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CLUSTERS AND EXTENDED ARRAYS WITH METAL IONS AND NITROGEN DONOR LIGANDS

presented by

Cristian Saul Campos Fernandez

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Major professor

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CLUSTERS AND EXTENDED ARRAYS WITH METAL IONS AND NITROGEN DONOR LIGANDS

By

Cristian Saul Campos Fernández

AN ABSTRACT OF A DISSERTATION

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

DOCTOR OF PHILOSPHY

Department of Chemistry

2001

Professor Kim R. Dunbar

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ABSTRACT

CLUSTERS AND EXTENDED ARRAYS WITH METAL IONS AND NITROGEN DONOR LIGANDS

By

Cristian Saul Campos Fernández

The study of nitrogen heterocyclic ligands in coordination chemistry has experienced a steady increase in the last thirty years. The increasing versatility of synthetic methods used in the preparation of ligands has permitted increasingly more complex molecules to be assembled. The work reported in this thesis involves the systematic study of the chemistry of five diimine ligands that have not been investigated thoroughly to date. These are 2-2-pyridyl-1,8-naphthyridine (pynp), 3,6-bis-pyridyltetrazine (bptz), 2,2'-bis-bipyridyl-azo (abpy), 1,3,6-trispyridyl-triazine (tptaz), and 2,3,5,6 tetrapyridyl pyrazine (tppz).

The chemistry of the bptz ligand was explored with a variety of first row transition metals, with the result being the high yield syntheses of cyclic coordination compounds (metallocyclophanes). The formation of these cyclic entities rather than polymeric materials or dinuclear complexes is attributed, in great degree, to the choice of the anion which functions as a template in the self-assembly of the cationic metallocyclophanes. Anions that are similar in size and geometry, e.g. $[BF_4]$ and $[ClO_4]$, yield molecular squares, whereas the larger anion, $[SbF_6]$, leads to the assembly of a molecular pentagon. The existence of these species in solution was demonstrated by ¹⁹F

MR studies Zabra (CH)CN . ment in the solution ta the formation of Ri Colland Cullis t The chemistry sports that opportunity n the synthesis and Manna that car taleenty species. In porton, namely as has vein the comp she first of its kind -Naphthyndine Masphine, hall de or c dine purp ligands ir tarrochemistry that terronicality "innove be reversible one ; ا ^زځندټرط،تر(۲۹:۲۵م.ترو Deng fully delocalized ^{I chavior is} found.

NMR studies conducted on the diamagnetic metallocyclophane, $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8)$, the results of which indicate that the encapsulated anion is present in the solution form of the compound. Electrospray mass spectrometry revealed that the formation of these metallocyclophanes with other transition metals such as Mn^{II}, Fe^{II}, Co^{II} and Cu^{II} is feasible, but that they are not as stable as the Ni^{II} and Zn^{II} analogs.

The chemistry of tppz has languished for almost two decades, most likely due to reports that coordination of more than one metal center was not possible. We embarked on the synthesis and characterization of a series of mononuclear tppz compounds $[M(tppz)_2]^{n+}$ that can potentially be used as building blocks for the synthesis of higher nuclearity species. In addition, a new application for this ligand was discovered in our laboratory, namely as a linker for metal-metal compounds to give molecular rectangles. In this vein, the compound $[Rh_4(O_2CCH_3)_2(tppz)_2(CH_3OH)_4][PF_6]_6$ was prepared which is the first of its kind in the M-M bond field.

Naphthyridine based ligands have been used relatively infrequently compared to phosphine, halide or carboxylate derivatives in metal-metal bond chemistry. The presence of two pynp ligands in the dimetal units $[M_2]^{4+}$ (M = Mo^{II}, Ru^{II} and Rh^{II}) allows for a rich electrochemistry that is not observed for most metal-metal compounds with more electronically "innocent" ligands. In the case of two of the new compounds in this study, four reversible one electron ligand based reductions, are observed. The compound $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2$ shows Class III Robin-Day behavior with all four electrons being fully delocalized throughout the molecule, whereas in the $[Mo_2]^{4+}$ derivative, Class II behavior is found.

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This work would not have been possible without the support of my advisor Dr. Kim Dunbar, whose constant support, understanding and patience allowed me to overcome several obstacles during my graduate student years. I also wish to thank all the staff members and Dunbar students at Michigan State University as well as Texas A&M University who taught me laboratory skills and the use of many techniques. I would also like to extend special thanks to Lisa Thompson and John Koomen who greatly helped me with theoretical and mass spectrometry studies at the latter stages of my career at Texas A&M. In addition, I will like to extend special thanks to the members of my research group, Rodolphe Clèrac and Jose Ramón Galan Máscaros for their invaluable help with magnetic measurements and Brad Smucker, Kemal Catalan and Elizabeth Lozada for the good moments that we spent in the lab. In general, I would like to thank to all of the Dunbar group members who I met throughout the last six years.

I would also like to acknowledge a very special person in my life, someone who influenced my life greatly and taught me the importance of education; my grandmother. She cannot be with me at this important moment of my life, but all the times that we talked about the importance of education really encouraged me to pursue post graduate studies in chemistry.

Finally, I will like to give thanks to my family who supported me even though they never quite understand what I was doing here. Without their support and encouragement I would have never had the will power to finish this difficult task.

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LIST OF SYMBOLS AND ABBREVIATIONS

Å	Ångström
Аbру	2-azo-bis-pyridyl
Ag/AgCl	Silver-silver chloride reference electrode
В	Boltzmann constant
BarF ₄	Tetrakis(3,5-bis(triflouromethyl)phenyl)
	borate
Bopd	2,5-(2-pyridyl)-1,3,4-oxadiazole
Bptz	3,5-bis-pyridyl- 1,2,4,6-tetrazine
Bpnp	2-7 bis-(2-pyridyl)-1,8 naphthyridine
Вру	2,2'-bipyridine
Bpym	2,2' bipyrimidine
br	broad
cm	centimeter
CV	cyclic voltammetry
℃	degree centigrade
d	doublet (NMR)
δ	parts per million (ppm)
E ₁₂	half-wave potential
Ep,a	anodic peak potential
Ep,a Ep,c	anodic peak potential cathodic peak potential
Ep,a Ep,c emu	anodic peak potential cathodic peak potential electromagnetic unit

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ε	molar extinction coefficcient
g	Lande factor
G	Gauss
h	hour
Н	Hamiltonian
НОМО	Highest Occupied Molecular Orbital
(M)Hz	(mega)hertz
IR	infrared
J	Exchange parameter
K	Kelvin
LUMO	Lowest Unoccupied Molecular Orbital
m	medium
Μ	moles per liter
mg	milligram
min	minute
MLCT	metal-to-ligand charge transfer
mL	milliliter
mmol	millimole
m/z	mass-to-charge ratio
μ	bridging ligand
N	Avodagro's constant
nm	nanometer
np	naphthyridine

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NMR	nuclear magnetic resonance
otf	trifluoromethanesulfonate
	(triflate, CF ₃ SO ₃ ⁻)
phen	phenanthroline
ррт	parts per million
рупр	2-2'-pyridyl-1,8 naphthyridine
S	singlet (NMR), strong (IR)
sh	shoulder
SQUID	Super Quantum Interference Device
TBABF ₄	tetra-n-butylammonium tetraflouroborate
TBAPF ₆	tetra-n-butylammonium
	hexafluorophosphate
TBAI	tetra-n-butylammonium iodide
TBAIO₄	tetra-n-butylammonium periodate
THF	tetrahydrofuran
Tptaz	1,3,6-trispyridyl-triazine
Тррz	2,3,5,6 tetrapyridyl pyrazine
tpy	2,2';6',2"-terpyridine
UV	ultraviolet
V	Volt
ν	frequency
vs	versus, very strong



weak

ZFS

Zero-field splitting

Chapter I

Introduction

I

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I. Background

Nitrogen Heterocyclic Ligand Chemistry

The use of nitrogen heterocyclic ligands in coordination chemistry has witnessed a steady increase in the last four decades. The versatility of synthetic methods used to prepare these molecules has allowed chemists to design increasingly complex derivatives with different applications in mind. Among the ligands that have been investigated are the common diimine ligands such as 2,2'-bipyridyl (Figure 1a), 1,10-phenanthroline (Figure 1b), 2,2':6',2"-terpyridine (Figure 1c) as well as more elaborate ones such as 1,3,5-[tris[4'-(2,2':6',2"-terpyridinyl)] benzene (Figure 1d).¹

One of the most simple and well studied coordination compounds based on diimine ligands is the tris-chelate complex $[Ru(bpy)_3]^{2+,2}$ In general, coordination compounds of this type based on the 2,2 bipyridine motif exhibit strong luminescence in solution at room temperature, and have a powerful photosensitization capacity for electron and energy-transfer processes.³ The photoluminescent excited state is a strong reductant as well as an excellent oxidant due to the presence of an electron deficient d⁵ metal center and an excess electron located in the ligand network in the excited state. Modifications to the 2,2' bipyridine unit permits one to tune of the redox potentials of the ligands over a significantly wide range.⁴ Such strategies have allowed for the synthesis of Ru(II) complexes that are either good oxidants or reductants in the excited state.²

a

Figure 1. [(b)] (d)]

a



b



c



Figure 1. Drawing of the ligands (a) 2,2'-bipyridine, (b) 1,10-phenanthroline, (c) 2,2':6',2"-terpyridine and (d) 1,3,5-tris[4'-2,2':6,2"-terpyridinyl]benzene.

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Mixed Valency in Ligand-Bridged Metal Assemblies

Mixed-valence materials that contain several redox sites in more than one oxidation state have attracted the interest of chemists for many years. Robin and Day⁷ defined three broad classes of mixed-valence materials that are referred to as Class I, II and III compounds. Class I mixed-valence species are those in which the interaction between redox centers bridged by a ligand is so weak that the mixed-valence material exhibits the properties observed for isolated mononuclear species. For Class III compounds, the opposite is encountered, namely the interaction between the two centers is so strong that the properties of individual redox centers are not observed, but rather new properties characteristic of the coupled redox units are exhibited, i.e., the system is delocalized. Intermediate between these two categories are Class II materials that exhibit redox characteristics which are slightly altered from the properties of the isolated units; these are referred to as partially delocalized systems.

Cyclic voltammetry is an invaluable tool for establishing the placement of any compound within the Robin-Day classification scheme. Based on the precedence of Taube's work, it is possible to define a comproportionation equilibrium constant, K_c, for

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the equilibrium between two valence states; the separation between two successive reversible redox potentials allows for its calculation as shown in equation $1.^{8}$

$$\begin{bmatrix} \mathbf{X} \\ \mathbf{X} \\ \mathbf{X} \end{bmatrix} + \begin{bmatrix} \mathbf{X} \\ \mathbf{X} \\ \mathbf{X} \end{bmatrix}^{2} = 2 \begin{bmatrix} \mathbf{X} \\ \mathbf{X} \\ \mathbf{X} \end{bmatrix}^{-}_{, \mathbf{K}_{c}}$$
(Eq. 1)
where
$$\ln \mathbf{K}_{c} = \left(\frac{\exp \Delta E_{V_{2}} (\operatorname{in} \mathbf{mV})}{25.69} \right)$$

If there is no communication between the redox centers (Class I), the K_c constant is $\leq 10^2$. In the case of complete delocalization between the redox centers, K_c is very large, $\geq 10^6$. The intermediate situation, in which there is electronic coupling but not full delocalization, yield K_c values in the range $10^2 < K_c < 10^5$.

II. New Applications of Bipyridine and Terpyridine Chemistry

One of the current challenges in chemistry is the manipulation of noncovalent interactions in the design of new materials in a manner akin to Nature. Chemists are striving to design building blocks, often called tectons, that self-assemble into larger conglomerates with the ability to store information in the form of electronic, magnetic or redox properties.⁹ Much of the supramolecular chemistry in recent years has involved the self-assembly of metal containing molecules with the use of polydentate nitrogen ligands. The work reported in this dissertation involves the application of nitrogen heterocyclic chemistry in areas where they have not been traditionally employed. Specifically, the research involves the coordination chemistry of the five ligands in Figure 2. These include (a) 2-2-pyridyl-1,8-naphthyridine (pynp), (b) 3,6-bis-pyridyl-1,2,4,6-tetrazine



Figure 2. Schematic drawing of the ligands (a) 2-2-pyridyl-1,8 naphthyridine (pynp), (b) 3,6-bis-pyridyl- 1,2,4,6-tetrazine (bptz), (c) 2-azo-bis pyridyl (abpy), (d) 1,3,6-trispyridyl-triazine (tptaz) and (e) 2,3,5,6 tetrapyridyl pyrazine (tppz).

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(bptz), (c) azo-2,2'-bipyridine (abpy), (d) 1,3,6-trispyridyl-triazine (tptaz), and (e) 2,3,5,6 tetrapyridyl-pyrazine (tppz). In the past, such ligands have been used mainly in reactions with Ru(II) and Os(II) centers,¹⁰ but in the present work, they are used to assemble arrays of paramagnetic first row metal ions and low valent second row transition metal ions that form metal-metal bonds.





The ligands have been chosen on the basis of their demonstrated ability to produce compounds with interesting electronic and redox properties.¹¹ Ligand *a* (pynp) bridges dinuclear units through the naphthyridine unit, thereby allowing for the formation of molecules with the dimetal core " $[M_2(pynp)_2]^{2+}$ ". Ligands *b-e* possess two or more coordinating domains that permit the synthesis of polymetallic arrays in the form of

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cyclic units or polymers. Ligands **b** (bptz) and **c** (abpy) share some common features, *i.e.*, both can be envisioned as bis-pyridyl units joined by either one or two azo (tetrazine) groups (scheme 1).¹¹ The azo group possesses low lying π^* orbitals (LUMO) that are suitable for promoting good electronic communication between metal centers.¹¹

In the case of ligands d (tptaz) and e (tppz), the triazine and pyrazine rings are known to provide a good π pathway for electronic or magnetic coupling. Both ligands possess terpyridine coordination sites.¹²

Each chapter in this dissertation describes the chemistry of a specific ligand and its application in the design of tectons (building blocks) and their intended use in building larger molecules. The dissertation is organized into four chapters including the introduction.

A. Bipyridine-based ligands in Paramagnetic Arrays

Supramolecular Chemistry of polytopic bpy ligands

The design of arrays with the goal of exploring electronic or magnetic coupling between metal centers has been under intense investigation in the last three decades.¹³ The synthesis of large heterocyclic receptors (ligands) with multiple coordination domains (polytopic), has enabled chemists to design large molecules that exhibit new properties as a result of cooperative effects between the constituent building blocks. An excellent example of this approach can be found in the family of materials known as metallodendrimers (Figure 3).¹⁴ Progress in this field requires the availability of molecular components (building blocks) with well-defined structures and properties.



n = 0, 1, 2, 3



Figure 3. Some examples of metallodendrimers.¹²

This approach has major drawbacks, namely multistep procedures similar to a typical organic covalent approach, which results in low yields for the synthesis of large molecules. The self-assembly of large organic molecules in living organisms takes place thorough collective weak forces including ion-pairing,¹⁵ hydrophobic or hydrophilic interactions,¹⁶ hydrogen-bonding,¹⁷ host-guest interactions,¹⁸ π -stacking,¹⁹ and donor-acceptor interactions.²⁰ By manipulating these supramolecular forces, the linkage of small units (molecules) with useful characteristics to form large entities (supramolecular



Figure 4. Supramolecular chemistry hierarchy¹⁸

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species) can be more efficiently achieved. Supramolecular chemistry is described as the chemistry of the "*intermolecular bond*", as defined by J. M Lehn.²¹

The driving force in supramolecular chemistry is the self-assembly of larger entities from specifically engineered smaller building blocks. Once these smaller entities have been assembled, they may perform complex functions such as light harvesting,²² conversion of light into chemical²³ or electrical energy²⁴, or function as memory devices.²⁵ Supramolecular systems are often categorized according to different levels of hierarchy. Primary structure corresponds to small building blocks that are referred to as <u>tectons</u>. In purely organic supramolecular structures, tectons aggregate via noncovalent bonds to generate polymolecular aggregates called supermolecules. These supermolecules can, in turn, associate with one another to render gigantic macroscopic conglomerates (Figure 4).^{26a}

Specific Supramolecular Interactions: Anions as Templates

As described in the previous section, non-covalent interactions (hydrogen bonding, π stacking, van der Waals interactions, cation or anion interactions) play an essential role in the assembly of supramolecular structures. Of particular relevance to this dissertation is the use of anions as templates in the assembly of metallocyclophanes. Templating is one of the more efficient procedures for self-assembly at the disposal of the chemist. It involves the use of temporary or permanent 'helper" species, of organic or inorganic nature, to assist in the process of assembly. The vast majority of the template effect cases reported in the literature are cation related.²⁷ Among these, crown ether chemistry is the most prominent. By comparison, the study of anion templates is much less common, and there are relatively few cases reported in the literature to date.²⁸



Chapter II describes self-assembly processes in which the divergent ligand, 3,6-bis pyridyl-tetrazine (bptz) permits the self-assembly of metallocyclophanes of different nuclearities. The bptz ligand is a bis-bipyridine chelate that is capable of assembling metal cations into cyclic olygomers or polymers. The overwhelming factor in dictating the outcome of the reaction was found to be the size and shape of the anion. The results presented in Chapter II constitute an important contribution to the area of metallocyclophane chemistry and underscore the role of the anion choice in forming a specific nuclearity for cationic assemblies. It is important to point out that previous research in the formation of cationic molecular square has not address the role of the anion (scheme 2).

11.

Divergent Metal Precursor with six labile positions

Divergent Bridging Ligand With two trans binding sites

Scheme 2.

B. Terpyridine ligands in Paramagnetic Arrays

Despite their outstanding photochemical properties, $[M(bpy)_3]^{2+}$ complexes present two major drawbacks as building blocks for polymetallic arrays, namely stereo and/or geometric isomerism. The use of ligands with the tpy (tpy = terpyridine)
coordination unit are advantageous from the geometric point of view, namely $[M(tpy)_2]^{n+}$ complexes are achiral.²⁹ Synthetic tailoring of tpy based ligands has allowed chemists to design ligands with multiple tpy binding sites. For example the tris-tpy ligand depicted in Figure 1d forms large polymetallic arrays based solely on coordination bonds.^{3,4,5,6} The main goal of this chemistry is the construction of nanosized components by a "bottom-up" approach, i.e., beginning with molecular components. The molecules are highly branched tree-like species commonly called dendrimers and are designed with specific properties such as the capability to absorb visible light, to luminesce, or to undergo reversible multielectron redox processes. Extensive research has been carried out in this area³⁰ with Ru(II) and Os(II)³¹ being incorporated into building blocks called diads (two metal centers) and triads (three metal centers) based on $[M(tpy)_2]^{2+}$ type units that can function as photosensitizers.³²



Figure 5. Schematic drawing of the molecule [(tpy)Ru(tppz)Ru(tpy)]⁴⁺.

One of the more important characteristics of metallo-tpy arrays is that they exhibit mixed-valence behavior.³³ For example, the complex [(tpy)Ru(tppz)Ru(tpy)]⁴⁺ with two

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equivalent Ru(II) centers (Figure 5)¹⁷ exhibits two oxidation couples corresponding to Ru(II)/Ru(III) and Ru(III)/Ru(III) species. The large $\Delta E_{\frac{1}{2}}$ value for the oxidation processes is evidence for strong delocalization through the tppz ligand (Figure 2e) which stabilizes the mixed valence state Ru(II)/Ru(III).

In addition to homometallic systems, multibranched ligands can be used to synthesize heterometallic systems, *e.g.*, $[(tpy)Ru(tppz)IrCl_3]^{2+.17}$ In this case the ruthenium center is the light absorbing site whereas the Ir(III) center is a catalytic center. These types of mixed-metal systems present the possibility for developing supramolecular complexes with widely varying functions due to the different metal centers. In this manner, compounds with new properties that arise from cooperative effects are being discovered.

As previously mentioned, polymetallic arrays often undergo multiple electron redox processes. This versatility in redox chemistry can be envisioned as providing a switching control, namely the possibility of turning a particular intermolecular interaction "on" or "off". Conceivably one could affect the strength of different binding sites by means of redox chemistry, thereby allowing for control over variables such as nuclearity or binding specificity towards a specific analyte (i.e., a sensor).³⁴ Constable and coworkers offer an excellent example of this approach wherein the nuclearity of a complex depends upon the redox state of the chelated metal ion.³⁵

One important aspect of supramolecular compounds based on coordination bonds is that the presence of metal atoms in the building blocks generates new types of molecular interactions, which are characteristic of inorganic systems. The self-assembly approach for the design of metal-based supramolecules offers an alternative to the

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classical organic route, in which one building block is added in each step of the synthesis. This process takes advantage of metal-ligand interactions that are fairly kinetically labile. The resulting supramolecular entities are often obtained in high yields and require fewer steps than equivalent covalent syntheses. The reversibility of the coordination bonds present in the assembly contribute to a defect-free product because the intermediates are in equilibrium with each other as the final, more thermodynamically stable compound is being formed³⁶



Figure 6. Schematic drawings of metal tppz building blocks.

Ligands based on the terpyridine binding motif have not been used extensively to connect first row transition metals. Chapter III is devoted to the self-assembly of paramagnetic metal ions of the 3d elements with the ligand tppz (Figure 2e). The general

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goal is to probe the magnetic behavior of metal-tpy arrays. The tppz molecule, reported in 1959 by Lion and coworkers,³⁷ possesses two tpy coordination domains that allow for the preparation of dimetallic or higher order metal-arrays. Three precursors of the type $[M(tppz)_2][X]_2$ (where $M = Co^{2+}$, Fe^{2+} , Ni^{2+} and $X = [NO_3]^-$, $[ClO_4]^-$, $[PF_6]^-$ and $[BF_4]^-$) were synthesized (Figure 6). They exhibit different degrees of electronic coupling between the two tppz units ranging from complete delocalization (Class III) for $[Fe(tppz)_2][ClO_4]_2$ to no electronic interaction at all in the case of $[Ni(tppz)_2][NO_3]_2$.



Figure 7. Schematic drawing of the molecule [Rh₄(O₂CCH₃)₂(tppz)₂(CH₃OH)₄][PF₆]₆.

The mononuclear building blocks $[M(tppz)_2]^{n+}$ posses two dangling tpy binding sites for further coordination to other metal ions. In addition to the electrochemical behavior, some of the molecules exhibit interesting magnetic properties, for example

Figure 8. Ditiss (ipi_)

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[Co(tppz)₂][PF₆]₂ exhibits spin crossover behavior. Besides the mononuclear compounds,

dinuclear $[Ni_2(tppz)(CH_3CN)_6][BF_4]_2$ polymer of and the form a а $[Co_2(tppz)(CH_3CN)_2Cl_2][BF_4][PF_6]_{\infty}$ synthesized structurally were also and characterized.

An unexpected application for tppz is reported in chapter III, namely as a bridge between two metal-metal bonded units (M-M). Earlier reports by Pruchnick and coworkers³⁸ indicated that two tpy ligands can bind to one dirhodium unit, *viz*, in the compound $[Rh_2(O_2CCH_3)(tpy)_2]Cl_2$. This result prompted us to attempt the use of tppz to link two $[Rh_2]^{4+}$ units, which we believed could occur to give and open structure. Instead the linkage of two $[Rh_2(O_2CCH_3)]^{3+}$ units led to the formation of a molecular rectangle composed of short Rh-Rh bonded sides and long Rh-tppz-Rh sides (Figure 7).

C. Dual Bipyridine/Terpyridine ligands



Figure 8. Different functionalities in the ligands (a) 1,3,6-trispyridyl-triazine (tptaz) and (b) 2-azo-bispyridyl (abpy).

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Chapter III also contains a brief account of the coordination chemistry of the ligand 2,4,6-tris-pyridyl triazine (tptaz) with first row transition metals. The ligand can be envisioned as being a combination of two different coordination motifs, namely bpy and tpy (Figure 8a).

In this part of the chapter, we reported the syntheses of three mononuclear compounds in which the metal is bound to the tpy domain and the bpy site is free to be used to coordinate to other metal ions. Cyclic voltammetric studies reveal a rich electrochemistry for these mononuclear complexes, the most interesting example being the $[Fe(tptaz)_2]^{2+}$ compound which displays four reversible one-electron reductions, and an oxidation corresponding to $Fe^{II} \rightarrow Fe^{III}$. The electrons added to the molecule are partially delocalized throughout the tptaz molecules as determined from the electrochemical data. A few dinuclear compounds with this ligand have been reported, but minimal characterization was reported.³⁹ The inductive effect on the triazine ring with binding of the first metal center decreases the basicity of the nitrogen atom of the open coordination site, but the possibility of accessing reduced species will increase the probability of coordinating a second metal. This will be explored in future studies.

D. Azopyridine based ligands in Paramagnetic Arrays

Chapter II includes a brief description of the synthesis and characterization of dinuclear compounds with the ligand azo-2,2'-bipyridine (abpy) (Figure 8b) which possesses low lying π^* orbitals based on high electron density located at the coordinating N centers.⁴⁰ This characteristic allows the abpy ligand to function as a molecular bridge between metal centers.⁴¹ Previous studies with metals such as Ru(II) and Os(II) have

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revealed that there is strong electronic coupling (a large comproportionation constant, K_c) indicating good stability for the mixed-valence species with these metals.

Dinuclear complexes with the abpy spacer have a short distance between metal centers as compared to ligands with similar coordination capabilities such as bptz (chapter II), bpym and bppz. Another noteworthy aspect to consider is that the abpy can be reduced to a stable radical spacer in coordination compounds e.g. in the compounds $[Cu_2(\mu-\eta^4-abpy\cdot-)(Ph_2P(CH_2)_6PPh_2)][BF_4]^{42}$ and $[Os(abpy\cdot-)(Br)(CO)(PPh_3)_2]^{43}$ (Figure 10). Three different compounds were synthesized with this ligand, namely the dinuclear compounds $[Cu_2(abpy)(CH_3CN)_8][BF_4]_4$ and $[Ni_2(abpy)(CH_3CN)_2][NO_3]_4$ and the polymeric material $[Cu(abpy)_2]_{\infty}$.



Figure 9. Compounds with the radical form of the ligand abpy.^{39,40}

III. Naphthyridine Ligands in Metal-Metal Bonded

Compounds

The realization of the existence of a quadruple bond in [ReCl₈]²⁻ by F. A Cotton and coworkers⁴⁴ marked a major event in the history of transition metal chemistry. Before



Figure 10. Molecular orbitals for M-M species.



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this fundamental discovery, a debate regarding the existence of M-M bonding had been going on for nearly ten years. Originally, the determination of the X-ray structure of $[Re_2(CO)_{10}]$ by Dahl, Ishishi and Rundle in 1957⁴⁵ provided evidence of the existence of the M-M bond with bridging groups between the metal centers, but the elucidation of the X-ray structure of $[Re_2Cl_8]^2$ led to the realization that low valent metals can form very short, unbridged contacts in their compounds. This fact has been born out in thousands of other examples of M-M bonded compounds that have been prepared since the 1960's.⁴⁶ A simple model of the atomic orbital overlap to form molecular orbitals in M-M compounds is shown in Figure 10.



Figure 11. Schematic drawing of the series $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (M = Mo(II), Ru(II) and Rh(II)).

From the early 1960's, and continuing to the present day, there has been a great deal of interest in M-M bond chemistry, much of it being conducted with carboxylate, phosphine and halide ligands. We noted that there has been comparatively little M-M

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chemistry with non-innocent ligands such as polypyridyl (bpy, terpy etc.,) and related ligands.⁴⁷ Even less research has been performed with ligands such as naphthyridine and its derivatives, presumably because they are not commercially available and their syntheses are not trivial. As part of the dissertation, the ligand pynp 2-(2-pyridyl)-1,8-naphthyridine (pynp) was synthesized and use to prepare three dinuclear compounds that comprise a homologous series, namely $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (Figure 11).

Chapter IV of this dissertation describes the syntheses and characterization of metal-metal bonded compounds of pynp that show unusual redox behavior. These may be envisioned as building blocks that could be taken to the next hierarchical level, *e. g.*, a cyclic oligomer. The electrochemical behavior of the $[M_2(O_2CR_2)_2(pynp)_2]^{2+}$ series is quite different than that exhibited by their carboxylate counterparts $[M_2(O_2CR_4)_4]^{2+}$ (where $M = Mo^{2+}$, Ru^{2+} , Rh^{2+}) which do not display a rich redox chemistry. This series exemplifies the three different cases of mixed-valence behavior on the Robin-Day scale.¹⁷ [Ru₂(OAc)₂(pynp)₂][PF₆]₂ displays Class III behavior with the electrons being completely delocalized over the two pynp units; $[Mo_2(OAc)_2(pynp)_2][BF_4]_2$ displays class II behavior, with the four electrons being partially delocalized, and finally $[Rh_2(OAc)_2(pynp)_2][BF_4]_2$ is a fully localized system (class I).

These compounds represent unprecedented building blocks for the construction of supramolecular metal-metal compounds through substitution of the equatorial carboxylate ligands (Figure 12)⁴⁸ with the appropriate linker. A macrocycle that incorporates redox active M-M units is expected to exhibit unusual electronic properties



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Figure 12. Possible outcome of linking four cis- $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$ units.

not observed in metal-metal compounds with ligands that do not promote delocalization

of electrons between the metals and the ligands.

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Chapter II

Coordination Chemistry of Nitrogen Heterocycles with

Bis-Bypyridine Functionalities.

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I. Introduction

The self-assembly of metal cations with nitrogen heterocyclic bridging ligands is a central theme in supramolecular chemistry aimed at developing light-harvesting assemblies of electronically coupled metal centers.^{1,2,3,4} Applications of metal complexes with delocalized π -ligand systems include their use as electron "propagating" components for inner-sphere electron-transfer reactions between metals,⁵ as building blocks for magnetic materials,⁶ models for metalloenzymes,⁷ and precursors to lowdimensional conducting polymers.⁸ One such ligand that bears promise for such applications is 3,6 bis(2-pyridyl)tetrazine (bptz), (Figure 13a).⁹ It has been noted that metal-coordinated bptz can be reduced to form stable anion radicals and that the metals are strongly coupled through the both the neutral and reduced forms of the ligand.¹⁰



Figure 13. Schematic drawing of (a) 3,6 bis(2-pyridyl)tetrazine (bptz) and (b) 2,2' bispyridyl azo (abpy).

Studies in our laboratories,¹¹ have revealed another application for the bptz molecule, namely as a cis-directing, bis-bipyridine chelate that promotes the selfassembly of cyclic oligomers with metal ions.¹¹ The high interest in cyclic molecules or metallocyclophanes as they are often called, stems from their promise in host-guest

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chemistry,^{12a,b} photochemistry^{12c,d} and catalysis.^{12e} A number of successful methods have been used to prepare cyclic molecules based on transition metals, most notably the use of late transition metal, square-planar metal complexes to prepare molecular squares.^{13, 14}

One obvious region of the periodic table for expanding molecular square chemistry is in the octahedral cations of the first-row transition series.¹⁵ Our goals are to explore this possibility and to understand how self-assembly between these relatively labile metal cations and multidentate ligands is controlled. A main parameter that influences the outcome of these self-assembly reactions is the rigidity of the linkers, as well illustrated by the synthesis of molecular grids.¹⁶ In some cases, however, two or more products ensue from a single metal/ligand stoichiometry. The structure of the product can be difficult to predict because it depends on subtle factors¹⁷ such as interligand stacking interactions,^{17a} or the participation of non-convalently bonded cations¹⁸ or anions¹⁹ as templates in the assembly process. In the present chemistry, the formation of molecular squares is evidently controlled to some extent by the anions which act as templates.¹⁹

This chapter describes a new family of molecular squares of general formula $[M_4(bptz)_4(CH_3CN)_8]^{8+}$ (M = Ni²⁺ or Zn²⁺) along with the pentagon $[Ni_5(bptz)_5(CH_3CN)_{10}]^{10+}$. In addition to extensive characterization by mass spectroscopy, single crystal X-ray data were used to verify structures for Ni²⁺ and Zn²⁺ compounds. Among the new compounds prepared are unprecedented, partially solvated squares and pentagons. The difference between obtaining one product versus another was shown to be entirely on the choice of counterion. It was also demonstrated that, under certain conditions, one can obtain dimers and polymers from the same reactions that lead to the

squates. The metal tons w In ac here also e arters.^N ar ampounds . se ubpy as mpioving m. it this work. I Chara ijelie voltarr It some case tharacterize : Methods and All e Setlenk-line esception of and toluene . P:Os. The st_ were purchasi MniCH3CN Zu CH₂CN
squares. These results are incontrovertible evidence that the self-assembly reactions of metal ions with bptz are controlled by subtle factors.

In addition to bptz chemistry, reactions of the related ligand abpy (Figure 13b) were also explored. The azo group permits good electronic coupling between metal centers,²⁰ and, in light of the presence of low lying π^* orbitals, a facile reduction of azo compounds is favored. The possibility of ligand reduction has prompted researchers to use abpy as a radical linker in coordination compounds which is advantageous for improving magnetic superexchange.²¹ Three compounds were isolated and characterized in this work, namely two dinuclear compounds of Ni(II) and Cu(II), and a polymer Cu(I).

Characterization of the new compounds in this chapter by X-ray crystallography, cyclic voltammetry, spectroscopic techniques, and magnetic measurements is presented. In some cases, electrospray mass spectroscopy was used in lieu of a crystal structure to characterize the products.

II. Experimental Section

Methods and Starting Materials.

All operations were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. All solvents were pre-dried over 4 Å molecular sieves with the exception of acetonitrile, which was pre-dried over 3 Å molecular sieves. Diethyl ether and toluene were freshly distilled over Na/K, and methylene chloride was distilled over P_2O_5 . The starting materials [Ni(H₂O)₆][ClO₄]₂ [Ni(H₂O)₆][NO₃]₂ and [Zn(H₂O)₆][ClO₄]₂ were purchased from Aldrich and used as received. The precursors [Ni(CH₃CN)₆][BF₄]₂, [Mn(CH₃CN)₄][BF₄]₂, [Cu(CH₃CN)₄][BF₄]₂, [Ni(CH₃CN)₆][SbF₆]₂, and [Zn(CH₃CN)₄][BF₄]₂ were synthesized by published methods.²² The bptz ligand was

repired Physical 40 Vana spectrome officined w the Departm en a finely ಷಿಷ್ಣಾಣ್ಯಂ entrospray Nanospiray 1 Bio:MultiVia aproximate) lonispray vo taltulations http://mem.be [Ni4(bptz)4(C The sa ^{ace:onitrile} an ²⁰¹¹Se of I hu solution was [N.405ptz)4(C] prepared from a literature method⁹ and recrystallized from benzene. The abpy ligand was synthesized as reported with minor modifications.²³

Physical Measurements.

The ¹H, ¹¹B, and ¹⁹F NMR spectra were recorded on either a XL-300 or XL-400 Varian NMR spectrometer. IR spectra were measured on a Nicolet 740 FT-IR spectrometer as Nujol mulls on KBr plates. Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL (housed in the Department of Chemistry at Texas A&M University). Measurements were performed on a finely ground polycrystalline sample. Data were corrected for the sample holder and diamagnetic contributions were calculated from Pascal constants.²⁴ Positive ion electrospray mass spectra were acquired using a Sciex Qstar Pulsar with a Protana Nanospray ion source. Data were acquired with TOFMA 2.0RC3 and analyzed with BioiMultiView 1.5RC3. Acetonitrile solutions of the metal complexes were diluted to approximately 10 μ M, and a 7.0 μ l was loaded into a Au/Pd coated, silica spray needle. Ionspray voltage was set between 900 and 1200 volts. Theoretical isotope ratio calculations were performed using ISOPRO3.0 (Senko, M. Sunnyvale, CA, http://members.aol.com/msmssoft/)

$[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ (1).

The salt $[Ni(CH_3CN)_6][BF_4]_2$ (100 mg, 0.209 mmol) was dissolved in 20 mL of acetonitrile and treated with solid bptz (50 mg, 0.209 mmol) under nitrogen. Over the course of 1 hour, the solution changed from a pale blue to a dark brown-green color. The solution was stirred overnight and then layered with toluene to yield crystals of $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ ·4CH₃CN within a three-day period; yield, 105 mg (84%). IR

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KB: mulle 1263 (w.), 19 0.15 ppm +s Zn₄ bptz 4 The of acetomicm hour stimm, solution was with CH₂Cl₂ penod: yield 1450 (w). 14 8.30 ppm (t intense ((s), 1868, ([Zn₁() Ni4(bptz)4(The s acetonithle a Over the cou ^{color.} T Nu(bptz)4(C reaction solu ^{acetonitrile}: y ¹⁶⁰³ (w), 146 (KBr mull) cm⁻¹: 3457 (s), 2321 (w), 2320 (w), 1605 (w), 1458 (vs), 1407 (s), 1376 (m), 1263 (w), 1068 (vs), 791 (w), 736 (w), 721 (w), 611 (w). ¹⁹F NMR 52.73 ppm (br,s), ¹¹B 0.18 ppm (s). ES-MS: m/z =1780 ([Ni₄(bptz)₄][BF₄]₇)⁺, 878 ([Ni₄(bptz)₄][BF₄]₆)²⁺.

$[Zn_4(bptz)_4(CH_3CN)_8] [BF_4]_8(2).$

The reagent $[Zn(CH_3CN)_6][BF_4]_2$ (150 mg, 0.309 mmol) was dissolved in 20 mL of acetonitrile, and bptz (73 mg, 0.309 mmol) solid was added under nitrogen. During a 1 hour stirring period, the solution changed from a colorless to an orange color. The solution was stirred for an additional 12 hours without further change, and then layered with CH₂Cl₂ to yield crystals of $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8 \cdot 4CH_3CN$ within a three-day period; yield; 125 mg, (67%). IR (KBr mull) cm⁻¹: 3400 (w,br), 1607 (w), 1504 (m, br), 1460 (w), 1404 (w),1377 (w), 1054 (s, b), 721(w). ¹H NMR 9.25 ppm (d), 8.55 ppm (t), 8.30 ppm (t), 8.10 ppm (d), 2.67 ppm (s) ¹¹B NMR -0.25 ppm (weak) (s), -1.60 ppm (intense) (s), ¹⁹F NMR. -151.2 ppm (weak) (s), -151.2 ppm (intense) (s). ES-M.S: m/z = 1868; ([Zn₂(bptz)][BF₄]₃)⁺, 621.9; ([Zn(bptz)][BF₄])⁺, 386.01

$[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$ (3).

The salt $[Ni(H_2O)_6][ClO_4]_2$ (100 mg, 0.309 mmol) was dissolved in 20 mL of acetonitrile and treated with solid bptz (73 mg, 0.309 mmol) under anaerobic conditions. Over the course of 1 hour, the solution changed from a light green to a dark brown-green color. The solution was stirred overnight. Crystals of $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$ ·3CH₃CN·C₄H₈O can be isolated by either layering the reaction solution with toluene or by slow diffusion of diethyl ether or THF into acetonitrile; yield, 120 mg (62 %). IR (KBr mull) cm⁻¹: 2320 (w), 2318 (w), 2072 (w), 1603 (w), 1460 (s), 1377 (m), 1405 (w), 1261 (w), 1098 (br,s), 798 (w), 722 (w). ES-

<u>M.S.</u> m. z Noprz : [Zn₄ bptz) The aetoritrile yeld an or Z-, 5212 .diffusion of 367. IR (15. br., 959 評問 (d), Zr. bptz :: 1531.9; Zr.; bp:z ; ^{96.9}: ([Zr.: Nis(bptz)5(The acetonitrile the course c Solution wa • Nis Bplz)s(1 ⁽⁸²⁹⁷⁾, IR (1 ¹⁰⁸² (w), 1

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M.S: m/z = 1868; $([Ni_4(bptz)_4][ClO_4]_7)^+$, 1376; $([Ni_3(bptz)_3][ClO_4]_5)^+$, 1140; $([Ni_3(bptz)_2][ClO_4]_5)^+$, 884.9; $([Ni_2(bptz)_2][ClO_4]_3)^+$, 629; $([Ni(bptz)_2][ClO_4])^+$.

