PART I

THE PREPARATION AND OPTICAL AND ELECTRON SPIN RESONANCE SPECTRA OF SOME HEXACHLORO AND PENTACHLOROALKOXO VANADATES (IV)

PART II

THE INVESTIGATION OF THE APPARENT THERMOCHROMISM OF SOME VANADIUM (III) COMPLEXES

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Major professor

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ABSTRACT

PART I

THE PREPARATION AND
OPTICAL AND ELECTRON SPIN RESONANCE SPECTRA OF
SOME HEXACHLORO AND PENTACHLOROALKOXO VANADATES(IV)

By

Robert Deane Bereman

A new class of crystalline vanadium(IV) compounds, the pentachloroalkoxovanadates(IV), has been prepared and characterized. The alkoxo group was methoxo, ethoxo, n-propoxo, or n-butoxo, while the cation was tetramethylammonium, tetraethylammonium, or pyridinium. The relative stabilities of the complexes are dependent on the cations. The color of all the complexes is golden.

Two new salts of the hexachlorovanadate(IV) ion were also prepared. The tetramethylammonium and tetraethylammonium hexachlorovanadates(IV) were prepared by adding a solution of VCl_4 in thionyl chloride to a solution of the tetraalkylammonium chloride in thionyl chloride.

The pentachloroalkoxovanadates(IV) were prepared by the addition of one equivalent of the appropriate alcohol to a slurry of the tetraalkylammonium or pyridinium hexachlorovanadate(IV) in an acetonitrile - ethyl ether mixture. The alkoxo complexes could be converted to the appropriate hexachloro complex by the addition of HCl or thionyl chloride and thus indicated the absence of a vanadyl species.

Magnetic studies indicated Curie-Weiss paramagnetism and verified the presence of the vanadium(IV) ion with $3d^1$ configuration. The infrared spectra of the complexes were in agreement with the formulation $V(OR)Cl_5^{-2}$, showing characteristic alkoxide C-O absorptions in the region 1000-1100 cm^{-1}. The ultraviolet-visible spectra of the alkoxides consisted of two peaks around 14,000 cm^{-1} while the spectra of the hexachlorovanadates(IV) had an asymmetric peak around 15,500 cm^{-1}. The reflectance spectrum of each of the complexes agreed with the solution spectrum.

Attempts to prepare a tetrachlorodialkoxovanadate(IV) species as well as other examples of the pentachloroalkoxovanadate(IV) species were unsuccessful.

A complete investigation of the electron spin resonance spectra of the pure solids, solutions and frozen solutions (glasses) of the pentachloroalkoxovanadates(IV) and hexachlorovanadates(IV) was carried out. Trends in the hyperfine splitting constants as well as in some g values were observed in going from the methoxide to the n-butoxide. The observed g and A values were used to calculate the coefficients in a simple molecular orbital scheme. The two molecular orbitals made up of the d_{xy} and $d_{x^2-y^2}$ metal orbitals became more covalent in going from the methoxo to the n-butoxo complex. The molecular orbital made up of the metal d_{xz} or d_{yz} metal orbitals became more ionic. The unpaired electron density in each of the four equatorial

ligand $3p_{\pi}$ orbitals was calculated from the molecular orbital coefficients. The density increased along the series (methoxide to n-butoxide) as was expected.

PART II

THE INVESTIGATION OF THE APPARENT THERMOCHROMISM OF SOME VANADIUM(III) COMPLEXES

Several crystalline octahedral vanadium(III) complexes of the general type $[(C_2H_5)_4N]VBr_{4-x}Cl_x \cdot 2CH_3CN$ where x = 0-4 were prepared and investigated. The color of the complexes changes gradually from yellow for the $[(C_2H_5)_4N]VCl_4 \cdot 2CH_3CN$ complex to red-brown for $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$ complex. All the complexes have the unusual property of being yellow at 77^0K.

The ultraviolet-visible spectra of the solid complexes were investigated at several temperatures in an attempt to explain the color changes. A large charge transfer band at approximately 20,000 cm^{-1} for the $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$ complex shifts to a shorter wavelenth and narrows slightly to produce the color change. Spectra at 300^0K, 195^0K, and 77^0K show the shift is gradual.

Magnetic studies indicated temperature dependent paramagnetism and verified the presence of the vanadium(III) ion with $3d^2$ configuration. No abrupt changes were found in magnetic behavior as the color of the complexes changed.

The Cl nuclear quadrupole resonance spectra of the $[(C_2H_5)_4N]VCl_4 \cdot 2CH_3CN$ complex gave two peaks at 77^0K. The position of these peaks shift only slightly when the sample is warmed to room temperature. No Cl nuclear quadrupole resonance signal could be obtained on any of the other complexes.

The infrared spectra were also investigated at room temperature and 77^0K. Only minor differences in the spectra were noted. Most of the peaks due to metal-ligand vibrations as well as those due to the acetonitrile group could be assigned.

