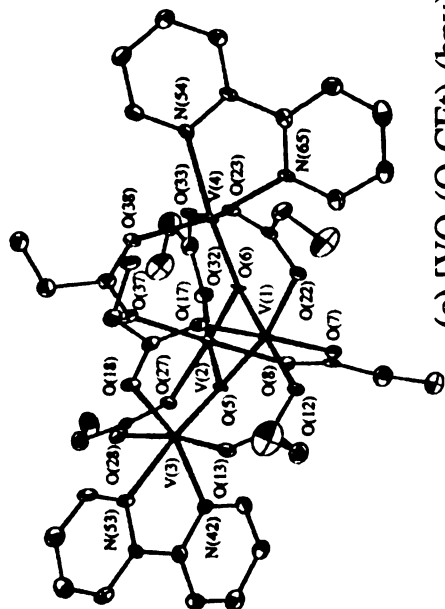
In order to explore the possibility of using such molecules as data storage media, new clusters displaying larger values of S and $|D|$ must be prepared.



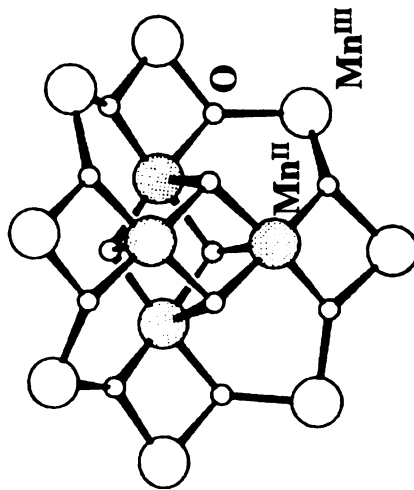
(a) $[\text{Fe}_4(\text{OCH}_3)_6(\text{C}_{11}\text{H}_{19}\text{O}_2)]$



(b) $[\text{Fe}_{19}(\text{C}_8\text{O}_5\text{N}_1\text{H}_{15})_{10}(\mu_3\text{-OH})_6(\mu_3\text{-OH})_8(\mu_3\text{-O})_6(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}]$



(c) $[\text{VO}_2(\text{O}_2\text{CEt})_7(\text{bpy})_2]^+$



(d) $\text{Mn}_{12}\text{O}_{12}$ core from $[\text{Mn}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4\text{O}_{12}]$

Figure 1.10. Examples of metal-oxo clusters that exhibit single molecule magnetism. (a^{12f}, b^{12h}, c^{12e}, d^{12b})

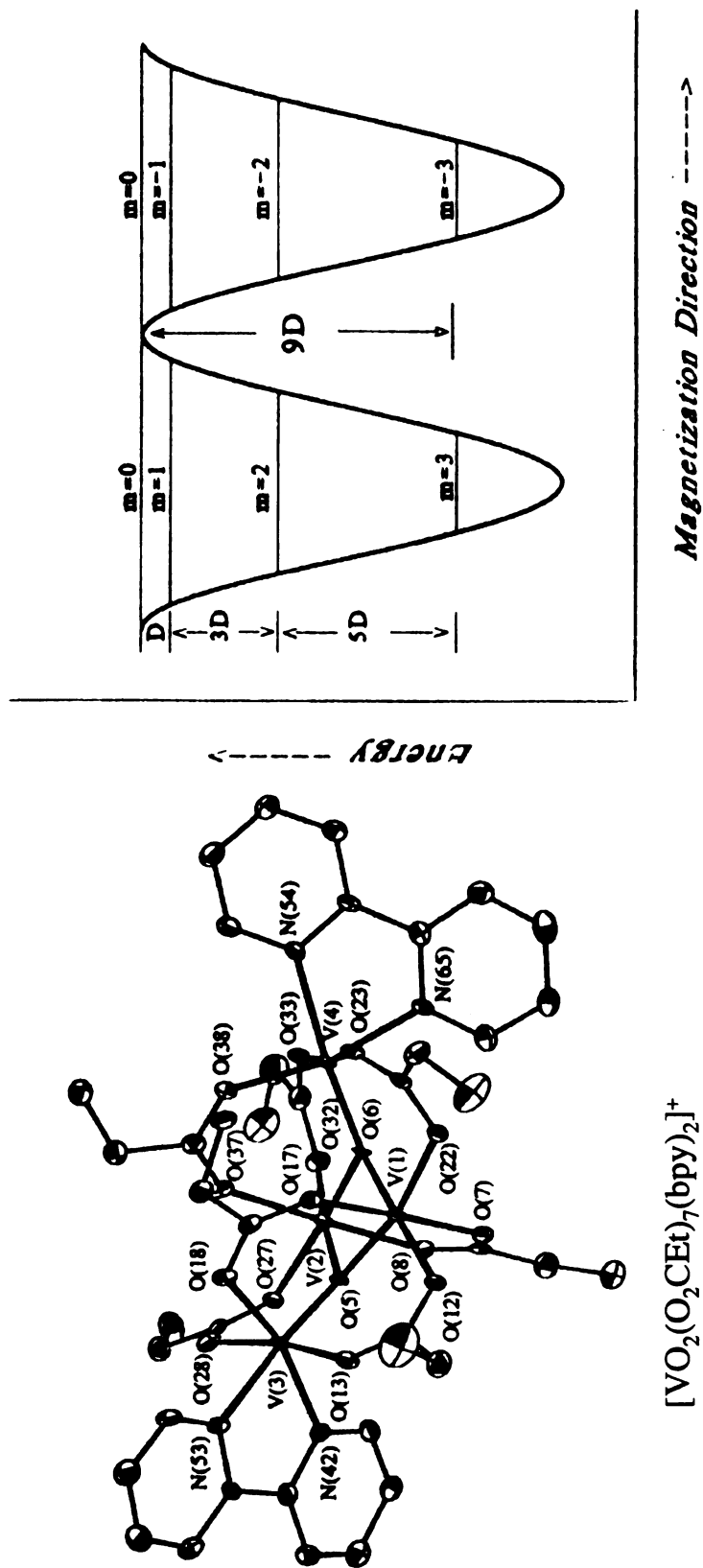


Figure 1.11. Double-well potential energy vs magnetization direction diagram for $[\text{VO}_2(\text{O}_2\text{CEt})_7(\text{bpy})_2]^+$ ($S = 3$). The thermal barrier for reversal of magnetization direction from $m_s = 3$ to $m_s = -3$ is $|9D|$.^{12e}

Using orthogonality as a guide, a maximum of $S = 10$ is possible with the eight metal atom cube motif if the corners are composed of four metal atoms with t_{2g}^3 electron configurations and four with $t_{2g}^6 e_g^2$ configurations. The magnetic anisotropy necessary for high $|D|$ values is tied to the shape of the cluster and the anisotropy inherent to the metal ions (single ion anisotropy).^{11,12} Simply put, the requirements for increasing magnetic anisotropy are the use of metal atoms with single ion anisotropy ($-D$) and cluster shapes that are not highly symmetrical. Whether high symmetry molecular cubes will exhibit single molecule magnetic phenomena is an open question, although the high symmetry certainly is not a good sign. An insufficient number of single molecule magnets have been prepared to predict how high spin transition metal cyanide cubes will behave.

In the vein of attempting to prepare open-shell heterometallic cubes as molecular analogs to Prussian Blue, an alternative structural motif for an expanded cubic cluster is that of Super Prussian Blue (SPB).⁴ A segment of the expanded cube motif inherent to the polymeric SPD structure is presented in Figure 1.12. Adding open-shell metals in place of the Sn sites along the edges to the metals present in the corner positions would allow for the incorporation of 20 metal atoms, thereby enabling higher spin states than would be possible with a eight metal atom cube. A maximum S value of 26

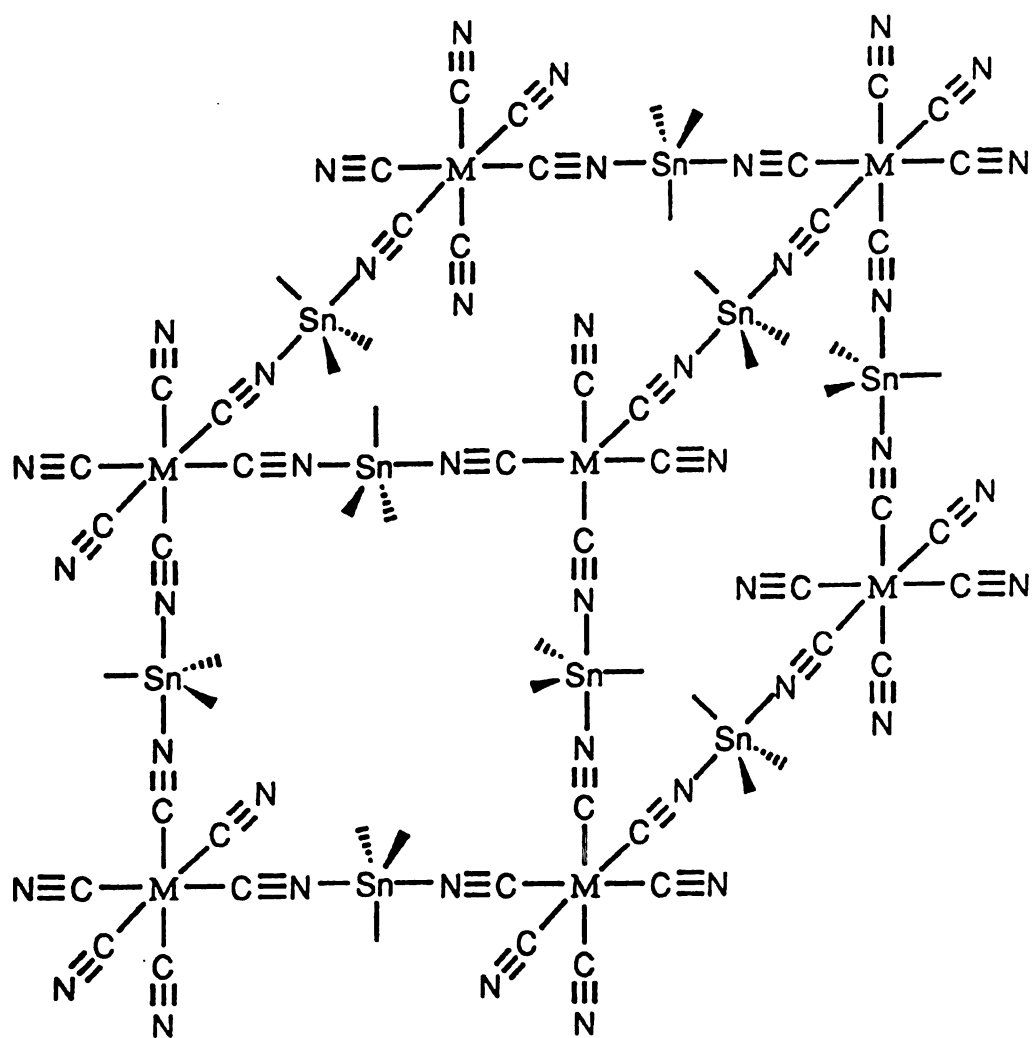


Figure 1.12. Schematic representation of the structure of Super Prussian Blue

would theoretically be possible if the metals along the edges had t_{2g}^3 electron configurations and the corner metals had $t_{2g}^6 e_g^2$ configurations. There is no precedent in the literature for a molecule of this type, but this approach is the subject of work that will be discussed in Chapter IV of this thesis.

B. Metal-metal bonded compounds with cyanide ligands

Despite the progress in developing the cyanide chemistry of the transition metals, one area that has remained largely unexplored is the preparation of metal-metal bonded compounds with cyanide ligands. Traditionally cyanide chemistry has been performed under aqueous conditions. This commonly involves a metathetic approach in which transition metal halides are reacted with alkali metal cyanides. In cases where the species involved were hydrolytically unstable, liquid ammonia or methanol media are used. Low oxidation states of the early transition metals are typically accessed by starting from the higher oxidation state compounds and reducing those either chemically using hydrazine or an alkali metal amalgam or electrochemically in the presence of excess cyanide. Such reaction conditions differ from the media used to conduct research on metal-metal bonded compounds. Most dimetallic complexes are not stable oxidatively or hydrolytically in solvents such as water. In addition, the alkali metal salts of cyanide are virtually

insoluble in the nonpolar, aprotic solvents commonly used in metal-metal bond chemistry.

The exclusion of cyanide as a routine ligand in metal-metal bond chemistry is, to an extent, understandable on the basis of the electronics of the ligand. It is intuitive to assume that the low-valent, electron-rich dinuclear cores would not be readily stabilized by a π -accepting ligand such as cyanide, and there is precedence in the literature that supports this hypothesis. The $\text{Mo}_2^{\text{II,II}}$ core has been shown to undergo cleavage in the presence of other π -acceptors such as CO, NO, and isocyanides.¹⁴ The $\text{W}_2^{\text{II,II}}$ and $\text{Re}_2^{\text{III,III}}$ cores have also been shown to display similar reactivities.^{15,16} An even less robust dimetallic core is $\text{Os}_2^{\text{III,III}}$ which is known to cleave in substitution reactions with a variety of ligands.¹⁶

Despite these difficulties, cyanide chemistry is not unknown in the area of metal-metal bond research (Figure 1.13). The reaction of $(\text{Cp})_2\text{Mo}_2(\text{CO})_4$ with cyanide, introduced as a methanolic solution of KCN, led to the addition product $\text{K}[(\text{Cp})_2\text{Mo}_2(\text{CO})_4\text{CN}]$.¹⁷ This compound constitutes the first reported example of cyanide binding in a semi-bridging mode (depicted in (c) of Figure 1.1). The equivalency of all the Cp groups in the NMR spectrum of this compound revealed this binding mode to be fluxional in a

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“windshield wiper” fashion on the NMR time scale. The crystal structure was reported in a subsequent publication.¹⁸

Similar reactivity was displayed in subsequent reactions of $[\text{Mn}_2\text{H}(\text{CH}_3\text{CN})(\text{CO})_5(\text{dppm})_2]^+$.¹⁹ The initial reaction with a methanol solution of KCN proceeded with displacement of the CH_3CN ligand to yield $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2]$. The subsequent reaction of this compound with the decarbonylation reagent $(\text{CH}_3)\text{NO}$ produced $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})(\text{dppm})_2]$. Neither of these cyano products has been structurally characterized, but spectroscopic evidence suggests that cyanide is present in the carbonyl extraction product in the semi-bridging mode as first observed in $\text{K}[(\text{Cp})_2\text{Mo}_2(\text{CO})_4\text{CN}]$.

The reactivity of $\text{M}_2(\text{OR})_6$ ($\text{M} = \text{Mo}, \text{W}$) compounds was investigated with one and two equivalents of $[n\text{-Bu}_4\text{N}][\text{CN}]$ in benzene and found to lead to the products $[n\text{-Bu}_4\text{N}][\text{M}_2(\text{CN})(\text{OR})_6]$ and $[n\text{-Bu}_4\text{N}]_2[\text{M}_2(\text{CN})_2(\text{OR})_6]$.²⁰ X-ray quality single crystals were not obtained, so assignments of the cyanide binding modes were made solely on the basis of infrared and ^{13}C NMR spectroscopic data. The mono-addition products were speculated to possess cyanide in the mode where bridging occurs only through the carbon atom in a fashion analogous to CO. This assignment was made primarily on the basis of NMR evidence which showed equal coupling to the two ^{183}W

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nuclei, and by comparison to the structural characterized carbonyl analog which has CO in the symmetrical bridging mode , $M(\mu\text{-CO})M$. While this bridging mode is common for CO, there are no reported examples of cyanide bridging in this manner. The known cyanide binding modes are presented in Figure 1.1. A more plausible explanation is the presence of cyanide in the semi-bridging mode which has been shown to be fluxional on the NMR time scale¹⁷ and would account for the ^{13}C NMR data observed for $[n\text{-Bu}_4\text{N}][\text{M}_2(\text{CN})(\text{OR})_6]$. The dicyano adducts were clearly formulated as containing only terminal cyanides based on the ^{13}C NMR data which revealed coupling of the cyanides to only one W nuclei.

One additional example of an unexpected semi-bridging cyano compound was obtained from the reaction of $[\text{Rh}_2(\text{NCS})(\text{CO})_2(\text{dppm})_2]\text{ClO}_4$ with CO which yields $[\text{Rh}_2(\mu\text{-CN})(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2]\text{ClO}_4$. In this product, a bridging CO has been added and the SCN^- group has been converted to CN^- .²¹ This compound was structurally characterized to confirm the semi-bridging cyanide binding mode.

Only two structurally characterized examples of metal-metal bonded compounds with terminal cyanides exist, viz., $[n\text{-Bu}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$ and $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_6(\text{dppm})_2]$ prepared in the Dunbar laboratories several years ago (Figure 1.14).²² The octacyanodimolybdate anion, $[\text{Mo}_2(\text{CN})_8]^{n-}$

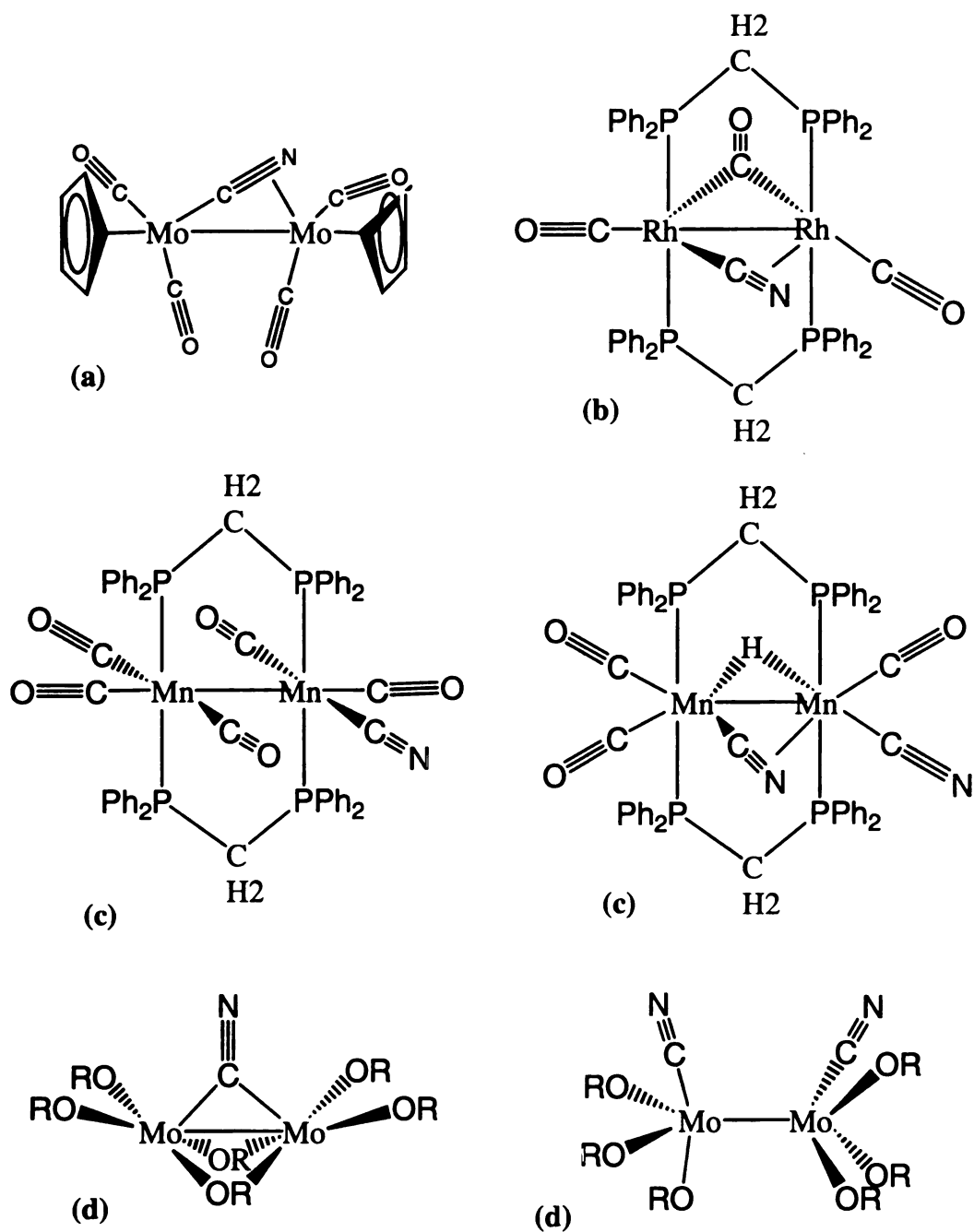


Figure 1.13. Representations of the metal-metal bonded compounds with cyanide ligands known prior to the research efforts carried out in the Dunbar laboratories. (a^{16} , b^{17} , c^{18} , d^{19})

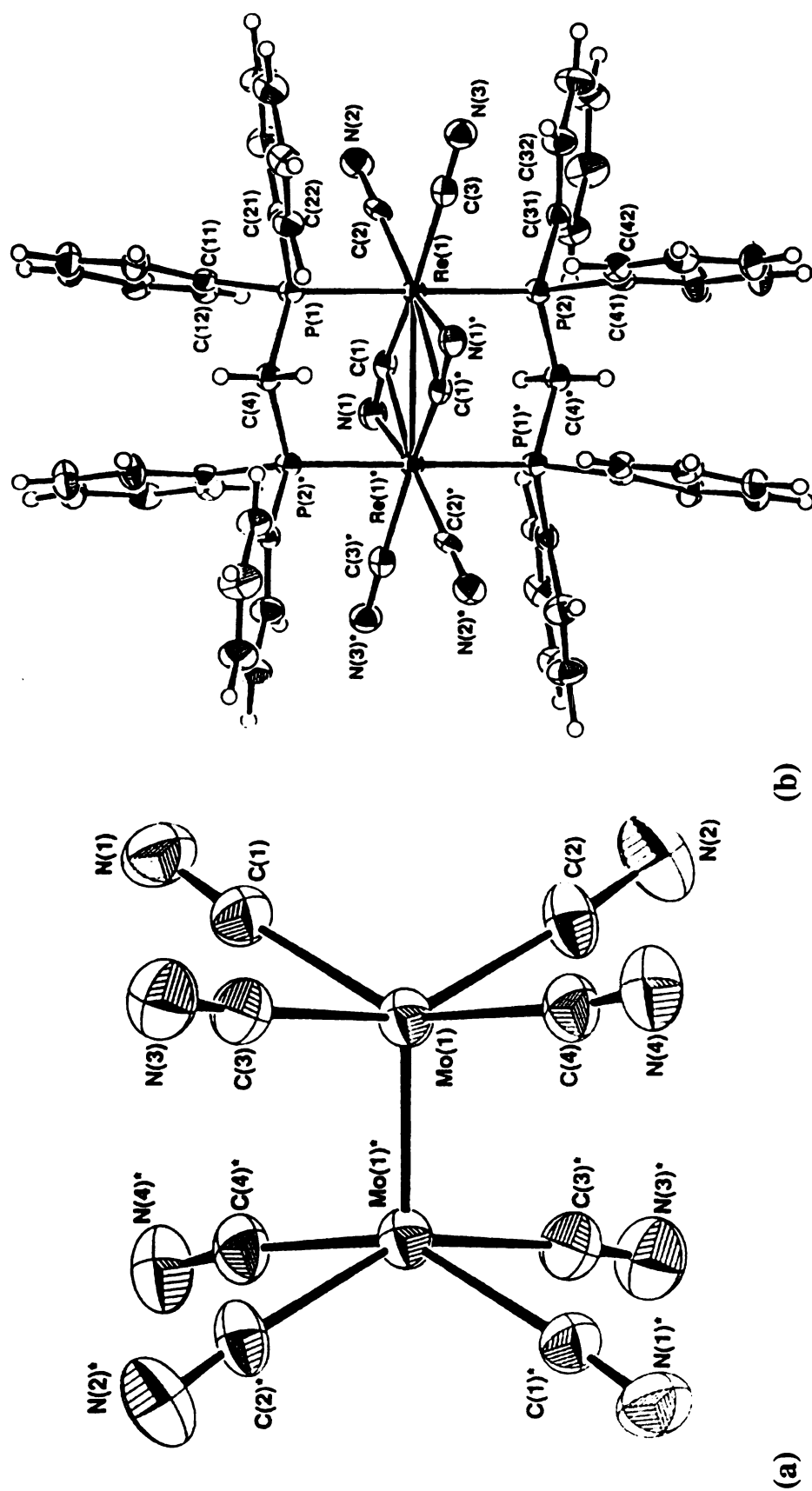


Figure 1.14. (a) Thermal ellipsoid plot of the molecular anion $[\text{Mo}_2(\text{CN})_8]^{4-}$. Atoms are represented at the 50% level. (b) Thermal ellipsoid plot of the molecular anion $[\text{Re}_2(\text{CN})_6(\text{dppm})_2]^{2-}$. Thermal ellipsoids for atoms in both structures are represented at the 50% level.²²

constitutes the only known homoleptic dinuclear cyanide complex in the literature, and the dirhenium compound is the only cyanide complex of the edge-sharing bioctahedral (ESBO) type. These examples notwithstanding, the full potential for the use of the cyanide ligand in metal-metal bond chemistry has not been significantly realized. One obvious area of impact is to advance the understanding of structure and bonding in simple molecules via synthesis and spectroscopic and structural characterization of novel compounds with cyanide ligands. This could in turn provide a source for exploration of a little developed area, namely the extension of multiply bonded molecular precursors into solid state materials with interesting properties.²³

C. Materials with open-shell metals coordinated to organic acceptor radicals

Antiferromagnetic exchange between strongly interacting magnetic centers of unequal spins is useful for designing bulk magnetic materials, as evidenced by the success of this approach in the Prussian Blue family of compounds, e.g. $V[Cr(CN)_6]_{0.86}$ which orders at $T_c = 315$ K. These compounds demonstrate the potential for preparing materials from molecular building blocks using mild solution methods. In the search for novel magnetic compounds, an alternative to metal cyanides that is amenable to

this facile solution synthesis is the preparation of materials that have both inorganic and organic components. Materials with open-shell metals and organic radicals can have spins on both the inorganic and organic components. Recent activity in this area of molecule-based materials has led to important achievements in a number of technologically important areas. Novel molecular and extended networks constructed from organic and inorganic building blocks have been found to behave as molecule-based conductors and superconductors²⁴, optically active compounds²⁵ and magnets.²⁶ Furthermore, the versatility of molecule-based materials allows for the design of “hybrid” materials with the possibility of the co-existence of properties, or even synergy between them.²⁷ In particular, magnetism has been one of the fields that has undergone significant development, with molecule-based magnetic materials that mimic and even improve on the properties of classic inorganic magnets (e.g. critical temperatures²⁸, coercive fields²⁹) having been reported.

A common feature of molecule-based magnets is the presence of polymeric networks of paramagnetic metals bridged by ligands capable of promoting magnetic interactions between the localized d-electrons. In addition to the different pathways for magnetic exchange through the ligand (σ versus π), it is important to consider the size of the linker, which is

typically inversely related to the strength of the interaction. Consequently, most examples of molecular-based magnets are based on ligands consisting of only a few atoms such as CN^- ³⁰, $\text{N}(\text{CN})_2^-$ ³¹, and $\text{C}_2\text{O}_4^{2-}$ ³². One strategy for inducing stronger magnetic interactions with longer linkers is to use organic radicals as ligands, due to the ability of unpaired electrons on the ligand to interact with those of the metals. Novel magnets have been obtained in this way with organic acceptors such as TCNE³³, and TCNQ³⁴ (Figure 1.15).

The reaction of $\text{V}(\text{C}_6\text{H}_6)_2$ with an excess of TCNE proceeds with reduction of the TCNE by the $\text{V}(\text{C}_6\text{H}_6)_2$ followed by loss of the C_6H_6 ligands to yield a black precipitate with the empirical composition $[\text{V}(\text{TCNE})_x] \cdot y\text{CH}_2\text{Cl}_2$ ($x \cong 2$, $y \cong 1/2$).^{33a} This compound has an ordering temperature, T_c , above room temperature and exhibits hysteresis with a coercive field of 60 G at room temperature. The critical temperature, in fact, exceeds 350 K, the thermal decomposition temperature of the sample, but was estimated to be ~400 K by a linear extrapolation of the magnetization to a temperature at which it would vanish.^{33a} Due to the structural disorder and variable composition of the magnetic material, a consequence of very low solubility and extreme air and water sensitivity, the detailed structure of $[\text{V}(\text{TCNE})_x] \cdot y\text{CH}_2\text{Cl}_2$ has yet to be elucidated, but the proposed local

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bonding about each TCNE and V center is depicted in Figure 1.16. Reactions of TCNE were carried out with other first row transition metals resulting in the preparation of the analogous $[M(\text{TCNE})_2]$ compounds of Fe, Mn, Co, and Ni.^{33c} The saturation magnetization, M_s , and ordering temperatures, T_c , for these products are presented in Table 1.2. These compounds did not display cooperative magnetic behavior at room temperature, but hysteresis was observed for $[M(\text{TCNE})_2]$ ($M = \text{Co}, \text{Ni}$) below the ordering temperature for both (44 K).

Binary transition metal compounds of the radical TCNQ have been prepared with Fe, Co, Mn, and Ni both with coordinated solvent, $M(\text{TCNQ})_2(\text{S})_2$, and as solvent free phases, $M(\text{TCNQ})_2$.³⁴ Preparation in water or alcohols led to two-dimensional polymers with extensive hydrogen bonding and π -stacking as evidenced by the crystal structure of $\text{Mn}(\text{TCNQ})_2(\text{CH}_3\text{OH})_2$ presented in Figure 1.17.³⁵ The TCNQ molecules exhibit two different structural types, namely σ -dimers resulting from direct C-C bond formation between two TCNQ radicals and face-to-face π -dimers. These coordinated solvent phases exhibited only Curie-Weiss paramagnetism.

The solvent free phases, $M(\text{TCNQ})_2$, were more difficult to structurally characterize, but were shown to form nanosize crystals as judged by TEM

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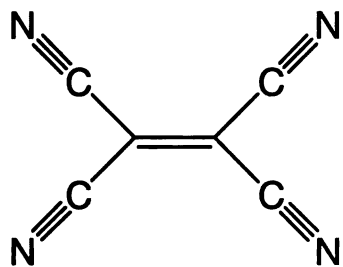
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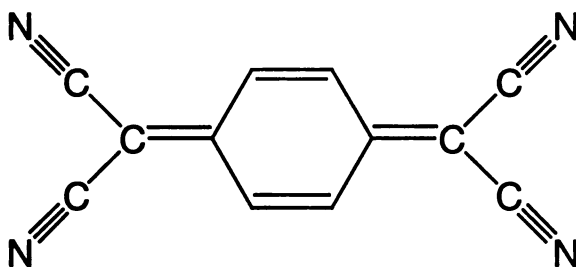
beha

glasse

with powder patterns indicative of tetragonal crystal systems. The Mn and Ni compounds exhibited an increase in magnetic susceptibility at low temperatures due to ferromagnetic coupling. The nature of this behavior is not clear-cut because a.c. magnetic susceptibility studies revealed a frequency dependence for the transition, which is indicative of either a spin-glass or superparamagnetic state but not a ferromagnet.³⁴ Spin glasses are characterized by ferromagnetic or antiferromagnetic interactions that through some degree of randomness or competing interactions cannot undergo a phase transition or ordering.³⁶ Attempts to fit the Mn(TCNQ)₂ magnetic data to the Arrhenius law gave E_a and v_0 values that were too large to have any physical meaning suggesting the magnetic properties in these compounds are not superparamagnetic in origin. Heat capacity measurements did not reveal a peak indicative of the phase transition of a ferromagnet, but the observed increase in susceptibility are more characteristic of ferromagnets than spin glasses. The nature of the magnetic behavior of these compounds appears to share characteristics of both spin glasses and ferromagnets.³⁴

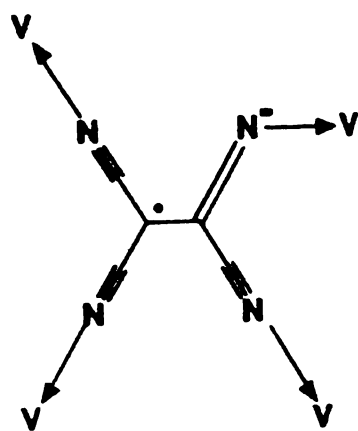


tetracyanoethylene (TCNE) $E_{1/2(\text{red})} = 0.34 \text{ V}$

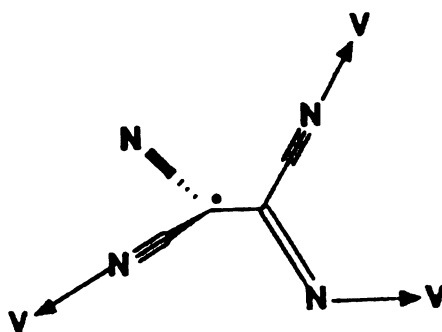


7,7,8,8-tetracyanoquinodimethane (TCNQ) $E_{1/2(\text{red})} = 0.28 \text{ V}$

Figure 1.15. Schematic representations of TCNE and TCNQ. The reported potentials are vs Ag/AgCl.



planar



twisted

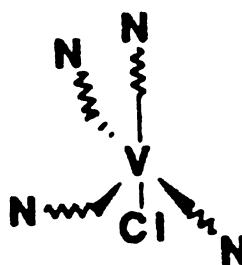
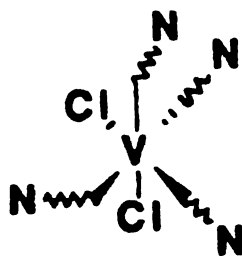
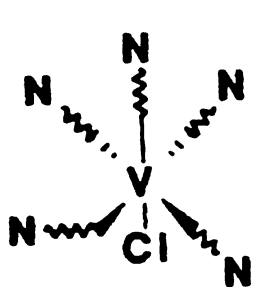
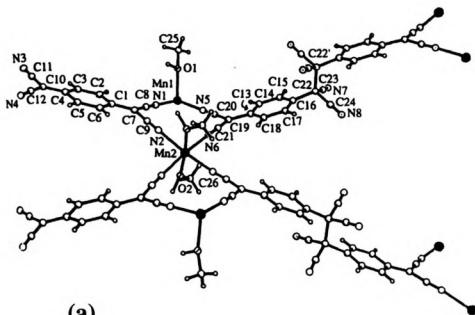


Figure 1.16. Proposed local bonding about each TCNE and V center in $[V(\text{TCNE})_x] \cdot y(\text{CH}_2\text{Cl}_2)$.^{33a}

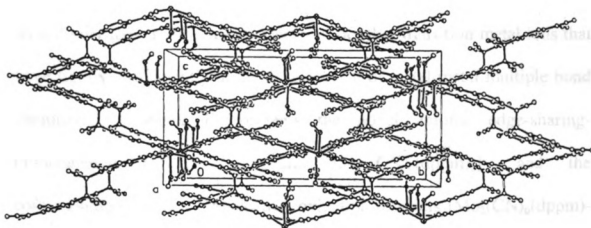
Table 1.2. Saturation magnetization, M_s , and ordering temperature, T_c , for $[M(\text{TCNE})_2] \cdot x\text{CH}_2\text{Cl}_2$ ($M = \text{V, Mn, Fe, Co, Ni}$)^{33a}

$[M(\text{TCNE})_2] \cdot x\text{CH}_2\text{Cl}_2$	M_s , (emu Oe mol ⁻¹) ^a	T_c , (K)
V	10, 300	~400
Mn	19, 000	107
Fe	16, 900	121
Co	8, 000	44
Ni	15, 800	44

^a recorded at 2 K



(a)



(b)

Figure 1.17. Views of the structure of $\text{Mn}(\text{TCNQ})_2(\text{CH}_3\text{OH})_2$:
 (a) a segment of one zig-zag chain (b) extended packing diagram projected down the a axis.

This dissertation describes the work relating to the preparation of cyanide and nitrile compounds with applications in solid state and cluster chemistry. Several approaches in developing this chemistry were undertaken. The first approach, detailed in Chapters II and III is focused on advancing the field of cyanide chemistry in the area of low valent metals that exhibit metal-metal bonding. Efforts to prepare homoleptic dinuclear cyanide compounds are presented in Chapter II. The synthesis and characterization of $[\text{Et}_4\text{N}]_4[\text{Re}_2(\text{CN})_8]$, which is only the second reported example of a dinuclear homoleptic cyanide compound of the type $[\text{M}_2(\text{CN})_m]^{n-}$, is presented along with discussions of the cyanide reactivity of other transition metal ions that have figured prominently in the development of metal-metal multiple bond chemistry. Chapter III presents the novel anionic edge-sharing-biooctahedral (ESBO) compound $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ and the corresponding one and two-electron oxidation products $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{1-}$ and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$. A computational study of these compounds lends insight into the nature of the semi-bridging mode adopted by the cyanides spanning the dimolybdenum core in these compounds and its influence on the metal-metal bond.

A new family of mononuclear transition metal cyanide and nitrile compounds prepared with the facial capping ligand 1-(hydro)trispyrazolborate are reported in Chapter IV. These compounds were designed for the preparation of molecular open-shell heterometallic cubes.

An alternative to transition metal cyanide building blocks for the preparation of clusters and extended systems is presented in Chapter V. In the vein of using organic radicals to link transition metal ions, the chemistry of hexazatriphenylene-hexacarbonitrile ($\text{HAT}-(\text{CN})_6$) was explored. The molecule $\text{HAT}-(\text{CN})_6$ is an aromatic system with three trigonally disposed N-N chelating sites that is capable of undergoing multiple reversible reduction processes. The deliberate reduction of $\text{HAT}-(\text{CN})_6$ to $[\text{HAT}-(\text{CN})_6]^-$ and $[\text{HAT}-(\text{CN})_6]^{2-}$ and the reactivity of these reduced species with transition metals will be presented.

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Chapter II

Nonaqueous cyanide chemistry of low valent transition metals that exhibit metal-metal bonding

1. Introduction

The use of transition metal cyanide compounds as building blocks for clusters and extended arrays is an active area of research.^{1,2} One of our goals is to extend the field of cyanide chemistry to low valent metals that exhibit metal-metal bonding. Such compounds are scarce, with the only examples prior to the work in our laboratories being $\text{K}[\text{Mo}_2(\mu\text{-CN})(\text{CO})_4(\text{Cp})_2]^{3-}$, $\text{Mn}_2(\mu\text{-CN})\text{H}(\text{CO})_5(\text{dppm})_2$,⁴ $[\text{n-Bu}_4\text{N}]_n[\text{M}_2(\mu\text{-CN})(\text{OR})_6]^{5-}$ ($n = 1, 2$) ($\text{M} = \text{Mo}$ or W), and $[\text{Rh}_2(\mu\text{-CN})(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2][\text{ClO}_4]_2$ ⁶ which contain one or two bridging cyanide ligands (Figure 1.14). Only two examples of metal-metal bonded compounds with terminal cyanides exist, viz., $[\text{n-Bu}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$ and $[\text{n-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_6(\text{dppm})_2]$ prepared in the Dunbar laboratories several years ago (Figure 1.14).⁷ The octacyanodimolybdate anion, $[\text{Mo}_2(\text{CN})_8]^{4-}$ constitutes the only known homoleptic dinuclear cyanide complex in the literature, and the dirhenium compound is the only cyanide complex of the edge-sharing bioctahedral (ESBO) type. These examples notwithstanding, the potential impact of incorporating cyanide into the chemistry of metal-metal bonded compounds has not been significantly realized. One obvious area of impact is advancement of understanding structure and bonding in simple molecules via synthesis and characterization of novel compounds

with cyanide ligands. This could in turn provide a source of compounds for exploring a undeveloped area, namely incorporation of multiply bonded molecular precursors into solid state materials. The bridging ability of cyanide is well documented to occur with mononuclear cyanide complexes, there is every reason to believe it will be the case with metal-metal bonded cyanide compounds as well.

The discovery of the unprecedented compounds $[n\text{-Bu}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$ and $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_6(\text{dppm})_2]$ prompted us to question whether other homoleptic dinuclear cyano compounds and anionic metal-metal bonded ESBO complexes with cyanide ligands could be isolated. This chapter reports the results of our investigations into extending the family of homoleptic dinuclear cyano compounds to include other transition metal ions that have figured prominently in the development of metal-metal multiple bond chemistry. These include the group 6 congeners of Mo^{II} , namely Cr^{II} and W_2^{II} as well as those in group 7 and 8, viz., Re^{III} and Os^{III} . In the course of these investigations, a previously undocumented reaction involving the $[\text{Et}_4\text{N}]^+$ and $[n\text{-Bu}_4\text{N}]^+$ salts of cyanide in nonpolar organic solvents was observed. The nature of this decomposition will be discussed in light of what is a feasible course of action to take when carrying out non-aqueous cyanide chemistry. In addition, the oxidative and hydrolytic

stability of $[n\text{-Bu}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$ was explored. A related topic, the preparation of a novel series of metal-metal bonded ESBO compounds with cyanide ligands is reported in Chapter III.

2. Experimental

A. Materials

All manipulations were carried out under an inert atmosphere using standard Schlenk-line techniques. Glassware was flame-dried under vacuum prior to use. Solvents were purified by conventional methods and were distilled under nitrogen prior to use. $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ ⁸ and $\text{W}_2(\text{O}_2\text{C}(\text{C}_6\text{H}_5))_4$ ⁹ were prepared according to published procedures. $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ was prepared by a modification of the reported procedure.¹⁰ $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ was prepared by an unpublished method developed in the Dunbar laboratories.¹¹ The salts $[n\text{-Bu}_4\text{N}][\text{CN}]$ and $[\text{Et}_4\text{N}][\text{CN}]$ were purchased from Aldrich. The salt $[n\text{-Bu}_4\text{N}][\text{CN}]$ was dried by heating the finely divided solid to 75°C under vacuum for 12 hours. The salt $[\text{Et}_4\text{N}][\text{CN}]$ was dried in a similar fashion but at 150°C.

B. Physical Measurements

Infrared spectra were recorded on solids suspended in Nujol between CsI plates in the range 4000-400 cm^{-1} on a Nicolet IR/42 Spectrometer and between 400-50 cm^{-1} on a Nicolet Magna-IR Series II 750 Spectrometer. ¹H

and ^{13}C NMR spectra were recorded on a Varian VXR 300s Spectrometer. Electronic absorption and near-IR spectra were measured on a Shimadzu UV-3101PC UV-Vis-NIR Scanning Spectrophotometer. Cyclic voltammetric studies were carried out with a CH Instruments Electrochemical Workstation in 0.1M $[n\text{-Bu}_4\text{N}][\text{BF}_4]/\text{CH}_3\text{CN}$ solutions at a Pt disk working electrode with Pt wire auxiliary and Ag/AgCl reference electrodes. Mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility, which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institute of Health.

C. Syntheses

(1) Attempted preparation of $[\text{Cr}_2(\text{CN})_8]^{4-}$

(i) Reactions of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$ and $[\text{Et}_4\text{N}][\text{CN}]$

Addition of a THF solution (20 mL) of $[n\text{-Bu}_4\text{N}][\text{CN}]$ (0.460 g, 1.716 mmol) to a pink THF solution (15 mL) of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ (0.100 g, 0.143 mmol) resulted in an immediate color change to green followed by yellow within fifteen seconds. The solution was concentrated to 10 mL before an aliquot of hexanes (10 mL) was added to precipitate the known

compound $[\text{n-Bu}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$ as a yellow solid. The solid was recovered by filtration and dried *in vacuo*. Yield 0.227 g (85%).

The reaction of $[\text{Et}_4\text{N}][\text{CN}]$ (0.133 g, 0.852 mmol) in THF (15 mL) with $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ (0.050 g, 0.071 mmol) in THF (10 mL) proceeded with the formation of a blue solution. The solution was concentrated to 10 mL before hexanes (10 mL) were added to precipitate $[\text{Et}_4\text{N}]_4[\text{Cr}(\text{CN})_6]$ as a blue solid. Exposure of the blue reaction solution to air or water results in a swift color change to yellow. Addition of hexanes (10 mL) induced the precipitation of $[\text{Et}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$ as a yellow solid. The precipitates are collected by filtration and dried *in vacuo*. Yield $[\text{Et}_4\text{N}]_4[\text{Cr}(\text{CN})_6]$ 0.051 g (79%) $[\text{Et}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$ 0.056 g (70%). $[\text{n-Bu}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$: $\nu_{\text{C}\equiv\text{N}}$: 2106 cm^{-1} ; $[\text{Et}_4\text{N}]_4[\text{Cr}(\text{CN})_6]$ ν_{CN} : 2089 cm^{-1} ; $[\text{Et}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$: ν_{CN} : 2110 cm^{-1} .

(2) Attempted preparation of $[\text{W}_2(\text{CN})_8]^{4-}$

(i) Reaction of $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ with $[\text{Et}_4\text{N}][\text{CN}]$

A THF solution (10 mL) of $[\text{Et}_4\text{N}][\text{CN}]$ (0.040 g, 0.259 mmol) was added to a THF solution (5 mL) of $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ (0.028 g, 0.032 mmol) which led to the formation of an orange solution and an orange precipitate (1). The precipitate was isolated by filtration and dried *in vacuo*. Yield 0.029 g.

When the reaction is carried out in CH_2Cl_2 under the same conditions an orange solution and orange precipitate (2) are also produced. Yield 0.036 g.

(1) $\nu_{\text{C}\equiv\text{N}}$: 2052 cm^{-1} ; ^1H NMR (CD_2Cl_2): $\{[\text{Et}_4\text{N}]^+\}$ - CH_2 -quartet 2.93 ppm, - CH_3 -triplet 0.94 ppm, UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}(\text{nm})(\epsilon(\text{M}^{-1} \text{ cm}^{-1}))$ 270, 488 (sh) (2) ν_{CN} : 2118 (sh), 2102, 2091 (sh) cm^{-1} .

(ii) Reaction of $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ with $[\text{n-Bu}_4\text{N}][\text{CN}]$

A CHCl_3 solution (10 mL) of $[\text{n-Bu}_4\text{N}][\text{CN}]$ (0.064 g, 0.238 mmol) was added to a CHCl_3 solution (5 mL) of $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ (0.025 g, 0.029 mmol), giving rise to an orange solution which was filtered, and concentrated to 2 mL. The solution was cooled to -30°C for several days to produce orange crystals that were identified by single crystal X-ray diffraction to be $[\text{n-Bu}_4\text{N}][\text{W}_6\text{O}_{19}]$. No other tractable products could be isolated from this reaction.

(3) Preparation of $[\text{Re}_2(\text{CN})_8]^{2-}$

(i) Reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$

and $[\text{n-Bu}_4\text{N}][\text{CN}]$

Addition of a CHCl_3 solution (10 mL) of $[\text{n-Et}_4\text{N}][\text{CN}]$ (0.138 g, 0.884 mmol) to a rapidly stirring suspension of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ (0.075 g, 0.111 mmol) in CHCl_3 (7 mL) produced a green solution and an oily green precipitate. The solution was decanted from the precipitate which was redissolved in CHCl_3 and re-precipitated with pentane to yield a green solid (3). Yield 0.065 g. X-ray quality single crystals of this compound have yet

to be obtained, but mass spectral and spectroscopic data support the formulation of this product as $[\text{Et}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$. Good elemental data to support this formula or its CHCl_3 solvate have not yet been obtained.

Addition of a CHCl_3 solution (10 mL) of $[\text{n-Bu}_4\text{N}][\text{CN}]$ (0.269, 1.00 mmol) to a rapidly stirring suspension of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ (0.075 g, 0.111 mmol) in CHCl_3 (7 mL) produced a dark purple solution. Addition of hexanes (8 mL) precipitated a dark red-purple solid 4A that was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 0.058 g. The solution was concentrated to 5 mL *in vacuo*. Addition of pentane (5 mL) precipitated a brown-green solid 4B. 4A Yield 0.058 g. 4B Yield 0.044 g.

(3): ν_{CN} : 2093 and 2079 cm^{-1} ; ^1H NMR (CD_3CN): $\{[\text{Et}_4\text{N}]^+\}$ - CH_2 -quartet 3.28 ppm, - CH_3 -triplet 1.27 ppm $\{\text{CHCl}_3\}$ 7.59 ppm; ^{13}C NMR (CD_3CN): $\{[\text{Et}_4\text{N}]^+\}$ - CH_2 - 53.43, - CH_3 - 8.34 ppm; UV-Vis (CH_3CN): $\lambda(\text{nm})$ 610; - FAB MS: $m/z = 710$ $\{[\text{Et}_4\text{N}][\text{Re}_2(\text{CN})_8]\}^-$; $E_{\text{p,c}} = -0.421$ V, $E_{\text{p,c}} -1.130$ V.

(4A): $\nu_{\text{C}\equiv\text{N}}$: 2210, 2112, 2100, 2073, 1907 cm^{-1} **(4B):** $\nu_{\text{C}\equiv\text{N}}$: 2091 and 2073 cm^{-1} ; ^1H NMR (CDCl_3): - CH_2 - 3.22, - CH_2 - 1.57, - CH_2 - 1.35, - CH_3 - 0.88 ppm; ^{13}C NMR (CDCl_3): 128.24, - CH_2 - 59.32, - CH_2 - 24.27, - CH_2 - 19.82, - CH_3 - 13.73 ppm; UV-Vis (CH_3CN): $\lambda(\text{nm})$ 345 (br) 605 (br).

(4) Attempted preparation of $[\text{Os}_2(\text{CN})_8]^{2-}$

(i) Reaction of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[\text{n-Bu}_4\text{N}][\text{CN}]$

Addition of a CHCl_3 solution (10 mL) of $[\text{n-Et}_4\text{N}][\text{CN}]$ (0.136 g, 0.847 mmol) to a rapidly stirring suspension of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ (0.075 g, 0.109 mmol) in CHCl_3 (7 mL) produced a green solution and an oily green precipitate. The solution was decanted from the solid which was, redissolved in CHCl_3 and re-precipitated with pentane to yield a green solid (5). Yield 0.068 g.

Addition of a CHCl_3 solution (10 mL) of $[\text{n-Bu}_4\text{N}][\text{CN}]$ (0.266 g, 0.999 mmol) to a rapidly stirring suspension of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ (0.085 g, 0.124 mmol) in CHCl_3 (7 mL) produced a green solution. Addition of hexanes (12 mL) precipitated a green solid (6) that was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 0.079 g. (5): ν_{CN} : 2112 (sh), 2106, 2085, 2070 (sh), 1870, and 1863 cm^{-1} ; ^1H NMR (CD_3CN): $\{[\text{Et}_4\text{N}]^+\}$ - CH_2 -quartet 3.21 ppm, - CH_3 -triplet 1.12 ppm; ^{13}C NMR (CD_3CN): $\{[\text{Et}_4\text{N}]^+\}$ - CH_2 - 53.43, - CH_3 - 8.34 ppm; UV-Vis (CH_3CN): $\lambda(\text{nm})$ 358, 526 (sh), 622 (sh), 700; A cyclic voltammogram of the compound in a 0.1M $[\text{n-Bu}_4\text{N}][\text{BF}_4]/\text{CH}_3\text{CN}$ solution did not reveal any electrochemical processes between +2.0 and -2.0 V. (6) $\nu_{\text{C}\equiv\text{N}}$: 2114, 2085, 2037, and 1869 cm^{-1} ; ^{13}C NMR (CD_3CN): 174.75, 80.02, 59.34, 24.56, 24.33, 20.27, 13.79 ppm.

(5) Reaction of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $(\text{CH}_3)_3\text{SiCN}$

A $(\text{CH}_3)_3\text{SiCN}$ (0.024 g, 0.234 mmol)/ THF (10 mL) mixture was added to a THF solution (10 mL) of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (0.050 g, 0.116 mmol) and allowed to stir for three days with the solution color gradually changing from yellow to red. Filtration of the solution was followed by concentration to 3 mL and addition of diethyl ether (10 mL) to precipitate a red-purple solid (7). The precipitate was isolated by filtration, washed with diethyl ether (2 x 5 mL) and dried *in vacuo*. Yield 0.040 g. ν_{CN} : 2116 cm^{-1} ; ^1H NMR (CD_3CN): 2.63 ppm; UV-Vis (CH_3CN): $\lambda(\text{nm})$ 540, 513.

(6) Stability studies of $[\text{Mo}_2(\text{CN})_8]^{4-}$

These reactions were carried out nonstoichiometrically with $[\text{Et}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$. The CH_3CN solvent for these studies was dried by passing it down an activated alumina column. Reactivity with $\text{O}_2(\text{g})$ under anhydrous conditions was investigated by passing the $\text{O}_2(\text{g})$ through a drying column prior to bubbling it through the $[\text{Et}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$ solution overnight. Deionized water for the hydrolytic stability test was deoxygenated by purging it with Ar prior to adding it to a CH_3CN solution of $[\text{Et}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$ which was stirred overnight. The solutions for both reactions were pumped to dryness *in vacuo* to give a green solid from the reaction with $\text{O}_2(\text{g})$ and a brown solid from the reaction with water. Green

solid: $\nu_{\text{C}\equiv\text{N}}$: 2197 and 2108 (sh) cm^{-1} ; brown solid $\nu_{\text{C}\equiv\text{N}}$: 2197, 2108 (sh), and 2079 cm^{-1} .

(7) Sample preparation for stability studies of $[n\text{-Bu}_4\text{N}][\text{CN}]$ and

$[\text{Et}_4\text{N}][\text{CN}]$ in organic media

$[\text{Et}_4\text{N}][\text{CN}]$ (0.030 g, 0.192 mmol) and $[n\text{-Bu}_4\text{N}][\text{CN}]$ (0.052 g, 0.192 mmol) were dissolved in 15 mL of THF, CHCl_3 , CH_2Cl_2 , acetone, NO_2CH_3 , and DMF. The samples were allowed to stand undisturbed for 48 hours during which all the solutions became a clear orange color. No reactivity differences were observed with the exclusion of light. $[\text{Et}_4\text{N}][\text{CN}]/\{\text{solvent}\}$: $\nu_{\text{C}\equiv\text{N}}$ (cm^{-1}): {THF} 2154, { CHCl_3 } 2148, { CH_2Cl_2 } 2150, {acetone} 2164, { NO_2CH_3 } 2152, {DMF} 2154; $[n\text{-Bu}_4\text{N}][\text{CN}]/\{\text{solvent}\}$: $\nu_{\text{C}\equiv\text{N}}$ (cm^{-1}): {THF} 2150, { CHCl_3 } 2150, { CH_2Cl_2 } 2153, {acetone} 2154, { NO_2CH_3 } 2152, {DMF} 2154;

3. Results and Discussion

A. Reactions of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ and $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ with

$[n\text{-Bu}_4\text{N}][\text{CN}]$ and $[\text{Et}_4\text{N}][\text{CN}]$

(1) Reactions of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$ and

$[\text{Et}_4\text{N}][\text{CN}]$

The reaction of 8 equivalents of cyanide with $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$, intended to lead to $[\text{Cr}_2(\text{CN})_8]^{4-}$, produced only a brown possibly polymeric

product, based on partial substitution. The reaction of twelve equivalents of $[n\text{-Bu}_4\text{N}][\text{CN}]$ with $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ proceeds with full substitution of the $(\text{O}_2\text{CCF}_3)^-$ groups but without retention of the metal-metal bond. This should not be unexpected because Cr-Cr bonds, while being amongst the shortest known, are notoriously weak. Within fifteen seconds after addition of the cyanide to the $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ precursor, the initial green color of the solution changed to yellow. Both $[\text{Cr}(\text{CN})_6]^{4-}$ (which is blue) and $[\text{Cr}(\text{CN})_6]^{3-}$ (which is yellow) are known compounds. This reaction appears to proceed with formation of $[\text{Cr}(\text{CN})_6]^{4-}$ which is then rapidly oxidized to $[\text{Cr}(\text{CN})_6]^{3-}$. This would account for the solution colors as the reaction proceeds to eventually yield $[n\text{-Bu}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$ as a yellow solid. The infrared spectrum of the product displayed the characteristic ν_{CN} mode at 2106 cm^{-1} .