$[Zn_4(bptz)_4(CH_3CN)_8][ClO_4]_8(4).$

The salt $[Zn(H_2O)_6][ClO_4]_2$ (100 mg, 0.269 mmol) was dissolved in 20 mL of acetonitrile and treated with bptz (64 mg, 0.269 mmol) under anaerobic conditions to vield an orange solution within 1 h. The solution was stirred overnight. Crystals of [Zn₄(bptz)₄(CH₃CN)₈][ClO₄]₈·3CH₃CN were obtained within 2 days by slow vapor diffusion of diethyl ether into an acetonitrile solution of the compound; yield, 60 mg (36%). IR (KBr mull) cm⁻¹: 3342 (w,br), 1604 (w), 1402 (w), 1377 (w), 1260 (w) 1098 (s, br), 959 (w), 790 (w), 721(w). ¹H NMR 9.26 ppm (d), 8.56 ppm (t), 8.35 ppm (t), 8.16 ppm (d), 2.65 ppm (s). ES-MS: m/z = 1893; $([Zn_4(bptz)_4][ClO_4]_7)^+$, 1656; $([Zn_4(bptz)_3][ClO_4]_7)^+$, 1161.8; $([Zn_4(bptz)_4][ClO_4]_7)^+$, 1630.8; $([Zn_3(bptz)_4][ClO_4]_5)^+$, $([Zn_3(bptz)_4][ClO_4]_4)^+,$ 1531.9; 1394.7; $([Zn_3(bptz)_3][ClO_4]_5)^+,$ 1295; $([Zn_3(bptz)_3][ClO_4]_4)^{\dagger}$, 1097.9; $([Zn_3(bptz)_3][ClO_4]_2)^{\dagger}$, 1132.9; $([Zn_2(bptz)_3][ClO_4]_5)^{\dagger}$, 896.9; $([Zn_2(bptz)_2][ClO_4]_3)^+$, 660; $([Zn_2(bptz)][ClO_4]_3)^+$, 635; $([Zn(bptz)_2][ClO_4])^+$.

$[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ (6).

The salt $[Ni(CH_3CN)_6][SbF_6]_2$ (250 mg, 0.322 mmol) was dissolved in 40 mL of acetonitrile and treated with bptz (77 mg, 0.322 mmol) under anaerobic conditions. Over the course of 1 hour, the solution changed from a pale blue to a brown-green color. The solution was stirred overnight and then layered with toluene to yield crystals of $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ ·2CH₃CN (6) within a three day period; yield, 240 mg (82%). IR (KBr mull) cm⁻¹: 2320 (w), 2319 (w), 1605 (w), 1303 (w), 1263 (w), 1153 (w), 1082 (w), 1022 (w), 970 (w), 789 (w). ES-MS: m/z =3584; ([Ni_5(bptz)_5][SbF_6]_9)⁺,

16-4.6: י בירי א [Mn/bptz || [Mr ad treated . ef 1 h. a pu reidish pow itäet attaet 96.1401 (w 22° Azo-Bip The . ragent 2-ar solution was slowly adde mixed, the r solution was ettracted with Maso₄, and :adissolved :: Pield 1.20 g Lmol.cm)

1674.6; $([Ni_5(bptz)_5][SbF_6]_8)^+$, 1528.7; $([Ni_5(bptz)_5][SbF_6]_8)^{2+}$, 1528.8; $([Ni_2(bptz)_3][SbF_6]_3)^+$, 1292.7; $([Ni_2(bptz)_2][SbF_6]_3)^+$, 1057.8; $([Ni_2(bptz)_2][SbF_6]_2)^+$. {[Mn(bptz)(CH₃CN)₂][BF₄]₂}, (7).

 $[Mn(CH_3CN)_4][BF_4]_2$ (290 mg, 0.74 mmol) was dissolved in 40 mL of acetonitrile and treated with bptz (174 mg, 0.61 mmol) under anaerobic conditions. Over the course of 1 h, a pale red precipitate began to form. The solution was stirred overnight, and a reddish powder of { $[Mn(bptz)_2(CH_3CN)_2][BF_4]$ } was collected by vacuum filtration under anaerobic conditions; yield, 123 mg (36%). IR (KBr mull) cm⁻¹: 2724 (w), 1605 (w), 1401 (w), 1376 (s), 1259 (w), 1062 (s, br), 722 (w).

2,2' Azo-Bipyridine (abpy).

The abpy ligand was synthesized as reported with some modifications.²³ The reagent 2-aminopyridine (5.0 g, 0.027 mol) was dissolved in 200 mL of water and the solution was cooled by placing it in an ice bath for one hour. This cold solution was slowly added to 600 mL of chilled NaOCl 5% aqueous. Once the two solutions are mixed, the reaction mixture developed a bright orange color within 5 minutes. The solution was stirred for one hour, after which time the bright orange solution was dried over MgSO₄, and the solvent was removed on a rotary evaporator. The orange solid was redissolved in hot hexanes and allowed to cool slowly. Orange crystals were obtained; yield 1.20 g (24 %). UV-Vis (acetonitrile, nm, c = 2.72×10^{-4} M): $\lambda = 450$, $\varepsilon = 4.8 \times 10^{2}$ L(mol·cm)⁻¹; $\lambda = 361$, $\varepsilon = 1.47 \times 10^{4}$ L(mol·cm)⁻¹; $\lambda = 203$, $\varepsilon = 5.29 \times 10^{2}$ L(mol·cm)⁻¹.

Ni: abpv As atternir it ässolved. solution, w addocal ? into the rea. IR KBrmu UV-Vis act (Cu₂tabpy) The aletonithie color charg Wernight, a the point of green cryst. • (*). 2323 | acetonithie × 104 L(mo

$[Ni_2(abpy)(CH_3CN)_2][NO_3]_4$ (12).

A sample of $[Ni(H_2O)_6][NO_3]_2$ (100 mg, 0.34 mmol) was dissolved in 30 mL of acetonitrile in a beaker. The pale green solution was stirred until the entire solid had dissolved, after which time a quantity of abpy (32 mg, 0.17 mmol) was added. The solution, which immediately changed to an intense green color, was stirred for 4 additional hours and then concentrated to 10 mL. Slow vapor diffusion of diethyl ether into the reaction solution afforded dark green crystals within 6 days; yield, 80 mg (75%). IR (KBr mull) cm⁻¹: 2724 (w), 1620 (w), 1147 (w), 1039 (w), 1022 (w), 801 (w), 722 (w). UV-Vis (acetonitrile, nm, c = 9.8 × 10⁻⁶M): $\lambda = 344$, $\varepsilon = 1.8 \times 10^4$ L(mol·cm)⁻¹.

[Cu₂(abpy)(CH₃CN)₆][BF₄]₄ (13).

The salt [Cu(CH₃CN)₄][BF₄]₂ (100 mg, 0.25 mmol) was dissolved in 20 mL of acetonitrile and treated with abpy (22 mg, 0.12 mmol) which led to an instantaneous color change from a blue to a pale green color. The reaction mixture was stirred overnight, after which time the solution was concentrated and treated with diethyl ether to the point of saturation. The solution was then placed in the freezer, and within 5 days green crystals were obtained; yield, 82 mg (80%). IR (KBr mull) cm⁻¹: 2724 (w), 2296 (w), 2323 (w), 1589 (w), 1261 (w), 1229 (w), 1027 (br,s), 805 (w), 722 (w). UV-Vis (acetonitrile, nm, c = 8.0×10^{-6} M): $\lambda = 351$, $\varepsilon = 2.7 \times 10^{4}$ L(mol·cm)⁻¹; $\lambda = 230$, $\varepsilon = 1.98 \times 10^{4}$ L(mol·cm)⁻¹.

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Data Collection and Refinement.

The X-ray data were collected on a SMART 1K area detector diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda_{\alpha} = 0.71073$ Å). The frames were integrated in the Siemens SAINT²⁵ software package and the data were corrected for absorption using the SADABS program.²⁶ The structures were solved using the direct-methods program SHELXS-97.²⁷ Crystal parameters and basic information pertaining to data collection and refinement are summarized in Table 1

[Ni₄(bptz)₄(CH₃CN)₈][BF₄]₈·4CH₃CN (1).

Crystals of $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8 \cdot 4CH_3CN$ were grown by slow diffusion of toluene into an acetonitrile solution of the title compound. A dark green prism of dimensions $0.05 \times 0.12 \times 0.25$ mm³ was secured on the tip of a glass fiber with Dow Corning silicone grease and cooled to 173(1) K in a cold N₂(g) stream. A total of 24786 reflections was collected, 16456 of which were unique. Five out of the eight [BF₄]⁻ ions were disordered, therefore restraints for chemically equivalent distances (B-F = 1.37Å) were applied. Displacement parameters of related fluorine positions were equated by means of constraints in order to minimize variables since the [BF₄]⁻ anions exhibit positional/rotational disorder patterns. The extensive disorder accounts for the slightly higher than usual R factors. The final full-matrix refinement was based on 9444 observed reflections with F₀>4 σ (F₀) that were used to fit 1554 parameters to give R1 = 0.0831 and wR2 = 0.1957. The goodness-of-fit index was 1.026 and the highest peak in the final difference map was 1.182 e⁻/Å⁻³.

Table I. Crystallographic Data för Compounds 1–15.

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	1	2	6	4	ĸ
empirical formula	C72H68B8F32N36Ni4	C ₇₂ H ₆₈ B ₈ F ₃₂ N ₃₆ Zn ₄	C74H73Cl8O33N36Ni4	C70H65Cl8O32N35Zn4	C ₂₈ H ₃₂ Cl ₄ O ₁₆ N ₁₄ Ni ₂
fw	2355.94	2393.58	2499.0	2453.7	1079.84
snace proun	P-1	P-1	P2./n	C2/c	P-1
a,Å	14.118(3)	13.924(5)	15.082(3)	20.377(4)	8.639(5)
b,Å	17.090(3)	17.071(5)	31.922(6)	16.634(3)	10.856(5)
c,A	21.774(4)	21.940(5)	22.305(5)	28.283(6)	12.362(5)
c	94.87(3)	94.458(5)	90	90	98.355(5)
ነዊ ;	91.43(3)	92.510(5)	104.11(3)	102.30(3)	104.675(5)
	97.47(3)	97.790(5)	90	90	97.317(5)
۲,Å ³	5186.6(2)	5144(3)	10415(4)	9366(3)	1093.2(9)
۲	2	2	4	4	2
D g/cm ³	1.516	1.544	1.619	1.795	1.60 8
	24786	63108	79465	44125	4433
total data unique data μ (mm ⁻¹)	16456 0.831	24635 1.039	25404 1.014	7997 1.34 8	3371 1.184
R indices	R1 = 0.0831	R1 = 0.0695	R1 = 0.0641	R1 = 0.0774	R1 = 0.0648
[l>4σ(1)] ^{ab}	wR2 = 0.1957	wR2 = 0.2017	wR2 = 0.1584	wR2 = 0.2244	wR2 = 0.1538
R indices	R1 = 0.1505	R1 = 0.1335	R1 = 0.2000	R1 = 0.1294	R1 = 0.1318
(all data)	wR2 = 0.2322	wR2 = 0.2614	wR2 = 0.2142	wR2 = 0.2636	wR2 = 0.1934
GOF	1.026	1.035	0.900	1.035	0.957

Table 1. Crystallographic Data for Compounds 1-15.

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empirical formula	C84H76 Sb10F60N42Nis	C ₁₈ H ₁₇ B ₂ F ₈ O ₁ N ₉ Mn ₁	C66N33H69Sb4B1P3F36 Nia	C ₆₈ N ₃₄ H ₆₂ I ₇ Cl ₁ O ₃₂ Ni	C ₂₈ N ₈ O ₄ H ₂₂ P ₂ F ₁₂ Co
fw	4324.7	782.84	3103.406	3024.574	865.99
snace oroin	C2/c	P-1	1222	C2/c	P-1
apare or our a. Å	17.933(4)	9.135(2)	14.762(3)	20.358(4)	8.383(2)
h.Å	28.314(6)	10.859(2)	17.869(4)	17.493(4)	9.933(2)
c. A	29.459(6)	14.631(3)	22.326(5)	28.123(6)	12.727(3)
	60	99.48(3)	60	60	68.31(3)
ძ ლი	104.82(3)	107.53(3)	90	98.53(3)	79.79(3)
ר :	60	102.27(3)	90	90	76.74(3)
Y V Å ³	14460(3)	1311.0(5)	5889(2)	9904(3)	953.4(3)
V,A 7	4	2	80	4	2
2 - /3	1.916	1.530	2.143	1.962	1.529
	36580	12882	5030	35238	10893
total data	12327	4480	3459	8434	4391
unique data µ (mm ⁻¹)	2.121	0.591	0.667	3.045	0.643
	R1 = 0.1160	R1 = 0.0617	R1 = 0.0668	R1 = 0.1063	R1 = 0.0561
K indices	wR2 = 0.3645	wR2 = 0.1494	wR2 = 0.0826	wR2 = 0.2895	wR2 = 0.1275
[]>4ơ(])]"	R1 = 0.1520	R1 = 0.1323	R1 = 0.1029	R1 = 0.1905	R1 = 0.0944
R indices (all data)	wR2 = 0.4049	wR2 = 0.1940	wR2 = 0.1926	wR2 = 0.3454	wR2 = 0.1436
GOF	1.069	0.933	1.048	1.161	1.020

Table 1. (cont'd)

Table 1. (cont'd)					
	11	12	13	14	15
empirical formula	$C_{24}N_8O_4H_{20}B_2F_8Cu$	C ₁₄ H ₁₄ N ₁₀ O ₁₂ Ni ₂	C ₂₆ N ₁₂ H ₃₂ B ₄ F ₁₆ Cu ₂	$C_{20}N_8H_{16}B_2F_8Cu_2$	C64H56F42I1N32Sb7Ni4
fw	721.622	631.707	986.92	605.55	3285.276
space group	P2 ₁ /c	P-1	P-1	P2(1)/n	1222
a,Å	10.270(2)	9.135(5)	10.340(5)	9.295(2)	14.932(3)
b,Å	10.910(2)	10.859(5)	10.659(5)	9.541(2)	18.136(4)
c, λ	13.480(3)	14.631(5)	10.659(5)	13.486(3)	22.527(5)
α	90	99.478(5)	64.234(5)	90	90
θ,	106.20(3)	107.533(5)	78.235(5)	91.58(3)	06
	90	102.266(5)	78.235(5)	90	06
V,Å ³	1450.4(5)	1311.0(1)	1026.9(8)	1195.5(4)	6100(2)
7	4	2	2	2	2
L Dg/cm ³ total data	1.652 9193	0.765 8160	1.565 7358	1.859 11151	1.839 19922
unique data	3467	3252	34 8 4	2040	5202
μ (mm ⁻¹)	0.852	0.752	1.141	1. 8 71	3.333
R indices	R1 = 0.0374	R1 = 0.0582	R1 = 0.0750	R1 = 0.0861	R1 = 0.0741
[I>4ơ(I)] ^{ab}	wR2 = 0.0943	wR2 = 0.1586	wR2 = 0.2053	wR2 = 0.2055	wR2 = 0.2283
R indices	R1 = 0.0564	R1 = 0.0636	R1 = 0.0860	R1 = 0.1574	R1 = 0.0816
(all data)	wR2 = 0.1042	wR2 = 0.1657	wR2 = 0.2166	wR2 = 0.2522	wR2 = 0.2391
GOF	1.080	1.092	1.058	0.987	1.092

 ${}^{a} R1 = \Sigma \left\| F_{0} \right\| - \left\| F_{c} \right\| / \Sigma \left\| F_{0} \right\| , {}^{b} wR2 = [\Sigma[w(F_{0}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{0}^{2})^{2}]]^{0.5}.$

$[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8 \cdot 4CH_3CN$ (2).

Single crystals of $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8 \cdot 4CH_3CN$ were obtained by slow diffusion of dichloromethane into an acetonitrile solution of the title compound. A light orange platelet of dimensions $0.11 \times 0.09 \times 0.24$ mm³ was mounted on the tip of a glass fiber with Dow Corning silicone grease and cooled to 110(1) K in a cold N₂(g) stream. A total of 63108 unique reflections was collected of which 24635 were unique. Two of eight of the [BF₄]⁻ ions were disordered, therefore restraints on chemically equivalent B-F (1.37 Å) bonds were applied. Displacement parameters of related fluorine atoms were constrained to minimize parameters. The final refinement was based on 13131 reflections with F₀>4 σ (F₀) that were used to fit 1394 parameters to give R1 = 0.0695 and wR2 = 0.2017. The goodness-of-fit index was 1.035 with the highest peak being 1.681 e⁷Å⁻³.

$[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8 \cdot 2CH_3CN \cdot C_4H_8O (3).$

Crystals of $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8 \cdot 2CH_3CN \cdot C_4H_8O$ were grown by slow vapor diffusion of THF into an acetonitrile solution of the compound. A dark green prism of dimensions $0.11 \times 0.08 \times 0.02 \text{ mm}^3$ was secured on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold N₂(g) stream at 110(1) K. Of the 79465 reflections that were collected, 25404 were unique. The final refinement was based on 9335 reflections with F₀>4 σ (F₀) that were used to fit 1384 parameters to give R1 = 0.0641 and wR2 = 0.1584. Restraints for the chemically equivalent distances were applied to the one disordered [ClO₄]⁻ (Cl-O = 1.44 Å). The displacement parameters of related oxygen positions were equated by means of constraints in order to minimize variables. The goodness-of-fit index was 0.9 and the highest peak in the final difference map was 1.541 e⁻/Å⁻³.

[2 1. \$ c. K 01 592 Cen æ]e rR2 2.127 للاليكا. [Ni₂t] of a f laie g ڏنڊ <u>ن</u> K Ti :e:ine للتعيين 间的

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$[Zn_4(bptz)_4(CH_3CN)_8][ClO_4]_8 \cdot 3CH_3CN (4).$

Light orange, single crystals of $[Zn_4(bptz)_4(CH_3CN)_8][ClO_4]_8$ ·3CH₃CN were grown by slow vapor diffusion of diethyl ether into a solution of the compound in acetonitrile. A platelet crystal of dimensions $0.1 \times 0.25 \times 0.03 \text{ mm}^3$ was placed on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold stream at 110(1) K. A total of 44125 reflections was collected of which 7997 were unique. Atoms C(19), C(20), C(33) and C(34) were heavily disordered, and were, therefore, refined isotropically. In addition, four of the eight [ClO₄]⁻ ions were disordered, and restraints on their distances were applied (Cl-O 1.44 Å). The final refinement was based on 4776 reflections with F₀>4 σ (F₀) that were used to fit 731 parameters to give R1 = 0.0764 and wR2 = 0.2218. The goodness-of-fit index was 1.024 and the highest peak in the final difference map was 1.410 e'/Å⁻³. The extensive disorder accounts for the higher than usual R factors.

$[Ni_2(bptz)(CH_3CN)_8][ClO_4]_4$ (5).

Single crystals of $[Ni_2(bptz)(CH_3CN)_8][ClO_4]_4$ were obtained by slow evaporation of a filtrate obtained after harvesting a bulk sample of $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$. A Pale green needle of dimensions $0.25 \times 0.03 \times 0.05 \text{ mm}^3$ was mounted on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold $N_2(g)$ stream at 110(1) K. The data set included 4433 reflections of which 3371 were unique. The final refinement was based on 1968 reflections with $F_0>4\sigma(F_0)$ that were used to fit 318 parameters to give R1 = 0.0648 and wR2 = 0.1538. The goodness-of-fit index was 0.957 with the highest peak being 0.733 e⁻/Å⁻³.

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$[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10} \cdot 2CH_3CN$ (6).

Crystals of (6) were grown by slow diffusion of a acetonitrile solution of $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ into dichloromethane. A green prism of approximate dimensions $0.13 \times 0.2 \times 0.05 \text{ mm}^3$ was secured on the tip of glass fiber with Dow Corning silicone grease and placed in a cold N₂(g) stream at 110(1) K. A total of 36580 reflections was collected of which 12327 were unique. Four of the ten $[SbF_6]^-$ ions were disordered and therefore required modeling in several orientations. Constraints on the Sb-F distances were applied (1.88 Å). Furthermore, the displacement parameters of related fluorine positions were equated by means of constraints in order to reduce parameters. The atoms Sb(1), F(1), F(2), F(3), F(4), F(5) and F(6) were refined isotropically. The final refinement cycle was based on 8016 reflections with F₀>4\sigma(F₀) that were used to fit 891 parameters which led to R1 = 0.1160 and wR2 = 0.3645 and a goodness-of-fit of 1.069. The highest peak in the final difference map is 4.551 e⁷Å³ and is associated with a disordered [SbF₆]⁻ anion. The extensive disorder accounts for the higher than usual R factors.

${[Mn(bptz)_2(CH_3CN)_2][BF_4]_2}_{\infty}$ (7).

Crystals of $\{[Mn(bptz)_2(CH_3CN)_2][BF_4]_2\}_{\infty}$ were grown by slow diffusion of a acetonitrile solution of $[Mn(CH_3CN)_4][BF_4]_2$ into a dichloromethane solution of bptz. A light-orange platelet of approximate dimensions $0.2 \times 0.1 \times 0.02 \text{ mm}^3$ was secured on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold N₂(g) stream at 110 (1)K. A total of 12882 reflections was collected of which 4480 were unique. The final least-squares refinement of 382 parameters based on 2339 reflections with F₀>4 σ (F₀) resulted in residuals of R1 = 0.0666 and wR2 = 0.1744 and a goodness-of-fit

index of 0.951. The final difference Fourier map revealed the highest peak to be 1.711 e⁻/Å³.

$[Ni_4(bptz)_4(CH_3CN)_8][BF_4][PF_6]_3[SbF_6]_4$ (8).

Single crystals of $[Ni_4(bptz)_4(CH_3CN)_8][BF_4][PF_6]_3[SbF_6]_4$ were grown by slow diffusion of a solution of $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ in acetonitrile into a solution of toluene that contained a mixture of $[TBA][BF_4]$ and $[TBA]PF_6$. Single crystals grew over a period of two weeks in a sealed glass tube of 5mm diameter. A crystal of dimensions $0.15 \times 0.8 \times 0.05$ mm³ was secured on the tip of a glass fiber with Dow Corning Silicone grease and placed in a cold $N_2(g)$ stream at 100(1) K. A total of 5030 reflections was collected of which 3459 were unique. The highest peak in the final difference map was 1.561 e⁻/Å⁻³. All of the anions present in the structure are disordered, thus restraints on chemically equivalent distances (B-F 1.409Å, Sb-F 1.820Å, P-F 1.622 Å) were applied. The tetraflouroborate anion displays a two-way positional/rotational disorder for the fluorine atoms. In addition, the B(1) atom is disordered over two different positions. Fluorine atoms F(7), F(8), F(9) coordinated to Sb(2) are involved in a two-way positional disorder; therefore, the displacement parameters of the opposite fluorine positions were equated by means of constraints in order to minimize variables. In the case of the [PF₆]⁻ anion, the displacement parameters of related fluorine atoms were also constrained. The final refinement cycle was based on 3459 reflections with $F_0 > 4\sigma(F_0)$ that were used to fit 419 parameters which led to R1 = 0.0765 and wR2 = 0.1075. The goodness-of-fit index was 1.030, and the highest peak in the final difference map was 1.25 e/Å³. Extensive disorder accounts for the slightly higher than usual R factors.

Nicoptz Сг Nappiz [B._N][IC bown rec a glass fi i0h1+K 034). C sotropica positional displacem order to 1 With Fur 0.063 ar the final tan usua Corbope C between 1 ^{lolue}ne sc ^{brown} pla ™th Dow lainx lea

$[Ni_4(bptz)_4(CH_3CN)_8][CIO_4][IO_4]_7 \cdot 2CH_3CN (9).$

Crystals of the product were grown by slow diffusion of a acetonitrile solution of $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$ into a toluene solution containing a large excess of $[Bu_4N][IO_4]$. Crystals grew at the interface of the two solvents within two weeks. A palebrown rectangular crystal of dimensions $0.3 \times 0.1 \times 0.06 \text{ mm}^3$ was mounted on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold $N_2(g)$ stream at 100(1) K. A total of 35238 reflections was collected of which 8434 were unique. Atoms C(34), C(32), O(6A) and O(8A) were heavily disordered, and were therefore refined isotropically. In addition, four of the $[IO_4]$ anions are involved in a two-way positional/rotational disorder. Restraints on I-O distances were applied (1.710 Å). The displacement parameters of related oxygen atoms were constrained to be equivalent in order to minimize variables. The final refinement cycle was based on 3996 reflections with $F_0 > 4\sigma F_0$ that were used to fit 727 parameters; this produced residuals of R1 = 0.1063 and wR2 = 0.2895. The goodness-of-fit index was 1.161, and the highest peak in the final difference map was $1.25 \text{ e}^{-1}\text{Å}^{3}$. The extensive disorder accounts for the higher than usual R factors.

$[C_0(bopd)_2(H_2O)_2][PF_6]_2$ (10).

Crystals of $[Co(bopd)_2(H_2O)_2][PF_6]_2$ grew as a side-product from the 1:1 reaction between $[Co(CH_3CN)_6][BF_4]_2$ and bptz. Slow diffusion of the reaction mixture into a toluene solution saturated with $[TBA][PF_6]$ afforded crystals of (10) within one week. A brown platelet of dimensions $0.06 \times 0.1 \times 0.09 \text{ mm}^3$ was secured on the tip of glass fiber with Dow Corning silicone grease and placed in a cold N₂(g) stream at 110(1) K. Fullmatrix least-squares refinement of 2950 reflections with F₀>4 σ (F₀) observed reflections

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ung 727 goodness-0.548 e''Å [Cu bopd C.<u>?</u> the of [C af dimensi Coming si reinement perimeters mier was : Ni:(abpy) Cŋ an acetoniti 0.32 × 0.13 and placed of which 3; With Fords ^{0.1054}. The Cap was 1.3 (Cu_l(abpy) Ligh placing an a using 727 parameters produced residuals of R1 = 0.0561 and wR2 = 0.1275. The goodness-of-fit index was 1.020, and the highest peak in the final difference map was $0.548 \text{ e}^{-1}\text{Å}^{-3}$.

$[Cu(bopd)_2(H_2O)_2][BF_4]_2$ (11).

Crystals of $[Cu(bopd)_2(H_2O)_2][BF_4]_2$ were obtained by slow diffusion of a 1:1 ratio of $[Cu(CH_3CN)_4][BF_4]_2$ and bptz in acetonitrile with toluene. A single green platelet of dimensions $0.15 \times 0.13 \times 0.08 \text{ mm}^3$ was mounted on the tip of glass fiber with Dow Corning silicone grease and placed in a cold N₂(g) stream at 110(1) K. The final refinement cycle was based on 2607 reflections with F₀>4 σ (F₀) that were used to fit 727 parameters. The final R values are R1 = 0.0582 and wR2 = 0.1586. The goodness-of-fit index was 1.092, and the highest peak in the final difference map was 0.595 e⁻/Å³.

$[Ni_2(abpy)(CH_3CN)_2][NO_3]_4$ (12).

Crystals of the product were grown by slow vapor diffusion of diethyl ether into an acetonitrile solution of the title compound. A dark brown prism of dimensions $0.2 \times 0.32 \times 0.13 \text{ mm}^3$ was secured on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold N₂(g) stream at 110(1) K. A total of 8160 reflections was collected of which 3252 were unique. The final refinement cycle was based on 2815 reflections with F₀>4 σ (F₀) that were used to fit 199 parameters which led to R1 = 0.0416 and wR2 = 0.1054. The goodness-of-fit index was 1.087, and the highest peak in the final difference map was 1.337 e⁻/Å³.

[Cu₂(abpy)(CH₃CN)₈][BF₄]₄(13)

Light green platelet crystals of $[Cu_2(abpy)(CH_3CN)_8][BF_4]_4$ were obtained by placing an acetonitrile solution of the compound in the freezer at -4 °C for a week. A

ight g <u>2</u>2238 7358 : 2907 r 00**-5**0 ie in {[Cuta silite atiges 2018re દ્રાજી wiect R.ect enci a l differe Nub Conth lavered xoidie ₩:th D ^{of} 199 light green platelet was secured on the tip of a glass fiber with Dow Corning silicone grease and placed in a N₂(g) stream at 110(1) K. The data collection involved a total of 7358 reflections of which 3484 were unique. The final refinement cycle was based on 2907 reflections with $F_0>4\sigma(F_0)$ that were used to fit 298 parameters which led to R1 = 0.0750 and wR2 = 0.2053. The goodness-of-fit index was 1.058, and the highest peak in the final difference map was 1.121 e⁻/Å³.

$\{[Cu(abpy)_2][BF_4]\}_{\infty}$ (14).

Crystals of $\{[Cu(abpy)_2][BF_4]\}_{\infty}$ grew over the period of three weeks from a solution of (13) layered with toluene. The crystals formed as dark green needles on the edges of the glass tube. A green needle of dimensions $0.05 \times 0.03 \times 0.12 \text{ mm}^3$ was covered with Paratone oil, secured on the tip of a glass fiber with Dow Corning silicone grease, and placed under a N₂(g) stream at 110 (1)K. A total of 11151 reflections was collected of which 2040 were unique. The final refinement cycle was based on 1096 reflections with F₀>4 σ (F₀) that were used to fit 181 parameters which led to R1 = 0.0861 and wR2 = 0.2055. The goodness-of-fit index was 0.987, and the highest peak in the final difference map was 1.361 e'/Å³.

$[Ni_4(bptz)_4(CH_3CN)_8][I][SbF_6]_7 (15).$

Single crystals of $[Ni_4(bptz)_4(CH_3CN)_8][I][SBF_6]_7$ grew over the period of one month from a solution of $[Ni_5(bptz)_5(CH_3CN)_{10}][SBF_6]_{10}$ in acetonitrile that had been layered with a toluene solution saturated with $[Bu_4N]I$. A light brown prism of approximate dimensions $0.1 \times 0.08 \times 0.2$ mm³ was mounted on the tip of a glass fiber with Dow Corning silicone grease and placed in a cold N₂(g) stream at 110 (1)K. A total of 19922 reflections was collected, of which 5202 were unique. The final refinement

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cycle was based on 4618 data points with $F_0>4\sigma(F_0)$ that were used to fit 396 parameters which led to R1 = 0.0741 and wR2 = 0.2283. The goodness-of-fit index was 1.092, and the highest peak in the final difference map was 2.094 e⁻/Å³.

III. Results and Discussion.

A. Self-Assembly of Molecular Squares.

A.1. Syntheses of $[M_4(bptz)_4(CH_3CN)_8][X]_8$ (M = Ni²⁺ and Zn²⁺) Compounds.

 $[\mathbf{M}(\mathrm{CH}_{3}\mathrm{CN})_{6}][X]_{2} + bptz \qquad \xrightarrow{\text{acetonitrile}} [M_{4}(bptz)_{4}(\mathrm{CH}_{3}\mathrm{CN})_{8}][X]_{8} \quad (Eq. 2)$ 4-8 hours

$$M = Ni^{2+}; X = [BF_4]^{-}: 70-80\%$$

$$M = Ni^{2+}; X = [ClO_4]^{-}: 60-65\%$$

$$M = Zn^{2+}; X = [BF_4]^{-}: 60-67\%$$

$$M = Zn^{2+}; X = [ClO_4]^{-}: 36\%$$

A major focus of this study was to prepare paramagnetic complexes with nitrogen heterocyclic ligands with the bptz ligand (Figure 13a). Previous studies indicated that **bPtz** showed promise for allowing electronic communication between metal centers of **class** III in the Robin-Day scale.²⁸ No reports of magnetic exchange using bptz have been ^{re}Ported however. With this goal in mind, we embarked on the study of self-assembly ^{re}actions of first row transition metals with bptz. Equation (2) summarizes the main ^{re}actions under investigation.

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N(II) metallocyclophanes.

Studies began with 1:1 reactions of $[Ni(CH_3CN)_6][BF_4]_2$ in acetonitrile under anaerobic conditions (Eq. 2). The reaction is essentially instantaneous as judged by a color change from a blue solution of $[Ni(CH_3CN)_6][BF_4]_2$ to a brown color upon addition of bptz. The Ni(II) products are stable under a variety of conditions. If the reaction is refluxed for a week, the product is obtained, unchanged, in quantitative yields. Furthermore, a 10:1 ratio of bptz to $[Ni(CH_3CN)_6][X]_2$ (X = $[BF_4]^-$ or $[ClO_4]^-$) still yields the tetrametallocyclophane as indicated by mass spectrometry and X-ray crystallography.

Identical reactions performed in acetone or nitromethane also yield the tetramers (*vide infra*) as corroborated by mass spectroscopy, but alcohols and water appear to limit the formation of metallocyclophanes; instead lower nuclearity species (monomers and dimers) or even polymers are obtained as evidenced again by mass spectrometric studies (*vide infra*) and also by insoluble solids.

Zn(II) metallocyclophanes.

Analogous results are obtained when Zn(II) is used in place of Ni(II) in these reactions. These metallocyclophanes are synthesized from the 1:1 reaction of bptz with $[Zn(CH_3CN)_4][BF_4]_2$ or $[Zn(H_2O)_6[ClO_4]_2$ in acetonitrile (Eq. 2). In both cases, the reaction solution changes from colorless to orange of addition of bptz. X-ray studies revealed that these species exist with either a $[BF_4]^-$ or a $[ClO_4]^-$ anion in the cavity of the molecular cation.

A main difference in the Ni(II) and Zn(II) chemistry with bptz was noted. There are drastic differences in the stability of these species in solution. Solutions of $[Zn_4(bptz)_4(CH_3CN)_8]^{8+}$ that are allowed to stand for more than three days begin to

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decompose with deposition of insoluble precipitates (polymers). A possible explanation is the greater lability of the Zn-N bonds, which allows for reversible coordination which could eventually lead to more insoluble oligomers/polymers with high concentrations. Moreover, unlike their Ni(II) analogues, the Zn(II) squares are sensitive to reaction conditions such as temperature, concentration and solvents. Dilute solutions favor the formation of the tetrametallocyclophane whereas highly concentrated solutions lead to insoluble materials presumably which are presumed to be polymers. Mass spectrometric studies (*vide infra*) indicate that the $[Zn_4]^{8+}$ product is not being formed in solvents other than acetonitrile. For example, reactions performed in nitromethane and acetone led to only low nuclearity species by mass spectrometry. It is worth pointing out that if the solutions of $[Zn_4(bptz)_4(CH_3CN)_8]^{8+}$ are stored at low temperature (0°C), the decomposition process is considerable delayed.

A.2. Spectroscopic and cyclic voltammetric studies of $[M_4(bptz)_4(CH_3CN)_8][X]_8 M = Ni, Zn; X = [BF_4]^{-}, [ClO_4]^{-}.$

The $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$ species exhibit two characteristic electronic **transitions** in their UV-Visible spectra. The first one occurs at 512 nm ($\varepsilon = 530 \text{ M}^{-1} \cdot \text{cm}^{-1}$) **and** is similar to a transition in the free bptz ligand, suggesting that this is a $\pi \rightarrow \pi^*$ ligand **based** transition. The second transition at 680 nm ($\varepsilon = 540 \text{ M}^{-1} \cdot \text{cm}^{-1}$) is characteristic of a **Laporte** forbidden d-d transition for Ni(II) compounds. The UV-Visible spectra for the $[Zn_4(bptz)_4(CH_3CN)_8]^{8+}$ salts, (2) and (4), exhibit only one transition at 540 nm with $\varepsilon = 270 \text{ M}^{-1} \cdot \text{cm}^{-1}$ which is assigned to a bptz $\pi \rightarrow \pi^*$ transition.

The $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ compound exhibits two weak stretches in the infrared spectrum at 2321 and 2325 cm⁻¹ which correspond to the v(C=N) modes from

ŝ ĉ. λ ĊſĊ X . 20 4 <u>.)-</u> 22 Poss). 2. 13 Nill Niel :00:00 Jista the bound acetonitriles. In addition, a broad and strong stretch at 1069 cm⁻¹ is observed, which corresponds to the v(B-F) mode of the tetrafluoroborates. The $[Zn_4(bptz)_4(CH_3CN)_8][X]_8$ compounds display a characteristic v(B-F) stretch at 1054 cm⁻¹ for (2) and 1098 cm⁻¹ for a v(Cl-O) stretch in the case of (4). The expected v(C=N) stretches were not observed, however, possibly because prolonged pumping led to the loss of the ligands in the solid state, due to the fact that they maybe weak to be observed.

Although previous work with dinuclear complexes of bptz²⁸ revealed good electronic communication between metal centers, (Class II or Class III Robin Day behavior),²⁹ cyclic voltammetric studies of the $[Ni_4]^{8+}$ species do not indicate significant electronic coupling between metal centers. The compounds $[Ni_4(bptz)_4(CH_3CN)_8][X]_8$ $(X = [BF_4]^{-}$ or $[ClO_4]^{-}$) exhibit a quasi-reversible ligand based reduction at $E_{1/2} = +0.4$ V and irreversible waves at $E_{p,c} = -1.95$ V and $E_{p,c} = -1.45$ V and $E_{p,a} = -0.62$ V. In a similar fashion, the Zn(II) squares do not exhibit communication between metal centers; compounds (2) and (4) display a quasireversible ligand based reduction at $E_{1/2} = 0.37$ V and irreversible waves at $E_{p,c} = -0.85$ V and $E_{p,c} = -1.4$ V followed by decomposition. It is POssible to rationalize the irreversible behavior by the fact that the tetrazine ring is not Planar which interrupts the π pathway for electronic communication.

A-3. X-ray crystallographic results.

Ni(II) molecular squares: $[Ni_4(bptz)_4(CH_3CN)_8][X]_8$; $X = [BF_4]^{-}$, $[ClO_4]^{-}$ and $[Ni_2(bptz)(CH_3CN)_8][ClO_4]_4$.

The molecular cation in compound (1) is presented in Figure 15 whereas compound (3) is depicted in Figure 16. $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ ·4CH₃CN (2) crystallizes in the triclinic space group $P\bar{1}$ and

1.1.1 à <u>וו</u>נ Ŀ Ŋ. Å. 20 15a <u>N</u>. itom Ćsio the id : traz iom 'elra", ^{10]}UM ំញាដ ed sh in the second $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8 \cdot 2CH_3CN \cdot C_4H_8O$ (4) crystallizes in the monoclinic space group P2₁/n. As expected, X-ray studies reveal that each Ni(II) center is in a distorted octahedral geometry with two bptz units coordinated in a cis fashion and two acetonitrile molecules completing the coordination environment.