Despite repeated attempts, the target $[\text{Cr}(\text{CN})_6]^{4-}$ could not be isolated from reactions of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$. The anion $[\text{Cr}(\text{CN})_6]^{4-}$ is known, but is said to be highly oxidatively unstable. The well known hygroscopic nature of $[n\text{-Bu}_4\text{N}]^+$ salts is most likely responsible for our inability to stabilize the Cr^{II} compound. Unfortunately the low thermal stability of $[n\text{-Bu}_4\text{N}][\text{CN}]$ precludes heating it above 75°C under vacuum to dry it, rendering anhydrous preparation extremely difficult. $[\text{Et}_4\text{N}][\text{CN}]$

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possessing much higher thermal stability enables samples to be heated under vacuum up to 150°C effectively facilitating anhydrous preparation.

The reaction of $[\text{Et}_4\text{N}][\text{CN}]$ with $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ in THF proceeds with formation of a blue solution. Addition of hexanes precipitated $[\text{Et}_4\text{N}]_4[\text{Cr}(\text{CN})_6]$ as a blue solid. The infrared spectrum of the product displayed the characteristic ν_{CN} mode at 2089 cm^{-1} . Exposure of the blue reaction solution to air or water resulted in a swift color change to yellow. Addition of hexanes induced the precipitation of $[\text{Et}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$ as a yellow solid which exhibits the characteristic ν_{CN} mode in the infrared spectrum at 2110 cm^{-1} .

(2) Reactions of $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$ and $[\text{Et}_4\text{N}][\text{CN}]$

(i) Reaction of $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$

Although we were unsuccessful in preparing the dinuclear Cr cyano compound, $[\text{Cr}(\text{CN})_8]^{4-}$ the group 6 transition metal, W was identified as a likely candidate for preparing the analogous anion $[\text{W}_2(\text{CN})_8]^{4-}$. The reaction of $[n\text{-Bu}_4\text{N}][\text{CN}]$ with $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ in CHCl_3 produced an orange solution, which, after concentration and chilling, produced orange crystals that were identified by single crystal X-ray diffraction studies to be $[n\text{-Bu}_4\text{N}][\text{W}_6\text{O}_{19}]$. Based on our observations in the Cr chemistry this result was not entirely unexpected because W^{II} compounds are also highly prone to

oxidation.¹² Consequently, inadvertent introduction of water, by the use of wet $[n\text{-Bu}_4\text{N}][\text{CN}]$ would promote formation of oxidized decomposition products.

(ii) Reactions of $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ with $[\text{Et}_4\text{N}][\text{CN}]$

The lack of an adequate method for drying $[n\text{-Bu}_4\text{N}][\text{CN}]$ for synthetic applications involving highly oxidatively unstable transition metal ions led us to explore $[\text{Et}_4\text{N}][\text{CN}]$ as an alternative in all reactions. The reaction of $[\text{Et}_4\text{N}][\text{CN}]$ with $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ in CH_2Cl_2 produced an orange solution and an orange precipitate (2). The Mid-IR spectrum of the orange precipitate displayed a broad stretch at 2102 with shoulders at 2118 and 2091 cm^{-1} . The breadth of the stretch at 2102 cm^{-1} and the presence of the two shoulders suggest the formation of multiple products that, despite the precautions taken in drying the $[\text{Et}_4\text{N}][\text{CN}]$, could include W oxo species.

To rule out the solvent as a possible oxidant, the reaction was repeated in THF, which was dried over Na and distilled under nitrogen immediately prior to its use. The reaction of $[\text{Et}_4\text{N}][\text{CN}]$ with $\text{W}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ in THF also produced an orange solution and orange precipitate (1) as did the reaction in CH_2Cl_2 , but the mid-IR spectrum of this precipitate displayed only a single sharp ν_{CN} mode at 2052 cm^{-1} indicating formation of a single W cyano

product. The result from this reaction underscores the need for scrupulous exclusion of water and oxygen from the reaction conditions.

The observed ν_{CN} mode for the W cyano product (1) is shifted by 18 cm^{-1} to lower energy from the $\nu_{\text{C}\equiv\text{N}}$ value of $[\text{Et}_4\text{N}][\text{CN}]$ at 2070 cm^{-1} . The ^1H NMR spectrum in CD_2Cl_2 displayed only the expected signals for the methylene and methyl groups of $[\text{Et}_4\text{N}]^+$ 2.93 ppm, 0.944 ppm indicating full displacement of the $(\text{O}_2\text{CC}_6\text{H}_5)^-$ groups.

The UV-visible spectrum displayed a strong absorption at 270 nm with a broad shoulder at 480 nm. The target product, $[\text{W}_2^{\text{II,II}}(\text{CN})_8]^{4-}$, with a d^4 - d^4 electronic configuration is expected to possess a metal-metal quadruple bond based on the conventional d-orbital overlap scheme.¹² The HOMO LUMO gap for $[\text{W}_2(\text{CN})_8]^{4-}$ would correspond to a transition between the δ and δ^* molecular orbitals of the W-W quadruple bond. The lowest energy absorption in the observed spectrum at 480 nm is not unreasonable for the $\delta \rightarrow \delta^*$ transition which we take as an indication the metal-metal bond could still be intact.^{12,14} The formation of mononuclear products from the reaction of W-W quadruply bonded compounds with π -acceptor ligands has been demonstrated.¹² The assignment of the (1) as $[\text{Et}_4\text{N}]_4[\text{W}(\text{CN})_6]$ or $[\text{Et}_4\text{N}]_4[\text{W}_2(\text{CN})_8]$ remains unclear. Both formulations are consistent with

the full displacement of the $(\text{O}_2\text{CC}_6\text{H}_5)^-$ groups indicated by the ^1H NMR spectrum and the single ν_{CN} observed in the infrared spectrum

B. Reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[\text{n-Bu}_4\text{N}][\text{CN}]$

(1) Product characterization from the reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$

In an effort to prepare $[\text{Et}_4\text{N}]_2[\text{M}_2(\text{CN})_8]$ ($\text{M} = \text{Re}, \text{Os}$), 8 equivalents of $[\text{Et}_4\text{N}][\text{CN}]$ in CHCl_3 were added to CHCl_3 suspensions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ which lead to the production of green solutions and green precipitates (3) (Re product) and 5 (Os product). Crystallization efforts have yet to yield X-ray quality single crystals other than $[\text{Et}_4\text{N}][\text{O}_2\text{CCH}_3]$ and $[\text{Et}_4\text{N}]\text{Cl}$, but several spectroscopic methods have been employed in the characterization of the green solids (3) and 5.

(i) Infrared and Nuclear Magnetic Resonance Spectroscopic Analysis

The characteristic $\nu_{\text{Os-O}}$ ($392, 346 \text{ cm}^{-1}$), $\nu_{\text{Re-O}}$ ($388, 356 \text{ cm}^{-1}$), $\nu_{\text{Os-Cl}}$ (248 cm^{-1}), $\nu_{\text{Re-Cl}}$ (221 cm^{-1}) modes of the $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ starting materials are absent from the Far-IR spectra of these green products which is a good indication of the full displacement of the $(\text{O}_2\text{CCH}_3)^-$ and Cl^- groups to yield homoleptic Re and Os cyanide compounds.

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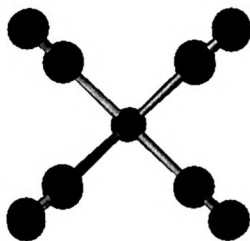
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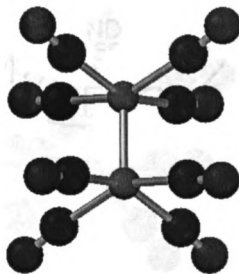
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The dirhenium core of $[\text{Re}_2^{\text{III,III}}(\text{CN})_8]^{2-}$ with a d^4 - d^4 electron configuration would be expected to have a metal-metal quadruple bond based on the conventional d-orbital overlap scheme.¹² The symmetry of the δ component of the quadruple bond would require an eclipsed configuration of the cyanide ligands. The two additional electrons present in a d^5 - d^5 diosmium core such as $[\text{Os}_2^{\text{III,III}}(\text{CN})_8]^{2-}$ would populate the δ^* M. O. thereby reducing the metal-metal bond order to 3, i.e. $\sigma^2 \pi^2 \delta^2 \delta^{*2}$. The cylindrical symmetry of the $\text{Os}\equiv\text{Os}$ triple bond would allow the cyanide ligands to assume a staggered configuration as found from example in $[\text{OsX}_8]^{2-}$.¹² The idealized point group symmetries of $[\text{Re}_2(\text{CN})_8]^{2-}$ and $[\text{Os}_2(\text{CN})_8]^{2-}$ (depicted in Figures 2.1 and 2.2) would be D_{4h} and D_{4d} , respectively, both of which would give rise to two IR active ν_{CN} modes (A_{2u} and E_u for $[\text{Re}_2(\text{CN})_8]^{2-}$ and B_2 and E_1 for $[\text{Os}_2(\text{CN})_8]^{2-}$). The mid-IR spectrum of the Re product (3) displayed ν_{CN} modes at 2089 and 2075 cm^{-1} which is consistent with the product being $[\text{Re}_2(\text{CN})_8]^{2-}$. The energies of the displayed ν_{CN} modes being higher than the 2070 cm^{-1} characteristic of free CN^- in $[\text{Et}_4\text{N}][\text{CN}]$ indicate that σ donation not π back bonding is dominating the Re cyanide bonding interactions. This was the case for the $\text{Mo}-\text{C}\equiv\text{N}$ interactions observed for $[\text{Mo}_2(\text{CN})_8]^{4-}$.⁷



(2)



(1)

Figure 2.1. A representation of the idealized eclipsed structure of $[\text{Re}_2(\text{CN})_8]^{2-}$ from a side-on perspective (1) and an end-on view (2)

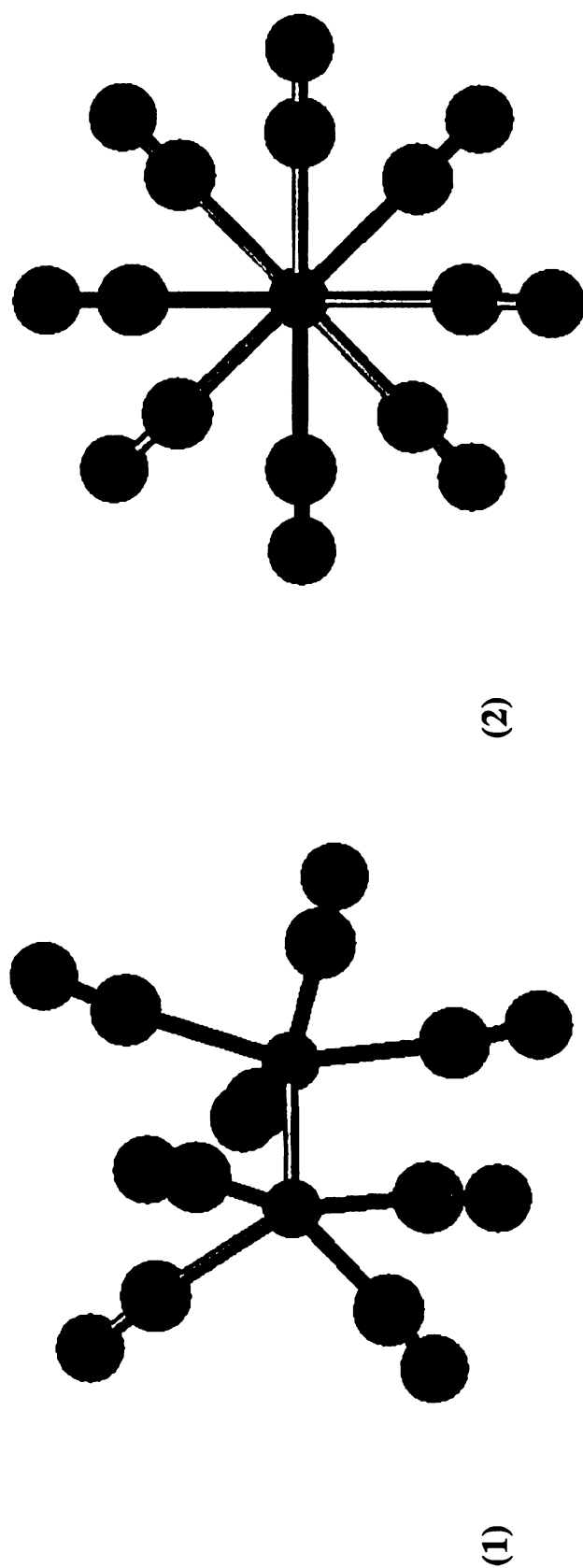


Figure 2.2. A representation of the predicted structure of the staggered anion $[\text{Os}_2(\text{CN})_8]^{2-}$ from a side-on perspective (1) and an end-on view (2)

The spectrum of the Os product (5) displays $\nu_{\text{C-N}}$ modes at 2112 (sh), 2106, 2085, 2070 (sh), 1870, and 1863. The numerous stretches spanning a wide energy range suggests that multiple products are present.

The ^1H and ^{13}C NMR spectra in CD_3CN of both the Re (3) and Os (5) products showed only the peaks expected for the methylene and methyl groups of the $[\text{Et}_4\text{N}]^+$ cations and small amounts of residual CHCl_3 from the reaction solvent. The signals in the ^1H NMR spectrum of the Re product (3) appeared at 3.28 ppm for the methylene quartet and 1.27 ppm the methyl triplet. The corresponding signals in the ^{13}C NMR were displayed at 53.43 and 8.34 ppm. The methylene and methyl signals in the ^1H and ^{13}C NMR spectra of the Os (5) product appeared at 3.21 and 1.12 ppm and 53.74 and 8.63 ppm respectively.

(ii) Electronic properties and cyclic voltammetric studies

The UV-visible spectrum of the Re product displays a broad absorption feature at 610 nm. The HOMO LUMO gap for the postulated product, $[\text{Re}_2(\text{CN})_8]^{2-}$, would correspond to the transition between the δ and δ^* molecular orbitals of the Re-Re quadruple bond. The observed absorbance at 610 nm while higher in energy than is common for the $\delta \rightarrow \delta^*$ transition of metal-metal bonded compounds based on the $\text{Re}_2^{\text{III,III}}$ core, is still

reasonable.¹² Comparison of the data to the dirhenium starting material is precluded by the insolubility of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$.

The UV-visible spectrum of the Os product (5) displayed electronic transitions at 358, 526 (sh), 622 (sh), 700 nm. The lack of $\text{Os}_2^{\text{III,III}}$ compounds with π -acid ligands makes it difficult to draw conclusions regarding the assignments, but we note that the $[\text{Os}_2\text{X}_8]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) family of compounds with π -donor halide ligands also exhibit numerous transitions in the range 250-750 nm.¹² The lowest energy transition in these molecules has been assigned to the $\delta^* \rightarrow \pi^*$ transition. Without other supporting data, however, the electronic absorption data for the Os product (5) does lend insight into the assignment of (5) as $[\text{Os}(\text{CN})_8]^{2-}$. The insolubility of the $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ starting material prohibits a comparison to the UV-visible data observed for this product.

A cyclic voltammetry study of the Re product (3) in a 0.1M [*n*-Bu₄N][BF₄]/CH₃CN of the Re product revealed two irreversible cathodic processes at -0.421 V and -1.130 V. The cyclic voltammogram of the Os compound did not reveal any electrochemical processes between +2.0 and -2.0 V. Reduction of the diosmium core from $\text{Os}_2^{\text{III,III}}$ to $\text{Os}_2^{\text{II,III}}$ is a common electrochemical feature of $\text{Os}_2(\text{O}_2\text{CR})_4\text{X}_2$ and $\text{Os}_2(\text{hp})_4\text{X}_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$) ($\text{X} = \text{Cl}, \text{Br}$) ($\text{hp} = 1\text{-hydroxypyridinate}$).¹² Curiously, the

$[\text{Mo}_2(\text{CN})_8]^{4-}$ compound is also electrochemically inactive in the window +2.0 V to -2.0 V.

(iii) Mass spectrometric analysis

The negative ion fast-atom bombardment (FAB) mass spectrometry studies of the Re and Os products were conducted in both nitrobenzyl alcohol (NBA) and glycerol matrices. The spectrum of the Re compound (3) in both matrices displayed a signal at 710 m/z corresponding to the fragment $\{[\text{Et}_4\text{N}][\text{Re}_2(\text{CN})_8]\}^-$. The observed signal is in agreement with the predicted isotope pattern for the fragment. No peaks in the spectra of the Os (5) compound in either matrix could be correlated with the target product $[\text{Et}_4\text{N}]_2[\text{Os}_2(\text{CN})_8]$ or any of its predicted fragments.

(2) Product characterization from the reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{n-Bu}_4\text{N}][\text{CN}]$

The reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{n-Bu}_4\text{N}][\text{CN}]$ proceeds along a different path than the analogous $[\text{Et}_4\text{N}][\text{CN}]$ reaction in that it produces a dark purple solution. Addition of pentane to this solution precipitated a red-purple solid (4A) that was separated by filtration. Concentration of the solution *in vacuo* and addition of pentane resulted in the isolation of a green-brown solid (4b). The green-brown solid is presumed to be the contaminated $[\text{n-Bu}_4\text{N}]^+$ salt of the green solid (3) isolated from the reaction

of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ that is formulated on the basis of ms spectroscopic data to be $[\text{Et}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$. Suitable conditions for purifying this green solid were not found, but the mid-IR spectrum displayed ν_{CN} modes at 2091 and 2073 cm^{-1} which are taken to be the same as the ν_{CN} modes at 2089 and 2075 cm^{-1} observed in the spectrum of the Re product (3). In addition, the $\nu_{\text{Re-O}}$ and $\nu_{\text{Re-Cl}}$ modes characteristic of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ are absent in the far-IR spectrum supporting the assignment of (4b) as contaminated $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$. No other ν_{CN} modes were present in the mid-IR of (4b) indicating that the impurity is not a Re cyanide compound but some other by-product. The mid-IR spectrum of the red-purple precipitate (4a) initially isolated in this reaction displayed multiple ν_{CN} modes at 2210, 2112, 2100, 2073, and 1907 cm^{-1} indicating that the formation of multiple Re cyanide products had occurred.

The reaction of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$ in CHCl_3 produced a dark green solution similar to the analogous $[\text{Et}_4\text{N}][\text{CN}]$ reaction. Addition of pentane to the solution induced the precipitation of a green solid (6). Similar to the green solid (5) obtained in the $[\text{Et}_4\text{N}][\text{CN}]$ reaction with $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, the product displays multiple ν_{CN} modes in the mid-IR spectrum at 2114, 2085, 2037, 1869 cm^{-1} . As stated, this is a good indication that multiple products are being formed. The possibility that

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these are homoleptic Os cyanide products is supported by the lack of $\nu_{\text{Os-O}}$ and $\nu_{\text{Os-Cl}}$ modes in the far-IR spectrum of (6).

(3) Summary of results from the reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$

(i) Reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$

The combined data from electronic absorption and infrared spectral measurements support the formulation of the green precipitate from the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with 8 equivalents of being $[\text{Et}_4\text{N}][\text{CN}]$ as $[\text{Et}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$. The far-IR spectrum is consistent with complete $(\text{O}_2\text{CCH}_3)^-$ and Cl^- displacement. The two $\nu_{\text{C-N}}$ modes of 2089 and 2075 cm^{-1} in the mid-IR are consistent with the expected D_{4h} symmetry of the eclipsed $[\text{Re}_2(\text{CN})_8]^{2-}$ anion. The signal in the negative ion FAB mass spectrum at 710 m/z that corresponds to the $\{[\text{Et}_4\text{N}][\text{Re}_2(\text{CN})_8]\}^-$ fragment provides valuable structural information. The 610 nm transition in the UV-visible spectrum is reasonable for the expected $\delta \rightarrow \delta^*$ transition based on a quadruple bond for the $\text{Re}_2^{\text{III,III}}$ core.

Infrared spectral evidence suggests that analogous reactions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[n\text{-Bu}_4\text{N}][\text{CN}]$ also produces $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$ (4b) along with additional Re cyanide compounds (4a). The increased

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solubility imbued by the $[n\text{-Bu}_4\text{N}]^+$ cation has thus far prevented isolation of pure $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$ from its by-products.

(ii) Reactions of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$

Electronic absorption and infrared spectral evidence suggests that reactions of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$ proceed with formation of mixtures of homoleptic Os cyanide compounds that may include mononuclear complexes, dinuclear species with eight or more cyanide ligands, or even higher nuclearity clusters. Disruption of the $\text{Os}\equiv\text{Os}$ triple bond is a likely reaction pathway,¹² as reactions involving displacement of the $(\text{O}_2\text{CCH}_3)^-$ groups from $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ typically lead to metal-metal bond cleavage. For example, although reactions of aqueous HX ($\text{X} = \text{Cl}, \text{Br}$) with $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ compounds lead to $[\text{Re}_2\text{X}_8]^{2-}$, treatment of $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$) with aqueous HCl or HBr lead only to $\text{Os}\equiv\text{Os}$ bond scission. Displacement of the $(\text{O}_2\text{CR})^-$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$) groups with retention of the $\text{Os}_2^{\text{III,III}}$ core to yield $[\text{Os}_2\text{X}_8]^{2-}$ (Cl, Br) was accomplished by passing dry gaseous HCl and HBr through suspensions of $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ in anhydrous ethanol. A similar approach involving HCN was not considered as an alternative means of preparing a diosmium cyanide compound due to safety concerns.

The mononuclear cyano complexes $[\text{Os}(\text{CN})_6]^{4-}$ and $[\text{Os}(\text{CN})_6]^{3-}$ have been reported but they are not well characterized.¹³ Attempts at preparing mononuclear $[\text{Os}(\text{CN})_n]^{m-}$ products from reaction of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with 12 or more equivalents of cyanide and refluxing led only to multiple products as evidenced by several ν_{CN} modes in the infrared spectra of these products.

C. Reactions of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $(\text{CH}_3)_3\text{SiCN}$

The reagent $(\text{CH}_3)_3\text{SiCN}$ was investigated as an alternative means for introducing CN^- into metal coordination environments, but suspensions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ in THF displayed no reactivity with $(\text{CH}_3)_3\text{SiCN}$, which presumably is not a strong enough cyanide transfer reagent for that type of heterogeneous reaction. The reaction of $(\text{CH}_3)_3\text{SiCN}$ with a THF solution of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ is slow, but did over the course of three days produce a solution color change from yellow to red. Addition of diethyl ether to this solution induced precipitation of a red-purple solid (7). The mid-IR spectrum of this solid displayed a single peak at 2116 cm^{-1} that was shifted 73 cm^{-1} lower in energy than the $\nu_{\text{C}\equiv\text{N}}$ mode at 2189 cm^{-1} observed for $(\text{CH}_3)_3\text{SiCN}$. The ^1H NMR spectrum revealed only a singlet at 2.63 ppm indicating $(\text{O}_2\text{CCH}_3)^-$ remains bound from which it can be inferred

that the metal-metal bond likely remains intact. This is supported by the UV-visible spectrum, which displays a 540 nm absorbance that is reasonable for the $\delta \rightarrow \delta^*$ transition of the Mo-Mo quadruple bond.

D. Stability studies of $[\text{Mo}_2(\text{CN})_8]^{4-}$

In contrast to what might be expected for a compound with eight π -acid ligands, especially given the low valency of the Mo center, $[\text{Mo}^{\text{II,II}}_2(\text{CN})_8]^{4-}$ is remarkably resistant to substitution or cleavage. Reactions with pyridine and Cl^- did not lead to any observable substitution of the cyanide ligands. Even extreme conditions such as refluxing in CO saturated toluene and dissolution in neat $\text{P}(\text{CH}_3)_3$ were not able to transform or decompose the compound.

Despite this inertness to substitution and metal-metal bond scission, $[\text{Mo}_2(\text{CN})_8]^{4-}$ has limited oxidative and hydrolytic stability. This was somewhat surprising given the fact that cyclic voltammetry experiments revealed that $[\text{Mo}_2(\text{CN})_8]^{4-}$ does not display any electrochemical processes in the range +2 V to -2 V (versus Ag/AgCl). Reactions of $[\text{Mo}_2(\text{CN})_8]^{4-}$ in dry CH_3CN with $\text{O}_2(\text{g})$ produced a green solid with the $\nu_{\text{C}\equiv\text{N}}$ modes shifted from 2109 and 2097 to 2197 and 2108 (sh) cm^{-1} . Reaction with deoxygenated, deionized water produced a brown solid with $\nu_{\text{C}\equiv\text{N}}$ modes shifted to 2197, 2108 (sh), and 2079 cm^{-1} . The identities of these products remain uncertain,

but the shifts of the $\nu_{\text{C}\equiv\text{N}}$ modes to higher energies indicate that the cyanide is either being oxidized to cyanate, OCN^- , or that the nitrogen end is being induced to coordinate perhaps as part of a metal-metal bond cleavage process. A mixture of products is possible as only a maximum of eight cyanate ligands could be generated by cyanide oxidation. If cyanate could not stabilize the dinuclear core, and cleavage were to occur, the coordination spheres of the Mo could contain various numbers of cyanate as well as some combination of solvent, water, or oxygen.

E. Stability studies of [*n*-Bu₄N][CN] and [Et₄N][CN] in organic media

Traditional cyanide chemistry is carried out in either aqueous or liquid ammonia media. Consequently, little is known about the interactions between nonpolar organic solvents and the cyanide anion. Our use of tetraalkylammonium cyanide salts in various organic media has led to observations of previously undocumented reactions. It was noted that a colorless reagent solution of [Et₄N][CN] in CH_2Cl_2 turned a clear orange within 24 h. Other solvents were investigated for similar reactivity with both [*n*-Bu₄N][CN] and [Et₄N][CN]. Reactions are signaled by a discoloration of the clear solution. The results of these studies are presented in Table 2.1.

The trend indicates that only the most polar solvents do not undergo a reaction with cyanide, with methanol being an exception. The explanation for this observation lies in considering ion-pairing and solvation of the cyanide anion. It is believed that these nonpolar solvents cannot sufficiently solvate the cyanide, thereby rendering it more strongly basic and hence reactive. The ability of methanol to stabilize the cyanide anion by engaging in hydrogen bonding interactions is believed to be the reason for its exception to the trend. In all cases, the $[n\text{-Bu}_4\text{N}]^+$ salt reacted more slowly. This is attributed to the ability of the butyl groups to fold back on each other in an umbrella fashion, thereby exposing the positively charged nitrogen and allowing for tighter ion pairing. This would better stabilize the cyanide anion and serve to slow the decomposition reaction.

Infrared spectroscopy was employed to elucidate the nature of these decomposition reactions. The pathway to decomposition of these tetraalkylammonium cyanides in nonpolar organic solvents is transfer of an alkyl group from the cation to the nitrogen end of cyanide to form the corresponding isocyanide and trialkyl amine. Infrared spectra of $[\text{Et}_4\text{N}][\text{CN}]$ /solvent solutions were obtained on neat samples placed between

Table 2.1. Decomposition of $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$ in organic solvents

Solvent	Dielectric Constant, ϵ	Decomposition of $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$
CHCl_3	4.72	yes
THF	7.58	yes
CH_2Cl_2	8.93	yes
Acetone	20.7	yes
MeOH	32.7	no
NO_2CH_3	35.9	yes
DMF	36.7	no
CH_3CN	38.8	no
DMSO	46.8	no

KBr plates. These spectra revealed the disappearance of the 2070 cm^{-1} $\nu_{\text{C}\equiv\text{N}}$ mode of $[\text{Et}_4\text{N}][\text{CN}]$ and the appearance of a slightly solvent dependent $\nu_{\text{C}\equiv\text{N}}$ mode that is in good agreement with the reported value of 2154 cm^{-1} for ethyl isocyanide (EtNC). The ν_{CN} modes (cm^{-1}) observed for the reactions of the various solvents were {THF} 2154, $\{\text{CHCl}_3\}$ 2148, $\{\text{CH}_2\text{Cl}_2\}$ 2150, {acetone} 2164, $\{\text{NO}_2\text{CH}_3\}$ 2152, and {DMF} 2154. The disappearance of the $[n\text{-Bu}_4\text{N}][\text{CN}]$ ν_{CN} mode at 2048 cm^{-1} and appearance of the $\text{C}\equiv\text{N}$ stretch characteristic of $n\text{-BuNC}$ (reported to be 2153 cm^{-1}) were observed in the spectra of the $[n\text{-Bu}_4\text{N}][\text{CN}]/\{\text{solvent}\}$ samples at {THF} 2150, $\{\text{CHCl}_3\}$ 2150, $\{\text{CH}_2\text{Cl}_2\}$ 2153, {acetone} 2154, $\{\text{NO}_2\text{CH}_3\}$ 2152, and {DMF} 2154 cm^{-1} . The appearance of the amines, R_3N ($\text{R} = n\text{-Bu, Et}$), is best monitored with ^1H NMR spectroscopy by observing the multiplet for the methylene groups α to the N atom. These signals appear at ~ 2.5 and ~ 2.4 ppm (solvent dependent) for Et_3N and $n\text{-Bu}_3\text{N}$ respectively. The equivalent methylene groups for the corresponding tetraalkylammonium cyanides and alkylisocyanides occur ~ 3.4 ppm. The ^1H NMR spectra of the samples also revealed the presence of additional signals in the range 0 to 4 ppm that cannot be assigned to any of the species described in the decomposition of the tetraalkylammonium cyanides indicating that while the amines, R_3N ($\text{R} = n\text{-Bu, Et}$), and isocyanides, RNC ($\text{R} = \text{Et, } n\text{-Bu}$), are the major products the

formation of additional products or further decomposition is likely occurring.

That alkyl group transfer to cyanide would take place with alkylation of the nitrogen end of cyanide in place of the carbon is surprising. However, the energies of the observed ν_{CN} modes preclude the possibility of nitrile formation as the final product in these reactions and are in good agreement with the reported values of EtNC and *n*-BuNC.

4. Conclusions

Reactions of 12 equivalents $[\text{Et}_4\text{N}][\text{CN}]$ and $[\text{n-Bu}_4\text{N}][\text{CN}]$ with $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ proceed with cleavage of the metal-metal bond and formation of $[\text{Cr}(\text{CN})_6]^{2-/3-}$ complexes. The oxidative instability of low valent transition metals such as Cr^{II} and W^{II} that exhibit metal-metal bonding necessitate the use of anhydrous reaction conditions that are accessible only with $[\text{Et}_4\text{N}][\text{CN}]$ and $(\text{CH}_3)_3\text{SiCN}$, but not $[\text{n-Bu}_4\text{N}][\text{CN}]$. The anion $[\text{Cr}(\text{CN})_6]^{4-}$ was prepared only from reactions with $[\text{Et}_4\text{N}][\text{CN}]$. Exposure of $[\text{Et}_4\text{N}]_4[\text{Cr}(\text{CN})_6]$ solutions to air or water led to oxidation and formation of $[\text{Et}_4\text{N}]_3[\text{Cr}(\text{CN})_6]$.

The electronic absorption, nuclear magnetic resonance, and infrared spectral characterization as well as mass spectrometric methods support the formulation of the green precipitate from the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$

with 8 equivalents of $[\text{Et}_4\text{N}][\text{CN}]$ as $[\text{Et}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$. Infrared spectroscopic evidence suggests that the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with 8 equivalents of $[n\text{-Bu}_4\text{N}][\text{CN}]$ proceeds with formation of several Re cyanide products, among them $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$. Electronic absorption and infrared spectral evidence suggests that reactions of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$ proceed with formation of multiple Os cyanide compounds.

It was found that $(\text{CH}_3)\text{SiCN}$ is not a sufficiently strong cyanide transfer reagent for heterogeneous reactions with suspensions of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, or $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$. A THF/ $(\text{CH}_3)\text{SiCN}$ solution, however, was able to slowly react with a THF solution of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ to produce a red product with a single $\nu_{\text{C-N}}$ mode. The nature of this product is under investigation.

Despite the resistance to substitution of the cyanides and metal-metal bond cleavage, $[\text{Mo}_2(\text{CN})_8]^{4-}$ has limited oxidative and hydrolytic stability. Acetonitrile solutions of $[n\text{-Bu}_4\text{N}]_4[\text{Mo}_2(\text{CN})_8]$ react with both deionized, deoxygenated water and dry oxygen in a manner that is suggestive of cyanide oxidation to cyanate.

The pathway to decomposition of $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$ in nonpolar organic solvents is the transfer of the alkyl group from the cation to the nitrogen end of cyanide to form RNC and R_3N . The inability of these

solvents to adequately solvate the cyanide anion is the driving force behind the reaction.

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water bath at 85-90°C for 4 hours. The solution was transferred to a large separatory funnel and extracted with diethyl ether (10 x 100 mL). Each time that fresh diethyl ether is added, the bottom layer must be dispensed into a beaker and the top layer discarded before the aqueous layer is returned to the separatory funnel. The yellow diethyl ether layer will become progressively become colorless. The red aqueous layer is emptied into a round-bottomed flask and reduced to a moist residue. Acetic acid (45 mL) and acetic anhydride (45 mL) are added and the solution is refluxed under an inert atmosphere for ~24 hours. The solution is cooled and filtered in air. Acetic acid followed by methanol and diethyl ether are used to wash the solid. The product is dried *in vacuo*. Yield is 2.84 g (70%).

11. In a dry box, CrCl_2 (0.750 g, 6.10 mmol) and NaO_2CCF_3 (1.66 g, 12.2 mmol) were transferred to a 100 mL Schlenk flask. The flask was removed from the dry box and 50 mL of THF was added. The suspension was refluxed for 10-12 hours. This produced a purple solution and a white (light green) precipitate. The purple solution was filtered and the THF removed under vacuum. The resulting purple solid was extracted with toluene and filtered again. The toluene was

removed to give a purple solid. The solid was dried under vacuum and transferred to a dry box for storage. Yield 1.77 g (83%).

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Chapter III

A new family of dimolybdenum compounds with cyanide and phosphine ligands

1. Introduction

Neutral and cationic ESBO compounds are well established families of compounds, but, prior to our results in the cyanide chemistry, anionic ESBOs were limited to one example, viz., $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]^-$. The discovery of the unprecedented compound $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_6(\text{dppm})_2]$ prompted us to question whether other anionic metal-metal bonded ESBO complexes with cyanide ligands could be isolated. Herein, the synthesis of the new anionic ESBO, $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$, produced from the reaction of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ and excess cyanide, is reported. Investigations of the electrochemistry of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) led to the isolation of the corresponding one and two-electron oxidation products, $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10) and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) respectively.

This homologous series of compounds presents an excellent opportunity to probe the ordering of the orbitals involved in metal-metal bond formation in edge-sharing bioctahedral (ESBO) compounds. In ESBO compounds, three d-d overlaps give rise to metal-metal bonds with σ , π , and δ components as well as the corresponding antibonding combinations (Figure 3.1). The δ and δ^* orbitals are generally considered to be sufficiently weak such that they may even be reversed in energy. This switching of the orbital order arises from the interaction of electron lone pair orbitals on the bridging

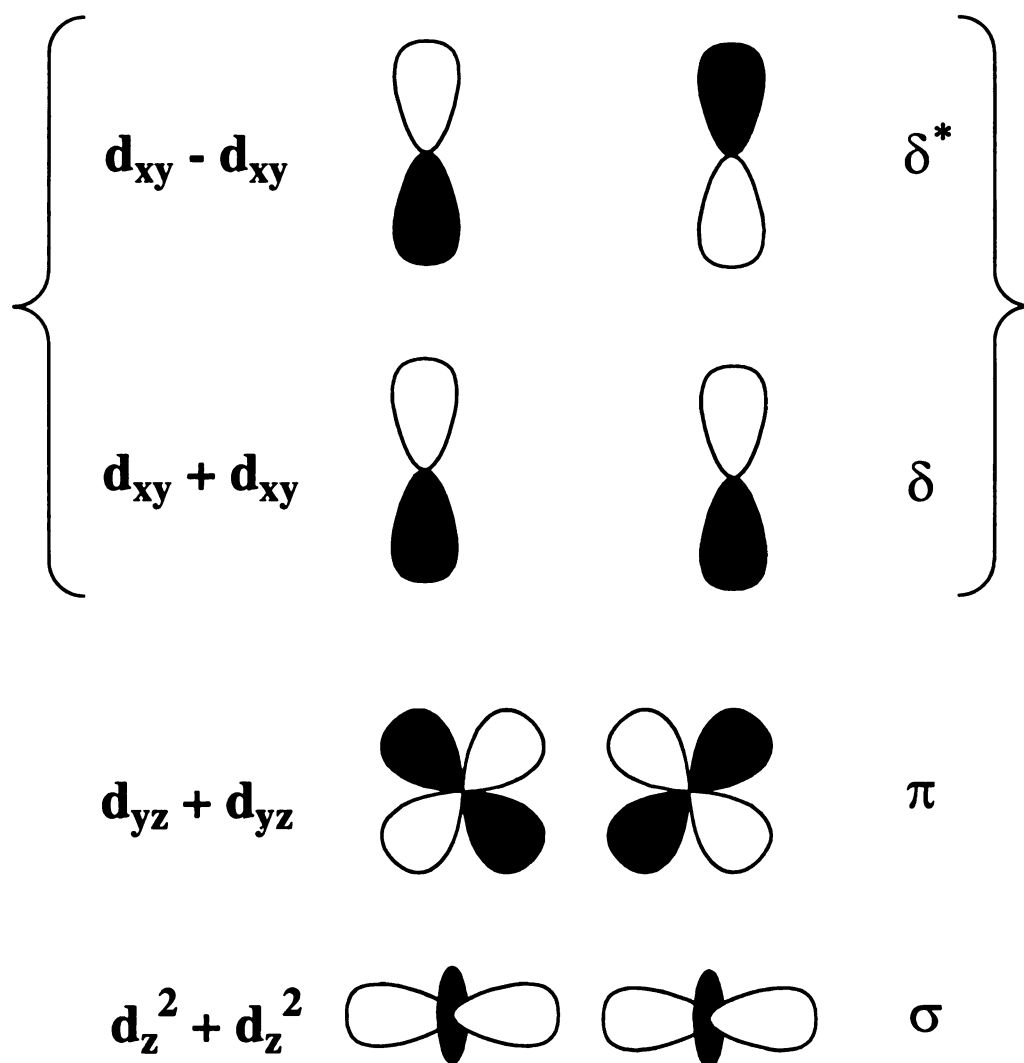


Figure 3.1. Schematic representation of the overlap of *d*-orbitals involved in metal-metal bond formation in an ESBO complex.

atoms with metal based d orbitals involved in metal-metal bond formation. Single crystal X-ray diffraction studies of (8), (10), and (11) as well as computational studies of the closed shell analogs $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ have helped lend insight into the nature of the semi-bridging mode adopted by the cyanides spanning the dimolybdenum cores of these ESBO compounds and its influence on the metal-metal bonding.

2. Experimental

A. Materials

All manipulations were carried out under an inert atmosphere using standard Schlenk-line techniques. Glassware was flame-dried under vacuum prior to use. Acetonitrile was dried over 3 Å sieves and diethyl ether was dried over Na. Both solvents were distilled under nitrogen prior to use. The compound $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ was prepared according to the literature method.¹¹ The reagent NOBF_4 was purchased from Aldrich and used without further purification. The salt $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ was prepared according to the literature method.¹²

B. Physical Measurements

Infrared spectra were recorded in the range 4000-400 cm^{-1} on a Nicolet IR/42 Spectrometer using KBr salt plates. ^1H and ^{31}P NMR spectra were recorded on Varian VXR 300s Spectrometer. Electronic absorption and

near-IR spectra were measured on a Shimadzu UV-3101PC UV-Vis-NIR Scanning Spectrophotometer. Cyclic voltammetry studies were carried out with a CH Instruments Electrochemical Workstation in 0.1M [*n*-Bu₄N][BF₄]/CH₃CN solutions at a Pt disk working electrode with a Pt wire auxiliary electrode and Ag/AgCl reference. Magnetic susceptibility measurements in the solid state were performed with the use of a Quantum Design superconducting quantum interference device (SQUID) magnetometer MPMS-5. Data were obtained on polycrystalline samples in the range of 2-300 K at 1000 G. Electron Paramagnetic Resonance spectra were recorded on a ESP300 E instrument equipped with an Oxford instrument Cryostat ESR900. Elemental analyses were performed on a Perkin Elmer Series II CHNS/O Analyzer. Mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institute of Health.

C. Syntheses

(1) Preparation of [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂], (8)

[*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] was prepared by combining 5 mL dichloromethane solutions of Mo₂Cl₄(dppm)₂ (0.200 g, 0.181 mmol) and [*n*-

Bu₄N][CN] (0.292 g, 1.087 mmol). Upon mixing, a dark red solution was obtained and the reaction was allowed to stir for 5 minutes. Addition of 10 mL of diethyl ether to the reaction solution induced the precipitation of a dark red microcrystalline solid, which was collected by filtration, washed with diethyl ether (3x10 mL), and dried *in vacuo*. Yield 0.145 g. (50%). ¹H NMR: -CH₂-pentet 4.08 ppm, phenyl multiplets 7.60 and 6.96 ppm; {¹H}³¹P NMR: 25.47 ppm; ν_{CN}: 2094, 2080, and 1936 cm⁻¹; UV-Vis (CH₃CN): λ_{max}(nm)(ε(M⁻¹ cm⁻¹)) 553 (1.9x10³) 333 (3.4x10⁵) *Anal.* Calcd for C₈₈H₁₁₄N₈P₄Mo₂: C, 66.01; H, 7.25; N, 7.00. Found: C, 65.18; H, 7.33; N 6.58.

(2) Preparation of [Et₄N]₂[Mo₂(CN)₆(dppm)₂], (9)

The salt [Et₄N]₂[Mo₂(CN)₆(dppm)₂] was prepared by combining 5 mL dichloromethane solutions of Mo₂Cl₄(dppm)₂ (0.200 g, 0.1810 mmol) and [Et₄N][CN] (0.170 g, 1.087 mmol). Upon mixing, the solution turned dark red and a dark red microcrystalline solid was observed to form. The solution was concentrated to 5 mL, and the product was collected by filtration and washed with dichloromethane (3x5 mL). The solid was then dried *in vacuo*. Yield 0.162 g. (65%). ¹H NMR: -CH₂-pentet 4.08 ppm, phenyl multiplets 7.60 and 6.96 ppm; {¹H}³¹P NMR: 21.0 ppm; ν_{CN}: 2094, 2080, and 1925 cm⁻¹; UV-Vis (CH₃CN): λ_{max}(nm)(ε(M⁻¹ cm⁻¹)) 553 (1.9x10³), 333 (3.4x10⁵)

Anal. Calcd for $C_{72}H_{84}N_8P_4Mo_2$: C, 62.79; H, 6.15; N, 8.14. Found: C, 62.48; H, 6.26; N 8.23.

(3) Preparation of $[n-Bu_4N][Mo_2(CN)_6(dppm)_2]$, (10)

Method i

$[n-Bu_4N][Mo_2(CN)_6(dppm)_2]$ was prepared by the drop-wise addition of 10 mL of an acetonitrile solution of $NOBF_4$ (0.015 g, 0.123 mmol) into 10 mL of an acetonitrile solution of $[n-Bu_4N]_2[Mo_2(CN)_6(dppm)_2]$ (0.165 g, 0.1031 mmol) that had been cooled to $-15\text{ }^{\circ}C$ by an ethylene glycol/dry ice bath. Upon complete addition of the $NOBF_4$ solution, the resulting green solution was allowed to warm to room temperature. The volume was reduced to 10 mL, the solution was filtered through Celite, and 10 mL of diethyl ether were added to induce precipitation. A green solid was recovered by filtration, washed with a 35/65% acetonitrile/diethyl ether solution (3x5mL), and dried *in vacuo*. Yield 0.112 g. (80%). ν_{CN} : 2108, and 1807 cm^{-1} ; UV-Vis (CH_3CN): $\lambda_{max}(nm)(\epsilon(M^{-1}\text{ cm}^{-1}))$ 429 (800) 780 (1.2×10^3). *Anal.* Calcd for $C_{72}H_{80}N_7P_4Mo_2$: C, 64.28; H, 5.95; N, 7.29. Found: C, 63.89; H, 6.17; N 6.98.

Method ii

$[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ can alternatively be prepared using $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ as an oxidizing agent. The drop-wise addition of 10 mL of an acetonitrile solution of $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ into 10 mL of an acetonitrile solution of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ that had been cooled to $-15\text{ }^\circ\text{C}$ in an ethylene glycol/dry ice bath produced a green solution. The resulting green solution was allowed to warm to room temperature, concentrated to 10 mL, then filtered through Celite. Diethyl ether (10 mL) was added to precipitate a green solid that was recovered by filtration then washed with a 35/65% acetonitrile/diethyl ether solution (3x5mL) and dried *in vacuo*. Typical yields are 80%.

(4) Preparation of $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (11)

$\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ was prepared by the dropwise addition of 20 mL of an acetonitrile solution of NOBF_4 (0.026 g, 0.227 mmol) into 10 mL of an acetonitrile solution of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (0.165 g, 0.1031 mmol) cooled to $-15\text{ }^\circ\text{C}$ by an ethylene glycol/dry ice bath. Upon complete addition of the NOBF_4 solution, a yellow-green solution with a small amount of a purple-red precipitate was observed. The solution was allowed to warm to room temperature and the purple-red precipitate was removed by filtration through Celite. The solution was concentrated to 10 mL which resulted in the precipitation of a yellow-green solid that was recovered by filtration,

washed with acetonitrile (3x5mL), and dried *in vacuo*. Yield 0.080 g. (70%). ν_{CN} : 2110, 2102 and 1807 cm^{-1} ; *Anal.* Calcd for $\text{C}_{56}\text{H}_{44}\text{N}_6\text{P}_4\text{Mo}_2$: C, 60.23; H, 3.97; N, 7.53. Found: C, 61.09; H, 4.25; N 7.32.

(5) Preparation of $\text{Ni}(\text{en})_2\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (12)

$\text{Ni}(\text{en})_2\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ was prepared by the addition of 10 mL of an acetonitrile solution of $[\text{Ni}(\text{en})_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ (0.035 g, 0.0625 mmol) to 10 mL of an acetonitrile solution of $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (0.100 g, 0.0625 mmol). Upon mixing of the solutions, a purple precipitate ensued which was recovered by filtration, washed with acetonitrile (3x5mL) and dried *in vacuo*. Yield 0.77 g (95%). ν_{CN} : 2096 (broad) and 1936 cm^{-1} *Anal.* Calcd for $\text{C}_{60}\text{H}_{60}\text{N}_{10}\text{P}_4\text{Mo}_2\text{Ni}_1$: C, 55.62; H, 4.67; N, 10.81. Found: C, 55.31; H, 4.45; N 10.39.

D. X-ray Crystallography

Single crystal X-ray structural determinations were performed on a Bruker SMART 1K CCD platform diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda_\alpha = 0.71069 \text{ \AA}$). The frames were integrated in the Bruker SAINT software package,¹³ and the data were corrected for absorption using the SADABS program.¹⁴ The structures were solved using the SHELXTL V.5.10 package.¹⁵ Crystallographic data for $[n\text{-}$

$\text{Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8), $[\text{n-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10), and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) are summarized in Table 1. Thermal ellipsoid plots for the structures of (8), (10), and (11) are displayed in Figures 2, 3, and 4. Selected bond distances and angles for (8), (10), and (11) are presented in Tables 2, 3, and 4. A comparison of the equatorial planes of the dimetal units in (8), (10), and (11) is illustrated in Figure 5. A metrical comparison of the three structures is presented in Table 5.

(1) $[\text{n-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$, (8)

(i) Data Collection and Reduction

Crystals of (8) were grown by slow diffusion of benzene into an acetonitrile solution of (8) in a sealed 8 mm O.D. glass tube. A dark red crystal of dimensions $0.44 \times 0.39 \times 0.07 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a monoclinic cell. A total of 6568 unique reflections was collected at 173 K using the ω -scan technique to a maximum 2θ value of 46.4° .

(ii) Structural Solution and Refinement

The space group was determined to be $C2/c$. The structure was solved by the SHELXS¹⁵ structure program and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. The

“softness” of the crystal resulted in poor diffraction which led to refinement limitations. With the exceptions of C31 and C2, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions. The high degree of thermal motion observed for the C3 and N3 atoms is attributed to librational disorder.¹⁶ Based on the appearance of the electron density maps of the region, it is unlikely that the bridging atoms are involved in a packing disorder of the molecule with two slightly different superimposed orientations of the ligand. Furthermore the unreasonably short C3-N3 bond length of 1.028 Å is an expected consequence of libration. The rather unlikely possibility of the bridging cyanide being bound through the N rather than C atom was considered and rejected on the basis of refinement statistics. When the atom bonded directly to the Mo atom in the bridging position was refined as a N atom instead of a C atom, the temperature factor became non-positive definite; the corresponding temperature factor of the C atom increased from 0.042 to 0.072.

(2) [*n*-Bu₄N][Mo₂(CN)₆(dppm)₂], (10)

(i) Data Collection and Reduction

Crystals of (10) were grown by slow evaporation in air of a benzene and

acetonitrile solution of (8). A green crystal of dimensions 0.38 x 0.25 x 0.07 mm³ was covered in Paratone oil and then mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a monoclinic cell. A total of 8462 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56°.

(ii) Structural Solution and Refinement

The space group was determined to be C2/c. The structure was solved by the SHELXS¹⁵ structure program and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located from the difference map and refined isotropically. The O1-H1WA and O1-H1WB distances were restrained to 0.85 Å.

(3) Mo₂(CN)₆(dppm)₂, (11)

(i) Data Collection and Reduction

Crystals of (11) were grown in an 8 mm O.D. glass tube by slow diffusion of an acetonitrile solution of (10) into nitromethane that was not dried or deoxygenated prior to use. A yellow-green crystal of dimensions 0.42 x 0.35 x 0.28 mm³ was covered in Paratone oil then mounted on the tip

of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a triclinic cell. A total of 6568 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56° .

(ii) Structural Solution and Refinement

The space group was determined to be P-1. The structure was solved by the SHELXS¹⁶ structure program and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were added in calculated positions.

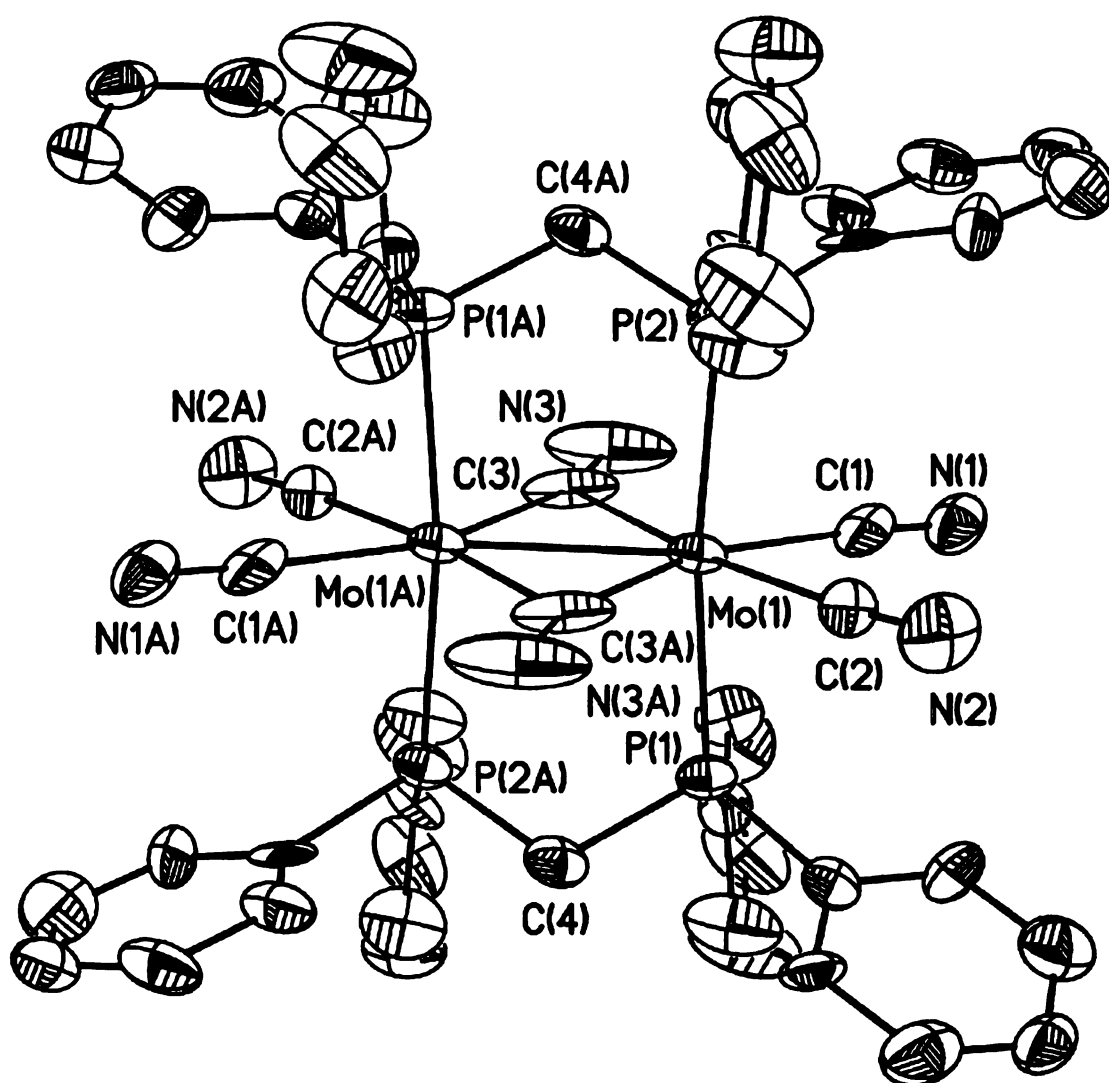


Figure 3.1. Thermal ellipsoid plot of $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$, (8) represented at the 50% probability level. Hydrogen atoms were removed for the sake of clarity.