Typical angles in compound (1) are [Ni(5C)-NiI-N(1C)] = 78.0 (2)° for the bptz binding, and [N(5)-Ni(1)-N(6)] = 89.4 (5)° for the acetonitrile interactions (Figure 15b). In terms of the Ni-N distances the Ni-N(tetrazine) is the longest bond, followed by the Ni-N(pyridyl) and finally Ni-N(acetonitrile); these distances are Ni(1)-N(5C), 2.098 (5) Å, Ni(1)-N(1C) 2.084 (6) Å, and Ni(1)-N(5) 2.035 (6) Å respectively (Figure 15b). The dimensions of the square are 6.87 Å on the edge and 9.69 Å along the diagonal (Figure 15a). The angle (θ) for average vertex the compound $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ 4CH₃CN (1) is 92.3° which represents a deviation of 2.3° from the ideal angle for a square (Figure 14). It is worth mentioning that each bptz unit is distorted in order to satisfy the coordination requirements. In compound (1), for example, the tetrazine ring shows distortions ranging from 1.86° to 11.70° (ω) (Figure 14). The tetrazine ring and the pyridyl are distorted from planarity as well, with angles ranging from the almost negligible 0.38° (almost coplanar) to 7.61° (ϕ) (Figure 14).

One of the most important aspects of the structure of (1) is the presence of a tetrafluoroborate anion inside the cavity. This anion has the correct surface area and \vee Olume to fit inside the cavity, which suggests its possible role as a template in the formation of this cyclic tetramer (Figure 15a and Figure 17a).¹⁹ A similar anion in size and shape such as [ClO₄]⁻ renders similar results, namely the assembly of a molecular square with an encapsulated anion (Figure 17).

Table2.Selected	bond dista	nces (Å) and	angles (°)	for
[Ni ₄ (bptz) ₄ (CH ₃ CN) ₈][BF ₄] ₈	3 [:] 4CH ₃ CN (1).			
Ni1-N5	2.035(6)	Ni2-N4	2.038	(7)
Nil-N6	2.045(6)	Ni2-N3	2.052	(6)
Nil-N1B	2.067(6)	Ni2-N2C	2.057	(6)
Nil-N1C	2.084(6)	Ni2-N2D	2.069	(6)
Nil-N5B	2.094(5)	Ni2-N3C	2.089	(5)
Nil-N5C	2.098(5)	Ni2-N6D	2.107	(6)
N5-Ni1-N6	89.4(2)	N1B-Ni1-N5B	77.6	(2)
N5-Ni1-N1B	96.4(2)	N1C-Ni1-N5B	88.6	(2)
N 6-Ni1-N1B	92.5(2)	N5-Ni1-N5C	86.1	(2)
N5-Ni1-N1C	97.5(2)	N6-Ni1-N5C	172.6	(2)
N6-Ni1-N1C	96.9(2)	N1B-Ni1-N5C	93.8	(2)
N1B-Ni1-N1C	163.2(2)	N1C-Ni1-N5C	78.0	(2)
N5-Ni1-N5B	173.8(2)	N5B-Ni1-N5C	95.8	(2)
N6-Ni1-N5B	89.3(2)			

Table3.Select[Ni4(bptz)4(CH3CN)8][ted bond dista [ClO ₄]8 [·] 2CH ₃ CN [·] C ₄ H ₈	nces (Å) and ₃ O (3).	angles	(°) for
N4B-Nil	2.083(5)	N2A-Ni2		2.089(5)
N 14-Ni1	2.040(6)	N2B-Ni2		2.082(5)
N6-Nil	2.077(5)	N12-Ni2		2.040(6)
N5B-Nil	2.083(5)	N6A-Ni2		2.057(5)
N 13-Ni1	2.029(6)	N6B-Ni2		2.073(5)
N2-Nil	2.078(5)	N11-Ni2		2.037(6)
N 13-Ni1-N14	90.5(2)	N3B-N4B-Ni 1		125.4(4)
N 13-Ni1-N6	97.2(2)	N6-Ni1-N4B		89.4(2)
N 14-Ni1-N6	96.1(2)	N2-Ni1-N4B		92.7(2)
N13-Ni1-N2	174.5(2)	N13-Ni1-N5B		91.5(2)
N14-Ni1-N2	87.2(2)	N14-Ni1-N5B		96.3(2)
N6-Ni1-N2	78.1(2)	N6-Ni1-N5B		164.7(2)
N13-Ni1-N4B	90.1(2)	N2-Ni1-N5B		93.7(2)
N14-Ni1-N4B	174.4(2)			



Figure 14. Schematic drawing of the distortions experienced by the ligand bptz in the tetrametallocyclophanes.

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Table 4.

	[Ni4(bptz)4(CH3CN)a][BF4]8	[Ni₄(bptz)₄(CH₃CN)₅][ClO₄]₅	[Zn4(bptz)4(CH3CN)8][BF4]8	[Zn4(bptz)4(CH3CN)8][ClO4]8
θ	92.3 °	94.1 °	93.8 °	97.4 °
÷	0.387.61°	1.10 — 6.86 °	1.295.35 °	5.24 — 10.14 °
3	1.86 — 11.70 °	1.70 — 12.66 °	1.35 — 4.74 °	4.40 —12.66 °



Figure 15. (a) Thermal ellipsoid representation of the cation in [Ni₄(bptz)₄(CH₅CN)₈][BF4]₈-4CH₅CN. (b) Asymmetric unit with 50% probability ellipsoids. Hydrogen atoms have been omitted for the sake of clarity.







 $\label{eq:Figure 17. Space filling diagrams of the cations in (a) [Ni_4(bptz)_A(CH_3CN)_8][BF_4]_8 4CH_3CN and (b) [Ni_4(bptz)_A(CH_5CN)_8][CIO_4]_8 C4H_5O with the encapsulated anion.$



Figure 18. Packing diagram of [Ni4(bptz)4(CH3CN)8][BF4]8.4CH3CN



Figure 19. Thermal ellipsoid representation of the cation at the 50% probability level in [Ni₂(bpt2)(CH₃CN)₈][ClO₄]₂. Hydrogen atoms have been omitted for the sake of clarity.

Ni1-N4A	2.044 (7)	Nil-N4D	2.072 (7)
Nil-Nl	2.069 (7)	Ni1-N2	2.073 (7)
Ni1-N4C	2.073 (7)	Nil-N4B	2.079 (7)
N4A-Ni1-N1	92.2 (3)	N4C-Ni1-N2	95.0 (3)
N4A-Ni1-N4C	92.0 (3)	N4D-Ni1-N2	90.4 (2)
N1-Ni1-N4C	171.8 (3)	N4A-Ni1-N4B	90.3 (3)
N4A-Ni1-N4D	177.9 (3)	N1-Ni1-N4B	92.1 (3)
N1-Ni1-N4D	89.8 (2)	N4C-Ni1-N4B	94.8 (3)
N4C-Nil-N4D	86.1 (3)	N4D-Ni1-N4B	88.9 (3)
N4A-Ni1-N2	90.8 (3)	N2-Ni1-N4B	170.1 (3)
N1-Ni1-N2	78.0 (3)		

Table 5. Selected bond distances (Å) and angles (°) for [Ni₂(bptz)₂(CH₃CN)₈][ClO₄]₄ (5).

The cation in compound (3) exhibits an octahedral geometry about each Ni(II) center, with two bptz units and two acetonitrile molecules coordinated in a cis fashion (Figure 16). The presence of an encapsulated perchlorate anion (47 Å³)^{19a} (Figure 17b) instead of a tetraflouroborate anion (38 Å³) results in larger distortions of the ligand units as compared to the previous Ni(II) tetramer (1). Complex (3) exhibits an average vertex angle (θ) of 94.05°, which is a 4.05° deviation from the ideal value for a square; this is **Compared to the 92.3° found in (1)**. The tetrazine ring also shows a larger distortion from **Plan**arity [12.66° (ω)], compared to the [BF₄]⁻ salt which is 11.67° (Figure 14). The **dih**edral angle between the planes of the pyridyl and tetrazine ring increases to 6.86° (ϕ). **The** Ni-N distances follow the same trend as the tetraflouroborate.

It was possible to isolate crystals of a minor product, namely $[N_{i_2(bptz)(CH_3CN)_8}][ClO_4]_4$ (5) (Figure 19) from a filtrate after isolation of (3). In this Case, each Ni(II) center exhibits a distorted octahedral geometry with the bptz unit COordinated in bidentate fashion and four acetonitrile molecules. The angle for the bptz binding is 78.0 (3)° [N(1)-Ni(1)-N(2)], and the average angle between the acetonitrile ligands is 90.4 [3]°. As in the case of (1) and (2), the tetrazine moiety and the pyridyl ring do not lie in the same plane. In this case there is an angle of 5.26° between planes of the two rings. The Ni-N distances follow the same trend as before with the longest Ni-N distance being the tetrazine ring Ni(1)-N(2) 2.073 (7) Å followed by the pyridyl nitrogen Ni(1)-N(1) 2.069 (7) Å; the shortest distance is to an acetonitrile ligand Ni(1)-N(4A) 2.044 (7) Å (Figure 19).

Zn(II) molecular squares: $[Zn_4(bptz)_4(CH_3CN)_8][X]_8$, $X = [BF_4]^{\circ}$, $[ClO_4]^{\circ}$.

Both of the Zn(II) molecular squares exhibit a distorted octahedral geometry. Crystals of $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8 \cdot 4CH_3CN$ (2) are triclinic, $P\overline{1}$ and those of $[Zn_4(bptz)_4(CH_3CN)_8][ClO_4]_8 \cdot 2CH_3CN$ (4) are monoclinic, C2/c. The metric parameters within (2) exhibit the same bonding trends as its Ni(II) counterpart, namely the tetrazine **nitrogen** exhibits the longest bond followed by the pyridyl and acetonitrile; the distances **are**; Zn(1)-N(1A) = 2.266(5)Å, Zn(1)-(5A) = 2.091(4) Å, and Zn(1)-N(10) = 2.077 Å (**Figure** 20b) respectively. The corresponding distances in (4) are Zn(1)-N(3) = 2.234 (4)Å, Zn(1)-N(1) = 2.144 (5) Å, and Zn(1)-N(11) = 2.045 (5)Å (Figure 21b). There is an **increase** in the M-N distances as compared to the Ni(II) species, as expected due to the **larg**er radius of Zn(II). Both $[Zn_4]^{8+}$ cations contain an encapsulated anion. The distances **bet** ween the Zn(II) centers in the two squares are 7.2 Å for (2) and (4) respectively (**Figure** 20 and Figure 21). The tetrazine rings in (2) exhibit a twist angle as large as 4.74° (**G**) and a torsion angle of 5.35° (ϕ) between the tetrazine and pyridyl rings (Figure 14). **In** (4), the tetrazine exhibits a torsion angle of 11.92° (ω) and an angle between the planes of the tetrazine and pyridyl ring of 10.14° (ϕ), which is the largest distortion among the

four structurally characterized squares (Figure 14).

Table 6 . Select [Zn ₄ (bptz) ₄ (CH ₃ CN) ₈]	ted bond dista [BF ₄] ₈ [:] 4CH ₃ CN (2).	ances (Å) and	angles	(°)	fc
Zn1-N9	2.070(5)	Zn2-N12		2.07	2(4)
Zn1-N10	2.077(5)	Zn2-N11		2.08	2(4)
Zn1-N5A	2.092(5)	Zn2-N6A		2.09	4(4)
Zn1-N6	2.131(5)	Zn2-N4B		2.29	3(4)
Zn1-N4	2.248(4)	Zn2-N5B		2.11	6(4)
Znl-N1A	2.262(4)	Zn2-N3A		2.25	5(4)
N9-Zn1-N10	92.95(18)	N10-Zn1-N4		172.53	(19)
N9-Zn1-N5A	98.29(18)	N5A-Zn1-N4		90.82	(17)
N10-Zn1-N5A	96.58(19)	N6-Zn1-N4		74.64	(16)
N9-Zn1-N6	102.67(18)	N9-Zn1-N1A		172.92	(18)
N10-Zn1-N6	98.91(18)	N10-Zn1-N1A		89.16	(16)
N5A-Zn1-N6	153.13(16)	N6-Zn1-N1A		83.65	(16)
N9-Zn1-N4	84.95(16)	N4-Zn1-N1A		93.79	(15)
Table 7. Selec	ted bond dista	nces (Å) and	angles	(°)	fc
ГаЫе 7 . Selec Zn₄(bptz)₄(CH ₃ CN)8]	ted bond dista [ClO ₄]8 [·] 3CH ₃ CN (4).	nces (Å) and	angles	(°)	fo
Table 7 . Selec Zn₄(bptz)₄(CH ₃ CN) ₈] Zn 1 -N11	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8)	nces (Å) and Zn2-N10	angles	(°) 2.011	f((10)
Table 7.Selec $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_4(bptz)_4(CH_3CN)_8]$	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9)	nces (Å) and Zn2-N10 Zn2-N9	angles	(°) 2.011 2.060	fo (10) (10)
Table 7. Selec Zn₄(bptz)₄(CH ₃ CN) ₈] Zn₄(bptz)₄(CH ₃ CN) ₈] I -N11 I -N13 I -N12	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6	angles	(°) 2.011(2.060 2.094	f((10) (10) (10)
Table 7. Selec $Zn_4(bptz)_4(CH_3CN)_8]$ n_1 -N11 n_1 -N13 n_1 -N12 n_1 -N1	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8	angles	(°) 2.011(2.060(2.094(2.10)	f((10) (10) (10) 7(9)
Table 7. Selection $Zn_4(bptz)_4(CH_3CN)_8$ Selection $Zn_4(bptz)_4(CH_3CN)_8$ Selection $Zn_1 - N11$ Selection $Zn_1 - N13$ Selection $Zn_1 - N13$ Selection $Zn_1 - N13$ Selection $Zn_1 - N12$ Selection $Zn_1 - N12$ Selection $Zn_1 - N13$ Selection $Zn_1 - N13$ Selection $Zn_1 - N13$ Selection $Zn_1 - N13$ Selection	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8) 2.237(8)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7	angles	(°) 2.011 2.060 2.094 2.10 2.24	f((10) (10) (10) (10) (10) 5(8)
Table 7. Selection $Zn_4(bptz)_4(CH_3CN)_8]$ $T_1 - N11$ $T_1 - N13$ $T_1 - N12$ $T_1 - N12$ $T_1 - N13$ $T_1 - N14$	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8) 2.237(8) 2.240(8)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7 Zn2-N7 Zn2-N2	angles	(°) 2.011(2.060) 2.094(2.10) 2.24(2.299)	f((10) (10) (10) (10) 5(8) (10)
Table 7. Selection $Zn_4(bptz)_4(CH_3CN)_8]$ $n1 - N11$ $n1 - N13$ $n1 - N12$ $n1 - N12$ $n1 - N13$ $n1 - N13$ $n1 - N13$ $n1 - N14$ $1 - N14$ $1 - N14$ $1 - Zn1 - N13$	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8) 2.237(8) 2.240(8) 88.8(4)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7 Zn2-N7 Zn2-N2 N12-Zn1-N3	angles	(°) 2.011(2.060(2.094(2.10) 2.24(2.299(92.)	f((10) (10) (10) 7(9) 5(8) (10) 5(3)
Table 7. Selection $Zn_4(bptz)_4(CH_3CN)_8]$ Cn1 -N11 Cn1 -N13 Cn1 -N12 I -N1 I -N14 I -Zn1-N13 I -Zn1-N12	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8) 2.237(8) 2.240(8) 88.8(4) 98.0(3)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7 Zn2-N7 Zn2-N2 N12-Zn1-N3 N1-Zn1-N3	angles	(°) 2.011 2.060 2.094 2.10 2.24 2.299 92. 74.	f((10) (10) (10) (10) 5(8) (10) 5(3) 4(3)
Table 7. Selec $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_1 - N11$ $n 1 - N13$ $n 1 - N12$ $n 1 - N12$ $n 1 - N13$ $n 1 - N14$ $1 1 - Zn1 - N13$ $1 1 - Zn1 - N13$ $1 2 - Zn1 - N12$ $1 3 - Zn1 - N12$	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.125(8) 2.139(8) 2.237(8) 2.240(8) 88.8(4) 98.0(3) 94.7(3)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7 Zn2-N7 Zn2-N2 N12-Zn1-N3 N1-Zn1-N3 N11-Zn1-N14	angles	(°) 2.011(2.060) 2.094(2.10) 2.24(2.299) 92.(74. 90.)	f((10) (10) (10) 7(9) 5(8) (10) 5(3) 4(3) 2(3)
Table 7. Selection $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_1 - N11$ $n_1 - N12$ $n_1 - N12$ $n_1 - N14$ $1 - Zn1 - N13$ $1 - Zn1 - N13$ $1 - Zn1 - N12$	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8) 2.237(8) 2.240(8) 88.8(4) 98.0(3) 94.7(3) 97.1(3)	nces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7 Zn2-N2 N12-Zn1-N3 N1-Zn1-N3 N11-Zn1-N14 N13-Zn1-N14	angles	(°) 2.0110 2.060 2.094 2.10 2.24 2.299 92. 74. 90. 169.	f((10) (10) (10) (10) (10) (10) (10) (10
Table 7. Selection $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_1 - N11$ $Zn_1 - N13$ $I - N12$ $I - N14$ $I - Zn1 - N13$ $I - Zn1 - N13$ $I - Zn1 - N12$ $I - Zn1 - N1$ $I - Zn1 - N1$	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8) 2.237(8) 2.240(8) 88.8(4) 98.0(3) 94.7(3) 97.1(3) 102.7(3)	Inces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N6 Zn2-N7 Zn2-N7 Zn2-N2 N12-Zn1-N3 N11-Zn1-N3 N11-Zn1-N14 N13-Zn1-N14 N12-Zn1-N14	angles	(°) 2.011 2.060 2.094 2.10 2.24 2.299 92. 74. 90. 169. 75.	f((10) (10) (10) (10) (10) (10) (10) (10
Table 7. Selec $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_1 - N11$ $n 1 - N13$ $n 1 - N12$ $n 1 - N12$ $n 1 - N13$ $n 1 - N14$ $1 1 - Zn1 - N13$ $1 1 - Zn1 - N13$ $1 2 - Zn1 - N12$ $1 3 - Zn1 - N12$ $1 3 - Zn1 - N12$ $1 3 - Zn1 - N1$ $1 2 - Zn1 - N1$	ted bond dista $[CIO_4]_8$ $^{3}CH_3CN$ (4). 1.957(8) 2.088(9) 2.125(8) 2.125(8) 2.139(8) 2.237(8) 2.240(8) 88.8(4) 98.0(3) 94.7(3) 97.1(3) 102.7(3) 157.1(3)	nnces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7 Zn2-N7 Zn2-N2 N12-Zn1-N3 N11-Zn1-N3 N11-Zn1-N14 N13-Zn1-N14 N12-Zn1-N14 N12-Zn1-N14	angles	(°) 2.011(2.060) 2.094(2.10) 2.24(2.299) 92. 74. 90. 169. 75. 87.	f((10) (10) (10) (10) 7(9) 5(8) (10) 5(3) (10) 5(3) 1(3) 8(3)
Table 7. Selection $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_4(bptz)_4(CH_3CN)_8]$ $Zn_1 - N11$ $I - N13$ $I - N12$ $I - N12$ $I - N12$ $I - N13$ $I - N14$ $I - Zn1 - N13$ $I - Zn1 - N12$ $I - Zn1 - N1$	ted bond dista [ClO ₄] ₈ ·3CH ₃ CN (4). 1.957(8) 2.088(9) 2.125(8) 2.139(8) 2.237(8) 2.240(8) 88.8(4) 98.0(3) 94.7(3) 97.1(3) 102.7(3) 157.1(3) 168.2(3)	nnces (Å) and Zn2-N10 Zn2-N9 Zn2-N6 Zn2-N8 Zn2-N7 Zn2-N7 Zn2-N2 N12-Zn1-N3 N11-Zn1-N3 N11-Zn1-N14 N13-Zn1-N14 N12-Zn1-N14 N1-Zn1-N14 N3-Zn1-N14	angles	(°) 2.011(2.060 2.094 2.10 2.24 2.299 92. 74. 90. 169. 75. 87. 97.	f((10) (10) (10) (10) (10) (10) (10) (5(3) (10) (10) (10) (10) (10) (10) (10) (10



(b) Asymmetric unit in [Zn₄(bpt2)₄(CH₅CN)₈][BF₄]s⁴CH₅CN at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity. Figure 20. (a)Thermal ellipsoid diagram of the cation in [Zn4(bptz)4(CH3CN)8][BF4]8-4CH3CN.



[Zn4(bptz)4(CH3CN)8][CIO4]8 CH3CN. Thermal ellipsoids are drawn at 50 % probability level, and hydrogen atoms have Figure 21. (a) Thermal ellipsoid digram of the cation in [Zn4(bptz)4(CH3CN)8][ClO4]8·CH3CN. (b) Asymmetric unit in been omitted for the sake of clarity.

Compound (2) displays an average vertex angle (θ) of 93.8° (Figure 14). In the perchlorate salt (4), this angle is 97.4°, which is the largest deviation in the tetrametallocyclophane series, namely 7.4°.

A.4. NMR studies

Thus far, support for an anion template effect in this chemistry is based solely in X-ray crystallography. The question that comes to mind is do these species exist in solution with an anion inside the cavity? The diamagnetic molecular square $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8$ is an ideal species for studying the solution behavior of these metallocyclophanes.

In order to check for the presence of encapsulated anions in solution, ¹⁹F and ¹¹B NMR studies were first performed on $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$, but it exhibited only one broad peak in both the ¹¹B and ¹⁹F NMR spectra due to the paramagnetism of the compound. On the other hand, the $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8$ derivative, being a diamagnetic species, is an ideal candidate for probing the behavior of these entities in solution by ¹⁹F NMR and ¹¹B NMR techniques.

If the anion resides in the cavity of the cation in solution, one would expect to observe two peaks for the two distinctive type of $[BF_4]^-$ anions: a major one, that corresponds to the 7 $[BF_4]^-$ anions outside the cavity and a minor one, that corresponds to the encapsulated one. The ¹¹B NMR spectrum of $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8$ contains resonances at -1.60 ppm and -0.20 ppm. Similarly, the ¹⁹F NMR spectrum displays two resonances, a major one at -151.2 ppm and the minor one at -151.0 ppm. The relative

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ĉ 12 T, 90 10 æ, 007 arg; cho áller X (Meta SUITA ring s integration of the peaks corresponding to the encapsulated and the free $[BF_4]^-$ anions in the ¹¹B and ¹⁹F NMR spectra are not exactly in the expected 7:1 ratio, but differences in relaxation times can account for this phenomenon.

A variable temperature ¹⁹F NMR experiment was performed from -44.0 up to 80.0 °C. (Figure 22). As the spectra in Figure 22 show, there are two resonances in the temperature of ~0 °C-60 °C. Broadening occurs at higher temperature due to faster exchange of the $[BF_4]^-$ inside the cavity and the "outer-sphere" anions. At lower temperature the broadening is attributed to solubility problems. Coalescence was not reached due to limitations of the solvent temperature range. The chemical shifts that occur over the temperature range are most likely due to differences in ion-pairing interactions with temperature.

The aforementioned NMR experiments provide evidence that the anions are retained in the cavity of the molecular squares in solution. With this evidence in hand, we conclude that the anion plays a role in the assembly of the molecular squares. If so, we argued, it should be possible to tune the size and shape of the metallocyclophane by the choice of the anion. In this vein, numerous anions with different sizes and shapes were attempted in this chemistry; among these are $[CF_3SO_3]^{-}$, $[PF_6]^{-}$, $[AlCl_4]^{-}$, $[IO_4]^{-}$, $[Barf]^{-}$, X⁻ (X = Cl⁻, Br⁻, I⁻). None of the previously mentioned anions led to a stable metallocyclophane as corroborated by ES-MS and the lack of crystalline materials suitable for X-ray analysis. By using the anion $[SbF_6]^{-}$, however, our goal of tuning the ring size of the oligomer was accomplished.

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B. A New Generation of Metallocyclophanes: Molecular Pentagons.

Both the $[ClO_4]^{-}$ and $[BF_4]^{-}$ anions promote the formation of molecular squares, presumably because of similarities in their sizes and shapes. Polygons of different nuclearities should be possible to obtain if the appropriate anion is used. As previously mentioned, different anions were used without success in terms of isolating a tractable product. The larger anion $[SbF_6]^{-}$, however, allowed for the assembly of a larger polygon, namely an unprecedented pentagon.

B.1. Synthesis of [Ni₅(bptz)₅(CH₃CN)₁₀][SbF₆]₁₀.

 $[Ni(CH_3CN)_6][SbF_6]_2$ was treated with bptz in a 1:1 ratio in acetonitrile which led to a color change from pale blue to dark orange within minutes. After two hours, a brownish green color persisted (Eq. 3). X-ray studies revealed the compound to be the unprecedented, partially solvated, molecular pentagon $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ ·2CH₃CN (6).

$$[Ni(CH_3CN)_6][SbF_6]_2 + bptz \xrightarrow{acetonitrile} [Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10} (Eq. 3)$$
4 hours
80-85% yield

As in the case of the $[Ni_4]^{8^+}$ compounds, the $[Ni_5]^{10^+}$ pentagon is stable in solution and, in fact, the compound is obtained in good yields even after one week of refluxing conditions. Different ratios of bptz to $[Ni(CH_3CN)_6][SbF_6]_2$ other than 1:1 do not affect the identity of the product, but they do lead to lower yields. The results were confirmed by mass spectrometry (*viole infra*) and X-ray crystallography.

Table 8. [Ni ₅ (bptz) ₅ (CH	Selected bond di 3CN)5][SbF6]10• 2CH3CN	stances (Å) (6).	and angles	(°)	for
Ni1-N16	2.035 (12) Ni2-N19		2.057	(14)
Ni1-N17	2.039 (14) Ni2-N18		2.054	(11)
Ni1-N3	2.058 (12) Ni2-N6		2.060	(11)
Nil-N4	2.062 (10) Ni2-N13		2.056	(11)
Ni1-N7	2.068 (10) Ni2-N1		2.077	(10)
Ni1-N11	2.093 (12)) Ni2-N14		2.066	(12)
N16-Ni1-N17	91.8 (5) N19-Ni2-N1	3	176.2	2 (5)
N16-Ni1-N3	96.5 (5) N18-Ni2-N13	3	87.0) (4)
N17-Ni1-N3	92.4 (5) N6-Ni2-N13		89.0) (4)
N16-Ni1-N4	174.9 (5) N19-Ni2-N1		89.8	3 (4)
N17-Ni1-N4	89.5 (5)) N18-Ni2-N1		176.1	(4)
N3-Ni1-N4	78.5 (4)) N6-Ni2-N1		78.2	2 (4)
N16-Ni1-N7	86.7 (4)) N18-Ni2-N14	1	93.5	i (4)
N17-Ni1-N7	177.8 (5) N6-Ni2-N14		162.4	l (4)
N3-Ni1-N7	89.5 (4)) N13-Ni2-N14	1	78.5	5 (4)
N4-Ni1-N7	92.1 (4)) N1-Ni2-N14		89.7	/ (4)
N16-Ni1-N11	93.9 (5)) N20#-Ni3-N2	20	90.8	(10)
N17-Ni1-N11	99.4 (5)) N20#1-Ni3-N	19	176.5	5 (6)
N3-Ni1-N11	164.0 (4)) N20#1-Ni3-N	19#1	88.9) (6)
N4-Ni1-N11	90.7 (4)) N20#1-Ni3-N	19	176.5	i (6)
N7-Ni1-N11	79.0 (4)) N9-Ni3-N9#2	l	91.6	5 (6)
N19-Ni2-N18	92.1 (5))			

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2,#2 -

x+2,y,-z+1/2

B.2. X-ray crystallographic results.

As in the case of the tetranuclear metallocyclophanes, the pentagon has an anion residing in the central cavity, in this case $[SbF_6]^-$ (Figure 23b), the presence of which is essential for the formation of the pentagonal unit. The six-coordinate Ni²⁺ ions are coordinated to two cis bptz ligands and two CH₃CN molecules in a distorted octahedral geometry. The M-N distances follow the same trend observed in the Ni(II) tetramers. The coordinated nitrogen atom of the tetrazine ring exhibits the longest Ni-N distance Ni(1)-







Е. Thermal Ellipsoid drawing at the 50% level of the asymmetric unit of [Ni₅(bptz)₅(CH₃CN)₁₀]¹⁰⁺ [Ni₅(bptz)₅(CH₃CN)₁₀][SbF₆]₁₀·2CH₃CN (6). Hydrogen atoms were omitted for the sake of clarity. 7 Figure



Figure 25. A skeletal view of the Ni₅(bptz)₅ pentagon superimposed on an ideal pentagon to emphasize the distortion of the ligands.



Figure 26. Packing diagram of [Ni₅(bptz)(CH₃CN)₁₀][SbF₆]₁₀.l

N(4) = 2.062 (10)Å followed by the pyridyl distance of 2.058 (12)Å and the Ni-NCCH₃ distance of 2.039 (14)Å (Figure 24).

It is worth mentioning that, although an ideal pentagon requires 108° vertices, the angles subtended by N-Ni-Ni edges are much smaller *e.g.* N(4)-Ni1)-N(7) = 92.1(4)° (Figure 25). In order to solve the problem created by using 90° disposed L-M-L building blocks to form a pentagon, the flexible bptz edges adopt 8.4° dihedral angles between the pyridyl and the tetrazine rings. In this way the overall angles between the Ni vertices of $92.1^{\circ} + (2 \times 8.4^{\circ}) = 108.9^{\circ}$ which is nearly ideal for a five-membered ring (Figure 25).

B.3. Spectroscopic and cyclic voltammetric studies.

The UV-Visible spectra exhibit two electronic transitions; the first one located at 510 nm ($\varepsilon = 270 \text{ M}^{-1} \cdot \text{cm}^{-1}$) is attributed to a $\pi \rightarrow \pi^*$ transition and a second at 690 nm ($\varepsilon = 260 \text{ M}^{-1} \cdot \text{cm}^{-1}$) is a forbidden d-d transition for Ni²⁺. Infrared spectroscopy revealed two weak stretches at 2350 and 2354 cm⁻¹ which correspond to the v(C=N) modes for the bound acetonitrile, and weak v(C-H) stretches below 900 cm⁻¹ from the aromatic pyridyl hydrogens.

Cyclic voltammetric studies in acetonitrile revealed a quasireversible ligand-based reduction at E_{y_2} = 0.28 V and an irreversible reduction at $E_{p,c}$ = -1.26 V. The lack of reversibility is attributed to the distortion from planarity of the tetrazine ring. There is an average distortion of 2.51° out of planarity for the tetrazine ring.

C. Chemistry of bptz with other 3d transition metals.



Figure 27. Possible outcomes for the reaction between bptz with an octahedral-metal precursor.

In addition to Ni(II) and Zn(II), reactions of bptz with other first row transition metals were investigated. In contrast to the previously discussed metals (Ni²⁺ and Zn²⁺), Mn(II), Fe(II), Co(II) and Cu(II) reactions tend to favor lower nuclearity species (monomers, dimers) as judged by mass spectroscopy or insoluble materials, although the tetranuclear product is formed to some degree as evidenced by mass spectroscopy.

For example Mn(II) forms a zig-zig polymer as determined by X-ray crystallography as well as a lower nuclearity species according to mass spectroscopy studies (*vide infra*). The ES-MS data show evidence of the presence of the " $[Mn_4(bptz)_4]^{8+m}$ unit in the first hour of the reaction, but, with time, an insoluble product begins to be deposited at the bottom of the reaction flask. Furthermore, the ES-MS data show evidence for higher concentration of dimers and monomers in marked contrast to the solutions of Ni(II) and Zn(II), in which the molecular squares are the main species even days after the reaction has been performed.

X- ray crystallographic studies of bptz products with Mn(II), Co(II), Cu(II).

Reactions of Mn(II) with bptz led to the isolation of the zig-zag polymeric material {[Mn(bptz)₂(CH₃CN)₂][BF₄]₂}_∞ (7) (Figure 28). In this compound, each Mn(II) center exhibits a distorted octahedral geometry with two bptz units coordinated in a cis fashion along with two acetonitrile ligands. As noted earlier in the case of the cyclic oligomers, the tetrazine and the pyridyl rings are not coplanar (dihedral angle = 5.32°) (Figure 28a) and the M-N distances follow the same trend as the metallocyclophanes with the shortest bond being to the acetonitrile ligand Mn(1)-N(4B) = 2.143 (6) Å, followed by the pyridyl interaction Mn(1)-N(1) = 2.230 (5) Å and finally the tetrazine interaction Mn(1)-N(2) = 2.320 (5)Å. The formation of the Mn²⁺ polymer (7) points out the fact that

both open and closed structures are formed in the reaction and that subtle factors such as identity of the metal, solvent and anion choice can promote one or the other of the two structures (Figure 27).

Mn1-N4B	2.142 (6)	Mn1-N1	2.230 (5)
Mn1-N4A	2.167 (6)	Mn1-N2A	2.309 (5)
Mn1-N1A	2.229 (6)	Mn1-N2	2.320 (5)
N4B-Mn1-N4A	93.7 (2)	NI-Mn1-N2A	88.19 (18)
N4B-Mn1-N1A	108.7 (2)	N4B-Mn1-N2	168.3 (2)
N4A-Mn1-N1A	101.4 (2)	N4A-Mn1-N2	86.0 (2)
N4B-Mn1-N1	97.2 (2)	N1A-Mn1-N2	82.77 (19)
N4A-Mn1-N1	99.2 (2)	N1-Mn1-N2	71.36 (19)
N1A-Mn1-N1	145.5 (2)	N2A-Mn1-N2	94.77 (18)
N4B-Mn1-N2A	87.1 (2)	N1A-Mn1-N2A	172.4 (2)
N4A- Mn1-N2A	71.24 (19)		.,

Table 9. Selected bond distances (Å) and angles (°) for $\{[Mn(bptz)_2(CH_3CN)_2][BF_4]_2\}_{\infty}$ (7).

It is worth mentioning another factor that should be taken into consideration in this chemistry, namely the tendency for bptz to undergo rearrangements in the presence of metal ions. For example, reactions of $[Cu(CH_3CN)_4][BF_4]_2$ and $[Co(CH_3CN)_6][PF_6]_2$ with bptz yield mononuclear complexes that contain the transformed ligand 2,5-(2-pyridyl)-1,3,4-oxadiazole (bopd) (Figure 29). The combination of an active metal and traces of water apparently promotes this rearrangement. Crystals of the compounds $[Cu(bopd)_2(H_2O)_2]^{2+}$ and $[Co(bopd)_2(CH_3OH)_2]^{2+}$ were obtained from layering the reaction mixtures in acetonitrile with toluene. The thermal ellipsoids plots for these compounds are depicted in Figure 29.



(a)



- **(b)**
- Figure 28. (a) Thermal ellipsoid diagram of a portion of the polymer $\{[Mn(bptz)_2(CH_3CN)_2]^{2+}\}_{\infty}$ at the 50% probability level, (b) asymmetric unit. Hydrogen atoms were omitted for the sake of clarity.



(a)



Figure 29. Thermal ellipsoid drawing of the mononuclear complexes (a) [Co(bopd)₂(CH₃OH)₂][PF₆]₂ and [Cu(bopd)₂(H₂O)][BF₄]₂ (b). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms were omitted for the sake of clarity.

D. Electrospray-MS studies of bptz reactions with Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} .

The metal/bptz products for Mn(II), Fe(II), Co(II) and Cu(II) were studied by the Electrospray mass spectroscopy technique. The following reactions were studied (Eq. 4).

$$[M(CH_{3}CN)_{6}][ClO_{4}]_{2} + bptz \xrightarrow{acetonitrile} [M_{4}(bptz)_{4}(CH_{3}CN)_{8}][ClO_{4}]_{8} (Eq. 4)$$
$$(M = Mn^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+})$$

As mentioned earlier, the polymeric material $\{[Mn(bptz)_2(CH_3CN)_2][BF_4]_2\}_{\infty}$ (Figure 28) was isolated in low yield (30%), but we were not able to isolate a cyclic oligomer (Figure 24). Mass-spectral studies of aged solutions of Mn(II) ions and bptz do not indicate the presence of tetranuclear products, but instead reveal the presence of monomers and dimmers. If MS data are collected immediately after the reaction has been performed, however there is evidence for the presence of $[Mn_4(bptz)_4][ClO_4]_7^{7+}$ (m/z = 1856.66) (Figure 30). One hour later, the same solution does not exhibit any signs of the molecular square. The yield of the insoluble materials (polymer) is low (30 %), after several hours, but afterseveral days, the yield increases to 50 %. These observations point to a lack of stability of the square $[Mn_4(bptz)_4(CH_3CN)_8]^{8+}$ which evidently decomposes into the polymeric form.

The Co(II), Fe(II) and Cu(II) analogues follow the same trend as Mn(II), as noted in Figures 31, 32 and 33. There is an indication of the formation of $[M_4(bptz)_4][ClO_4]_7^+$ $(M = Co^{2+}, Fe^{2+}, Cu^{2+})$ species, immediately after the reaction has been performed (Figure 31, 32, 33). An hour later, the signal for the parent ion has disappeared and only lower nuclearity species are observed. The solution data are compelling evidence that a major factor in controlling the outcome of these reactions is the metal identity. One could attribute this behavior to ion size. For example a large cation such as Mn(II) may not form a stable cyclic entity because the cavity inside the molecular square is too large for the $[BF_4]^-$ or $[ClO_4]^-$ to have the same stabilizing effect as they have with Ni(II) and Zn(II). In the case of Cu(II), the Jahn-Teller distortion could play a predominant role in the instability of the metallocyclophanes because of the weak interactions along the axial sites of the metal center. Finally, cations such as Co(II), Fe(II) may exhibit lower lability to their M-N bonds than Ni(II) or Zn(II); consequently, the self-healing mechanism that takes place in the high-yield assembly of the cyclic species may not be occurring. In these cases the kinetic product (polymeric form) would be favored instead.

Electrospray mass spectroscopy studies performed on solutions of $[Ni_4(bptz)_4(CH_3CN)_8][X]_8$ and $[Zn_4(bptz)_4(CH_3CN)_8][X]_8$, where $X = [BF_4]^-$ or $[ClO_4]^-$, in acetonitrile revealed the parent ion $[M_4(bptz)_4(CH_3CN)_8][X]_7^+$ ($M = Ni^{2+}$ or Zn^{+2}) and several fragmentation peaks (Figure 34). These species were detected in a solution that had been standing for more than a week, which is good evidence for the stability of these metallocyclophnes in solution.

The MS data in Figure 34 indicate that the products of the perchlorate salts are more stable in the gas phase than the $[BF_4]$ salts in that less fragmentation is observed for the perchlorate derivatives (3 and 4) (Figure 34 b and c), than for the tetrafluoroborate compounds (Figure 31a). Compound (2) is not stable enough in the gas phase to allow for the observation of the parent peak ($[Zn_4(bptz)_4][BF_4]_7^+$).


Figure 30. ESI-MS spectra of the 1:1 reaction between [Mn(H₂O)₆][ClO₄]₂ and bptz taken after 10 minutes



Figure 31. ESI-MS spectra of the 1:1 reaction between [Co(H₂O)₆][ClO₄]₂ and bptz taken after 10 minutes.



Figure 32. ESI-MS spectra of the 1:1 reaction between [Fe(H₂O)₆][ClO₄]₂ and bptz taken after 10 minutes.