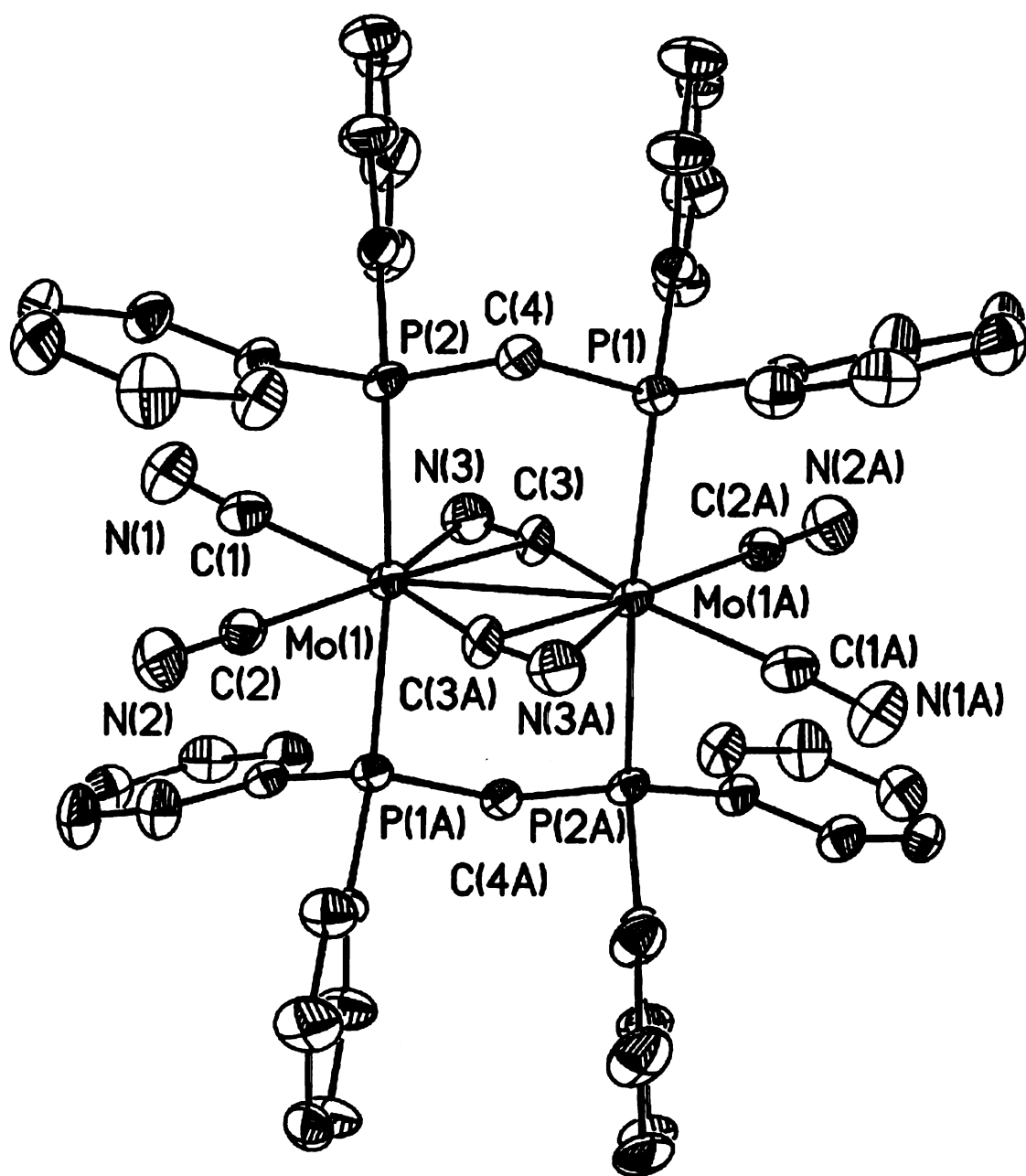


Figure 3.3. Thermal ellipsoid plot of the molecular anion $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{1-}$ in (10) at the 50% level. Hydrogen atoms have been removed for the sake of clarity.

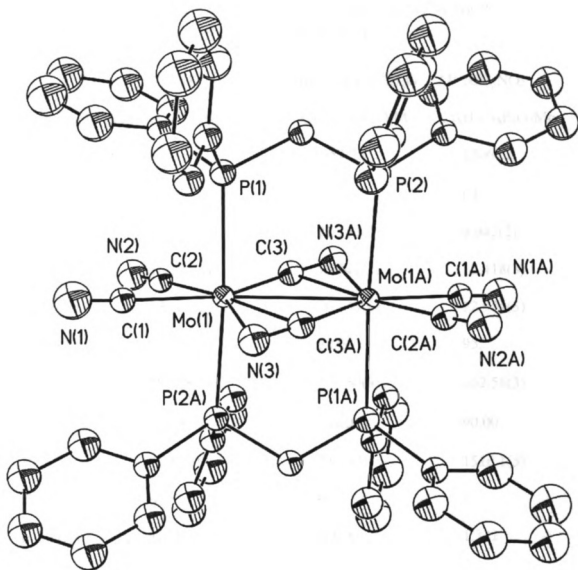


Figure 3.4. Thermal ellipsoid plot of the structure of $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (11) represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

Table 3.1. Crystallographic Data for [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] (**8**)·
2CH₃CN·2C₆H₆, [*n*-Bu₄N][Mo₂(CN)₆(dppm)₂] (**10**)·2CH₃CN·
2H₂O and Mo₂(CN)₆(dppm)₂ (**11**)·2CH₃NO₂.

	8 ·2CH ₃ CN·2C ₆ H ₆	10 ·2CH ₃ CN·2H ₂ O	11 ·2CH ₃ NO ₂
empirical formula	C ₁₀₄ H ₁₃₄ N ₁₀ P ₄ O ₂ Mo ₂	C ₇₆ H ₉₀ N ₉ P ₄ O ₂ Mo ₂	C ₅₈ H ₅₀ N ₈ P ₄ O ₂ Mo ₂
formula weight	1601.71	1359.25	1206.82
space group	C2/c	C2/c	P $\bar{1}$
a (Å)	27.505(6)	27.353(6)	9.942(2)
b (Å)	18.824(4)	10.741(2)	12.418(3)
c (Å)	23.108(5)	26.149(5)	12.934(3)
α (deg)	90.00	90.00	95.
β (deg)	102.58(3)	107.50(3)	102.58(3)
γ (deg)	90.00	90.00	90.00
V (Å ³)	9909(3)	7327(3)	1516.1(5)
Z	4	4	1
ρ _{calcd} (g/cm ³)	1.339	1.233	1.322
temperature, K	173	173	173
R ₁ ^a	0.0850	0.0602	0.0423
WR ₂ ^b	0.1357	0.1166	0.1049
Goodness-of-fit ^c	1.052	0.927	0.904

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b WR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}; \quad w = 1/\sigma^2(|F_o|)$$

$$^c \text{goodness-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

Table 3.2. Selected Bond Distances (Å) and Bond Angles (°) for [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] (8) · 2CH₃CN · 2C₆H₆

Bond Distances			
Mo(1) – Mo(1A)	2.709(2)	C(1) – N(1)	1.162(12)
Mo(1) – C(1)	2.167(13)	C(2) – N(2)	1.132(11)
Mo(1) – C(2)	2.186(11)	C(3) – N(3)	1.028(12)
Mo(1) – C(3)	2.199(12)	Mo(1) – P(1)	2.474(3)
Mo(1) – C(3A)	2.077(12)	Mo(1) – P(2)	2.470(3)
Bond Angles			
C(2) – Mo(1) – C(1)	81.7(4)	N(3) – C(3) – Mo(1)	117.1(14)
C(3) – Mo(1) – C(1)	163.5(4)	N(3) – C(3) – Mo(1A)	162.8(14)
C(3) – Mo(1) – C(2)	83.0(4)	P(1) – Mo(1) – P(2)	172.85(10)

Table 3.3. Selected Bond Distances (Å) and Bond Angles (°) for [*n*-Bu₄N][Mo₂(CN)₆(dppm)₂] (10) · 2CH₃CN · 2H₂O.

Bond Distance			
Mo(1) – Mo(1A)	2.8299(10)	C(1) – N(1)	1.153(6)
Mo(1) – C(1)	2.181(5)	C(2) – N(2)	1.151(5)
Mo(1) – C(2)	2.155(4)	C(3) – N(3)	1.161(5)
Mo(1) – C(3)	2.252(3)	Mo(1) – P(1)	2.542(1)
Mo(1) – C(3A)	2.032(4)	Mo(1) – P(2)	2.537(1)
Bond Angles			
C(2) – Mo(1) – C(1)	78.47(16)	N(3) – C(3) – Mo(1)	86.2(3)
C(3) – Mo(1) – C(1)	157.64(15)	N(3) – C(3) – Mo(1A)	168.2(3)
C(3) – Mo(1) – C(2)	80.75(15)	P(1A) – Mo(1) – P(2)	174.31(3)

Table 3.4. Selected Bond Distances (Å) and Bond Angles (°) for Mo₂(CN)₆(dppm)₂(11): 2CH₃NO₂

Bond Distances			
Mo(1) – Mo(1A)	2.9357(9)	C(1) – N(1)	1.153(6)
Mo(1) – C(1)	2.176(4)	C(2) – N(2)	1.151(5)
Mo(1) – C(2)	2.251(3)	C(3) – N(3A)	1.161(5)
Mo(1) – C(3)	2.087(4)	Mo(1) – P(1)	2.547(1)
Mo(1) – C(3A)	2.284(3)	Mo(1) – P(2)	2.557(1)
Bond Angles			
C(2) – Mo(1) – C(1)	81.08(11)	N(3) – C(3) – Mo(1)	165.8(3)
C(3) – Mo(1) – C(1)	80.22(12)	N(3) – C(3) – Mo(1A)	82.2(2)
C(3) – Mo(1) – C(2)	159.02(12)	P(1) – Mo(1) – P(2A)	176.90(3)

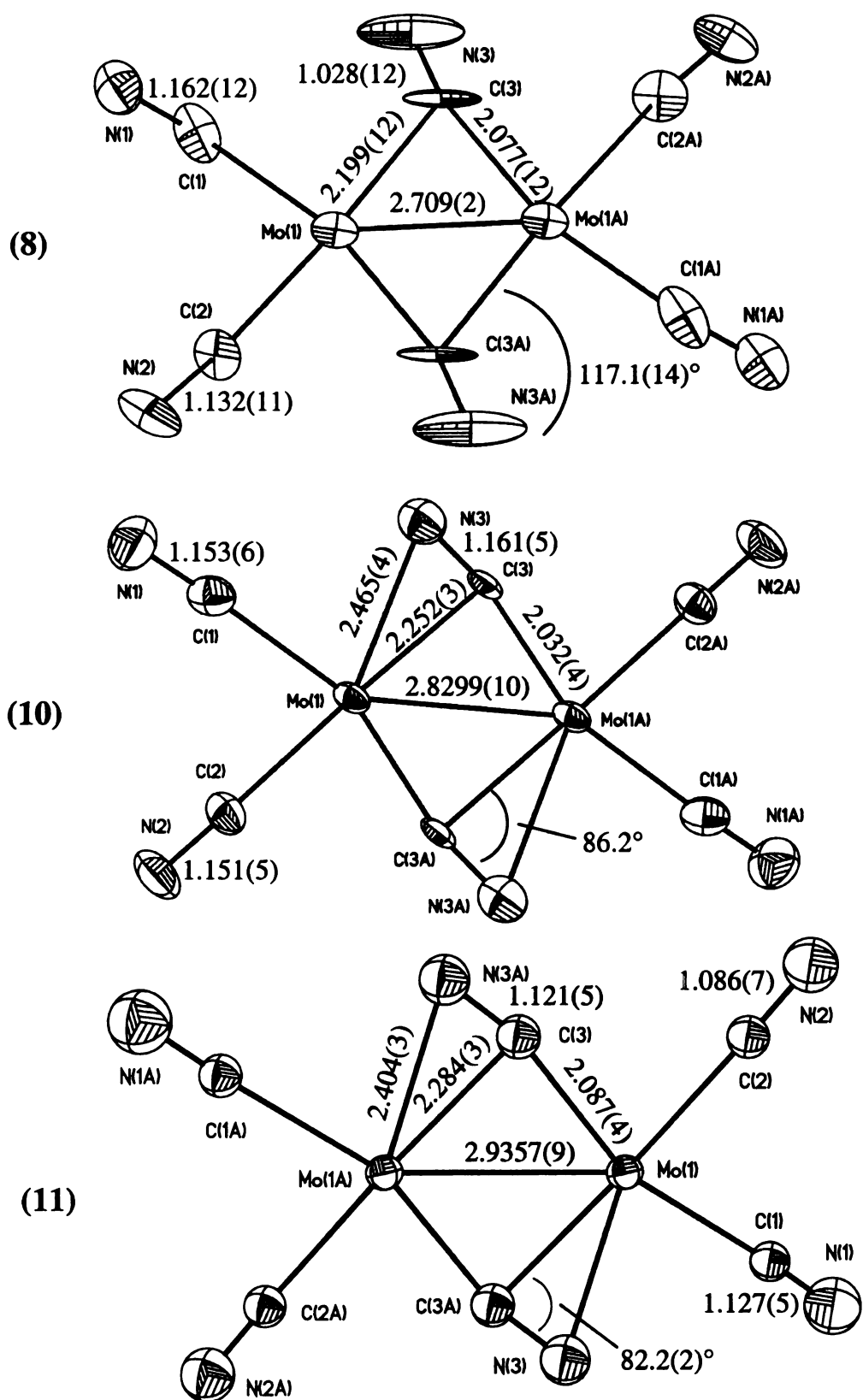


Figure 3.5. Views of the equatorial planes in (8), (10), and (11).

Table 3.5. Comparison of the metrical parameters for the equatorial planes of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (1), $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (3), and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (4).

	$\text{Mo}_2^{\text{II,II}}$ (1)	$\text{Mo}_2^{\text{II,III}}$ (3)	$\text{Mo}_2^{\text{III,III}}$ (4)
Bond Length (Å)			
Mo(1)-Mo(1A)	2.079(2)	2.8299(10)	2.9357(9)
Mo(1)-C(1)	2.167(13)	2.1811(5)	2.176(4)
Mo(1)-C(2)	2.186(11)	2.1554(4)	2.251(3)
Mo(1)-C(3)	2.077(12)	2.032(4)	-----
Mo(1)-C(3A)	-----	-----	2.087(4)
C(3)-N(3)	1.028(12)	1.161(5)	-----
C(3)-N(3A)	-----	-----	1.121(4)
Bond Angle (deg.)			
C(1)-Mo(1)-C(2)	81.7(4)	78.47(16)	81.08(11)
Mo(1)-C(3)-N(3)	117.1(14)	86.2(3)	-----
Mo(1)-C(3)-N(3A)	-----	-----	82.2(2)

Note: The structural solution of $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (4) necessitated the use of a different atom labeling scheme. In situations where this scheme differed between compound (4) and compounds (1) and (3) the corresponding bond length or angle is listed on the next line.

E. Theoretical Methods

Ab initio calculations with relatively large basis sets, including electron correlation using Density Functional Theory (DFT) with the Becke3 hybrid exchange functional¹⁷ and the Lee-Yang-Parr correlation (B3LYP)¹⁸ were carried out using the Gaussian 98 suite of programs.¹⁹ A quasi-relativistic effective core potential (ECP) with a small core (1s 2s 2p 3s 3p 3d) and the basis set of Hay and Wadt²⁰ were used for Mo in conjunction with the Dunning basis set on H, C and N.²¹ The LANL2DZ bases as implemented in G98 were used for the P atoms along with ECP of small core (1s 2s 2p). Extra *d*-polarization functions were supplied for P atoms.²² The multiplicities (2S+1) were restricted to one. Model compounds for (8), (10), and (11) with the phenyl groups of the dppm ligands replaced by hydrogens were employed. The geometries of the complexes were obtained from the corresponding single-crystal X-ray structures. An idealized P–H distance of 1.40 Å was used.

3. Results and Discussion

A. Preparation of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$,

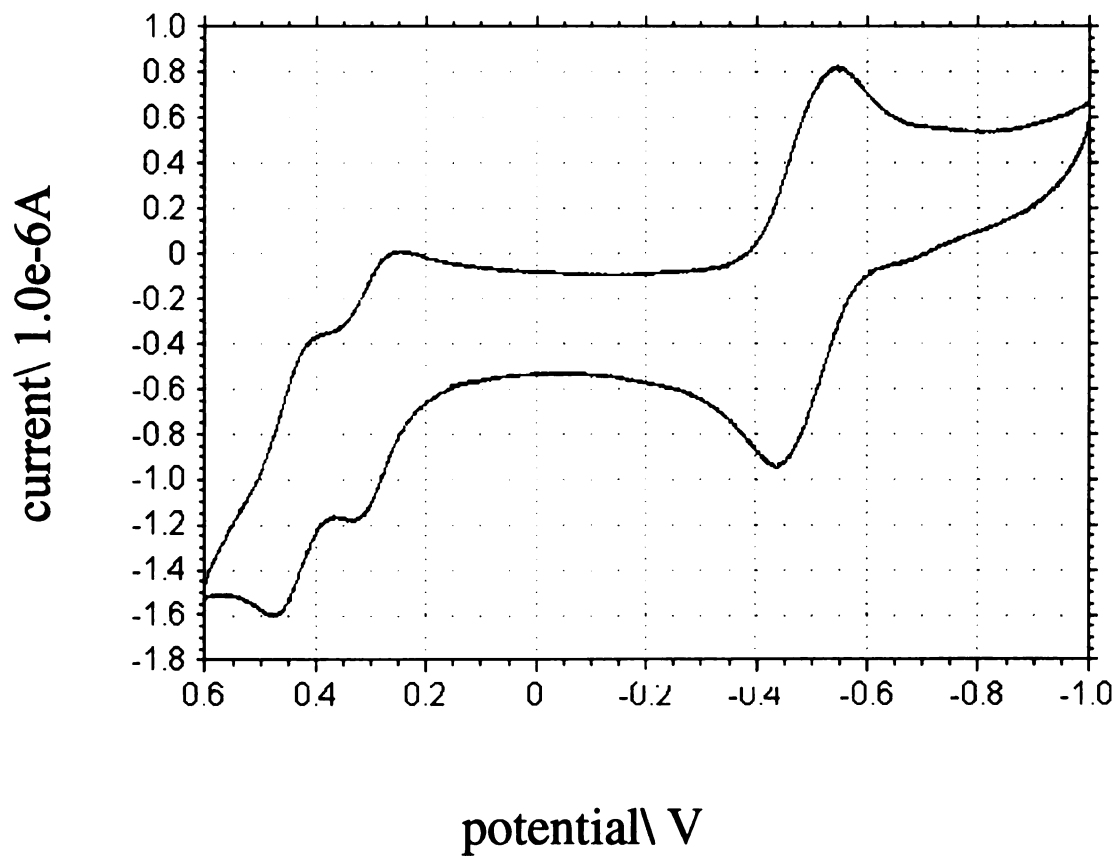
$[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$, and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$

The salt $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_6(\text{dppm})_2]$ was prepared by reacting $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with excess cyanide. The corresponding reaction of

$\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ with excess cyanide proceeds in an analogous fashion. The chloride ligands are displaced by cyanide and the metal complex accepts two additional cyanides that serve to bridge the dimolybdenum core. Prior to structural characterization, the presence of two different cyanide environments was confirmed by infrared spectroscopy (*vide infra*). The data indicated that the bridging cyanides adopt the semi-bridging mode that was observed in the structure of $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_6(\text{dppm})_2]$.

(1) Oxidation of $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$

Although $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) and $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2(\text{CN})_6(\text{dppm})_2]$ are isostructural and isoelectronic, their stabilities are quite different. The dianion $[\text{Re}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ is quite air stable and displays no redox activity by cyclic voltammetry. In contrast, the cyclic voltammogram of $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ (8) (Figure 3.6.) reveals two accessible oxidations. This is presumably the reason why $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ (8) slowly decomposes in dichloromethane to a green product which has not been isolated in sufficient purity to enable its identification, but whose color strongly supports that oxidation is occurring. This decomposition does not appear to occur in acetonitrile but efforts to prepare $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ (8) in acetonitrile lead only to the production of oily intractable products.



$$E_{1/2} = 0.448 \text{ V}$$

$$E_{1/2} = 0.291 \text{ V}$$

$$E_{1/2} = -0.490 \text{ V}$$

Figure 3.6. Cyclic voltammogram of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) in 0.1M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ /acetonitrile at a Pt disk electrode with a Pt wire auxiliary electrode and a Ag/AgCl reference electrode.

The observation that $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ decomposes in air prompted us to use deliberate chemical means to prepare the oxidation products represented in the electrochemistry. The one-electron oxidation product, $[n\text{-Bu}_4\text{N}][\text{Mo}_2^{\text{II,III}}(\text{CN})_6(\text{dppm})_2]$ (10), was prepared by reaction of an acetonitrile solution of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2]$ cooled to $-15\text{ }^\circ\text{C}$ with 1.2 equivalents of either NOBF_4 or $[\text{Cp}_2\text{Fe}][\text{BF}_4]$. All attempts to perform this reaction at room temperature led to a mixture of $[n\text{-Bu}_4\text{N}][\text{Mo}_2^{\text{II,III}}(\text{CN})_6(\text{dppm})_2]$ (10) and additional products which could not be isolated.

The two-electron oxidation product, $\text{Mo}_2^{\text{III,III}}(\text{CN})_6(\text{dppm})_2$ (11), was prepared under analogous conditions by using 2.2 equivalents of NOBF_4 . A small amount of red-purple precipitate was observed to form in this reaction which was too small in quantity to allow for characterization. It was removed by filtration through Celite.

B. Physical Methods Characterization of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8), $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10), and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11)

(1) Mass Spectrometry Studies

No evidence for the formation of partially substituted compounds was observed in the preparation of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8). Fast-atom bombardment (FAB) mass spectrometry in both nitrobenzyl alcohol and

glycerol matrices was conducted to investigate the possibility of incomplete cyanide/chloride metathesis. The mass spectra showed no evidence for the isotopic pattern characteristic of chlorine. Since $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10) and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) are prepared directly from (8), the purity of the parent compound ensures that the other two will also be free of chloride ligands. A peak at 1360 m/z corresponding to the ion $[\text{HMo}_2(\text{CN})_6(\text{dppm})_2]^{1-}$ was present in the negative ion FAB mass spectrum of (8).

(2) Cyclic Voltammetry Study of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$, (8)

Cyclic voltammetry was used to probe the redox properties of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8). Measurements were made in 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ acetonitrile solutions at a Pt disk electrode with a Ag/AgCl reference electrode. Under these experimental conditions, the ferrocene/ferrocenium couple occurs at $E_{1/2}(\text{Cp}_2\text{Fe}/[\text{Cp}_2\text{Fe}]^+) = 0.455$ V. Two oxidation waves $E_{1/2}(\text{ox})$ at +0.29(60) V and 0.45(70) V were observed along with a two-electron reduction $E_{1/2}(\text{red})$ at -0.49 (60) V. The separation of 160 mV between the two successive oxidations allows for the isolation of the mixed-valence complex. The compound $[\text{FeCp}_2][\text{BF}_4]$, which has a couple at 0.46 V under similar experimental conditions, was used to oxidize the $\text{Mo}^{\text{II,II}}$ complex to $\text{Mo}^{\text{II,III}}$ in complex (10). Although both the mixed-

valence complex **3** and the two-electron oxidation complex (11) could be isolated by using NOBF₄, the latter complex could not be obtained by the reaction of (8) with [FeCp₂][BF₄]. The potential that is required for the second oxidation is comparable to [FeCp₂][BF₄], but was achievable only by using NOBF₄. The origin of the two-electron reduction wave has not been established, but is presumed to be due to reduction of the Mo₂ unit.

(3) Infrared, Nuclear Magnetic Resonance, and Electronic Absorption Spectroscopic Studies

Prior to X-ray structural characterization, the presence of two cyanide environments in [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] (8) was confirmed by infrared spectroscopy and rationalized on the basis of group theoretical arguments and literature precedence. The localized D_{2h} symmetry of the four terminal cyanide ligands would be expected to give rise to two IR active vibrational modes (B_{1u} and B_{3u}). The ν_{CN} modes occur at 2094 and 2079 cm⁻¹ for the terminal cyanides and at 1936 cm⁻¹ for the bridging cyanides.

An infrared spectrum of crystals of [*n*-Bu₄N][Mo₂(CN)₆(dppm)₂] (10) exhibits two features at 2108 and 1807 cm⁻¹. The lack of a second stretch in the higher energy region implies that the symmetric and anti-symmetric stretches for the four terminal cyanides are degenerate. The ν_{CN} mode at

1807 cm^{-1} for the bridging cyanide in (10) represents a decrease of 129 cm^{-1} from the μ -cyano ν_{CN} observed in $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8).

The infrared spectrum of $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) exhibits ν_{CN} modes at 2110 and 2102 cm^{-1} for the terminal cyanides and a single feature at 1807 cm^{-1} for the bridging cyanide ligands. The removal of an additional electron from the $\text{Mo}_2^{\text{II,III}}$ core of $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10) lifts the degeneracy of the symmetric and anti-symmetric stretches of the terminal cyanides. The pronounced decrease in the ν_{CN} stretch from 1936 to 1807 cm^{-1} that was observed with the one electron oxidation of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) to (10) is not mimicked in the one electron oxidation of (10) to $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11). The ν_{CN} mode for the bridging cyanide in both (10) and (11) is $\sim 1807 \text{ cm}^{-1}$.

The observed increase in energy of the ν_{CN} modes for the terminal cyanides that accompanies oxidation of the dimolybdenum core from $\text{Mo}_2^{\text{II,II}}$ (2094, 2079 cm^{-1}) to $\text{Mo}_2^{\text{II,III}}$ (2108 cm^{-1}) and $\text{Mo}_2^{\text{III,III}}$ (2110, 2102 cm^{-1}) is consistent with the expected trend for π -acid capable ligands. As the Mo oxidation state increases, less electron density is available for donation to the π^* LUMO of cyanide through π -backbonding interactions. In contrast, the ν_{CN} modes for the bridging cyanides decrease as the Mo oxidation state increases. The semi-bridging mode exhibited in the structures of (8), (10),

and (11) requires attachment to one Mo through a σ interaction from the C end of cyanide and coordination to the other Mo through a side-on π interaction. This donation of π -electron density weakens the $C\equiv N$ and consequently lowers the frequency at which the mode corresponding to that stretch appears in the IR spectrum. The nature of this interaction and how its influenced by the oxidation state of the dimolybdenum core is examined more extensively in the proceeding sections which present a comparison of the structures of (8), (10), and (11) and the results of the computational studies carried out for $[Mo_2(CN)_6(dppm)_2]^{2-}$ (8) and $Mo_2(CN)_6(dppm)_2$ (11).

The 1H NMR spectrum of $[n-Bu_4N]_2[Mo_2(CN)_6(dppm)_2]$ (8) is typical of bis-dppm compounds with a symmetrical distribution of ligands in the equatorial plane.²³ The pentet for the methylene bridge of *trans* bis-dppm was identified at 4.08 ppm. The pentet arises from virtual coupling of the four equivalent methylene protons with four equivalent P nuclei. Multiplets for the dppm phenyl groups were observed at 7.60 and 6.96 ppm. The $^{31}P\{^1H\}$ spectrum of (8) recorded in acetonitrile at 22 °C relative to 85% H_3PO_4 showed a singlet at 25.5 ppm.

In accord with the assignment of the mixed valence $Mo_2^{II,III}$ core, the 1H NMR spectrum of $[n-Bu_4N][Mo_2(CN)_6(dppm)_2]$ (10) contained only broad signals indicative of paramagnetism. Likewise, the ^{31}P NMR spectrum

exhibited no signal. The poor solubility of $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (11) prevented analysis by NMR methods.

Electronic d-d transitions for $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) occur at 553 and 333 nm with ϵ values of 1.9×10^3 and $3.4 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ respectively. Electronic d-d transitions for $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$, (10) occur at 420 and 780 nm with ϵ values of 800 and $1.2 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ respectively. Since compounds (8) and (10) constitute the only examples of anionic Mo_2 (ESBO) compounds, assignments of these transitions cannot be made by analogy to similar compounds. The chromophores of the compounds located at 333 and 553 nm for (8) and 429 and 780 nm for (10) provide a convenient means for verifying the purity of samples of $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$, (10). Due to the solubility limitations of $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (11), analysis by UV-visible spectroscopic methods was not possible.

C. Spectroscopic Studies of $\text{Ni}(\text{en})_2\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (12)

The infrared spectrum of $\text{Ni}(\text{en})_2\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (12) exhibited a broad ν_{CN} mode at 2096 cm^{-1} and a more narrow feature at 1936 cm^{-1} . The presence of the lower energy mode is characteristic of the bridging cyanide in the $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ anion. The shift of the sharp terminal ν_{CN} modes of 2091 and 2080 cm^{-1} in (8) to the broad 2096 cm^{-1} feature observed

in (12) indicates that the Ni ion is coordinated to the terminal cyanides. This is further supported by the absence of the characteristic ν_{CN} modes of the bound acetonitrile in the $[\text{Ni}(\text{en})_2(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$ starting material. The neutrality of the product is inferred by the lack of the ν_{PF} modes in the infrared spectrum characteristic of $[\text{PF}_6]^-$. Magnetic susceptibility studies of (12) yielded a μ_{eff} value of 2.90 B. M. with $g = 2.05$. Plots of χT vs T and $1/\chi$ vs T are presented in Figure 3.9. These data are in good agreement with the proposed structure (Figure 3.8) of a 1-dimensional chain with alternating $[\text{Ni}(\text{en})_2]^{2+}$ and $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ units. The Ni^{II} centers are d^8 and octahedrally coordinated, which would be expected to produce a spin value of $S = 1$ for each Ni center. The observed μ_{eff} value is in the range expected for isolated, *i.e.* non-interacting, $S = 1$ spin centers. Thus, the equatorial plane of $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ acts as a bridge but does not enable magnetic communication to occur between the nearest neighbor Ni^{II} centers.

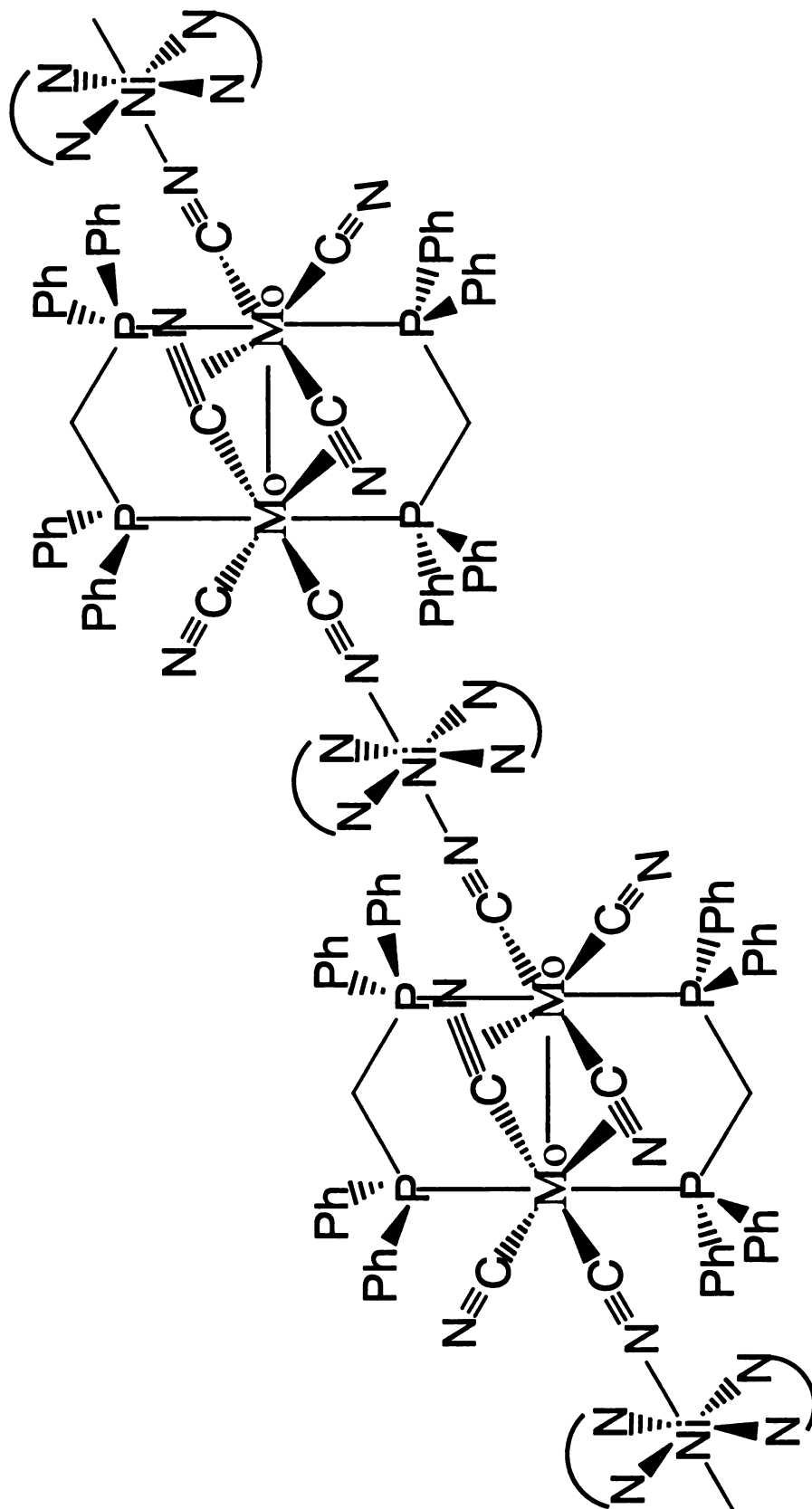


Figure 3.7. A segment of one possible structure for $\text{Ni(en)}_2\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (12)

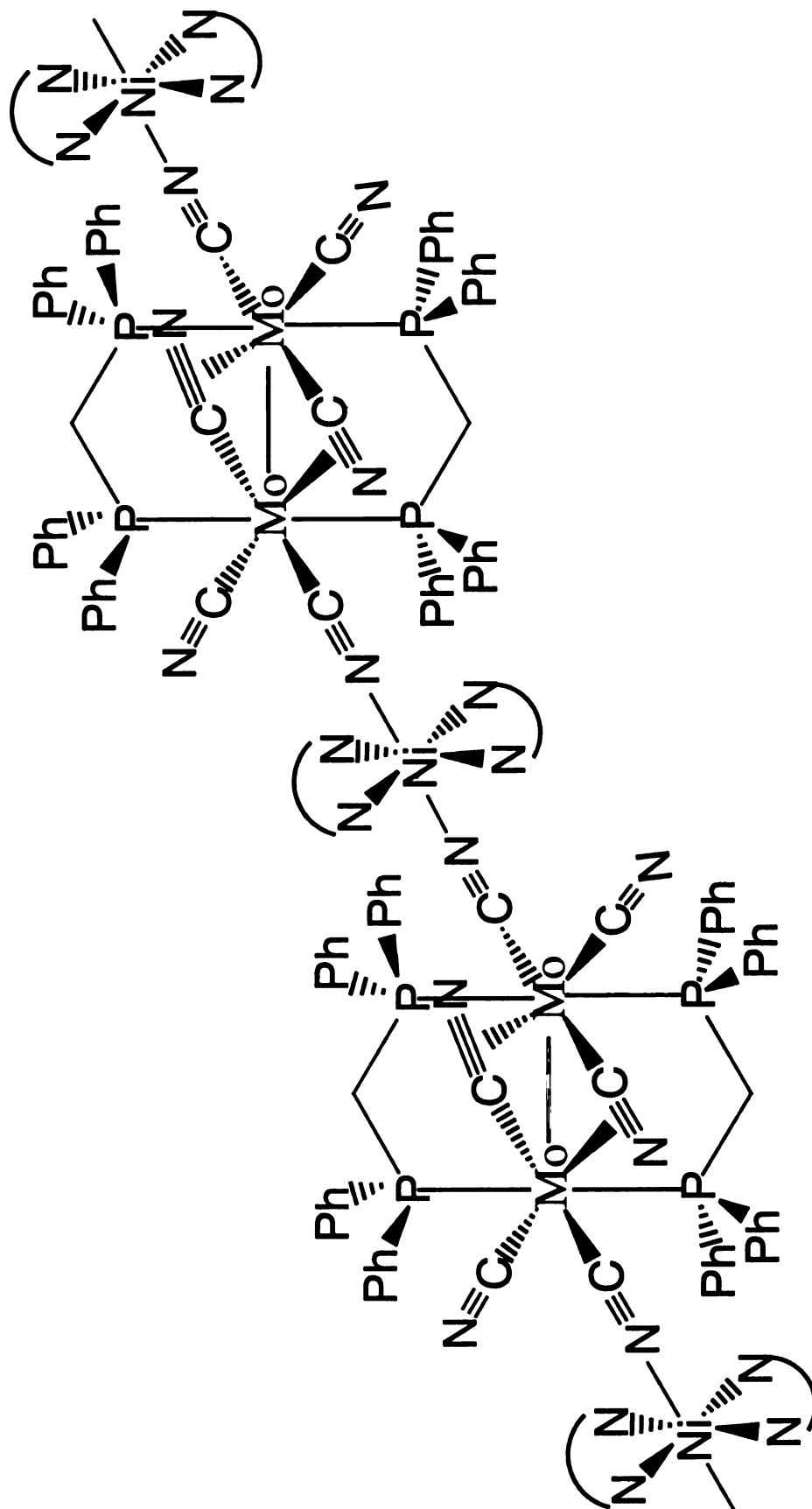


Figure 3.7. A segment of one possible structure for $\text{Ni}(\text{en})_2\text{Mo}_2(\text{CN})_6(\text{dppm})_2$, (12)

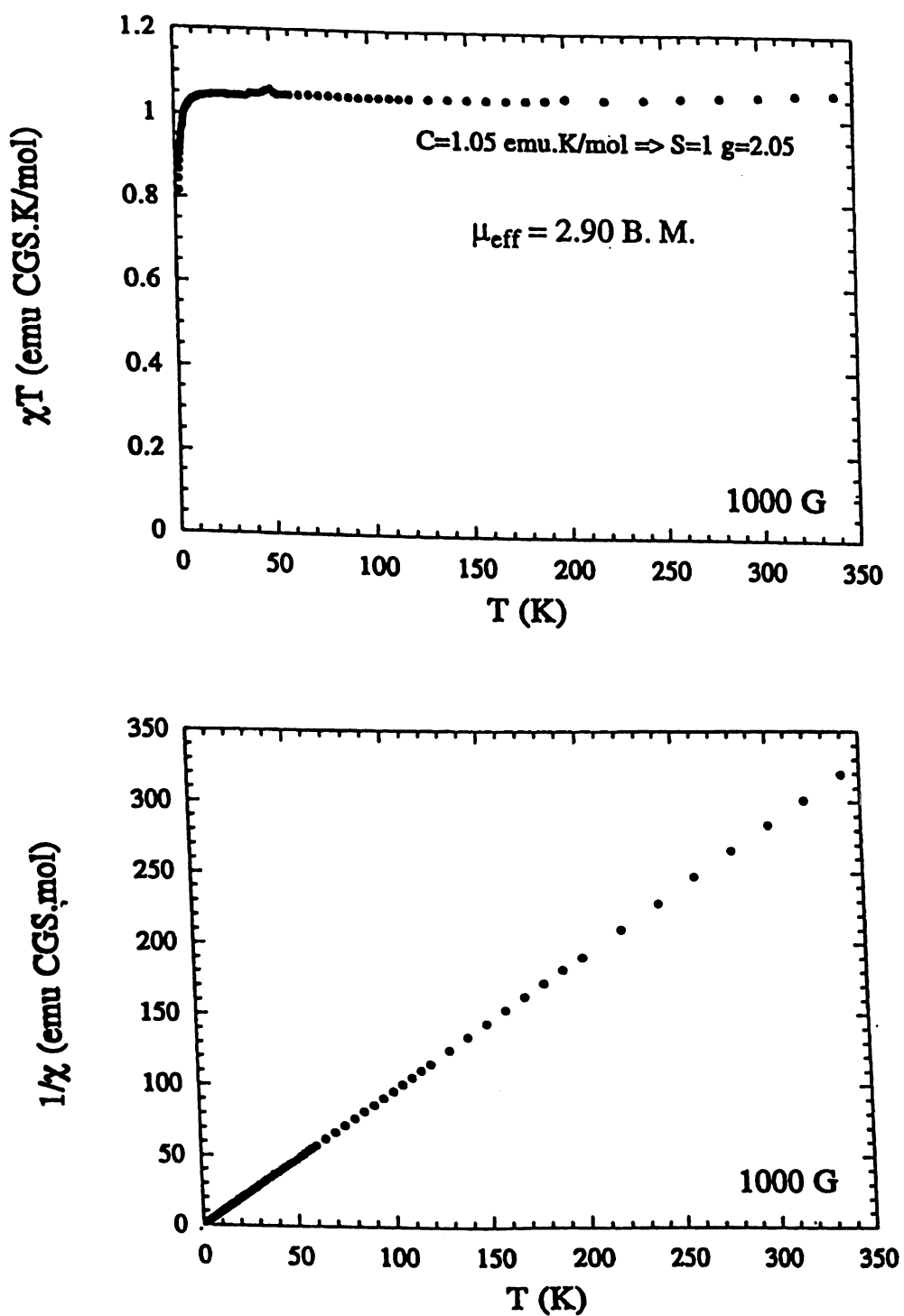


Figure 3.8. Plots of χT (emu CGS.mol) vs. temperature (K) and $1/\chi$ (emu CGS.mol) vs. temperature (K) for $\{\text{Ni}(\text{en})_2\text{Mo}_2(\text{CN})_6(\text{dppm})_2\}_n$ (12)

D. Molecular Structures

The molecular anions of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8), $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10), and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) consist of *trans*-dppm ligands that bisect an equatorial plane containing two molybdenum atoms as well as four terminal and two bridging cyanide ligands. In (8), the bridging ligands are coordinated through the carbon atom to the Mo-Mo unit in a slightly unsymmetrical fashion, whereas in (10) and (11) the binding mode is best described as semi-bridging with a nearly linear Mo(1A)-C(10) σ -bond and a side-on π interaction between C(10)N(10) and Mo(8). A schematic of this interaction is depicted in Figure 3.10.

A comparison of the metrical parameters associated with the bridging cyanides in $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) and $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10) illustrates the effect on these bonding interactions with reduction of the $\text{Mo}_2^{\text{II,II}}$ core to $\text{Mo}_2^{\text{II,III}}$. The different orientations of the bridging ligands in the two compounds are best appreciated by inspection of the Mo1-C3-N3 angles which are 117.1 (14)° and 86.2(10)° in (8) and (10) respectively. It is apparent from these structural differences, and from the bridging ν_{CN} mode which is lowered from 1936 cm^{-1} in (8) to 1807 cm^{-1} in (10), that oxidation of the Mo_2^{4+} core to Mo_2^{5+} is accompanied by an increase in π -bonding from the bridging

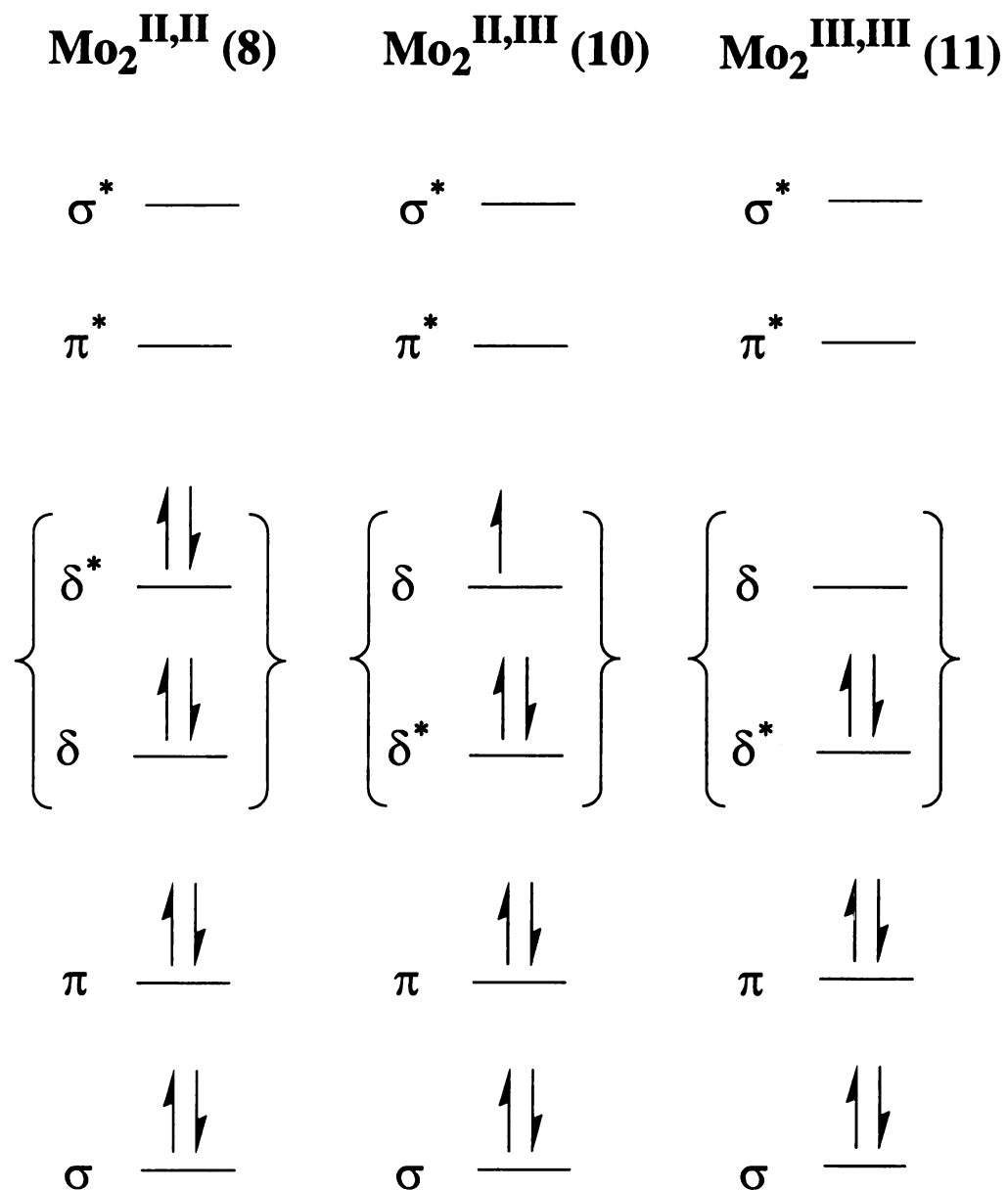


Figure 3.9. A schematic representation of the electronic configurations of compounds (8), (10), and (11).

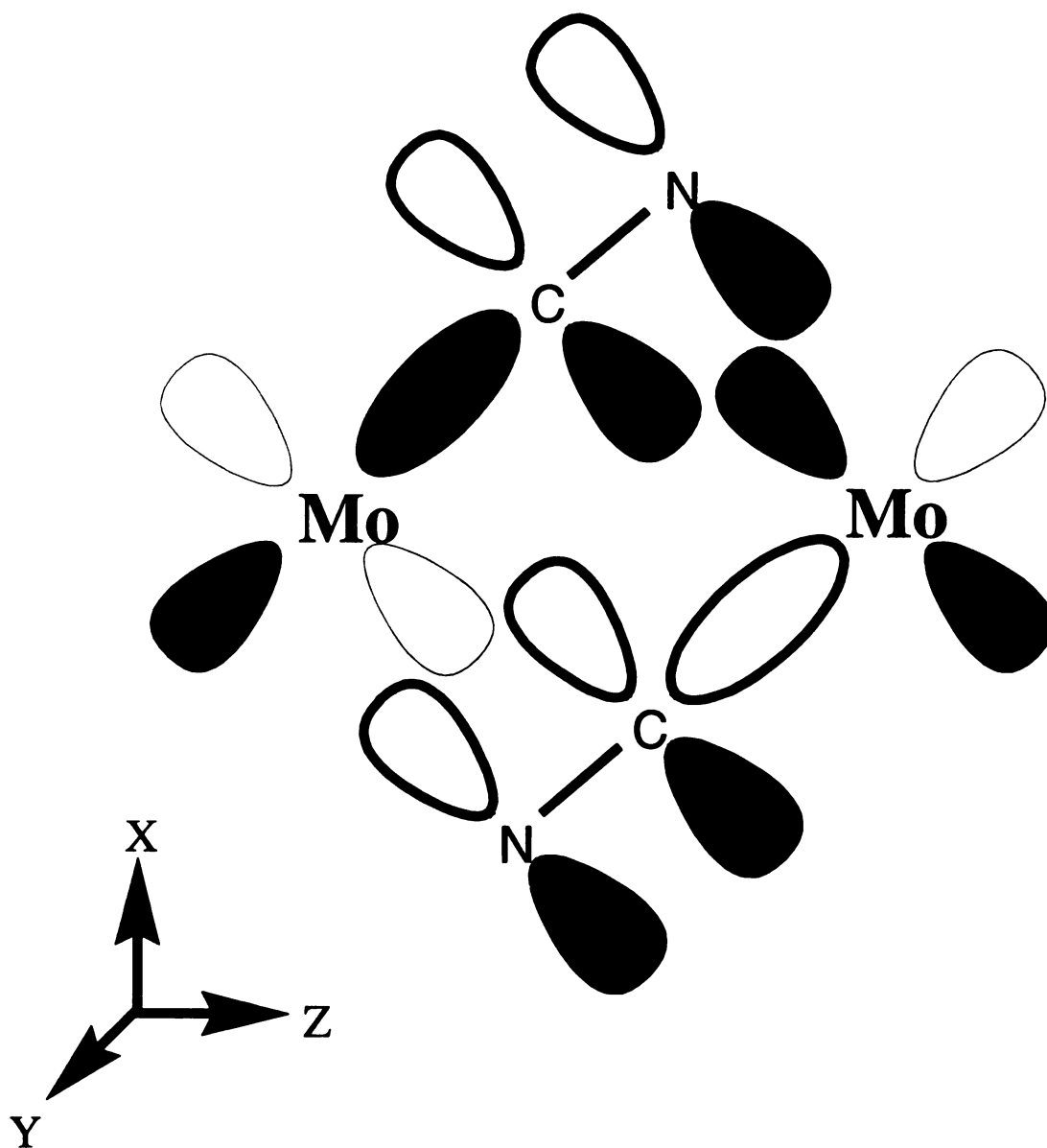


Figure 3.10. A schematic representation of the semi-bridging mode of cyanide with the molybdenum based d_{xz} orbitals interacting with the $p_x + p_x$ π bonding M.O. of the cyanide.

cyanide to the metal centers. A comparison of selected metrical parameters for $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8), $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10), and $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) is presented in Table 3.7.

Although the data set for $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) is of a lower resolution than that of $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10), a comparison of the metal-ligand bonding environment of the two compounds is nonetheless informative. According to the established M. O. bonding scheme for ESBO compounds, the electronic configurations of the $\text{Mo}_2^{\text{II,II}}$ and $\text{Mo}_2^{\text{II,III}}$ compounds are $\sigma^2\pi^2(\delta\delta^*)^4$ and $\sigma^2\pi^2(\delta\delta^*)^3$ respectively.^{8,9} Since the δ and δ^* orbitals are considered weak interactions and may even be reversed in their energies, a bond order of approximately two would be predicted for both. The increase in the metal-metal bond length in the Mo_2^{5+} compound versus the Mo_2^{4+} compound (2.8299(10) Å versus 2.709(9) Å) is attributed to an interaction between the semi-bridging cyanides and the molecular orbitals of the metal-metal bond. A detailed description of this interaction is provided with the results of the computational studies.

The increase in π -bonding from the bridging cyanide to the metal centers that accompanies oxidation of the Mo_2^{4+} core to Mo_2^{5+} is far more pronounced than the analogous increase that is observed upon oxidation of the Mo_2^{5+} core to Mo_2^{6+} (Figure 3.5). A comparison of the structures of $[n$ -

Bu₄N][Mo₂(CN)₆(dppm)₂] (10) and Mo₂(CN)₆(dppm)₂ (11) reveals that the orientations of the bridging ligands in those two compounds are only slightly different. The Mo(8)-C(10)-N(10) angle is 86.2(10)° in (10) and the equivalent angle in (11) Mo(8)-C(3A)-N(10) is 82.2(11)°. ²⁴ This similarity is also reflected in the energy of the bridging ν_{CN} mode, which is 1807 cm⁻¹ for both compounds. Despite this, the Mo-Mo distance in Mo₂(CN)₆(dppm)₂ (11) is increased to 2.9357(8) Å from 2.709(9) and 2.8299(10) Å for [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] (8), and [*n*-Bu₄N][Mo₂(CN)₆(dppm)₂] (10) respectively. The interactions between the semi-bridging cyanide and the molecular orbitals of the Mo-Mo bond would produce this result and, in fact, the computational studies presented support this hypothesis. An additional contributing factor could be d-orbital contraction resulting from the increase in positive charge of the dimolybdenum core that occurs with oxidation of the Mo₂^{II,III} core of (10) to Mo₂^{III,III} for Mo₂(CN)₆(dppm)₂ (11).

**E. Computational study of [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] (8),
and Mo₂(CN)₆(dppm)₂ (11)**

To gain a better understanding of the electronic structure and bonding in [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] (8) and Mo₂(CN)₆(dppm)₂ (11) computational studies were conducted. According to the established M.O. bonding scheme for ESBO compounds, the electronic configurations of the Mo₂^{II,II} (8) and

Mo₂^{III,III} (10) compounds are $\sigma^2\pi^2(\delta\delta^*)^4$ and $\sigma^2\pi^2(\delta\delta^*)^2$ respectively (Figure 6).^{8,9} The δ and δ^* are considered to be weak interactions, and may even be reversed in their energies. In accord with the bonding scheme, the computational studies predict that the HOMO and HOMO-1 levels for the Mo₂^{II,II} compound (8) are the δ^* and δ levels (Figure 3.11). For the compound Mo₂^{III,III} (10) the δ and δ^* M. O.'s are reversed in energy with δ^* as the HOMO and δ as the LUMO.

The contour diagrams of the frontier orbitals of the Mo₂^{II,II} (8) and Mo₂^{III,III} (11) systems are shown in Figure 7. The HOMO (no. 76) of the Mo₂^{II,II} system resembles a δ^* orbital resulting primarily from the out-of-phase interaction of d_{xy} orbitals on the metal atoms. No contribution from the p_x orbitals of N(10) and N(3A) were observed (Figure 7a). The HOMO-1 (no. 75) is a predominantly metal-based δ orbital arising from a bonding interaction between metal d_{xy} orbitals. The p_x orbitals of N(10) and N(3A) are involved in an antibonding interaction with the δ orbital (Figure 7b). The estimated separation between the occupied δ^* and δ orbitals is only 4.07 Kcal/mole. In contrast, the LUMO (No. 76) and HOMO (no. 75) of the Mo₂^{III,III} compound are δ and δ^* type orbitals respectively with an energy separation of 25.97 Kcal/mole. The coefficients of the atomic orbitals

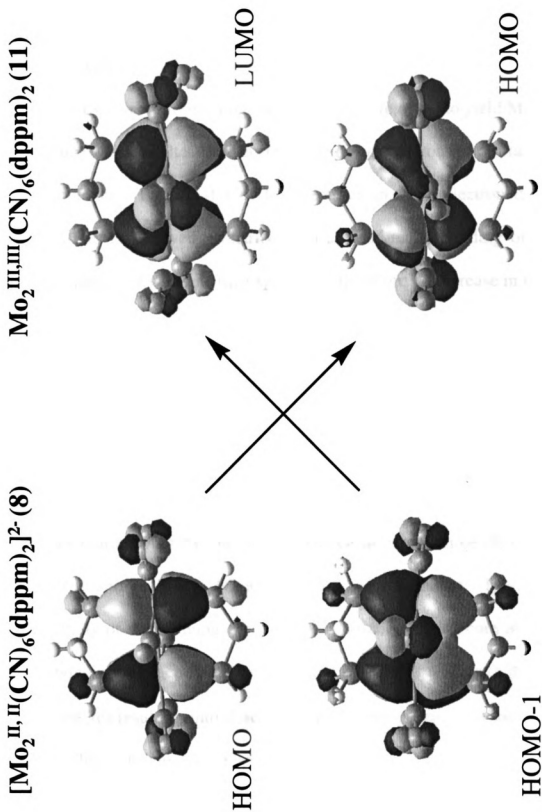


Figure 3.11. Representations of selected molecular orbitals for (8) and (11) as determined by Gaussian 98.

indicate that the HOMO's in (8) and (11) have similar parentage. The same is true for the HOMO-1 and LUMO of the $\text{Mo}_2^{\text{II,II}}$ and $\text{Mo}_2^{\text{III,III}}$ species respectively.