Figure 33. ESI spectra of the reaction between $[Cu(H_2O)_6][ClO_4]_2$ and bptz taken after 10 minutes.



Figure 34. ESI-MS spectra in acetonitrile of the metallocyclophanes (a) $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$, (b) $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$, and (c) $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8$.



Figure 35. ESI-MS spectra of the pentagon compound [Ni₅(bptz)₅(CH₃CN)₁₀][SbF₆]₁₀ dissolved in acetonitrile.



Figure 36. ESI-MS spectra of [Ni₄(bptz)₄(CH₃CN₃][ClO₄]₈ in different solvents. The peak being depicted is the parent ion.

Solutions of $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ (6) clearly show the signal for the parent ion $[Ni_5(bptz)_5][SbF_6]^{9+}$ at 3584 mass units (Figure 35). In addition, there are numerous fragmentation peaks corresponding to $[Ni_4]$, $[Ni_3]$ and $[Ni_2]$ species, as it can be observed in Figure 35.

All X-ray structures of the metallocyclophanes were performed on crystals grown in acetonitrile. A question that comes to mind is whether they exist in other solvents besides acetonitrile. Electrospray mass spectroscopy is an excellent technique for probing this question. Since the perchlorate salts were already known to be more stable in the gas phase (as noted earlier), ES-MS studies of these salts in different solvents were performed. Reactions of $[Ni(H_2O)_6][CIO_4]_2$ with bptz in a 1:1 ratio were performed in aprotic solvents such as nitromethane and acetone and evidence for the formation of the tetramers was obtained by mass-spectrometry (Figure 36). On the other hand, protic solvents such as alcohols or water do not promote the formation of the metallocyclophanes, instead only lower nuclearities were observed.

F. Interconversion of the $[Ni_5]^{10+}$ and $[Ni_4]^{8+}$.

With all of the above mentioned data in hand, the evidence for the predominant role of the anion in the assembly of these metallocyclophanes was compelling. Similar anions, in terms of size and geometry such as $[BF_4]^-$ and $[ClO_4]^-$ yield tetramers whereas the larger anion ($[SbF_6]^-$) produces the pentamer (6). Armed with this knowledge, we asked ourselves if it was possible to transform the pentamer into the tetramer by treating a pure sample of $[Ni_5]^{10+}$ with an excess of tetrafluoroborate or perchlorate in order to exchange the $[SbF_6]^-$, or to transform the $[Ni_4]^{8+}$ molecule into the $[Ni_5]^{10+}$ compound by reacting it with an excess of $[SbF_6]^-$. In order to test this hypothesis, two different

approaches were taken. In one case, a large excess of tetraflouroborate was added to a solution of $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ and allowed to stir for several days. In order to obtain crystallographic evidence for the outcome, layering experiments were performed and crystals were obtained. The results showed that the transformation to the tetramer $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8\cdot 4CH_3CN$ (1) had occurred. With the same idea in mind, experiments were performed with a mixture of $[TBA][BF_4]$ and $[TBA][PF_6]$ which lead to the isolation of the mixed anion salt $[Ni_4(bptz)(CH_3CN)_8][BF_4]][PF_6]_3[SbF_6]_4\cdot CH_3CN$ (8) (Figure 37). In this salt the only $[BF_4]^{-1}$ anion that is present is the one inside the cavity of the tetramer. Presumably, the $[SbF_6]^{-1}$ and $[PF_6]^{-1}$ anions are too large to occupy the cavity reside and, therefore, in the interstices between the squares.

It was found that the transformation of the molecular squares into the pentagon is not as facile as the reverse reaction. A layering of $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ or $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$ in acetonitrile with a saturated solution of $[Bu_4N][SbF_6]$ afforded only crystals of the tetramers. The lack of a transformation was corroborated by mass spectrometry. In order to attempt to force this transformation, a large excess of $[Bu_4N][SbF_6]$ was added to a solution of $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$ in acetonitrile (> 50:1 ratio) and the solution was refluxed for two days. Mass spectrometric studies revealed the transformation of the tetramer into the pentamer was successful in this case (Figure 39). The fact that the transformation of the pentagon into the square takes place under less forcing conditions is a good indication that the square nuclearity is more stable than its pentagon counterpart.

Table10.Sele $[Ni_4(bptz)_4(CH_3CN)_8]$	cted bond dist [BF4][PF6]3[SbF6]4•Cl	ances (Å) and H ₃ CN (8).	angles	(°)	for
Nil-N6	1.99(3)	Ni1-N3		2.1	0(2)
Ni1-N5	2.08(2)	Ni1-N4		2.10(2)	
Ni1-N2	2.09(2)	Ni1-N1		2.1	0(2)
N2-Ni1-N1	76.9(9) N3-Ni1-N4		77.6(8)		
N2-Ni1-N3	88.7(10)	0) N4-Ni1-N1		95.1(8)	
N2-Ni1-N4	92.6(9)) N5-Ni1-N1		91.0(9)	
N3-Ni1-N1	163.7(11)				
Table11.Sele[Ni4(bptz)4(CH3CN)8]	cted bond dista [ClO4][IO4]7 [·] 2CH3CN	ances (Å) and (9).	angles	(°)	for
Nil-NI4	2.045(14)	Ni2-N12		2.0	4(2)
N11-N13	2.043(13)	Ni2-N7		2.061	(17)
NII-NI	2.065(13)	N12-N6		2.075	(10)
N11-N8	2.068(15)	N12-N9		2.073	(14)
N11-N10	2.088(15)	NIZ-NII		2.084	(10)
N11-N2	2.090(13)	IN12-IN5		2.085	(14)
N14-Ni1-N13	86.2(6)	N12-Ni2-N7		96.	5(6)
N14-Ni1-N1	93.5(6)	N12-Ni2-N6		92.	6(6)
N13-Ni1-N1	93.6(5)	N7-Ni2-N6		162.	9(5)
N14-Ni1-N8	94.1(6)	N12-Ni2-N9		173.	2(6)
N13-Ni1-N8	92.5(5)	N7-Ni2-N9		77.	3(6)
N1-Ni1-N8	170.6(5)	N6-Ni2-N9		94.	1(5)
N1- Ni1-N10	171.9(5)	N12-Ni2-N11		90 .	0(6)
N1- Ni1-N10	92.6(6)	N7-Ni2-N11		99 .	9(6)
N1-Ni1-N10	94.6(5)	N6-Ni2-N11		94.	5(6)
N8-Ni1-N10	78.0(5)	N9-Ni2-N11		88.	3(6)
N14-Ni1-N2	87.7(5)	N12-Ni2-N5		91.	1(6)
N13-Ni1-N2	170.0(6)	N7-Ni2-N5		87.	7(5)
N1-Ni1-N2	78.9(5)	N6-Ni2-N5		77.	7(5)
N8-Ni1-N2	95.8(5)	N9-Ni2-N5		91.	5(5)
N10-Ni1-N2	94.6(5)	N11-Ni2-N5		172.	1(7)

A good example of the predominant role of the anions in the self-assembly is demonstrated by the addition of 50 equivalents of $[Bu_4N][IO_4]$ to a solution of



(a)

(b)



Figure 37. (a) Thermal ellipsoid drawing of the [Ni₄(bptz)₄(CH₃CN)₈][BF₄][SbF₆]⁶⁺ unit in [Ni₄(bptz)₄(CH₃CN)₈][BF₄][PF₆]₃[SbF₆]₄ with 50% probability ellipsoids, (b) space filling diagram and (c) asymmetric unit. Hydrogen atoms have been omitted for the sake of clarity.







Figure 38. (a) Thermal ellipsoid drawing of the [Ni₄(bptz)₄(CH₃CN)₈][ClO₄][IO₄]⁶⁺ unit in [Ni₄(bptz)₄(CH₃CN)₈][ClO₄][IO₄]₇ with 50% probability ellipsoids, (b) space filling diagram that emphasizes the molecular volume of the perchlorate versus the periodate and (c) asymmetric unit. Hydrogen atoms were omitted for the sake of clarity. $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$. The initial goal of the experiment was to obtain metallocyclophanes of nuclearities other than four or five. The outcome of the reaction, however, was the molecular square $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4][IO_4]_7$ (9) (Figure 38). Although the solution was saturated with $[IO_4]^-$ the compound retains a $[ClO_4]^-$ inside the cavity and exchanges only the outer anions.

E.S-MS studies of interconversion reactions.

Another aspect of this chemistry investigated by mass spectrometry is the conversion of $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ the pentagon into the molecular square in the presence of an excess of either $[BF_4]^-$ or $[ClO_4]^-$. This conversion was accomplished easily as previously mentioned and confirmed by X-ray crystallography, but the reverse transformation from the square into the pentagon did not take place under similar mild conditions.

A reaction that involved addition of a large excess of $[Bu_4N][SbF_6]$ to a solution of $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8$ with two days of reflux was followed by ESI-MS. As indicated by the data in Figure 39, the solution contains only $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$ in the earlier stages of the reaction (Figure 39a). After two days (under constant refluxing), there are signs of $[Ni_5(bptz)_5(CH_3CN)_{10}]^{10+}$ (Figure 39b), but the conversion is not complete. These data suggest that the molecular square is more stable that the molecular pentagon.



Figure 39. Conversion of the square into the pentagon by addition of an excess of [TBA][SbF₆] to a refluxing solution of [Ni4(bptz)4(CH3CN)8][ClO4]8. (a) represents the initial sample of the square and (b) represents the final solution.

G. 2,2' azo bipyridine Chemistry.

G.1. Synthesis of $[Ni_2(abpy)(CH_3CN)_2(NO_3)_4]$, $[Cu_2(abpy)(CH_3CN)_8][BF_4]_4$ and $\{[Cu_2(abpy)][BF_4]_2\}_{\infty}$ Compounds.

The compounds $[Ni_2(abpy)(CH_3CN)_2(NO_3)_4]$ (12) and $[Cu_2(abpy)(CH_3CN)_8][BF_4]_4$ (13) were synthesized in acetonitrile. The reactions proceed virtually instaneously upon the contact of both reagents. In marked contrast to previous reports, in which is stated that there is a large activation barrier for the coordination of a second metal center after the first metal is bound, the formation of the dinuclear species is relatively facile in this case.³⁰ Specifically $[Ni_2(abpy)(CH_3CN)_2(NO_3)_4]$ was synthesized by reaction of $[Ni(H_2O)_6][NO_3]_2$ with abpy in a 2:1 ratio in a beaker (Eq. 5). The reaction takes place rapidly as evidenced by the color change from pale blue to green within minutes. Crystals of the product were obtained by slow vapor diffusion of diethyl ether into the reaction mixture.

$$2[Ni(H_2O)_6][NO_3]_2 + abpy \xrightarrow{acetonitrile} [Ni_2(abpy)(CH_3CN)_2][NO_3]_4 (Eq. 5)$$

$$75\% \text{ yield}$$

 $2[Cu(CH_3CN)_4][BF_4]_2 + abpy \xrightarrow{acetonitrile} [Cu_2(abpy)(CH_3CN)_8][BF_4]_4 (Eq. 6)$ 80% yield

The compound $[Cu_2(abpy)(CH_3CN)_8][BF_4]_4$ (13) was synthesized under anaerobic conditions by dissolving two equivalents of $[Cu(CH_3CN)_4][BF_4]_2$ in acetonitrile, and adding one equivalent of abpy (Eq. 6). The reaction is fast, leading to a color change from pale blue to light green within minutes. Crystals of

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 $[Cu_2(abpy)(CH_3CN)_8][BF_4]_4$ (13) were obtained by saturating the solution with diethyl ether and placing it in the freezer. The compound $[Cu_2(abpy)(CH_3CN)_8][BF_4]_4$ (13) is not indefinitely stable and eventually decomposes to the polymer { $[Cu_2(abpy)][BF_4]_2$ }. In this process, Cu(II) is reduced to Cu(I) over the period of several months when the title compound in acetonitrile, is layered with toluene as judged by the isolation of { $[Cu(abpy)_2][BF_4]$ }. (14) crystals.

G.2. Spectroscopic and Electrochemical studies.

The abpy ligand possesses low lying π^* orbitals, which renders it an excellent electron acceptor. Early reports indicate that these compounds exhibit rich electrochemistry and interesting electronic properties.^{32,33} The ligand itself exhibits three electronic transitions in the UV-Visible region at $\lambda_{max} = 450$, 361 and 203 nm with ε values of 4.8×10^2 , 1.5×10^4 and 5.3×10^2 L(mol·cm)⁻¹, respectively. These transitions correspond to $\pi \rightarrow \pi^*$ transitions.

The compound $[Ni_2(abpy)(CH_3CN)_2(NO_3)_4]$ (12) displays only one electronic transition in the UV-Visible range, namely at $\lambda_{max} = 344$ nm which is assigned to an MLCT band given the ε value of 1.8×10^4 L(mol·cm)⁻¹. Its counterpart $[Cu_2(abpy)(CH_3CN)_8][ClO_4]_4$ (13) exhibits a similar transition at 351 nm with $\varepsilon = 1.5 \times 10^4$ L(mol·cm)⁻¹ along with a second electronic transition at higher energy, $\lambda_{max} = 230$ nm, $\varepsilon = 2.0 \times 10^4$ L(mol·cm)⁻¹.

The cyclic voltammogram of $[Ni_2(abpy)(CH_3CN)_2(NO_3)]_4$ (12) in acetonitrile exhibits two oxidation features at Ep,a = +0.62V and Ep,a = +0.4V with no associated return waves. In addition there are three reversible reductions located at $E_{\frac{1}{2}} = -0.10V$, $E_{\frac{1}{2}}$ = -0.4V and $E_{\frac{1}{2}} = -0.9V$. The dinuclear Cu(II) (13) compound also exhibits a rich electrochemistry with an irreversible oxidation at Ep,a = +1.10 V, reversible reductions at $E_{\nu_2} = 0.65V$, $E_{\nu_2} = +0.40V$ and a quasireversible reduction at $E_{\nu_2} = 0.0V$.

G.3. X-ray Crystallographic studies.

The molecular structure of $[Ni_2(abpy)(CH_3CN)_2(NO_3)_4]$ (12) is based on a distorted octahedral geometry around the metal centers (Figure 40). Each nickel(II) center is coordinated to one bidentate and one monodentate nitrate, an acetonitrile molecule, and an abpy ligand.

Table12.Selected[Ni2(abpy)(CH3CN)2(NO3)4	bond dist]·2CH₃CN (12).	ances (Å)	and	angles	(°)	in
Ni1-06	1.990(2) Ni1-O3				2.106(2)	
Nil-Nl	2.037(2)	Ni1-N2		2.121(2)		
Nil-N5	2.044(2)	Ni1-02			2.125	(2)
N5-Ni1-O3	86.69(9)	N5-Ni1-N2			170.06	(8)
O6-Ni1-N2	95.56(8)	O3-Ni1-N2			101.99	(8)
N1-Ni1-N2	76.45(9)	N1-Ni1-O3			162.44	(8)
O6-Ni1-N1	105.01(8)	06-Ni1-02		153.92(7)		
O6-Ni1-N5	88.82(9)	N1-Ni1-O2			101.01	(8)
N1-Ni1-N5	93.80(9)	O3-Ni1-O2			61.43	(8)
O6-Ni1-O3	92.55(8)	N2-Ni1-O2			88.74	(8)
N5-Ni1-O2	91.24(9)					

The Ni-N distance to the acetonitrile ligand is 2.044 (2) Å which is essentially the same as the distance in $[Ni_2(bptz)(CH_3CN)_8][ClO_4]_4$; (Ni(1)-N(5), 2.044 (7)Å) (Figure 19). The azo nitrogen distance to Ni(II) is the longest of the three Ni-N interactions at Ni(1)-N(2) = 2.121 (2)Å. Compared to a similar type of interaction in $[Ni_2(bptz)(CH_3CN)_8][ClO_4]_4$ in which there is a tetrazine ring instead of an azo linkage, this interaction is 0.04 Å longer.

The angles within the coordination sphere also provide some helpful insight into the distortion of the ligand environment of this compound. The binding angle for the chelating nitrate O(3)-Ni(1)-O(1) is 61.43 (8)°. The angle between the pyridyl and the acetonitrile ligand is close to the ideal value for an octahedron, (N(5)-Ni(1)-N(1) = 93.80 (2)°). The binding angle of abpy, N(1)-Ni(1)-N(2) of 76.45 (9)°, is very close to angles of coordinated bptz in [Ni₂(bptz)(CH₃CN)₈][ClO₄]₄ 78.10 (3)°. The two Ni(II) atoms are 4.942 Å apart, which is much shorter than the corresponding distance in [Ni₂(bptz)(CH₃CN)₈][ClO₄]₄, (6.904Å). An important feature to note in the structure of (12) is the elongation of the N=N bond by 0.025Å with (N(2)-N(2#) 1.271 Å), compared to the corresponding value in free abpy, (1.246 Å).³¹ This phenomenon indicates π -back donation from the Ni(II) centers into the π^* (abpy) orbital. This effect has been previously noted for coordination complexes of abpy with Cu(I).³²

(10).			
Cu1-N4	2.004(5)	Cu1-N6	2.318(5)
Cu1-N3	2.007(5)	Cu1-N2	2.403(5)
Cu1-N5	2.029(6)	Cu1-N1	2.032(5)
N6-Cu1-N2	166.00(18)	N3-Cu1-N6	94.4(2)
N4-Cu1-N3	174.83(19)	N5-Cu1-N6	87.03(19)
N4-Cu1-N5	91.6(2)	N1-Cu1-N6	94.59(19)
N3-Cu1-N5	86.9(2)	N4-Cu1-N2	86.35(18)
N4-Cu1-N1	89.5(2)	N3-Cu1-N2	89.35(19)
N3-Cu1-N1	91.8(2)	N5-Cu1-N2	106.66(18)
N5-Cu1-N1	178.01(19)	N1-Cu1-N2	71.79(18)
N4-Cu1-N6	90.41(19)		

Table 13. Selected bond distances (Å) and angles (°) for $[Cu_2(abpy)(CH_3CN)_8][BF_4]_2$ (13).

 $[Cu_2(azbpy)(CH_3CN)_8][BF]_4$ (13) exhibits typical parameters for a Cu(II) metal center in an distorted octahedral environment. It displays a Jahn-Teller distortion which

corresponds to the Cu-azo nitrogen interaction, Cu(1)-N(2) 2.403 (5)Å and the Cu-N acetonitrile interaction Cu(1)-N(6) 2.318 (5)Å along the z axis (Figure 41). The other four coordination sites are filled by three acetonitrile molecules, which exhibit an average Cu(1)-N distance of 2.013 [5] Å, and the pyridyl ring, Cu(1)-N(1) 2.032 (5) Å. The L-Cu-L binding angles are distorted from the ideal 90 or 180 ° expected for an octahedron. The angles N(2)-Cu(1)-N(5) = 106.6 (2)° and N(2)-Cu(1)-N(1) = 71.8 (2)° are typical values. The N-N distance in the azo group N(2)-N(2A), 1.277 (1) Å is indicative of π backdonation from the Cu(II) center into the π^* (abpy) orbital. This distance is 0.03 Å larger than the one found in free abpy, which is 1.246 (2)Å.³¹ The Cu(II) centers are separated by a distance of 5.408Å, which is 0.46 Å longer that the corresponding separation in the Ni(II) case, as expected for a larger metal radius.

Table 14. Selected bond distances (Å) and angles (°) in $\{[Cu(abpy)_2][BF_4]_2\}_{\infty}$ (14).				
Cul-N4	1.934(9)	Cu1-N1	2.060(9)	
Cu1-N3	2.009(9)	N3-N3A	1.300(16)	
Cu1-N2	2.009(9)	N3-C9	1.396(13)	
N4-Cu1-N3	146.5(4)	N2-Cu1-N1	135.6(4)	
N4-Cu1-N2	117.1(4)	N3-N3A-Cu1	115.7(9)	
N3-Cu1-N2	79.5(3)	C9-N3-Cu1	129.0(7)	
N4-Cu1-N1	77.8(4)	C1-N1-Cu1	131.2(7)	
N3-Cu1-N1	111.9(3)	C5-N1-Cu1	113.0(7)	

Finally, $\{[Cu(abpy)_2][BF_4]_2\}_{\infty}$ (14) is a 1-D polymer with Cu(I) ions instead of Cu(II). As expected for Cu(I), the metal center exhibits a distorted tetrahedral geometry (Figure 42). This is illustrated by the angles observed between the pyridyl-azo, N(3)-Cu(1)-N(1) = 111.9 (3)°, and the two pyridyl groups N(1)-Cu(1)-N(2) = 135.6 (4)°, which are far from the ideal 109.5° for a tetrahedron. The distance N(3)-N(3#) = 1.300 Å













to the azo group is evidently involved in appreciable π back-donation from the Cu(I), as expected for an electron rich d¹⁰ center. The N=N distance is 0.054 Å, which is nearly twice the lengthening observed for the Ni(II) and Cu(II) complexes.

IV. Future work

Reactions of the metallocyclophanes.

In our search for supramolecular compounds with interesting properties, an interesting family of metallocyclophanes was isolated. A close look at the structures reveal the presence of two acetonitrile ligands on each metal center as emphasized in Figure 43. Substitution of these molecules by organic linkers may allow the formation of higher nuclearity species (Figure 43). With this goal in mind, several bridging ligands were reacted; these include 1,4' phenyldiamine, pyrazine, cyanide, 4,4'-azo-bipyridine, 2,2'-bipyrimidine, 4,4'-bipyridine, 1,4'-benzonitrile and thiocyanide. Reactions of $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ with a large excess of either $[Bu_4N][CN]$ or bpym led to the isolation of the compounds $[Bu_4N]_2[Ni(CN)_4]$ and $[Ni(bpym)_3][BF_4]_2$ as verified by X-ray crystallography.

Halides (Cl⁻, Br⁻ and I⁻) react to yield insoluble species in acetonitrile. The reaction is effectively instaneous, and IR/spectral analyses of the precipitates reveal the disappearance of the v(C=N) and v(B-F) modes that are normally observed for $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$. It is worth mentioning at this point, that reactions of the pentagon with halides are much slower, with eventual precipitation of an insoluble precipitate that lacks C=N stretches. Moreover, in the case of reactions of the pentagon $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ with I⁻, there is more than one product. After the initial insoluble solid is removed, the remaining light green solution affords crystals when

layered with toluene. The crystals are the unexpected compound $[Ni_4(bptz)_4(CH_3CN)_8][I][SbF_6]_7$ (Figure 44) in which the central cavity is occupied by an iodide atom. The iodide ion is another anion which has the correct size to occupy the cavity of the molecular square. Attempts to synthesize this compound by using NiI₂ as the source of Ni(II), led to only an insoluble, material which is either a polymer or a neutral square.

Other organic linkers that appear to react with the $[Ni_4]^{8+}$ square are isocyanide and oxalate. In both cases, there is a disappearance of the characteristic v(C=N) mode with precipitation of insoluble products. This can be attributed to the formation of either neutral species that are insoluble in acetonitrile or molecular grids, which would not be soluble. Unfortunately, attempts to obtain crystals by layering experiments or by slow vapor diffusion were unsuccessful.

Ni1-N6	2.026(10)	Nil-N4	2.098(10)
Ni1-N3	2.052(11)	Ni1-N1	2.100(11)
Ni1-N2	2.066(9)	Ni1-N7	2.130(17)
N6-Ni1-N3	96.7(4)	N2-Ni1-N1	78.1(4)
N6-Ni1-N2	174.2(4)	N4-Ni1-N1	94.6(4)
N3-Ni1-N2	89.1(4)	N6-Ni1-N7	90.4(5)
N6-Ni1-N4	91.9(4)	N3-Ni1-N7	94.3(4)
N3-Ni1-N4	79.0(4)	N2-Ni1-N7	88.4(4)
N2-Ni1-N4	89.9(4)	N4-Ni1-N7	173.1(4)
N6-Ni1-N1	96.2(4)	N1-Ni1-N7	91.5(4)
N3-Ni1-N1	165.8(4)		

Table 15. Selected bonds (Å) and angles (°) for [Ni₄(bptz)₄(CH₃CN)₈][I][SbF₆]₇ (15).

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,z ; #2 x,-y,-z #3 -x+1,-y,z; #4 -x+1,y,-z; #5 -x+1,y,-z+1

Other organic linkers that were used in pursuit of linked metallocyclophanes are 1,4 disubstitued benzenes, such as 1,4 benzonitrile and 1,4 phenyldiamine. These ligands



Figure 43. Schematic drawing of the molecular square and pentagon with indicated sites for substitution.





Figure 44. (a) Thermal ellipsoid plot of the cation in [Ni₄(bptz)₄(CH₃CN)₈][I][SbF₆]₇ (15) at the 50% probability ellipsoid level, (b) space filling diagram with the iodine anion inside the metallocyclophane and (c) asymmetric unit. Hydrogen atoms have been omitted for the sake of clarity.

did not react swiftly as was the case for reactions of halides or cyanide, but, under refluxing conditions for 4 hours, there was a noticeable color change. Layering experiments and slow vapor diffusion have thus far been unsuccessful in leading to single crystals growth. IR data of the products reveal an absence of nitrile stretches, indicating that the substitution of the acetonitrile molecules has occurred.

Finally, the use of neutral ligands such as pyrazine, 4,4'-azo-bipyridine and 4,4'bipyridine do not appear to react with $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ in acetonitrile, even with a large excess of the ligands under refluxing conditions. Reaction solutions afforded crystals of only the starting materials $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$ and the linking ligand.

V. Conclusions

The metallocyclophanes presented in this work are outstanding examples of how subtle factors such as anion choice, solvent and metal identity can lead to differences in self-assembly reactions. Molecular squares ($[Ni_4]^{8+}$ or $[Zn_4]^{8+}$) and the pentagons ($[Ni_5]^{10+}$) are obtained in good yields when the precursor salts that contain tetraflouroborate, perchlorate or hexaflouroantimonate anions are reacted in 1:1 ratio with bptz. In addition to acetonitrile, other solvents such as nitromethane and acetone allow for the formation of these metallocyclophanes as evidenced by ESI-MS (Figure 36). These results are attributed to the match between the size of the cavity formed by the $[M_4]$ or $[M_5]$ cyclic unit and the anion.¹⁹ The tetramers $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$ and $[Zn_4(bptz)_4(CH_3CN)_8]^{8+}$ have a cavity size that is well-matched with a $[BF_4]^-$, $[ClO_4]^-$ and $[I]^-$.^{19a} The use of a much larger anion, $[SbF_6]^-$ (71 Å³),^{19a} led to the pentagon metallacyclophane, $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}^-2CH_3CN$ (6). On the contrary, when anions such as, $[CF_3SO_3]^-$, $B\{C_6H_3(CF_3)_2\}_4^-$, $[PF_6]^-$, $[AlCl_4]^-$, $[NO_3]^-$ and $[SO_4]^{2-}$ were

used, the formation of $[M_4]^{8+}$ and $[M_5]^{10+}$ entities is precluded; instead lower nuclearity or polymers are assembled.

Molecular pentagons versus squares can be favored, in solution and in the solidstate simply by altering the anion present in solution. Transformations between molecular square $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$ and the molecular pentagon $[Ni_5(bptz)_5(CH_3CN)_{10}]^{10+}$ can be achieved by adding an excess of the anion needed for the assembly; $[SbF_6]^-$ for the first case and $[BF_4]^-$ or $[ClO_4]^-$ for the second. The fact that the nuclearity of these macrocyclos can be interchanged is excellent evidence of the predominant role of anion as a template. The conversion of the pentagon into the square takes place under mild conditions whereas the opposite (square \rightarrow pentagon) requires refluxing for two days (Figure 39). These results indicate that the squares are more stable than the pentagon.

The diamagnetic tetramer $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8$ allows for the study of these entities in solution by means of ¹⁹F NMR and ¹¹B NMR spectroscopy. Both NMR experiments show two peaks, one corresponding to the encapsulated and the other to the exterior $[BF_4]^-$ anions, thereby proving the existence of these entities in solution. Coalescence could not achieved in a variable ¹⁹F NMR experiment, presumably due to the formation of aggregates between the metallocyclophanes in solution when the temperature is varied (Figure 22).

Mass spectrometric studies of the products of different Ni(II) salts $([Ni(CH_3CN)_6][X]_2 \ X = anions)$ with bptz show that only those reactions that involve the $[BF_4]^{-}$, $[ClO_4]^{-}$, $[SbF_6]^{-}$ anions yield tetramers or pentamers respectively; all others appear to be leading only to lower nuclearity species or polymer formation. Tetrametallocyclophanes with Co(II), Fe(II), Cu(II) and Mn(II) are formed initially, as

verified by ES-MS (Figures 30 through 33), but they are not stable in solution. Decomposition takes within a few minutes to one hour, with entities of lower nuclearity or polymers being formed.

It was noted that the bptz ligand is prone to side-reactions in the presence of water and Co(II) or Cu(II) which apparently assist in the tetrazine ring-opening and formation of a five-membered ring (2,5-di(2-pyridyl)-1,3,4-oxadiazole). This is evidenced by the isolation of the mononuclear compound $[Cu(bopd)_2(H_2O)_2][BF_4]_2$ and $[Co(bopd)_2(CH_3OH)_2][BF_4]_2$ (Figure 29).

The new $[M_4]^{8+}$ and $[M_5]^{10+}$ molecules are of an unprecedented type of partially solvated molecular metallocyclophanes. The presence of labile CH₃CN ligands on the periphery of these molecules allows for their use as building blocks for larger molecules for the elaboration of 2-D square grids (Figure 43).

First-row transition metal coordination compounds with abpy do not exhibit as good electronic coupling as their counterparts in the second and third row transition metals. ²⁰ A good approach to improve the capabilities of the abpy as a molecular bridge for first-row transition metals would be the use of the radical form of abpy instead. Previous studies with Cu(II) and Fe(II) have demonstrated that this approach affords mixed-valence species.^{32,33}

Dinuclear compounds of Ru(II) and Os(II) with abpy are difficult to obtain and require tedious and lengthy synthesis, but the mononuclear species were obtained in high yields. The large activation barrier to the formation of abpy-bridge dimers from monomeric precursors has previously been attributed to steric interactions between the 6 and 6' protons of the bridge and the coordinating nitrogen atoms of adjacent ligands.³³ In

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the case of the dimers of Ni(II) and Cu(II), however, they are obtained in large yields just by stirring for a few hours followed by crystallization without any forcing conditions.

VI. References

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Chapter III

Reactivity of the Ligands 2,3,5,6 tetrapyridyl pyrazine (tppz)

and 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptaz) with

Paramagnetic First Row Metal Ions
I. Introduction

In the last thirty years, the scientific community has witnessed a growth of research in the area of supramolecular chemistry. One of the main approaches in this field is to use predesigned "building blocks" to assemble larger structures. In order to build more elaborate molecules, the building blocks must possess reactive sites at which further chemistry can take place. One of the simple ligands that has been used with these goals in mind is 2,3,5,6-tetrapyridylpyrazine (tppz) (Figure 45). The tppz ligand was synthesized in 1959 by Goodwin and Lions, who reported a series of monodentate compounds of the type $[M(tppz)_2]^{2+}$ (M = first row transition metals) with little characterization to verify their nature.¹ At the time, it was believed that once the ligand tppz was coordinated to one metal, binding to the second site would not occur. This prediction was based on the belief that the four pendant 2-pyridyl rings would not be stable in a coplanar arrangement with the central diazine ring.



Figure 45. Schematic drawing of the ligand 2,3,5,6-tetrapyridylpyrazine (tppz).

For almost thirty years the tppz ligand was largely ignored due to these early predictions, and it was not until 1988 that Thummel and coworkers started using the ligand to prepare compounds such as $(tpy)Ru(tppz)Ru(tpy)]^{4+}$, work which demonstrated that coordination of a second metal was indeed possible.² A series of compounds with Ru(II), Os(II), Ir(II), Rh(II) and tppz were synthesized and characterized during the next 15 years, with the ultimate aim being to use them as photosentizers.³ In addition to displaying photoluminescence, some of these species exhibit strong electronic coupling, which is an excellent indication that this bridging ligand permits delocalization of electronic density between metal centers. Within this category, the compound [(NH₃)₃Ru(tppz)Ru(NH₃)]⁴⁺ is the best example, with a comproportionation constant K_c





Figure 46. The three coordination sites in Tptaz.

of 2.8×10^8 based on cyclic voltammetric studies. This qualifies the compound as class III (completely delocalized) on the Robin-Day scale.⁴

Concomitant with the research on the reaction of the second and third row transition metal with tppz, Stoeckli-Evans and co-workers undertook reactivity studies with first row metals.⁵ "Monomers" and "dimers" such as $[M_2(tppz)_2(L)_6]^{4+}$, $[M(tppz)]_2^+$ (M= Ni²⁺, Cu²⁺; L = H₂O) were prepared and found to exhibit significant antiferromagnetic coupling.⁵ There were no reported attempts, however, to use these compounds as building blocks for higher nuclearity species.

Work in our laboratories on the tppz ligand focuses on two main areas: (a) the synthesis of paramagnetic building blocks with first row transition metals and (b) the self-assembly of molecular rectangles with metal-metal bonded cores, a novel application for this ligand. In related chemistry, exploratory chemistry with the ligand tptaz (2,4,6-Tris(2-pyridyl)-1,3,5-triazine) is also being conducted. The tptaz ligand possesses three coordination sites (tridentate, bidentate and monodentate) according to the number of donor nitrogen atoms (three, two and one, respectively) as shown in Figure 46. Given the multiple coordination sites on tptaz, it can act simultaneously as a tridentate and a bidentate ligand. Dinuclear compounds of this type have been synthesized with Co(II),⁶ Hg(I),⁷ and Ru(II)⁸ ions. It is worth mentioning, however, that the coordination of the triazine ring by the inductive effect of the first metal, and also because of steric interactions between the hydrogen atoms and the metal ion.⁹

In the chapter, the syntheses of precursors to be used as building blocks for the preparation of multinuclear metal complexes are reported. Three compounds were

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synthesized in quantitative yields, namely $[Ni(tptaz)(CH_3CN)_2(H_2O)][BF_4]_2$ (12), $[Fe(tptaz)_2][ClO_4]_2$ (13) and $[Mn(tptaz)(phen)][CF_3SO_3]_2$ (14). A detailed characterization of these compounds including magnetic measurements, cyclic voltammetry, UV-Visible spectroscopy and X-ray crystallography is presented. A description of our attempts to form larger supramolecular entities will be presented along with a rationale for the outcome and possible future approaches to succeed in this goal.

II. Experimental Section

Preparation of Compounds. Methods and Materials.

All operations were performed under a nitrogen atmosphere using standard Schlenk line techniques unless otherwise indicated. All solvents were pre-dried over 4 Å molecular sieves with the exception of acetonitrile, which was pre-dried over 3 Å molecular sieves. Diethyl ether and toluene were freshly distilled over Na/K, acetonitrile was distilled over 3 Å molecular sieves and methylene chloride was distilled over P₂O₅. The starting materials [Ni(H₂O)₆[ClO₄]₂, [Mn(H₂O)₆[ClO₄]₂ and [Fe(H₂O)₆[ClO₄]₂ were purchased from Aldrich and used without further purification. The solvated compounds [Ni(CH₃CN)₆][BF₄]₂ and [Co(CH₃CN)₆][PF₆]₂ were synthesized by published methods.¹⁰ The tppz ligand was prepared from a literature method and recrystallized from pyridine.²

Physical Measurements.

IR spectra were performed on a Nicolet 740 FT-IR spectrometer using KBr plates and samples were suspended in Nujol mulls. The magnetic susceptibility measurements were obtained with a Quatum Design SQUID MPMS-XL magnetometer. Measurements were performed on finely ground polycrystalline samples. Data were corrected for the sample holder, and the experimental diamagnetic contribution was calculated from the Pascal constants.¹² Electrochemical measurements were carried out by using an EG&G Princeton Applied Research Model 362 scanning potentiostat in conjunction with a BAS Model RXY recorder. Cyclic voltammetry was performed in CH₃CN containing 0.1 M tetra-*n*-butylammonium hexaflourophosphate (TBAPF₆) as the supporting electrolyte. The working electrode was a BAS Pt disk electrode. The ferrocene couple occurs at 0.52 V vs. Ag/AgCl under the same experimental conditions.

Synthesis

2,3,5,6-tetrapyridylpyrazine (tppz).

In a 500 mL round-bottomed flask, a 90 g sample of NH₄O₂CCH₃ was thoroughly mixed with 20 g of α -pyrodoin (C₁₂N₂O₂H₁₀). This mixture was slowly heated to 180 °C in an oil bath for two hours. After the first hour of refluxing, yellow crystals began to appear in the brown melt. The thick brown solution was filtered to give a yellow solid which was washed with a large quantity of diethyl ether. The solid was recrystallized from pyridine; yield 4.8g (27 %) m.p 284°C. ¹H NMR (CDCl₃): three multiplets centered at 7.30, 7,85 and 8.45 ppm. UV-Visible (acetonitrile, nm, c = 2.47 × 10⁻⁵M): $\lambda_{max} = 320$, $\varepsilon = 2.62 \times 10^4 \text{ L(mol·cm)}^{-1}$; $\lambda_{max} = 274$, $\varepsilon = 2.6 \times 10^4 \text{ L(mol·cm)}^{-1}$. IR (KBr mull) cm⁻¹, 1680 (w), 1288 (w), 1138 (w), 1061 (w), 992 (w), 748 (m), 789 (w), 724 (w).

2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptaz).

The tptaz ligand was synthesized from a previously published method with some modifications.¹¹ The reagent 2-cyano pyridine (6.0 g, 0.058 mol) was loaded in a round-bottomed flask and mixed thoroughly with NaH (0.1g, 0.004 mol) under nitrogen. This mixture was heated at 165 °C until the entire solid had melted and then refluxed at 170 °C

for one hour. At this point the melt had turned black. The solid was extracted with hot benzene and recrystallized by slow evaporation; yield 3.0g (50%).

$[Ni(tppz)_2][NO_3]_2$ (16).

The salt $[Ni(H_2O)_6][NO_3]_2$ (100 mg, 0.344 mmol) was dissolved in 20 mL of acetonitrile, and two equivalents of tppz were added (270 mg, 0.69 mmol). Within a few minutes a drastic color change from blue to yellow ensued, and a precipitate appeared at the bottom of the vessel. The reaction mixture was stirred overnight after which time the precipitate was removed by suction filtration. The filtrate was layered with toluene to afford crystals of $[Ni(tppz)_2][NO_3]_2$ within one week; yield, 190 mg (58%). IR (KBr mull) cm⁻¹, 2723 (w), 1598 (w), 1250 (w), 1204 (w), 1149 (w), 1096 (w), 1015 (w), 743 (w), 722 (w). UV-Vis (acetonitrile, nm, c = 1.9×10^{-5} M): $\lambda_{max} = 355$, $\varepsilon = 4.3 \times 10^{4}$ L(mol·cm)⁻¹; $\lambda_{max} = 298 \varepsilon = 4.0 \times 10^{4}$ L(mol·cm)⁻¹).

[Co(tppz)₂][PF₆]₂·2CH₃CN (17).

The precursor $[Co(CH_3CN)_6][PF_6]_2$ (100 mg, 0.2 mmol) was dissolved in 20 mL of acetonitrile in a 50 mL round-bottomed flask, and the resulting pink solution was treated with tppz (155 mg, 0.4 mmol). The solution immediately changed to a red color. It was stirred under nitrogen overnight, after which time it was layered with toluene to afford red rectangular crystals; yield, 213 mg (90%). IR (KBr mull) cm⁻¹, 2726 (w), 1317 (w), 1250 (w), 1152 (w), 840 (s,b), 722 (m), 687 (w). UV-Vis (acetonitrile, nm, c = 1.5×10^{-4} M): $\lambda_{max} = 520$, $\varepsilon = 2.3 \times 10^{3}$ L(mol·cm)⁻¹; $\lambda_{max} = 484$, $\varepsilon = 2.3 \times 10^{3}$ L(mol·cm)⁻¹.

$[Fe(tppz)_2][ClO_4]_2$ (18).

The salt $[Fe(H_2O)_6][ClO_4]_2$ 100 mg (0.276 mmol) was dissolved in 30 mL of acetonitrile in a beaker. To this clear solution was added 215 mg (0.553 mmol) of tppz

which led to an instantaneous color change from a clear solution to a dark blue. The blue solution was stirred for 4h, and the volume was decreased by half. The reaction mixture was layered with diethyl ether and blue crystals were obtained within a week; yield, 230 mg (81%). IR (KBr mull) cm⁻¹, 2723 (w), 1320 (w), 1220 (w), 1078 (s,b), 722 (m), 619 (w). UV-Vis (acetonitrile, nm, c = 7.4×10^{-6} M): $\lambda_{max} = 568$, $\varepsilon = 3.7 \times 10^{3}$ L(mol·cm)⁻¹; $\lambda = 341$, $\varepsilon = 4.0 \times 10^{4}$ L(mol·cm)⁻¹; $\lambda_{max} = 242.5$, $\varepsilon = 4.4 \times 10^{4}$ L(mol·cm)⁻¹.

$[Mn(tppz)_2][ClO_4]_2$ (19).

A sample of $[Mn(H_2O)_6][ClO_4]_2$ (100 mg, 0.277 mmol) was placed in a beaker and dissolved in 30 mL of acetonitrile. To this clear solution was added 215 mg (0.55 mmol) of tppz. The solution turned a pale yellow color within a couple of minutes, was stirred for two hours, and finally concentrated to one-half of its original volume. The solution was layered with diethyl ether and a crop of pale yellow crystals was harvested in two days; yield, 215 mg (75%). IR (KBr mull) cm⁻¹, 2723 (w), 1303 (w), 1155 (w), 1099 (s,b), 1012 (m), 722 (w). UV-Vis (acetonitrile, nm, c = 2.9×10^{-5} M): $\lambda_{max} = 351$, ε = 4.1×10^4 L(mol·cm)⁻¹; $\lambda_{max} = 290$, $\varepsilon = 3.5 \times 10^4$ L(mol·cm)⁻¹.

$[Ni(tppz)_2][ClO_4]_2$ (20).

A quantity of $[Ni(H_2O]_6[ClO_4]_2$ (100 mg, 0.275 mmol) was dissolved in 30 mL of acetonitrile in a beaker and treated with two equivalents of tppz (215 mg, 0.549 mmol). The pale blue solution immediately turned yellow. The solution was stirred for four hours, reduced in volume to 15 mL, and layered with toluene to obtain yellow needles; yield, 275 mg (83%). IR (KBr mull) cm⁻¹, 2723 (w), 1568 (w), 1301 (w), 1246 (w), 1148 (w), 1080 (s,b), 788 (w), 769 (m), 723 (w). UV-Vis (acetonitrile, nm, c = 1.4×10^{-5} M): $\lambda_{max} = 355$, $\varepsilon = 4.3 \times 10^4$ L(mol·cm)⁻¹; $\lambda_{max} = 298 \varepsilon = 4.0 \times 10^4$ L(mol·cm)⁻¹.

$[Ni_2(tppz)(CH_3CN)_6][BF_4]_4(21).$

The salt [Ni(CH₃CN)₆][BF₄]₂ (100 mg, 0.2 mmol) was placed in a Schlenk flask under nitrogen and dissolved in 20 mL of freshly distilled acetonitrile. The stirring pale blue solution was treated with tppz (39 mg, 0.1 mmol) which led to a color change to brown-yellow. After stirring overnight, the solution was concentrated, diethyl ether was added, and the solution was chilled to -10 °C. Crystals of [Ni₂(tppz)₂(CH₃CN)₆][BF₄]₄ grew over a period of two weeks; yield, 145 mg (66%). IR (KBr mull) cm⁻¹, 3450 (b,m), 2725 (w), 2316 (m), 1600 (w), 1311 (w), 1301 (w), 1260 (w), 1209 (w), 1018 (s,b), 787 (w), 750 (w), 722 (m). UV-Vis (acetonitrile, nm, c = 1.3×10^{-5} M): $\lambda_{max} = 354$, $\varepsilon = 2.5 \times 10^{4}$ L(mol·cm)⁻¹; $\lambda_{max} = 292 \varepsilon = 2.4 \times 10^{4}$ L(mol·cm)⁻¹; $\lambda = 241$, $\varepsilon = 4.2 \times 10^{4}$ L(mol·cm)⁻¹.

$[Rh(tppz)_2][BF_4]_3$ (23).

A sample of $[Rh_2(CH_3CN)_{10}][BF_4]_3$ 100 mg (0.12 mmol) was loaded into a roundbottomed flask under nitrogen and dissolved in 20 mL of acetonitrile. The orange solution was stirred until the entire solid had dissolved. After which time, 93 mg (0.24 mmol) of tppz were added. This produced a drastic change of color from orange to a dark brown within minutes. The reaction mixture was stirred overnight, and the solution was concentrated and treated with diethyl ether to the point of saturation. The vessel was placed in the freezer, and a microcrystalline compound was collected within five days; yield, 75 mg (48%). IR (KBr mull) cm⁻¹, 1653 (s), 1565 (s), 1155 (w), 1014 (w), 839 (w), 722 (w). UV-Vis (acetonitrile, nm, c = 1.8×10^{-5} M): $\lambda_{max} = 749$, $\varepsilon = 2.9 \times 10^{3}$ L(mol·cm)⁻¹ ; $\lambda_{max} = 517 \varepsilon = 1.6 \times 10^{4}$ L(mol·cm)⁻¹; $\lambda_{max} = 437$, $\varepsilon = 1.4 \times 10^{4}$ L(mol·cm)⁻¹, $\lambda_{max} = 405$, $\varepsilon = 1.4 \times 10^{4}$ L(mol·cm)⁻¹.

[Rh₂(O₂CCH₃)₂(tppz)₂(CH₃OH)₄][PF₆]₆·CH₃OH (24).

A quantity of $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ (100 mg, 0.13 mmol) was dissolved in 20 mL of CH₃OH, and the purple solution was stirred until the entire solid had dissolved. After this time, tppz (52 mg, 0.13 mmol) was added, and the solution was heated to 60 °C to dissolve the tppz. The solution changed to a dark green color within 20 minutes, after which time the heating was ceased and diethyl ether was added to the saturation point. A microcrystalline powder was collected after two days; yield, 65 mg (48%). IR (KBr mull) cm⁻¹, 2724 (w), 1170 (w), 1034 (w), 1846 (s), 769 (w), 722 (w).

$[Co_2(tppz')_2][Co_2Cl_7][PF_6]$ (25).

To a sample of CoCl₂ (100 mg, 0.78 mmol) dissolved in 30 ml of acetonitrile was added tppz (301 mg, 0.78 mmol). An immediate color change from intense blue to a dark green color ensued, and after ten minutes an orange insoluble solid began to deposit on the bottom of flask. The solution was stirred overnight under nitrogen, and the solution was separated from the solid by suction filtration. At this point, the solution was concentrated, and green crystals of the product were obtained by slow vapor diffusion of diethyl ether into acetonitrile within three days; yield, 280 mg (52%). IR (KBr mull) cm⁻¹, 2722 (w), 1585 (w), 1298 (w), 1251 (w), 1143 (w), 1060 (w), 1034 (w), 795 (w), 746 (w). UV-Vis (acetonitrile, nm, c = 2.74×10^{-4} M): $\lambda_{max} = 679.5$, $\varepsilon = 3.77 \times 10^{2}$ L(mol·cm)⁻¹.

$[Ni(tptaz)(CH_3CN)_2(H_2O)][BF_4]_2$ (27).

A sample of $[Ni(CH_3CN)_6][BF_4]_2$ (100 mg, 0.21 mmol) was dissolved in 20 mL of acetonitrile, and tptaz (65 mg, 0.2 mmol) was added to the stirring solution which affected a color change from bright blue to yellow-green. The reaction mixture was

stirred overnight under nitrogen and layered with toluene. (Note that the acetonitrile should not be anhydrous, otherwise crystals do not grow.) Crystals grew over the period of a week; yield, 80 mg (62%). IR (KBr mull) cm⁻¹, 3483 (b,m), 2325 (w), 2298 (w), 1377 (s), 1258 (w), 1060 (w), 1066 (b,s), 773 (w), 722 (w). UV-Vis (acetonitrile, nm, c = 4.96×10^{-5} M): $\lambda_{max} = 293$, $\varepsilon = 5.9 \times 10^{4}$ L(mol·cm)⁻¹, $\lambda_{max} = 253$, $\varepsilon = 2.5 \times 10^{2}$ L(mol·cm)⁻¹.

[Fe(tptaz)₂][ClO₄]₂ (28).

The salt [Fe(H₂O₆)][ClO₄]₂ (100 mg, 0.28 mmol) was dissolved in 30 mL of acetonitrile in a beaker and treated with tptaz (175 mg, 0.56 mmol). The solution, which immediately developed an intense blue color, was stirred for five hours and then concentrated to 15 mL. Blue platelet crystals were obtained by slow diffusion of diethyl ether into the reaction mixture in acetonitrile; yield, 215 mg (82%). IR (KBr mull) cm⁻¹, 1573 (w), 1356 (w), 1258 (w), 1083 (b,s), 768 (w), 622 (w). UV-Vis (acetonitrile, nm, c = 4.6×10^{-5} M): $\lambda_{max} = 568$, $\varepsilon = 6.1 \times 10^{2}$ L(mol·cm)⁻¹, $\lambda_{max} = 341$, $\varepsilon = 6.5 \times 10^{3}$ L(mol·cm)⁻¹, $\lambda_{max} = 243$, $\varepsilon = 4.3 \times 10^{3}$ L(mol·cm)⁻¹.

$[Mn(tptaz)(phen)(H_2O)][O_3SCF_3]_2$ (29).

A sample of Mn(phen)₂(O₃SCF₃)₂ (100 mg, 0.14 mmol) was loaded into a roundbottomed Schlenk flask under nitrogen and dissolved in 20 mL of freshly distilled acetonitrile. The colorless solution was stirred for a few minutes until the solid had dissolved, and tptaz (44 mg, 0.14 mmol) was added, giving a pale green solution. The reaction mixture was stirred overnight and concentrated. Crystals of the product were obtained by slow vapor diffusion of diethyl ether into the acetonitrile solution; yield, 110 mg (91%). IR (KBr mull) cm⁻¹, 1533 (w), 1274 (w), 1222 (w), 1151 (w), 1028 (w), 635 (w). UV-Vis (acetonitrile, nm, c = 6.3×10^{-6} M): $\lambda_{max} = 292$, $\varepsilon = 5.0 \times 10^{4}$ L(mol·cm)⁻¹, $\lambda_{max} = 272$, $\varepsilon = 7.0 \times 10^{4}$ L(mol·cm)⁻¹, $\lambda_{max} = 227$, $\varepsilon = 6.7 \times 10^{4}$ L(mol·cm)⁻¹.

X-ray data collection and Refinement.

X-ray structural studies were performed on crystals of (16)-(29) on a SMART 1K area detector diffractometer equipped with graphite monochromated Mo K α radiation (λ_{α} = 0.71073 Å). The frames were integrated in the Siemens SAINT software package,¹³ and the data were solved using the direct-methods program SHELXS-97.¹⁴ Crystal data are listed for compounds (16)-(29) in Table 16.

$[Ni(tppz)_2][NO_3]_2$ (16).

Single crystals of $[Ni(tppz)_2][NO_3]_2$ (16) were grown by slow diffusion of dichloromethane into an acetonitrile solution of the title compound. A light yellow rectangular crystal of dimensions $0.01 \times 0.04 \times 0.2 \text{ mm}^3$ was secured on the tip of a glass fiber with silicone grease and transferred to the Bruker Smart CCD system. The crystal was cooled to 110 ± 2 K during the data collection via a cold stream of nitrogen gas. A of total 22900 reflections collected of was which 4086 were unique. The two [NO₃]⁻ ions were heavily disordered, therefore restraints for chemically equivalent distances (N-O 1.203 Å) were applied. The final fullmatrix, least-squares refinement was based on 3344 observed reflections with $F_0>4\sigma(F_0)$ which were used to fit 379 parameters to give R1 = 0.0895 and wR2 = 0.2484. The goodness-of-fit index was 0.999 and the highest peak in the final difference map was 1.450 $e^{-1}A^{-3}$. The extensive disorder accounts for the slightly higher than usual R factors.

ic Data for Compounds 16-2	29.		
16	17	18	19
C ₅₀ H ₃₅ N ₁₅ O ₆ Ni ₁	C ₅₀ H ₃₅ N ₁₃ P ₂ F ₁₂ Co ₁	C48H32N12Cl2O8Fe1	C48H32N12Cl2O8Mn1
999.225	1166.175	1030.119	1030.720
C2/c	C2/c	P21/c	I4-2d
27.080(5)	11.701(5)	14.128(3)	13.653(2)
14.524(5)	30.340(5)	18.108(4)	13.653(2)
13.138(5)	14.159(5)	19.873(4)	28.424(6)
60	60	06	06
112.082(5)	100.406(5)	96.83(3)	06
60	06	06	06
4788(3)	4944(3)	5048.1(2)	5298
4	4	4	4
0.392	1.568	1.489	1.292
0.242	0.510	0.478	0.411
22900	11742	25468	13232
4086	4176	85599	2261
R1 = 0.0895	R1 = 0.0605	R1 = 0.0766	R1 = 0.1352
wR2 = 0.2484	wR2 = 0.1014	wR2 = 0.1925	wR2 = 0.3510
R1 = 0.1024	R1 = 0.1015	R1 = 0.1907	R1 = 0.1855
wR2 = 0.2649	wR2 = 0.1146	wR2 = 0.2338	wR2 = 0.3771
0.999	1.083	0.922	1.292
	ic Data for Compounds 16-2 16 C ₅₀ H ₃₅ N ₁₅ O ₆ Ni ₁ 999.225 C ₅₀ H ₃₅ N ₁₅ O ₆ Ni ₁ 999.225 C2/c 27.080(5) 14.524(5) 13.138(5) 90 112.082(5) 90 112.082(5) 90 4788(3) 4788(3	ic Data for Compounds 16-29. 16 17 16 17 IG 17 IG IG IG IG IG IG IG IG	ic Data for Compounds 16-29. 16 16 17 18 16 17 18 C ₅₀ H ₃₅ N ₁₅ O ₆ Ni ₁ C ₅₀ H ₃₅ N ₁₃ P ₂ F ₁₂ Co ₁ 18 99.225 1166.175 P2/rC 99.225 1166.175 P2/rC 99.225 11.701(5) 14.128(3) 14.524(5) 30.340(5) 18.108(4) 13.138(5) 90 96.83(3) 90 13.138(5) 96.83(3) 90 12.082(5) 96.83(3) 90 12.082(5) 96.83(3) 90 12.082(5) 96.83(3) 90 96.83(3) 96.83(3) 90 96.83(3) 96.83(3) 90 96.83(3) 96.83(3) 90 96.83(3) 96.83(3) 91 1742 25468 112.082 873(4) 90 96.853(3) 91 973(4) 90 96.83(3) 91 973(4) 90 96.83(3) 112.082 96.83(3) 91 973(4) 90 96.83(3) 91 973(4) 91 96.83(3) 11

Table 16 (cont'd)				
	20	21	22	23
empirical formula	C ₅₀ H ₃₅ N ₁₃ O ₈ Cl ₂ Ni ₁	C ₃₈ H ₃₇ N ₁₃ B ₄ F ₁₆ Ni ₂	$C_{29}H_{24}N_8B_1P_1F_{10}Cl_4Co_2$	C ₅₆ H ₄₆ N ₁₄ B ₃ F ₁₂ O ₁ Rh ₁
fw	1073.146	1139.212	973.921	1294.312
space group	P2(1)/n	C2/c	C2/c	C222(1)
a,Å	11.783(2)	19.135(4)	13.470(3)	17.991(4)
b,Å	29.819(6)	14.694(3)	18.346(4)	19.836(4)
c,Å	14.066(3)	19.345(4)	16.999(3)	33.970(7)
α	06	06	06	<u> </u>
β	101.38(3)	109.83(3)	107.85(3)	90
. ~	06	06	06	90
V, A^3	4845.0(2)	5116.7(2)	3998.6(1)	12123(4)
Z ,	4	4	7	8
D e/cm ³	1.440	1.536	1.707	1.459
и (mm ⁻¹)	0.579	0.840	1.226	0.373
total data	44378	21891	34759	39610
unique data	8270	6042	6762	14580
R indices	R1 = 0.0749	R1 = 0.0531	R1 = 0.0807	R1 = 0.0725
[]>2مر(])] ^{عل}	wR2 = 0.1974	wR2 = 0.1123	wR2 = 0.2458	wR2 = 0.1861
R indices	R1 = 0.1396	R1 = 0.0759	R1 = 0.1127	R1 = 0.1444
(all data)	wR2 = 0.2254	wR2 = 0.1229	wR2 = 0.2789	wR2 = 0.2317
GOF	0.983	1.074	1.049	0.942

	24	25	26	27
empirical formula	C ₅₆ H ₅₀ N ₁₂ O8P6F ₃₆ Rh4	C48N12H32Cl7P1F6C04	$C_{34}H_{28}B_2F_8N_8Cl_2Co_2$	C22H19N8B2F8O1Ni1
fw	2299.794	1401.766	910.0535	644.75
space group	C2/c	P-31c	P2(1)/c	P-1
a,Å ¯	15.604(5)	15.817(2)	10.903(2)	9.484(5)
b,Å	23.279(5)	15.817(2)	18.434(4)	11.694(5)
c,Å	21/081(5)	21.022(4)	9.321(2)	13.438(5)
ъ	6 0	90	06	111.440(5)
3	110.158(5)	<u> </u>	90.00(3)	95.790(5)
- ~	6 0	120) 06	91.690(5)
$v.A^3$	7189(3)	4554.6(1)	1873.4(7)	1376.(6)
2	4	4	2	0
D 2/cm ³	1.859	1.699	1.604	1.553
u (mm ⁻¹)	1.110	1.362	1.106	0.792
total data	32269	21108	13051	16965
unique data	6137	3754	4485	6596
R indices	R1 = 0.0786	R1 = 0.0519	R1 = 0.0475	R1 = 0.0532
[]>4 ₆ (])] ^{ab}	wR2 = 0.1906	wR2 = 0.0938	wR2 = 0.1119	wR2 = 0.1389
R indices	R1 = 0.1110	R1 = 0.1584	R1 = 0.0801	RI = 0.0937
(all data)	wR2 = 0.2085	wR2 = 0.1813	wR2 = 0.1275	wR2 = 0.1583
GOF	1.086	1.052	0.979	0.995

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Table 16 (cont'd)

	28	29
empirical formula	C42H33N12Cl2O8Fe1	C43H30F8N18O10S6Mn
fw	879.402	1162.18
space group	P-1	P-1
a,Å	10.395(5)	13.103(3)
b,Å	12.079(5)	16.400(3)
c,Å	18.203(5)	19.636(4)
ъ	107.433(5)	111.05(3)
ß	90.261(5)	97.90(3)
	92.602(5)	108.46(3)
V,Å ³	2178.0(1)	3581.9(1)
Z	7	2
D g/cm ³	1.529	1.616
u (mm ⁻¹)	0.542	0.578
total data	25468	16569
unique data	8599	8412
R indices	R1 = 0.0608	R1 = 0.0564
[1>46(1)] ^{ab}	wR2 = 0.1610	wR2 = 0.1272
R indices	R1 = 0.0898	R1 = 0.1237
(all data)	wR2 = 0.2029	wR2 = 0.1500
GOF	1.130	0.905
^a R1 = $\Sigma F_0 - F_c /\Sigma $	$F_0 . bwR2 = [\Sigma[w(F_0^2 - F$	${}_{\rm c}^{2}{}^{$

$[Co(tppz)_2][PF_6]_2(17).$

X-ray quality crystals of $[Co(tppz)_2][PF_6]_2$ were grown by slow diffusion of toluene into an acetonitrile solution of $[Co(tppz)_2][PF_6]_2$ in a thin pyrex tube. A red platelet with dimensions $0.15 \times 0.2 \times 0.1 \text{ mm}^3$ was mounted on a glass fiber using Dow-Corning silicone grease and cooled down to 173 ± 2 K during data collection via a cold stream of nitrogen gas. A total of 11742 reflections was collected, of which 4176 were unique. The final full-matrix least-squares refinement was based on 2916 observed reflections with F₀>4 σ (F₀) that were used to fit 356 parameters to give R1 = 0.0605 and wR2 = 0.1014. The goodness-of-fit index was 1.083 and the highest peak in the final difference map was 0.396 e⁻/Å⁻³.

$[Fe(tppz)_2][ClO_4]_2$ (18).

Single crystals of $[Fe(tppz)_2][ClO_4]_2$ were obtained by slow vapor diffusion of diethyl ether into an acetonitrile solution of $[Fe(tppz)_2][ClO_4]_2$. Data were collected on a dark-blue, rectangle shaped crystal with dimensions of $0.3 \times 0.05 \times 0.25$ mm³ which was mounted on the tip of a glass fiber, secured with silicone grease and placed under a stream of N₂(g) at 110 ± 2 K. A total of 25468 reflections was collected, of which 8599 were unique. Both $[ClO_4]^-$ anions exhibit a 2-fold rotational disorder. In order to solve this problem, restraints for chemically equivalent distances (Cl-O 1.415 Å) were applied. The final full-matrix least-squares refinement was based on 3312 observed reflections with F₀>4 σ (F₀) which were used to fit 647 parameters to give R1 = 0.0766 and wR2 = 0.1925. The goodness-of-fit index was 0.922 and the highest peak in the final difference map was 1.322 e⁻/Å⁻³. The extensive disorder accounts for the slightly high R factor.

$[Mn(tppz)_2][ClO_4]_2$ (19).

Crystals of the title compound were obtained by slow diffusion of toluene into an acetonitrile solution of the title compound. A pale yellow crystal of dimensions $0.2 \times 0.4 \times 0.25 \text{ mm}^3$ was mounted on the tip of a glass fiber with silicone grease and placed in a cold N₂(g) stream at 110 ± 2K. A total of 13232 reflections were collected, of which 2261 were unique. The final full-matrix refinement was based on 2033 observed reflections with F₀>4 σ (F₀) which were used to fit 163 parameters to give R1 = 0.1352 and wR2 = 0.3510. The goodness-of-fit index was 1.29 and the highest peak in the final difference map was 0.898 e⁻/Å⁻³.

$[Ni(tppz)_2][ClO_4]_2$ (20).

X-rays quality crystals of $[Ni(tppz)_2][ClO_4]_2$ were grown by slow diffusion of toluene into an acetonitrile solution of $[Ni(tppz)_2][ClO_4]_2$ in a thin pyrex tube (diameter = 3 mm). A pale yellow needle of dimensions $0.05 \times 0.2 \times 0.06$ mm³ was placed on the tip of a glass fiber, secured with silicone grease, and placed in a N₂(g) stream at 298 ±2 K. A total of 44378 reflections was collected, of which 8270 were unique. One of the $[ClO_4]^-$ anions exhibits a two-fold rotational disorder. In order to solve this problem, restraints for chemically equivalent distances (Cl-O 1.529 Å) were adopted. The final full-matrix, least-squares refinement was based on 3735 observed reflections with F₀>4 σ (F₀) which were used to fit 675 parameters to give R1 = 0.0749 and wR2 = 0.1979. The goodness-of-fit index was 0.983 and the highest peak in the final difference map was 0.939 e'/Å⁻³. As the previous cases, this disorder accounts for the slightly higher R factor.

[Ni₂(tppz)(CH₃CN)₆][BF₄]₄·CH₃CN (21).

Single crystals of (21) were grown by treating a saturated solution of $[Ni_2(tppz)(CH_3CN)_6][BF_4]_4$ in acetonitrile with diethyl ether and placing it in the freezer for two weeks at -5 °C. Crystals formed at the bottom of the flask. A dark yellow platelet with dimensions $0.1 \times 0.24 \times 0.07$ mm³ was covered in paratone oil and quickly mounted on the tip of glass fiber due to the rapid solvent loss. It was secured with Dow Corning silicone grease and placed under a N₂(g) stream at 173 ± 2K. A total of 21891 reflections was collected, of which 6042 were unique. The final full-matrix least-squares refinement was based on 4706 observed reflections with F₀>4 σ (F₀) which were used to fit 343 parameters to give R1 = 0.0531 and wR2 = 0.1123. The goodness-of-fit index was 1.074 and the highest peak in the final difference map was 0.622 e'/Å⁻³.

${[Co_2(tppz)(CH_3CN)_2Cl_4][PF_6][BF_4]}_{\infty}(22).$

Good quality crystals of (22) were obtained by slow diffusion of an acetonitrile solution of the title compound into dichloromethane. A red platelet of dimensions $0.2 \times 0.15 \times 0.08 \text{ mm}^3$ was mounted on the tip of a glass fiber and and placed in a N₂(g) cold stream at 110 ±2 K. A total of 34759 reflections was collected, of which 6762 were unique. The [PF₆]⁻ anions are involved in a two-fold rotational disorder, therefore restraints on the chemically equivalent distances (P-F 1.580 Å) were applied. The final full-matrix refinement was based on 4538 observed reflections with F₀>4 σ (F₀) which were used to fit 563 parameters to give R1 = 0.0807 and wR2 = 0.245. The goodness-offit index was 1.049 and the highest peak in the final difference map was 0.837 e⁷/Å⁻³. This disorder accounts for the high R factor of the refinement of the structure.

$[Rh(tppz)_2][BF_4]_3$ (23).

Single crystals of $[Rh(tppz)_2][BF_4]_3$ were obtained by slow vapor diffusion of diethyl ether into an acetonitrile solution of the title compound. A brown platelet of dimensions $0.02 \times 0.01 \times 0.05$ mm³ was secured on the tip of a glass fiber with silicone grease and placed under a N₂(g) stream at 110 ± 2 K. At the end of the data collection, a total of 39610 reflections had been collected, of which 14580 were unique. The final full-matrix refinement was based on 7715 observed reflections with F₀>4 σ (F₀) which were used to fit 799 parameters to give R1 = 0.0725 and wR2 = 0.1861. The goodness-of-fit index was 0.942 and the highest peak in the final difference map was 1.169 e⁻/Å⁻³.

$[Rh_4(O_2CCH_3)_2(tppz)_2(CH_3OH)_4][PF_6]_6$ (24).

Single crystals of $[Rh_4(O_2CCH_3)_2(tppz)_2(CH_3OH)_4][PF_6]_6$ were obtained by slow diffusion of a toluene solution saturated with $[Bu_4N][PF_6]$ into a solution of the title compound in methanol in a thin pyrex tube (diameter = 3 mm). Crystals grew over a period of two months. A green rectangular platelet of dimensions $0.06 \times 0.03 \times 0.1$ mm³ was mounted on the tip of a glass fiber with silicone grease and placed in a N₂(g) cold stream at 173 ± 2K. At the end of the data collection, a total of 32269 reflections was collected, of which 6137 were unique. Two $[PF_6]^-$ anions are involved in a three-fold rotational disorder. In order to solve this problem, restraints on chemically equivalent distances (P-F 1.671 Å) were applied, and the atoms were refined isotropically. The carbon atoms C(16) and O(4) were also refined isotropically. The final full-matrix, leastsquares refinement was based on 4599 observed reflections with $F_0>4\sigma(F_0)$ which were used to fit 493 parameters to give R1 = 0.0786 and wR2 = 0.1906. The goodness-of-fit index was 1.086, and the highest peak in the final difference map was 2.067 e⁻/Å⁻³, which is not located near any other atoms. The high degree of disorder accounts for the slightly high R factor present in the final refinement.

$[Co_2(tppz')_2]PF_6][Co_2Cl_7]$ (25).

X-ray quality crystals of $[Co_2(tppz')_2][PF_6][Co_2Cl_7]$ were isolated by slow diffusion of toluene into an acetonitrile solution of the title compound in a thin pyrex tube (diameter = 3 mm). A dark green platelet of dimensions $0.09 \times 0.04 \times 0.2$ mm³ was mounted on a tip of glass fiber, secured with silicone grease, and placed in a N₂(g) cold stream at 110 ± 2K. A total of 21108 reflections were collected, of which 3754 were unique. The final full-matrix, least-squares refinement was based on 2310 observed reflections with F₀>4 σ (F₀) which were used to fit 194 parameters to give R1 = 0.0519 and wR2 = 0.1584. The goodness-of-fit index was 1.052 and the highest peak in the final difference map was 0.735 e'/Å⁻³.

$[Co(tpy)_2Cl_2][BF_4]_2$ (26).

X-ray quality crystals were obtained by slow diffusion of toluene into an acetonitrile solution of (26). A pale-red prism of dimensions $0.08 \times 0.23 \times 0.075 \text{ mm}^3$ was mounted on tip of a glass fiber, secured with silicone grease, and placed in a N₂(g) cold stream at 110 ± 2 K. During the data collection process, a total of 13051 reflections was collected, of which 4485 were unique. The final full-matrix, least-squares refinement was based on 2999 observed reflections with F₀>4 σ (F₀) which were used to fit 253 parameters to give R1 = 0.0475 and wR2 = 0.1119. The goodness-of-fit index was 0.979 and the highest peak in the final difference map was 0.939 e'/Å⁻³.

$[Ni(tptaz)(CH_3CN)(H_2O)][BF_4]_2$ (27).

Crystals suitable for X-ray crystallography analysis were obtained by slow diffusion of toluene into an acetonitrile solution of the title compound. A light-green prism of dimensions $0.33 \times 0.22 \times 0.4 \text{ mm}^3$ was secured on a tip of a glass fiber with silicone grease and placed in a stream of cold N₂(g) at 110 ± 2K. During the data collection a total of 16965 reflections was collected, of which 6596 were unique. The final full-matrix, least-squares refinement was based on 4144 observed reflections with F₀>4 σ (F₀) that were used to fit 379 parameters to give R1 = 0.0532 and wR2 = 0.1389. The goodness-of-fit index was 0.995 and the highest peak in the final difference map was 0.948 e⁻/Å⁻³.

[Fe(tptaz)₂][ClO₄]₂ (28).

In order to obtain crystals suitable for X-ray crystallography, diethyl ether was gently layered over a solution of the title compound in acetonitrile. Crystals grew over a period of 5 days. An intense blue colored needle of dimensions $0.5 \times 0.21 \times 0.15$ mm³ was mounted on a tip of a glass fiber, secured with silicone grease and placed in a N₂(g) cold stream at 110 ± 2 K. A total of 25468 reflections was collected, of which 8599 were unique. The final full-matrix, least-squares refinement was based on 7393 observed reflections with F₀>4 σ (F₀) that were used to fit 647 parameters to give R1 = 0.0766 and wR2 = 0.1925. The goodness-of-fit index was 0.891 and the highest peak in the final difference map was 1.322 e⁷Å⁻³.

$[Mn(tptaz)(phen)(H_2O)][Mn(tptaz)(phen)(H_2O)][CF_3SO_3]_4 (29).$

Suitable quality single crystals were obtained by slow vapor diffusion of diethyl ether into an acetonitrile solution of the title compound. A light yellow platelet of dimensions $0.3 \times 0.11 \times 0.35 \text{ mm}^3$ was mounted on the tip of a glass fiber with silicone grease and placed in a N₂(g) cold stream at 110 ± K. A total of 16569 reflections was collected, of which 8412 were unique. The final full-matrix, least-squares refinement was based on 8412 observed reflections with F₀>4 σ (F₀) that were used to fit 991 parameters to give R1 = 0.056 and wR2 = 0.1237. The goodness-of-fit index was 0.983 and the highest peak in the final difference map was 1.427 e⁻/Å⁻³.

II. Results and discussion

A.
$$[M(tppz)_2]^{2+}$$
 Series $(M = Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+})$:

A.1. Synthesis.

A series of compounds of general formula $[M(tppz)_2]^{2+}$ was synthesized by reacting the salts $[M(H_2O)_6][ClO_4]_2$ (M = Ni²⁺, Mn²⁺, Fe²⁺), $[Ni(H_2O)_6][NO_3]_2$ and $[Co(CH_3CN)_6][PF_6]_2$ with two equivalents of tppz in acetonitrile (Eqs. 7 and 8). The reactions were performed in air with the exception of the Co(II) reaction, which was performed under nitrogen. All reactions proceed with a dramatic color change that occurs within minutes of mixing the reagents.



Experimental conditions such as the anion appear to play a major role in the chemistry as judged by the Ni(II) reaction with tppz. The mononuclear complex $[Ni(tppz)_2]^{2+}$ is formed in yields that exceed 80% when perchlorate is used (Eq. 7), but, when $[NO_3]^-$ is used, the yield is only about 58% (Eq. 7) and a significant amount of insoluble, presumably polymeric material is formed. Interesting, when the anion is $[BF_4]^-$, the dinuclear complex $[Ni_2(tppz)(CH_3CN)_6][BF_4]_4$ is the main product of the reaction. In a deliberate attempt to prepare the dinuclear compound $[Ni_2(tppz)(CH_3CN)_6][CIO_4]_4$, different ratios of Ni(II): tppz were used, but all attempts were unsuccessful; regardless of changes in temperature or concentration the sole product was still $[Ni(tppz)_2][CIO_4]_2$. It is apparent that the anion is playing a dominant role in determining whether the nuclearity of the product is monuclear, dinuclear or polymeric.

Solvent is another variable that is important in this chemistry. The compound $[Co(tppz)_2][PF_6]_2$ was obtained in yields greater than 75% (Eq. 8) in acetonitrile, but, if an alcohol or acetone is used instead, the yield drops to less than 50% and insoluble solids are obtained. The same situation is encountered for Fe(II) and Ni(II) as well. It should be emphasized that attempts to synthesize the dinuclear species $[M_2(tppz)(CH_3CN)_6][X]_4$ (M = Co²⁺, Fe²⁺, Mn²⁺; X = [PF_6]⁻, [ClO₄]⁻) were unsuccessful regardless of the ratio of reagents or solvent utilized.

A.2. Spectroscopic and cyclic voltammetric studies.

As indicated from the data in Table 17, compounds (16) through (20) exhibit characteristic MLCT transitions as expected for polypyridine coordination compounds. The tppz moiety with its low lying π^* orbitals are easily accessible for electron promotion from the metal d electrons. The Ni(II) compounds (16) and (20) exhibit two transitions at 355 nm and 298 nm that are assigned to MLCT transitions; the transitions exhibit ε values of ~ 4.3 × 10⁴ mol(L·cm)⁻¹. The cobalt derivative (17) displays two MLCT transitions as well located at 520 and 484 nm with ε values of 2.3 × 10³ mol(L·cm)⁻¹. In the case of [Fe(tppz)₂][ClO₄]₂ (18), there are three MLCT transitions located at 568, 341 and 242 nm; their respective ε values are 3.7 × 10³, 4.0 × 10⁴ and 4.4 × 10⁴ mol(L·cm)⁻¹. Finally, [Mn(tppz)₂][ClO₄]₂ (19) exhibits two MLCT transitions located at 352 and 290 nm with ε values of 4.1 × 10⁴ and 3.5 × 10⁴ mol(L·cm)⁻¹ respectively.

Table 17. UV-Visible data for compounds (16)-(20).					
	λ(nm)	ε mol(L·cm) ⁻¹			
$[Ni(tppz)_2][X]_2 (16) X = [NO_3]^T (20) X = [ClO_4]^T$	298 355	4.3×10^4 4.3×10^4			
(17) [Co(tppz) ₂][PF ₆] ₂	520 484	2.3×10^{3} 2.3×10^{3}			
(18) [Fe(tppz) ₂][ClO ₄] ₂	568 341 243	$ \begin{array}{r} 3.7 \times 10^{3} \\ 4.0 \times 10^{4} \\ 4.4 \times 10^{4} \end{array} $			
(19) [Mn(tppz) ₂][ClO ₄] ₂	352 290	4.1×10^4 3.5×10^4			

Cyclic voltammetry confirmed the accessibility of the π^* orbitals in compounds (16)-(19). shows a very rich electrochemistry in the range 0 to -1.8 volts. Compound $[Fe(tppz)_2][ClO_4]_2$ (18) exhibits the most impressive electrochemical properties with four

reversible reduction couples and a reversible oxidation. The oxidation couple occurs at $E_{\frac{1}{2}} = +1.37$ V and corresponds to the oxidation of Fe(II) to Fe(III). The ligand-based reductions occur in the range -0.4 to -1.8 V at $E^{(1)}_{\frac{1}{2}} = -0.77$, $E^{(2)}_{\frac{1}{2}} = -1.04$, $E^{(3)}_{\frac{1}{2}} = -1.50$ and $E^{(4)}_{\frac{1}{2}} = -1.67$ V (Figure 47). These cyclic voltammetry measurements allow for the



Figure 47. Cyclic voltammogram for [Fe(tppz)₂][ClO₄]₂ in acetonitrile with 0.1 M [n-Bu₄N][PF₆].

calculation of the comproportionation constant (K_c) for the stability of the mixed-valence intermediates as each ligand is reduced.⁴ The comproportionation constant for the first two couples is 3.7×10^4 , whereas the second set of reductions gives a value of 7.5×10^2 (scheme 3). These equilibrium constants correspond to class II and class I borderline behavior for the stability of the mixed valence species, respectively. In the first case, the electrons are partially delocalized throughout the system, therefore the mixed valence intermediate is moderately stable. In the latter case, the mixed valence species is rather unstable and corresponds to nearly insulating behavior.

$$[Fe(tppz)_2]^{2+} \qquad \underbrace{+e}_{-e} \qquad [Fe(tppz)_2]^{4+} \qquad K_c = 3.7 \times 10^4$$

$$[Fe(tppz)_2]^+ \qquad \underbrace{+e}_{-e^-} \qquad [Fe(tppz)_2]$$

$$[Fe(tppz)_2] \qquad \underbrace{+e^{-}}_{-e^{-}} \qquad [Fe(tppz)_2]^{-}$$

$$K_c = 7.5 \times 10^2$$

$$[Fe(tppz)_2]^{-1} \qquad \underbrace{+e}_{-e} \qquad [Fe(tppz)_2]^{2-1}$$

Scheme 3.

The Ni(II) derivative, $[Ni(tppz)_2][ClO_4]_2$ (20), exhibits three redox events, namely a reversible reduction at $E_{\frac{1}{2}} = -0.79$ V, follow by a irreversible cathodic wave at $E_{p,c} = -1.2$ V and finally a quasireversible reduction at $E_{\frac{1}{2}} = -1.61$ V with subsequent decomposition of the reduced species. These data represent an electrochemical, chemical, electrochemical (ECE) series of processes.¹⁵

 $[Mn(tppz)_2][ClO_4]_2$ displays an irreversible couple at E = +1.22 V attributed to the oxidation of Mn(II) to Mn(III) with the subsequent decomposition of the main species. Two reversible ligand based reductions were observed, the first one being at $E_{1/2} = -1.1$ V which involves one electron, and the second one located at $E_{1/2} = -1.7$ V that involves two electrons.