The two electron oxidation of the $\text{Mo}_2^{\text{II,II}}$ core of (8) to yield $\text{Mo}_2^{\text{III,III}}$ (11) produces a clear alteration in the ordering of the frontier orbitals in these compounds. The LUMO of (11) testifies that the electron density, on oxidation, is removed primarily from a metal-metal bonding orbital. The consequence of which is the experimentally observed increase in the metal-metal bond length.

The stabilization of the δ^* orbital and destabilization of the δ orbital on oxidation of $\text{Mo}_2^{\text{II,II}}$ compound (8) is readily understood by considering the interaction of the orbitals of the bridging cyanides with the metal based 4d orbitals. The reduction in the Mo1 – C3A – N3 and Mo1A – C3 – N3A angles that accompany one- and two-electron oxidation of (8) respectively result in shorter Mo1 – N3 and Mo1A – N3A distances. The more close proximity of the bridging cyanides to the dimolybdenum core increases the antibonding interaction of the p_x orbitals of N3 and N3A with the δ orbital (Figure 7c) resulting into destabilization of this orbital. It should be noted here although similar interaction is present in the $\text{Mo}_2^{\text{II,II}}$ compound

(HOMO-1) it is considerably more influential in the oxidized species due to shorter Mo1 – N3 and Mo1A – N3A distances.

The semi-bridging orientation of the bridging cyanides also help in stabilizing the δ^* orbital. The p_x orbitals of the C3A and C3 atoms are involved in a favorable bonding interaction with d_{xy} orbitals of Mo1A and Mo1 respectively (Figure 7d). Such interaction is virtually absent in complex (8) where each cyanide bridges the two metal centers in a nearly symmetric fashion.

The net effect is the stabilization of the HOMO of the $\text{Mo}_2^{\text{II,II}}$ compound such that upon oxidation it remains the HOMO for the $\text{Mo}_2^{\text{III,III}}$ compound. The low-lying HOMO-1 for $\text{Mo}_2^{\text{II,II}}$, on oxidation, experiences destabilizing interactions and becomes the LUMO for $\text{Mo}_2^{\text{III,III}}$. The loss of the δ bonding contribution to the metal-metal bond results in the observed increase of the Mo–Mo distance in $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) vs $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ (8).

4. Conclusions

Under anaerobic conditions, the reaction of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ with $[\text{R}_4\text{N}][\text{CN}]$ ($\text{R} = \text{Et}$ or $n\text{-Bu}$) proceeds with complete displacement of the four chloride ligands and addition of two cyanides to yield $[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2]^{2-}$ (8). The cyanide ligands spanning the dimolybdenum core have adopted a rare semi-bridging mode, with cyanide

bound through a σ bond to one Mo atom through the carbon atom and to the other Mo atom through a side-on π interaction. As evidenced by the cyclic voltammogram. $[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2]^{2-}$ (8) is easily oxidized. The careful use of one and two equivalents of the oxidant NOBF_4 led to the preparation of the one and two-electron oxidation products of (8), viz., $[\text{Mo}_2^{\text{II,III}}(\text{CN})_6(\text{dppm})_2]^{1-}$ (10) and $\text{Mo}_2^{\text{III,III}}(\text{CN})_6(\text{dppm})_2$ (11).

The oxidation state of the dimolybdenum core strongly influences the bonding interactions of the bridging cyanides. The side-on π interaction of the semi-bridging cyanides in the one electron oxidation product $[n\text{-Bu}_4\text{N}][\text{Mo}_2^{\text{II,III}}(\text{CN})_6(\text{dppm})_2]$ (10) are significantly more prominent than in the parent compound $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2]$ (8). The removal of an electron from (10) to give $\text{Mo}_2^{\text{III,III}}(\text{CN})_6(\text{dppm})_2$ (11) further increases the π interaction but only slightly so. The strength of the interaction between the semi-bridging cyanide and the metal-metal bond in (10) as compared to (8) results in a switching of the order of the δ and δ^* orbitals in $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11).

The spatial arrangement of the terminal cyanide ligands in $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8), $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (9) and, $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (10) is such that interactions with Lewis acids to form larger assemblies are possible. The poor solubility of

$\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11) precludes its use in this manner. In this regard, the reaction of (8) with $[\text{Ni}(\text{en})_2(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$ was carried out. The compound $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]$ (8) reacts with $[\text{Ni}(\text{en})_2(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$ to form a product that is formulated as neutral one-dimensional polymer composed of $\{[\text{Ni}(\text{en})_2][\text{Mo}_2(\text{CN})_6(\text{dppm})_2]\}_n$ repeating units. The $[\text{Mo}_2(\text{CN})_6(\text{dppm})_2]^{2-}$ units act as a bridge, but do not enable magnetic communication to occur between the nearest neighbor Ni^{II} centers.

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Chapter IV

Transition metal cyanide and nitrile compounds with

1-(hydro)trispyrazolylborate

1. Introduction

The assembly of molecular precursors to form nanoscale molecules is becoming an active area of research in magnetochemistry.¹ This interest stems from the demonstration of a phenomenon similar to superparamagnetism in large spin paramagnetic clusters that exhibit magnetic anisotropy. Several mixed valence Mn clusters with carboxylate bridges constitute one family of compounds with high ground state spin values that have been prepared for the purposes of investigating single molecule magnetic phenomenon (Figure 1.10).² These have been shown to display properties such as hysteresis and quantum tunneling of the magnetization. Unfortunately, traditional cluster chemistry such as the Mn carboxylate clusters suffers from the limitation that, *a priori*, reliable prediction of the structure and composition of the resulting products is often not possible. An unaddressed synthetic challenge in this area is the design of synthetic routes to high-spin magnetic clusters with predetermined structures. This level of synthetic control was recently demonstrated by the independent work of Rauchfuss (Figures 1.7 and 1.8) and Long (Figure 1.9) in the preparation and crystallization of molecular “boxes” (“cubes”).^{3,4} The corners of the molecules consist of eight metal atoms with bridging cyanides along the sides. The remaining three coordination sites on the metal atom

corners were occupied by the facial capping ligands Cp^* or triazacyclononane (tacn) respectively.

In both previously reported cases the molecular cubes are diamagnetic, being composed of Rh^{III} and Co^{III} in the case of $[(\text{Cp})_4(\text{C}_5(\text{Me})_4\text{Et})_4\text{Co}_4\text{Rh}_4(\text{CN})_{12}][\text{PF}_6]_4$ and Co^{III} in the case of $[(\text{tacn})_8\text{Co}_8(\text{CN})_{12}][\text{CF}_3\text{SO}_3]$. We initiated an effort to prepare paramagnetic heterometallic cubes with both eight and twenty metal atom boxes. The boxes with eight metal atom corners are one expected product from the combination of four “corner” precursors that contain facially arranged dangling cyanides with four “corner” precursors that contain good leaving groups in the same facial arrangement. Displacement of the leaving groups by the nitrogens of the dangling cyanides would result in closure and formation of the desired molecular box. The twenty metal atom boxes would consist of the corner precursors described above, but instead of twelve cyanide edges, the edges consist of units of the type *trans*- $\text{M}(\text{L})_4(\text{CN})_2$. Schematics of the proposed assembly of 8 and 20 metal atom molecular boxes are depicted in Figures 4.1 and 4.2 respectively.

The first step in this chemistry is to prepare the appropriate building blocks. This chapter presents the results of these efforts to prepare divalent and trivalent corner and edge building block compounds. The most

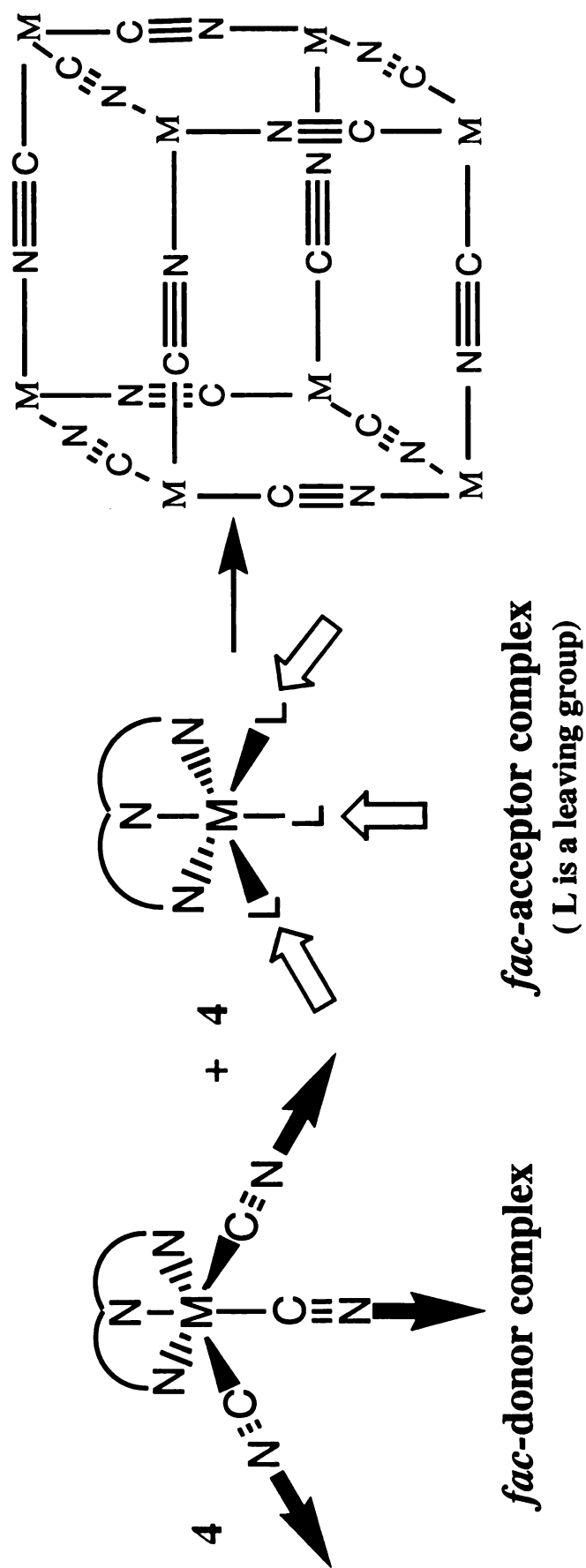


Figure 4.1. Schematic representation of the assembly of an eight metal atom molecular box. The corner capping groups were omitted for the sake of clarity.

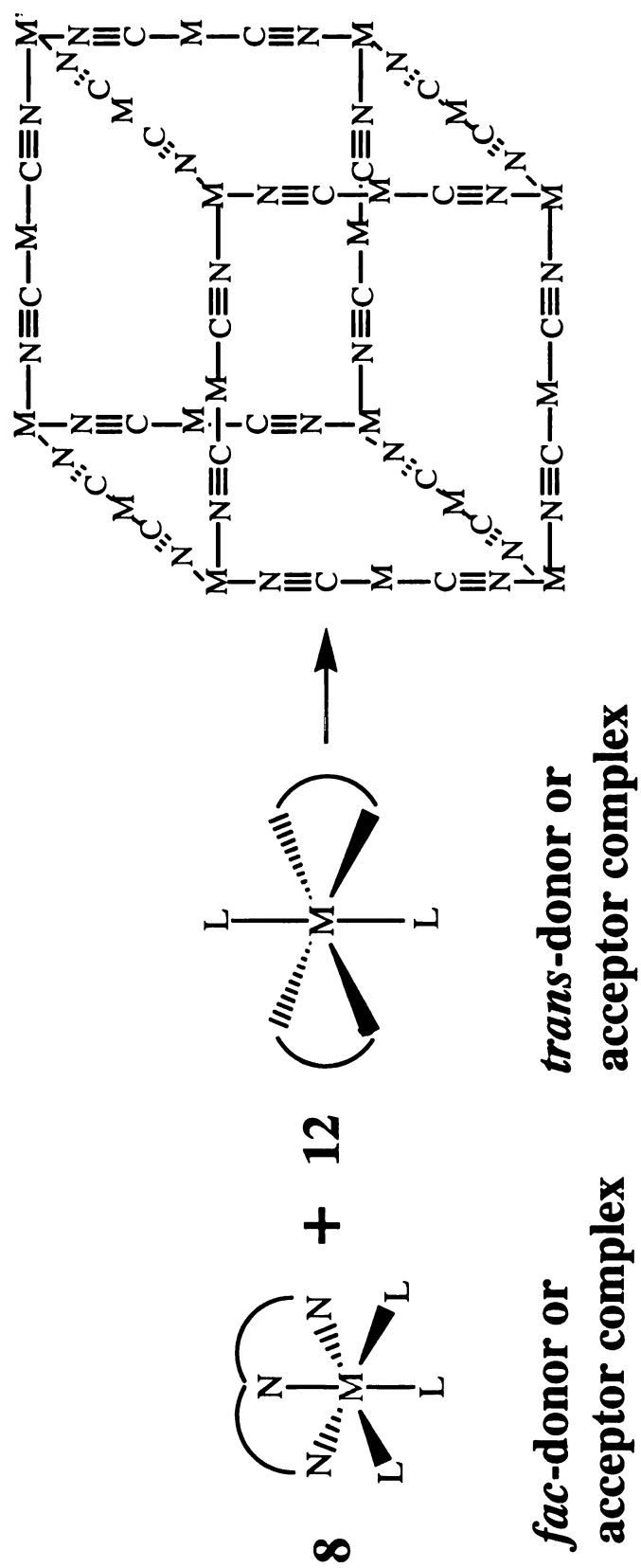


Figure 4.2. Schematic representation of the assembly of a twenty metal atom molecular box. The corner capping groups and bidentate ligands of the edge building blocks were omitted for the sake of clarity.

promising results in the use of these compounds to assemble molecular boxes will also be discussed.

The chapter focuses on building blocks of the metals V^{III} , Cr^{III} , Mo^{III} , Mn^{II} , and Co^{II} . Precursor compounds of Fe^{III} , Fe^{II} , and Ni^{II} will be presented in the dissertation of Jennifer A. Smith another student on the project.²²

2. Experimental

A. Materials

All manipulations were carried out under an inert atmosphere using standard Schlenk-line and dry box techniques. All glassware was flame-dried under vacuum prior to use. Solvents were purified by conventional methods and were distilled under nitrogen prior to use. Acetonitrile solvated transition metal complexes of the type $[M(CH_3CN)_x](PF_6)_2$ ($x = 4, 6$),^{5a} $VCl_3(THF)_3$,^{5b} $CrCl_3(THF)_3$,^{5b} and $MoBr_3(THF)_3$ ^{5c} were prepared according to the literature methods. The reagents KCN, $AgPF_6$, and $TlPF_6$ were purchased from Aldrich and used as received. The facial capping ligand that was used for all the corner precursors is 1-(hydro)trispyrazolylborate (Tp) which was prepared as its $Na[Tp]$ and $K[Tp]$ salts from the literature method.⁶

B. Physical Measurements

Infrared spectra were recorded on solids suspended in Nujol between KBr plates in the range 4000-400 cm^{-1} on a Nicolet IR/42 Spectrometer or between CsI plates in the range between 400-50 cm^{-1} on a Nicolet Magna-IR Series II 750 Spectrometer. Electronic absorption and near-IR spectra were measured on a Shimadzu UV-3101PC UV-Vis-NIR Scanning Spectrophotometer. Magnetic susceptibility measurements in the solid state were performed with the use of a Quantum Design superconducting quantum interference device (SQUID) magnetometer MPMS-5. Data were obtained on polycrystalline samples in the range of 2-300 K at 1000 G. Elemental analyses were performed on a Perkin Elmer Series II CHNS/O Analyzer. Mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility, which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institute of Health.

C. Syntheses

(1) Preparation of $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13) and $\text{K}[(\text{Tp})\text{CrCl}_3]$ (14)

The compound $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13) was prepared by a modification of the literature method reported for $[\text{Ph}_4\text{As}][(\text{Tp})\text{CrCl}_3]$.⁷ A THF solution (30 mL) of $\text{Na}[\text{Tp}]$ (0.063 g, 0.208 mmol) was added to a 30 mL THF solution

of $\text{CrCl}_3(\text{THF})_3$ (0.100 g, 0.268 mmol). The resulting green solution was stirred for thirty minutes and concentrated to 10 mL. Hexanes (10 mL) were added to precipitate a green solid that was collected by filtration, washed with diethyl ether, (3 x 5 mL) and dried *in vacuo*. Yield 0.100 g (95%). $\text{K}[(\text{Tp})\text{CrCl}_3]$ (14) was prepared from the reaction of $\text{CrCl}_3(\text{THF})_3$ (0.100 g, 0.268 mmol) with $\text{K}[\text{Tp}]$ (0.068 g, 0.268 mmol) as described for $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13). Yield 0.105 g (96%). $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13): $\nu_{\text{Cr-Cl}}$: 340 and 330 cm^{-1} ; $\nu_{\text{B-H}}$: 2490 cm^{-1} ; UV-Vis (THF): $\lambda(\text{nm})(\epsilon(\text{M}^{-1}\text{ cm}^{-1}))$ 600 (77); *Anal.* Calcd for $\text{C}_9\text{H}_{10}\text{N}_6\text{Cl}_3\text{B}_1\text{Cr}_1\text{Na}_1$: C, 27.40; H, 2.56; N, 21.30. Found: C, 27.85; H, 2.72; N 21.08. $\text{K}[\text{CrCl}_3(\text{Tp})]$ (14): $\nu_{\text{Cr-Cl}}$: 331 and 310 cm^{-1} ; $\nu_{\text{B-H}}$: 2490 cm^{-1} ; *Anal.* Calcd for $\text{C}_9\text{H}_{10}\text{N}_6\text{Cl}_3\text{BCrK}$: C, 26.33; H, 2.45; N, 20.47. Found: C, 26.95; H, 2.35; N 21.03.

(2) Preparation of $(\text{Tp})\text{MoBr}_2(\text{THF})$, (15)

A THF solution (20 mL) of $\text{Na}[\text{Tp}]$ (0.200 g, 0.850 mmol) was added to a 40 mL THF solution of $\text{MoBr}_3(\text{THF})_3$. The resulting dark yellow solution was refluxed overnight, concentrated to 10 mL, and filtered through Celite. A dark yellow solid was obtained by reducing the solution to dryness *in vacuo*. The solid was extracted with 60 mL of THF and filtered again through Celite. The solution was reduced to dryness, washed with diethyl ether, (3 x 5 mL) and dried *in vacuo*. Yield 0.459 g (75%). $\nu_{\text{Mo-Br}}$: 263 cm^{-1}

¹; $\nu_{\text{B-H}}$: 2480 cm^{-1} ; UV-Vis (THF): $\lambda(\text{nm})(\epsilon(\text{M}^{-1} \text{cm}^{-1}))$ 376 (80.0) 308 (100);

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{N}_6\text{Br}_2\text{B}_1\text{O}_1\text{Mo}_1$: C, 28.87; H, 3.35; N, 15.54. Found: C, 28.40; H, 3.22; N 15.80.

(3) Preparation of $[(\text{Tp})\text{Mn}(\text{CH}_3\text{CN})_3][\text{PF}_6]$, (16) and

$[(\text{Tp})\text{Co}(\text{CH}_3\text{CN})_3][\text{PF}_6]$, (17)

The following procedure works for the preparation of both (16) and (17), the only difference being the use of $[\text{Mn}(\text{CH}_3\text{CN})_4][\text{PF}_6]_2$ (0.438 g, 0.847 mmol) to prepare (16) or $[\text{Co}(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$ (0.457 g, 0.847 mmol) to prepare (17). An acetonitrile solution (30 mL) of Na[Tp] (0.200 g, 0.847 mmol) was added dropwise to a 30 mL acetonitrile solution of the appropriate $[\text{M}(\text{CH}_3\text{CN})_x][\text{PF}_6]_2$ starting material. The solution was then concentrated to ~30 mL and placed in the freezer (-5 °C) overnight to induce complete precipitation of NaPF_6 as a white precipitate. The cold solution was filtered through Celite to remove the precipitate. Diethyl ether (60 mL) was added and the solution was cooled to -5 °C overnight to yield the product $[\text{Mn}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]$ (16) as a white solid or $[\text{Co}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]$ (17) as a yellow-orange solid. Yields 0.215 g (54%) (16) and 0.228 g, (50%) (17). $[\text{Mn}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]$, (16): $\nu_{\text{C}\equiv\text{N}}$: 2312 and 2284 cm^{-1} ; $\nu_{\text{B-H}}$: 2469 cm^{-1} ; $\nu_{\text{P-F}}$: 869 cm^{-1} ; UV-Vis (CH_3CN): $\lambda(\text{nm})(\epsilon(\text{M}^{-1} \text{cm}^{-1}))$ 331 (~1). $[\text{Co}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]$, (17): $\nu_{\text{C}\equiv\text{N}}$: 2315 and

2280 cm^{-1} ; $\nu_{\text{B-H}}$: 2498 cm^{-1} ; $\nu_{\text{P-F}}$: 839 cm^{-1} ; UV-Vis (CH_3CN): $\lambda(\text{nm})(\epsilon(\text{M}^{-1} \text{cm}^{-1}))$ 468 (83.2), 515 (22.5).

(4) Preparation of $[(\text{Tp})\text{Mo}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$, (18)

$[(\text{Tp})\text{Mo}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (18) was prepared by bromide abstraction from $(\text{Tp})\text{MoBr}_2(\text{THF})$ (15). An acetonitrile solution (30 mL) of AgPF_6 (0.205 g, 0.814 mmol) was added to an acetonitrile solution (30 mL) of (15) (0.220 g, 0.407 mmol) and allowed to stir overnight. Aluminum foil was used to exclude light from the reaction. The resulting precipitate was removed by filtration through Celite. The solution was reduced to 10 mL before 30 mL of diethyl ether was added to precipitate the product as a yellow solid. This solid was extracted with acetonitrile (30 mL) and filtered through Celite. Addition of diethyl ether (30 mL) followed by cooling the solution to $-5\text{ }^\circ\text{C}$ overnight led to precipitation of the product, which was collected by filtration, washed with 10 mL of diethyl ether, and dried *in vacuo*. Yield was 0.293 g (79%). $\nu_{\text{C}\equiv\text{N}}$: 2318 and 2284 cm^{-1} ; $\nu_{\text{B-H}}$: 2527 cm^{-1} ; $\nu_{\text{P-F}}$: 841 cm^{-1} ; UV-Vis (CH_3CN): $\lambda(\text{nm})(\epsilon(\text{M}^{-1} \text{cm}^{-1}))$ 455 (broad) (966).

(5) Preparation of $[(\text{Tp})\text{V}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$, (19)

The compound $[(\text{Tp})\text{V}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (19) was prepared by chloride abstraction from $(\text{Tp})\text{VCl}_2(\text{THF})$ which was prepared according to the

literature method.⁸ An acetonitrile solution (40 mL) of $\text{VCl}_2(\text{THF})(\text{Tp})$ (0.320 g, 0.788 mmol) was combined with an acetonitrile solution (30 mL) of TiPF_6 (0.558 g, 1.58 mmol). The procedure described for $[(\text{Tp})\text{Mo}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (18) was also followed for this reaction. A dark yellow solid was recovered to give a yield of 0.320 g (60%). $\nu_{\text{C}\equiv\text{N}}$: 2326 and 2295 cm^{-1} ; $\nu_{\text{B-H}}$: 2532 cm^{-1} ; $\nu_{\text{P-F}}$: 845 cm^{-1} UV-Vis (CH_3CN): $\lambda(\text{nm})(\epsilon(\text{M}^{-1} \text{cm}^{-1}))$ 480 (115) 330 (75).

(6) Preparation of $\text{K}[(\text{Tp})\text{Cr}(\text{CN})_3]$, (20)

A methanol solution (30 mL) of KCN (0.150 g, 2.28 mmol) was added dropwise (about 1 drop/second) with vigorous stirring to a methanol solution (30 mL) of $\text{K}[(\text{Tp})\text{CrCl}_3]$ (14) (0.312 g, 0.760 mmol). Complete addition of KCN produces a cloudy pink solution, which was filtered through Celite and reduced to dryness to give a pink solid. This solid was extracted with 30 mL of acetonitrile and filtered again through Celite. The solution was then concentrated to 5 mL and 25 mL of diethyl ether was added to yield a pink solid. Yield 0.250 g (80%). $\nu_{\text{C}\equiv\text{N}}$: 2135 cm^{-1} ; $\nu_{\text{B-H}}$: 2492 cm^{-1} ; UV-Vis (CH_3CN): $\lambda(\text{nm})(\epsilon(\text{M}^{-1} \text{cm}^{-1}))$ 322 (75), 365 (60), and 410 (45).

(7) Preparation of *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$, (21)

An acetonitrile solution of TiPF_6 (20 mL) (0.150 g, 0.423 mmol) was added to a 20 mL acetonitrile suspension of *trans*- $\text{NiCl}_2(\text{en})_2$ (0.053 g, 0.212

mmol) and allowed to stir overnight. The resulting cloudy blue solution was filtered through Celite and concentrated to 5 mL before 25 mL of diethyl ether was added to precipitate a purple-blue solid. The solid was extracted with 20 mL of acetonitrile and filtered through Celite. Concentration of this solution to 5 mL followed by addition of 30 mL of diethyl ether produced a purple-blue product. The solid was collected by filtration, washed with 10 mL of diethyl ether and dried *in vacuo*. Yield 0.068 g (90%). $\nu_{\text{C}\equiv\text{N}}$: 2312 and 2284 cm^{-1} ; $\nu_{\text{P-F}}$: 880 cm^{-1} ; UV-Vis (CH_3CN): $\lambda(\text{nm})(\epsilon(\text{M}^{-1} \text{cm}^{-1}))$ 880 (65), 536 (75), 339(25).

(8) Reaction of $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13) with MPF_6 ($\text{M} = \text{Ag}^{1+}$ or Tl^{1+})

Reactions of $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13) (0.150 g, 0.380 mmol) were carried out under the same conditions with both AgPF_6 (0.288 g, 1.14 mmol) and TlPF_6 (0.403 g, 1.14 mmol). An acetonitrile solution (30 mL) of MPF_6 ($\text{M} = \text{Ag}^{1+}$ or Tl^{1+}) was added to 30 mL of an acetonitrile solution of $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13) and allowed to stir overnight. Aluminum foil was used to exclude light from the reaction involving AgPF_6 . Both reactions produced cloudy pink solutions that were filtered through Celite and concentrated to 5 mL. Cooling these solutions to $-5\text{ }^\circ\text{C}$ for three days resulted to the deposition of pink crystals. Single crystal X-ray diffraction studies revealed these compounds to be the monohalide abstraction products, $(\text{Tp})\text{CrCl}_2(\text{CH}_3\text{CN})$.

Equivalents of AgPF_6 and TiPF_6 were incorporated into the products from these reactions to give $\{(\text{Tp})\text{CrCl}_2(\text{CH}_3\text{CN})\}_2 \cdot \text{AgPF}_6$ (22) and $\{(\text{Tp})\text{CrCl}_2(\text{CH}_3\text{CN})\}_2 \cdot \text{TiPF}_6$ (23). No other tractable products could be isolated from these reactions.

(9) Reaction of $[(\text{Tp})\text{V}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (19) and 3 $[n\text{-Bu}_4\text{N}][\text{CN}]$

An acetonitrile solution (30 mL) of $[n\text{-Bu}_4\text{N}][\text{CN}]$ (0.339 g, 1.26 mmol) was added dropwise (~1 drop / second) to a 30 mL acetonitrile solution of $[(\text{Tp})\text{V}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (19) (0.285 g, 0.421 mmol). The resulting light orange solution was filtered through Celite and concentrated to 20 mL and cooled to -5°C overnight producing colorless needle shaped crystals. These were determined by a single crystal X-ray diffraction unit cell determination to be $[n\text{-Bu}_4\text{N}][\text{PF}_6]$. The solution was separated by filtration, concentrated to 5 mL, and cooled to -5°C overnight producing a red crystalline product. Single crystal X-ray diffraction revealed these to be $\text{V}(\text{Tp})_2 \cdot 1/3\text{CH}_3\text{CN} \cdot 1/6\text{Et}_2\text{O}$ (24). No other tractable products could be isolated from the reaction.

(10) Reaction of $\text{K}[(\text{Tp})\text{Cr}(\text{CN})_3]$ (20) with $[(\text{Tp})\text{Ni}(\text{CH}_3\text{CN})_3][\text{BF}_4]$ ²²

An acetonitrile solution (30 mL) of $\text{K}[\text{Cr}(\text{CN})_3(\text{Tp})]$ (20) (0.050 g, 0.131 mmol) was added to a 30 mL acetonitrile solution of $[(\text{Tp})\text{Ni}(\text{CH}_3\text{CN})_3][\text{BF}_4]$ (0.063 g, 0.131 mmol). A pink precipitate was

observed to form within 30 seconds. This was collected by filtration and washed with acetonitrile (3 x 5 mL.). Yield 0.035 g. $\nu_{\text{C}\equiv\text{N}}$: 2174 cm^{-1} ; $\nu_{\text{B-H}}$: 2494 cm^{-1} .

D. X-ray Crystallography

Single crystal x-ray structural determinations were performed on a Bruker SMART 1K CCD platform diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The frames were integrated in the Bruker SAINT software package⁹, and the data were corrected for absorption using the SADABS program.¹⁰ The structures were solved using the SHELXTL V.5.10 package.¹¹ Pertinent crystallographic data for $\text{Na}[\text{CrCl}_3(\text{Tp})]$ (13), $(\text{Tp})\text{MoBr}_2(\text{THF})$ (15), $[(\text{Tp})\text{Co}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ (17), $[(\text{Tp})\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$ (21), $(\text{Tp})\text{CrCl}_2(\text{CH}_3\text{CN})\cdot\text{AgPF}_6\cdot 2 \text{ CH}_3\text{CN}$ (22), $(\text{Tp})\text{CrCl}_2(\text{CH}_3\text{CN})\cdot\text{TiPF}_6\cdot 2 \text{ CH}_3\text{CN}$ (23), and $\text{V}(\text{Tp})_2\cdot 1/3\text{CH}_3\text{CN}\cdot 1/6\text{Et}_2\text{O}$ (24) are presented in Tables 4.1-4.7. Thermal ellipsoid plots are provided in Figures 4.3-4.10.

(1) $\text{Na}[(\text{Tp})\text{CrCl}_3]$, (13)

(i) Data Collection and Reduction

Cooling a concentrated THF solution of (13) overnight in dry ice produced green X-ray quality single crystals. A crystal of dimensions 0.22 x 0.31 x 0.35 mm^3 was covered in Paratone oil and mounted on the tip of a

glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a hexagonal cell. A total of 2891 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.10° .

(ii) Structural Solution and Refinement

From the systematic absences, the space group was determined to be $P6_3/m$. The structure was solved by the SHELXS program and refined by full matrix least-squares refinement using the SHELXL97 refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to C(1), C(2), and C(3) of the pyrazol ring were placed in calculated positions. The hydrogen atom on B(1) was identified from the difference map. The crystal diffracted poorly which lead to refinement limitations ($R_{\text{int}} = 0.1121$ and $R_\sigma = 0.1435$). The final cycle of full matrix least squares refinement was based on 3695 observed reflections with $F_o > 4 \sigma(F_o)$ and 93 parameters to give $R1 = 0.1272$ and $wR2 = 0.3441$ and a goodness-of-fit value of 1.113.

The molecular structure of $[\text{CrCl}_3(\text{Tp})]^-$ was identified to be the expected six-coordinate compound. All atoms were located and refined with anisotropic thermal parameters yielding reasonable temperature factors. The high R factors are a consequence of the low data quality and residual

electron density, the magnitude of which suggests the unassigned atoms are carbon, nitrogen, or oxygen. This unassigned electron density localized around the exterior of Na(2) could not be satisfactorily modeled.

(2) (Tp)MoBr₂(THF), (15)

(i) Data Collection and Reduction

Crystals were grown by cooling a concentrated THF solution of (15) overnight at -5°C . A yellow crystal of dimensions $0.23 \times 0.13 \times 0.13 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a monoclinic cell. A total of 8571 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.61° .

(ii) Structural Solution and Refinement

The space group was determined to be $P2_1/n$ from the systematic absences. The structure was solved by the SHELXS structure program using direct methods and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to the pyrazol rings and the atom B(1) were located from the difference map. The THF hydrogen atoms were placed in calculated positions. The final

cycle of full matrix least squares refinement was based on 3695 observed reflections with $F_o > 4 \sigma(F_o)$ and 257 parameters to give $R1 = 0.0315$ and $wR2 = 0.0707$ and a goodness-of-fit value of 1.028.

(3) $[\text{Co}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]$, (17)

(i) Data Collection and Reduction

Crystals were grown by cooling a 50/50 mixture of acetonitrile/diethyl ether solution that contained (17) for several days at -5°C . An orange crystal of dimensions $0.35 \times 0.45 \times 0.50 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection obtained corresponded to a rhombohedral cell. A total of 5453 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.64° .

(ii) Structural Solution and Refinement

From the systematic absences, the space group was determined to be $R\bar{3}c$. The structure was solved by the SHELXS¹⁶ structure program using direct methods and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. Other than atoms F(1) and F(2) all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom bound to B(1), was located from the difference map. All additional hydrogen atoms were placed in calculated positions. The final

cycle of full matrix least squares refinement was based on 962 observed reflections with $F_o > 4 \sigma(F_o)$ and 93 parameters to give $R1 = 0.1443$ and $wR2 = 0.3998$ and a goodness-of-fit value of 2.545. The high R factors are a consequence of a $[PF_6]^-$ disorder that could not be adequately modeled.

(4) *trans*-[Ni(CH₃CN)₂(en)₂][PF₆], (21)

(i) Data Collection and Reduction

Crystals were grown by cooling a concentrated acetonitrile solution of (21) overnight at -5°C . A purple-blue crystal of dimensions $0.50 \times 0.49 \times 0.35 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a monoclinic cell. A total of 2551 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 57.01° .

(ii) Structural Solution and Refinement

The space group was determined to be $P2_1/n$ from the systematic absences. The structure was solved by the SHELXS structure program using direct methods and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to atoms N2 and N3 were located from the difference map whereas the

hydrogen atoms coordinated to C2, C3, and C4 were added in calculated positions. The final cycle of full matrix least squares refinement was based on 2551 observed reflections with $F_o > 4 \sigma(F_o)$ and 149 parameters to give $R1 = 0.0496$ and $wR2 = 0.1427$ and a goodness-of-fit value of 1.094.

(5) (Tp)CrCl₂(CH₃CN)•AgPF₆•2 CH₃CN, (22)

(iii) Data Collection and Reduction

Crystals were grown from cooling a concentrated acetonitrile solution of (22) for three days at $-5\text{ }^{\circ}\text{C}$. A red crystal of dimensions $0.51 \times 0.42 \times 0.43\text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a triclinic cell. A total of 10086 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.68° .

(iv) Structural Solution and Refinement

The space group was determined to be P-1. The structure was solved in the SHELXS program using direct methods and refined by full matrix least-squares refinement using the SHELXL97 refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters and all the hydrogen atoms were added in calculated positions. The final cycle of full matrix least squares refinement was based on 5962 observed reflections with

$F_o > 4 \sigma(F_o)$ and 523 parameters to give $R1 = 0.0618$ and $wR2 = 0.1793$ and a goodness-of-fit value of 1.170.

(6) (Tp)CrCl₂(CH₃CN)•TIPF₆•2 CH₃CN, (23)

(i) Data Collection and Reduction

Crystals were grown by cooling a concentrated acetonitrile solution of (23) for three days at -5°C . A red crystal of dimensions $0.35 \times 0.40 \times 0.20 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a monoclinic cell. A total of 19209 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.67° .

(ii) Structural Solution and Refinement

From the systematic absences, the space group was determined to be Cc. The structure was solved by the SHELXS program using direct methods and refined by full matrix least-squares refinement using the SHELXL97 refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms coordinated to the boron of the Tp groups were located in the difference map whereas all other hydrogen atoms were placed in calculated positions. The final cycle of full matrix least squares refinement was based on 9090 observed reflections with $F_o > 4$

$\sigma(F_o)$ and 531 parameters to give $R1 = 0.0263$ and $wR2 = 0.0587$ and a goodness-of-fit value of 0.965.

(7) $V(Tp)_2 \cdot 1/3CH_3CN \cdot 1/6Et_2O$, (24)

(i) Data Collection and Reduction

Crystals were grown by cooling overnight the concentrated acetonitrile reaction solution containing $[(Tp)V(CH_3CN)_3][PF_6]$ (19) and three equivalents of $[n-Bu_4N][CN]$ at $-5^\circ C$. A dark red crystal of dimensions $0.31 \times 0.17 \times 0.17 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a triclinic cell. A total of 9592 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 57.01° .

(ii) Structural Solution and Refinement

The space group was determined to be P-1. The structure was solved by the SHELXS program using direct methods and refined by full matrix least-squares refinement using the SHELXL97 refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms coordinated to B(1), B(2), and B(3) were located from the difference map whereas all other hydrogen atoms were added in calculated positions. The final cycle of full matrix least squares refinement was based

on 7559 observed reflections with $F_o > 4 \sigma(F_o)$ and 532 parameters to give $R1 = 0.0465$ and $wR2 = 0.1361$ and a goodness-of-fit value of 1.030.

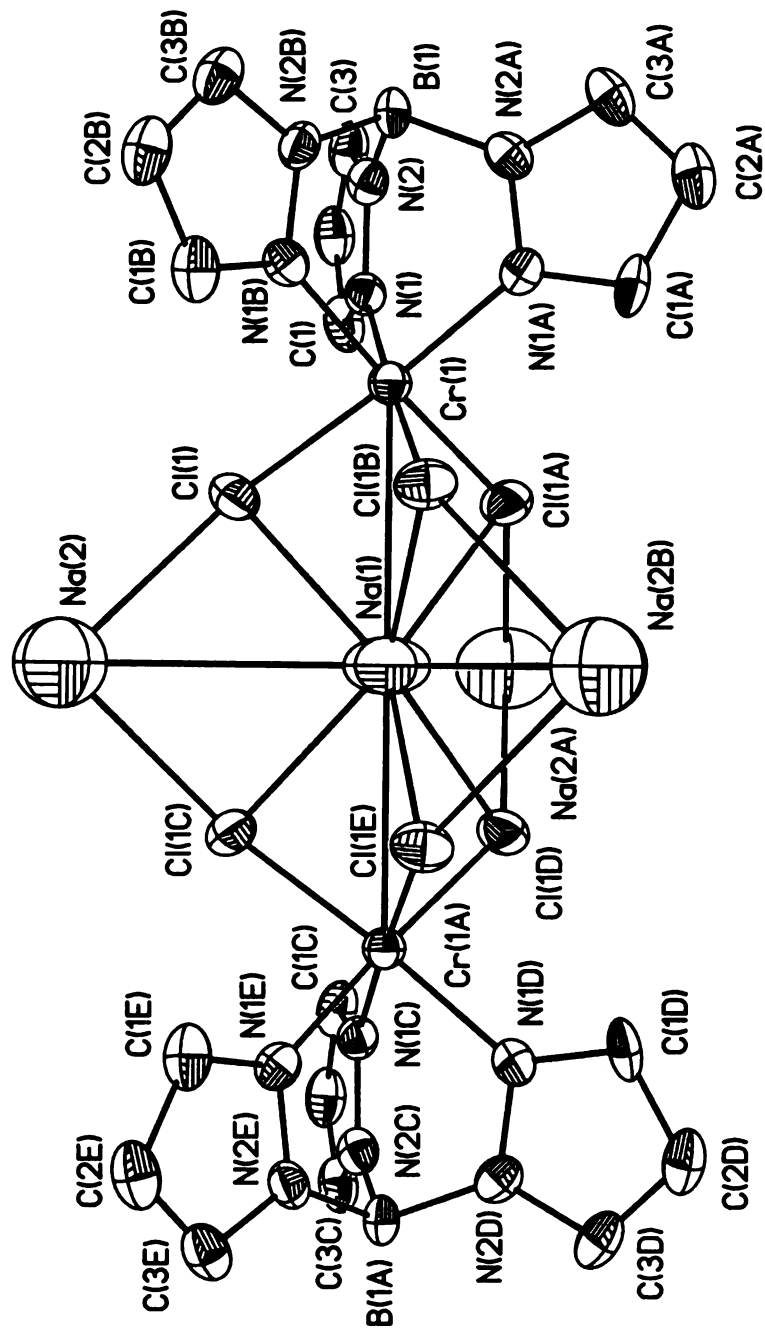


Figure 4.3. Thermal ellipsoid plot of the structure of $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13). All atoms were represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

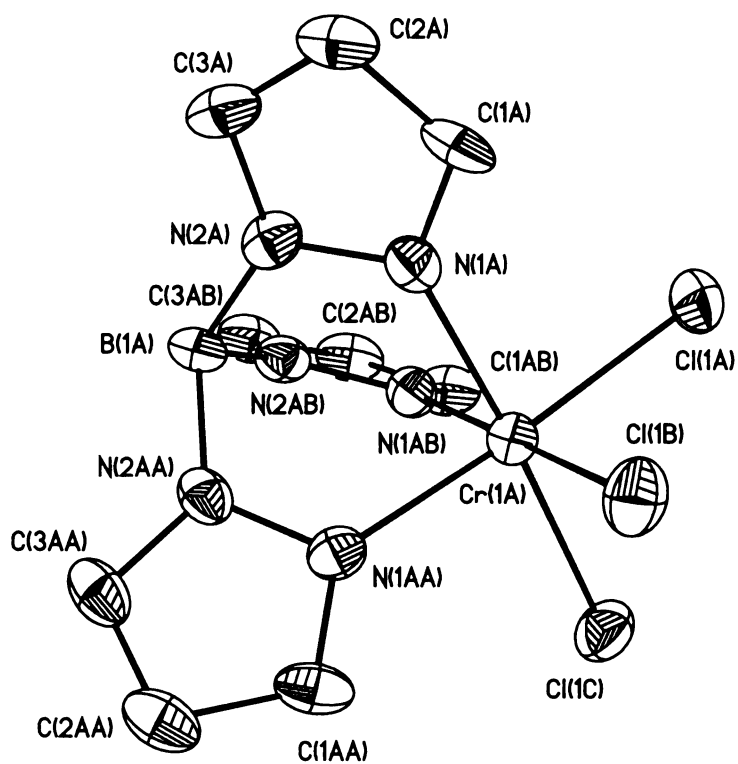


Figure 4.4. Thermal ellipsoid representation of the molecular anion $[(\text{Tp})\text{CrCl}_3]^-$ from (13). All atoms are represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

Table 4.1. Summary of crystallographic data for Na[(Tp)CrCl₃], (13)

formula	C ₉ H ₁₀ N ₆ Cl ₃ B ₁ Cr ₁ Na ₁
formula weight	410.88
space group	P6(3)/m
a, Å	11.4255(16)
b, Å	11.4255(16)
c, Å	22.124(4)
α, deg.	90.00
β, deg.	90.00
γ, deg.	120.00
V, Å ³	2501.2(7)
Z	6
^d calc, g/cm ³	1.762
μ (Mo Kα), cm ⁻¹	1.214
temperature, K	173
trans. factors, max., min.	1.00, 0.757
R ₁	0.1263
wR ₂	0.3078
goodness-of-fit	1.101

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\Sigma w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

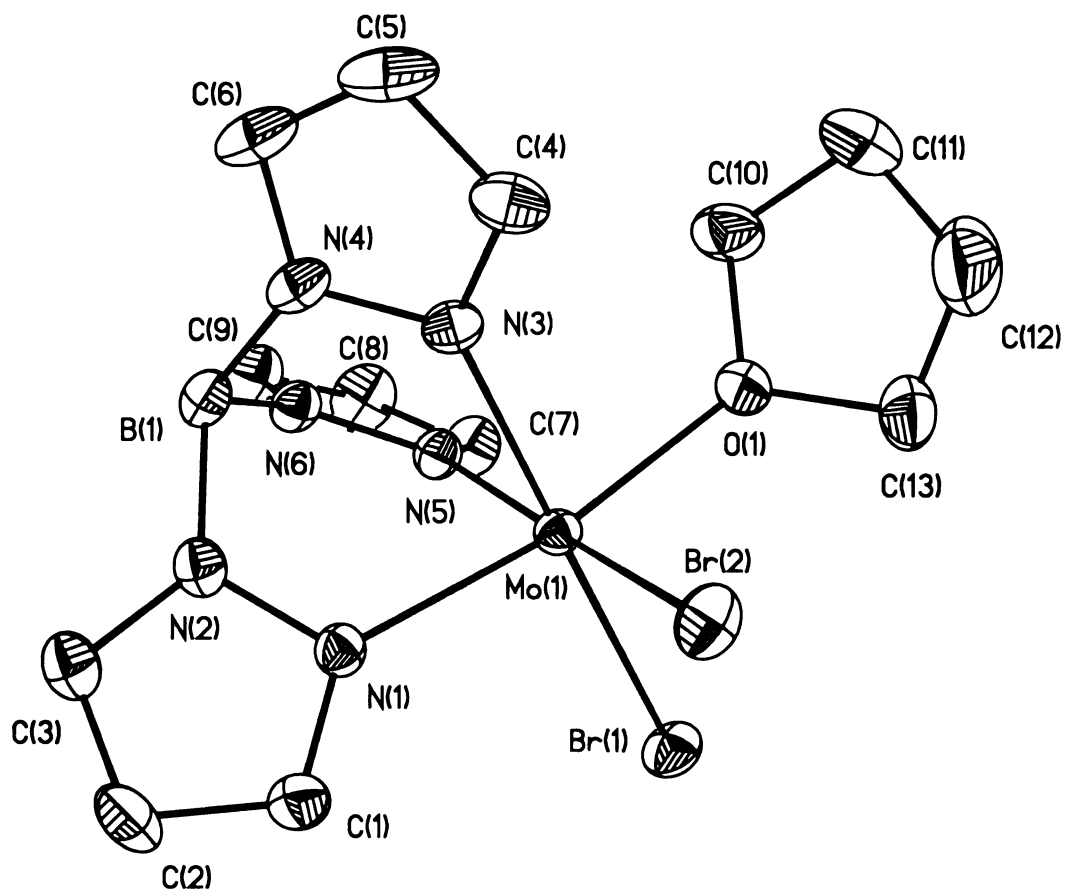


Figure 4.5. Thermal ellipsoid plot of the structure of (Tp)MoBr₂(THF) (15). All atoms are represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

Table 4.2. Summary of crystallographic data for (Tp)MoBr₂(THF), (15)

formula	C ₁₃ H ₂₀ N ₆ B ₁ Br ₂ O ₁ Mo ₁
formula weight	542.92
space group	P2(1)/n
a, Å	9.894(2)
b, Å	12.601(3)
c, Å	15.208(3)
α, deg.	90.00
β, deg.	101.12(3)
γ, deg.	90.00
V, Å ³	1806.5(6)
Z	4
d _{calc} , g/cm ³	1.938
μ (Mo Kα), cm ⁻¹	5.013
temperature, K	173
trans. factors, max., min.	1.00, 0.768
R ₁	0.0315
wR ₂	0.0661
goodness-of-fit	1.028

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

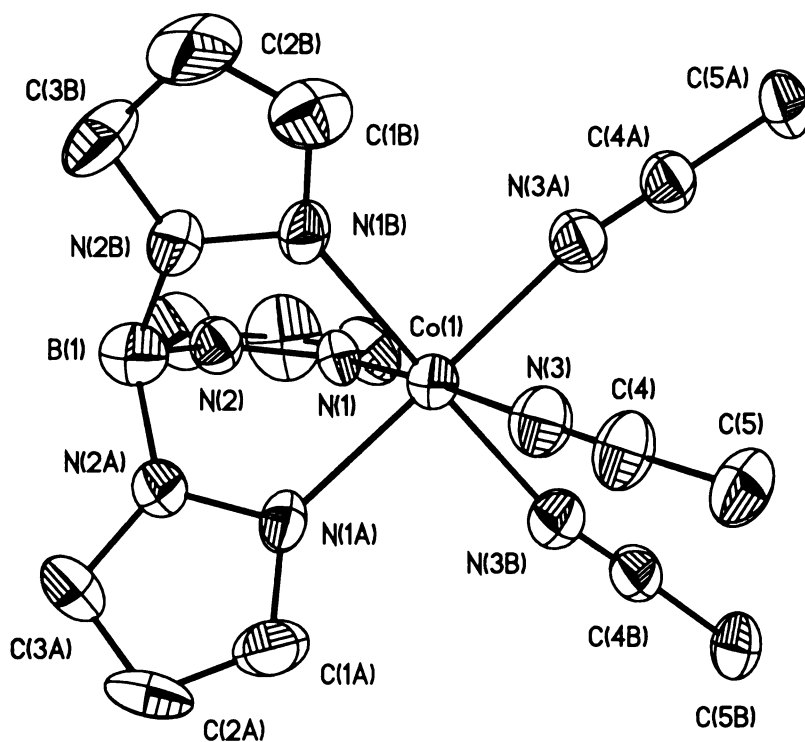


Figure 4.6. Thermal ellipsoid representation of the molecular cation $[(\text{Tp})\text{Co}(\text{CH}_3\text{CN})_3]^+$ from (17). All atoms are represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

Table 4.3. Summary of crystallographic data for [(Tp)Co(CH₃CN)₃][PF₆], (17)

formula	C ₁₅ H ₁₉ N ₉ B ₁ P ₁ F ₆ Cr ₁
formula weight	540.10
space group	R-3c
a, Å	21.568(3)
b, Å	21.568(3)
c, Å	21.568(3)
α, deg.	30.868(17)
β, deg.	30.868(17)
γ, deg.	30.868(17)
V, Å ³	2342.38(7)
Z	4
^d calc, g/cm ³	1.532
μ (Mo Kα), cm ⁻¹	0.870
temperature, K	173
trans. factors, max., min.	1.00, 0.743
R ₁	0.1443
wR ₂	0.3998
goodness-of-fit	2.545

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

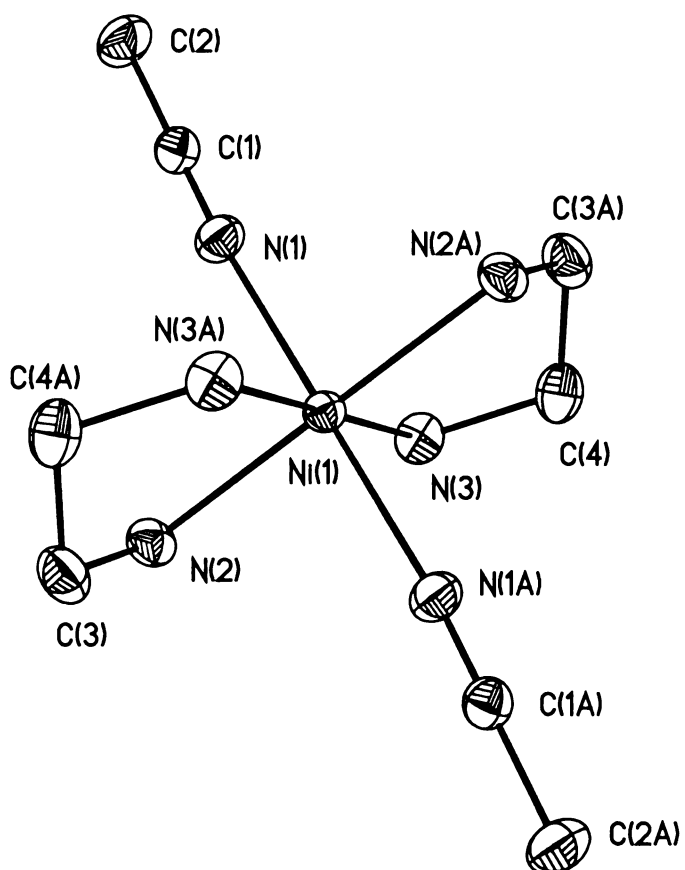


Figure 4.7. Thermal ellipsoid plot of the cation of *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$ (21). All atoms are represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

Table 4.4. Summary of crystallographic data for *trans*-[Ni(CH₃CN)₂(en)₂][PF₆]₂, (21)

formula	C ₈ H ₂₂ N ₆ P ₂ F ₁₂ Ni ₁
formula weight	550.97
space group	P2(1)/n
a, Å	8.8538(18)
b, Å	10.106(2)
c, Å	11.815(2)
α, deg.	90.00
β, deg.	107.57(3)
γ, deg.	90.00
V, Å ³	1007.8(4)
Z	2
^d calc, g/cm ³	1.816
μ (Mo Kα), cm ⁻¹	1.237
temperature, K	173
trans. factors, max., min.	1.00, 0.768
R ₁	0.0496
wR ₂	0.1404
goodness-of-fit	1.094

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\Sigma w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

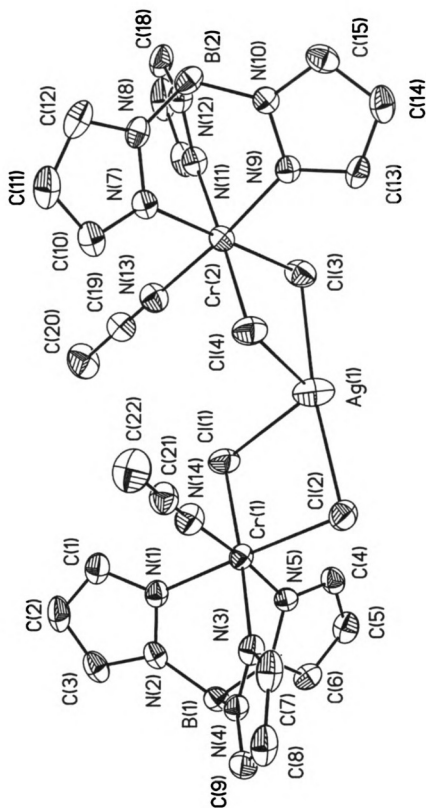


Figure 4.8. Thermal ellipsoid plot of the structure of the metal complex in $\{(Tp)CrCl_2(CH_3CN)\}_2AgPF_6 \cdot 2CH_3CN$ (22). All atoms are represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

Table 4.5. Summary of crystallographic data for
 $\{(\text{Tp})\text{CrCl}_2(\text{CH}_3\text{CN})\}_2\text{AgPF}_6 \cdot 2(\text{CH}_3\text{CN})$, (22)

formula	$\text{C}_{26}\text{H}_{32}\text{N}_{16}\text{Cl}_4\text{B}_2\text{P}_1\text{F}_6\text{Cr}_1\text{Ag}_1$
formula weight	1036.98
space group	P-1
a, Å	12.713(3)
b, Å	12.709(3)
c, Å	15.090(3)
α , deg.	82.96(3)
β , deg.	82.94(3)
γ , deg.	63.22(3)
V, Å ³	2153.9(7)
Z	2
^d calc, g/cm ³	2.240
μ (Mo K α), cm ⁻¹	3.064
temperature, K	173
trans. factors, max., min.	1.00, 0.827
R ₁	0.0618
wR ₂	0.1636
goodness-of-fit	1.170

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

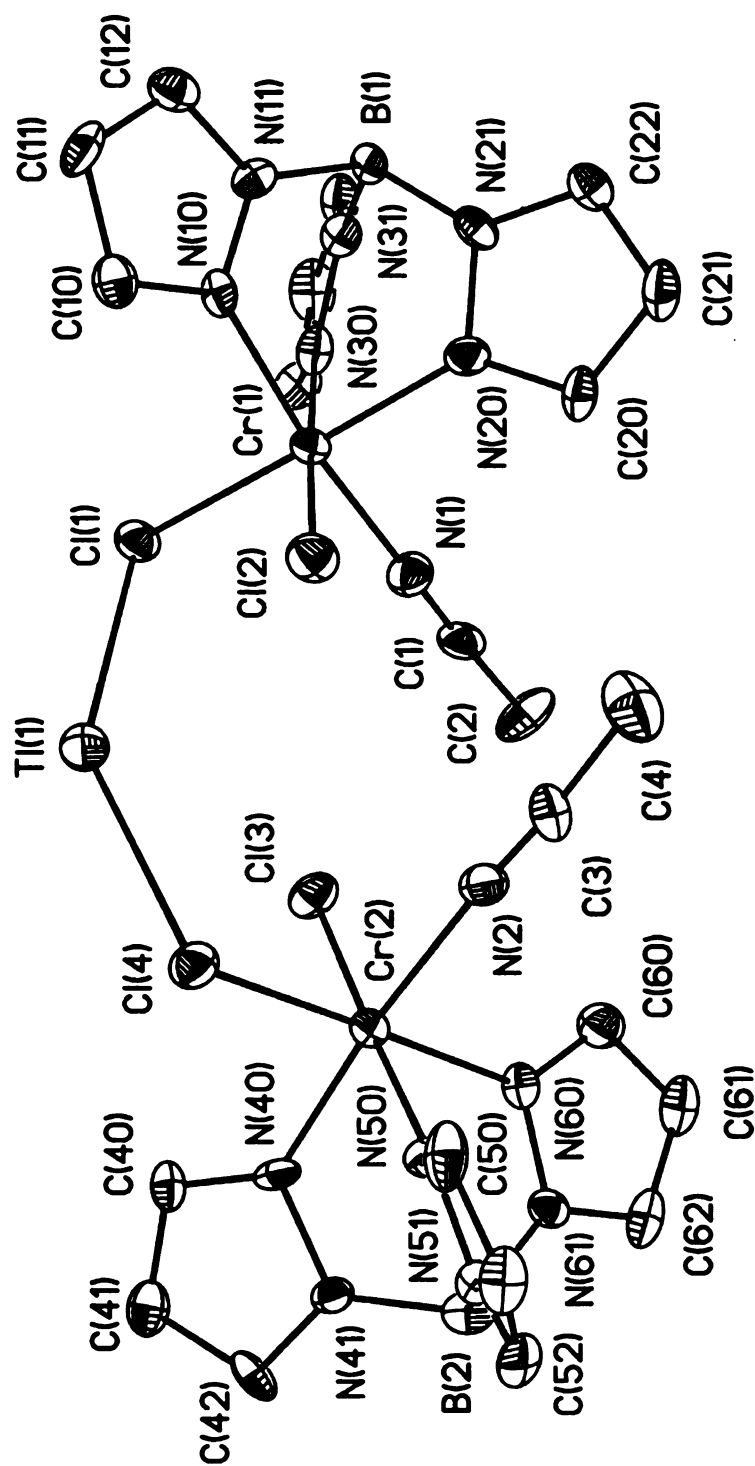
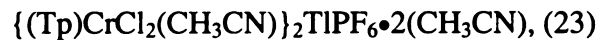


Figure 4.9. Thermal ellipsoid plot of the structure of $\{(Tp)CrCl_2(CH_3CN)\}_2TIPF_6 \cdot 2CH_3CN$ (23). All atoms are represented the 50% level. Hydrogen atoms were removed for clarity.

Table 4.6. Summary of crystallographic data for

formula	$\text{C}_{26}\text{H}_{32}\text{N}_{16}\text{Cl}_4\text{P}_1\text{F}_6\text{Cr}_1\text{Ti}_1$
formula weight	1133.08
space group	Cc
a, Å	22.473(5)
b, Å	12.791(3)
c, Å	15.180(5)
α , deg.	90.00
β , deg.	99.74(3)
γ , deg.	90.00
V, Å ³	4300.6(15)
Z	8
^d calc, g/cm ³	2.132
μ (Mo K α), cm ⁻¹	8.371
temperature, K	173
trans. factors, max., min.	1.00, 0.725
R ₁	0.0263
wR ₂	0.0587
goodness-of-fit	0.965

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\Sigma w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

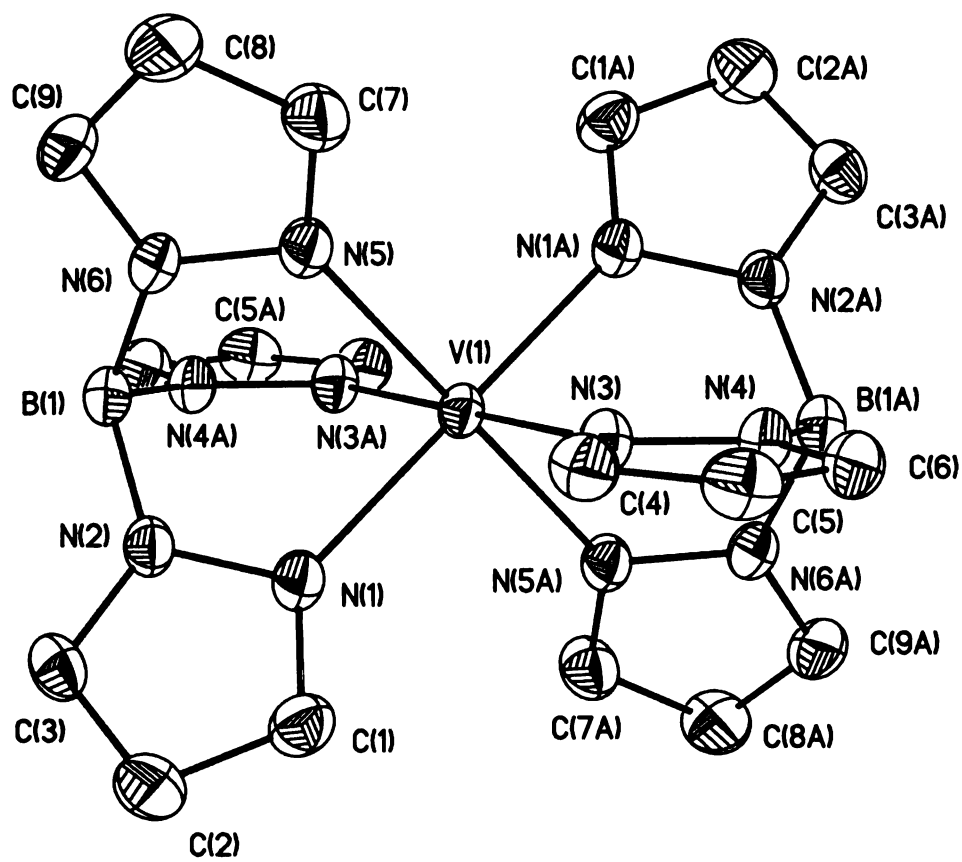


Figure 4.10. Thermal ellipsoid plot of the structure of $V(Tp)_2$ (24). All atoms are represented at the 50% level. Hydrogen atoms were removed for the sake of clarity.

Table 4.7. Summary of crystallographic data for $V(Tp)_2 \cdot 1/6Et_2O \cdot 1/3CH_3CN$, (24)

formula	$C_{60}H_{73}N_{37}B_6O_1V_3$
formula weight	1444.26
space group	P-1
a, Å	10.595(2)
b, Å	15.045(3)
c, Å	15.472(3)
α , deg.	63.57(3)
β , deg.	73.35(3)
γ , deg.	77.08(3)
V, Å ³	2102.4(7)
Z	3
d_{calc} , g/cm ³	1.486
μ (Mo K α), cm ⁻¹	1.214
temperature, K	173
trans. factors, max., min.	1.00, 0.889
R ₁	0.0465
wR ₂	0.1267
goodness-of-fit	1.030

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$$

4. Results and Discussion

A. Synthetic Issues in the Design of New Paramagnetic Building Blocks

(1) Corner Building Block Compounds for Molecular Cubes

One category of building block compounds contains acetonitrile as a leaving group. Acetonitrile readily coordinates to transition metals ions, but with sufficient lability such that these solvates have been used extensively as a source of transition metal ions in synthetic chemistry. The dissociation of the acetonitrile ligands opens up vacant coordination sites for catalysis, and allows transition metals to be introduced into extended arrays formed by condensation reactions with polydentate ligands.¹²

The facial capping ligand employed for all of the corner building block compounds is 1-hydrotrispyrazolylborate (Tp), one of the so-called “scorpionate ligands”. The Tp ligand is a tridentate, monoanionic ligand that has been used extensively in transition metal and main group coordination chemistry.¹³ In terms of its role in chemistry, it is similar to the Cp family that has been used successfully by Rauchfuss in the preparation of a molecular box. Both Cp⁻ and Tp⁻ donate 6 electrons, occupy three coordination sites, and are monoanionic. Tp is a representative of the “first generation” of scorpionate ligands.¹³ The “second generation” is characterized by substitution of the hydrogens in the three or three and five

positions of the pyrazol rings. Common substituents are methyl, *tert*-butyl, isopropyl, phenyl, and tolyl although several others have been reported.¹³ The additional steric bulk provided by these substituents serves to influence the coordination number of metals to which they are bound. These substituents also often impart improved solubility for Tp compounds in organic solvents. In spite of this advantage, substituted Tp ligands were not extensively explored in this project due to the fact that metal coordination numbers less than six are not conducive to forming molecular cubes. Even in cases of substituted Tp ligands where the metal coordination number remained six, the prospect of adding steric repulsion to the entropy barrier for cube assembly was a disadvantageous factor in their use.

(2) Edge Building Block Compounds for Molecular Cubes

In addition to precursors with *trans* solvent molecules such as *trans*-[Ni(CH₃CN)₂(en)₂][PF₆]₂ (21), a suitable dicyanide compound exists in the literature. The compound *trans*-V(CN)₂(dmpe)₂ was prepared according to the published method.¹⁴ but the use of this compound suffers from several problems. Both the V^{II} center and chelating phosphine ligands, dmpe, are extremely air and moisture sensitive which prohibits the use of any water in assembly reactions involving this compound. The benefits of employing water as a solvent or co-solvent in preparing metal cyanide compounds have

been amply demonstrated.¹⁵ Additionally, the question of steric interactions from the dmpe ligands that would point to the interior of the 20 metal atom cube must be considered. A modeling study using the Spartan program¹⁶ was used to evaluate the possibility that steric problems would prevent cube assembly with the *trans*-V(CN)₂(dpme)₂ compound. A similar study was also carried out on a proposed eight metal atom cube with (Tp)M corners. The results of these efforts are presented in Figure 4.11. Both models show that little void space exists but that perhaps steric factors will not totally preclude the formation of the proposed molecules.

B. Preparation of Na[(Tp)CrCl₃] (13), K[(Tp)CrCl₃] (14), and (Tp)MoBr₂(THF) (15)

The metal trihalide tris-THF adducts, MX₃(THF)₃ (X = Cl, Br) provided a convenient source of trivalent transition metal starting materials. Both of these reactions were expected to proceed with displacement of the THF by the tridentate Tp to form the corresponding [(Tp)MX₃]¹⁻ compounds. The reaction of CrCl₃(THF)₃ with Na[Tp] or K[Tp] followed this scheme and led to the expected compound Na[(Tp)Cr(Cl)₃] (13). The analogous reaction with MoBr₃(THF)₃, however, did not proceed in the same manner. Tp added to the Mo^{III} center displacing the three THF ligands, but a Br is also lost and the neutral product MoBr₂(THF)(Tp) (15) is isolated.

(1)



(2)



Figure 4.11. Space-filling models generated by the Spartan program for the (1) 8 metal atom and (2) 20 metal atom molecular boxes. The feature of primary interest is the lack of void space present within the cube interiors.

The reaction of Tp with $\text{CrCl}_3(\text{THF})_3$ occurs almost immediately upon addition of $\text{Na}[\text{Tp}]$ or $\text{K}[\text{Tp}]$. The reaction with $\text{MoBr}_3(\text{THF})_3$ proceeds more slowly and requires an overnight reflux. The additional time for the Mo reaction is a consequence of the geometries of the $\text{MX}_3(\text{THF})_3$ starting materials. The compound $\text{CrCl}_3(\text{THF})_3$ is a *fac* isomer which is the necessary geometry for addition of Tp whereas $\text{MoBr}_3(\text{THF})_3$ is a *mer* isomer which requires substitution with isomerization.

The rate of addition of $\text{Na}[\text{Tp}]$ was a synthetic consideration that required monitoring due to unwanted production of $\text{M}(\text{Tp})_2$. Avoidance of these by-products played a central role in the development of the reactions of $[\text{M}(\text{CH}_3\text{CN})_x]^{n+}$ with $\text{Na}[\text{Tp}]$ and will be discussed further in section 4(C). During the isolation of $\text{Na}[(\text{Tp})\text{Cr}(\text{Cl})_3]$ (13) from reactions in which the $\text{Na}[\text{Tp}]$ was added rapidly, a small amount of yellow-orange precipitate was isolated and determined to be $[\text{Cr}(\text{Tp})_2]\text{Cl}$.¹³ This impurity is minimized by slow addition of $\text{Na}[\text{Tp}]$ to $\text{CrCl}_3(\text{THF})_3$.

C. Preparation of $[(\text{Tp})\text{Mn}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ (16) and

$[(\text{Tp})\text{Co}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ (17)

The acetonitrile solvates, $[\text{Mn}(\text{CH}_3\text{CN})_4][\text{PF}_6]_2$ and $[\text{Co}(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$, provide a convenient source of divalent transition metal starting materials for Tp chemistry. The reactions of these compounds with $\text{Na}[\text{Tp}]$ proceed

rapidly $[(\text{Tp})\text{M}(\text{CH}_3\text{CN})_3]^+$. The $[\text{PF}_6]^{1-}$ anion is weakly coordinating and sufficiently stable that the cationic metal centers do not abstract fluorides.

As mentioned in section 4(B), the formation of the undesired by-product $\text{M}(\text{Tp})_2$ is a synthetic obstacle that had to be addressed in the preparation of these compounds. The stability of the $[(\text{Tp})\text{M}(\text{CH}_3\text{CN})_3]^{1+}$ complexes was observed to be heavily concentration dependent. If the reaction solutions are too concentrated ligand redistribution occurs to give $\text{M}(\text{Tp})_2$ complexes and $[\text{M}(\text{CH}_3\text{CN})_x]^{n+}$. This limitation was overcome by isolation of $[(\text{Tp})\text{M}(\text{CH}_3\text{CN})_3]^{1+}$ salts from solution by addition of diethyl ether to moderately concentrated solutions of the compounds.

D. Preparation of $\text{K}[(\text{Tp})\text{Cr}(\text{CN})_3]$, (20)

$\text{K}[(\text{Tp})\text{CrCl}_3]$ (14) served as a convenient starting material for the tri-cyanide analog $\text{K}[(\text{Tp})\text{Cr}(\text{CN})_3]$ (20). Reaction of (14) with the tetraalkylammonium cyanides, $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$, proved to be unreliable for reproducible preparation of tractable products. KCN proved to be an effective alternative, in that there is no possibility of a mixture of cations moreover the by-product, KCl, is more easily removed from the solution than the tetraalkylammonium chlorides. The poor solubility of KCN in non-polar organic solvents necessitated carrying out the reaction in methanol.

The ligand field strength of cyanide is high and the tendency of Tp to yield $M(\text{Tp})_2$ compounds requires careful monitoring of the addition rate of the cyanide reagent to $K[(\text{Tp})\text{CrCl}_3]$ (14). By adding KCN via cannula dropwise at a rate of ~1 drop per second the reaction proceeds as desired to yield $[(\text{Tp})M(\text{CN})_3]$.

Crystals of $K[(\text{Tp})\text{Cr}(\text{CN})_3]$ (20) were grown several times from cooling concentrated acetonitrile solutions of the compound. Unfortunately the crystals proved to be remarkably unstable once removed from the solution. Precautions including the use of DOW Silicone grease, Paratone oil, and a nitrogen purged glove bag with microscope and liquid nitrogen cooled mounting stage were employed in mounting these for single-crystal X-ray diffraction analysis. Despite these efforts, all attempts to obtain a single crystal X-ray data set invariably led to loss of crystallinity. The loss of crystallinity is most likely due to loss of interstitial solvent.

E. Preparation of $[(\text{Tp})\text{Mo}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (18),

$[(\text{Tp})\text{V}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (7), and *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$, (21)

One method to prepare precursors with labile solvent ligands, involved the coordination of Tp to the homoleptic acetonitrile solvated transition metal cations, $[M(\text{CH}_3\text{CN})_n]^{2+}$ ($M = \text{Mn}, \text{Co}$; $n = 4, 6$). This was a convenient approach for the divalent transition metal ions, but the trivalent

metal ions are not particularly stable as $[M(\text{CH}_3\text{CN})_n]^{3+}$ compounds. In the cases of $(\text{Tp})\text{MoBr}_2(\text{THF})$ (15) and $(\text{Tp})\text{VCl}_2(\text{THF})$ suitable trivalent precursors were prepared from $\text{MX}_3(\text{THF})_3$. A suitable edge precursor was prepared from *trans*- $\text{NiCl}_2(\text{en})_2$. Abstraction of the halides from $(\text{Tp})\text{MX}_2(\text{THF})$ and $\text{NiCl}_2(\text{en})_2$ in acetonitrile with AgPF_6 or TlPF_6 results in the formation of $[(\text{Tp})\text{Mo}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (18), $[\text{V}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]_2$ (19), and *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$ (21). Acetonitrile occupied the metal coordination sites vacated by the halides, which were easily removed MCl ($\text{M} = \text{Ag}, \text{Tl}$). Obviously since acetonitrile was present in sufficient excess, it replaces the THF ligands that were originally coordinated to the Mo and V starting materials.

For the preparation of the compounds $[(\text{Tp})\text{V}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (19) and *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$ (21) both Ag^{1+} and Tl^{1+} are suitable halide abstraction reagents, but removal of the Br^- from $(\text{Tp})\text{MoBr}_2(\text{THF})$ (15), required the use of Ag^+ . Even under refluxing conditions the Tl^+ ion proved to be unable to effect complete halide abstraction.

F. Reaction of $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13) with MPF_6 ($\text{M} = \text{Ag}^{1+}$ or Tl^{1+})

After the successful preparation of $[\text{M}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]$ ($\text{M} = \text{Mo}^{\text{III}}$ (18), or V^{III} (19)), attempts were made to prepare the analogous Cr^{III} compound by chloride abstraction from $\text{Na}[(\text{Tp})\text{CrCl}_3]$ (13) with AgPF_6 and

TiPF₆. The change in solution color from green to pink for the Na[(Tp)CrCl₃] (13) starting material clearly indicated that a reaction was taking place but, only the products representing a single halide abstraction event, namely {(Tp)CrCl₂(CH₃CN)}₂AgPF₆•2CH₃CN (22) and {(Tp)CrCl₂(CH₃CN)}₂TiPF₆•2CH₃CN (23), could be isolated from these reactions. The presence of unreacted Ag⁺ and Ti⁺ reagents explains their presence in (22) and (23).

Further attempts to isolate the desired product, [(Tp)Cr(CH₃CN)₃]²⁺ by varying the reaction conditions (e.g. increasing the reaction time) were unsuccessful. Refluxing to make transition metal Tp compounds was avoided due to the inevitable redistribution reactions resulting in the formation of M(Tp)₂ by-products.

In retrospect, the fact that [(Tp)Cr^{III}Cl₃]⁻ is not a suitable precursor to [Cr^{III}(CH₃CN)₃(Tp)]²⁺, in spite of the successful preparation of [M^{III}(CH₃CN)₃(Tp)]²⁺ (M = Mo (18), V (19)) is not so unexpected in retrospect. The compound MoBr₃(THF)₃ and VCl₃(THF)₃ exhibit different reactivity with NaTp from that of CrCl₃(THF)₃ in that the neutral species (Tp)MX₂(THF) is formed spontaneously (M = Mo, V). The reaction with Cr, however, proceeds with retention of all three halides to yield the anionic [(Tp)CrCl₃]⁻ species, an indication that the Cr^{III} center is more Lewis acidic

and less labile than the V^{III} or Mo^{III} and therefore less able to be stabilized as a dicationic complex with Tp and three neutral, weakly donating acetonitrile ligands.

G. Preparation of $V(Tp)_2 \cdot 1/3CH_3CN \cdot 1/6Et_2O$, (24)

The crystalline by-product $V(Tp)_2 \cdot 1/3CH_3CN \cdot 1/6Et_2O$ was isolated from the acetonitrile reaction of $[V(CH_3CN)_3(Tp)][PF_6]$ (19) and 3 $[n-Bu_4N][CN]$ a reaction that was intended to yield $[V(CN)_3(Tp)]^{1-}$. It is not clear whether the target product was formed at all because the only tractable product that could be isolated from this reaction is $V(Tp)_2$. An interesting aspect of this reaction relates to the fact that vanadium is in the +3 oxidation state in the starting material and +2 in the $V(Tp)_2$ product. The disproportionation of $[V(CN)_7]^{4-}$ to V^{II} and V^{IV} cyano species in the presence of water has been reported.¹⁷ It is possible that $[n-Bu_4N][CN]$, which is very difficult to dry, could have introduced water into this reaction. The V^{II} generated by disproportionation under cyanide deficient conditions (only three equivalents of the cyanide starting material being available) could have been a target for free Tp thereby leading to $V(Tp)_2$. The $M(Tp)_2$ compounds are thermodynamically quite stable, which translates to a “dead-end” side reaction in this case.

H. Reaction of $K[(Tp)Cr(CN)_3]$ (20) and $[(Tp)Ni(CH_3CN)_3][BF_4]$ ²²

The reaction of an acetonitrile solution of $K[(Tp)Cr(CN)_3]$ (20) with an acetonitrile solution of $[(Tp)Ni(CH_3CN)_3(Tp)][BF_4]$ produced a pink precipitate within thirty seconds. The product was collected by filtration and washed with acetonitrile. The target product of this reaction is the eight metal atom molecular box, $Cr_4Ni_4(CN)_{12}(Tp)_8$ and, indeed, spontaneous precipitation of a product is in accord with a neutral product. The fact that the solid formed so quickly did not allow for single crystal x-ray diffraction studies, but the infrared spectroscopic evidence is encouraging (*vide infra*).

I. Physical Methods Characterization

(1) Infrared and Electronic Absorption Spectroscopic Studies

In all cases, the paramagnetism of the compounds under investigation prohibited structural characterization by NMR Spectroscopy, but single crystal X-ray diffraction and infrared spectroscopy were informative methods for helping one to assign a formula and/or a molecular structure. The use of group theoretical arguments and the localized molecular symmetry of characteristic infrared active bond stretching modes provide information for identifying the structures of these compounds. The M-X (X = halides) and the $C\equiv N$ in acetonitrile and cyanide are especially helpful in this regard. In addition, the ν_{B-H} mode in the Tp^- ligand is a convenient

marker. A comparison of the energies of the $\nu_{\text{B-H}}$ and $\nu_{\text{C}\equiv\text{N}}$ modes in the starting materials and products was also quite informative.

The infrared spectra of $\text{Na}[(\text{Tp})\text{CrCl}_3]$, (13) and $\text{K}[(\text{Tp})\text{CrCl}_3]$ (14) exhibit two $\nu_{\text{Cr-Cl}}$ modes at 340 and 330 cm^{-1} and 331 and 310 cm^{-1} respectively. The $\nu_{\text{B-H}}$ mode at 2490 cm^{-1} which is common to both (13) and (14) was shifted to lower energy from the 2500 cm^{-1} observed for NaTp. The two observed $\nu_{\text{Cr-Cl}}$ features are in agreement with the group theoretical prediction of two IR active modes, A_1 and E, for the idealized C_{3v} symmetry of the Cr-Cl bonds. The displacement of the THF ligand was supported by the disappearance of the THF $\nu_{\text{C-O}}$ modes observed at 1012 and 855 cm^{-1} in the starting material.

A broad $\nu_{\text{Mo-Br}}$ mode at 263 cm^{-1} was observed in the infrared spectrum of $(\text{Tp})\text{MoBr}_2(\text{THF})$ (15). The $\nu_{\text{B-H}}$ feature at 2480 cm^{-1} was shifted to lower energy from the 2500 cm^{-1} stretch for Na[Tp]. Group theoretical analysis predicts two observed $\nu_{\text{Mo-Br}}$ modes, namely A_1 and B_1 , for the idealized C_{2v} symmetry of the Mo-Br bonds. The 20 cm^{-1} width at half-height of the $\nu_{\text{Mo-Br}}$ stretch indicates that the two expected modes are degenerate, thereby giving rise to a single overlapping peak. The UV-Visible spectrum of $(\text{Tp})\text{MoBr}_2(\text{THF})$ (15) in THF displayed absorptions at 376 (80.0) and 308 (100) nm ($\text{L mol}^{-1} \text{cm}^{-1}$).

One expects two IR active modes, A_1 and E, for the idealized C_{3v} symmetry of the $C\equiv N$ bonds in CH_3CN in the spectra of $[(Tp)Mn(CH_3CN)_3][PF_6]$ (16) and $[(Tp)Co(CH_3CN)_3][PF_6]$ (17). Indeed, the ν_{CN} modes appear at 2312, 2284 cm^{-1} and 2315, 2280 cm^{-1} for (16) and (17) respectively. These values are shifted from the ν_{CN} features located at 2322, 2293 cm^{-1} and 2316, 2292 cm^{-1} observed in the Mn and Co starting materials respectively. The ν_{B-H} modes are located at 2469 cm^{-1} for (16) and 2498 for (17).

The UV-Visible spectrum of $[(Tp)Mn(CH_3CN)_3][PF_6]$ (16) in acetonitrile displays an absorbance at 331 nm with an ϵ value of $\sim 1 \text{ L mol}^{-1} \text{ cm}^{-1}$. This low value is expected on the basis of the d^5 high-spin electronic configuration of octahedral Mn^{II} , which leads to only spin forbidden transitions being possible. The UV-Visible spectrum of $[(Tp)Co(CH_3CN)_3][PF_6]$ (17) in CH_3CN displayed absorbances at 515 (23) and 468 (83) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$).

The infrared spectra of $[(Tp)Mo(CH_3CN)_3][PF_6]_2$ (18) and $[(Tp)V(CH_3CN)_3][PF_6]_2$ (19) showed two $\nu_{C\equiv N}$ modes at 2318, 2284 cm^{-1} and 2326, 2295 cm^{-1} respectively. The ν_{B-H} mode for (18) is at 2527 cm^{-1} and is shifted to higher energy from the 2500 observed for $Na[Tp]$ and the 2480 cm^{-1} stretch found for $(Tp)MoBr_2(THF)$ (15). The ν_{B-H} mode for (19)

at 2532 cm^{-1} is similarly shifted to higher energy from the corresponding values observed for $\text{Na}[\text{Tp}]$ and $(\text{Tp})\text{VCl}_2(\text{THF})$. The two observed $\nu_{\text{C}\equiv\text{N}}$ modes are in agreement with the group theoretical prediction of two IR active modes, namely A_1 and E , for the idealized molecular C_{3v} symmetry of $[(\text{Tp})\text{M}(\text{CH}_3\text{CN})_3]^+$. The UV-Vis spectra in acetonitrile displayed a broad peak at $455\text{ (966) nm (L mol}^{-1}\text{ cm}^{-1}\text{)}$ for $[(\text{Tp})\text{Mo}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (18) and peaks at 480 (115) and $330\text{ (75) nm (L mol}^{-1}\text{ cm}^{-1}\text{)}$ for $[\text{V}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]_2$ (19).

The infrared spectrum of $\text{K}[\text{Cr}(\text{CN})_3(\text{Tp})]$ (20) exhibited a single $\nu_{\text{C}\equiv\text{N}}$ stretching feature at 2135 cm^{-1} instead of the usual two modes. The presence of a single stretch indicates that the symmetric and anti-symmetric ν_{CN} stretching modes are degenerate.¹⁸ The $\nu_{\text{B-H}}$ mode was observed at 2496 cm^{-1} . The absence of $\nu_{\text{Cr-Cl}}$ modes in the far IR of this compound confirmed complete cyanide displacement of the chlorides. The UV-Visible spectrum revealed absorptions at 322 (75) , 365 (60) , and $410\text{ (45) nm (L mol}^{-1}\text{ cm}^{-1}\text{)}$.

A single IR active mode, B_{1u} , for the idealized D_{2h} symmetry of the $\text{C}\equiv\text{N}$ bonds of the CH_3CN ligands in *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$ (21) is expected, but in fact two stretches at 2312 and 2284 cm^{-1} were observed. The two stretches would be consistent with a C_{2v} symmetry for the $\text{C}\equiv\text{N}$ bonds for the *cis* isomer of this compound, but the crystal structure was

obtained on the *trans* isomer. We reasoned that one possibility is that both isomers could be present in the reaction solution with the *trans* isomer preferentially crystallizing. This hypothesis was explored by preparing an IR sample from a batch of the *trans* isomer crystals. This sample produced a spectrum with the same two stretches. A solution infrared spectrum, however, revealed a single $\nu_{\text{C}\equiv\text{N}}$ mode at 2293 cm^{-1} indicating the two stretches are a consequence of solid state splitting which lowers the site symmetry from the idealized D_{2h} . The UV-visible spectrum in acetonitrile contains transitions at 880 (65), 536 (75), 339(25) nm ($\text{L mol}^{-1}\text{ cm}^{-1}$).

(2) Mass Spectrometric Analysis of [(Tp)Mn(CH₃CN)₃][PF₆] (16) and [(Tp)Co(CH₃CN)₃][PF₆] (17)

Fast-atom bombardment (FAB) mass spectrometry in both nitrobenzyl alcohol (NBA) and glycerol matrices was conducted on Samples of [(Tp)Mn(CH₃CN)₃][PF₆] (16) and [(Tp)Co(CH₃CN)₃][PF₆] (17). NBA proved the more successful of the two matrices. The parent ion peaks in the spectra for (15) and (16) were 268.09 and 272.12 m/z respectively, which correspond to the fragments $[\text{Mn}(\text{Tp})]^{1+}$ and $[\text{Co}(\text{Tp})]^{1+}$. The bound acetonitrile ligands appear to be easily lost under these conditions. A second fragment could be also be assigned to the prominent peaks at 360.13 and 364.15 m/z in the spectra of (15) and (16). These correspond to

$[\text{Mn}(\text{CH}_3\text{CN})_2\text{F}(\text{Tp})]^{1+}$ and $[\text{Co}(\text{CH}_3\text{CN})_2\text{F}(\text{Tp})]^{1+}$, species produced by fluoride abstraction from $[\text{PF}_6]^-$.¹⁹

(3) Magnetic Susceptibility Studies

Magnetic susceptibility studies were conducted to establish the expected ground state spin values for the new paramagnetic molecular building blocks. This information is useful for predicting the number of unpaired electrons that a product will possess based on the metal precursor combinations chosen for a given molecular box assembly reaction.

A magnetic susceptibility study of $[\text{Mn}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]$ (16) gave a μ_{eff} value of 5.90 B.M. with $g = 1.99$. The symmetrical $t_{2g}^3 e_g^2$ electron configuration of the Mn^{II} center leads to μ_{eff} and g values that are in good agreement with the predicted spin-only values of 5.90 B.M. and $g \sim 2$.

The $[\text{BF}_4]^-$ salt of $[\text{Co}(\text{CH}_3\text{CN})_3(\text{Tp})]^{1+}$ (17) with a Co^{II} center exhibits a μ_{eff} value of 3.69 B.M. with $g = 1.90$. The spin-only value for an $S = 3/2$ ground state would exhibit a $\mu_{\text{eff}} = 3.87$ for $g \cong 2$. The $t_{2g}^3 e_g^2$ configuration of the Co^{II} leads to spin-orbital coupling and typically lower moments than the spin-only value. The compound $[\text{V}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{PF}_6]_2$ (19) exhibits a room temperature μ_{eff} value of 3.06 B.M. with $g = 2.15$. An octahedral d^2 V^{III} compound with $S = 1$ with no spin-orbit effects should exhibit a $\mu_{\text{eff}} =$

2.83 for $g \cong 2$.²⁰ The experimentally observed values are consistent with literature reports of other octahedral V^{III} and Co^{II} compounds.^{20,21}

A magnetic susceptibility study of $[(Tp)Mo(CH_3CN)_3][PF_6]_2$ (18) revealed a room temperature μ_{eff} value of 3.45 B.M. with $g = 1.78$. An idealized $S = 3/2$ octahedral d^3 Mo^{III} ion with no spin orbit coupling effects would be expected to exhibit a μ_{eff} value of 3.87 B.M (for $g \cong 2$). This assumption for second and third row transition metal ions, however, is not generally valid because spin-orbit coupling contributions tend to be significantly greater than with the respective 3d congeners.²⁰ The observed deviations in μ_{eff} and g for the Mo^{III} center were expected and reasonable based on literature precedence.²⁰

Magnetic susceptibility studies of $K[Cr(CN)_3(Tp)]$ (20) revealed a room temperature μ_{eff} value of 3.62 B.M. with $g = 1.89$. A μ_{eff} value of 3.87 would be expected for an idealized octahedral d^3 Cr^{III} ion with a spin value of $S = 3/2$ assuming no spin orbital coupling contribution. The symmetrical filling of the t_{2g} orbitals would be expected to minimize spin-orbital coupling contributions. However, the six coordinate Cr^{III} center is not rigorously octahedral from a symmetry standpoint, as three coordination sites occupied by the tridentate nitrogen donor ligand Tp and the other three are filled by cyanide ligands. In addition, the expected μ_{eff} value for Cr^{III} complexes is

generally higher than observed due to spin-orbit coupling stemming from the mixing of excited states, which have orbital degeneracy, with the non-degenerate ground state.²⁰

The edge building block *trans*-[Ni(CH₃CN)₂(en)₂][PF₆] (21) exhibits a room temperature μ_{eff} value of 2.98 B.M. with $g = 2.12$. The experimentally observed μ_{eff} and g values deviate from the predicted spin-only values of 2.83 B.M. and $g \cong 2$, but are consistent with literature reports of other octahedral Ni^{II} compounds.^{20,21}

(4) Characterization of the product from the reaction of

K[(Tp)Cr(CN)₃] (20) and [(Tp)Ni(CH₃CN)₃][BF₄]²²

The infrared spectrum of the pink precipitate from this reaction exhibited only a single ν_{CN} mode at 2174 cm⁻¹. This is in accord with a highly symmetrical structure such as the target product an eight metal atom molecular box, namely (Tp)₈Cr₄Ni₄(CN)₁₂, in which all the cyanides reside in the same environment. A structural schematic is depicted in Figure 4.1. The increase of 31 cm⁻¹ for the ν_{CN} mode of the product relative to the K[Cr(CN)₃(Tp)] (20) starting material (2174 versus 2135 cm⁻¹) is an expected consequence in the switch of cyanide from dangling to bridging mode. This shift to higher energy is attributed to both the kinematic coupling that occurs when a second mass is attached to the CN unit as well

as to the fact that the lone pair electron density localized on the nitrogen is antibonding with respect to the $\text{C}\equiv\text{N}$ triple bond. The ν_{CN} force constant increases upon donation from this orbital to a Lewis acid. Furthermore a $\nu_{\text{B-H}}$ mode at 2494 cm^{-1} was observed in accord with the conclusion the Tp ligand is still bound to the metals in the product. The appearance of the stretch at 2494 cm^{-1} is within resolution of the $\nu_{\text{B-H}}$ modes of 2492 and 2496 for the starting materials $\text{K}[\text{Cr}(\text{CN})_3(\text{Tp})]$ (20) and $[\text{Ni}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{BF}_4]$. The poor solubility of this product precludes solution characterization such as UV-visible analysis. Elemental analysis of the product did not fit the expected formula, nor did it correspond to any identifiable products.

Magnetic susceptibility studies of this product led to moments that are lower than predicted value for $(\text{Tp})_8\text{Cr}_4\text{Ni}_4(\text{CN})_{12}$. The lack of definitive structural information prevents any further detailed interpretation of this reaction.

Table 4.8. Properties of Building Block Compounds

Corner Building Blocks	Infrared (cm ⁻¹)		Moment μ _{eff} (B.M.)	UV-Visible λ _{max} (nm)(ε)
	ν _{C≡N}	ν _{B-H}		
<i>Accepting</i>				
[V(CH ₃ CN) ₃ (Tp)](PF ₆) ₂	2326, 2295	2532	3.06	480{115}
[Mo(CH ₃ CN) ₃ (Tp)](PF ₆) ₂	2318, 2284	2527	3.45	455{966}
[Mn(CH ₃ CN) ₃ (Tp)](PF ₆)	2312, 2284	2469	5.90	331{1.2}
[Co(CH ₃ CN) ₃ (Tp)](PF ₆)	2315, 2280	2498	3.69	468{83.2}
<i>Donating</i>				
K[Cr(CN) ₃ (Tp)]	2135	2492	3.62	322{75}
Side Building Blocks				
<i>Accepting</i>				
[Ni(CH ₃ CN) ₂ (en) ₂](PF ₆)	2312, 2284	N/A	2.98	536{75}

J. Molecular Structures

(1) Na[(Tp)CrCl₃], (13)

The molecular anion [(Tp)CrCl₃]¹⁻ consists of an octahedrally coordinated Cr^{III} ion with three sites being occupied by facially arranged chlorides and the other three sites being occupied by the face capping ligand Tp. The octahedron is relatively undistorted with a N(1)-Cr(1)-Cl(1) angle of 90.49°. The Na(1) is coordinated to the facial chlorides from two [(Tp)CrCl₃]¹⁻ anions with a trigonal prismatic geometry. The Na(2) resides in the plane of Na(1) and is disordered over three sites such that it bridges the edges of the “NaCl₆” trigonal prism. The separation distance between Na(1) and Na(2) is 3.89 Å. The Na(1) atom is situated on a mirror plane and three fold axis of rotation. Selected bond distances and angles are presented in Table 4.9.

(2) (Tp)MoBr₂(THF), (15)

In this compound, Tp occupies three facial coordination sites of the octahedral Mo center. The Mo(1)-N(1), N(3), and N(5) distances of 2.139, 2.163, and 2.158 Å respectively are longer than the Cr-N distance of 2.033 Å observed in (13). The shorter Mo(1)-N(1) distance relative to the corresponding Mo distance to N(3) and N(5) is attributed to the presence of a *trans* THF to N(1) as compared to Br⁻ ligands which are present in

positions *trans* to N(3) and N(5) respectively. The bond differences reflect the superior π -donating ability of Br⁻ versus THF ligands. The octahedron is slightly distorted with N(1)-Mo(1)-Br(1) and N(1)-Mo(1)-Br(2) angles of 96.81° and 93.35° respectively. Selected bond distances and angles are presented in Table 4.10.

(3) [(Tp)Co(CH₃CN)₃][PF₆], (17)

The molecular cation [(Tp)Co(CH₃CN)₃]¹⁺ consists of an octahedrally coordinated cobalt atom with three sites occupied by *fac*-CH₃CN groups and the face capping Tp ligand. The Co-N bonds are slightly non-linear with a Co(1)-N(3)-C(4) angle of 167.2(8)°. The octahedron is distorted as reflected by the angle N(3)-Co(1)-N(1) angle = 95.3(3)°. The Co atom resides on a three-fold axis of symmetry and the [PF₆]⁻ counterions are located in two positions in the structure. One [PF₆]⁻ is located between two [Co(CH₃CN)₃(Tp)]⁺ cations which are oriented such that the three facial CH₃CN are directed towards the anion. The second [PF₆]⁻ anion is positioned between the Tp ligands of two adjacent [Co(CH₃CN)₃(Tp)]⁺ cations. The P atoms reside on the mirror planes of the 3 bar axis. Selected bond distances and angles are presented in Table 4.11.

(4) *trans*-[Ni(CH₃CN)₂(en)₂][PF₆]₂, (21)

The molecular structure of (21) is composed of an octahedral nickel center with two *trans* CH₃CN and two *trans* bidentate ethylenediammine ligands. The nickel atom resides on an inversion center. The Ni-N(CH₃CN) interactions are slightly non-linear as evidenced by the Ni(1)-N(1)-C(1) angle of 173.4°. The octahedron is distorted in the plane of the ethylenediammine ligands with an obtuse N(2)-Ni(1)-N(3) angle of 97.12°. Selected bond distances and angles are presented in Table 4.12.

(5) {(Tp)CrCl₂(CH₃CN)}₂AgPF₆•2CH₃CN (22) and

{(Tp)CrCl₂(CH₃CN)}₂TlPF₆•2CH₃CN (23)

The structures of (22) and (23) are essentially identical except for of the coordination numbers of the Ag and Tl respectively. The Cr atoms in both structures are octahedrally coordinated with three facially oriented coordination sites being occupied by Tp. Two Cl⁻ atoms and one acetonitrile ligand complete the coordination sphere of each Cr atom. Two (Tp)CrCl₂(CH₃CN) moieties are connected in each structure by the coordination of the Cl⁻ to Ag or Tl respectively. In (22) four Cl⁻ ligands are bound to a Ag atom. In (23) only one Cl⁻ from each (Tp)CrCl₂(CH₃CN) moiety is bound to the Tl⁺ ion. The Ag⁺ coordination environment is best described as a highly distorted see-saw shape with Cl(1)-Ag(1)-Cl(2) and

Cl(3)-Ag(1)-Cl(4) angles of 79.41° and 79.31° respectively. The Cl(1)-Ti(1)-Cl(4) bridge is bent at an angle of 147.96°. The pyrazol rings of the Tp ligands of the two (Tp)CrCl₂(CH₃CN) moieties bridged by the metals in (22) and (23) are staggered relative to each other. Selected bond distances and angles for {(Tp)CrCl₂(CH₃CN)}₂AgPF₆•2CH₃CN (22) are presented in Tables 13 and 14. Selected bond distances and angles for {(Tp)CrCl₂(CH₃CN)}₂TiPF₆•2CH₃CN (23) are presented in Tables 4.15 and 4.16.

(6) V(Tp)₂•1/6Et₂O•1/3CH₃CN, (24)

The crystal structure of (24) consists of three V(Tp)₂ units, an acetonitrile solvent molecule, and a disordered diethyl ether molecule. The coordination sphere of each V atom is occupied by two Tp ligands in a staggered formation. The octahedral coordination of the V atoms is essentially undistorted with all the V atoms residing on inversion centers. The diethyl ether molecule is disordered and was therefore modeled with a 50% occupancy. Selected bond distances and angles are presented in Table 4.17.

Table 4.9. Bond lengths [Å] and angles [deg] Na[(Tp)CrCl₃], (13)

Cr(1A)-N(1A)	2.033(7)
Cr(1A)-Cl(2A)	2.349(2)
Cr(1A)-Na(1A)	3.318(2)
Cl(2A)-Na(1A)	2.798(2)
Cl(2A)-Na(2A)	2.98(3)
Na(1A)-Na(2A)	3.84(4)
B(1A)-N(2A)	1.542(9)
N(1A)-C(1A)	1.330(10)
N(1A)-N(2A)	1.369(9)
C(1A)-C(2A)	1.410(12)
C(2A)-C(3A)	1.370(13)
N(1A)-Cr(1A)-Cl(2A)	91.23(18)
N(1A)-Cr(1A)-Na(1A)	127.88(18)
Cl(2A)-Cr(1A)-Na(1A)	56.10(7)
Cr(1A)-Cl(2A)-Na(1A)	79.74(7)
Cr(1A)-Cl(2A)-Na(2A)	143.8(8)
Na(1A)-Cl(2A)-Na(2A)	83.1(6)
Cl(2A)-Na(1A)-Cr(1A)	44.17(4)
Cl(2A)-Na(1A)-Na(2A)	50.5(2)
Cr(1A)-Na(1A)-Na(2A)	90.000(9)
Cl(2A)-Na(2A)-Na(1A)	46.4(5)
C(1A)-N(1A)-N(2A)	106.3(6)
C(1A)-N(1A)-Cr(1A)	133.1(6)
N(2A)-N(1A)-Cr(1A)	120.6(5)
C(3A)-N(2A)-N(1A)	109.9(7)
C(3A)-N(2A)-B(1A)	131.0(8)
N(1A)-N(2A)-B(1A)	119.1(7)
N(1A)-C(1A)-C(2A)	110.6(7)
C(3A)-C(2A)-C(1A)	104.7(7)
N(2A)-C(3A)-C(2A)	108.6(7)

Table 4.10. Bond lengths [Å] and angles [deg] for (Tp)MoBr₂(THF), (15)

Mo(1)-N(1)	2.139(3)
Mo(1)-N(3)	2.163(3)
Mo(1)-N(5)	2.158(2)
Mo(1)-O(1)	2.163(2)
Mo(1)-Br(1)	2.5747(7)
Mo(1)-Br(2)	2.5732(6)
B(1)-N(2)	1.549(4)
B(1)-N(4)	1.556(5)
B(1)-N(6)	1.551(4)
N(1)-Mo(1)-N(3)	84.00(10)
N(1)-Mo(1)-N(5)	84.60(10)
N(1)-Mo(1)-O(1)	170.26(9)
N(1)-Mo(1)-Br(1)	96.81(7)
N(1)-Mo(1)-Br(2)	93.35(7)
N(2)-B(1)-N(4)	108.1(3)
N(2)-B(1)-N(6)	108.4(3)
N(3)-Mo(1)-Br(1)	178.10(7)
N(3)-Mo(1)-Br(2)	88.74(7)
N(5)-Mo(1)-N(3)	85.64(10)
N(5)-Mo(1)-O(1)	87.53(10)
N(5)-Mo(1)-Br(1)	92.71(7)
N(5)-Mo(1)-Br(2)	174.19(7)
N(6)-B(1)-N(4)	107.7(3)
O(1)-Mo(1)-N(3)	89.69(10)
O(1)-Mo(1)-Br(1)	89.29(7)
O(1)-Mo(1)-Br(2)	93.93(7)
Br(2)-Mo(1)-Br(1)	92.937(15)

Table 4.11. Bond lengths [$\text{\AA}$] and angles [deg] for $[(\text{Tp})\text{Co}(\text{CH}_3\text{CN})_3][\text{PF}_6]$, (17)

Co(1)-N(1)	2.115(8)
Co(1)-N(3)	2.146(9)
B(1)-N(2)	1.537(12)
N(1)-C(1)	1.346(13)
N(1)-N(2)	1.349(10)
N(2)-C(3)	1.343(13)
N(3)-C(4)	1.129(12)
N(1A)-Co(1)-N(1B)	86.7(3)
N(1A)-Co(1)-N(1)	86.7(3)
N(1B)-Co(1)-N(1)	86.7(3)
N(1B)-Co(1)-N(3B)	95.3(3)
N(1B)-Co(1)-N(3B)	177.0(3)
N(1)-Co(1)-N(3B)	91.2(3)
N(1A)-Co(1)-N(3A)	177.0(3)
N(1B)-Co(1)-N(3A)	91.2(3)
N(1)-Co(1)-N(3A)	95.3(3)
N(3B)-Co(1)-N(3A)	86.9(3)
N(1A)-Co(1)-N(3)	91.2(3)
N(1B)-Co(1)-N(3)	95.3(3)
N(1)-Co(1)-N(3)	177.0(3)
N(3B)-Co(1)-N(3)	86.9(3)
N(3A)-Co(1)-N(3)	86.9(3)
N(2)-B(1)-N(2A)	108.3(1)
N(2)-B(1)-N(2B)	108.3(1)
N(2A)-B(1)-N(2B)	108.3(1)

Table 4.12. Bond lengths [Å] and angles [deg] for
trans-[Ni(CH₃CN)₂(en)₂][PF₆]₂, (21)

Ni(1)-N(1)	2.134(2)
Ni(1)-N(2)	2.121(2)
N(1)-C(1)	1.141(4)
N(2)-C(3)	1.495(4)
N(3)-C(4)	1.491(4)
C(1)-C(2)	1.460(4)
Ni(1)-N(3)	2.109(2)
N(2)-Ni(1)-N(1)	91.05(9)
N(3)-Ni(1)-N(1)	89.60(9)
N(3)-Ni(1)-N(2)	97.12(9)
C(1)-N(1)-Ni(1)	173.4(2)
C(3)-N(2)-Ni(1)	107.88(17)
C(4)-N(3)-Ni(1)	107.65(17)
N(1)-C(1)-C(2)	179.7(4)

Table 13. Bond lengths [Å] {CrCl₂(CH₃CN)(Tp)}₂AgPF₆•2 CH₃CN, (22)

Ag(1)-Cl(1)	2.7176(18)
Ag(1)-Cl(2)	2.5814(16)
Ag(1)-Cl(3)	2.5796(16)
Ag(1)-Cl(4)	2.7171(18)
Cr(1)-N(1)	2.023(4)
Cr(1)-N(3)	2.056(4)
Cr(1)-N(5)	2.025(4)
Cr(1)-N(14)	2.055(5)
Cr(1)-Cl(1)	2.3345(16)
Cr(1)-Cl(2)	2.3482(18)
Cr(2)-N(7)	2.025(4)
Cr(2)-N(9)	2.025(4)
Cr(2)-N(11)	2.053(4)
Cr(2)-N(13)	2.063(5)
Cr(2)-Cl(3)	2.3486(18)
Cr(2)-Cl(4)	2.3367(16)
B(1)-N(2)	1.551(7)
B(1)-N(4)	1.549(7)
B(1)-N(6)	1.551(7)
B(2)-N(8)	1.549(7)
B(2)-N(10)	1.553(7)
B(2)-N(12)	1.557(7)
N(13)-C(19)	1.148(7)
N(14)-C(21)	1.147(7)

Table 14. Bond angles [deg] for {CrCl₂(CH₃CN)(Tp)}₂AgPF₆•2 CH₃CN, (22)

Cl(2)-Ag(1)-Cl(4)	104.85(5)
Cl(2)-Ag(1)-Cl(1)	79.31(5)
Cl(3)-Ag(1)-Cl(1)	104.97(5)
Cl(3)-Ag(1)-Cl(2)	172.86(5)
Cl(3)-Ag(1)-Cl(4)	79.41(5)
Cl(4)-Ag(1)-Cl(1)	108.57(6)
N(1)-Cr(1)-N(3)	86.29(17)
N(1)-Cr(1)-N(14)	90.32(18)
N(1)-Cr(1)-Cl(1)	89.81(13)
N(1)-Cr(1)-Cl(2)	177.23(12)
N(3)-Cr(1)-N(14)	88.11(18)
N(3)-Cr(1)-Cl(1)	176.07(13)
N(3)-Cr(1)-Cl(2)	91.39(13)
N(5)-Cr(1)-N(1)	87.55(17)
N(5)-Cr(1)-N(3)	86.71(17)
N(5)-Cr(1)-N(14)	174.52(18)
N(5)-Cr(1)-Cl(1)	92.64(12)
N(5)-Cr(1)-Cl(2)	93.82(13)
N(14)-Cr(1)-Cl(1)	92.40(14)
N(14)-Cr(1)-Cl(2)	88.10(14)
Cl(1)-Cr(1)-Cl(2)	92.52(6)
Cr(1)-Cl(1)-Ag(1)	90.33(6)
Cr(1)-Cl(2)-Ag(1)	93.45(6)
Cr(2)-Cl(3)-Ag(1)	93.44(6)
Cr(2)-Cl(4)-Ag(1)	90.24(6)
N(4)-B(1)-N(2)	106.2(4)
N(4)-B(1)-N(6)	106.6(4)
N(6)-B(1)-N(2)	107.5(4)
C(19)-N(13)-Cr(2)	173.8(5)
C(21)-N(14)-Cr(1)	173.9(4)

Table 4.15. Bond lengths [Å] for {(Tp)CrCl₂(CH₃CN)}₂TiPF₆•2CH₃CN, (23)

Tl(1)-Cl(1)	3.081(2)
Tl(1)-Cl(4)	3.088(2)
Cr(1)-N(1)	2.055(8)
Cr(1)-N(10)	2.056(7)
Cr(1)-N(20)	2.017(7)
Cr(1)-N(30)	2.067(7)
Cr(1)-Cl(1)	2.337(3)
Cr(1)-Cl(2)	2.321(3)
Cr(2)-N(2)	2.067(8)
Cr(2)-N(40)	2.033(7)
Cr(2)-N(50)	2.044(7)
Cr(2)-N(60)	2.045(6)
Cr(2)-Cl(3)	2.327(3)
Cr(2)-Cl(4)	2.332(3)

Table 4.16. Angles [deg] for {(Tp)CrCl₂(CH₃CN)}₂TiPF₆•2CH₃CN, (23)

Cl(1)-Ti(1)-Cl(4)	147.96(2)
N(1)-Cr(1)-N(10)	172.5(3)
N(1)-Cr(1)-N(30)	88.2(3)
N(1)-Cr(1)-Cl(1)	89.5(2)
N(1)-Cr(1)-Cl(2)	92.3(3)
N(10)-Cr(1)-N(30)	85.9(3)
N(10)-Cr(1)-Cl(1)	95.1(2)
N(10)-Cr(1)-Cl(2)	93.4(2)
N(20)-Cr(1)-N(1)	88.9(3)
N(20)-Cr(1)-N(10)	86.0(3)
N(20)-Cr(1)-N(30)	85.5(3)
N(20)-Cr(1)-Cl(1)	174.7(2)
N(20)-Cr(1)-Cl(2)	91.8(2)
N(30)-Cr(1)-Cl(1)	89.3(2)
N(30)-Cr(1)-Cl(2)	177.3(2)
Cl(2)-Cr(1)-Cl(1)	93.32(10)
N(2)-Cr(2)-Cl(3)	91.6(2)
N(2)-Cr(2)-Cl(4)	89.8(2)
N(40)-Cr(2)-N(2)	174.3(3)
N(40)-Cr(2)-N(50)	88.3(3)
N(40)-Cr(2)-N(60)	86.8(3)
N(40)-Cr(2)-Cl(3)	91.9(2)
N(40)-Cr(2)-Cl(4)	94.5(2)
N(50)-Cr(2)-N(2)	88.0(3)
N(50)-Cr(2)-N(60)	86.6(3)
N(50)-Cr(2)-Cl(3)	177.8(2)
N(50)-Cr(2)-Cl(4)	88.7(2)
N(60)-Cr(2)-N(2)	88.7(3)
N(60)-Cr(2)-Cl(3)	91.2(2)
N(60)-Cr(2)-Cl(4)	175.1(2)
Cl(3)-Cr(2)-Cl(4)	93.48(10)

Table 4.17. Bond lengths [$\text{\AA}$] and angles [deg] $\text{V(Tp)}_2 \cdot 1/6\text{Et}_2\text{O} \cdot 1/3\text{CH}_3\text{CN}$,
(24)

V(1)-N(13)	2.168(2)
V(1)-N(15)	2.1708(17)
V(1)-N(17)	2.1840(19)
V(2)-N(7)	2.1656(18)
V(2)-N(9)	2.1546(19)
V(2)-N(11)	2.178(2)
V(3)-N(1)	2.177(2)
V(3)-N(3)	2.165(2)
V(3)-N(5)	2.1861(18)
B(1)-N(14)	1.563(3)
B(2)-N(10)	1.562(3)
B(2)-N(12)	1.558(3)
B(3)-N(2)	1.561(3)
B(3)-N(6)	1.558(3)
N(13)-V(1)-N(15)	94.79(7)
N(13)-V(1)-N(17)	93.81(7)
N(15)-V(1)-N(17)	84.56(7)
N(7)-V(2)-N(11)	95.04(8)
N(9)-V(2)-N(7)	94.29(7)
N(9)-V(2)-N(11)	86.37(7)
N(1)-V(3)-N(5)	85.32(7)
N(3)-V(3)-N(1)	94.36(7)
N(3)-V(3)-N(5)	95.04(7)
N(12)-B(2)-N(10)	109.72(18)
N(6)-B(3)-N(2)	108.41(18)

5. Conclusions:

Reactions of Na[Tp] with the homoleptic acetonitrile solvated transition metal ions, $[\text{Mn}(\text{CH}_3\text{CN})_4][\text{PF}_6]_2$ and $[\text{Co}(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$ proved to be effective in preparing the divalent, solvated corner building block compounds $[(\text{Tp})\text{Mn}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ (16) and $[(\text{Tp})\text{Co}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ (17). The trivalent precursors $(\text{Tp})\text{MoBr}_2(\text{THF})$ and $(\text{Tp})\text{VCl}_2(\text{THF})$ were useful as precursors to the higher oxidation state building blocks compounds $[(\text{Tp})\text{Mo}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (18) and $[(\text{Tp})\text{V}(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (19). The cyanide corner building block compound $\text{K}[(\text{Tp})\text{Cr}(\text{CN})_3]$ (20) was prepared from $\text{K}[(\text{Tp})\text{CrCl}_3]$ (14). All efforts to prepare the cation $[(\text{Tp})\text{Cr}(\text{CH}_3\text{CN})_3]^+$ by chloride abstraction from $[(\text{Tp})\text{CrCl}_3]^-$ produced only the monochloride abstraction product $(\text{Tp})\text{CrCl}_2(\text{THF})$.