Finally, $[Co(tppz)_2][PF_6]_2$ (17) exhibits two reversible ligand based reductions and a reversible oxidation. The oxidation couple occurs at $E_{\frac{1}{2}} = +0.41$ V and corresponds to an oxidation of Co(II) to Co(III). The reduction, at $E^{(1)}_{1/2} = -0.28$ V and $E^{(2)}_{1/2} = -1.18$ V each correspond to a two electron process.

A.3. X-ray crystallographic results.

In the mononuclear compounds, the metal centers reside in highly distorted octahedral environments, as indicated by the angle between the pyridyl moiety and the pyrazine unit with the metal center. This value averages $\sim 80^{\circ}$ as compared to the expected 90° for an ideal octahedron; the specific angles for the Mn(II), Fe(II), Co(II) and Ni(II) compounds are 72.3° (2), 81.4° (3), 79.2° (8) and 78.3°(2) respectively (Figures 49-53). The average M-N distances to the pyrazine moiety for the different compounds are 1.870 [3], 1.892 [4], 1.986 [3] and 2.228 [4] Å for Fe(II), Co(II), Ni(II) and Mn(II) respectively. The M-N distances to the pyridyl moiety are 1.952 [4], 2.052 [3], 2.094 [4] and 2.241 Å for Fe(II) Co(II), Ni(II) and Mn(II) respectively. The gradual increase in the M-N distances is due to an increase in the radii of the metal centers.

The ligand unit itself undergoes considerable distortion upon coordination. The pyrazine ring is not planar in any of the compounds, as determined from X-ray structural determinations (**(()**) (Figure 48). The greatest distortion is found in [Co(tppz)₂][PF₆]₂·CH₃CN (17); in this case, there is a torsion angle of 10.7° (ϕ). The second largest distortion is exhibited by $[Ni(tppz)_2][ClO_4]_2$ (20), with a value of 9.8° (ϕ), followed by $[Mn(tppz)_2][ClO_4]_2$, 5.5° (ϕ), and finally the smallest distortion is found in $[Fe(tppz)_2][ClO_4]_2$ (18) at 4.8° (ϕ) (Table 18). The planes between the coordinated pyridyl groups are not coplanar in these compounds with the exception of $[Fe(tppz)_2][ClO_4]_2$ (18). In the Fe²⁺ compound, the pyridyls rings are nearly coplanar with a dihedral angle of only 0.2°. The Mn²⁺ and Co²⁺ analogues display the largest deviation from coplanarity with 13.5 and 13.2° angles respectively (κ , Table 18). The compound $[Ni(tppz)_2][ClO_4]_2$ (**20**) displays a deviation of 6.12° (κ , Table 18). The non-coordinated pyridyl rings exhibit much larger dihedral angles (β) between the planes (Figure 48) These values are 13.7°, 44.3°, 58.2° and 72.8° for Co^{II}, Ni^{II}, Mn^{II} and Fe^{II} respectively (β , Table 18) (Figure 48).

Table 18. Values of the distortions exhibited by the tppz ligand by coordination to Co(II) (17), Ni(II) (16), Mn(II) (19) and Fe(II) (18).						
	φ (°)	θ (°)	β (°)	κ (°)		
$\left[\operatorname{Co}(\operatorname{tppz})_2\right]^{2+}$	10.7	44.9	13.74	13.2		
[Ni(tppz) ₂] ²⁺	9.8	66.9	44.3	6.1		
[Mn(tppz) ₂] ²⁺	5.5	63.4	58.2	13.5		
[Fe(tppz) ₂] ²⁺	4.8	59.6	72.8	0.2		





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Tahle 10	Selected hond	distances (\mathring{A})	and angles (°)	for [Ni(tonz	100 - 100
Table 17.	Sciected bond	uistances (A)	and angles ()	ioi [ini(ippz	

Ni1-N(2)#1	2.002(4)	Ni1-N6	2.093(5)
Ni1-N2	2.002(4)	Nil-Nl	2.118(4)
Ni1-N(6)#1	2.093(4)	Ni1-N(1)#1	2.118(4)
N2-Ni1-N(2)#1	177.7(2)	N6-Ni1-N1	98.37(16)
N(2)#1-Ni1-N(6)#1	104.01(16)	N(6)#1-Ni1-N1	155.49(16)
N2-Ni1-N(6)#1	77.63(16)	N1-Ni1-N(1)#1	83.0(2)
N(2)#1-Ni1-N6	77.63(16)	N2-Ni1-N1	78.05(16)
N2-Ni1-N6	104.01(16)	N6-Ni1-N(1)#1	155.49(16)
N6-Ni1-N(6)#1	90.4(2)	N(6)#1-Ni1-N(1)#1	98.37(16)
N(2)#1-Ni1-N1	100.22(16)		. ,

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+1/2

Col-N2	1.859(4)	Col-N6	2.134(3)
Col-N5	1.925(4)	Co1-N(1) #1	1.970(3)
Col-N1	1.970(3)	Co1-N(6)#1	2.134(3)
N1-Co1-N(1)#1	164.49(17)	N(1)#1-Co1-N(6)#1	94.33(12)
N2-Co1-N(6)#1	100.80(8)	N2-Co1-N(6)#1	100.80(8)
N5-Co1-N(6)#1	79.20(8)	N5-Co1-N6	79.20(8)
N1-Co1-N(6)#1	88.57(12)	N1-Co1-N6	94.33(12)
N2-Co1-N5	180.02(5)	N1-Co1-N(6)#1	88.57(12)
N2-Co1-N1	82.25(8)	N6-Co1-N(6)#1	158.39(16)
N5-Co1-N1	97.75(8)	N5-Co1-N1	97.75(8)
N2-Co1-N(1)#1	82.25(8)		

Table 20. Selected bond distances (Å) and angles (°) for [Co(tppz)₂][PF₆]₂·CH₃CN (17).

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2







Figure 50. Thermal ellipsoid representation of cation in [Co(tppz)₂][PF₆]₂·CH₃CN (17) with 50 % ellipsoids. Hydrogen atoms have been omitted for the sake of clarity.

Fe1-N2	1.865(6)	Fe1-N3	1.952(7)
Fe1-N12	1.876(6)	Fe1-N7	1.954(6)
Fe1-N11	1.945(6)	Fe1-N1	1.955(6)
N2-Fe1-N12	178.6(3)	N11-Fe1-N7	162.3(3)
N2-Fe1-N11	98.3(3)	N3-Fe1-N7	88.6(3)
N12-Fe1-N11	81.4(3)	N2-Fe1-N1	81.4(3)
N2-Fe1-N3	81.5(3)	N12-Fe1-N1	100.0(3)
N12-Fe1-N3	97.2(3)	N11-Fe1-N1	87.0(3)
N11-Fe1-N3	94.2(3)	N3-Fe1-N1	162.8(3)
N2-Fe1-N7	99.4(3)	N7-Fe1-N1	95.4(3)
N12-Fe1-N7	80.9(3)		

Table 21. Selected bond distances (Å) and angles (°) for [Fe(tppz)₂][ClO₄]₂ (18).

Table 22. Selected bond distances (Å) and angles (°) for [Mn(tppz)₂][ClO₄]₂ (19).

Mn(1)-N(2)#1	2.227(8)	Mn(1)-N(1)#1	2.241(11)
Mn(1)-N(2)	2.227(8)	Mn(1)-N(1)#2	2.241(11)
Mn(1)-N(1)	2.241(11)	Mn(1)-N(1)#3	2.241(11)
N(2)#1-Mn1-N2	180.0	N(1)#1-Mn1-N(1)#2	144.7(4)
N(2)#1-Mn1-N(1)#1	72.3(2)	N1-Mn1-N(1)#2	95.29(12)
N2-Mn1-N(1)#1	107.7(2)	N(2)#1-Mn1-N(1)#3	107.7(2)
N(2)#1-Mn1-N(1)	107.7(2)	N2-Mn1-N(1)#3	72.3(2)
N2-Mn1-N1	72.3(2)	N(1)#1-Mn1-N(1)#3	95.29(12)
N(1)#1-Mn1-N1	95.29(12)	N1-Mn1-N(1)#3	144.7(4)
N(2)#1-Mn1-N(1)#2	72.3(2)	N(1)#2-Mn1-N(1)#3	95.29(12)
N2-Mn1-N(1)#2	107.7(2)		

Symmetry transformations used to generate equivalent atoms: #1 y,-x+1,-z ; #2 -y+1,x,-z #3 -x+1,-y+1,z; #4 x+0,-y+1/2,-z+1/4

Another aspect that should be considered is that the nitrogen atoms of the noncoordinated, pyridyls rings are rotated away from each other, and do not form a terpy coordination environment.

The final angle to note in these compounds is the one between the coordinated and non-coordinated pyridyl rings. These deviations from coplanarity are quite large (θ in



Figure 51. Thermal ellipsoid representation of the molecular cation in [Fe(tppz)₂][ClO₄]₂ (18) with 50% probability ellipsoids. Hydrogen atoms have omitted for the sake of clarity.



Figure 52. Thermal ellipsoid diagram of the cation in [Mn(tppz)₂][ClO₄]₂·CH₃CN (19) with the unique unit atoms labeled with 50% ellipsoids. Hydrogen atoms were omitted for the sake of clarity. Table 18 and Figure 48). All the values are near 60° with the exception of the Co^{II} analogue. The specific values are 44.9°, 59.6°, 63.4° and 66.9° for Co^{II}, Fe^{II}, Mn^{II} and Ni^{II} respectively. This deviation is in response to the steric interaction between the 2' hydrogen atoms of the pyridyl rings.

It is obvious from the X-ray structures of compounds (16)-(20) that the tppz moiety in these complexes experiences a great deal of distortion upon coordination. This observation helps to explain the difficulties encountered in using these as precursors for the self-assembly of larger supramolecular entities and the lack of electronic coupling between the two ligands, as evidenced by spectroscopic methods and cyclic voltammetry as previously discussed.

Table 23. Selected bond distances (Å) and angles (°) for [Ni(tppz) ₂][ClO ₄] ₂ (20).					
Ni1-N2	1.981(4)	Ni1-N3A	2.091(5)		
Ni1-N2A	1.990(5)	Nil-N1A	2.094(5)		
Ni1-N3	2.082(5)	Nil-Nl	2.101(5)		
N2-Ni1-N2A	176.46(19)	N3-Ni1-N1A	94.99(18)		
N2-Ni1-N3	78.70(18)	N3A-Ni1-N1A	157.24(19)		
N2A-Ni1-N3	99.59(18)	N2-Ni1-N1	78.39(18)		
N2-Ni1-N3A	97.81(18)	N2A-Ni1-N1	103.36(18)		
N2A-Ni1-N3A	78.99(18)	N3-Ni1-N1	157.05(18)		
N3-Ni1-N3A	88.30(18)	N3A-Ni1-N1	96.09(19)		
N2-Ni1-N1A	104.92(18)	N1A-Ni1-N1	89.63(18)		
N2A-Ni1-N1A	78.26(19)				


Figure 53. Thermal ellipsoid drawing of the molecular cation in [Ni(tppz)₂][CIO₄]₂ (20) with 50% probability ellipsoids. Hydrogen atoms have been omitted for the sake of clarity.

B. Synthesis of the dinuclear compound [Ni₂(tppz)(CH₃CN)₆][BF₄]₄.

B.1. Synthesis

In all previous cases, attempts to synthesize a dinuclear compound of the form $[M_2(tppz)(CH_3CN)_6][X]_4$ where $M = Mn^{II}$, Fe^{II} and Co^{II} were unsuccessful regardless of the ratio of reagents, solvent, anion or temperature conditions. The exception to this situation is Ni^{II}. In this particular case, the choice of anion appears to play an important role in whether the product is mononuclear or dinuclear, as previously discussed. In the presence of $[BF_4]^-$, the dinuclear product is formed rather than the mononuclear form. The reaction was performed under anaerobic conditions in acetonitrile in a 2:1 ratio of $[Ni(CH_3CN)_6][BF_4]_2$ and tppz (Eq. 9).

$$2[Ni(CH_3CN)_6][BF_4]_2 + tppz \qquad \longrightarrow [Ni_2(tppz)(CH_3CN)_6][BF_4]_4 \quad (Eq. 9)$$

yield: 66%

The reaction proceeds instantaneously, with the solution changing from a pale blue to a dark yellow color within minutes. Solvent is another variable that has to be taken into consideration. Alcohols and water promote the formation of insoluble products. Aprotic solvents, such as acetone or dichloromethane promote the formation of the mononuclear form as indicated by IR and UV-Visible spectroscopies. The only conditions that appear to favor the assembly of the dinuclear complex are the combination of CH_3CN and $[BF_4]^-$

Crystals of $[Ni_2(tppz)(CH_3CN)_6][BF_4]_4$ were obtained by adding diethyl ether to a concentrated solution of the compound in acetonitrile and placing it in the freezer at

-10°C for 10 days. The crystals are highly hygroscopic and readily decompose in the presence of moisture.

B.2. Spectroscopic and cyclic voltammetric studies.

UV-Visible spectroscopic studies of the dinuclear compound $[Ni_2(tppz)(CH_3CN)_6][BF_4]_4$ in acetonitrile led to the observation of three electronic transitions. Two of the transitions are nearly identical to the mononuclear species $[Ni(tppz)_2][ClO_4]_2$ (20) and appear at $\lambda_{max} = 354$ and 292 nm with $\varepsilon = 2.5 \times 10^4$ and 2.4 $\times 10^4$ L·(mol·cm)⁻¹ respectively. In addition to the previous two transitions, there is a third feature at $\lambda_{max} = 241$ nm ($\varepsilon = 4.2 \times 10^4$ (L·(mol·cm)⁻¹). As in the previous case, these transitions can be assigned to MLCT transitions between the metal center and low lying π^* orbitals in tppz.

The cyclic voltammogram exhibits one reversible reduction at $E_{\nu_2} = -0.4$ V, a quasireversible reduction at $E_{\nu_2} = -1.10$ V and a reduction wave at $E_{p,c} = -1.5$ volts without accompanying wave. These studies indicate that weak electronic coupling between the two Ni^{II} centers is occurring. As will be pointed out in the next section, the weak coupling can be attributed to the disruption of planarity of the pyrazine ring upon coordination of both Ni^{II} centers, with the subsequent disruption of the π -system.

B.3. X-ray crystallographic studies.

The Ni^{II} center resides in a highly distorted octahedral geometry with the angle between the pyridyl and pyrazine rings and the metal center of N(3)-Ni(1)-N(2) = 78.1 (3)° (Figure 60). The angle between the acetonitrile ligands is close to the ideal value 90° (N(5)-Ni(1)-N(6) = 88.3 (2)°). The shortest M-N distance is to the pyrazine ligand at Ni(1)-N(2) = 2.025 (2) Å, followed by the M-N(CH₃CN) distances at an average value of





2.083 [3] Å. The longest M-N distance is to the pyridyl ring (2.104 [3] Å). The two coordinated pyridyl rings are not coplanar to each other, possessing a dihedral angle of 9.2 °. The central pyrazine ring is twisted at an angle of 12.9°.

Ni1-N2	2.025(2)	Nil-Nl	2.100(2)
Ni1-N5	2.043(2)	Ni1-N3	2.108(2)
Ni1-N6	2.090(3)	Ni1-N4	2.115(3)
N2-Ni1-N5	177.31(10)	N5-Ni1-N1	100.08(9)
N2-Ni1-N6	89.94(9)	N6-Ni1-N1	94.64(9)
N5-Ni1-N6	88.26(10)	N2-Ni1-N3	78.06(8)
N2-Ni1-N1	78.08(8)	N5-Ni1-N3	103.84(9)

Table 24. Selected bonds (Å) and angles (°) for [Ni₂(tppz)(CH₃CN)₆][BF₄]₄·CH₃CN (21).

C. Reactivity studies of $[M(tppz)_2]^{2+}$ (M = Ni^{II}, Fe^{II}, Co^{II}, Mn^{II}) and $[Ni_2(tppz)(CH_3CN)_6]^{4+}$.

As stated earlier, the goal of synthesizing and characterizing the mononuclear species $[M(tppz)_2]^{2+}$ and the dinuclear compounds represented by $[Ni_2(tppz)(CH_3CN)_6]^{4+}$ is to use them in the assembly of extended arrays. Several approaches were undertaken to connect these precursors through their accessible coordination sites, (see Figure 6, Chapter I). One attempt involved the reaction of $[Ni_2(tppz)(CH_3CN)_6]^{4+}$ with two equivalents of the mononuclear species $[Co(tppz)_2]^{2+}$, with the aim of synthesizing the tetranuclear species $[(tppz)Co(tppz)Ni(tppz)Ni(tppz)Co(tppz)]^{8+}$. Various reaction conditions were used, including different solvents such as acetonitrile, acetone, dichloromethane and alcohols, and various temperature conditions. The outcome in every case was the isolation of mononuclear species such as $[Ni(tppz)_2]^{2+}$, $[Co(tppz)_2]^{2+}$ as corroborated by X-ray crystallography. Another approach that was taken is to use

FeCl₃(tpy) as the source of the second coordinating metal. In this particular case, Fe(tpy)Cl₃ was reacted with the $[M(tppz)_2]^{2+}$ complexes in a 2:1 ratio. The products that were isolated are $[Fe(tppz)_2]^{2+}$, Fe(tppz)Cl₂ and $[Fe(tpy)_2]^{2+}$, which result from ligand redistribution and reduction of Fe(III) to Fe(II). These results indicate the that the $[Fe(tppz)_2]^{2+}$ species is quite stable.

Additional attempts to prepare oligomers were performed in which the included reactions of [M(tppz)2]2+ with two equivalents of $[M(CH_3CN)_6][X]_2$ or $[M(H_2O)_6][X]_2$ $(M = Ni^{II}, Co^{II}, Fe^{II}; X = [BF_4]^{-}, [ClO_4]^{-})$. This reaction is based on the fact that two the dangling coordination sites on $[M(tppz)_2]^{2+}$ cations could allow for a trinuclear product to be assembled. In most cases, an insoluble product was obtained, suggesting that a polymer or higher order oligomer is being formed. On several occasions, crystals were isolated, but these were inevitably the mononuclear species $[M(tppz)_2][X]_2$.

D. Reactions of CoCl₂ with tppz and tpy ligands.

D.1. Synthesis.

After noting that $[Co(tpp2)_2][PF_6]_2$ (17) exhibits spin-crossover behavior we became interested in adding two additional Co(II) centers at the open coordination sites to produce a trinuclear complex (Figure 55). The presence of three Co^{II} ions instead of one could lead to cooperative spin crossover or even multiple step spin crossover. In pursuit of the proposed trinuclear compound, a Co^{II} starting material that possesses three open coordinating sites, namely [mer-Co(tpy)(CH₃CN)₃][BF₄]₂ was used. In an attempt to prepare the unknown compound [Co(tpy)(CH₃CN)₃][BF₄]₂, CoCl₂ was treated in a 1:1 ratio with tpy in order to first prepare [Co(tpy)Cl₂(CH₃CN)]. The next step was to abstract the Cl⁻ ions from [Co(tpy)Cl₂(CH₃CN)] with AgBF₄ in acetonitrile so that the compound [Co(tpy)(CH₃CN)₃][BF₄]₂ could be obtained.



Figure 55. Schematic drawing of the proposed synthesis of $[Co_3(tpy)_2(tppz)_2]^{6+}$ from the reaction of $[Co(tppz)_2][PF_6]_2$ with two equivalents of $[Co(tpy)(CH_3CN)_3][BF_4]_2$.

We reasoned that this mononuclear partially solvated species, would be an ideal building block because of the presence of the tpy capping ligand. Instead of the anticipated $[Co(tpy)(CH_3CN)_3][BF_4]_2$ compound however, the dinuclear compound $[Co_2(tpy)_2(CH_3CN)_2Cl_2][BF_4]_2$ (26) with two bridging Cl⁻ ions was obtained instead. The



Figure 56. Rearrangment of the tppz ligand in the presence of CoCl₂.

reaction of $[Co_2(tpy)_2(CH_3CN)_2Cl_2][BF_4]_2$ with $[Co(tppz)_2][BF_4]_2$ in the presence of an excess of $[n-Bu_4N][PF_6]$ afforded the polymer $\{[Co_2(tppz)_2(CH_3CN)_2Cl_2][BF_4][PF_6]\}_{\infty}$ (22). The product is a 1-D chain with alternating bridging $Co(\mu-Cl)_2Co$ and Co(tppz)Co units.

Once the existence of $\{[Co_2(tppz)_2(CH_3CN)_2Cl_2][BF_4][PF_6]\}_{\infty}$ (22) had been confirmed by X-ray crystallography, a more direct route to its synthesis was attempted. The polymeric material CoCl₂ was used as the source of Co^{II} and reacted in 1:1 ratio with tppz. The outcome of this reaction is an unexpected rearrangement of the tppz moiety, as shown in Figure 63. This ligand rearrangement allows for the coordination of two Co(II) centers in a molecular square (Figure 66).

D.2. Spectroscopic and cyclic voltammetric studies.

The cyclic compound $[Co_2(tppz')_2][PF_6][Co_2Cl_7]$ (25) displays two electronic transitions in the UV-visible spectrum, at $\lambda_{max} = 680$ nm ($\varepsilon = 3.7 \times 10^2$ L·(mol·cm)⁻¹) and $\lambda_{max} = 588$ nm ($\varepsilon = 3.7 \times 10^2$ L·(mol·cm)⁻¹). Both transitions can be assigned to MLCT transitions in which electrons from the d orbitals of the metal are promoted to the low lying π^* LUMO of the tppz ligand.

The cyclic voltammogram displays an irreversible reduction wave at $E_{p,c} = -0.75$ V; there is no evidence of an oxidation of the metal up to 2.0 V.

D.3. X-ray crystallographic studies.

In the tpy derivative $[Co_2Cl_2(tpy)_2(CH_3CN)_2][BF_4]_2$ (26), the Co(II) center resides in a highly distorted octahedral environment as illustrated in Figure 57. The pyridyl and the pyrazine interaction with the metal is N(1)-Co(1)-N(2) = 76.15 (3)°, which is a 13.8° deviation from an ideal 90° angle. The acetonitrile and the pyrazine moieties are separated by N(4)-Co(1)-N(2) = 99.92 (2)°, which is a 9.9° deviation from ideal octahedral coordination. Finally, the two bridging chlorine angle Cl(1)-Co(1)-Cl(1)* = $86.24 (3)^{\circ}$. The Co-N distances (in increasing order) are N(2)-Co(1) = 2.078 (3) Å, N(4)-Co(1) = 2.127 (3)Å, and N(1)-Co(1) = 2.146 (3)Å for pyrazine, acetonitrile and pyridyl interactions, respectively. The metal centers are 3.562 Å apart. It is worth noting that the midpoint of the dinuclear unit resides on an inversion center; thus, only one-half of the molecule is unique.

Table 25. Selected bond distances (Å) and angles (°) for[Co2Cl2(tpy)2(CH3CN)2][BF4]2. (26).			
Co1-N2	2.078(3)	Col-Nl	2.150(3)
Col-N4	2.127(3)	Col-Cll	2.3679(9)
Col-N3	2.141(3)	Co1-Cl2	2.510(1)
N2-Co1-N4	99.92(10)	N3-Co1-N1	151.36(10)
N2-Co1-N3	75.64(10)	N2-Co1-Cl1	172.58(7)
N4-Co1-N3	90.67(10)	N4-Co1-Cl1	87.29(8)
N2-Co1-N1	76.15(10)	N3-Co1-Cl1	102.68(7)
N1-Co1-Cl1	105.93(8)	N2-Co1-Cl1	86.49(7)
N4-Col-N1	89.38(10)	N4-Co1-Cl1	173.17(7)

The compound $\{[Co_2Cl_2(tppz)(CH_3CN)_2][BF_4][PF_6] \cdot CH_2Cl_2\}_{\infty}$ (22) was obtained from the reaction of $[Co_2Cl_2(tpy)(CH_3CN)_2][BF_4]_2$ (26) in a 2:1 ratio with acetonitrile. This $[Co(tppz)_2][PF_6]_2$ in compound is similar to $[Co_2Cl_2(tpy)(CH_3CN)_2][BF_4]_2$ (26), but, in this case, the tpy ligands have been substituted by tppz units, which allows for the growth of a 1-D polymer (Figure 58). The Co(II) centers are linked on one side by bridging Cl⁻ ions and on the other side by a tppz unit. The two Co(II) centers linked by the Cl- ions are 3.509 Å apart from each other, which is 0.053 Å shorter than in the dinuclear compound [Co₂(tpy)Cl₂(CH₃CN)₂][BF₄]₂





(26) (Figure 57). The distance between Co^{II} centers linked by the tppz unit is much larger, namely 6.792 Å, which is nearly twice the distance between Co^{II} centers bridged by two Cl⁻ ions. Each metal center is in a very distorted octahedral coordination environment that consists of one tppz, one CH₃CN and two Cl⁻ ions. Three of the coordination sites are occupied by the tppz ligand, one by an acetonitrile molecule, and finally two bridging chlorine atoms (Figure 64).

Table	26.	Selected bond di {[Co ₂ (tppz)(CH ₃ CN) ₂ C	stances (Å) [2][BF4][PF6] · CH	and angles H ₂ Cl ₂ } _∞ (22).	(°)	for
Col-N5		2.085(6)	Co2-N2		2.08	1(6)
Col-N6		2.102(6)	Co2-N1		2.114	4(6)
Col-N8		2.112(7)	Co2-N7		2.122	2(7)
Col-N4		2.113(6)	Co2-N3		2.120	5(6)
Col-Cll		2.326(2)	Co2-Cl2		2.319	9(2)
Col-Cl2		2.563(2)	Co2-Cl1		2.56	1(2)
N5-Co1-	N6	75.4(2)	N2-Co2-N1		76.'	7(2)
N5-Col-	N8	95.8(2)	N2-Co2-N7		94.9	9(2)
N6-Co1-	N8	88.5(2)	N1-Co2-N7		91.9	9(2)
N5-Col-	N4	76.0(2)	N2-Co2-N3		75.2	2(2)
N6-Co1-	N4	151.3(2)	N1-Co2-N3		151.7	7(2)
N8-Col-	N4	92.2(2)	N7-Co2-N3		87.3	3(2)
N5-Co1-	Cll	171.72(16)	N2-Co2-Cl2		171.67((17)
N6-Col-	Cll	103.63(16)	N1-Co2-Cl2		102.70	(16)
N8-Col-	Cll	92.34(19)	N7-Co2-Cl2		93.46((19)
N4-Co1-	Cll	105.01(16)	N3-Co2-Cl2		105.60((16)
N5-Col-	Cl2	83.65(16)	N2-Co2-Cl1		83.34((16)
N6-Col-	Cl2	89.66(17)	N1-Co2-Cl1		90.10	(16)
N8-Co1-	Cl2	178.12(19)	N7-Co2-Cl1		176.91	(19)
N4-Col-	Cl2	89.47(16)	N3-Co2-Cl1		89.80	(17)
Cl1-Co1	-Cl2	88.14(7)				

The angle between the pyridyl and pyrazine ring in this polymer is 75.7 [3]°, which represents a 14.3° difference from the ideal value of 90°. The two chlorine atoms are asymmetrically bound, as evidenced by the two distances Co(1)-Cl(1) = 2.326 (2)Å



(a) Thermal ellipsoid representation of the 1-D polymer {[Co₂Cl₂(tppz)₂(CH₃CN)₂][BF₄][PF₆]}_~ (22) with 50% probability ellipsoids. (b) Asymmetric unit diagram with 50% probability ellipsoids. Figure 58.

and Co(1)-Cl(2) = 2.563 (2)Å. In the case of the Co(2)-Cl angles, the inverse situation is encountered (Figure 58). The Cl(2)-Co(1)-N(4) angle is 89.5 (2)°, which is close to the ideal value of 90°. On the other hand, the Cl(1)-Co(1)-N(6) angle is 103.6 (2)°, which is a large deviation from 90°. The M-N distance trend was the same as that observed in $[Co_2(tpy)Cl_2(CH_3CN)_2][BF_4]_2$ (26). The angles are Co(1)-N(5) = 2.086 (6) Å, Co-N(6)/(4) = 2.108 [3] Å, and Co(1)-N(8) = 2.113 (6)Å for pyrazine, pyridyl and acetonitrile interactions, respectively.

(25).	and distances (A) and	d angles (°) for	{ [Co ₂ (tppz ⁺) ₂][PF ₆][Co ₂ Cl ₇]
Col-N1	2.112(3)	Col-N2A	2.149(3)
Col-N1A	2.112(3)	Col-N2B	2.149(3)
Col-N1B	2.112(3)	Col-N2C	2.149(3)
N1-Co1-N1A	98.86(11)	N1-Co1-N2B	88.64(12)
N1-Co1-N1B	98.86(11)	N2A-Co1-N2	95.84(12)
N1A-Co1-N1B	98.86(11)	N1A-Co1-N2C	171.99(12)
N1-Co1-N2	88.64(12)	N1B-Co1-N2C	88.64(12)
N1A-Co1-N2	77.05(12)	N1B-Co1-N2C	77.05(12)
N1B-Co1-N2	171.99(12)	N2B-Co1-N2C	95.84(12)
N1A-Co1-N2B	77.05(12)	N2-Co1-N2C	95.84(12)
N1B-Co1-N2B	171.99(12)		. ,

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In $[Co_2(tppz')_2][PF_6][Co_2Cl_7]$ (25), the tppz' ligand is the result of a rearrangement of tppz in the presence of CoCl₂ (Figure 59). The rearranged tppz ligand is composed of two equivalent units linked by a C-C tether (Figure 59a). Each one of these units is composed of a pyridyl ring joined to a six-membered ring which is fused to a five-membered ring (Figure 59). These two equivalent units can rotate around the C-C bond that links them together, which allows them to coordinate to two Co(II) metal centers 90° from each other. Two more units can be added to complete the cyclic unit



asymmetric unit and (e) packing diagram with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Figure 59. Thermal ellipsoid diagram of [Co₂(tppz')₂][Co₂Cl₇][PF₆] (25) (a) ligand unit, (b) and (c) metallocyclophane, (d)

viewed in Figure 62a. The distance Co(1)-N(2) = 2.149 Å is longer than the metal interaction to the fused rings at Co(1)-N(1) = 2.112 Å. The metal center resides in a highly distorted octahedral geometry composed of three equivalent chelating interactions from a pyridyl and a five-membered ring. The angle between the pyridyl and the five membered ring $N(1^*)-Co(1)-N(2) = 77.1$ (2)° (Figure 59).

E. Reactions of cis- $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ and $[Rh_2(CH_3CN)_{10}][BF_4]_4$ with tppz.

E.1. Synthesis

A careful search of the literature in the last 40 years reveals that tppz has been used exclusively in mononuclear metal complexes.^{16,1} Reports by Pruchnnik and coworkers¹⁷ and observations in our own laboratories with bipyridine and terpyridine ligand on [Rh₂]⁴⁺ prompted us to react tppz with metal-metal bonded compounds. In one such reaction, [Rh₂(O₂CCH₃)₂(CH₃CN)₆][BF₄]₂ was selected as a source of Rh₂⁴⁺ because of its availability and stability. The reaction with tppz was performed in a 1:1 ratio in H₂O. At room temperature no reaction was observed, but, with heating, the purple solution of the starting material gradually changes to a pale brownish red color and finally to green. At this point, the reaction must be ceased, otherwise cleavage of the metal-metal bond with concomitant oxidation to Rh(III) bond takes place, as evidenced by isolation of $[Rh(tppz)_2]^{3+}$. The product is recovered by evaporation of the H₂O. A methanol solution of the product was layered with toluene and green platelet crystals were observed to grow over a period of two months (yield 15%). X-ray studies revealed that the "dimer of dimers" these crystals are [Rh₄(O₂CCH₃)₂(tppz)₂(CH₃OH)₄][PF₆]₆·CH₃OH (**24**).

 $[Rh_4]^{4+}$ With successful isolation the compound the of from $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ we turned to another source for the $[Rh_4]^{4+}$ core, namely [Rh₂(CH₃CN)₁₀][BF₄]₄. The 1:1 reaction between [Rh₂(CH₃CN)₁₀][BF₄]₄ and tppz was performed in acetonitrile, and, upon mixing, the orange solution changed immediately to a brown color solution from which the mononuclear Rh^{III} species, was isolated $[Rh(tppz)_2][BF_4]_3$. In an attempt to avoid the presumed disproportionation reaction, the reaction was performed at low temperature and in the absence of light, but we were not able to avoid the formation of $[Rh^{III}(tppz)_2]^{3+}$. The fate of the other half of the reaction, namely the Rh¹ species is not known.

E.2. Spectroscopic studies.

The mononuclear species $[Rh(tppz)_2][BF_4]_3$ (23) exhibits interesting electronic spectral properties. Four electronic transitions were located in the range of 200-800 nm. The lowest energy transition occurs at $\lambda_{max} = 749$ nm ($\varepsilon = 2.9 \times 10^3$ L·(mol·cm)⁻¹). The others appear at $\lambda_{max} = 517$ nm ($\varepsilon = 1.6 \times 10^4$ L·(mol·cm)⁻¹), at $\lambda_{max} = 437$ nm ($\varepsilon = 1.4 \times 10^4$ L·(mol·cm)⁻¹), and at $\lambda_{max} = 405$ nm ($\varepsilon = 1.45 \times 10^4$ L·(mol·cm)⁻¹). All of these transitions are presumed to be MLCT transitions based on their high molar absorptivity coefficients.

E.3. X-ray crystallographic studies.

Compound (24), $[Rh_4(O_2CCH_3)_2(tppz)_2(CH_3OH)_4][PF_6]_6$ ·CH₃OH, consists of a rectangular unit based on two Rh-Rh bonds and two M-tppz edges. The coordination sphere of the Rh^{II} ions consists of three nitrogen atoms from the tppz ligand, two oxygen atoms, (one from the bridging acetate and the other from a methanol molecule), and finally the Rh-Rh bond (Figure 61). The angle between the pyridyl and pyrazine

nitrogens, Rh(2)-N(2)-N(3) is 81.2 (3)°. The N(1)-Rh(2)-N(3) = 160.3 (3)° angle, which involves the pyridyl rings, is far from the ideal 180°. The shortest of the three Rh-N distances is the Rh-pyrazine distance of Rh(2)-N(2) = 1.934 (7) Å, followed by the Rh-pyridyl distance Rh(2)-N = 2.030 [8] Å (Figure 60).

Table 28.	Selected bonds dist [Rh ₄ (O ₂ CCH ₃) ₂ (tppz) ₂ (Cl	ances (Å) and H ₃ OH) ₄][PF ₆] ₆ ·CH ₃ O	angles (°) for H (24).
Rh1-N2A	1.929(7)	Rh2-N2	1.934(7)
Rh1-N1A	2.041(7)	Rh2-N1	2.010(8)
Rh1-O2	2.054(7)	Rh2-N3	2.047(8)
Rh1-O3	2.245(7)	Rh2-O1	2.053(7)
Rh1-Rh2	2.6058(11)	Rh2-O4	2.216(8)
N2A-Rh1-N3A	81.7(3)	N2-Rh2-N1	80.7(3)
N2A-Rh1-N1A	81.0(3)	N2-Rh2-N3	81.2(3)
N3A-Rh1-N1A	160.6(3)	N1-Rh2-N3	160.3(3)
N2A-Rh1-O2	179.0(3)	N2-Rh2-O1	178.5(3)
N3A-Rh1-O2	98.8(3)	N1-Rh2-O1	100.2(3)
N1A-Rh1-O2	98.4(3)	N3-Rh2-O1	97.8(3)
N2A-Rh1-O3	93.0(3)	N2-Rh2-O4	95.3(3)
N3A-Rh1-O3	88.4(3)	N1-Rh2-O4	89.6(3)
N1A-Rh1-O3	83.8(3)	N3-Rh2-O4	84.4(3)
O2-Rh1-O3	86.2(3)	O1-Rh2-O4	83.5(3)
N2A-Rh1-Rh2	95.9(2)	N2-Rh2-Rh1	96.2(2)
N3A-Rh1-Rh2	91.2(2)	N1-Rh2-Rh1	90.6(2)
N1A-Rh1-Rh2	99.3(2)	N3-Rh2-Rh1	99.0(2)
O2-Rh1-Rh2	85.0(2)	O1-Rh2-Rh1	85.0(2)
O3-Rh1-Rh2	171.0(2)	O4-Rh2-Rh1	168.4(2)

The molecular cation is a rectangle in which each Rh-Rh unit is a short edge of the rectangle and tppz units are the long edges. The Rh-Rh bond distance is 2.606 (1)Å, which is within the expected range for a Rh-Rh single bond.¹⁸ The distance between tppz bridged Rh^{II} atoms along is 6.749 Å and the diagonal of the rectangle is 6.977 Å. The tppz units are highly distorted, with the planes of the two coordinating pyridyl units on the same Rh atom forming a dihedral angle of 27.4°. The pyrazine ring exhibits a dihedral









angle of 19.46 °. A close look at the space filling diagram in Figure 68 shows the remarkably good fit of the two twisted tppz units in this molecule.

Table	29.	Selected [Rh(tppz) ₂	bond di][BF ₄] ₃ ·2CH	istances (Å) and I ₃ CN·C₄H ₈ O (23).	angles (°) for
Rh1-N2	A		1.962(6)	N2-C19	1.345(10)
Rh1-N2			1.975(6)	N4-C7A	1.347(10)
Rh1-N3			2.035(7)	N4A-C13A	1.348(9)
Rh1-N1			2.032(7)	N4-C13	1.335(10)
Rh1-N1	0A		2.054(6)	N4-C7	1.355(10)
Rh1-N3	Α		2.066(7)	N2A-C19A	1.334(10)
N2-N6			1.334(9)		· · ·
N2A-Rh	1-N2		178.0(3)	N3-Rh1-N10A	91.3(3)
N2A-Rh	1-		100.7(3)	N1-Rh1-N10A	91.8(3)
N2-Rh1-	-N3		80.3(3)	N2A-Rh1-N3A	80.7(2)
N2A-Rh	1-N1		98.9(3)	N2-Rh1-N3A	97.5(3)
N2-Rh1-	-N1		80.2(3)	N3-Rh1-N3A	91.9(3)
N3-Rh1-	-N1		160.4(2)	N1-Rh1-N3A	91.3(3)
N2A-Rh	1-N10A		80.5(3)	N10A-Rh1-N3A	161.2(2)
N2-Rh1-	-N10A		101.3(3)		

Compound (23) contains a mononuclear Rh(III) cation in a distorted octahedral geometry (Figure 69). The angle between the pyrazine and pyridyl rings and the Rh atom is N(1)-Rh(1)-N(2) = 80.2 °, which is much less than the ideal 90°. The angle N(1)-Rh(1)-N(3) between two pyridyl rings is 160.4°, also far from the ideal. The tppz experiences severe distortions, with two of the non-coordinating pyridyl rings forming an angle of 37.11° between them. The pyrazine ring is twisted by 9.68 °. In the case of coordinated and non-coordinated pyridyl rings, they are twisted as far as possible at 48.31 °. The driving force for this is most likely the steric interaction of the 4,4' hydrogen atoms.