The solvated edge building block, *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$ (21) was prepared by chloride abstraction from *trans*- $\text{NiCl}_2(\text{en})_2$. A suitable *trans*-cyanide edge precursor, *trans*- $\text{V}(\text{CN})_2(\text{dmpe})_2$, was identified from the literature and prepared according to the published method.¹⁴

The successful synthesis of several divalent and trivalent corner and edge building block compounds provides an opportunity to explore different charges for the resulting molecular cubes. The main point is that dependent upon precursor selection, the cubes could be either neutral or cationic.

The Spartan program was used to conduct a modeling study to evaluate whether steric interactions would prevent cube assembly with the compounds under investigation. A molecular model was constructed for both the eight and twenty metal atom cubes. The results of these efforts revealed that sufficient void space exists inside the cubes such that steric factors will not play a prohibitive role in the assembly process.

Finally, self-assembly reactions of two types of building block compounds were investigated. The most promising of these reactions based on infrared spectroscopic data is the reaction of four equivalents each of $\text{K}[\text{Cr}(\text{CN})_3(\text{Tp})]$ (20) and $[\text{Ni}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{BF}_4]$ which is leading to a product that has only a single cyanide stretch.

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Chapter V

Investigations of the reduction chemistry of $\text{HAT}-(\text{CN})_6$ and reactivity of the reduced species with transition metals

1. Introduction

A common feature of molecule-based magnets is the presence of polymeric networks of paramagnetic metals bridged by ligands capable of promoting magnetic interactions between the localized d-electrons. In addition to the different pathways for magnetic exchange through the ligand (σ versus π), it is important to consider the size of the linker which is typically inversely related to the strength of the interaction. Consequently, most examples of molecular-based magnets are based on ligands consisting of only a few atoms such as CN^- ¹, $\text{N}(\text{CN})_2^-$ ², and $\text{C}_2\text{O}_4^{2-}$ ³. One strategy for inducing stronger magnetic interactions with longer linkers is to use organic radicals as ligands, due to the ability of unpaired electrons on the ligand to interact with those of the metals. Novel magnets have been obtained in this manner with organic acceptors such as TCNE⁴ and TCNQ⁵.

In the vein of our use of organoradical linkers such as TCNQ, the hexanitrile derivative of 1,4,5,8,9,11-hexazatriphenylene, namely hexaazatriphenylene-hexacarbonitrile ($\text{HAT}-(\text{CN})_6$) (Figure 5.1), offers interesting possibilities for preparing new magnetic materials with first row transition metals. The cyclic voltammogram of $\text{HAT}-(\text{CN})_6$ in acetonitrile,

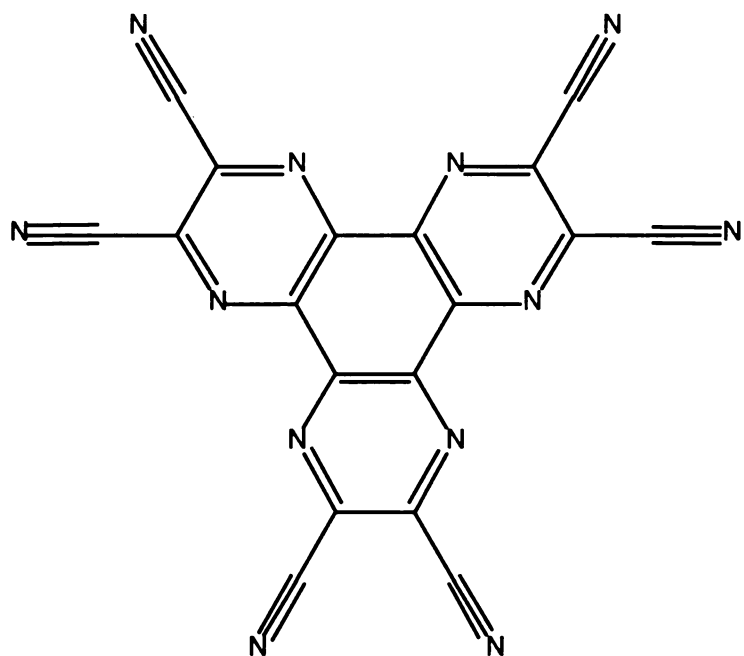


Figure 5.1. A representation of the structure of HAT-(CN)₆ (25)

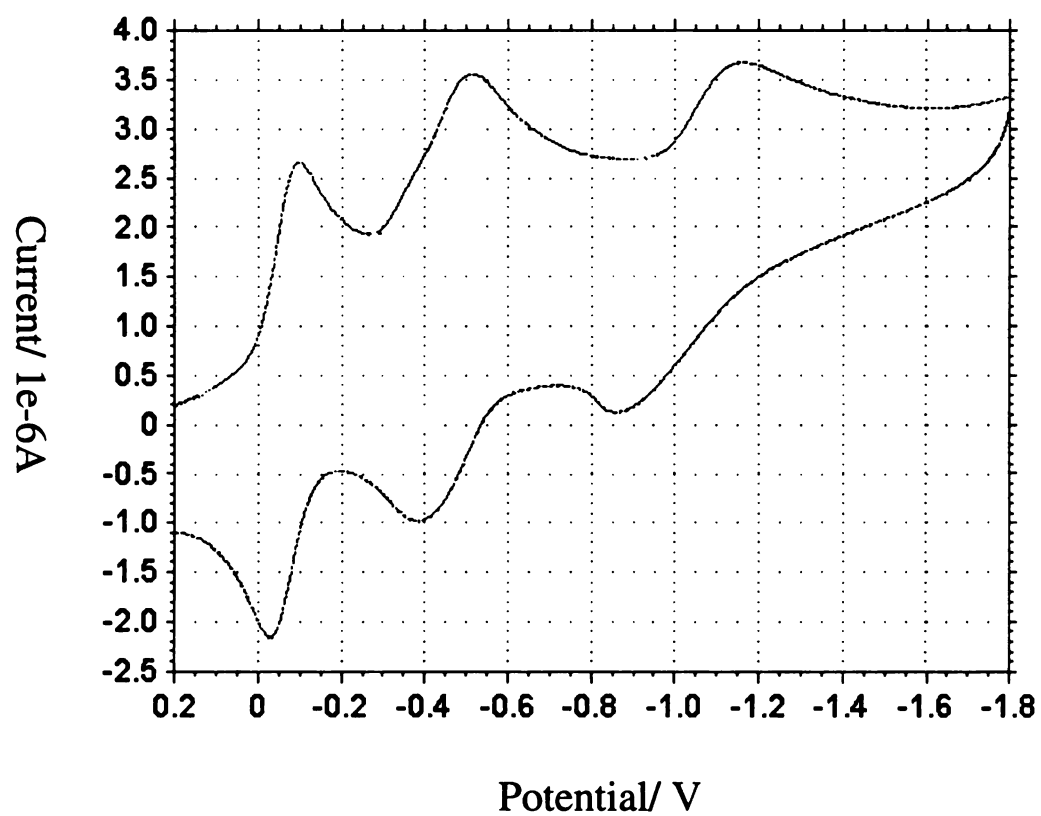


Figure 5.2. Cyclic Voltammogram of HAT-(CN)₆ (25) performed in acetonitrile vs Ag/AgCl.

versus Ag/AgCl, reveals two reversible one-electron reductions located at $E_{1/2} = -0.064$ V and -0.450 V. Reduction by a third electron leads to decomposition as evidenced by an irreversible cathodic feature at -1.16 V (Figure 5.2).¹² The accessibility of the first two redox processes renders $[\text{HAT}-(\text{CN})_6]^-$ and $[\text{HAT}-(\text{CN})_6]^{2-}$ viable candidates for isolation as paramagnetic ligands. In considering the two possible coordination modes of this ligand, the chelating bipyridine moieties in the central rings are expected to be favored over monodentate coordination at the terminal nitrile functionalities. With this situation, the coordination of up to three metals is possible, which would result in a triangular arrangement. Depending upon the metal/ligand ratio, one may anticipate different solid state architectures and molecular species to be formed. During the course of our studies, we noted the report of the compound $\{[\text{Cu}(\text{dppe})]_3[\text{HAT}-(\text{CN})_6]\}$ in which the $[\text{HAT}-(\text{CN})_6]^-$ ligand is chelated to three metal ions.¹³ This is the only compound of the $[\text{HAT}-(\text{CN})_6]^-$ radical that has been reported to date. In this case, however, the magnetic interaction of metal spins through the $[\text{HAT}-(\text{CN})_6]^-$ core could not be probed, since the Cu(I) centers are diamagnetic.

This chapter is a report our studies on the deliberate reduction of $\text{HAT}-(\text{CN})_6$ to $[\text{HAT}-(\text{CN})_6]^-$ and $[\text{HAT}-(\text{CN})_6]^{2-}$ and the reactivity of these reduced species with transition metals. A computational study investigating

the one and two electron reduction products of $\text{HAT}(\text{CN})_6$ was conducted in collaboration with Professor J. E. Jackson of Michigan State University. In addition, EPR studies were conducted in collaboration with Dr. Andrew Ichimura at Michigan State University. The results of these efforts with $\text{HAT}(\text{CN})_6$, $[\text{HAT}(\text{CN})_6]^-$, and both the singlet and triplet electronic configurations of $[\text{HAT}(\text{CN})_6]^{2-}$ will be discussed.

2. Experimental

A. Materials

All solvents were of reagent grade quality and were dried by conventional methods. All manipulations were carried out under an inert atmosphere using standard Schlenk-line and dry box techniques. The molecule $\text{HAT}(\text{CN})_6$ (25) was prepared according to the literature method and recrystallized from a methanol/acetonitrile solution.⁶ The compounds Cp^*Fe , Cp_2Co , and $[\text{Cp}_2\text{Co}][\text{PF}_6]$ were purchased from Strem and used as received. The salts $\text{M}(\text{ClO}_4)_2 \cdot 6(\text{H}_2\text{O})$ ($\text{M} = \text{Mn}, \text{Co}, \text{and Ni}$) were purchased from Aldrich and used without further purification.

B. Physical Measurements

Cyclic Voltammetric (CV) experiments were carried out on a CH Instruments Electrochemical Work Station with a Ag/AgCl reference electrode, a Pt disk working electrode, and a Pt wire auxiliary electrode in

0.1 M [*n*-Bu₄N][PF₆] acetonitrile solutions. Infrared spectra were recorded on solids suspended in Nujol on CsI plates using a Nicolet IR/42 FT-IR spectrometer. Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker Electron Spin Resonance ESP300 E instrument equipped with an Oxford instrument Cryostat ESR900 in the range 4.2-300 K. Variable temperature magnetic susceptibility data were obtained in the range 2-300 K on polycrystalline samples using a Quantum Design, Model MPMS-XL housed in the Department of Physics at Michigan State University.

C. Syntheses

(1) Preparation of HAT-(CN)₆•C₇H₈•CH₃CN, (26)

A sample of HAT-(CN)₆ (0.020 g, 0.052 mmol) was dissolved in 5 mL of acetonitrile and treated with toluene (5 mL). The resulting orange solution was filtered and concentrated by slow evaporation under nitrogen to yield green crystals of HAT-(CN)₆•C₇H₈•CH₃CN (26). $\nu_{\text{CN}} = 2243 \text{ cm}^{-1}$.

(2) Preparation of Co(HAT(CN)₄O₂)(H₂O)₄•4H₂O, (27)

Orange crystals of Co(HAT(CN)₄O₂)(H₂O)₄•4H₂O (27), were obtained by slow evaporation in air of a solution containing Co(ClO₄)₂•6(H₂O) (0.013g, 0.034 mmol) dissolved in 2 mL of deionized water and HAT-(CN)₆ (0.008

g, 0.021 mmol) dissolved in 2 mL of acetonitrile. Yield 0.006 g (60%) $\nu_{\text{CN}} = 2229 \text{ cm}^{-1}$.

(3) Preparation of $\text{Ni}[\text{HAT}(\text{CN})_4\text{O}_2](\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, (28) and

$\text{Mn}[\text{HAT}(\text{CN})_4\text{O}_2](\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, (29)

The compounds $\text{Ni}[\text{HAT}(\text{CN})_4\text{O}_2](\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ (28) and $\text{Mn}[\text{HAT}(\text{CN})_4\text{O}_2](\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, (29) were prepared as crystalline products under the same conditions as $\text{Co}(\text{HAT}(\text{CN})_4\text{O}_2)(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, (27) from the reaction of $\text{Ni}(\text{ClO}_4)_2 \cdot 6(\text{H}_2\text{O})$ (0.013 g, 0.034 mmol) or $\text{Mn}(\text{ClO}_4)_2 \cdot 6(\text{H}_2\text{O})$ (0.013 g, 0.033 mmol) with $\text{HAT}(\text{CN})_6$ (0.008 g, 0.021 mmol). (28) Yield 0.005 g (50%) $\nu_{\text{CN}} = 2229 \text{ cm}^{-1}$. (29) Yield 0.005 g (50%) $\nu_{\text{C}\equiv\text{N}} = 2229 \text{ cm}^{-1}$.

(4) Preparation of $\{(\text{Cp}_2\text{Fe})_3[\text{HAT}(\text{CN})_6]\} \cdot \text{CH}_3\text{CN}$, (30)

Crystals of $\{(\text{Cp}_2\text{Fe})_3[\text{HAT}(\text{CN})_6]\} \cdot \text{CH}_3\text{CN}$ (30), were prepared by mixing acetonitrile solutions of ferrocene (0.100 g, 0.528 mmol) and $\text{HAT}(\text{CN})_6$ (0.068 g, 0.176 mmol). Concentration of this solution either *in vacuo* or by evaporation in air resulted in the formation of dark green crystals. $\nu_{\text{C}\equiv\text{N}} = 2243 \text{ cm}^{-1}$.

(5) Preparation of $\{[(\text{Cp})_2\text{Co}][\text{PF}_6]\}_3\text{HAT}(\text{CN})_6$ (31)

The compound $\{[(\text{Cp})_2\text{Co}][\text{PF}_6]\}_3\text{HAT}-(\text{CN})_6$ (31) was prepared by mixing acetonitrile solutions of $[\text{Cp}_2\text{Co}][\text{PF}_6]$ (0.100 g, 0.528 mmol) and $\text{HAT}-(\text{CN})_6$ (0.068 g, 0.176 mmol). Concentration of this solution by slow evaporation under nitrogen results in the deposition of dark green crystals (31). $\nu_{\text{C}\equiv\text{N}} = 2243 \text{ cm}^{-1}$.

(6) Preparation of $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT}-(\text{CN})_6]_2\} \cdot 3\text{C}_6\text{H}_6$, (32)

Addition of a THF solution (10 mL) of $[n\text{-Bu}_4\text{N}][\text{I}]$ (0.432 g, 1.17 mmol) to a THF solution of $\text{HAT}-(\text{CN})_6$ (0.075 g, 0.195 mmol) produced a green solution. Heating was required for complete reagent dissolution. Concentration of the solution to ~7 mL precipitated unreacted $[n\text{-Bu}_4\text{N}][\text{I}]$ as a white crystalline solid. After removal of the $[n\text{-Bu}_4\text{N}][\text{I}]$ by filtration, benzene (15 mL) was added. Green needle-shaped crystals of $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT}-(\text{CN})_6]_2\} \cdot 3\text{C}_6\text{H}_6$, (32) were obtained after the solution had been standing undisturbed for two days. $\nu_{\text{C}\equiv\text{N}} = 2243, 2228 \text{ cm}^{-1}$

(7) Preparation of $[\text{CoCp}_2][\text{HAT}-(\text{CN})_6]$, (33)

$[\text{CoCp}_2][\text{HAT}-(\text{CN})_6]$ (33), was prepared by mixing acetonitrile solutions of $\text{HAT}-(\text{CN})_6$ (0.304 g, 0.793 mmol) and cobaltocene (0.050 g, 0.264 mmol). The solution was concentrated and tetrahydrofuran added to precipitate the green product, which was collected by filtration, washed with

tetrahydrofuran followed by diethyl ether, and dried *in vacuo*. Yield 0.113 g (75%). $\nu_{\text{C}\equiv\text{N}} = 2214 \text{ cm}^{-1}$. The EPR spectrum of a solid sample at 4K shows an isotropic signal at $g = 2.0084$ and a line-width of 7 G. *Anal.* Calcd for $\text{C}_{28}\text{N}_{12}\text{H}_{10}\text{Co}_1$: C, 58.65; H, 1.76; N, 29.31. Found: C, 58.78; H, 1.92; N, 28.88.

(8) Preparation of $[\text{CoCp}_2]_2[\text{HAT}-(\text{CN})_6]$ (34)

The compound $[\text{CoCp}_2]_2[\text{HAT}-(\text{CN})_6]$ (34) was prepared by combining acetonitrile solutions of $\text{HAT}-(\text{CN})_6$ (0.075 g, 0.195 mmol) and cobaltocene (0.111 g, 0.585 mmol). The blue-green product precipitated from solution with concentration and was collected by filtration, washed with tetrahydrofuran followed by diethyl ether, and dried *in vacuo*. Yield 0.126 g (85%). $\nu_{\text{C}\equiv\text{N}} = 2195 \text{ cm}^{-1}$. *Anal.* Calcd for $\text{C}_{38}\text{N}_{12}\text{H}_{20}\text{Co}_2$: C, 59.86; H, 2.64; N, 22.04. Found: C, 58.95; H, 2.81; N, 22.49.

(9) Preparation of $[\text{M}][\text{HAT}-(\text{CN})_6]_2$ (M = Co (35), Zn (36))

$[\text{M}][\text{HAT}-(\text{CN})_6]_2$ (M = Co (35) or Zn(36)) complexes were prepared by the reaction of an excess of the metal powder or chips with a vigorously stirred acetonitrile solution of $\text{HAT}-(\text{CN})_6$ (0.200 g, 0.520 mmol). The resulting dark blue-green solutions are filtered through Celite and reduced to dryness. The solid was washed with dichloromethane followed by diethyl

ether and dried *in vacuo*. Co[HAT-(CN)₆]₂ (35): Yield 0.365 g (85%). $\nu_{\text{C}\equiv\text{N}}$ = 2210 cm⁻¹; The results of EPR studies are presented in the results and discussion section of this chapter. *Anal.* Calcd. for C₃₆N₂₄Co: C, 52.25; N, 40.62. Found: C, 51.32; N, 39.95. Zn[HAT-(CN)₆]₂ (36): Yield 0.368 g (85%) $\nu_{\text{C}\equiv\text{N}}$ = 2212 cm⁻¹; *Anal.* Calcd. for C₃₆N₂₄Zn: C, 51.84; N, 40.31. Found: C, 51.06; N, 39.73.

D. X-ray Crystallography

Single crystal X-ray structural analyses were performed on a Bruker SMART 1K CCD platform diffractometer with graphite monochromated MoK_α radiation (λ_{α} = 0.71069 Å).¹³ The frames were integrated in the Bruker SAINT software package¹³, and the data were corrected for absorption using the SADABS program.¹³ The structures were solved using the SHELXTL V.5.10 package.¹³ Pertinent crystallographic data and refinement parameters are provided in Tables 5.1–5.3.

(1) HAT-(CN)₆•toluene•CH₃CN, (26)

(i) Data Collection and Reduction

Green X-ray quality single crystals were obtained by slow evaporation of an acetonitrile/toluene 50/50 solution of HAT-(CN)₆ under nitrogen. A crystal of dimensions 0.25 x 0.15 x 0.05 mm³ was covered in Paratone oil

and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a monoclinic cell. A total of 6174 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.56° .

(ii) Structural Solution and Refinement

From the systematic absences, the space group was determined to be $P2_1/c$. The structure was solved by the SHELXS structure program and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions. The crystal diffracted poorly which lead to refinement limitations ($R_{\text{int}} = 0.1401$ and $R_g = 0.1381$). The final cycle of full matrix least-squares refinement was based on 2724 observed reflections with $F_o > 4 \text{ sig}(F_o)$ and 361 parameters to give $R1 = 0.0932$ and $wR2 = 0.2592$ and a goodness-of-fit value of 1.042.

(2) $\text{Co}(\text{HAT}(\text{CN})_4\text{O}_2)(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, (27), $\text{Ni}[\text{HAT}(\text{CN})_4\text{O}_2](\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ (28), and $\text{Mn}[\text{HAT}(\text{CN})_4\text{O}_2](\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ (29)

(i) Data Collection and Reduction

Orange X-ray quality single crystals of the isostructural compounds (27), (28), and (29) formed from aerial evaporation of solutions of HAT-(CN)₆ dissolved in CH₃CN and M(ClO₄)₂•6H₂O (M = Mn, Co, Ni) dissolved in water. Crystals of dimensions 0.75 x 0.22 x 0.13 mm³ (27), 0.40 x 0.09 x 0.09 mm³ (28), and 0.25 x 0.12 x 0.11 mm³ (29) were covered in Paratone oil and mounted on the tips of glass fibers with silicone grease. The cell constants and orientation matrix for data collection obtained for all three compounds corresponded to triclinic cells. Totals of 13414, 13477, and 1350 unique reflections were collected for (27), (28), and (29) at 173 K using the ω -scan technique to a maximum 2 θ value of 56.76°.

(ii) Structural Solution and Refinement

The space group for all three structures was determined to be P-1. The structures were solved by the SHELXS structure program and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located from the difference map. The final cycle of full matrix least-squares refinement for (27) was based on 3199 observed reflections with $F_o > 4 \text{ sig}(F_o)$ and 398 parameters to give $R1 = 0.0541$ and $wR2 = 0.1252$ and a goodness-of-fit value of 1.023. The final cycle of full matrix least squares refinement for (28) was based on

2884 observed reflections with $F_o > 4 \text{ sig}(F_o)$ and 398 parameters to give $R1 = 0.0556$ and $wR2 = 0.1126$ and a goodness-of-fit value of 0.913. The final cycle of full matrix least-squares refinement for (29) was based on 3546 observed reflections with $F_o > 4 \text{ sig}(F_o)$ and 385 parameters to give $R1 = 0.0608$ and $wR2 = 0.1773$ and a goodness-of-fit value of 1.211.

(3) $\{(\text{Cp}_2\text{Fe})_3[\text{HAT}-(\text{CN})_6]\} \cdot \text{CH}_3\text{CN}$, (30)

(i) Data collection and reduction

Green X-ray quality single crystals were obtained by evaporation in vacuo of an acetonitrile solution of $\text{HAT}-(\text{CN})_6$ and Cp_2Fe . A crystal of dimensions $0.55 \times 0.49 \times 0.35 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a trigonal crystal system. A total of 7587 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.48° .

(ii) Structural Solution and Refinement

The space group was determined to be P3 from the systematic absences. The structure was solved by the SHELXS structure program and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. With the exceptions of C102 and C112 all non-hydrogen atoms were refined with anisotropic thermal parameters. The

hydrogen atoms were placed in calculated positions. The final cycle of full matrix least-squares refinement was based on 6109 observed reflections with $F_o > 4 \text{ sig}(F_o)$ and 378 parameters to give $R1 = 0.0890$ and $wR2 = 0.2335$ and a goodness-of-fit value of 1.420.

(4) $\{([Cp_2Fe][PF_6])_3[HAT-(CN)_6]\}$, (31)

(i) Data collection and reduction

Green X-ray quality single crystals were obtained by evaporation under nitrogen of an acetonitrile solution of $HAT-(CN)_6$ and $[Cp_2Co][PF_6]$. A crystal of dimensions $0.20 \times 0.15 \times 0.05 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a monoclinic cell. A total of 6819 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.56° .

(ii) Structural Solution and Refinement

The space group was determined to be $C2$ from the systematic absences. The structure was solved by the SHELXS structure program and refined by full matrix least-squares refinement using the SHELXL97 structure refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were placed in calculated

positions. The crystal diffracted poorly which led to refinement limitations ($R_{\text{int}} = 0.1017$ and $R_{\sigma} = 0.1461$). The final cycle of full matrix least-squares refinement was based on 3636 observed reflections with $F_o > 4 \text{ sig}(F_o)$ and 347 parameters to give $R1 = 0.1021$ and $wR2 = 0.2666$ and a goodness-of-fit value of 1.05.



(i) Data collection and reduction

The addition of benzene to the green THF reaction solution of $[n\text{-Bu}_4\text{N}]\text{I}$ and $\text{HAT}(\text{CN})_6$ led to the deposition of green X-ray quality single crystals of $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT}(\text{CN})_6]_2\} \cdot 3\text{C}_6\text{H}_6$, (32) after two days. A crystal of dimensions $0.60 \times 0.20 \times 0.20 \text{ mm}^3$ was covered in Paratone oil and mounted on the tip of a glass fiber with silicone grease. The cell constants and orientation matrix for data collection corresponded to a rhombohedral cell. A total of 9061 unique reflections were collected at 173 K using the ω -scan technique to a maximum 2θ value of 56.65° .

(ii) Structural Solution and Refinement

The space group was determined to be $R\bar{3}$ from the systematic absences. The structure was solved by the SHELXS structure program and refined by full matrix least-squares refinement using the SHELXL97 structure

Table 5.1. Summary of crystallographic data for HAT-(CN)₆•C₇H₈•CH₃CN (26){(FeCp₂)₃[HAT-(CN)₆]}•CH₃CN (30), and{([FeCp₂][PF₆])₃[HAT-(CN)₆]}•CH₃CN (31)

formula	C ₂₇ H ₁₁ N ₁₃	C ₅₀ H ₃₃ N ₁₃ Fe ₃	C ₄₈ H ₃₀ N ₁₂ P ₃ F ₁₈ Co ₃
formula weight	517.49	983.44	1386.54
space group	P2(1)/c	P3	C2
a, Å	20.618(4)	16.673(2)	25.780(5)
b, Å	7.3790(15)	16.673(2)	14.903(3)
c, Å	17.362(4)	9.878(2)	7.5610(15)
α, deg.	90.00	90.00	90.00
β, deg.	104.53(3)	90.00	90.85(3)
γ, deg.	90.00	120.00	90.00
V, Å ³	2556.9(9)	2378.0(7)	2904.5(10)
Z	4	2	2
^d calc, g/cm ³	1.344	1.373	1.585
μ (Mo Kα), cm ⁻¹	1.09	9.52	1.032
temperature, K	173	173	173
R ₁	0.0932	0.0890	0.1017
wR ₂	0.2127	0.2335	0.2666
goodness-of-fit	1.042	1.420	1.052

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

Table 5.2. Summary of crystallographic data for {Co[HAT-(CN)₄O₂(H₂O)₄}.4H₂O (27), {Ni[HAT-(CN)₄O₂(H₂O)₄}.4H₂O (28) and {Mn[HAT-(CN)₄O₂(H₂O)₄}.4H₂O (29)

formula	C ₁₆ H ₂₀ N ₁₀ O ₁₀ Co ₁	C ₁₆ H ₂₀ N ₁₀ O ₁₀ Ni ₁	C ₁₆ H ₂₀ N ₁₀ O ₁₀ Mn ₁
formula weight	571.32	571.09	576.32
space group	P-1	P-1	P-1
a, Å	8.571(2)	8.546(2)	8.570(3)
b, Å	10.065(2)	10.072(2)	10.094(2)
c, Å	13.571(3)	13.493(3)	13.571(3)
α, deg.	81.78(3)	82.07(3)	82.55(3)
β, deg.	77.43(3)	77.53(3)	77.51(3)
γ, deg.	85.70(3)	85.49(3)	85.78(3)
V, Å ³	1129.8(4)	1121.7(4)	1135.3(4)
Z	2	2	2
^d calc, g/cm ³	1.692	1.691	1.690
μ (Mo Kα), cm ⁻¹	8.43	9.43	8.30
temperature, K	173	173	173
R ₁	0.0541	0.0556	0.0608
wR ₂	0.1252	0.1126	0.1773
goodness-of-fit	1.023	0.913	1.211

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\Sigma w(|F_o| - |F_c|)^2 / N_{\text{obs}} - N_{\text{parameters}}]^{1/2}$$

Table 5.3. Summary of crystallographic data for $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT}(\text{CN})_6]_2\} \cdot 3\text{C}_6\text{H}_6$, (32)

formula	$\text{C}_{102}\text{H}_{126}\text{N}_{27}\text{I}_4$
formula weight	2237.9
space group	R3
a, Å	26.690(4)
b, Å	26.690(40)
c, Å	13.676(3)
α , deg.	90.00
β , deg.	90.00
γ , deg.	120.00
V, Å ³	8437(2)
Z	3
d_{calc} , g/cm ³	1.175
μ (Mo K α), cm ⁻¹	1.155
temperature, K	173
trans. factors, max., min.	1.000, 0.607
R ₁	0.1094
wR ₂	0.2679
goodness-of-fit	0.993

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$\text{goodness-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

refinement program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions. The final cycle of full matrix least-squares refinement was based on 4096 observed reflections with $F_o > 4 \text{ sig}(F_o)$ and 361 parameters to give $R1 = 0.1094$ and $wR2 = 0.3291$ and a goodness-of-fit value of 0.993.

3. Results and Discussion.

A. Chemistry of neutral HAT-(CN)₆

(1) Molecular Structure of HAT-(CN)₆

The HAT-(CN)₆ molecule is a strongly electron-deficient heterocycle. One consequence of this is that it avoids self- π -complexation in its neutral form. Crystals obtained from a methanol/acetonitrile mixture by J.R. Galán-Mascarós, a postdoctoral fellow in the Dunbar laboratories, revealed that neutral HAT-(CN)₆ molecules have no tendency to stack, rather they are significantly offset with respect to one another, forming staircase-like chains (Figure 5.3). The intermolecular spacing is 3.75 Å, which is larger than the expected van der Waals radii sum of 3.54 Å.⁷ The overall crystal packing is primarily dominated by perpendicular CN- π interactions which leads to a complicated, but highly symmetric, 3D hexagonal arrangement as illustrated in Figure 5.4.

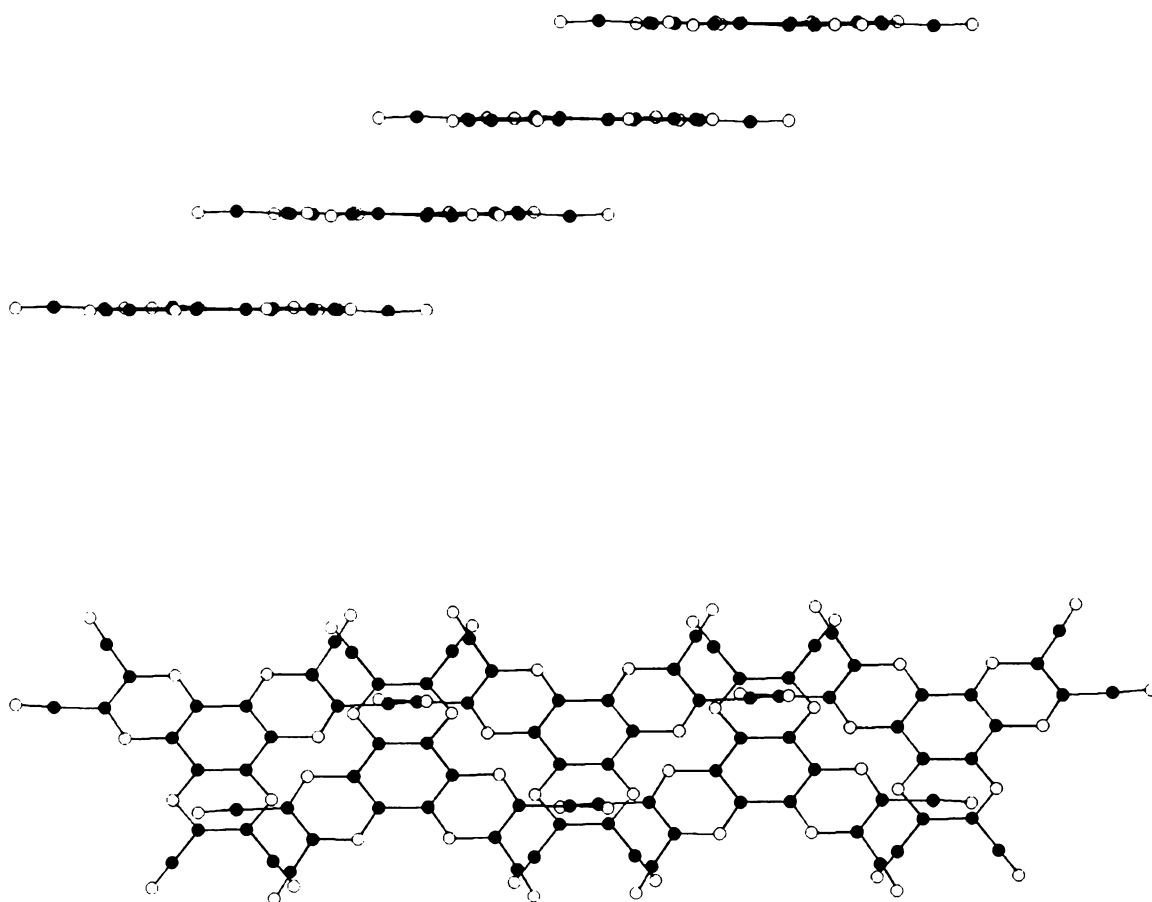


Figure 5.3. Two different views of one of the HAT-(CN)₆ chains in (25).

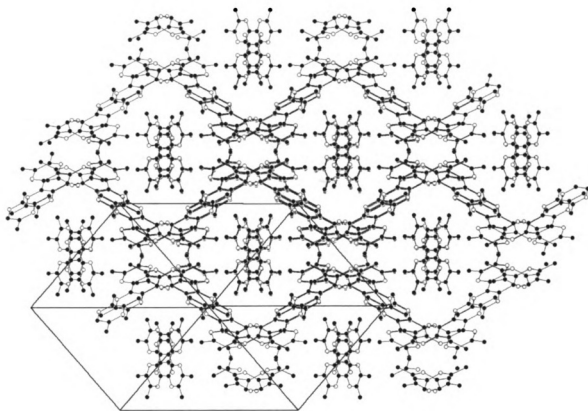


Figure 5.4. A view of the 3D packing arrangement of HAT-(CN)₆ molecules in (25).

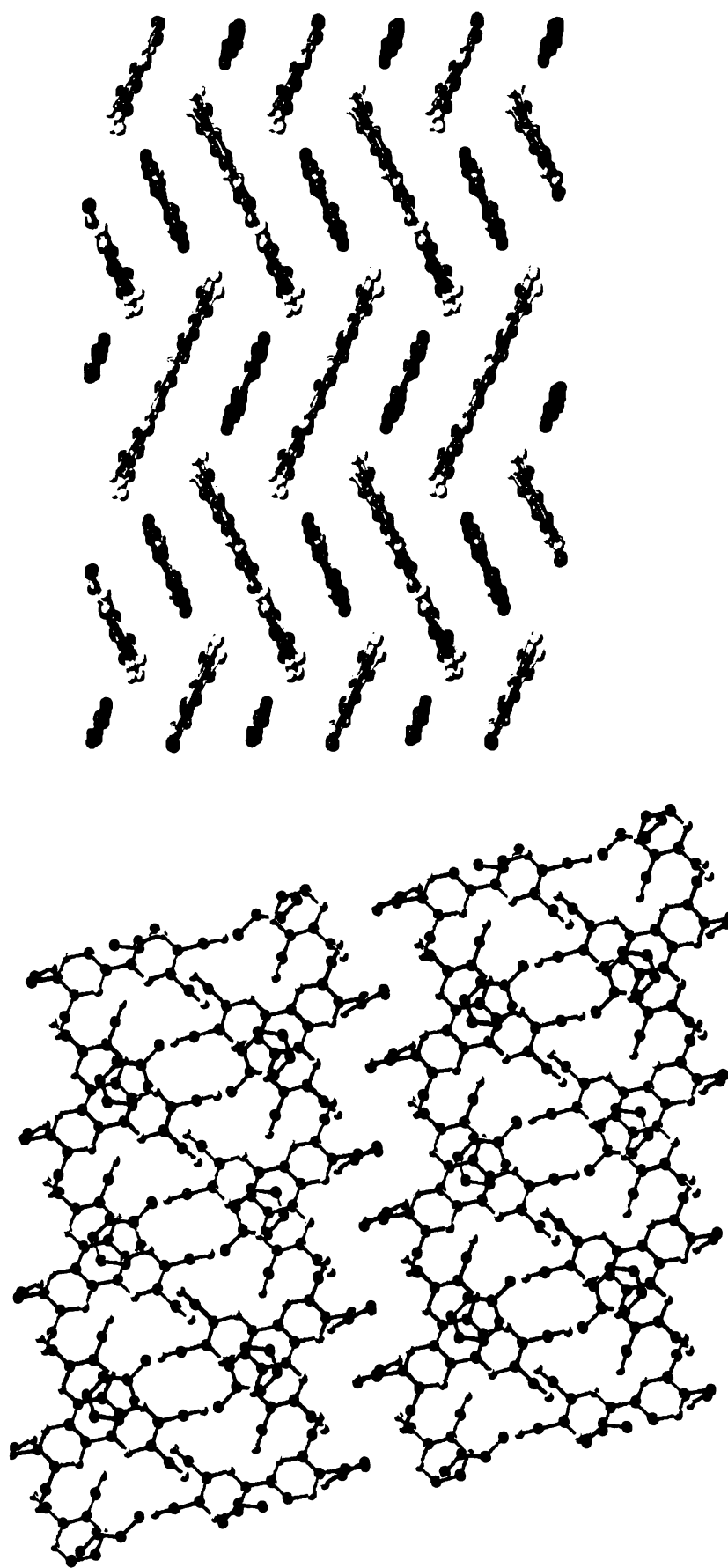


Figure 5.5. A view of the structure of the packing in HAT-(CN)₆•C₇H₈•CH₃CN (26) looking down the *b* axis (left) and *a* axis (right).

Slow evaporation of a 50/50 acetonitrile/toluene solution under nitrogen resulted in a second crystalline form of HAT-(CN)₆ (25) (Figure 5.5). Single crystal X-ray diffraction analysis revealed the incorporation of both toluene and acetonitrile molecules into the interstices of the structure. The packing motif consists of angled, interpenetrating columns of alternating HAT-(CN)₆ and toluene molecules. The toluene molecules reside below HAT-(CN)₆ bipyridine moieties. The incorporation of toluene combined with the interpenetrating nature of the columns precludes any self- π -complexation of HAT-(CN)₆. The acetonitrile molecules reside in the channels defined by three nearest-neighbor HAT-(CN)₆/toluene columns.

(2) The templating effect of FeCp₂ and [CoCp₂][PF₆] on the crystal structures of HAT-(CN)₆

Ferrocene was initially employed as a potential reducing agent for HAT-(CN)₆, but it proved to be an insufficiently strong reductant for this purpose. The green crystalline product that was isolated from this reaction was shown by single-crystal X-ray crystallography to be the 3:1 phase {(FeCp₂)₃[HAT-(CN)₆]}.CH₃CN (30) (Figure 5.6). Support for the neutral assignment for the HAT-(CN)₆ molecules in this compound comes from the $\nu_{C\equiv N}$ mode at 2243 cm⁻¹ in the infrared spectrum. It appears that the

ferrocene molecules act as templates in the formation of a layered structure with a trigonal motif. Within a given layer, the ferrocene molecules reside in the spaces adjacent to the chelating bipyridine moieties of HAT-(CN)₆. Adjacent layers are staggered such that the ferrocene in one layer lies underneath the cyano groups of the HAT-(CN)₆ in the layer above it.

The metallocene salt, [CoCp₂][PF₆], also proved to be a capable template for the formation of a layered structure with neutral HAT-(CN)₆. Slow evaporation under nitrogen of an acetonitrile solution of [CoCp₂][PF₆] and HAT(CN)₆ produced green crystals that were determined by single crystal X-ray diffraction to be the 3:1 phase {[CoCp₂][PF₆]}₃HAT-(CN)₆ (31) (Figure 5.7). The packing in this structure consists of columns composed of alternating layers of HAT-(CN)₆ and three [PF₆]⁻ anions. The P atoms of the [PF₆]⁻ are centered underneath the NC-C_(ring). The [PF₆]⁻ anions are oriented with the 3-fold rotation axis of the octahedra perpendicular to the HAT-(CN)₆. The [CoCp₂]⁺ cations reside in the channels defined by three nearest neighbor HAT-(CN)₆/[PF₆]⁻ columns and are slightly canted such that the Cp rings are not parallel to the HAT-(CN)₆ layers. Unlike the {(FeCp₂)₃[HAT(CN)₆]}.CH₃CN (30) structure with the neutral metallocene FeCp₂, the cationic [CoCp₂]⁺ do not occupy the space adjacent to the bipyridine moieties but reside in the plane of the [PF₆]⁻ counteranions.

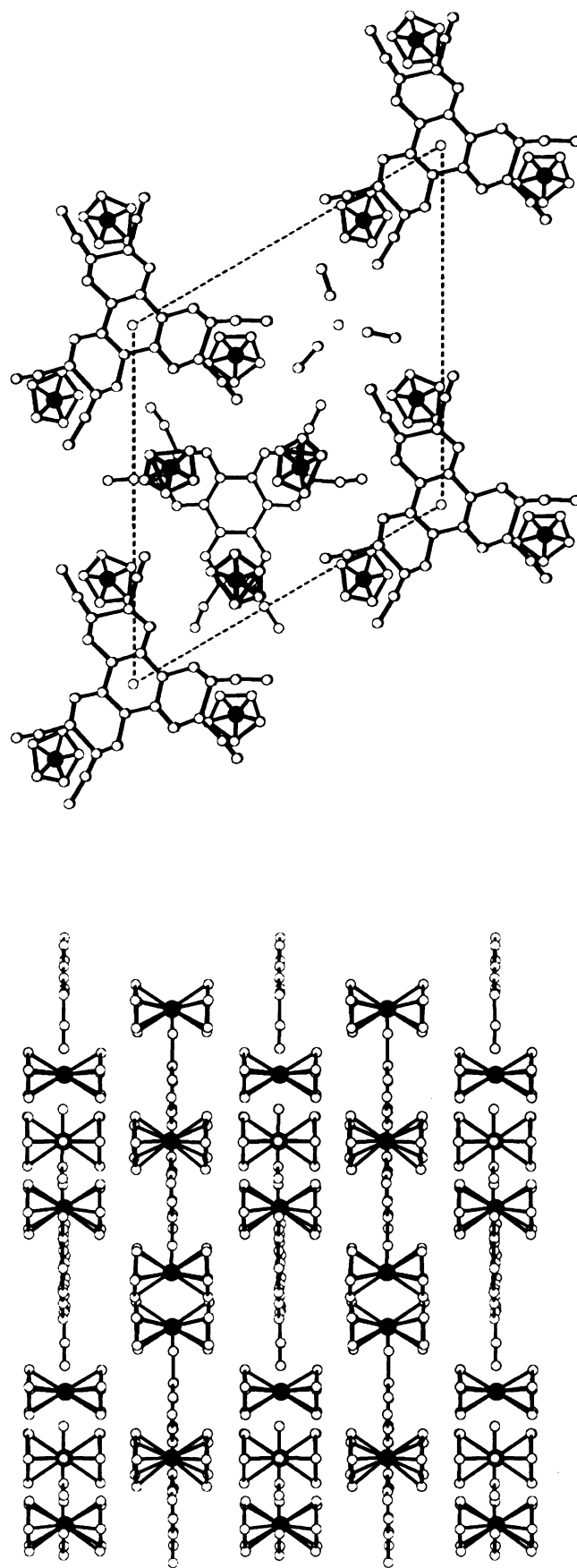


Figure 5.6. Views of the packing in the crystal structure of $\{(\text{FeCp}_2)_3[\text{HAT}-(\text{CN})_6]\} \cdot \text{CH}_3\text{CN}$ (30) viewed down the *a* axis (left) and *c* axis (right).

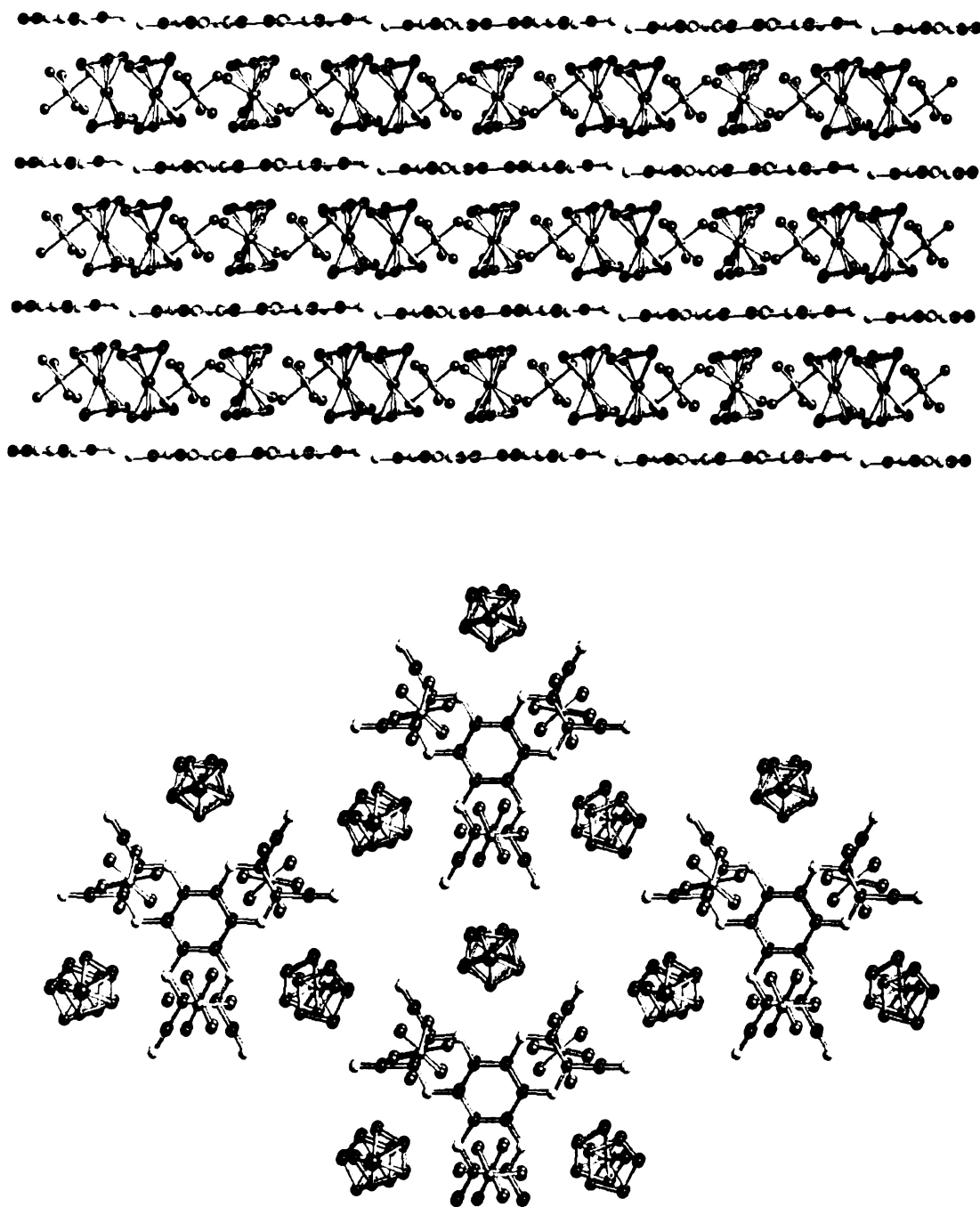


Figure 5.7. Views of the packing in the crystal structure of $\{([Cp_2Co][PF_6])_3[HAT(CN)_6] \bullet CH_3CN\}$ (31) looking down the *b* axis (top) and the *c* axis (bottom).

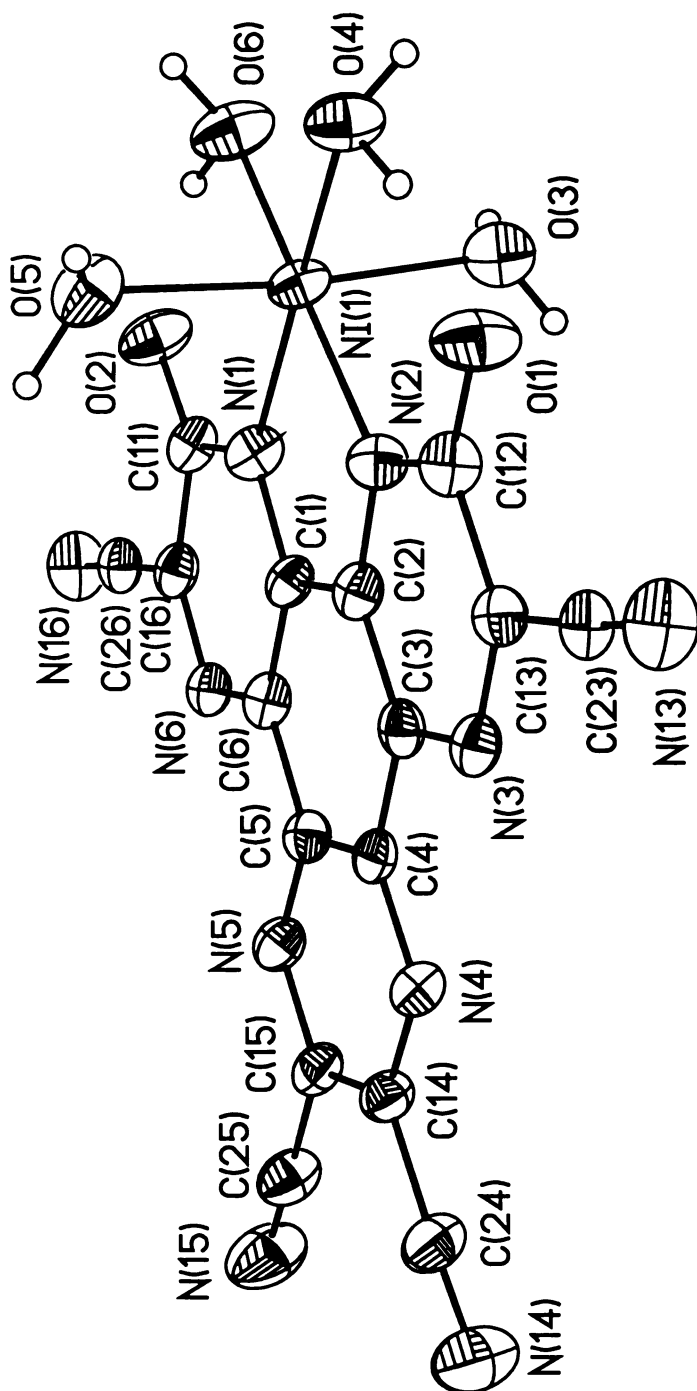


Figure 5.8. A thermal ellipsoid plot of the structure of $\text{Ni}(\text{HAT}(\text{CN})_4\text{O}_2)(\text{H}_2\text{O})_4$ (29). All atoms are represented at the 50% level. Compound (29) is isostructural with compounds $\{\text{Co}[\text{HAT}(\text{CN})_4\text{O}_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}\}$ (27) and $\{\text{Mn}[\text{HAT}(\text{CN})_4\text{O}_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}\}$ (28).