Figure 62. Representation of the cation in [Rh(tppz)₂](BF4]₃·C4H8O·2CH₃CN (23) with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for the sake of clarity.

F. A hybrid ligand of 2,2' azobypyridine and tetrapyridyl pyrazine: 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptaz).

F.1. Synthesis

The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptaz) contains three possible coordination sites as depicted in Figure 46. The most likely candidate for the first coordination is the tridentate site. The three compounds isolated in this work are mononuclear species with tptaz using only the tridentate coordination site. In all cases, formation of the product is the same, regardless of the ratio of reagents or reaction conditions used.

$$[Ni(CH_3CN)_6][BF_4]_2 + tptaz \xrightarrow{CH_3CN} [Ni(tptaz)(CH_3CN)_2(H_2O)][BF_4]_2 \quad (Eq. 10)$$

yield: 62%

$$[Fe(H_2O)_6][ClO_4]_2 + 2 \text{ tptaz} \xrightarrow{CH_3CN} [Fe(tptaz)_2][ClO_4]_2 \qquad (Eq. 11)$$

yield: 82%

$$[Mn(phen)_2][CF_3SO_3]_2 + tptaz \xrightarrow{CH_3CN} [Mn(tptaz)(H_2O)][CF_3SO_3]_2 \qquad (Eq. 12)$$

yield: 91%

In a typical reaction, $[Ni(CH_3CN)_6][BF_4]_2$ was dissolved in acetonitrile to form a bright blue solution, and one equivalent of tptaz was added. The color of the reaction changed to pale yellow and finally to pale yellow green within 8 hours (Eq. 10). Layering of the solution with toluene, benzene or diethyl ether affords crystals of $[Ni(tptaz)(CH_3CN)_2(H_2O)_2][BF_4]_2$ within days. It must be pointed out that the acetonitrile cannot be completely dry, otherwise, the compound will not crystallize. Several attempts to coordinate a second Ni^{II} center to the already formed $[Ni(tptaz)(CH_3CN)_2(H_2O)_2]^{2+}$ (27)

molecule were unsuccessful. This may be due to the inductive effect of the first metal on the triazine ring, which renders the triazine ring much less basic.

The compound $[Fe(tptaz)_2][ClO_4]_2$, (28), results from the reaction of $[Fe(H_2O)_6][ClO_4]_2$ with tptaz in a 1:2 ratio (Eq. 11). The reaction takes place instantaneously, with the color changing from a colorless Fe(II) solution to a deep blue solution within minutes. All attempts to prepare polynuclear compounds by varying the reaction conditions were unsuccessful. Crystals of the mononuclear compound were obtained by layering with diethyl ether or THF or by slow evaporation of the reaction mixture.

For the synthesis of $[Mn(tptaz)(phen)(H_2O)][O_3SCF_3]_2$ (29), a slightly different approach was taken. Instead of using a "naked" cation (in which all six coordination sites are occupied by labile water or acetonitrile molecules), $[Mn(phen)_2](O_3SCF_3]_2$ was employed. This precursor contains four coordination sites occupied by phenanthroline molecules (capping ligands), and two sites occupied by weakly coordinating triflate ([CF₃SO₃⁻]) anions. By using this precursor, it was intended that the tptaz would coordinate in its middle bidentate coordination site (Figure 46), allowing for the coordination of a second metal center in a subsequent step in the tridentate site. The reaction was performed anaerobically, with a 1:1 ratio of $[Mn(phen)_2(O_3SCF_3]_2]$ and tptaz in acetonitrile (Eq. 12). The reaction was instantaneous, as judged by an immediate color change to light yellow. The outcome of the reaction is the mononuclear species $[Mn(tptaz)(phen)(H_2O)][O_3SCF_3]_2$ (29) in which the tptaz ligand is coordinated through its major coordination site (tpy mode), which requires the displacement of one phenanthroline molecule. Further attempts to coordinate a second Mn^{II} metal center on the available bpy coordination site (middle coordination site, Figure 46) by adding an excess of either $[Mn(CH_3CN)_4][BF_4]_2$ or $[Mn(phen)_2(O_3SCF_3]_2]$ (with and without refluxing) were unsuccessful. The mononuclear product was always obtained as evidenced by X-ray crystallographic studies.

F.2. Spectroscopic and cyclic voltammetric studies

UV-Visible spectroscopy of $[Ni(tptaz)(CH_3CN)_2(H_2O)_2][BF_4]_2$ $[Fe(tptaz)_2][ClO_4]_2$, $[Mn(tptaz)(phen)(H_2O)][O_3SCF_3]_2$ revealed numerous electronic transitions. The tptaz ligand exhibits two electronic transitions in the UV region, the lowest energy one being at $\lambda_{max} = 279$ nm ($\varepsilon = 3.0 \times 10^4$ L·(mol·cm)⁻¹) and the higher energy one at $\lambda_{max} = 244$ nm ($\epsilon = 3.0 \times 10^4$ L·(mol·cm)⁻¹). Both transitions are assigned to $\pi \rightarrow \pi^*$ electronic transitions. [Ni(tptaz)(CH₃CN)₂(H₂O)][BF₄]₂ (27) displays two electronic transitions at $\lambda_{max} = 293$ nm ($\varepsilon = 5.9 \times 10^4$ L·(mol·cm)⁻¹) and $\lambda_{max} = 253$ nm (ε = 2.5 \times 10² L·(mol·cm)⁻¹). The transition at λ = 293 nm corresponds to a MLCT transition, based on its location and its absorption coefficient. The higher energy transition at $\lambda_{max} = 253$ nm is assigned to a $\pi \rightarrow \pi^*$ transition of the ligand. $[Fe(tptaz)_2][ClO_4]_2$ (28) exhibits three electronic transitions in the UV-Visible spectrum at λ_{max} values of 568 nm, 341 nm and 243 nm with ε values of 6.1×10^2 , 6.5×10^5 and 4.3×10^3 L·(mol·cm)⁻¹, respectively. The two lower energy transitions are assigned to MLCT transition and the higher energy one at $\lambda_{max} = 243$ nm is a $\pi \rightarrow \pi^*$ transition, as inferred comparison the free ligand spectra. Finally. from a to $[Mn(tptaz)(phen)(H_2O)][O_3SCF_3]_2$ (29) displays three electronic transitions at $\lambda_{max} = 227$ and 272 nm (assigned to $\pi \rightarrow \pi^*$ electronic transitions) and at $\lambda_{max} = 292$ nm, attributed to a MLCT transition. The ε values are 5.0×10^4 , 7.0×10^4 , and 6.7×10^4 L·(mol·cm)⁻¹ for $\lambda_{max} = 292$, 272 and 227 nm, respectively.

Table 30. UV-Visible spectroscopic data for compounds (27)-(29).			
	λ(nm)	ε L·(mol·cm) ⁻¹	
	279	3.0×10^{4}	
Tptaz	244	3.0×10^4	
	293	5.9×10^{4}	
$[Ni(tptaz)(CH_3CN)(H_2O)][BF_4]_2$	253	2.5×10^2	
	568	6.1×10^2	
[Fe(tptaz) ₂][ClO ₄] ₂	341	6.5×10^{5}	
	243	4.3×10^{3}	
	227	6.7×10^4	
[Mn(tptaz)(phen)(H ₂ O)][O ₃ SCF ₃] ₂	272	7.0×10^4	
	292	5.0×10^{4}	

The presence of energetically accessible π^* orbitals leads to a rich electrochemistry for these molecules. Cyclic voltammetric studies show that $[Fe(tptaz)_2][ClO_4]_2$ (28) exhibits the richest electrochemistry. The free ligand exhibits only a reversible reduction ($E_{\nu_2} = -1.2$ V), but upon coordination to Fe(II), four one-electron reductions became accessible as depicted in Figure 63. The four one-electron reductions of $[Fe(tptaz)_2][ClO_4]_2$ (28), are found within the range -0.4 to -1.85 V. These reduction couples occur at $E^{(1)}_{\nu_2} = -0.62$, $E^{(2)}_{\nu_2} = -0.75$, $E^{(3)}_{\nu_3} = -1.47$ and $E^{(4)}_{\nu_3} = -1.71$ V (Figure 63). In addition, there is an irreversible oxidation at E = +1.54 V that corresponds to the oxidation of Fe(II) to Fe(III). An examination of the separation of the four couples allows for the calculation of the comproportionation constants for the two intermediates

as shown in scheme 4, based on the Robin and Day approach.¹⁹ The first two couples lead to a comproportionation constant of 1.57×10^2 , which corresponds to a value on the borderline of class I and II. For the next two reversible couples, the K_c is 1.14×10^4 , which falls in the category of class II (Scheme 4).



Figure 63. Cyclic voltammogram of [Fe(tptaz)₂][ClO₄]₂ in 0.1 M TBAPF₆ acetonitrile at a Pt disk electrode versus Ag/AgCl.

In marked contrast to the Fe(II) derivatives, $[Mn(tptaz)(phen)(H_2O)][O_3SCF_3]_2$ (29) exhibits only one reversible reduction at $E_{1/2} = -1.47$ V. There are three irreversible waves at $E_{p,c} = -0.55$, -0.72 and -0.80 V without corresponding anodic return waves.

Finally, $[Ni(tptaz)(CH_3CN)_2(H_2O)][BF_4]_2$ exhibits a reversible reduction at $E^{1/2} =$ -0.5 V and a cathodic wave at $E_{p,c} = -1.03V$ with a return wave at E = -0.85V.

$$[Fe(tptaz)_2]^{2+} \qquad \underbrace{+e}_{-e} \qquad [Fe(tptaz)_2]^{+} \\ K_c = 1.57 \times 10^2$$

$$[Fe(tptaz)_2]^+ -e^- [Fe(tptaz)_2]$$

$$[Fe(tptaz)_{2}] \qquad \underbrace{+e^{-}}_{-e^{-}} \qquad [Fe(tptaz)_{2}]^{-}$$

$$[Fe(tptaz)_{2}]^{-} \qquad \underbrace{+e^{-}}_{-e^{-}} \qquad [Fe(tptaz)_{2}]^{2-}$$



F.3. X-ray crystallographic studies.

The compound $[Ni(tptaz)(CH_3CN)_2(H_2O)][BF_4]_2$ (27) consists of a Ni^{II} center in distorted octahedral geometry (Figure 71). The coordination sphere is composed of two acetonitrile molecules, one water molecule and tptaz ligand coordinated at the tpy site (Figure 70). The shortest Ni-N bond is to the nitrogen of the triazine ring, (Ni(1)-N(2) = 1.982 (3)Å), followed by the acetonitrile interaction (2.037 [3]Å). The longest distance is to the pyridyl rings at an average Ni-N distance of 2.134 [3]Å. The angle between the pyridyl and pyrazine rings and the nickel center is N2-Ni1-N1 = 77.05 (11)°, which is far from the ideal 90°. The angle between the pyridyl and the acetonitrile ligands is N(1)-Ni(1)-N(8) = 103.17 (11)°. The two trans pyridyls are 154.1° apart from each other,

which is 25.9° from the expected 180°. With respect to the open middle coordination site,

Table 31. Selected bond distances (Å) and angles (°) for [Ni(tptaz)(CH ₃ CN)(H ₂ O)][BF ₄] ₂ (27).				
Ni1-N2	1.982(3)	Ni1-O1	2.063(2)	
Ni1-N8	2.027(3)	Ni1-N3	2.134(3)	
Nil-N7	2.047(3)	Nil-Nl	2.135(3)	
N2-Ni1-N8	179.70(12)	N7-Ni1-N3	89.08(11)	
N2-Ni1-N7	91.51(12)	01-Ni1-N3	91.66(10)	
N8-Ni1-N7	88.29(12)	N2-Ni1-N1	77.05(11)	
N2-Ni1-O1	88.84(11)	N8-Ni1-N1	103.17(11)	
N8-Ni1-O1	91.37(11)	N7-Ni1-N1	90.68(11)	
N7-Ni1-O1	179.24(11)	01-Ni1-N1	88.74(10)	
N2-Ni1-N3	77.05(11)	N3-Ni1-N1	154.09(11)	
N8-Ni1-N3	102.72(11)			

the dihedral angle between the triazine and pyridyl rings is only 9.4°.

In compound $[Fe(tptaz)_2][ClO_4]_2$ (28), two tptaz units are present in the coordination sphere. The Fe^{II} center resides in a distorted octahedral environment (Figure 72). The longest Fe(1)-N interaction is to the pyridyl ring, with an average value of 1.984 [3]Å, followed by the triazine with an average value of 1.862 [3]Å. The angles throughout the coordination sphere reflect the distortion from an ideal octahedron. The angle between the pyridyl and triazine units and the Fe^{II} center is 80.10 [12]° (almost a 10° difference from the ideal 90°). The coordinated pyridyl rings of the same tptaz molecule are 160.2° apart from each other, which is a 19.8° deviation from the expected 180°.

The compound $\{[Mn(tptaz)(phen)(H_2O)][CF_3SO_3]_2\}\{[Mn(tptaz)(phen)(H_2O)][CF_3SO_3]_2\}\cdot H_2O$ (29) crystallizes in the P-1 space group with two independent co-crystallized molecules. Both

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molecules contains a Mn(II) ion, but they exhibit different geometries. The first molecule consists of a Mn^{II} ion in a distorted octahedral environment (Figure 74) whereas the second molecule contains a heptacoordinate Mn(II) ion.

Table 32. Selected bond distances (Å) and angles (°) for [Fe(tptaz) ₂][ClO ₄] ₂ ·2CH ₃ CN (28).				
Fe1-N2	1.859(3)	Fe1-N3A	1.983(3)	
Fe1-N2A	1.865(3)	Fel-Nl	1.988(3)	
Fe1-N3	1.981(3)	Fel-N1A	1.989(3)	
N2-Fe1-N2A	178.23(13)	N3-Fe1-N1	160.38(12)	
N2-Fe1-N3	80.30(12)	N3A-Fe1-N1	93.28(12)	
N2A-Fe1-N3	101.08(12)	N2-Fe1-N1A	98.87(12)	
N2-Fe1-N3A	101.12(12)	N2A-Fe1-N1A	79.99(12)	
N2A-Fe1-N3A	80.05(12)	N3-Fe1-N1A	93.03(12)	
N3-Fe1-N3A	89.42(12)	N3A-Fe1-N1A	159.99(12)	
N2-Fe1-N1	80.11(12)	N1-Fe1-N1A	91.04(12)	
N2A-Fe1-N1	98.53(12)			

A close look at the molecule with seven ligands shows that it has pentagonal bipyramidal geometry (Figure 73). The equatorial plane is occupied by the tptaz nitrogens atoms (N(1), N(2), N(3)), a nitrogen from the phenanthroline N(7), an oxygen from a triflate O(4), and finally the water molecule O(7). In an ideal case, each atom in the pentagon should be 72° apart, which is close to what is observed in the structure. Some characteristic angles found in this plane are N(1)-Mn(2)-N(7) = 76.61 (11)°, N(1)-Mn(2)-N(2) = 67.00 (10)°, N(3)-Mn(2)-N(2) = 69.24 (11)° and O(3)-Mn(2)-N(7) = 75.11 (11)°. The two axial sites are occupied by a triflate molecule weakly coordinated through an oxygen atom, Mn(2)-O(4) = 2.164 (3)Å, and a nitrogen from the phenanthroline ring Mn(2)-N(8) = 2.277 (3)Å. The molecule with the octahedral geometry (Figure 74) does not contain a coordinated triflate molecule; its coordination sphere is composed of a





tptaz, a phen, and a water molecule. The tptaz ligand and one of the phenanthroline nitrogen atoms occupy the equatorial plane. The axial sites are filled by a water molecule and the remaining nitrogen from the phenanthroline. The tptaz and phenanthroline ligands impose rigid geometric requirements as judged by the angles involving tptaz $(N(2A)-Mn(1)-N(1A) = 70.5 (1)^{\circ})$ and phenanthroline $(N(8A)-Mn(1)-N(7A) = 75.7 (1)^{\circ})$ are far from the ideal 90° in an octahedral environment. Consequently, these coordination requirements affect the rest of the bonding, *e.g.*, $O(14)-Mn(1)-N(8A) = 162.3 (1)^{\circ}$. The shortest Mn(1)-N distance is to the triazine ring of the tptaz, Mn(1)-N(2A) = 2.224 (3) Å, followed by the phenanthroline ring with an average M-N distance of 2.255 [3] Å. Finally, the longest interaction is to the pyridyl rings at an average M-N distance of 2.360 [3]Å.

Table 33. Selected bond distances (Å) and angles (°) for ${[Mn(tptaz)(phen)(H_2O)][CF_3SO_3]_2} {[Mn(tptaz)(phen)(H_2O)][CF_3SO_3]_2} .$			
Mn1-014	2.170(3)	Mn2-O4	2.164(3)
Mn1-N2A	2.224(3)	Mn2-N7	2.276(3)
Mn1-N7A	2.241(3)	Mn2-N8	2.277(3)
Mn1-N8A	2.269(3)	Mn2-N2	2.339(3)
Mn1-N3A	2.345(3)	Mn2-N3	2.357(3)
Mn1-N1A	2.375(4)	Mn2-O3	2.511(3)
Mn2-N1	2.569(3)		
O14-Mn1-N2A	97.47(11)	N7A-Mn1-N1A	124.58(12)
Ol4-Mnl-N7A	89.76(11)	N8A-Mn1-N1A	90.74(11)
N2A-Mn1-N7A	163.60(11)	N3A-Mn1-N1A	142.25(11)
Ol4-Mnl-N8A	162.30(10)	O4-Mn2-N7	102.21(11)
N2A-Mn1-N8A	99.20(11)	O4-Mn2-N8	169.22(11)
N7A-Mn1-N8A	75.73(12)	N7-Mn2-N8	74.69(12)
O14-Mn1-N3A	91.77(10)	O4-Mn2-N2	89.00(10)
N2A-Mn1-N3A	72.00(12)	N7-Mn2-N2	140.09(11)
N7A-Mn1-N3A	93.16(12)	N8-Mn2-N2	87.20(11)
N8A-Mn1-N3A	99.00(11)	O4-Mn2-N3	100.15(10)
O14-Mn1-N1A	89.24(11)	N7-Mn2-N3	142.70(11)
N2A-Mn1-N1A	70.46(12)	N8-Mn2-N3	87.92(11)



at the 50% probability level Hydrogen atoms have been omitted for the sake of clarity. Figure 66. Thermal ellipsoid plot of the six coordinate Mn^{ll} ion in





IV. Conclusions

The ligand 2,3,5,6-tetrapyridylpyrazine (tppz) possesses two tridentate coordination sites which in principle can allow for the assembly of metal arrays. In our attempts to prepare such metal arrays, the mononuclear series $[M(tppz)_2][X]_2$ (M = Ni²⁺, Co^{2+} , Fe^{2+} , Mn^{2+} ; X = ClO₄⁻, PF₆⁻, NO₃⁻) was obtained by the reactions of $[M(S)_6]^{2+}$ (S = CH₃CN or H₂O) cations with two tppz ligands. The products exhibit interesting properties in their own right, and could give rise to interesting properties by associative effects if extended metal arrays can be obtained.

Magnetic studies of $[Co(tppz)][PF_6]_2$ (17) revealed that this compound exhibits spin-crossover behavior. Previous studies with Co^{II} and tpy derivatives have indicated similar behavior.²⁰ The low spin configuration is obtained at T = 55K with S = 1/2 and the high spin configuration is reached at T = 260 K with S = 3/2. From a structural point of view, $[Co(tppz)_2][PF_6]_2$ presents a major difference from other spin-crossover Co(II) complexes, namely the availability of coordination sites for further chemistry. This compound is ideal as a potential building block for the construction of higher nuclearity species that incorporate a building block with spin-crossover behavior.

A cyclic voltammogram of $[Fe(tppz)_2][ClO_4]_2$ shows five fully reversible redox couples, which is quite remarkable. The four reductions indicate electronic communication between the two ligands. Calculation of the comproportionation constants show class I/II behavior for the first two reduction couples with $K_c = 7.5 \times 10^2$. The next two reduction couples exhibit class II behavior with $K_c = 3.7 \times 10^4$ (Scheme 3).

Attempts to synthesize the dinuclear products $[M_2(tppz)_2(CH_3CN)_6]^{+4}$ (M = Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}) were unsuccessful except in the case of $[Ni_2(tppz)(CH_3CN)_6][BF_4]_4$. The
reaction was performed with a 1:2 ratio of tppz and $[Ni(CH_3CN)_6][BF_4]_2$. The identical reactions performed with any other anions *e.g* ($[ClO_4]^-$, $[PF_6]^-$, $[NO_3]^-$) did not afford this product, but produced only $[Ni(tppz)_2]^{2+}$ instead. The choice of anion evidently plays a major role in the self-assembly process.

Reactions of tppz with $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ led to the isolation of a novel rectangle in which the longest sides are occupied by the tppz ligand units and the shorter sides are defined by the two Rh-Rh bonds. In the case of $[Rh_2(CH_3CN)_{10}][BF_4]_4$ reactions, one observes only metal-metal cleavage and disproportionation with isolation of $[Rh(tppz)_3][BF_4]_3$.

In the tptaz chemistry, all of the metal ions coordinate only to the major tridentate site. In principle, it should still be possible to use these building blocks in further chemistry based on metal coordination to the bpy site.

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Chapter IV

A Homologous Series of Redox-Active, Dinuclear Cations $[M_2(O_2CCH_3)_2(pynp)]^{2+}$ (M = Mo, Ru, Rh) with the Bridging Ligand 2-(2-Pyridyl)-1,8-naphthyridine (pynp).

I. Introduction

In our quest for nitrogen heterocyclic ligands that are capable of spanning a dinuclear unit, we found several references on the use of cavity-shaped ligands such as 2-(2-pyridyl)-1,8-naphthyridine $(pynp)^{I}$ 2,7-bis(2-pyridyl)-1,8-naphthyridine and (bpnp)^{6(a);(d)-(g)} (Figure 68). The pynp and bpnp molecules are relatively rigid tridentate and tetradentate ligands, that possess, in addition to the naphthrydine bridging unit, one or two pyridyl binding sites that can be used to bind to the axial positions of a dimetal unit. The pynp ligand (Figure 68) can act as a tridentate combination bridging/chelating ligand as in the case of $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ or a chelating, bpy mode in the case of [Rh₂(pynp)₃Cl₂][PF₆]·CH₃CN.^{1b} These compounds were found to exhibit interesting electronic properties, but, in the intervening years since these examples were published, no additional reports of M-M bonded pynp compounds have appeared in the literature, and only one X-ray structure has been reported.^{1c} This chapter is devoted to the study of the coordination chemistry of 2-(2-pyridyl)-1,8-naphthyridine (pynp) with $[Mo_2]^{4+}$, $[Ru_2]^{4+/5+}$ and $[Rh_2]^{4+}$ dimetal complexes and a comparison of the structures and redox properties of the homologous series $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (M = Mo, Ru, and Rh).



Figure 68. Schematic drawings of the bpnp and pynp ligands.

II. Experimental Section

All manipulations were performed under an inert atmosphere with the use of standard Schlenk-line techniques. Acetonitrile was freshly distilled over 3Å molecular sieves and methanol was pre-dried over 4Å molecular sieves and then distilled over NaOMe. The solvents diethyl ether and toluene were freshly distilled over Na/K amalgam. The ligand 2-(2-pyridyl)-1,8-naphthyridine (pynp) was prepared by a modified literature procedure.² The starting materials $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$,³ $[Mo_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ ^{3,4} and $Ru_2(O_2CCH_3)_4Cl^5$ were prepared by literature methods.

Physical Measurements.

¹H NMR spectra were obtained on a Varian VXR 300-MHz spectrometer Gemini-200. Electrochemical measurements were carried out by using an H CH Electrochemical Analyser model 620A. Cyclic voltammetry experiments were performed in CH₃CN containing 0.1M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The working electrode was a BAS Pt disk electrode, the reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The ferrocene couple occurs at $E_{1/2} = {}^{+}0.52V$ vs Ag/AgCl under the same experimental conditions. Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL (housed in the Department of Chemistry at Texas A&M University). Data was collected in the temperature range 1.8-350 K at 1000 G on finely divided polycrystalline samples. The raw data was corrected for the contribution of the sample holder and the diamagnetism of the constituent atoms by the use of Pascal constants.⁶

Theoretical Details.

A companion theoretical study for the experimental work in this chapter was performed by Dr. Lisa Thompson at Texas A&M University. The compounds, $[M(O_2CCH_3)_2(pynp)_2]^{2+}$ (where M = Mo²⁺, Ru²⁺, Rh²⁺) (**30-32**), without the solvent molecules, were subjected to density functional theory (DFT) calculations⁷ with the Becke3 hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP).⁸ Details of the calculation are contained in Appendix I, which is provided as supporting information.

Syntheses

Preparation of 2-(2-pyridyl)-1,8-naphthyridine (pynp).

The preparation of pynp requires the precursor 2-aminonicotinaldehyde, which must be freshly prepared and used immediately after isolation to avoid self-condensation side reactions.

2-aminonicotinaldehyde.

The method of Caluwe and co-workers² was followed with some modifications. Nicotinamide (9.1 g, 0.07 mmol) was mixed with 13.0 g (0.11 mmol) of ammonium sulfamate in a round-bottomed flask equipped with a condenser. The temperature was slowly increased to 150 °C until the entire solid had melted. At this point the temperature was continuously increased until it reached 200 °C, after which time the reaction was allowed to reflux for 8.5 h. The grayish-white solid obtained from this procedure was washed with copious amounts of water and diethyl ether to remove unreacted nicotinamide and sulfamate. The remaining solid was refluxed in 75 mL of 4N HCl for 6.5 hours and the solution was made basic (pH ~ 9.0) by adding portions of a saturated NaOH solution. The resulting solution was subjected to four extractions with diethyl ether, and the combined extracts were dried over anhydrous MgSO₄ for one hour. The diethyl ether was evaporated and the remaining light yellow solid was sublimed at 60 °C under vacuum to obtain pure 2-aminonicotinaldehyde; yield, 3.1g (34%). This product must be stored in an inert atmosphere at 0 °C to avoid self-condensation reactions. IR (KBr mull) cm⁻¹: 3412 (br,w), 2924 (br,w), 2750 (w), 1669 (w), 1624 (w), 1568 (w), 1458 (w), 1402 (w), 1377 (w), 1296 (w), 1273 (w), 1194 (w), 1136 (w), 912 (w), 775 (w), 675 (w), 623 (w). ¹H NMR spectrum in CDCl₃ at 25 °C: δ 9.82 (s, OH), 8.22 (dd), 7.78 (dd), 6.95 (b), 6.72 (dd) ppm.

Preparation of 2-(2-pyridyl)-1,8-naphthyridine (pynp).

An amount of freshly prepared 2-aminonicotinaldehyde (1.6 g, 14.8 mmol) was placed in a Schlenk flask under nitrogen and dissolved in 25 mL of freshly distilled ethanol. To this solution was added 1.0 mL of 2-acetyl-pyridine. The solution was refluxed under nitrogen and treated with one drop of a freshly prepared methanolic solution saturated with NaOH. A color change from yellow to a pale brown-yellow immediately ensues. The solution was refluxed overnight under nitrogen and the solution was concentrated to one half of its original volume. White crystals were observed to form after a few hours; yield, 1.1 g (43 %). IR (KBr mull) cm⁻¹: 1550 (m), 1520 (w), 1470 (s), 1350 (m), 1050 (w), 850 (w), 800 (m), 750 (w). ¹H NMR spectrum in CD₃CN at 25 °C, δ 9.1 (q), 8.75 (m), 8.68 (d,d), 8.45 (d), 8.36 (d,d), 7.95 (t,d), 7.56 (q), 7.48 (m) ppm.

$[Mo_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ (30).

A sample of $[Mo_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ (0.2 g, 0.27 mmol) was dissolved in 20 mL of CH₃CN and treated with 114 mg (55 mmol) of pynp, which leads to a color change from a light pink to a dark green. After 12 h, the solution was concentrated and diethyl ether was added to the point of saturation. The solution was then placed in a refrigerator to yield green platelets; yield, 0.145 g (75 %). IR (KBr mull) cm⁻¹: 2924 (br, s), 2725(w), 1606(w), 1557(w), 1518(w), 1458(s), 1377(s), 1316(w), 1263(w), 1217(w), 1146(w), 1057(br, s), 854(w), 816(w), 781(w), 721(w), 679(w), 521(w) cm⁻¹. ¹H NMR spectrum in CD₃CN at 25 °C: δ 9.05 (d, pynp), 8.85 (dd, pynp), 8.68 (d), 8.2 (td, pynp), 7.72 (m, pynp), 7.66 (m, pynp), 7.52(m, pynp), 2.65(s, CH₃-acetate) ppm.

$Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2$ (31).

The starting material $[Ru_2(O_2CCH_3)_4]Cl$ (0.150 g, 0.32 mmol) was dissolved in 20 mL of MeOH and treated with 0.131 g (0.64 mmol) of pynp. The initial dark brown solution instantaneously turned to a dark blue color. This solution was stirred overnight and the volume was decreased to ~ 10 mL, after which time diethyl ether was added to produce a dark blue crystalline powder. Yield 0.103 g (60%). IR (Nujol, KBr): 2700 (br,s), 2350 (w), 1450 (s), 1380 (s), 1300 (br,w), 845 (br,s), 780 (br,s), 710 (w), 580 (w). 'H The NMR signals of the product were broad and featureless. $[Rh_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ (32).

A sample of $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ (0.1 g, 0.13 mmol) was treated with 0.056 g (0.27 mmol) of pynp in 20 mL of CH₃CN which led to an instantaneous color change from pale red to intense red. After stirring overnight, the volume was reduced to 5 mL and the solution was layered with toluene. A crop of red crystals was harvested after three days. Yield 0.077 g (70%). IR (Nujol, KBr): 2926 (br, s), 2725 (w), 1604 (w), 1650 (w), 1523 (w), 1462 (s), 1377 (w), 1315 (w), 1265 (w), 1147 (w), 1059 (w), 1012 (w), 841 (w), 779 (w), 736(w), 715 (w), 559 (w). ¹H NMR spectrum in CD₃CN at 25 °C:

200

δ 9.70 (d, pynp), 8.87 (dd, pynp), 8.70 (d, pynp), 8.60 (m, pynp), 8.45 (dd, pynp), 8.35 (td, pynp), 7.48(q, pynp), 2.25 (s,CH₃-acetate) ppm.

X-ray data collection and Refinement.

Geometric and intensity data for compound (30) were collected on a Rigaku AFC6S diffractometer equipped with a graphite-monochromated Mo K α ($\lambda_{\alpha} = 0.71069$ Å) radiation source. All calculations were performed with VAX computers on a cluster network using Texsan software package of the Molecular Structure Corporation.⁹ X-ray structural studies for compounds (31)-(33) were performed on a SMART 1K area detector diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda \alpha = 0.71073$ Å). The frames were integrated in the Siemens SAINT software package,¹⁰ and the data was solved using the direct-methods program SHELXS-97.¹¹ Crystal data are listed for compounds (30)-(33) in Table 34.

Mo₂(O₂CCH₃)₂(pynp)₂][BF₄]₂·3CH₃CN (30).

X-ray quality crystals were obtained within three days from a saturated solution of the title compound in acetonitrile with diethyl ether at -5 °C. A green rectangular crystal of dimensions $0.80 \times 0.4 \times 0.25$ mm³ was covered with silicone grease and mounted on the tip a glass fiber. Cell constants were obtained from a least squares refinement using 25 carefully centered reflections in the range 29<20<37°. Data were collected at -100 ± 1 °C, by using the ω scan method, in the range 4≤20≤47°. A total of 7493 reflections was collected of which 7200 were unique. The final full-matrix refinement was based on 4162 observed reflections with F₀>4 σ (F₀) that were used to fit 550 parameters to give R1 = 0.0598 and wR2 = 0.1690. The goodness-of-fit index was 0.999 and the highest peak in the final difference map was 1.017 e'/Å⁻³.

empirical formula	30 C ₃₆ H ₃₃ B ₂ F ₈ N9O4M0 ₂	31 C32H32P2F12N6O6Ru2	32 C37H36B2F8N6O4Rh2	33 C ₃₈ H ₃₆ P ₁ B ₁ F ₁₀ N ₁₀ O4Rh ₂
fw	1021.21	1004.87	1008 16	1123 611
space group	P21/c	C2/c		10.0011 D 1
a,Å	15.134(5)	14.2228(7)	13 400/2)	r-I 17 526/37
b,Å	14.301(6)	20.3204(9)	21 670(3)	12 116(2)
c,Å	19.990(6)	14.1022(7)	(c)2(c) 13 776(7)	13 786(2)
σ	6	06	10.1 ±0(±)	13./03(3) 07 57(3)
ß	108 06(1)	05 144(1)	01 8/5/3/	(5)75.78
2		22.144(1)	(7)000(7)	77.70(3)
Υ.,	90	90	60	85.76(3)
V,Å ³	4113(3)	4059.3(3)	3973.9(8)	2.193.0(8)
Ζ	4	8	4	2
D g/cm ³	1.649	1.808	1.685	
μ (mm ⁻¹)	0.697	0.931	0.916	0 884
total data	7493	9867	7670	23918
unique data	7200	3429	3203	9970
R indices	R1 = 0.0598	R1 = 0.0617	R1 = 0.1062	R1 = 0.0678
[]>2σ(])] ^{ab}	wR2 = 0.1690	wR2 = 0.170	wR2 =0.2365	wR2 = 0.1642
R indices	R1 = 0.1545	R1 = 0.0812	R1 = 0.1773	R1 = 0.1250
(all data)	wR2 = 0.2064	wR2 = 0.1798	wR2 = 0.2809	wR2 = 0.1881
GOF	1.017	1.078	1.117	0.980

Table 34. Crystallographic Data for Compounds 30-33.

 ${}^{a} R1 = \Sigma \left\| F_{0} \right\| - \left\| F_{c} \right\| / \Sigma \left\| F_{0} \right\| , {}^{b} wR2 = \left[\Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{0}^{2})^{2}] \right]^{0.5}.$

$Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2 \cdot CH_3OH (31)$

X-ray quality crystals were grown by layering a methanol solution of the title compound with toluene. A blue platelet of dimensions $0.11 \times 0.07 \times 0.05 \text{ mm}^3$ was secured on the tip of a glass fiber with silicone grease and placed in a N₂(g) stream at 173 \pm 1 K. A total of 9867 reflections was collected of which 3429 were unique. A disordered [PF₆]⁻ anion required modeling in three different orientations. Final least-square refinement of 242 parameters and 3203 data resulted in residuals of wR1 = 0.0812 and wR2 = 0.1798. The goodness-of-fit index was 1.078 and the highest peak in the final difference map was 0.952 e⁻/Å³.

Rh₂(O₂CCH₃)₂(pynp)₂][BF₄]₂·C₇H₈ (32)

X-ray quality crystals were obtained by slow diffusion of an acetonitrile solution of the title compound into toluene. A red, rectangular crystal of dimensions $0.05 \times 0.06 \times$ 0.15 mm^3 was covered with silicone grease, secured on the tip a glass fiber, and cooled to 173 ± 2 K. A total of 7670 reflections was collected of which 3203 were unique. Final least-squares refinement of 294 parameters and 1840 data resulted in residuals of wR1 = 0.1062and wR2 = 0.2365 and a goodness-of-fit of 1.117. A final difference Fourier map revealed the highest peak to be 0.952 e⁻/Å³.

$[Rh_2(O_2CCH_3)_2(pynp)_2(CH_3CN)_2][BF_4][PF_6]\cdot 2CH_3CN$ (33).

Suitable crystals for X-ray crystallography were obtained by slow diffusion of a solution of $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ in acetonitrile layered over a solution of pynp in dichloromethane. A pale red prism of dimensions $0.15 \times 0.05 \times 0.1 \text{ mm}^3$ was covered with silicone grease, mounted on the tip of a glass fiber and placed in a N₂(g) cold stream at 173 ± 2 K. A total of 23918 reflections was collected, of which 9970 were

unique. Final least-squares refinement of 598 parameters and 5987 reflections resulted in residuals of wR1 = 0.0678 and wR2 = 0.1642 and a goodness-of-fit of 0.980. A final difference Fourier map revealed the highest peak to be 2.209 $e^{7}/Å^{3}$ which is associated with a disordered [PF₆]⁻.

III. Results and Discussion.

A. A homologous series of redox-active dinuclear compounds.

A.1. Synthesis of compounds $[M_2(O_2CCH_3)_2(pynp)]^{2+}$, $M = [Mo]^{2+}$, $[Ru]^{2+}$, $[Rh]^{2+}$. Synthesis of compounds $[M_2(O_2CCH_3)_2(pynp)]^{2+}$, $M = Mo^{2+}$, Ru^{2+} , Rh^{2+} .

Reactions of pynp with $[Mo_2(O_2CCH_3)(CH_3CN)_6][BF_4]_2^{10}$, $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2^{11}$, and $Ru_2(O_2CCH_3)_4Cl^5$ carried out in a 1:2 metal/ligand ratio (Eqs. 13, 14) reactions proceed instantaneously as judged by the color changes that occur within minutes of mixing the reagents.

$$[M_{2}(OAc)_{2}(CH_{3}CN)_{6}][BF_{4}]_{2} + 2 \text{ pynp} \xrightarrow{CH_{3}CN} [M_{2}(OAc)_{2}(\text{pynp})_{2}][BF_{4}]_{2} \quad (Eq. 13)$$

M = (a) Mo²⁺, (b) Rh²⁺ yield: a = 75%
b = 70%

$$[Ru_{2}(OAc)_{4}]Cl + 2 pynp \qquad \xrightarrow{CH_{3}OH} [Ru_{2}(OAc)_{2}(pynp)_{2}][PF_{6}]_{2} \quad (Eq. 14)$$

$$[n-Bu_{4}N][PF_{6}] \qquad yield: 60\%$$

___ _

The pale violet solution of $[Mo_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ solution changes to a bright green color, the purple solution of $[Rh_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ changes to a pale red color, and finally the brown solution of $Ru_2((O_2CCH_3)_4Cl$ first changes to a dark purple color and later reverts to dark blue. X-ray and NMR studies (*vide infra*) revealed that the reactions proceed by displacement of the equatorial acetonitrile ligands in the former two cases and, in the case of the diruthenium chemistry, a loss of two acetate ligands accompanied by a reduction from $[Ru_2]^{5+}$ to $[Ru_2]^{4+}$.

The replacement of acetonitrile molecules the six on $[M_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ to yield $[M_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ (M = Rh, Ru) occurs in methanol, ethanol and acetone regardless of the use of different ligand/metal ratios or reaction temperature. In the case of the [Mo₂]⁴⁺ complex, however, decomposition occurs at higher temperatures. The synthesis of the dinuclear [Ru₂]⁴⁺ complex is best performed in alcohols, as reactions preformed in acetonitrile and acetone lead to much lower yields. In the case of the reaction of [Rh₂(O₂CCH₃)₂(CH₃CN)₆][BF₄]₂ with pynp, the side-product $[Rh_2(O_2CCH_3)_2(pynp)_2(CH_3CN)_2][BF_4][PF_6]\cdot 2CH_3CN$ (33) was isolated and characterized by single crystal X-ray methods.

A.2. X-ray crystallographic studies.