Table 5.4. Bond lengths [$\text{\AA}$] for $\{\text{Co}(\text{HAT}(\text{CN})_4\text{O}_2(\text{H}_2\text{O})_4)\cdot 4\text{H}_2\text{O}$ (27)

Co(1)-O(3)	2.124(3)
Co(1)-O(4)	2.095(3)
Co(1)-O(5)	2.122(4)
Co(1)-O(6)	2.081(3)
Co(1)-N(1)	2.146(3)
Co(1)-N(2)	2.144(3)
C(1)-N(1)	1.355(4)
C(1)-C(2)	1.472(4)
C(1)-C(6)	1.403(4)
C(2)-N(2)	1.359(4)
C(2)-C(3)	1.400(4)
C(3)-N(3)	1.377(4)
C(3)-C(4)	1.450(4)
C(4)-N(4)	1.346(4)
C(4)-C(5)	1.438(4)
C(5)-N(5)	1.345(4)
C(5)-C(6)	1.449(4)
C(6)-N(6)	1.374(4)
C(11)-O(1)	1.244(4)
C(11)-N(1)	1.384(4)
C(11)-C(16)	1.473(5)
C(12)-O(2)	1.252(4)
C(12)-N(2)	1.371(4)
C(12)-C(13)	1.466(5)
C(13)-N(3)	1.322(4)
C(13)-C(23)	1.437(4)
C(14)-N(4)	1.341(4)
C(14)-C(15)	1.423(4)
C(14)-C(24)	1.458(5)
C(15)-N(5)	1.341(4)
C(15)-C(25)	1.451(5)
C(16)-N(6)	1.322(4)
C(16)-C(26)	1.444(4)
C(23)-N(13)	1.155(4)
C(24)-N(14)	1.148(4)
C(25)-N(15)	1.144(4)
C(26)-N(16)	1.157(4)

Table 5.5. Bond angles [deg] for {Co(HAT(CN)₄O₂(H₂O)₄}•4H₂O (27)

O(3)-Co(1)-N(1)	95.88(12)
O(3)-Co(1)-N(2)	172.35(12)
O(4)-Co(1)-O(3)	92.21(13)
O(4)-Co(1)-O(5)	90.40(13)
O(4)-Co(1)-N(1)	171.11(11)
O(4)-Co(1)-N(2)	94.44(11)
O(5)-Co(1)-O(3)	86.57(15)
O(5)-Co(1)-N(1)	93.73(12)
O(5)-Co(1)-N(2)	89.62(13)
O(6)-Co(1)-O(3)	88.84(14)
O(6)-Co(1)-O(4)	86.87(14)
O(6)-Co(1)-O(5)	174.57(13)
O(6)-Co(1)-N(1)	89.63(13)
O(6)-Co(1)-N(2)	95.27(12)
N(2)-Co(1)-N(1)	77.74(10)
O(1)-C(11)-N(1)	122.6(3)
O(1)-C(11)-C(16)	121.9(3)
N(1)-C(11)-C(16)	115.6(3)
O(2)-C(12)-N(2)	122.3(3)
O(2)-C(12)-C(13)	121.0(3)
N(2)-C(12)-C(13)	116.7(3)
C(1)-N(1)-C(11)	118.7(3)
C(1)-N(1)-Co(1)	114.2(2)
C(11)-N(1)-Co(1)	127.0(2)
C(2)-N(2)-C(12)	117.8(3)
C(2)-N(2)-Co(1)	114.6(2)
C(12)-N(2)-Co(1)	127.6(2)

Table 5.6. Bond lengths [Å] for {Ni(HAT(CN)₄O₂(H₂O)₄}•4H₂O (29)

Ni(1)-O(3)	2.067(4)
Ni(1)-O(4)	2.060(3)
Ni(1)-O(5)	2.061(3)
Ni(1)-O(6)	2.069(3)
Ni(1)-N(1)	2.092(3)
Ni(1)-N(2)	2.095(3)
C(1)-N(1)	1.350(5)
C(1)-C(6)	1.395(5)
C(1)-C(2)	1.470(5)
C(2)-N(2)	1.348(5)
C(2)-C(3)	1.396(5)
C(3)-N(3)	1.370(4)
C(3)-C(4)	1.446(5)
C(4)-N(4)	1.338(4)
C(4)-C(5)	1.427(5)
C(5)-N(5)	1.350(4)
C(5)-C(6)	1.441(5)
C(6)-N(6)	1.363(4)
C(11)-O(2)	1.238(4)
C(11)-N(1)	1.385(5)
C(11)-C(16)	1.461(5)
C(12)-O(1)	1.251(4)
C(12)-N(2)	1.374(4)
C(12)-C(13)	1.452(5)
C(13)-N(3)	1.318(4)
C(13)-C(23)	1.444(5)
C(14)-N(4)	1.339(5)
C(14)-C(15)	1.409(5)
C(14)-C(24)	1.459(5)
C(15)-N(5)	1.333(5)
C(15)-C(25)	1.454(5)
C(16)-N(6)	1.311(4)
C(16)-C(26)	1.449(5)
C(23)-N(13)	1.138(5)
C(24)-N(14)	1.134(5)
C(25)-N(15)	1.136(5)
C(26)-N(16)	1.143(5)

Table 5.7. Bond angles [deg] for {Ni(HAT(CN)₄O₂(H₂O)₄}•4H₂O (29)

O(3)-Ni(1)-O(6)	87.22(17)
O(3)-Ni(1)-N(1)	94.10(13)
O(3)-Ni(1)-N(2)	89.74(15)
O(4)-Ni(1)-O(3)	89.36(14)
O(4)-Ni(1)-O(5)	86.75(15)
O(4)-Ni(1)-O(6)	91.50(16)
O(4)-Ni(1)-N(1)	172.62(14)
O(4)-Ni(1)-N(2)	94.16(13)
O(5)-Ni(1)-O(3)	173.87(15)
O(5)-Ni(1)-O(6)	88.15(15)
O(5)-Ni(1)-N(1)	90.31(14)
O(5)-Ni(1)-N(2)	95.26(13)
O(6)-Ni(1)-N(1)	95.17(14)
O(6)-Ni(1)-N(2)	173.55(14)
N(1)-Ni(1)-N(2)	79.36(11)
N(2)-C(2)-C(3)	123.9(3)
O(2)-C(11)-N(1)	122.6(3)
O(2)-C(11)-C(16)	122.0(3)
N(1)-C(11)-C(16)	115.4(3)
O(1)-C(12)-N(2)	121.9(3)
O(1)-C(12)-C(13)	121.6(3)
N(2)-C(12)-C(13)	116.5(3)
C(1)-N(1)-C(11)	118.1(3)
C(1)-N(1)-Ni(1)	113.9(2)
C(11)-N(1)-Ni(1)	127.9(3)
C(2)-N(2)-C(12)	117.7(3)
C(2)-N(2)-Ni(1)	113.8(2)
C(12)-N(2)-Ni(1)	128.5(3)
C(13)-N(3)-C(3)	116.0(3)
C(4)-N(4)-C(14)	116.8(3)
C(15)-N(5)-C(5)	116.6(3)
C(16)-N(6)-C(6)	116.7(3)

Table 5.8. Bond lengths [$\text{\AA}$] for $\{\text{Mn}(\text{HAT}(\text{CN})_4\text{O}_2(\text{H}_2\text{O})_4)\cdot 4\text{H}_2\text{O}$ (28)

Mn(1)-O(4)	2.163(3)
Mn(1)-O(6)	2.186(4)
Mn(1)-O(3)	2.192(4)
Mn(1)-O(5)	2.224(4)
Mn(1)-N(1)	2.280(3)
Mn(1)-N(2)	2.286(3)
N(1)-C(11)	1.381(4)
N(2)-C(2)	1.354(4)
N(2)-C(12)	1.369(4)
N(3)-C(13)	1.318(4)
N(3)-C(3)	1.368(4)
N(4)-C(14)	1.340(4)
N(4)-C(4)	1.356(4)
N(5)-C(15)	1.349(4)
N(6)-C(16)	1.322(4)
N(6)-C(6)	1.363(4)
C(1)-C(2)	1.478(4)
C(1)-N(1))	1.353(4)
C(3)-C(2)	1.404(4)
C(4)-C(3)	1.449(4)
C(5)-N(5)	1.344(4)
C(5)-C(4)	1.426(4)
C(5)-C(6)	1.452(4)
C(6)-C(1)	1.401(5)
C(12)-C(13)	1.459(4)
C(15)-C(14)	1.411(4)
C(15)-C(25)	1.453(5)
C(16)-C(26)	1.444(4)
C(16)-C(11)	1.453(5)
C(23)-N(13)	1.161(4)
C(23)-C(13)	1.440(4)
C(24)-N(14)	1.142(5)
C(24)-C(14)	1.451(5)
C(25)-N(15)	1.146(5)
C(26)-N(16)	1.165(4)
O(1)-C(11)	1.252(4)
O(2)-C(12)	1.249(4)

Table 5.9. Bond angles [deg] for {Mn(HAT(CN)₄O₂(H₂O)₄}•4H₂O (28)

O(3)-Mn(1)-N(1)	95.54(15)
O(3)-Mn(1)-N(2)	166.75(15)
O(3)-Mn(1)-O(5)	85.78(19)
O(4)-Mn(1)-O(6)	87.33(14)
O(4)-Mn(1)-O(3)	100.29(16)
O(4)-Mn(1)-O(5)	91.06(14)
O(4)-Mn(1)-N(1)	163.79(11)
O(4)-Mn(1)-N(2)	91.67(11)
O(5)-Mn(1)-N(1)	93.59(12)
O(5)-Mn(1)-N(2)	88.35(12)
O(6)-Mn(1)-O(5)	175.86(14)
O(6)-Mn(1)-O(3)	90.74(19)
O(6)-Mn(1)-N(1)	88.99(12)
O(6)-Mn(1)-N(2)	95.52(12)
N(1)-Mn(1)-N(2)	72.97(10)
C(1)-N(1)-C(11)	118.0(3)
C(1)-N(1)-Mn(1)	116.3(2)
C(11)-N(1)-Mn(1)	125.6(2)
C(2)-N(2)-C(12)	117.9(3)
C(2)-N(2)-Mn(1)	116.28(19)
C(12)-N(2)-Mn(1)	125.8(2)
O(1)-C(11)-N(1)	121.5(3)
O(1)-C(11)-C(16)	122.0(3)
N(1)-C(11)-C(16)	116.4(3)
N(2)-C(12)-C(13)	116.9(3)
O(2)-C(12)-N(2)	122.2(3)
O(2)-C(12)-C(13)	120.9(3)

(3) Reactivity Studies of HAT-(CN)₆ with M(ClO₄)₂•6H₂O (M = Mn, Co, or Ni)

Although the bipyridine binding sites of neutral HAT-(CN)₆ are expected to be rather weak ligands due to the electron withdrawing effects of the cyano groups, reactions with first row transition metal ions were carried out to probe the possibilities of coordination. When a mixture of water/acetonitrile solutions of M(ClO₄)₂•6H₂O were reacted with HAT-(CN)₆ the new

compounds M(HAT(CN)₄O₂)(H₂O)₄ (M= Mn, Co, Ni) were isolated (Figure 5.8). The ease of formation of these compounds underscores the fact that coordinated HAT-(CN)₆ is hydrolytically unstable. As the structures of these compounds revealed HAT-(CN)₆ undergoes cleavage of the two activated nitrile groups adjacent to the coordinated metal center. The result is a di-anionic oxygen ligand. The coordination sphere of the octahedral metal center in these compounds is completed by water molecules.

B. Chemical reduction of HAT-(CN)₆

(1) Reactivity with [*n*-Bu₄N][I]

The well known ability of iodide to act as a reducing agent in solution with the formation of polyiodide species such as I₃⁻ led us to explore the [*n*-Bu₄N]⁺ salt as a reducing agent for HAT-(CN)₆. Addition of [*n*-Bu₄N][I] to

a THF solution of HAT-(CN)₆ produces a green solution which is indicative of the presence of [HAT-(CN)₆][−]. Addition of benzene led to isolation of the crystalline product $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT-(CN)}_6]_2\} \cdot 3\text{C}_6\text{H}_6$ (32) after three days. Single crystal X-ray diffraction analysis revealed an unusual structure that consists of stacks with four different repeating layers and channels defined by the positions of the stacks (Figures 5.9 and 5.10). The first of the four repeating layers consists of a HAT-(CN)₆ molecule with three [n-Bu₄N]⁺ cations occupying the space adjacent to the bipyridine moieties. The next layer is formed by three iodide ions each of which is centered under the C-C bond in NC-C_(ring) positions on HAT-(CN)₆. Molecules of HAT-(CN)₆ constitute the third layer. The fourth layer consists of an iodine atom positioned under the center ring of HAT-(CN)₆ and three benzene molecules that are located under the HAT-(CN)₆ cyano groups. This ABCD packing pattern repeats throughout the crystal. Finally, the [n-Bu₄N]⁺ ions occupy the channels forming a sheath around each stack.

The determination of this structure prompted us to explain the fact that only three [n-Bu₄N]⁺ ions are available for four I[−] ions. The mid-IR spectrum of crystals of $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT-(CN)}_6]_2\} \cdot 3\text{C}_6\text{H}_6$ (32) revealed the presence of ν_{CN} modes at 2243 and 2228 cm^{−1}. The 2243 cm^{−1} feature is characteristic of neutral HAT-(CN)₆, but the lower energy ν_{CN} mode

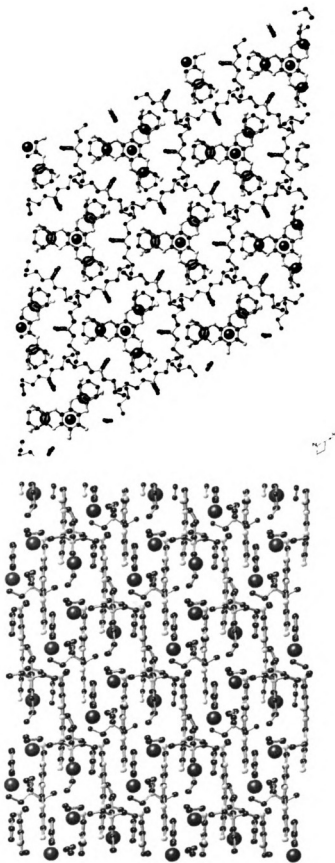
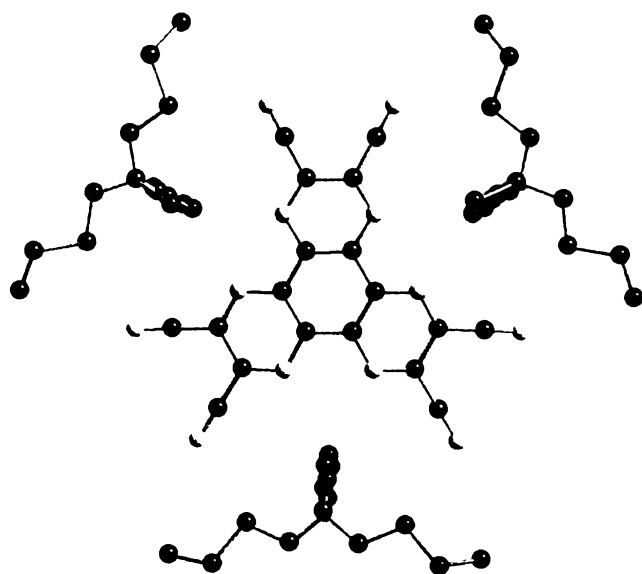
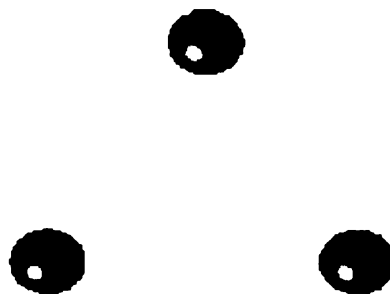


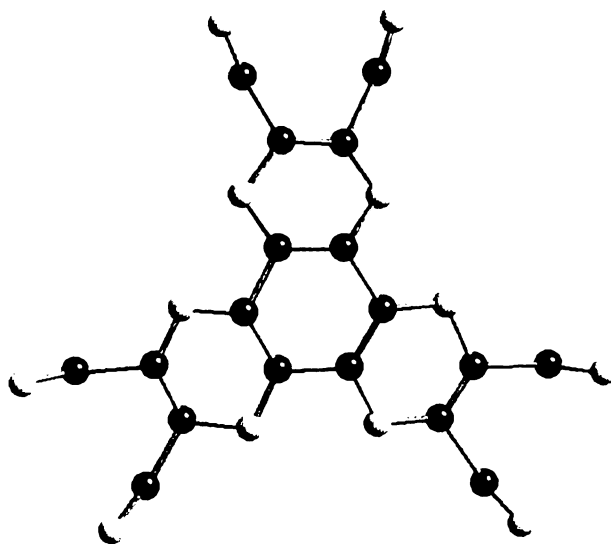
Figure 5.9. Views of the packing in the crystal structure of $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT}(\text{CN})_6]_2\} \cdot 3\text{C}_6\text{H}_6$ (32) looking down the *b* axis (left) and the *c* axis (right).



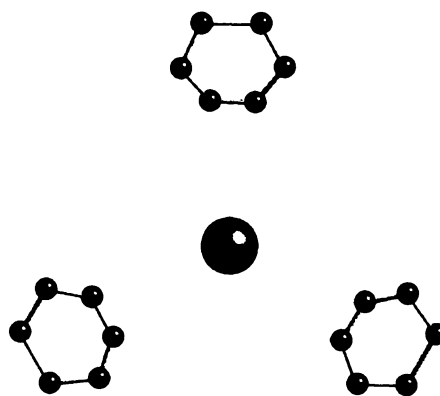
A



B



C



D

Figure 5.10. Representations of the layers that compose the columns present in the crystal structure of $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT}(\text{CN})_6]_2\} \cdot 3\text{C}_6\text{H}_6$ (32).

indicates that donation of electron density to HAT-(CN)₆ is occurring. The crystallographic evidence suggests this is occurring from a charge transfer interaction involving HAT-(CN)₆ and the an I atom of the fourth repeat layer. The distance of the I atom to the C atoms of the center ring in the HAT-(CN)₆ above it is slightly less (3.65 Å versus 3.69 Å) than the distance to the equivalent carbon atoms in the HAT-(CN)₆ below it. Reactions of this type have been reported for iodine atoms in the literature.²⁰

(2) Reactivity with FeCp^{*}₂ and CoCp₂

The inability of FeCp₂ to reduce HAT-(CN)₆ led to try the more strongly reducing FeCp^{*}₂. The FeCp^{*}/[FeCp^{*}₂]⁺ couple at -0.070 V suggests that FeCp^{*}₂ is capable of the one electron reduction of HAT-(CN)₆ to [HAT-(CN)₆]⁻ which occurs at E_{1/2} = -0.064 V. Acetonitrile solutions of FeCp^{*}₂ (yellow) treated with HAT-(CN)₆ (orange) produced a green solution characteristic of the radical [HAT-(CN)₆]⁻, but the system is in equilibrium, and the process of electron transfer from FeCp^{*}₂ to HAT-(CN)₆ is evidently not strongly product favored. If one cools the solution to -5°C the equilibrium shifts back to the reactants, neutral HAT-(CN)₆ and neutral FeCp^{*}₂. With the loss of the [HAT-(CN)₆]⁻ and [(Cp^{*})₂Fe]⁺ chromophores, the solution reverts to orange-yellow. The potentials of the (Cp^{*})₂Fe/[(Cp^{*})₂Fe]⁺ and HAT-(CN)₆/[HAT-(CN)₆]⁻ redox couples are

solvent dependent which effects the electron transfer process. In THF, two reversible reductions and one irreversible cathodic process are again observed for HAT-(CN)₆, but the potentials are shifted to more positive potentials occurring at 0.051, -0.429, and -1.06 V respectively. Combining THF solutions of (Cp^{*})₂Fe and HAT-(CN)₆ produces no color change indicating the lower dielectric constant of THF as compared to acetonitrile does not facilitate reduction of HAT-(CN)₆.

A more convenient and successful approach to chemical reduction of HAT-(CN)₆ is to use CoCp₂ which is theoretically capable of reducing HAT-(CN)₆ to both the mono-radical [HAT-(CN)₆]⁻ and the di-anionic [HAT-(CN)₆]²⁻ forms. The compound [CoCp₂][HAT-(CN)₆] was isolated as a green powder from the reaction of cobaltocene with an excess of HAT-(CN)₆. Although single crystals have not yet been obtained, some characteristic features of the [HAT-(CN)₆]⁻ radical were identified. The IR spectrum contains a $\nu_{C\equiv N}$ mode at 2214 cm⁻¹, which represents a shift to lower energy from neutral HAT-(CN)₆ (2243 cm⁻¹). This is analogous to the shifts observed for other organic radicals with C≡N groups.²⁰ The EPR spectrum of a solid sample of [CoCp₂][HAT-(CN)₆] at 4 K shows a typical isotropic resonance for an organic radical (S = 1/2), with a g value of 2.0084

and a narrow line-width of 7 G. These data indicate the $[\text{HAT}-(\text{CN})_6]^{1-}$ radicals are not strongly dimerized in the solid state, perhaps due to the formation of integrated stacks with π - π interactions between the cations and anions.

The reaction of neutral $\text{HAT}-(\text{CN})_6$ with an excess of CoCp_2 yields the salt $[\text{CoCp}_2]_2[\text{HAT}-(\text{CN})_6]$. The dianion is extremely sensitive to the presence of air or water, which renders its characterization difficult. The IR spectrum contains a characteristic $\nu_{\text{C}\equiv\text{N}}$ mode at 2195 cm^{-1} , which is lower in energy by 19 cm^{-1} relative to the monoradical $[\text{HAT}-(\text{CN})_6]^\cdot$ and 48 cm^{-1} relative to neutral $\text{HAT}-(\text{CN})_6$.

(3) Reactivity Studies of $\text{HAT}-(\text{CN})_6$ with Co and Zn

An alternative method for preparing binary transition metal compounds of $[\text{HAT}-(\text{CN})_6]^\cdot$ is the direct reaction of $\text{HAT}-(\text{CN})_6$ with first row transition metals such as Co and Zn. The resulting dark blue-green powders are soluble in polar organic solvents such as acetonitrile which suggests that discrete species are being formed. Although X-ray quality single crystals have not been obtained, several spectroscopic characterization techniques have been employed that support their formulation as the compounds $\text{M}[\text{HAT}-(\text{CN})_6]_2$ ($\text{M} = \text{Co}$ (35), Zn (36)) (Figure 5.10). The $\nu_{\text{C}\equiv\text{N}}$ stretching

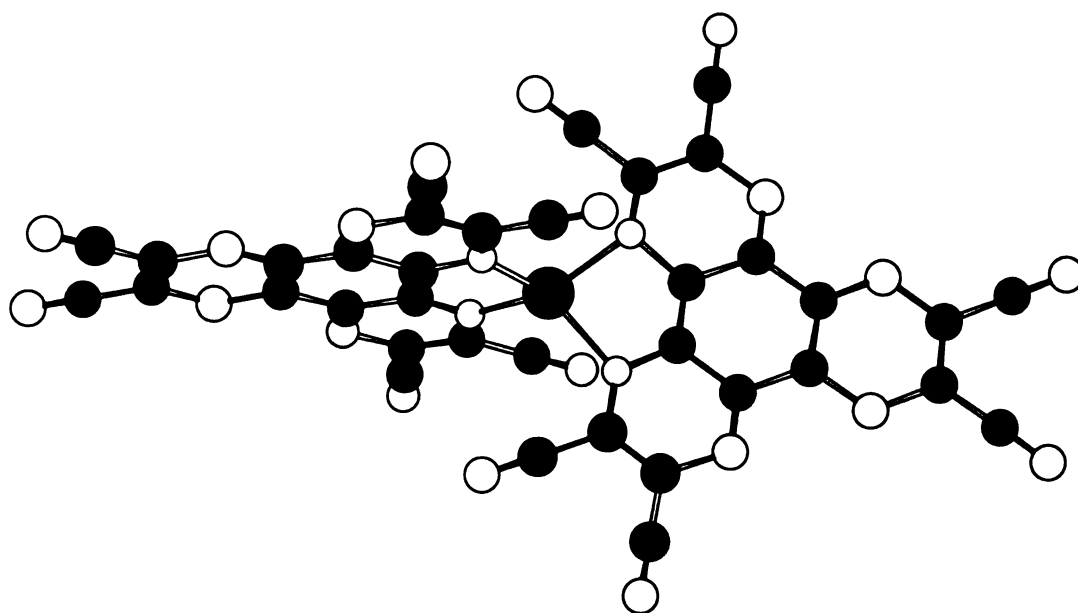


Figure 5.11. A structural representation of $\text{Co}[\text{HAT}-(\text{CN})_6]_2$ (35) and $\text{Zn}[\text{HAT}-(\text{CN})_6]_2$ (36) illustrating the steric bulk of the CN groups.

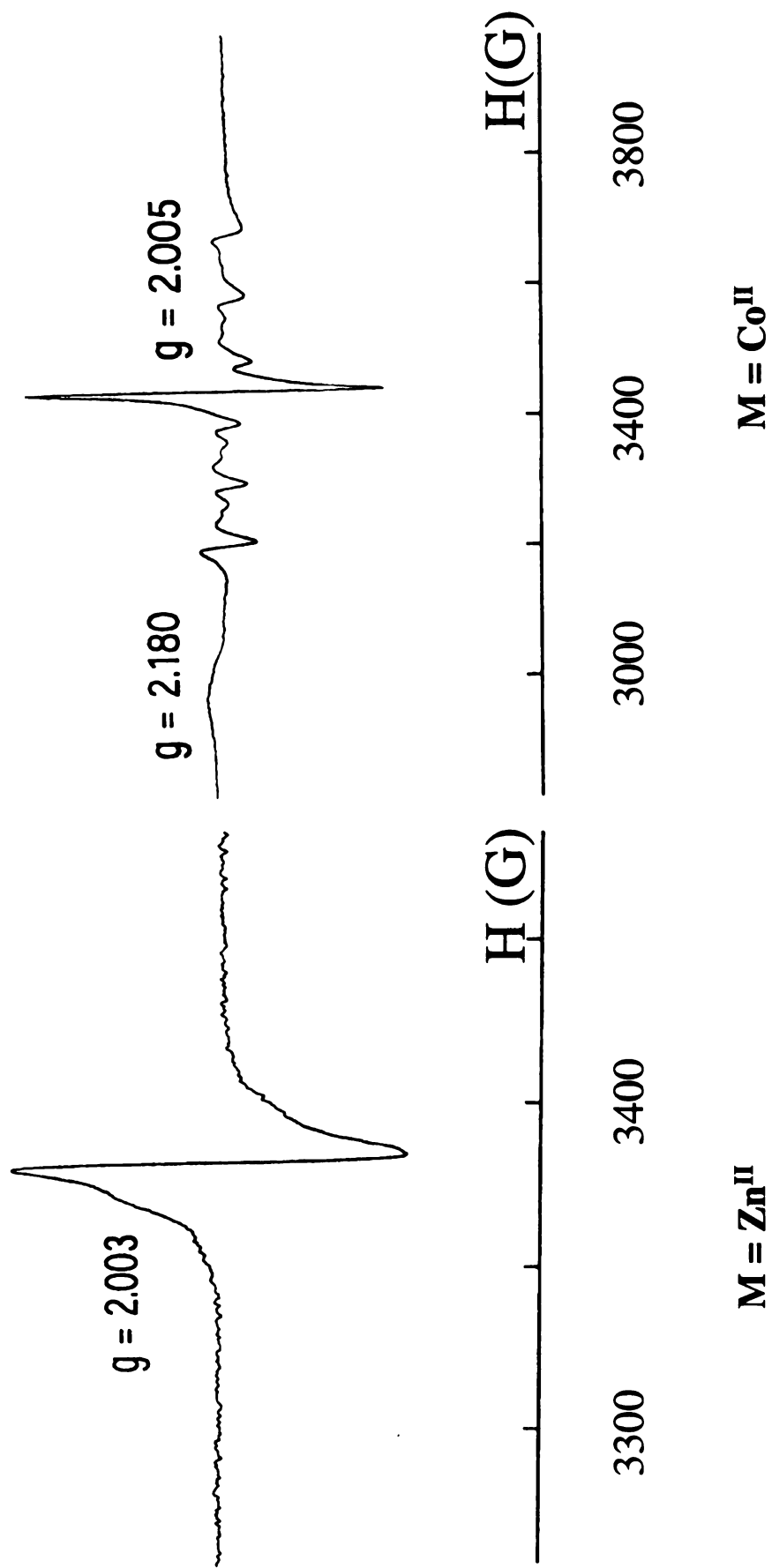


Figure 5.12. X-Band EPR Spectra of $\text{M}(\text{HAT}-(\text{CN})_6)_2$ ($M = \text{Zn}$ or Co) recorded on $\text{CH}_3\text{CN}/\text{toluene}$ frozen solutions at 77 K.

modes of 2210 and 2212 cm^{-1} are consistent with the presence of $[\text{HAT}-(\text{CN})_6]^-$. Both compounds are EPR silent in the solid state, but spectra obtained in acetonitrile/toluene frozen solutions at 4 K EPR active. The spectrum of the Zn compound consists of a single isotropic feature at $g = 2.0031$ with $\Delta H = 15 \text{ G}$ (Figure 5.12). Hyperfine coupling would not be expected due to the low natural abundance of ^{67}Zn (4%). On the other hand, ^{59}Co with $I = 7/2$ is 100% abundant, consequently the EPR signal of $\text{Co}[\text{HAT}-(\text{CN})_6]_2$ shows hyperfine coupling to the Co nucleus at $g = 2.0051$ with $\Delta H = 480 \text{ G}$ (Figure 5.12). Additionally, a broad signal was observed for the $S = 3/2$ Co^{II} ion at $g = 2.180$. This g value is in good agreement with the one obtained from magnetic susceptibility studies of the compound, which revealed a high temperature moment of $\mu_{\text{eff}} = 4.2 \text{ B.M.}$ with $g = 2.17$. These data indicate that the Co centers are magnetically isolated from each other. As confirmed by EPR spectroscopy, there is no contribution to the magnetization from $[\text{HAT}-(\text{CN})_6]^-$, presumably due to intermolecular interactions in the solid state. The Zn compound is rendered diamagnetic in the solid state due to these stacking interactions.

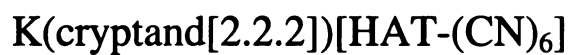
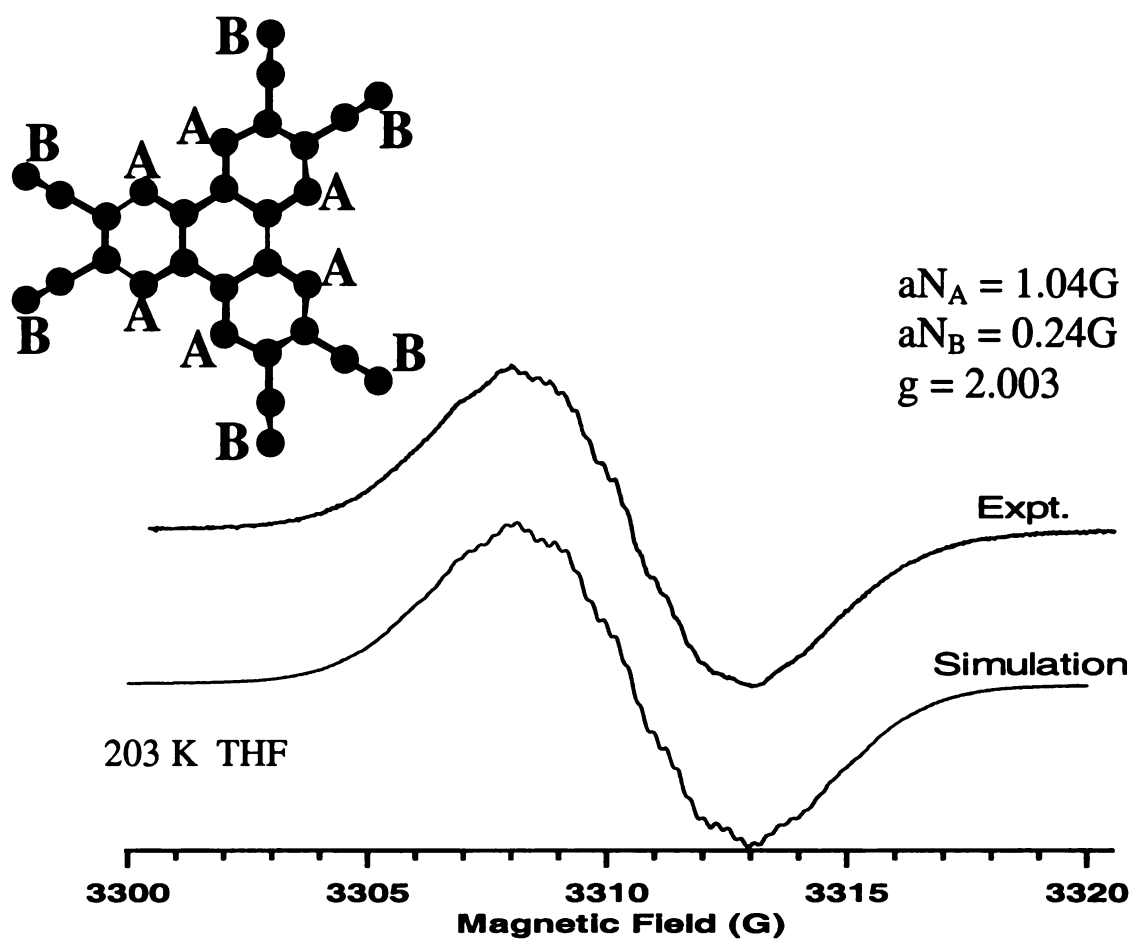


Figure 5.13. The experimental and simulated EPR spectra of $\text{K}(\text{cryptand}[2.2.2])[\text{HAT}-(\text{CN})_6]$ recorded in THF at 203 K.

(4) Potassium reduction of HAT-(CN)₆

The reaction of HAT-(CN)₆ with one equivalent of K in dimethylimidazole (DMI) produces a green solution of K[HAT-(CN)₆]. The EPR spectrum of this solution is identical to the spectrum (Figure 5.13) of K(cryptand[2.2.2])[HAT-(CN)₆] that was first recorded by A. Ichimura.²¹ The narrow line-width of 5 G and the g value of 2.003 are characteristic of organic radicals. The hyperfine coupling to the nitrogen atoms is weak yet sufficiently well resolved to identify the hyperfine coupling constants of $aN_A(\text{ring nitrogens}) = 1.04 \text{ G}$ and $aN_B(\text{nitrile nitrogens}) = 0.24 \text{ G}$. A simulation of the [HAT-(CN)₆][•] EPR spectrum (Figure 5.13) provided a good fit to the experimental data. The low intensity of the hyperfine coupling is attributed to several factors that modulate the line-width. In the simulation, the hyperfine splitting pattern is the same on both halves of the spectrum, but in the experimental spectrum the high field side is less well-resolved. This is common for molecules undergoing slow molecular tumbling. Additionally, hyperfine anisotropy of π -radicals is generally quite large and is one of the terms that contributes to the expression for the line-width under conditions of slow molecular tumbling and short correlation times.²²

The reaction of HAT-(CN)₆ with two equivalents of K in DMI produces a green solution that is proposed to be [K]₂[HAT-(CN)₆]. The results of computational studies presented in Section 4 of this chapter indicate that [HAT(CN)₆]²⁻ should exhibit a triplet ground state. The most compelling experimental evidence in support of this electronic ground state configuration is the observation of a half-field signal at 1685 G in the EPR spectrum recorded at 4.2K (Figure 5.15). This line corresponds to the $\Delta m_s = 2$ transition that can only originate from a triplet electronic state.²² The transition is quantum-mechanically forbidden, but zero field splitting (zfs) generally relaxes the selection rule that dictates only transitions with $\Delta m_s = \pm 1$ are allowed. The weak intensity of the signal is consistent with the one line signal observed in the high field region near $g \approx 2$ (Figure 5.15). Given three energy levels, -1, 0, and +1, and the $\Delta m_s = \pm 1$ selection rule two EPR transitions would be expected for a triplet (Figure 5.14). In situations where the zfs parameter, D, is small, however, the two lines can collapse to give a spectrum with only one line.²² The intensity of the half-field, forbidden, transition scales with D so triplet spectra with a single line in the high-field region would be expected to have a weak $\Delta m_s = 2$ transition.

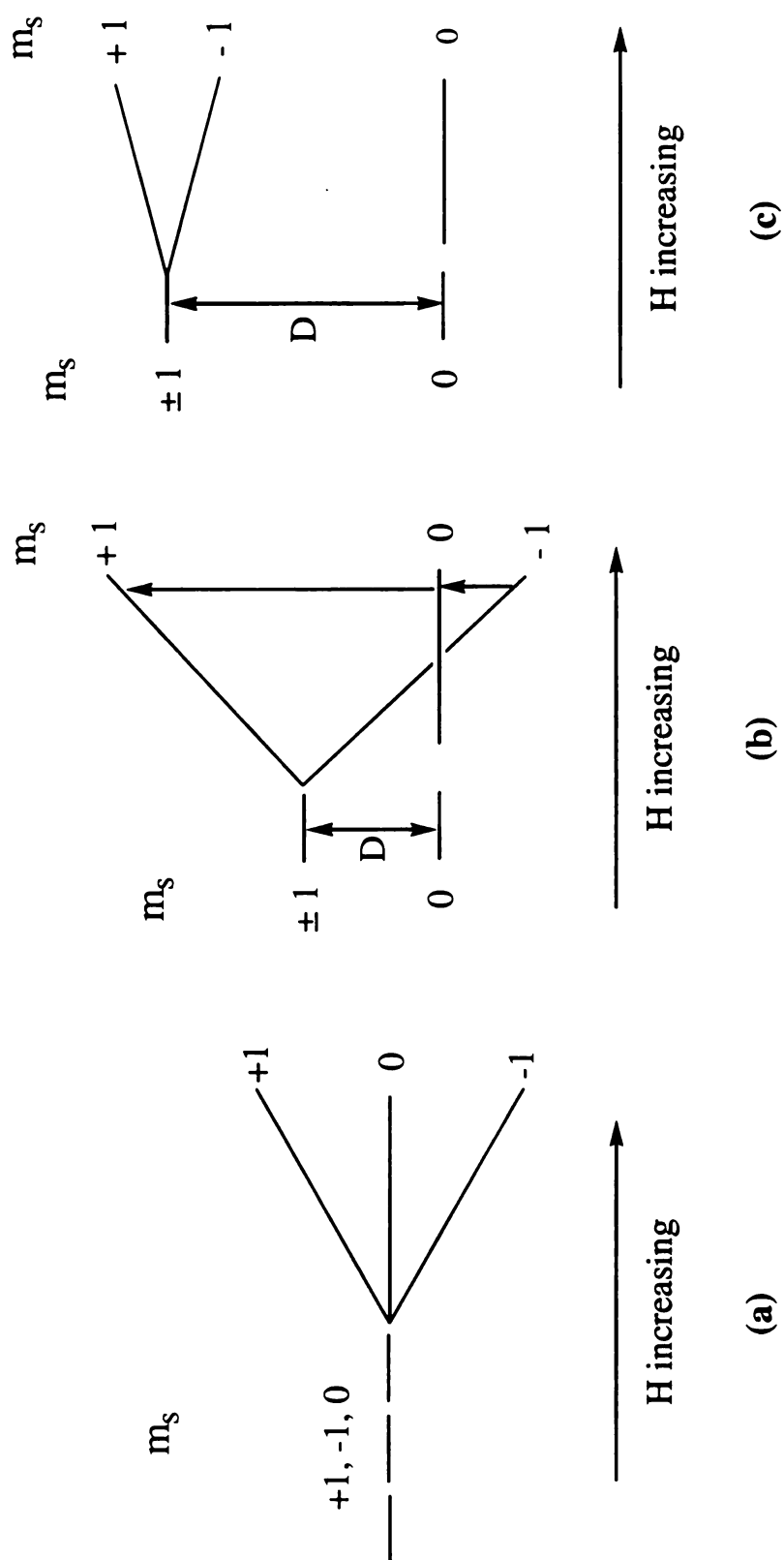


Figure 5.14. The effects of zero-field splitting (ZFS) on the expected EPR transitions of a triplet state species. (a) no ZFS (b) moderate ZFS (c) large ZFS

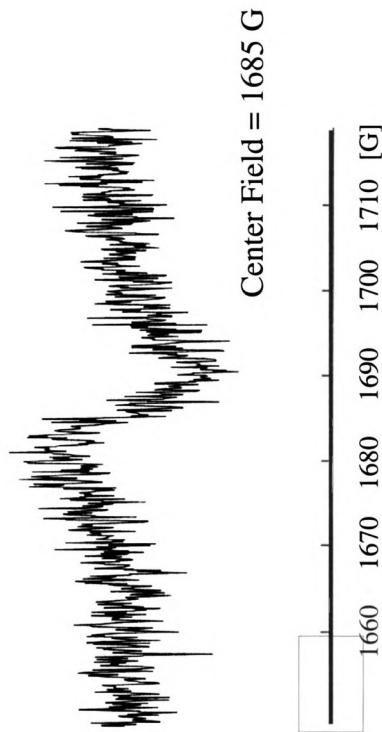


Figure 5.15. Half-field transition in the EPR spectrum of the product from the reaction of $\text{HAT}(\text{CN})_6$ with 2 equivalents of K. The spectrum was recorded in dimethylimidazole at 4.2 K.

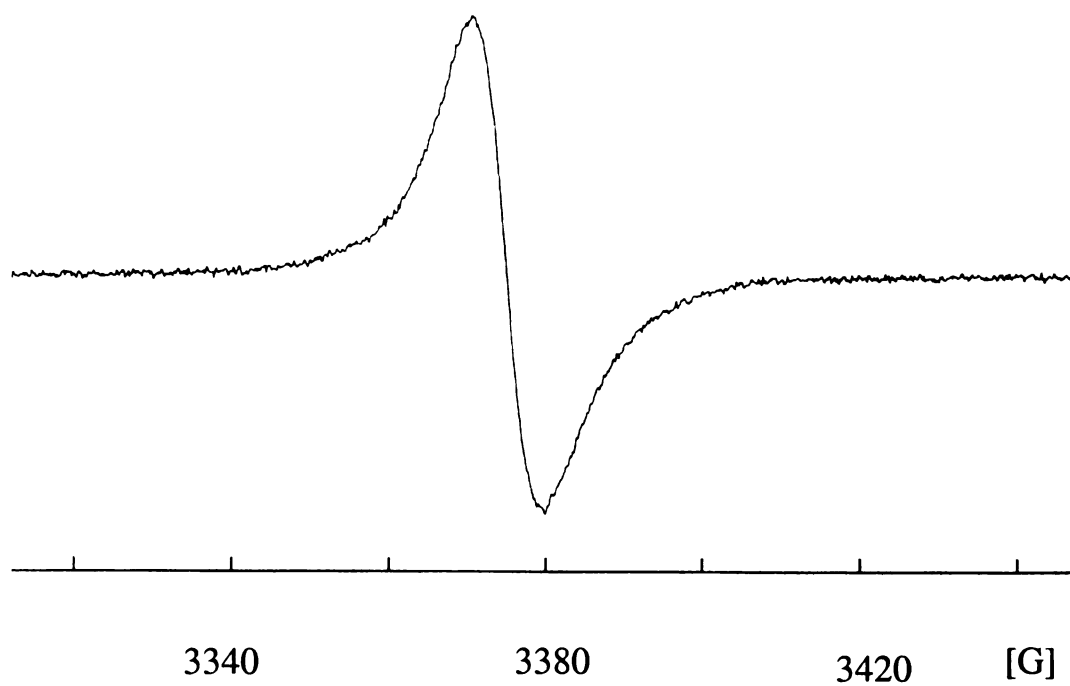


Figure 5.16. The frozen solution EPR spectrum of the reaction of $\text{HAT}-(\text{CN})_6$ with 2 equivalents of K in dimethylimidazole recorded at 4.2 K.

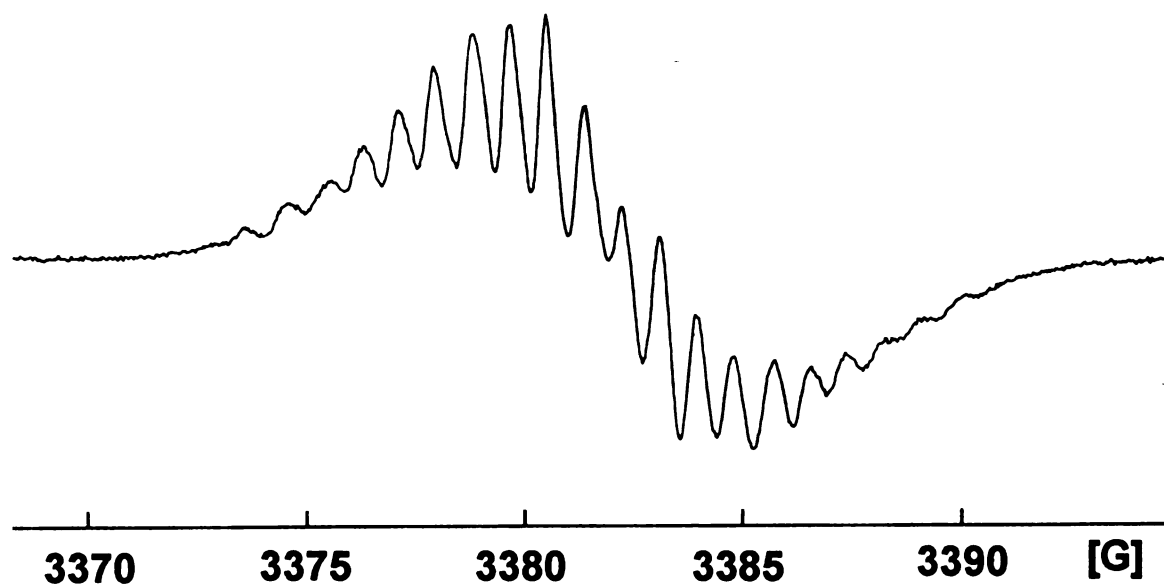


Figure 5.17. The solution EPR spectrum of the reaction of $\text{HAT}-(\text{CN})_6$ with 2 equivalents of K. The spectrum was recorded in DMI at room temperature.

The solution EPR spectrum in DMI at room temperature is displayed in Figure 5.17. The even number of hyperfine lines is inconsistent with what should be produced by a molecule such as $\text{HAT}(\text{CN})_6$ which contains an even number of N atoms with $I = 1$ nuclear spin values. This situation should give rise to a signal with an odd number of lines and therefore a hyperfine line at the center. The even number of hyperfine lines implies additional coupling, possibly to K, however the hyperfine coupling constant of the additional nucleus would have to be equal to the nitrogen hyperfine or some multiple of it to give the observed signal. The origin of the hyperfine coupling observed in this spectrum is still unresolved.

C. Reaction of $[\text{HAT}(\text{CN})_6]^-$ with transition metal ions

Reactions of $[\text{CoCp}_2][\text{HAT}(\text{CN})_6]$ with divalent first row transition metal ions such as Mn^{II} , Fe^{II} , Co^{II} , and Ni^{II} in acetonitrile at room temperature yield dark green precipitates. The high degree of insolubility of these products in common solvents suggests the presence of extended structures. Assuming that the preferred $[\text{HAT}(\text{CN})_6]^-$ binding mode is through the chelating N-N sites and that the nitrile groups are sufficiently bulky to force the tetrahedral versus octahedral geometry (Figure 5.11), the expected stoichiometry for the binary metal- $[\text{HAT}(\text{CN})_6]$ coordination polymers would be 3:2. The presence of the $[\text{HAT}(\text{CN})_6]^-$ radical and the

absence of $[\text{CoCp}_2]^+$ was verified by IR spectroscopy, but the low crystallinity of these samples precluded a structural study. It remains unknown if the compounds are discrete or polymeric, and if the solid state structure is controlled solely by metal-ligand interactions or also by ligand-ligand interactions. The magnetic measurements for these compounds revealed only paramagnetic behaviour characteristic of the metal ions with no contributions from the ligand. This fact taken, together with the absence of significant magnetic exchange between localized moments in the metal ions in all cases, suggests π - π dimerization of the ligand in the solid state. Such a situation would yield diamagnetic “dimers” ($S = 0$) similar to many other salts of organic radicals.⁸

4. Computational Studies of HAT-(CN)₆ and its reduction products

Density Functional Theory computations were carried out using the Gaussian 98 Program. Geometric optimization using Cartesian coordinates and frequency calculations were conducted for neutral HAT-(CN)₆, the mono-anion radical $[\text{HAT}-(\text{CN})_6]^{1-}$, and both the singlet and triplet states of the di-anion $[\text{HAT}-(\text{CN})_6]^{2-}$. The theory level and basis set employed were UB3LYP and 6-31G respectively.

Although the parameters for the geometric optimizations were set up so as to permit the $[\text{HAT}-(\text{CN})_6]^{0/1-/2-}$ molecules to undergo Jahn-Teller distortion, all four species remained planar. It should be noted that optimizations for the radical mono-anion and the singlet di-anion are not true minimizations because the frequency calculations yielded an imaginary frequency. These geometries would best be called transition states but these could be merely rotational transition states and not necessarily vibrational in nature. The maximum force, RMS force, maximum displacement, and RMS displacement terms of all four optimizations did, however, converge as required. This suggests that any energy differences produced by additional calculations would be negligible.

A slight Jahn-Teller distortion was observed for the radical $[\text{HAT}-(\text{CN})_6]^\cdot$. As mentioned previously, the radical remained planar with only a slight in-plane elongation along two of the C_2 axes which lowers the molecular symmetry from D_{3h} to C_{2v} . A representation of the distortion is depicted in Figure 5.18.

The energies of the four $\text{HAT}-(\text{CN})_6$ species were determined. The lowest of these was neutral $\text{HAT}-(\text{CN})_6$ which lies 78.559 kcal/mol below the mono-anion radical $[\text{HAT}-(\text{CN})_6]^\cdot$. The triplet di-anion is 1.354 kcal/mol above the mono-anion and 3.663 kcal/mol below the singlet

dianion. Though the singlet-triplet gap is small, these calculations support that $[\text{HAT}-(\text{CN})_6]^{2-}$ should favor slightly a triplet ground state.

The molecular orbitals for $\text{HAT}-(\text{CN})_6$, $[\text{HAT}-(\text{CN})_6]^\cdot$, and both the singlet and triplet electronic configurations of $[\text{HAT}(\text{CN})_6]^{2-}$ were determined. The degenerate HOMO's and LUMO's of neutral $\text{HAT}-(\text{CN})_6$ are depicted in Figure 5.19. The molecular orbital calculations revealed that HOMO of $[\text{HAT}(\text{CN})_6]^\cdot$ (Figure 5.20) strongly resembles one of the $\text{HAT}-(\text{CN})_6$ LUMO's. The other $\text{HAT}-(\text{CN})_6$ LUMO becomes the LUMO+1 of $[\text{HAT}(\text{CN})_6]^\cdot$ and not, as might have been expected, the LUMO. This could be due to the Jahn-Teller distortion observed for the radical $[\text{HAT}(\text{CN})_6]^\cdot$. The degenerate HOMO's of the triplet $[\text{HAT}(\text{CN})_6]^{2-}$ (presented in Figure 5.21) split and become the HOMO and LUMO of the singlet $[\text{HAT}(\text{CN})_6]^{2-}$ species (depicted in Figure 5.22).

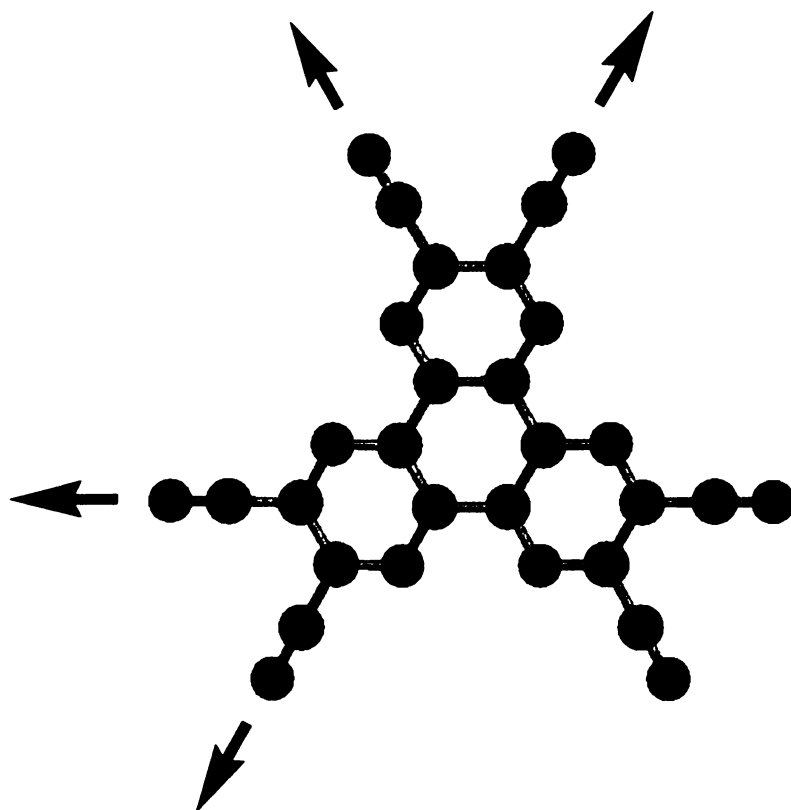
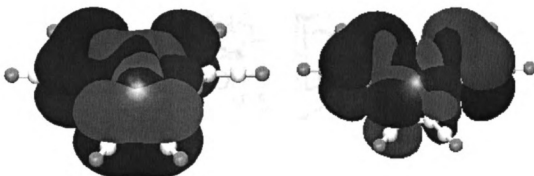


Figure 5.18. A representation of the Jahn-Teller elongation predicted for the radical [HAT-(CN)₆][•] by a DFT computational study conducted with Gaussian 98.



LUMO's $E = -0.16958$



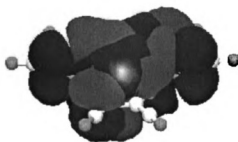
HOMO's $E = -0.32472$

Figure 5.19. Representations of the frontier molecular orbitals of $\text{HAT}(\text{CN})_6$ as determined by a DFT computational study conducted with the Gaussian 98 program. The energies are reported in Hartree units.



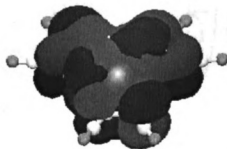
LUMO

E = -0.04008



LUMO+1

E = -0.03917



HOMO

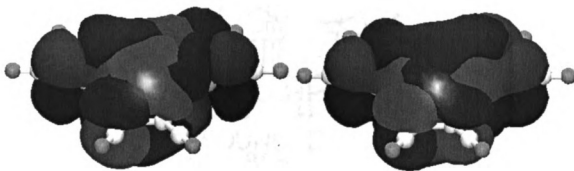
E = -0.08086

Figure 5.20. Representations of the frontier molecular orbitals of $[\text{HAT}-(\text{CN})_6]^-$ as determined by a DFT computational study conducted with the Gaussian 98 program. The energies are reported in Hartree units.



LUMO

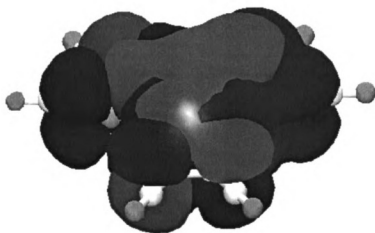
$E = 0.09175$



HOMO's

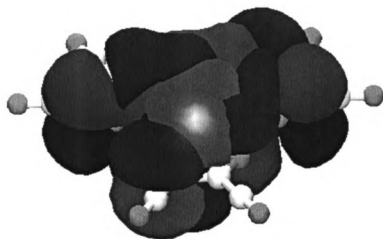
$E = 0.04106$

Figure 5.21. Representations of the frontier molecular orbitals for the triplet electronic configuration of $[\text{HAT}-(\text{CN})_6]^{2-}$ as determined by a DFT computational study conducted with the Gaussian 98 program. The energies are reported in Hartree units.



LUMO

$E = 0.08782$



HOMO

$E = 0.05138$

Figure 5.22. Representations of the frontier molecular orbitals for the singlet electronic configuration of $[\text{HAT}-(\text{CN})_6]^{2-}$ as determined by a DFT computational study conducted with the Gaussian 98 program. The energies are reported in Hartree units.

5. Conclusions

The metallocenes, FeCp_2 and $[\text{CoCp}_2][\text{PF}_6]$, proved to be capable templates for the formation of layered structures of with $\text{HAT}-(\text{CN})_6$. Convenient outer-sphere chemical reduction routes of $\text{HAT}-(\text{CN})_6$ to the radical $[\text{HAT}-(\text{CN})_6]^\cdot$ species and the dianion $[\text{HAT}-(\text{CN})_6]^{2-}$ have been documented. Transition metals can also be used as reducing agents, but in these cases complexation of the metal with the reduced $\text{HAT}-(\text{CN})_6$ species occurs. Discrete, soluble paramagnetic complexes are obtained by direct reaction of $\text{HAT}-(\text{CN})_6$ with Co and Zn. Insoluble, polymeric binary salts were obtained from reactions of divalent transition metals with the pre-reduced $[\text{HAT}-(\text{CN})_6]^\cdot$ anion. The structures of these salts are not known, but they show magnetic behavior indicative of a dimerization of the $[\text{HAT}-(\text{CN})_6]^\cdot$ radicals in the solid state.

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Chapter VI

Conclusions

In this thesis project, progress was made in advancing the field low-valent transition metal cyanide chemistry that including compounds that exhibit metal-metal bonding. Electronic absorption, NMR, and infrared spectral characterization as well as mass spectrometric methods support that the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with 8 equivalents of $[\text{Et}_4\text{N}][\text{CN}]$ proceeds to yield $[\text{Et}_4\text{N}]_2[\text{Re}_2(\text{CN})_8]$ (3), which is only the second example of a $[\text{M}_2(\text{CN})_8]^{n-}$ compound. The reaction of $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ or $[n\text{-Bu}_4\text{N}][\text{CN}]$ proceeds with cleavage of the metal-metal bond and formation of $[\text{Cr}(\text{CN})_6]^{2-/3-}$ rather than the desired dinuclear anion $[\text{Cr}_2(\text{CN})_8]^{4-}$. The results of electronic absorption and infrared spectroscopy indicate that reactions of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $[\text{Et}_4\text{N}][\text{CN}]$ and $[n\text{-Bu}_4\text{N}][\text{CN}]$ proceed with formation of multiple cyanide containing products. The instability of low valent transition metals such as Cr^{II} and W^{II} towards oxidation necessitate the use of anhydrous reaction conditions that are accessible only with $[\text{Et}_4\text{N}][\text{CN}]$ and $(\text{CH}_3)_3\text{SiCN}$, but not with $[n\text{-Bu}_4\text{N}][\text{CN}]$.

A family of edge-sharing bioctahedral (ESBO) dimolybdenum cyanide compounds with phosphine co-ligands was prepared. Under anaerobic conditions, the reaction of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ with $[\text{R}_4\text{N}][\text{CN}]$ ($\text{R} = \text{Et}$ or $n\text{-Bu}$) proceeds with cyanide displacement of the chloride ligands and addition of

two cyanides to yield the tetraalkylammonium salt of $[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2]^{2-}$ (8) (Figure 3.1). The two (μ -CN) groups spanning the dimolybdenum core are in the rarely observed semi-bridging mode with cyanide being bound to one Mo through a σ -bond and to the other Mo atom through a side-on π interaction (Figures 3.10). As evidenced by the cyclic voltammogram displayed in Figure 3.6 $[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2]^{2-}$ (8) is easily oxidized. The deliberate use of one and two equivalents of the oxidant NOBF_4 led to the preparation of the oxidation products $[\text{Mo}_2^{\text{II,III}}(\text{CN})_6(\text{dppm})_2]^{1-}$ (10) and $\text{Mo}_2^{\text{III,III}}(\text{CN})_6(\text{dppm})_2$ (11) (Figures 3.3 and 3.4).

The oxidation state of the dimolybdenum core strongly influences the bonding interactions of the bridging cyanides. The side-on π interaction of the semi-bridging cyanides in the one electron oxidation product $[n\text{-Bu}_4\text{N}][\text{Mo}_2^{\text{II,III}}(\text{CN})_6(\text{dppm})_2]$ (10) are significantly more prominent than in the parent compound $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2^{\text{II,II}}(\text{CN})_6(\text{dppm})_2]$ (8) (Figure 3.5 and Table 3.7). The removal of an electron from $[\text{Mo}_2^{\text{II,III}}(\text{CN})_6(\text{dppm})_2]^-$ (10) to give $\text{Mo}_2^{\text{III,III}}(\text{CN})_6(\text{dppm})_2$ (11) further increases the π interaction but to a smaller degree than what was observed in going from the $\text{Mo}_2^{\text{II,II}}$ to $\text{Mo}_2^{\text{II,III}}$ species (Figures 3.5 and Table 3.7).

The spatial arrangement of the terminal cyanide ligands in these new compounds is such that interactions with Lewis acids to form larger assemblies are possible. In this regard, the reaction of [*n*-Bu₄N]₂[Mo₂(CN)₆(dppm)₂] (8) with [Ni(en)₂(CH₃CN)₂][PF₆]₂ (21) was found to form a neutral one-dimensional polymer with {[Ni(en)₂][Mo₂(CN)₆(dppm)₂]}_n (12) repeating units (Figure 3.8). The [Mo₂(CN)₆(dppm)₂]²⁻ units act as a bridge, but do not enable magnetic communication to occur between the nearest neighbor Ni^{II} centers (Figure 3.9).

A family of mononuclear transition metal cyanide and nitrile compounds with the facial capping ligand 1-(hydro)trispyrazolborate were designed for the preparation of molecular, open-shell, heterometallic cubes (Figures 4.1 and 4.2). The Na[Tp] and homoleptic acetonitrile solvated transition metal ions, [Mn(CH₃CN)₄][PF₆]₂ and [Co(CH₃CN)₆][PF₆]₂ proved to be effective in preparing the divalent, solvated corner building block compounds [(Tp)Mn(CH₃CN)₃][PF₆] (16) and [(Tp)Co(CH₃CN)₃][PF₆] (17) (Figure 4.6). The trivalent precursors (Tp)MoBr₂(THF) (15) (Figure 4.5) and (Tp)VCl₂(THF) were useful as precursors to the higher oxidation state building blocks compounds [(Tp)Mo(CH₃CN)₃][PF₆]₂ (18) and [(Tp)V(CH₃CN)₃][PF₆]₂ (19). The cyanide corner building block compound

$\text{K}[(\text{Tp})\text{Cr}(\text{CN})_3]$ (20) was prepared from $\text{K}[(\text{Tp})\text{CrCl}_3]$ (14). The solvated, edge building block, *trans*- $[\text{Ni}(\text{CH}_3\text{CN})_2(\text{en})_2][\text{PF}_6]_2$ (21) (Figure 4.7) was prepared by chloride abstraction from *trans*- $\text{NiCl}_2(\text{en})_2$.

The Spartan program was used to conduct a computer modeling study to evaluate whether steric interactions would prevent cube assembly with the compounds under investigation. A molecular model was constructed for both the eight and twenty metal atom cubes (Figure 4.11). The results of these efforts revealed that sufficient void space exists inside the cubes such that steric factors will not play a prohibitive role in the assembly process.

Self-assembly reactions of two types of building block compounds were investigated. Based on infrared spectroscopic data, the most promising of these is the reaction of four equivalents each of $\text{K}[\text{Cr}(\text{CN})_3(\text{Tp})]$ (20) and $[\text{Ni}(\text{CH}_3\text{CN})_3(\text{Tp})][\text{BF}_4]$ which leads to a product that exhibits only a single, sharp cyanide stretch.

The aromatic molecule with trigonally disposed chelating sites, hexazatriphenylene-hexacarbonitrile ($\text{HAT}-(\text{CN})_6$), and its reduced species were explored as organic linkers for transition metal ions. The metallocenes, FeCp_2 and $[\text{CoCp}_2][\text{PF}_6]$, proved to be capable templates for the formation of layered structures with $\text{HAT}-(\text{CN})_6$ (Figures 5.6 and 5.7). Convenient outer-sphere chemical reduction routes of $\text{HAT}-(\text{CN})_6$ to the radical $[\text{HAT}-(\text{CN})_6]^\cdot$

$(\text{CN})_6]^-$ species and the dianion $[\text{HAT}-(\text{CN})_6]^{2-}$ have been documented. Transition metals can also be used as reducing agents, but, in these cases, complexation of the metal with the reduced $\text{HAT}-(\text{CN})_6$ species occurs. Discrete, soluble paramagnetic complexes are obtained by direct reaction of $\text{HAT}-(\text{CN})_6$ with Co (35) and Zn (36) (Figure 5.11). Insoluble, polymeric binary salts were obtained from reactions of divalent transition metals with the pre-reduced $[\text{HAT}-(\text{CN})_6]^-$ anion. The structures of these salts are not known, but they show magnetic behavior indicative of a dimerization of the $[\text{HAT}-(\text{CN})_6]^-$ radicals in the solid state. Computational studies predict that $[\text{HAT}-(\text{CN})_6]^{2-}$ should exhibit a triplet ground state. Experimental evidence to this effect was obtained from EPR spectroscopic studies that led to the observation of a half-field signal for $\text{K}_2[\text{HAT}-(\text{CN})_6]$ which can only arise from a triplet electronic state (Figure 5.14).

Appendices

Table A.1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_2(\text{CN})_6(\text{dppm})]\cdot 2\text{CH}_3\text{CN}\cdot 2\text{C}_6\text{H}_6$ (8)

	x	y	z	U(eq)
Mo(1)	2479(1)	2720(1)	-572(1)	26(1)
P(1)	3498(1)	2348(2)	-105(1)	31(1)
P(2)	1450(1)	3122(1)	-1176(2)	30(1)
N(1)	2231(4)	2205(5)	-2092(5)	44(3)
N(2)	2762(4)	4188(4)	-1122(5)	55(3)
N(5)	3028(6)	3175(9)	-2910(9)	126(6)
N(3)	1981(4)	1361(5)	-750(7)	88(5)
N(4)	1768(4)	1112(4)	-3881(5)	39(2)
C(1)	2300(4)	2355(6)	-1564(7)	41(3)
C(2)	2682(4)	3703(6)	-898(5)	34(3)
C(3)	2205(5)	1718(6)	-348(7)	45(4)
C(4)	3928(4)	2370(5)	864(5)	35(3)
C(11)	3920(4)	2932(5)	-300(6)	33(3)
C(12)	4281(4)	3466(6)	140(6)	40(3)
C(13)	4578(5)	3894(6)	-60(8)	59(4)
C(14)	4517(5)	3816(7)	-684(8)	57(4)
C(15)	4130(5)	3297(8)	-1132(7)	64(4)
C(16)	3838(5)	2871(6)	-940(7)	52(4)
C(21)	3667(5)	1476(5)	-303(6)	35(3)
C(22)	4234(5)	1294(7)	-53(7)	69(4)
C(23)	4368(6)	631(9)	-193(8)	97(6)
C(24)	3938(7)	147(7)	-571(7)	73(5)
C(25)	3382(6)	322(6)	-819(7)	61(4)
C(26)	3232(5)	984(6)	-695(6)	43(3)
C(31)	1232(5)	4033(5)	-1188(5)	29(3)
C(32)	646(5)	4221(6)	-1559(6)	60(4)
C(33)	473(6)	4903(8)	-1544(7)	71(4)
C(34)	899(7)	5414(7)	-1179(7)	68(4)
C(35)	1493(6)	5245(6)	-797(7)	76(5)
C(36)	1647(5)	4545(5)	-807(6)	47(4)
C(41)	1015(4)	2917(6)	-2112(6)	33(3)
C(42)	944(5)	3418(6)	-2593(6)	44(3)
C(43)	688(5)	3244(7)	-3274(8)	63(4)
C(44)	483(5)	2569(8)	-3509(6)	56(4)
C(45)	544(5)	2059(6)	-3037(7)	50(4)
C(46)	816(4)	2235(6)	-2341(6)	44(3)
C(51)	2381(5)	1356(5)	-3327(6)	52(4)
C(52)	2854(5)	801(6)	-3028(6)	55(4)

C(53)	3432(5)	1083(6)	-2412(7)	72(4)
C(54)	3912(6)	544(7)	-2143(7)	100(5)
C(55)	1745(5)	819(6)	-4504(6)	52(4)
C(56)	1155(5)	611(6)	-5115(7)	69(4)
C(57)	1203(6)	266(7)	-5675(7)	83(5)
C(58)	601(6)	32(8)	-6290(7)	107(6)
C(59)	1360(5)	1767(6)	-4084(6)	66(4)
C(60)	1470(6)	2335(7)	-4449(7)	87(5)
C(61)	1049(7)	2972(7)	-4704(9)	100(5)
C(62)	502(6)	2899(9)	-5287(9)	147(9)
C(63)	1559(5)	555(6)	-3589(7)	55(4)
C(64)	1664(5)	663(6)	-2903(6)	54(4)
C(65)	1353(6)	91(6)	-2766(7)	68(4)
C(66)	1507(7)	75(7)	-2070(8)	109(6)
C(70)	255(7)	3005(8)	2529(10)	105(6)
C(71)	519(6)	2395(10)	2556(8)	103(6)
C(72)	259(8)	1759(8)	2535(13)	158(9)
C(73)	2930(7)	2751(12)	-4320(8)	97(6)
C(74)	2460(10)	3167(8)	-4788(12)	94(6)
C(75)	2041(8)	2911(11)	-5446(12)	98(6)
C(76)	2697(7)	3401(9)	-2840(9)	89(5)
C(77)	2268(6)	3710(7)	-2758(7)	91(5)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$), and occupancies for $[n\text{-Bu}_4\text{N}][\text{Mo}_2(\text{CN})_6(\text{dppm})_2] \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ (10)

	x	y	z	U(eq)
Mo(1)	2203(1)	1878(1)	-467(1)	19(1)
P(1)	2222(1)	2408(1)	1015(1)	19(1)
P(2)	1609(1)	978(1)	19(1)	19(1)
N(1)	1151(2)	1781(4)	-1519(2)	47(1)
N(2)	2249(2)	-960(3)	-940(2)	43(1)
N(3)	1901(2)	4052(3)	-544(2)	37(1)
N(4)	5000	4985(4)	2500	28(1)
N(5)	160(2)	5583(6)	-1720(2)	86(2)
C(1)	1525(2)	1861(4)	-1169(2)	30(1)
C(2)	2236(2)	27(4)	-773(2)	28(1)
C(3)	2217(2)	3826(3)	-146(2)	26(1)
C(4)	1921(2)	912(4)	746(2)	22(1)
C(11)	2544(2)	2095(4)	1723(2)	23(1)
C(12)	2729(2)	925(4)	1916(2)	31(1)
C(13)	2978(2)	760(5)	2456(2)	37(1)
C(14)	3037(2)	1738(5)	2810(2)	38(1)
C(15)	2857(2)	2905(5)	2624(2)	44(1)
C(16)	2619(2)	3077(4)	2079(2)	35(1)
C(21)	1679(1)	3358(3)	1052(2)	22(1)
C(22)	1350(2)	2923(4)	1324(2)	36(1)
C(23)	929(2)	3617(5)	1351(2)	42(1)
C(24)	843(2)	4768(4)	1109(2)	36(1)
C(25)	1166(2)	5217(4)	841(2)	42(1)
C(26)	1581(2)	4514(4)	809(2)	33(1)
C(31)	989(2)	1695(3)	-39(2)	24(1)
C(32)	655(2)	1129(5)	203(2)	37(1)
C(33)	194(2)	1685(6)	188(2)	48(1)
C(34)	66(2)	2824(6)	-63(2)	54(2)
C(35)	388(2)	3382(5)	-309(3)	49(1)
C(36)	849(2)	2820(4)	-301(2)	35(1)
C(41)	1432(2)	-641(3)	-162(2)	22(1)
C(42)	1007(2)	-894(4)	-597(2)	30(1)
C(43)	883(2)	-2119(4)	-763(2)	33(1)
C(44)	1193(2)	-3083(4)	-503(2)	37(1)
C(45)	1621(2)	-2837(4)	-80(2)	42(1)
C(46)	1743(2)	-1622(4)	94(2)	32(1)
C(50)	5068(2)	4180(4)	2045(2)	33(1)
C(51)	5517(2)	3296(5)	2185(2)	42(1)

C(52)	5578(2)	2700(5)	1677(2)	49(1)
C(53)	5772(3)	3601(7)	1331(3)	66(2)
C(54)	4527(2)	5770(4)	2245(2)	32(1)
C(55)	4346(2)	6624(4)	2608(2)	38(1)
C(56)	3796(2)	7060(5)	2315(2)	44(1)
C(57)	3393(2)	6078(6)	2298(3)	53(2)
C(61)	953(3)	4778(6)	-1954(3)	58(2)
C(60)	500(2)	5223(5)	-1826(2)	51(1)
O(1)	2878(1)	8575(3)	1176(2)	44(1)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table A.3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Mo}_2(\text{CN})_6(\text{dppm})_2$ (11)

	x	y	z	U(eq)
Mo(1)	5199(1)	3894(1)	5303(1)	20(1)
P(1)	6815(1)	4655(1)	7170(1)	22(1)
P(2)	6404(1)	6973(1)	6539(1)	22(1)
C(1)	3992(3)	2874(3)	6035(3)	26(1)
C(2)	6552(3)	2464(3)	5497(3)	24(1)
C(3)	3784(3)	4997(3)	5605(3)	26(1)
C(4)	6420(3)	6047(3)	7587(2)	26(1)
C(11)	6589(4)	3887(3)	8260(3)	27(1)
C(12)	7357(6)	2991(4)	8500(4)	62(1)
C(13)	7147(7)	2349(4)	9272(4)	84(2)
C(14)	6175(6)	2594(4)	9803(4)	59(1)
C(15)	5375(5)	3450(4)	9545(4)	55(1)
C(16)	5594(4)	4103(4)	8785(3)	45(1)
C(21)	8738(3)	4727(3)	7445(3)	29(1)
C(22)	9610(4)	5227(4)	8449(3)	50(1)
C(23)	11066(5)	5260(5)	8662(4)	73(2)
C(24)	11646(5)	4792(5)	7899(5)	74(2)
C(25)	10816(4)	4297(4)	6915(4)	56(1)
C(26)	9351(4)	4261(3)	6685(3)	37(1)
C(31)	8282(3)	7344(3)	6745(3)	29(1)
C(32)	9030(4)	8101(3)	7612(3)	45(1)
C(33)	10465(5)	8349(4)	7769(4)	60(1)
C(34)	11153(4)	7849(4)	7083(4)	58(1)
C(35)	10416(4)	7095(4)	6238(4)	50(1)
C(36)	8979(4)	6839(3)	6060(3)	37(1)
C(41)	5787(3)	8234(3)	7049(3)	26(1)
C(42)	5271(4)	8346(3)	7930(3)	39(1)
C(43)	4779(5)	9339(3)	8237(4)	51(1)
C(44)	4814(4)	10209(3)	7663(3)	45(1)
C(45)	5332(5)	10108(3)	6787(3)	48(1)
C(46)	5808(4)	9124(3)	6468(3)	42(1)
N(1)	3310(3)	2360(3)	6379(3)	43(1)
N(2)	7285(4)	1825(3)	5609(3)	55(1)
N(3)	6793(3)	4262(3)	4279(2)	37(1)
C(50)	8818(15)	8307(9)	11889(9)	210(6)
N(50)	8398(11)	8232(7)	10719(6)	163(4)
O(1)	8163(8)	7462(6)	10157(5)	167(3)
O(2)	8350(20)	9123(9)	10480(10)	501(15)

C(51)	572(6)	402(5)	5250(5)	96(2)
N(51)	572(6)	402(5)	5250(5)	96(2)
O(3)	1710(7)	137(5)	5308(5)	65(2)
O(4)	197(8)	1284(6)	5771(6)	77(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table A.4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Na}[(\text{Tp})\text{CrCl}_3]$, (13)

	x	y	z	U(eq)
Cr(1A)	-3333	3333	6000(1)	25(1)
Cl(2A)	-3348(2)	5032(2)	6593(1)	39(1)
Na(1A)	-3333	3333	7500	89(4)
Na(2A)	-1780(40)	7190(30)	7500	133(11)
B(1A)	-3333	3333	4563(7)	24(3)
N(1A)	-4753(6)	3302(6)	5436(3)	28(1)
N(2A)	-4592(6)	3321(6)	4823(3)	29(2)
C(1A)	-5906(8)	3295(8)	5531(4)	34(2)
C(2A)	-6518(8)	3290(8)	4977(4)	37(2)
C(3A)	-5647(8)	3313(8)	4545(4)	35(2)
O(1)	10(40)	6480(40)	7500	257(17)
O(2)	-4090(90)	7510(60)	7500	520(50)
O(3)	-470(90)	9080(30)	6466(15)	430(30)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (Tp)MoBr₂(THF), (15)

	x	y	z	U(eq)
Mo(1)	289(1)	1449(1)	2364(1)	16(1)
Br(2)	1153(1)	-375(1)	2998(1)	28(1)
Br(1)	1534(1)	1292(1)	1031(1)	28(1)
B(1)	-2792(4)	2356(3)	2370(3)	24(1)
N(1)	-1653(3)	834(2)	1693(2)	20(1)
N(2)	-2846(3)	1326(2)	1808(2)	23(1)
N(3)	-751(3)	1637(2)	3482(2)	22(1)
N(4)	-2028(3)	2102(2)	3341(2)	24(1)
N(5)	-583(3)	2973(2)	1924(2)	21(1)
N(6)	-1925(3)	3191(2)	1974(2)	22(1)
O(1)	2050(2)	2294(2)	3104(2)	33(1)
C(1)	-2031(4)	-4(3)	1153(2)	26(1)
C(2)	-3455(4)	-57(3)	916(3)	34(1)
C(3)	-3938(4)	794(3)	1336(2)	29(1)
C(4)	-382(4)	1473(3)	4368(2)	30(1)
C(5)	-1389(4)	1844(3)	4811(2)	38(1)
C(6)	-2413(4)	2231(3)	4144(2)	32(1)
C(7)	-102(4)	3840(3)	1558(2)	28(1)
C(8)	-1120(4)	4602(3)	1377(3)	37(1)
C(9)	-2258(4)	4168(3)	1640(2)	30(1)
C(10)	1994(4)	3202(3)	3695(2)	35(1)
C(11)	3007(5)	2931(4)	4546(3)	64(2)
C(12)	3754(5)	1943(6)	4314(3)	86(2)
C(13)	3436(4)	1879(3)	3333(3)	42(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^2$), and occupancies for $[(\text{Tp})\text{Co}(\text{CH}_3\text{CN})_3][\text{PF}_6]$, (17)

	x	y	z	U(eq)
Co(1)	973(1)	973(1)	973(1)	31(1)
B(1)	1486(4)	1486(4)	1486(4)	47(5)
N(1)	1028(8)	2714(8)	-193(8)	34(2)
N(2)	1302(9)	2697(9)	196(9)	38(2)
N(3)	806(9)	-745(9)	2223(9)	41(2)
C(1)	872(13)	3930(12)	-1303(11)	52(3)
C(2)	1008(16)	4658(13)	-1623(13)	70(4)
C(3)	1321(14)	3859(12)	-652(12)	59(4)
C(4)	620(11)	-1496(11)	2741(11)	41(3)
C(5)	415(11)	-2517(12)	3421(12)	45(3)
P(1)	0	0	0	38(2)
P(2)	2500	2500	2500	43(2)
F(1)	100(200)	-1140(90)	650(160)	800(90)
F(2)	3910(30)	2050(30)	1990(30)	341(15)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *trans*-[Ni(CH₃CN)₂(en)₂][PF₆]₂, (21)

	x	y	z	U(eq)
Ni(1)	0	0	5000	16(1)
N(1)	2172(3)	-986(2)	5114(2)	24(1)
N(2)	1232(3)	1517(2)	6154(2)	22(1)
N(3)	48(3)	889(2)	3396(2)	24(1)
C(1)	3291(3)	-1504(3)	5057(2)	22(1)
C(2)	4729(4)	-2163(4)	4989(3)	33(1)
C(3)	1050(3)	1270(3)	7353(2)	28(1)
C(4)	-1159(4)	209(3)	2408(3)	29(1)
P(1)	1467(1)	4587(1)	3325(1)	24(1)
F(1)	803(4)	5870(2)	3774(3)	67(1)
F(2)	1507(5)	5347(3)	2149(3)	83(1)
F(3)	2141(3)	3286(2)	2846(2)	46(1)
F(4)	1531(5)	3773(3)	4482(2)	80(1)
F(5)	3243(4)	5066(3)	3944(4)	82(1)
F(6)	-266(3)	4052(3)	2660(3)	71(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (Tp)CrCl₂(CH₃CN)•AgPF₆•2CH₃CN, (22).

	x	y	z	U(eq)
Tl(1)	1802(1)	2638(1)	4067(1)	30(1)
Cr(2)	3219(1)	495(1)	3887(1)	17(1)
Cr(1)	389(1)	494(1)	4247(1)	18(1)
Cl(1)	772(1)	1973(2)	5052(2)	25(1)
Cl(2)	998(1)	721(2)	3171(2)	28(1)
Cl(3)	2608(1)	717(2)	4966(2)	26(1)
Cl(4)	2836(1)	1971(2)	3083(2)	26(1)
P(1)	1806(2)	6264(1)	4066(3)	37(1)
N(1)	1028(4)	-406(6)	5030(6)	28(2)
N(2)	2573(3)	-415(6)	3112(5)	24(2)
N(3)	1098(4)	3717(8)	2176(6)	46(2)
N(4)	2617(5)	5552(8)	6781(8)	85(3)
N(10)	-333(3)	1255(5)	3505(5)	18(1)
N(11)	-886(3)	884(5)	3453(4)	18(1)
N(20)	26(3)	-824(5)	3653(5)	22(2)
N(21)	-596(3)	-983(5)	3523(5)	20(2)
N(30)	-176(3)	237(5)	5169(4)	20(1)
N(31)	-748(3)	-51(5)	4893(5)	21(2)
N(40)	3914(3)	1275(5)	4640(5)	19(1)
N(41)	4505(3)	896(5)	4673(5)	19(1)
N(50)	3766(3)	245(6)	2959(4)	22(2)
N(51)	4362(3)	-72(5)	3224(5)	18(2)
N(60)	3583(3)	-839(5)	4497(4)	17(1)
N(61)	4186(3)	-997(5)	4619(5)	18(1)
C(1)	1370(4)	-900(7)	5504(6)	27(2)
C(3)	2260(4)	-917(6)	2653(6)	26(2)
C(2)	1769(4)	-1554(8)	6139(7)	41(2)
C(4)	1808(5)	-1510(8)	2045(7)	42(2)
C(5)	1046(4)	4505(9)	1832(8)	39(2)
C(6)	963(4)	5483(7)	1349(5)	37(2)
C(7)	2536(4)	4488(10)	6345(7)	42(3)
C(8)	2458(5)	3732(9)	5990(8)	48(3)
C(10)	-368(4)	2155(6)	3036(6)	25(2)
C(11)	-971(4)	2358(7)	2696(6)	29(2)
C(12)	-1281(4)	1549(7)	2977(6)	25(2)
C(20)	272(4)	-1667(6)	3289(6)	24(2)
C(21)	-182(4)	-2358(7)	2946(6)	31(2)
C(22)	-725(4)	-1899(7)	3105(6)	22(2)

C(30)	-71(4)	286(7)	6068(6)	25(2)
C(31)	-611(5)	24(7)	6356(7)	36(2)
C(32)	-1017(4)	-190(7)	5597(6)	28(2)
C(40)	3961(4)	2155(6)	5101(6)	22(2)
C(41)	4566(4)	2382(7)	5447(6)	27(2)
C(42)	4898(4)	1559(6)	5150(6)	24(2)
C(50)	3702(4)	281(6)	2060(6)	28(2)
C(51)	4213(4)	0(6)	1735(6)	25(2)
C(52)	4636(4)	-209(7)	2502(5)	22(2)
C(60)	3346(4)	-1655(7)	4833(6)	27(2)
C(61)	3791(4)	-2357(7)	5194(6)	30(2)
C(62)	4313(4)	-1917(7)	5045(6)	27(2)
B(2)	4598(4)	-164(8)	4254(6)	21(2)
B(1)	-992(4)	-185(7)	3900(6)	18(2)
F(1)	2427(3)	6288(6)	4749(5)	66(2)
F(2)	1177(4)	6269(6)	3408(6)	73(2)
F(3)	1804(5)	7523(2)	4051(7)	60(1)
F(4)	1432(4)	6312(7)	4888(5)	78(2)
F(5)	2128(4)	6244(7)	3226(5)	78(2)
F(6)	1793(7)	5029(2)	4069(10)	96(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for
(Tp)CrCl₂(CH₃CN)•TlPF₆•2CH₃CN, (23)

	x	y	z	U(eq)
Tl(1)	1802(1)	2638(1)	4067(1)	30(1)
Cr(2)	3219(1)	495(1)	3887(1)	17(1)
Cr(1)	389(1)	494(1)	4247(1)	18(1)
Cl(1)	772(1)	1973(2)	5052(2)	25(1)
Cl(2)	998(1)	721(2)	3171(2)	28(1)
Cl(3)	2608(1)	717(2)	4966(2)	26(1)
Cl(4)	2836(1)	1971(2)	3083(2)	26(1)
P(1)	1806(2)	6264(1)	4066(3)	37(1)
N(1)	1028(4)	-406(6)	5030(6)	28(2)
N(2)	2573(3)	-415(6)	3112(5)	24(2)
N(3)	1098(4)	3717(8)	2176(6)	46(2)
N(4)	2617(5)	5552(8)	6781(8)	85(3)
N(10)	-333(3)	1255(5)	3505(5)	18(1)
N(11)	-886(3)	884(5)	3453(4)	18(1)
N(20)	26(3)	-824(5)	3653(5)	22(2)
N(21)	-596(3)	-983(5)	3523(5)	20(2)
N(30)	-176(3)	237(5)	5169(4)	20(1)
N(31)	-748(3)	-51(5)	4893(5)	21(2)
N(40)	3914(3)	1275(5)	4640(5)	19(1)
N(41)	4505(3)	896(5)	4673(5)	19(1)
N(50)	3766(3)	245(6)	2959(4)	22(2)
N(51)	4362(3)	-72(5)	3224(5)	18(2)
N(60)	3583(3)	-839(5)	4497(4)	17(1)
N(61)	4186(3)	-997(5)	4619(5)	18(1)
C(1)	1370(4)	-900(7)	5504(6)	27(2)
C(3)	2260(4)	-917(6)	2653(6)	26(2)
C(2)	1769(4)	-1554(8)	6139(7)	41(2)
C(4)	1808(5)	-1510(8)	2045(7)	42(2)
C(5)	1046(4)	4505(9)	1832(8)	39(2)
C(6)	963(4)	5483(7)	1349(5)	37(2)
C(7)	2536(4)	4488(10)	6345(7)	42(3)
C(8)	2458(5)	3732(9)	5990(8)	48(3)
C(10)	-368(4)	2155(6)	3036(6)	25(2)
C(11)	-971(4)	2358(7)	2696(6)	29(2)
C(12)	-1281(4)	1549(7)	2977(6)	25(2)
C(20)	272(4)	-1667(6)	3289(6)	24(2)
C(21)	-182(4)	-2358(7)	2946(6)	31(2)
C(22)	-725(4)	-1899(7)	3105(6)	22(2)

C(30)	-71(4)	286(7)	6068(6)	25(2)
C(31)	-611(5)	24(7)	6356(7)	36(2)
C(32)	-1017(4)	-190(7)	5597(6)	28(2)
C(40)	3961(4)	2155(6)	5101(6)	22(2)
C(41)	4566(4)	2382(7)	5447(6)	27(2)
C(42)	4898(4)	1559(6)	5150(6)	24(2)
C(50)	3702(4)	281(6)	2060(6)	28(2)
C(51)	4213(4)	0(6)	1735(6)	25(2)
C(52)	4636(4)	-209(7)	2502(5)	22(2)
C(60)	3346(4)	-1655(7)	4833(6)	27(2)
C(61)	3791(4)	-2357(7)	5194(6)	30(2)
C(62)	4313(4)	-1917(7)	5045(6)	27(2)
B(2)	4598(4)	-164(8)	4254(6)	21(2)
B(1)	-992(4)	-185(7)	3900(6)	18(2)
F(1)	2427(3)	6288(6)	4749(5)	66(2)
F(2)	1177(4)	6269(6)	3408(6)	73(2)
F(3)	1804(5)	7523(2)	4051(7)	60(1)
F(4)	1432(4)	6312(7)	4888(5)	78(2)
F(5)	2128(4)	6244(7)	3226(5)	78(2)
F(6)	1793(7)	5029(2)	4069(10)	96(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{V(Tp)}_2 \cdot 1/3\text{CH}_3\text{CN} \cdot 1/6\text{Et}_2\text{O}$, (24)

	x	y	z	U(eq)
V(1)	5000	5000	0	21(1)
V(2)	5000	5000	5000	23(1)
V(3)	0	10000	5000	22(1)
B(1)	1823(2)	5672(2)	437(2)	23(1)
B(2)	5437(3)	7143(2)	3135(2)	31(1)
B(3)	-2311(2)	9395(2)	4420(2)	27(1)
O(1)	6853(3)	8783(2)	-678(2)	54(1)
N(1)	-1026(2)	10890(1)	3795(1)	27(1)
N(2)	-1952(2)	10464(1)	3671(1)	26(1)
N(3)	1933(2)	10426(1)	4109(1)	27(1)
N(4)	2774(2)	10628(1)	4518(1)	27(1)
N(5)	85(2)	8769(1)	4591(1)	28(1)
N(6)	-1040(2)	8643(1)	4391(1)	28(1)
N(7)	5438(2)	3525(1)	4996(1)	28(1)
N(8)	5152(2)	2710(1)	5887(1)	28(1)
N(9)	4148(2)	5658(1)	3712(1)	28(1)
N(10)	4456(2)	6594(1)	3010(1)	29(1)
N(11)	6848(2)	5531(1)	3991(1)	29(1)
N(12)	6788(2)	6475(1)	3242(1)	30(1)
N(13)	3532(2)	4363(1)	1343(1)	25(1)
N(14)	2220(2)	4762(1)	1362(1)	24(1)
N(15)	6462(2)	4966(1)	754(1)	24(1)
N(16)	7768(2)	4635(1)	455(1)	23(1)
N(17)	6034(2)	3547(1)	74(1)	25(1)
N(18)	7404(2)	3441(1)	-165(1)	24(1)
N(30)	-1084(7)	9192(5)	1127(5)	154(3)
C(1)	-959(2)	11808(2)	3053(2)	34(1)
C(2)	-1833(3)	11983(2)	2440(2)	41(1)
C(3)	-2432(2)	11113(2)	2854(2)	32(1)
C(4)	2591(2)	10564(2)	3177(2)	30(1)
C(5)	3850(2)	10856(2)	2978(2)	34(1)
C(6)	3929(2)	10888(2)	3844(2)	31(1)
C(7)	1018(2)	8037(2)	4463(2)	38(1)
C(8)	511(3)	7444(2)	4180(2)	44(1)
C(9)	-792(3)	7852(2)	4146(2)	36(1)
C(10)	5901(2)	3155(2)	4299(2)	32(1)
C(11)	5912(2)	2117(2)	4721(2)	38(1)
C(12)	5427(2)	1863(2)	5726(2)	34(1)

C(13)	3263(2)	5400(2)	3408(2)	31(1)
C(14)	2990(2)	6164(2)	2512(2)	35(1)
C(15)	3758(2)	6901(2)	2291(2)	34(1)
C(16)	8143(2)	5207(2)	3959(2)	35(1)
C(17)	8934(3)	5933(2)	3207(2)	42(1)
C(18)	8036(2)	6727(2)	2768(2)	38(1)
C(19)	3547(2)	3585(2)	2230(2)	31(1)
C(20)	2259(2)	3471(2)	2823(2)	36(1)
C(21)	1449(2)	4231(2)	2248(2)	30(1)
C(22)	6413(2)	5154(2)	1540(2)	29(1)
C(23)	7681(2)	4947(2)	1754(2)	31(1)
C(24)	8507(2)	4620(2)	1052(2)	26(1)
C(25)	5665(2)	2647(2)	332(2)	32(1)
C(26)	6784(3)	1949(2)	265(2)	39(1)
C(27)	7861(2)	2486(2)	-57(2)	32(1)
C(30)	-359(6)	9435(4)	1388(4)	93(2)
C(31)	506(5)	9753(4)	1681(4)	88(2)
C(41)	8276(4)	7289(3)	-629(3)	52(1)
C(42)	7512(5)	7890(4)	-101(5)	72(2)
C(43)	5445(8)	10306(5)	-938(7)	122(3)
C(44)	6007(7)	9352(4)	-165(5)	84(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table A.11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for HAT-(CN)₆•C₇H₈•CH₃CN, (26)

	x	y	z	U(eq)
N(1)	3938(2)	10507(5)	5480(2)	28(1)
N(2)	3011(2)	9179(5)	4221(2)	31(1)
N(3)	1665(2)	8866(5)	4298(2)	30(1)
N(4)	1279(2)	10374(5)	5543(2)	26(1)
N(5)	2230(2)	11849(5)	6865(2)	26(1)
N(6)	3583(2)	11758(5)	6866(2)	26(1)
N(21)	5621(2)	11257(6)	6032(2)	47(1)
N(22)	2896(2)	7249(6)	2378(3)	51(1)
N(23)	1012(2)	6647(6)	2527(2)	47(1)
N(24)	-163(2)	11246(6)	6074(2)	42(1)
N(25)	1176(2)	13208(6)	7981(3)	54(1)
N(26)	5170(2)	12704(6)	8005(3)	51(1)
N(38)	936(3)	9613(7)	747(3)	71(2)
C(1)	3297(2)	10480(6)	5544(2)	23(1)
C(2)	2806(2)	9757(6)	4887(2)	25(1)
C(3)	2145(2)	9658(6)	4918(2)	23(1)
C(4)	1944(2)	10400(6)	5576(2)	24(1)
C(5)	2420(2)	11147(6)	6238(2)	23(1)
C(6)	3117(2)	11143(6)	6231(2)	24(1)
C(11)	4382(2)	11124(6)	6104(2)	26(1)
C(12)	2524(2)	8392(6)	3598(2)	28(1)
C(13)	1878(2)	8266(6)	3645(2)	27(1)
C(14)	1103(2)	11101(6)	6146(2)	25(1)
C(15)	1578(2)	11821(6)	6815(2)	26(1)
C(16)	4214(2)	11735(6)	6800(2)	27(1)
C(21)	5077(2)	11204(6)	6059(3)	32(1)
C(22)	2732(2)	7754(6)	2927(3)	32(1)
C(23)	1389(2)	7378(6)	3021(3)	31(1)
C(24)	388(2)	11170(6)	6113(3)	31(1)
C(25)	1357(2)	12603(6)	7469(3)	34(1)
C(26)	4736(2)	12304(6)	7476(3)	33(1)
C(31)	3490(3)	10564(6)	-494(3)	40(1)
C(32)	2824(3)	10963(7)	-756(4)	57(2)
C(33)	2388(3)	10533(8)	-283(4)	66(2)
C(34)	2618(3)	9708(8)	453(4)	61(2)
C(35)	3293(3)	9323(7)	715(4)	54(2)
C(36)	3719(3)	9733(7)	249(3)	46(1)
C(37)	3974(3)	11061(9)	-988(4)	69(2)

C(38)	471(3)	9263(8)	932(3)	55(2)
C(39)	-143(3)	8845(9)	1171(4)	73(2)

U(eq) is defined as one third of the trace of the orthogonalized
Uij tensor.

Table A.12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Co}(\text{HAT}(\text{CN})_4\text{O}_2)(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ (27)

	x	y	z	U(eq)
Co(1)	-1735(1)	-2219(1)	1629(1)	33(1)
C(1)	-1427(4)	-2646(3)	3792(2)	24(1)
C(2)	-3084(4)	-2113(3)	3834(2)	23(1)
C(3)	-4088(4)	-1939(3)	4773(2)	22(1)
C(4)	-3526(3)	-2293(3)	5715(2)	21(1)
C(5)	-1915(4)	-2829(3)	5675(2)	23(1)
C(6)	-879(4)	-2999(3)	4700(2)	22(1)
C(11)	1041(4)	-3303(4)	2792(3)	29(1)
C(12)	-5079(4)	-1311(4)	2939(3)	27(1)
C(13)	-6081(4)	-1125(3)	3937(2)	24(1)
C(14)	-3940(4)	-2464(3)	7452(2)	25(1)
C(15)	-2357(4)	-3020(3)	7417(2)	26(1)
C(16)	1559(4)	-3642(3)	3767(3)	25(1)
C(23)	-7678(4)	-571(3)	3946(2)	22(1)
C(24)	-5021(4)	-2248(4)	8411(3)	33(1)
C(25)	-1722(4)	-3401(4)	8331(3)	32(1)
C(26)	3170(4)	-4189(3)	3751(3)	25(1)
N(1)	-512(3)	-2778(3)	2859(2)	29(1)
N(2)	-3544(3)	-1815(3)	2928(2)	26(1)
N(3)	-5632(3)	-1423(3)	4818(2)	24(1)
N(4)	-4517(3)	-2105(3)	6605(2)	25(1)
N(5)	-1355(3)	-3192(3)	6532(2)	25(1)
N(6)	659(3)	-3508(3)	4675(2)	23(1)
N(13)	-8942(4)	-119(3)	3898(2)	40(1)
N(14)	-5870(4)	-2060(4)	9163(2)	48(1)
N(15)	-1186(4)	-3694(4)	9038(3)	50(1)
N(16)	4442(4)	-4640(3)	3785(3)	44(1)
O(1)	1942(3)	-3488(3)	1967(2)	43(1)
O(2)	-5609(3)	-1014(3)	2142(2)	41(1)
O(3)	278(4)	-2541(4)	449(2)	54(1)
O(4)	-3252(3)	-1755(3)	596(2)	41(1)
O(5)	-1089(4)	-187(4)	1406(2)	45(1)
O(6)	-2283(4)	-4215(3)	1702(3)	44(1)
O(10)	-5013(4)	-4514(4)	990(3)	60(1)
O(11)	-1873(4)	972(4)	3151(3)	62(1)
O(12)	-2252(5)	-5912(5)	3480(3)	72(1)
O(13)	-2223(7)	0(8)	-1017(7)	196(4)

Table A.13. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Mn}(\text{HAT}(\text{CN})_4\text{O}_2)(\text{H}_2\text{O})_4 \bullet 4\text{H}_2\text{O}$, (28)

	x	y	z	U(eq)
Mn(1)	1613(1)	2217(1)	3470(1)	38(1)
N(3)	5583(3)	1438(2)	167(2)	24(1)
N(4)	4496(3)	2108(3)	-1620(2)	26(1)
O(2)	5542(3)	1003(3)	2831(2)	41(1)
N(2)	3492(3)	1823(3)	2051(2)	27(1)
C(5)	1895(4)	2837(3)	-696(2)	24(1)
N(5)	1349(3)	3213(3)	-1552(2)	28(1)
N(6)	-681(3)	3517(3)	282(2)	27(1)
C(4)	3489(3)	2302(3)	-726(2)	23(1)
C(23)	7628(4)	585(3)	1034(2)	25(1)
C(3)	4050(4)	1951(3)	212(2)	24(1)
C(12)	5018(4)	1307(3)	2037(2)	27(1)
C(6)	840(3)	3013(3)	275(2)	24(1)
C(1)	1373(4)	2662(3)	1184(2)	26(1)
C(2)	3032(4)	2124(3)	1151(2)	25(1)
C(13)	6025(3)	1132(3)	1044(2)	23(1)
O(5)	996(4)	86(4)	3640(3)	52(1)
N(1)	438(3)	2795(3)	2110(2)	31(1)
O(1)	2020(3)	3518(3)	2978(2)	49(1)
C(15)	2367(4)	3030(3)	-2438(2)	28(1)
O(6)	2142(4)	4314(3)	3420(3)	54(1)
C(16)	-1592(4)	3662(3)	1185(3)	28(1)
C(26)	-3201(4)	4204(3)	1193(3)	30(1)
C(24)	5016(4)	2246(3)	-3418(3)	31(1)
O(4)	3336(4)	1729(3)	4431(2)	52(1)
N(13)	8897(4)	131(3)	1084(2)	36(1)
C(11)	-1101(4)	3331(3)	2151(3)	32(1)
N(14)	5865(4)	2041(4)	-4161(2)	46(1)
C(25)	1771(4)	3452(4)	-3359(3)	35(1)
C(14)	3934(4)	2474(3)	-2467(2)	26(1)
N(16)	-4492(4)	4648(3)	1180(3)	43(1)
N(15)	1265(4)	3803(4)	-4069(3)	55(1)
O(3)	-575(5)	2483(6)	4623(4)	83(2)
O(10)	5009(4)	4535(4)	4050(3)	61(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ni}(\text{HAT}-(\text{CN})_4\text{O}_2)(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, (29)

	x	y	z	U(eq)
Ni(1)	-6738(1)	2709(1)	-3349(1)	26(1)
C(1)	-6435(4)	2320(4)	-1218(3)	20(1)
C(2)	-8090(4)	2859(4)	-1191(3)	21(1)
C(3)	-9093(4)	3057(3)	-253(3)	20(1)
C(4)	-8536(4)	2723(3)	693(3)	20(1)
C(5)	-6932(4)	2186(3)	659(3)	21(1)
C(6)	-5887(4)	1996(4)	-308(3)	21(1)
C(11)	-3973(4)	1629(4)	-2205(3)	23(1)
C(12)	-10080(4)	3652(4)	-2094(3)	25(1)
C(13)	-11071(4)	3863(4)	-1103(3)	22(1)
C(14)	-8957(4)	2564(4)	2432(3)	24(1)
C(15)	-7385(5)	2009(4)	2401(3)	25(1)
C(16)	-3462(4)	1333(4)	-1229(3)	22(1)
C(23)	-12681(4)	4423(4)	-1097(3)	23(1)
C(24)	-10041(5)	2784(4)	3397(3)	32(1)
C(25)	-6751(5)	1632(4)	3323(3)	32(1)
C(26)	-1838(4)	792(4)	-1234(3)	23(1)
N(1)	-5526(3)	2167(3)	-2150(2)	24(1)
N(2)	-8545(3)	3131(3)	-2097(2)	23(1)
N(3)	-10630(3)	3582(3)	-217(2)	22(1)
N(4)	-9529(4)	2921(3)	1580(2)	24(1)
N(5)	-6374(4)	1821(3)	1524(2)	24(1)
N(6)	-4355(3)	1490(3)	-328(2)	21(1)
N(13)	-13931(4)	4875(3)	-1141(3)	38(1)
N(14)	-10850(5)	2992(4)	4150(3)	51(1)
N(15)	-6215(5)	1329(4)	4027(3)	53(1)
N(16)	-577(4)	346(4)	-1198(3)	39(1)
O(1)	-10604(3)	3927(3)	-2899(2)	37(1)
O(2)	-3068(3)	1420(3)	-3024(2)	35(1)
O(3)	-6113(4)	4686(4)	-3578(3)	36(1)
O(4)	-8195(4)	3177(4)	-4394(3)	34(1)
O(5)	-7300(4)	743(3)	-3289(3)	37(1)
O(6)	-4771(4)	2352(4)	-4495(3)	41(1)
O(10)	-7234(4)	5338(4)	-5795(3)	58(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.15. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$), and occupancies for $\{(\text{Cp}_2\text{Fe})_3\text{HAT}(\text{CN})_6\cdot\text{CH}_3\text{CN}\}$ (30)

	x	y	z	U(eq)
Fe(1)	4562(1)	3328(2)	3460(2)	37(1)
Fe(2)	817(1)	3336(2)	8458(2)	51(1)
C(40)	1067(13)	4270(18)	6853(16)	107(8)
C(34)	1076(13)	4161(19)	10112(16)	107(7)
C(36)	1180(14)	2898(17)	6828(13)	91(7)
C(32)	1155(10)	2909(12)	10157(12)	61(4)
C(37)	1693(13)	3970(20)	6816(15)	93(6)
C(33)	1648(11)	3887(15)	10197(14)	76(5)
C(35)	104(15)	3357(18)	10100(13)	104(8)
C(38)	157(12)	2575(16)	6859(16)	91(6)
C(31)	200(12)	2645(13)	10125(16)	90(6)
C(39)	72(12)	3324(13)	6829(12)	72(5)
N(7)	5727(6)	4288(6)	8448(7)	25(2)
N(8)	4718(6)	2345(6)	8450(8)	33(2)
C(29)	3326(7)	2348(8)	8468(11)	38(2)
C(24)	4336(7)	2858(8)	8454(9)	35(2)
C(30)	4330(7)	4367(8)	8482(13)	42(3)
C(27)	6158(5)	3838(8)	8469(8)	32(2)
C(28)	4755(7)	3827(6)	8462(9)	26(2)
N(1)	2566(7)	1955(6)	8440(10)	48(2)
N(2)	3868(14)	4698(13)	8457(14)	111(6)
C(26)	5672(6)	2851(6)	8468(7)	24(2)
N(4)	4650(6)	6127(6)	3464(9)	44(2)
N(5)	7891(16)	9288(15)	3456(9)	145(10)
C(53)	4056(6)	6422(6)	3453(10)	43(2)
C(41)	0	0	7640(20)	75(6)
C(42)	0	0	9270(30)	83(6)
N(3)	6733(11)	6313(7)	3498(12)	52(2)
C(1)	6620(9)	8414(6)	3452(13)	35(2)
N(11)	0	0	10650(20)	133(11)
C(2)	5553(7)	6828(6)	3460(9)	38(2)
N(9)	5154(8)	8033(9)	3468(17)	86(4)
C(49)	4274(7)	7345(6)	3446(10)	46(2)
C(54)	6228(7)	6554(6)	3462(8)	42(2)
C(52)	5801(6)	7818(9)	3453(10)	65(3)
C(101)	3889(11)	3392(11)	5141(11)	55(4)
C(102)	4480(13)	2558(13)	5122(17)	78(4)
C(103)	5278(8)	3355(9)	5105(12)	54(3)

C(104)	3808(17)	2640(20)	5154(18)	150(13)
C(105)	4979(15)	4093(7)	5119(9)	110(8)
C(111)	4487(10)	2532(8)	1786(13)	76(5)
C(113)	5290(7)	3377(8)	1792(13)	57(3)
C(114)	4062(10)	3599(12)	1813(12)	144(13)
C(115)	5046(11)	4092(6)	1795(9)	97(8)
C(112)	3737(9)	2654(10)	1811(19)	90(5)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.16. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$), and occupancies for $\{[(\text{Cp})_2\text{Co}][\text{PF}_6]\}_3\text{HAT}-(\text{CN})_6$, (31)

	x	y	z	U(eq)
Co(1)	1998(1)	8176(1)	-45(2)	41(1)
Co(2)	0	12159(1)	0	47(1)
P(1)	0	8560(3)	0	38(1)
P(2)	1201(1)	4971(2)	-84(4)	39(1)
F(1)	-209(4)	7805(6)	326(10)	80(3)
F(2)	-209(6)	9297(6)	1319(12)	112(5)
F(3)	539(3)	8538(7)	1022(12)	84(3)
F(7)	746(4)	4822(10)	1211(11)	116(5)
F(8)	1660(4)	5143(10)	-1384(12)	109(4)
F(9)	837(4)	5546(8)	-1383(10)	97(4)
F(10)	1382(5)	5822(7)	985(12)	104(4)
F(11)	1555(5)	4428(9)	235(12)	118(5)
F(12)	1072(10)	4115(7)	-1153(15)	183(9)
N(1)	4456(3)	12765(5)	5109(11)	31(2)
N(2)	3929(3)	11181(6)	5135(12)	29(2)
N(3)	4464(3)	9537(6)	5010(11)	30(2)
N(4)	2678(3)	10405(8)	5249(16)	52(3)
N(5)	3456(4)	8051(6)	5073(17)	51(3)
N(6)	4220(4)	15011(7)	5121(15)	47(3)
C(1)	4728(4)	11997(6)	5064(12)	24(2)
C(2)	4448(4)	11163(7)	5069(12)	25(2)
C(3)	4725(3)	10340(7)	5016(12)	27(2)
C(4)	3958(4)	9567(7)	5070(14)	30(2)
C(5)	3690(3)	10390(8)	5124(12)	28(2)
C(6)	4721(4)	13521(7)	5063(13)	33(2)
C(7)	4438(4)	14350(8)	5147(14)	34(2)
C(8)	3129(4)	10411(8)	5197(14)	37(2)
C(9)	3688(4)	8710(8)	5050(14)	37(3)
C(21)	939(10)	7250(20)	-2080(30)	113(9)
C(22)	2317(7)	8110(30)	-2480(20)	155(13)
C(23)	019(11)	8856(13)	-2320(30)	107(9)
C(24)	1471(18)	8527(16)	-1970(30)	184(18)
C(25)	1496(9)	7695(13)	-1850(20)	86(7)
C(26)	2240(10)	7524(18)	2150(30)	102(7)
C(27)	2552(8)	8170(20)	1790(30)	101(7)
C(28)	2296(10)	9068(14)	1680(30)	97(7)
C(29)	1743(8)	8827(13)	2230(20)	83(5)
C(30)	718(10)	7885(18)	2420(20)	107(8)

C(31)	8(8)	12987(13)	2120(30)	137(9)
C(32)	477(8)	12511(16)	1910(30)	161(13)
C(33)	363(9)	11585(16)	1980(30)	139(10)
C(34)	-175(9)	11488(14)	2230(30)	173(14)
C(35)	-395(7)	12355(14)	2320(20)	106(7)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.17. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$), for $\{([n\text{-Bu}_4\text{N}][\text{I}])_3[\text{I}][\text{HAT}-(\text{CN})_6]_2 \cdot 3\text{C}_6\text{H}_6, (32)$

	x	y	z	U(eq)
I(1)	7468(1)	2532(1)	2189(1)	102(1)
I(2)	0	0	3798(1)	148(1)
C(1)	542(4)	547(3)	1338(6)	39(2)
N(1)	-16(4)	1030(4)	1312(6)	50(2)
N(2)	1042(3)	1043(4)	1315(6)	51(2)
C(2)	-2(4)	542(4)	1340(6)	44(2)
C(3)	18(7)	539(5)	6281(7)	68(3)
C(4)	1031(4)	1520(4)	1269(6)	41(2)
N(3)	-30(7)	1005(7)	6308(7)	82(3)
C(5)	529(6)	542(5)	6284(7)	69(3)
C(6)	482(4)	1514(4)	1272(7)	46(2)
N(4)	1053(5)	1030(6)	6311(7)	89(4)
C(7)	499(5)	2058(6)	1219(10)	68(3)
C(8)	1559(5)	2065(5)	1214(9)	63(3)
C(9)	475(17)	1475(11)	6357(11)	118(8)
C(10)	976(12)	1510(7)	6355(12)	118(8)
C(13)	1568(13)	2060(13)	6422(16)	195(16)
N(5)	1978(4)	2493(5)	1151(12)	98(4)
N(6)	513(6)	2491(5)	1158(13)	107(5)
C(12)	485(15)	2084(16)	6445(16)	167(11)
C(14)	8693(7)	1326(7)	3039(11)	87(4)
N(9)	8518(4)	1487(4)	2059(8)	68(3)
C(16)	8742(11)	2095(10)	2060(20)	139(8)
C(17)	9354(10)	2474(8)	2020(20)	162(11)
C(19)	8748(6)	1262(6)	1305(12)	87(4)
C(20)	8636(8)	1375(8)	279(14)	111(5)
C(21)	7944(10)	1302(11)	2061(16)	133(8)
N(7)	609(18)	2559(10)	6370(30)	249(18)
C(22)	8940(40)	1130(30)	-510(15)	440(60)
N(8)	1947(12)	2549(9)	6390(20)	199(11)
C(23)	8810(20)	1190(20)	-1530(20)	340(30)
C(24)	9497(13)	3138(13)	2110(40)	211(16)
C(25)	10010(30)	3599(18)	1700(50)	540(80)
C(26)	1089(8)	1728(9)	3804(14)	107(5)
C(27)	649(10)	1744(10)	3807(15)	113(5)
C(28)	539(12)	2127(12)	3820(20)	156(8)
C(29)	1596(13)	2162(12)	3810(20)	161(9)
C(30)	993(18)	2660(20)	3790(30)	220(14)

C(31)	1590(20)	2670(20)	3760(30)	222(15)
C(32)	8510(20)	1460(20)	3970(30)	260(20)
C(33)	7514(7)	638(9)	2030(20)	159(11)
C(35)	6836(12)	489(15)	2110(30)	217(17)
C(37)	6370(20)	60(40)	1740(60)	670(110)
C(34)	8800(30)	1150(30)	4900(30)	330(30)

$U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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