The molecular structures of the dinuclear cations for compounds (30)-(32) are essentially identical, as indicated by X-ray crystallography (Figures 69-72). The compounds consist of a dimetal unit spanned by two cis tridentate pynp ligands, in addition to two bridging acetate ligands. Such a series of compounds is convenient for studying the effect on structure and properties of a non-innocent ligand such pynp in a series of related dinuclear compounds. One interesting aspect to consider is the axial interaction between the metal and the nitrogen donor of the pyridyl unit. The pseudoaxial pyridine interaction is relatively long in all three cases, with M-N distances ranging from 2.204 (4) to 2.439 (8) Å and M-M-N_{ax} angles in the range 159.01[2] to 169.6(3)°. Compound [Mo₂(O₂CCH₃)₂(pynp)₂][BF₄]₂·3CH₃CN (**30**) exhibits the longest axial M-N distance of 2.439 [8]Å as expected for a [Mo₂]⁴⁺ quadruply-bonded complex.¹² In the case of $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2.2CH_3OH$ (**31**) complex, the axial interaction is of an intermediate value, Ru(1)-N(3)Å 2.237(7)Å, which is consistent with the fact that this species is a doubly-bonded compound. Finally, $[Rh_2(O_2CCH_3)_2(pynp)_2][BF_4]_2.C_7H_8$ (**32**) exhibits the shortest axial interaction, 2.204 (4) Å (Rh(1)-N(3), as expected for the compound with the weakest M-M bond trans-influence.¹²

The strength of the axial interation is closely tied to the M-M distance, as well illustrated by this series of compounds. The quadruply-bonded compound $[Mo_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ $3CH_3CN$ (30) exhibits a M-M bond distance of 2.124(1) Å, whereas the reported M-M distance for the parent molecule $Mo_2(O_2CCH_3)_4$ is 2.0934(8) Å.¹³ The lengthening of the metal-metal bond by 0.03 Å is attributed primarily $[Ru_2]^{4+}$ derivative the axial interaction. The in this series to $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2.2CH_3OH$ (31) exhibits a Ru-Ru distance of 2.298 (1)Å, which is slightly longer than the corresponding distances in [Ru₂(O₂CCH₃)₄(THF)₂] and $[Ru_2(O_2CCH_3)_4(H_2O)_2]$ which are 2.261(3) and 2.265(3)Å, respectively.¹⁴ This lengthening can be attributed to the fact that the pyridyl ring is a better axial donor than THF or H₂O. Finally, in $[Rh_2(O_2CCH_3)_2(pynp)_2][BF_4]_2.C_7H_8$ (32) the Rh-Rh distance is 2.408 (2)Å which is well within the expected values for a Rh-Rh single bond.¹⁷ This distance is 0.04 Å longer than the corresponding distance in $Rh_2(O_2CC_3H_7)_4$ ¹⁵ which is the only dirhodium tetra-carboxylate compound without axial coordination to be structurally characterized. The lengthening of the M-M bond is due to the donation of the pyridyl moiety into the σ^* antibonding orbital of the $[Rh_2]^{4+}$ unit.

The $M-N_{eq}$ interactions with the naphthyridine bridges are considerably shorter than the $M-N_{ax}$ interactions by comparison, and they decrease as the radius of the metal

ion decreases. Since Mo^{II} possesses the largest radius, the M-N distances are the longest with the averages being 2.211[8] Å followed by Ru^{II} with 2.072[5] Å and finally Rh^{II} with 2.018 [4]Å.

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Table35.Sele $[Mo_2(O_2CCH_3)_2(pynp)]$	ected bond dist)2][BF4]2·3CH3CN (3	ances (Å) and)).	angles	(°) for
NG1 02	2.029/(/)	M-2 02		2 002/()
Mo1-03	2.088(6)	M02-02		2.092(0)
Mol-Ol	2.114(6)	M02-04		2.150(6)
Mol-Mo2	2.124(1)	MOZ-NZ		2.165(8)
Mol-No	2.184(8)	Mo2-N5		2.245(7)
Mol-NI	2.251(7)	Mo2-N4		2.450(8)
Mol-N3	2.429(8)			
O3-Mo1-O1	88.4(2)	O2-Mo2-N2		88.5(3)
O3-Mo1-Mo2	93.5(2)	Mo1-Mo2-N2		94.7(2)
O1-Mo1-Mo2	89.66(17)	O4-Mo2-N2		174.9(3)
O3-Mo1-N6	88.1(3)	O2-Mo2-N5		175.9(3)
Ol-Mol-N6	174.3(3)	Mo1-Mo2-N5		90.7(2)
Mo2-Mo1-N6	95.1(2)	O4-Mo2-N5		91.2(3)
O3-Mo1-N1	174.7(3)	N2-Mo2-N5		92.0(3)
O1-Mo1-N1	87.6(3)	O2-Mo2-N4		106.6(3)
Mo2-Mo1-N1	90.1(2)	Mo-Mo2-N4		158.7(2)
N6-M01-N1	95.5(3)	O4-Mo2-N4		84.1(3)
O3-Mo1-N3	106.1(3)	N2-Mo2-N4		93.4(3)
01-Mo1-N3	84.3(3)	N5-Mo2-N4		69.3(3)
Mo2-Mo1-N3	159.33(19)	C1-O1-Mo1		119.8(6)
N6-M01-N3	92.2(3)	C1-O2-Mo2		116.8(5)
N1-Mo1-N3	69.9(3)	C2-O3-Mo1		116.5(6)
O2-Mo2-Mo1	93.33(18)	C2-O4-Mo2		118.7(6)
O2-Mo2-O4	88.0(2)	C4-N1-Mo1		121.6(6)
Mo1-Mo2-O4	89.20(19)	C8-N1-Mo1		119.9(6)



Figure 69. Thermal ellipsoid plot at the 50% level of the cation in [Mo₂(O₂CCH₃)₂(pynp)₂][BF₄]₂·CH₃CN (30). Hydrogens have been omitted for the sake of clarity.

Table 36.	Selected bond dist [Ru ₂ (O ₂ CCH ₃) ₂ (pynp) ₂][P	ances (Å) and F ₆] ₂ .2CH ₃ OH (31).	angles (°) for
Rul-Rul	2.298(1)	Rul-Nl	2.071(5)
Ru1-O2	2.054(5)	Ru1-O1	2.089(5)
Ru1-N2	2.072(5)	Ru1-N3	2.237(7)
O2-Ru1-N2	90.2(2)	O1-Ru1-N3	87.6(2)
O2-Ru1-N1	176.7(2)	O2-Ru1-Ru1	91.22(14)
N2-Ru1-N1	93.0(2)	N2-Ru1-Ru1	91.16(15)
N2-Ru1-O1	175.6(2)	N1-Ru1-Ru1	89.44(15)
N1-Ru1-O1	90.9(2)	O1-Ru1-Ru1	86.91(14)
N2-Ru1-N3	95.3(2)	N3-Ru1-Ru1	163.7(2)

As noted earlier, in addition to the [Rh₂]⁴⁺ dinuclear complex with two tridentate by-product pynp units, a was isolated, namely $[Rh_2(O_2CCH_3)_2(pynp)_2(CH_3CN)_2][BF_4][PF_6]\cdot 2CH_3CN$ (33). This compound cocrystallizes product from reaction as a side the that produces $[Rh_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$. In this compound, the dirhodium unit possess one pynp ligand coordinated in the tridentate fashion and a second pynp ligand that acts as a monodentate ligand to an axial position through one of the N atoms of the naphthyridine unit (Figure 72). The pseudo-axial distance (Rh(1)-N(4)) between the η^1 -pynp ligand and the metal center is 2.158 (5) Å, which is 0.16 Å larger than the Rh-pyridyl interaction Rh(2)-N(3) 1.997 (5) Å. The weaker Rh-N interaction is presumably due to the weaker donor character of the naphthyridine nitrogen atom compared to the pyridine nitrogen unit.



Figure 70. Thermal ellipsoid plot of the cation in [Ru₂(O₂CCH₃)₂(pynp)₂][PF₆]₂·CH₃OH (31) at the 50% probability level. Hydrogen atoms have been omitted for the sake clarity.

Table 3	7.	Selected [Rh ₂ (O ₂ CC	bond H ₃) ₂ (pyn)	dista p)2][B]	nces $F_4]_2.C_7$	(Å) H ₈ (32).	and	angles	(°)	for
Rh1-Rh1			2.4075((18)	Rh1-	N1			2.045	(12)
Rh1-N2			1.985((12)	Rh1-	01			2.051	(11)
Rh1-O2			2.036((11)	Rh1-	N3			2.204	(11)
N2-Rh1-O2	•		90.2	2(5)	O2-R	h1-N3			90.4	1(4)
N2-Rh1-N1			92.0	D(5)	N1-R	h1-N3			95.0	5(4)
O2-Rh1-N1			173.8	3(4)	01-R	h1-N3			101.1	7(4)
N2-Rh1-O1			178.7	7(4)	N2-R	h1-Rh1			91.	1(3)
O2-Rh1-O1			88.6	5(4)	O2-R	hl-Rhl			86.9	9(2)
N1-Rh- O1			89.2	2(4)	N1-R	h1-Rh1			87.3	3(3)
N2-Rh1-N3			78.9	9(4)	01-R	h1-Rh1			88.3	3(2)

Table	38.	Selected bond [Rh ₂ (O ₂ CCH ₃) ₂ (p	d distances (Å) a pynp) ₂ (CH ₃ CN) ₂][BF ₄ [PF ₆]	and angles (°) 1 [·] 2CH ₃ CN (33) .	for
Rh1-N8		2.034(6)	Rh1-N4	2.158(5)	
Rh1-O1		2.084(5)	Rh1-O3	2.176(5)	
Rh1-N1		2.134(6)	Rh2-N3	1.997(5)	
N8-Rh1-	·O1	178.02(17)	N1-Rh1-O3	174.15(17)	
N8-Rh1-	N1	95.6(2)	N4-Rh1-O3	94.77(19)	
Ol-Rhl-	N1	85.1(2)	N8-Rh1-Rh2	93.27(14)	
N8-Rh1-	N4	95.5(2)	Ol-Rhl-Rh2	88.46(12)	
Ol-Rhl-	N4	82.67(19)	N1-Rh1-Rh2	97.86(14)	
N1-Rh1-	N4	90.9(2)	N4-Rh1-Rh2	166.96(15)	
N8-Rh1-	·O3	85.3(2)	O3-Rh1-Rh2	76.30(11)	
Ol-Rhl-	·O3	94.23(18)			



Figure 71. Thermal ellipsoid plot of the cation in [Rh₂(O₂CCH₃)₂(pynp)₂][BF₄]₂·C₇H₈
 (32) at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity.



Figure 72. Thermal ellipsoid plot of the cation in [Rh₂(O₂CCH₃)₂(pynp)₂(CH₃CN)₂][BF₄][PF₆]₂·2CH₃CN (32) at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity.

A.3. Theoretical calculations.

To gain insight into the electronic structure of the series $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (compounds (**30**), (**31**), and (**32**)), single point energy calculations were performed by Dr. Lisa Thompson at Texas A&M University for the dication, neutral and dianion of these complexes at the B3LYP level of theory. An orbital analysis of the calculated orbital occupancy for the dication of $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$, $[Ru_2(O_2CCH_3)_2(pynp)_2]^{2+}$, and $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$, showed the expected metal orbital occupancy of $\sigma^2 \pi^4 \delta^2$, $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*1} \pi^{*1}$, and $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*4}$ respectively. Details of the findings as they pertain to the experimental findings in this chapter are found in Appendix I. Only a summary of how the results of the calculations support the spectroscopic and electrochemical results is included in the relevant sections.

A.4. UV-	Visible	and NMR	spectrosco	pic studies.
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Table 39. UV-Visible data for compounds (30)-(32)					
	λ _{max} nm	ε L·(mol·cm) ^{−1}			
[Mo ₂ (O ₂ CCH ₃) ₂ (pynp) ₂ [BF ₄] ₂ (30)	432 857	1.8×10^3 4.8×10^2			
$[Ru_2(O_2CCH_3)_2(pynp)_2[PF_6]_2$ (31)	327 671	3.4×10^4 3.6×10^4			
$[Rh_2(O_2CCH_3)_2(pynp)_2[BF_4]_2$ (32)	278 355 451	$ \begin{array}{c} 3.1 \times 10^{4} \\ 8.7 \times 10^{3} \\ 2.4 \times 10^{3} \end{array} $			

The electronic spectra for the three compounds in the series $[M_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ were recorded in acetonitrile in the range 800-200 nm (Table 6). The spectrum for $[Mo_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ (30) exhibits an electronic transition in the visible range at 432 nm which is a characteristic energy for a $\delta \rightarrow \delta^*$ transition for a quadruply-bonded $Mo_2^{II,II}$ complex^{16,17} but the ε value is uncharacteristically high at 1.8 x 10^3 L·M⁻¹cm⁻¹ an order of magnitude greater than the typical values, suggesting the involvement of ligand character. The dinuclear [Ru₂]⁴⁺ complex (31) exhibits two electronic transitions located at 327 nm ($\varepsilon = 3.4 \times 10^4 \text{ L} \cdot \text{M}^ ^{1}$ cm⁻¹) and 671 nm ($\epsilon = 3.6 \times 10^{4} \text{ L} \cdot \text{M}^{-1}$ cm⁻¹). The dirhodium compound $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (32) displays three transitions located at 278, 355 and 451 nm with ε values of 3.1 x 10⁴, 8.7 x 10³ and 2.4 x 10³ L·M⁻¹cm⁻¹ respectively.

The aforementioned electronic spectral data indicate that the new compounds exhibit very different electronic properties than the parent tetracarboxylate species. Electronic transitions for $[Mo_2(O_2CCH_3)_4$ are located at 435 nm ($\varepsilon \approx 10^2 \text{ L} \cdot \text{M}^{-1} \text{ cm}^{-1}$), ¹⁷ for Rh₂(O₂CCH₃)₄]L₂ at $\lambda = 552 \text{ nm}$ ($\varepsilon \approx 2 \times 10^2 \text{ L} \cdot \text{M}^{-1} \text{ cm}^{-1}$) and $\lambda = 437 \text{ nm}$ ($\varepsilon \approx 1 \times 10^2 \text{ L} \cdot \text{M}^{-1} \text{ cm}^{-1}$), ¹⁸ and finally for Ru₂^{II,II}(O₂CCH₃)₄ at $\lambda_{max} = 448 \text{ nm}$ ($\varepsilon \approx 6 \times 10^2 \text{ L} \cdot \text{M}^{-1} \text{ cm}^{-1}$). ¹).¹² Clearly the presence of the two pynp ligands has perturbed the electronic structure of the HOMOand/or LUMO levels, a possibility that was probed by theoretical calculations (Appendix I).

¹H NMR Spectroscopy.

¹H NMR spectroscopic studies of the two diamagnetic compounds $[Mo_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ (30) and $[Rh_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ (32) in CD₃CN support the existence of the intact cations $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$ and

 $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ in solution. The ¹H NMR spectrum for $[Mo_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ displays an upfield singlet at $\delta = 2.65$ ppm for the acetate CH₃ groups and seven resonances between $\delta = 7.5$ -9.0 ppm for the aromatic pynp protons. The $[Rh_2]^{4+}$ complex (32) exhibits a similar pattern, with an upfield singlet located at $\delta = 2.25$ ppm and aromatic resonances in the range 7.5-9.7 ppm. The presence of only one acetate environment in each case and the 1:1 integration of acetate:pynp ligands is in accord with the solid-state structure.

A.5. Cyclic voltammetric studies.

Electrochemical studies of Compounds (**30**)-(**32**) were performed by the cyclic voltammetry technique in acetonitrile solutions (Figure 73). The cyclic voltammogram of $[Mo_2(O_2CCH_3)_2(CH_3CN)_6][BF_4]_2$ ·3CH₃CN (**30**) exhibits four reversible reduction couples located at $E_{1/2}^{(1)} = -0.43V$, $E_{1/2}^{(2)} = -0.67 V$, $E_{1/2}^{(3)} = -1.34V$ and $E_{1/2}^{(4)} = -1.66V$ (Figure 6). In addition, an irreversible oxidation occurs at $E_{pa} = 0.86V$. The most salient point about these data is that the second reduction occurs at a potential that is 240 mV more negative than the first couple. This corresponds to a comproportionation constant, K_c , for this reaction of 1.2×10^4 (scheme 5), which was class II behavior according to the Robin-Day classification.¹⁹ Likewise the second set of one-electron reductions are coupled as judged by the fact that the fourth one-electron reduction occurs at a potential that is 320 mV higher than the third reduction process (K_c value of 2.70 x 10^5) (Scheme 5). These comproportionation constants are in the range of what has been observed for weakly coupled systems.

The compound $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2$ (31) also exhibits four reversible one-electron ligand based reductions; these are located at $E_{1/2}^{(1)} = -0.43$ V, $E_{1/2}^{(2)} = -0.82$ V, $E_{1/2}^{(3)} = -1.40$ V and $E_{1/2}^{(4)} = -1.84$ V (Figure 73). The second reduction is shifted to a more negative potential by 390 mV relative to the first one. This separation corresponds to a comproportionation constant of $K_c = 3.9 \times 10^6$, an indication that the unpaired electron is delocalized over the two pynp units (Class III, Robin-Day behavior).¹⁹ Analogously the third and fourth reductions occur at a separation of 420 mV, which leads to a calculated K_c value of 2.7 x 10⁷. This also corresponds to class III behavior (Scheme 5). In addition, the compound displays a reversible couple at $E_{1/2} = 0.85V$ which corresponds to the oxidation from $[Ru_2]^{4+}$ to $[Ru_2]^{5+}$.

$$\begin{bmatrix} M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2} \end{bmatrix}^{2+} \qquad \underbrace{+e^{-}}_{-e^{-}} \qquad \begin{bmatrix} M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2} \end{bmatrix}^{+} \qquad E^{(1)}_{\frac{1}{2}} \\ M = a) Mo, & K_{c}(a) = 1.2 \times 10^{4} \\ K_{c}(b) = 3.9 \times 10^{6} \\ \begin{bmatrix} M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2} \end{bmatrix}^{+} \qquad \underbrace{+e^{-}}_{-e^{-}} \qquad \begin{bmatrix} M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2} \end{bmatrix} \qquad E^{(2)}_{\frac{1}{2}} \\ E^{(2)}_{\frac{1}{2}} \end{bmatrix}$$

$$[M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2}] \xrightarrow{+e-} [M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2}]^{-} E^{(3)}_{\frac{1}{2}}$$

$$K_{c}(a) = 2.7 \times 10^{5}$$

$$K_{c}(b) = 2.7 \times 10^{7}$$

$$[M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2}]^{-} \xrightarrow{+e-} [M_{2}(O_{2}CCH_{3})_{2}(pynp)_{2}]^{2-} E^{(4)}_{\frac{1}{2}}$$

Scheme 5

In contrast to the previous two cases, $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}(31)$ exhibits only two reduction features in the cyclic voltammogram; these are located at $E_{1/2}^{(1)} = -0.78$ V and $E_{1/2}^{(2)} = -1.42$ V (Figure 6c). The first reduction process is associated with a two-



Figure 73. Cyclic voltammograms for compounds (30)-(32) in acetonitrile with 0.1 M [n-Bu₄N][PF₆] at a Pt disk electrode versus Ag/AgCl.

electron process whereas the latter one is a one-electron process as determined by coulometry and differential pulse voltammetry (Figure 74).

A homologous series such as the present one is an ideal situation for making comparisons based on the differences in metal frontier orbitals. The cyclic voltammetry results for the Mo₂(II,II) and Ru₂(II,II) complexes indicate stable mixed-valence intermediates of the type $[M_2(O_2CCH_3)_2(pynp)_2]^+$ and $[M_2(O_2CCH_3)_2(pynp)_2]^-$, whereas for the Rh₂(II,II) complex, the mixed valence states are not stable. In order to understand this situation, theoretical calculations were performed (Appendix I), and the results indicated that the dirhodium compound is undergoing decomposition as the LUMO is becoming populated during the reduction processes. In the case of the stable reduced forms of Mo₂(II,II) and Ru₂(II,II), however, the calculations reveal that the ratios of the changes in energy between orbitals *before and after* reduction are in excellent agreement with the observed differences in potential between the two sets of reductions (neutral/2e⁻ reduction and 2e⁻ reduction).



Figure 74. Diferential pulse voltammogram of [Rh₂(O₂CCH₃)₂(pynp)₂][BF₄]₂ in 0.1 M TBAPF₆ acetonitrile at a Pt disk electrode versus Ag/AgCl.

A 6. Magnetic studies.

In this series, only $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2$ (**31**) is paramagnetic. According to previous studies on various $[Ru_2]^{4+}$ compounds, the ground state spin value is S = 1.²⁰ In order to understand the magnetic behavior of these compounds, it is necessary to understand that a large zero-field splitting is expected due to spin-orbit coupling.^{24b} The actual data for $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2$ confirms this prediction. Figure 75 presents



Figure 75. Plot of χT versus T (red) and χ versus T (blue) for $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2$ at an applied field of 1000 G.

the data in two different ways, namely as χ vs T and χ T vs T plots. The plot of χ T versus T shows a constant decrease as the temperature decrease due to the zero field splitting present in this compound. The plot of χ versus T displays an increase in susceptibility

below 30 K that can be attributed to a small amount of paramagnetic impurity (probably the oxidized Ru(II)-Ru(III) species) which must be taken into account for modeling the magnetic behavior of compound $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2$. In order to fit this experimental data to a theoretical expression of the magnetic susceptibility for an anisotropic S = 1 system, which accounts for the small paramagnetic impurity and the Tip observed, the equation 14 was used.

$$\chi = (2Ng_{\rm M}^{2}\mu_{\rm B}^{2}/3\kappa T)\{[e^{-x} + (2/x)(1 - e^{-x})]/(1 + 2e^{-x})\} + Tip + P/T (Eq. 14)$$

In equation 14 x = D/ κ T accounts for the zero field splitting and g_M was assigned a value of 2, these assignments were based on previous studies done in [Ru₂]⁺⁴ systems.²⁴

III. Conclusions

Extensive research over the past forty years has been carried out on the tetracarbox vlate family of compounds of general formula $M_2(O_2CCH_3)_4$ (M= Mo²⁺, Ru²⁺, Rh²⁺).¹⁷ Although these compounds are useful starting materials for a variety of M-M bonded derivatives, they do not exhibit extensive redox chemistry or unusual electronic properties. In sharp contrast, the new compounds in this study that contain two pyridyl naphthyridine ligands pynp in addition to two acetate ligands display vastly different behavior. In particular, $[Mo_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ ·3CH₃CN (30) and $[Ru_2(O_2CCH_3)_2(pynp)_2][PF_6]_2 \cdot CH_3OH$ (31) exhibit four, reversible one-electron reduction processes. In the case of the $[Mo_2]^{4+}$ compound (30) the four reductions indicate Class II behavior based on the Robin and Day scale.¹⁹ For the [Ru₂]⁴⁺ compound. the potentials of the four, one-electron reduction couples signify Class III behavior, namely a fully delocalized system.

Density functional theoretical calculations (Appendix I) lend supporting evidence for the correlation between the degree of mixing of the metal-based orbitals with the ligand orbitals and the degree of delocalization of the electrons upon reduction. The Ru₂(II,II) complex exhibits the highest degree of mixing, thus the larger comproportionation constants are observed.

The capability of pynp to coordinate as either a tridentate or bidentate ligand had earlier been suggested, but not substantiated with X-ray evidence. This work presents the first well-characterized example of the monodentate coordination mode for the pynp ligand, which is a likely intermediate in the eventual stabilization of the tridentate form.

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APPENDIX I

Density Functional Calculations on LIST COMPOUNDS.

In order to gain insight into the electronic structure of the compounds $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$, single point energy calculations were performed at the B3LYP level of theory for the dication, neutral and dianion versions of all three complexes. In the case of the Ru(II) analog, calculations were also performed on the monocation and monoanion species. Analyses of the calculated orbital occupancies for the dications $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$, $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$, and $[Ru_2(O_2CCH_3)_2(pynp)_2]^{2+}$ supports the electronic configurations of $\sigma^2 \pi^4 \delta^2$, $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*2}$, and $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*4}$ respectively.

Correlation with electronic transitions

The calculated energy differences between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels for each of the three new compounds from DFT (*vide infra*) calculations are in good to reasonable agreement with the aforementioned experimental data. In all cases, the lowest energy transition is one that involves little to significant metal-to-ligand charge transfer (MLCT), which is in accord with the higher ε values than those reported for similar metal-metal bonded compounds. The calculated energy difference of the LUMO and the HOMO of the dication for complexes (**30**), (**31**), and (**32**), corresponds to the lowest energy transitions found in the UV-visible spectra for these species (Figure 76). In the case of $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (**30**), the lowest energy transition is a $\delta \rightarrow \delta^*$ transition, with a calculated (E_{LUMO}-E_{HOMO}) energy gap of 33.6 kcal/mol as compared to the experimental value of 33.3 kcal/mol. The extinction coefficient for this transition ($\varepsilon = 4.75 \times 10^2 \text{ LM}^-$

¹cm⁻¹) is an order of magnitude greater than those typically found for a pure $\delta \rightarrow \delta^*$ transition. The calculation indicates that the ligand character of the LUMO involved in the first electronic transition of $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$ is much greater than the ligand character of the HOMO (Table 40). From these results, it is possible to conclude that the lowest energy transition involves a metal-to-ligand charge transfer (MLCT), which are much more intense than pure d-d transitions.

The lowest energy transition for $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ was calculated to be a transition from a metal-based π^* orbital to a ligand-based π^* orbital (M_{π^*} -> L_{π^*}) with a value of 63.9 kcal/mol. This is in good agreement with the experimental value of 63.4 kcal/mol (Figure 76). The ε value is 2.4 X 10³ LM⁻¹ cm⁻¹ which is an order of magnitude larger than the ε value for the first transition of $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$. This finding is consistent with an increase in MLCT character for $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ as compared to $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (Table 40). Finally, the lowest energy transition for $[Ru_2(O_2CCH_3)_2(pynp)_2]^{2+}$ was also calculated to be a $M_{\pi^*} \rightarrow L_{\pi^*}$ transition (MLCT) with an energy of 59.3 kcal/mol. The experimental value is 42.6 kcal/mol, which is in reasonable agreement with the calculations (Figure 76). The MLCT character for Ru_2^{2+} is calculated to be slightly smaller than for Rh_2^{2+} which is consistent with the slightly smaller extinction coefficient for Ru_2^{2+} ($\epsilon = 3.1 \times 10^4 LM^{-1} cm^{-1}$) compared to Rh_2^{2+} ($\epsilon =$ 3.1 X 10^4 LM⁻¹ cm⁻¹). An overestimation of the excitation energy is not entirely unexpected for this type of estimation, as the correlation energy at the excited electron is not used, but it is somewhat surprising given the close agreement of the calculated and experimental results for the other two compounds. Obviously, solvation of $[Ru_2(O_2CCH_3)_2(pynp)_2]^{2+}$ could lead to subtle geometry changes, which affects the
validity of comparing calculations performed on parameters taken from the solid-state structure with electronic spectral measurements measured in solution. One other point that should be emphasized is that the dication of $[Ru_2(O_2CCH_3)_2(pynp)_2]^{2+}$ is an unrestricted open-shell calculation with two unpaired electrons (S = 1 with the alpha and beta orbitals optimized independently), whereas $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$ and $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ were both closed shell calculations (S = 0).

Correlation with Electrochemistry.

DFT single point energy calculations on the X-ray crystal structure of the dications were performed for three different oxidation states of the Mo and Rh compounds, namely $[Mo_2(O_2CCH_3)_2(pynp)_2]^{(2+/0/2-)}$, $[Rh_2(O_2CCH_3)_2(pynp)_2]^{(2+/0/2-)}$ and five different oxidation states of the Ru(II) compound $[Ru_2(O_2CCH_3)_2(pynp)_2]^{(2+/1+/0/1-/2-)}$. These calculations were analyzed and compared to the electrochemical potentials for the reduction of the three parent compounds $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$. An open-shell calculation was unavoidable for $[Ru_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (31), because the ground state was determined experimentally to be a triplet (S = 1), therefore, 1e⁻ and 2e⁻ reductions were calculated. A single point energy calculation was performed on both the singlet (S = 0) and triplet (S = 1) for (32), and the triplet was found to be 35.4 kcal/mol lower in energy, in agreement with the magnetic measurements. For compounds $[Mo_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (30) and $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (32), 2e⁻ reductions were simulated instead of 1e⁻ reductions to decrease the difficulty of the computations. The 2e⁻ reductions produce compounds with all electrons spin-paired (S = 0), while 1e⁻ reductions would produce open-shell (S = 1/2) species for (30) and (32), which are harder to compute than the closed-shell species (S=0).

To correlate the calculated energetics with the observed electrochemistry the change in the $\Delta E(LUMO - HOMO)$ (energy difference between the HOMO and LUMO) of the unreduced species and the $\Delta E(HOMO - HOMO-1)$ of the reduced species was originally calculated with the expectation that the larger the calculated change the larger the splitting in the 1e⁻ reduction potentials. It was found that the absolute change in orbital energy differences did not correlate due to the lack of solvation of the charge in the gas phase calculations. In an attempt to compensate for the effect that the change in charge has on the orbital energetics, the difference in the change in the frontier orbital energies. For example, the normalized change in orbital energy (NCOE) for the 2e⁻ reduction of [Mo₂(O₂CCH₃)₂(pynp)₂]²⁺ is shown in equation 15.

$$\frac{\left(E_{HOMO}^{2+} - E_{LUMO}^{2+}\right) - \left(E_{HOMO-1}^{0} - E_{HOMO}^{0}\right)}{\frac{1}{2}\left(\left(E_{HOMO}^{2+} - E_{LUMO}^{2+}\right) + \left(E_{HOMO-1}^{0} - E_{HOMO}^{0}\right)\right)}$$
(Eq. 15)

According to this approach, the calculated NCOE values should be proportional to the splitting of the 1e⁻ reduction potentials in the cyclic voltammetry for this series of compounds. The relevant orbital energies, differences and NCOE values for compound (31) are listed in Table 41. As mentioned previously, $[Ru_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (31) is paramagnetic with two unpaired electrons (S=1), unlike the $[Mo^{4+}]$ (30) and $[Rh^{4+}]$ (32) derivatives. Since the ground state of the $[Ru^{4+}]$ complex is an open-shell calculation, the four 1e⁻ reductions in this series were calculated, as apposed to only calculating two 2e⁻ reductions. The NCOE for the 1e⁻ reduction of the dication of (31) was calculated to be 0.45, which indicates a fairly large splitting of the 1e⁻ process (0e⁻/1e⁻ to 1e⁻/2e⁻ reduction potentials). The NCOE for the 1e⁻ reduction of the neutral species was calculated to be 0.66, indicating a larger splitting of the second 1e⁻ process (2e⁻/3e⁻ to 3e⁻/4e⁻ reduction potentials). The cyclic voltammogram for (31) exhibits four 1e⁻ reductions with separations of $\Delta E_{1/2} = 390 \text{mV}$ (1e⁻/2e⁻) and $\Delta E_{1/2} = 420 \text{mV}$ (3e⁻/4e⁻), which is consistent with the calculated larger splitting of the second 1e⁻ process.

To determine if the modeling of 2e⁻ reductions would produce the same trend found when modeling the 1e⁻ reductions, the NCOE values for the 2e⁻ reduction of the dication and neutral species of (**31**) were calculated. The NCOE value for the 2e⁻ reduction of the dication was calculated to be 0.70, and the NCOE value for the 2e⁻ reduction of the neutral species was calculated to be 0.88, which also indicates that the splitting of the second 1e⁻ process should be larger than the first. Therefore, modeling the 1e⁻ process with a 2e⁻ reduction should also give a qualitative description of the splitting of the two 1e⁻ reduction potentials.

The orbital energies, differences and NCOE for compounds (30) and (32) are listed in Table 42. For the dinuclear complex (30), the NCOE for the first 2e⁻ reduction is 0.59, and for the second 2e⁻ reduction, the NCOE is 0.73. The cyclic voltammogram for $[Mo_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ also exhibits four 1e⁻ reductions with separations of $\Delta E_{1/2}$ = 240mV (1e⁻/2e⁻) and $\Delta E_{1/2}$ = 320mV (3e⁻/4e⁻). The NCOE for the second 2e⁻ reduction is larger than for the first 2e⁻ reduction, in agreement with the experimental results, which has a larger splitting of the second 1e⁻ process. The calculated NCOE values for both of the 1e⁻ processes of (30) are smaller than the corresponding NCOE calculated using the 2e⁻ reduction method for (31), a result that is also in agreement with the smaller splitting found in the cyclic voltammetry of (30).

For the complex $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (32), the NCOE for the first 2e⁻ reduction is 0.16, and for the second 2e⁻ reduction is 1.77. As previously mentioned, the cyclic voltammogram for the $[Rh_2(O_2CCH_3)_2(pynp)_2]^{2+}$ complex (32) is very distinct from its $[Mo_2]^{4+}$ (30) and $[Ru_2]^{4+}$ (31) counterparts. The calculated NCOE value for the 2e' reduction of $[Rh_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ (32) is much smaller than the NCOE values calculated for (30) or (32); which is consistent with the fact that the first two 1e⁻ reductions occur at nearly the same potential; this is entirely consistent with the electrochemical data. The NCOE value of 1.77 calculated for the second le process (3e) /4e⁻) for (32) indicates that the splitting of the 1e⁻ reduction potentials should be extremely large (Table 42). A differential pulse voltammetry (DPV) experiment performed on $[Rh_2(O_2CCH_3)_2(pynp)_2][BF_4]_2$ revealed that the first reversible process is a 2e⁻ reduction, whereas the second quasi-reversible couple is only a 1e⁻ reduction (Figure 73) in agreement with the calculated NCOE value. The orbital occupation for the neutral species of the $[Rh_2]^{4+}$ dinuclear complex (32) is $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*4} L(\pi^{*2})$ and the LUMO is an anti-bonding interaction of the metal- δ^* with a ligand- π^* orbital. Based on the fact that the electrochemical processes for this complex is quasi-reversible and that the second reduction is only a 1e⁻ reduction, it appears that the neutral species $Rh_2(O_2CCH_3)_2(pynp)_2$ begins to decompose upon occupation of the anti-bonding LUMO. Overall, the calculated NCOE values, as calculated by the 2e⁻ reduction method, for complexes, (30), (31), and (32), are in qualitative agreement with the experimentally determined splitting of the le reduction potentials, shown in the cyclic voltmmograms.

Table 40. Ratio of Metal to Ligand (M/L) and Ligand to Metal (L/M) character of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as calculated at the B3LYP level of theory for the dication $[M_2(O_2CCH_3)_2(pynp)_2]^{2+}$ (M = Mo²⁺, Ru²⁺ and Rh²⁺) of (**30**), (**31**), and (**32**).

	НОМО	LUMO	НОМО	LUMO
	M/L	M/L	L/M	L/M
Mo(+2)	1.63	0.36	0.61	2.74
$Ru(+2)^a$	1.53	0.01	0.65	9.87
Rh(+2)	1.33	0.09	0.75	11.5

^a HOMO and LUMO for the alpha molecular orbitals.

Table 41. Orbital Energies (hartrees) and Ratios for Important Molecular Orbitals in singlet (S = 0) dinuclear complex Mo(II) (30) and dinuclear complex Rh(II) (32), dication, neutral and dianion species.

	C1	C2	C3	ΔE^{a}	ΔE^{b}	NCOE	NCOE
M ₂ (+2)	НОМО	LUMO	LUMO+1	ΔEı	ΔE_3		
M ₂ (O)	HOMO-1	НОМО	LUMO	ΔE_3	ΔE₄	$\Delta_{1,3}^{c}$	
M ₂ (-2)	HOMO-2	HOMO-1	НОМО	ΔE_5	ΔE_{6}		Δ _{4,6}
Mo ₂ (+2)	-0.3745	-0.3193	-0.3042	0.055	0.015		
Mo ₂ (O)	-0.1447	-0.1148	-0.0807	0.030	0.034	0.59	
Mo ₂ (-2)	0.0713	0.1030	0.1189	0.032	0.016		0.73
Rh ₂ (+2)	-0.4109	-0.3090	-0.3062	0.103	0.003		
Rh ₂ (O)	-0.1870	-0.1003	-0.0791	0.087	0.021	0.16	
Rh ₂ (-2)	0.0435	0.1210	0.1223	0.078	0.001		1.77

^a ΔE_n = (orbital energy in column C2 – orbital energy in column C1) ^b ΔE_m = (orbital energy in column C3 – orbital energy in column C2)

^c
$$\Delta_{x,y} = \frac{\Delta E_x - \Delta E_y}{\frac{1}{2} (\Delta E_x + \Delta E_y)}$$

[Ru ₂ (O ₂ C	(CH ₃) ₂ (pynp C1	(1)2 ²⁺ (31), dr	oublet (S = C3	= 1/2) (31) ⁽¹⁺ C4	ΔE^{a}	l singlet ΔE^{b}	ΔE^{c}	11 ^(0/2-)	NCOE
Ru(+2)	ОМОН	LUMO	LUMO+1	LUMO+2	ΔE_1	ΔE_2	ΔE_3		
Ru(+1)	HOMO-1	OMOH	LUMO	LUMO+1	ΔE_4	ΔE ₅	ΔE_6	$\Delta_{1,4}$	
Ru(0)	HOMO-2	HOMO-1	ОМОН	LUMO	ΔE_7	ΔE_8	ΔE_9		
Ru(-1)	HOMO-3	HOMO-2	HOMO-1	ОМОН	ΔE_{10}	ΔE_{11}	ΔE_{12}		ΔΕ9,12
Ru(-2)	НОМО-3	HOMO-2	I-OMOH	ОМОН	ΔE13	ΔE14	ΔΕ15		ΔΕ9,15
ku(+2) ^a	-0.3921	-0.3110	-0.3041	-0.2991	0.081	0.007	0.005		
Ru(+1) ^b	-0.2790	-0.2275	-0.1927	-0.1894	0.051	0.035	0.003	0.45	
Հս(0) ^ª	-0.1558	-0.1307	-0.1136	-0.0747	0.025	0.017	0.039		
ku(-1) ^c	-0.0445	-0.0256	-0.0160	0.0035	0.019	0.010	0.020		0.66
ku(-2) ^a	0.0749	0.1082	0.1119	0.1270	0.033	0.004	0.015		0.88
$ \begin{array}{l} E_m = (0) \\ E_n = (0) \\ E_p = (0) \\ Alpha = \\ \end{array} $	rbital energ. rbital energy rbital energy Beta orbital	y in column y in column in column energies, ^e E	C2 – orbital C3 – orbital C4 – orbital 3eta orbitals	energy in co energy in co energy in co	olumn C olumn C olumn C	(1) (3)		⁸ Al _I ⊿ _^	$\frac{\text{oha orbitals}}{x} = \frac{\Delta E_x - \Delta E_y}{\frac{1}{2} \left(\Delta E_x + \Delta E_y \right)}$

he Pertinent Molecular Orbitals in triplet $(S = 1)$	= 1/2) (31) ^(1+/1-) . and singlet (S = 0) 31 ^(0/2-) .
able 42. Molecular Orbital Energies for the	Ru ₂ (O ₂ CCH ₃) ₂ (pynp) ₂] ²⁺ (31), doublet (S