PART I

THE PREPARATION AND OPTICAL AND ELECTRON SPIN RESONANCE SPECTRA OF SOME HEXACHLORO AND PENTACHLOROALKOXO VANADATES(IV)

PART II

THE INVESTIGATION OF THE APPARENT THERMOCHROMISM OF SOME VANADIUM(III) COMPLEXES

By

Robert Deane Bereman

A THESIS

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INTRODUCTION

Much recent interest has centered on the investigation d^1 transition elements involving oxyions of the type $M^{(n+2)+}$ where $M^{(n+2)+}$ is Cr^{+5}, Mo^{+5}, W^{+5} or V^{+4}. The lide complexes of these ions have been studied and it is ll established that there is substantial π-bonding be- een the metal and oxygen atoms.[1-7] The relatively simple tical and magnetic properties which arise from a single paired electron and C_{4v} symmetry have made these systems rticularly appealing. The bonding and molecular orbitals interest in the vanadyl (VO^{++}) systems have been dis- ssed in detail by Ballhausen and Gray.[8] The bonding in other systems has been treated by various authors.[1-7]

Alcohol solutions are among the few solvent systems in ch one can work with d^1 transition element halides and id the formation of oxyions. Recent work in this labor- ry has been concerned with the preparation and character- tion of d^1 transition element alkoxides and complexes taining alkoxides as ligands.[9-16]

It was decided that vanadium(IV) chloro-alkoxides would of interest because of the large amount of work which has done on the vanadyl systems. The pentachloroalkoxo- date(IV) ion should be six-coordinate and the metal to

xygen bond would formally be a single bond. A study of a eries of these complexes in which the alkoxide group is hanged would show the effect on the bonding parameters of hanging the donating strength of the oxygen. The effect n the molecular orbital parameters of changing the donating trength of the halide by changing from F^- to Cl^- to r^- has been shown in the case of the pentahalo(oxo)molyb- ate(IV) ion.[1]

HISTORICAL

Vanadium(IV) Chemistry

Of those d^1 transition elements which have been vestigated, vanadium in the tetravalent state has cer-inly been the most thoroughly studied. Vanadium(IV) normally bonded to oxygen to give the familiar vanadyl $^{++}$) unit. The vanadium-oxygen bond has been shown to essentially a double bond, V=O, *i.e.* in $VO(H_2O)_5^{+2}$, there four water molecules in a plane with a V-O distance 2.3 Å; while perpendicular to this plane is the V=O d of length 1.67Å.[17] The multiplicity of the bond ses from the flow of electron density $O(p_\pi) \longrightarrow V(d_\pi)$. ause of the strong V-O π-bonding in oxovanadium(IV) plexes, the interpretation of the electronic spectra is as simple as it would be for an ordinary octahedral plex. There are presently unresolved differences of ion as to the exact ordering of the orbitals.[18]

Sidgwick[19] provides a suitable review of vanadium co-nation complexes through 1949. Excellent and compre-ive reviews of oxovanadium(IV) compounds have recently ared.[20,21] Somewhat fewer examples exist of vanadium(IV) on-vanadyl systems. The reaction of vanadium(IV)

alides with nitrogen and oxygen bases has been surveyed
y Fowles.[22] Bridgland, et al.[23] caused vanadium tetra-
hloride and vanadium tetrafluoride to react with a variety
f N-containing and O-containing ligands which did not con-
ain protonic hydrogens and obtained complexes of the general
ype VX_4L and VX_4L_2. All of the complexes are readily
drolyzed and oxidized in air. Vanadium tetrachloride also
rms 1:1 or 1:2 adducts with sulfur[24,25], selenium[26],
osphorous[27] and arsenic[28,29] donor molecules. Nicholls[30]
fers a thorough review of non-vanadyl complexes since
49.

Solvolytic reaction of vanadium(IV) chloride with
cohols and phenols causes cleavage of two V-Cl bonds,
rming the dichloroalkoxides. The general properties of
ese compounds have been reviewed by Nicholls.[30]

The alkoxides formed by the aliphatic alcohols are dark green solids, dimeric in boiling benzene. These dimers probably contain hexa-coordinate vanadium with a structure consisting of two octahedra sharing a common edge through alkoxide bridges. They cannot be sublimed, but on heating at 150° C/0.1 mm they yield the oxychloride alkoxides, $[V_2OCl_3(OR)_3]$. The tert-butyl and tert-amyl alkoxides are most conveniently prepared by alkoxide ion exchange with isopropoxides.

Bradley and Menta[31] and Thomas[32] have prepared a
iety of tetraalkoxovanadates(IV). These compounds are
mally prepared by causing tetrakis(dimethylamide)vana-
e(IV) or tetrakis(diethylamide)vanadate(IV) to react with
hols. Primary, secondary, and tertiary alkoxides of this
e have been prepared. The tertiary and secondary alkoxides

are predominantly monomeric in benzene. However, tetramethoxovanadate(IV) is apparently a trimer in benzene which is the limiting degree of association for an octahedrally-coordinated metal alkoxide. Chamberlain, et al.[33] prepared tetrakis(triphenylsiloxy)vanadium(IV) from vanadium tetrachloride and sodium tetraphenylsilanolate. The liquid, ethyl analogue was prepared by Thomas[34] from vanadium(IV) diethylamide and triethylsilanol in benzene.

Only two previous examples of anionic, octahedral, non-vanadyl vanadium(IV) complexes exist. Potassium, rubidium, and cesium hexafluorovanadate(IV) were prepared from vanadium(IV) fluoride and the appropriate fluoride salt in selenium tetrafluoride or by fluorination of the appropriate pentafluorovanadate(III) salt.[35] Six salts of the hexachlorovanadate(IV) ion have been prepared. Gutmann[36] first identified the hexachlorovanadate(IV) ion by the conductimetric titration of potassium chloride with vanadium tetrachloride in iodine monochloride. Subsequent conductimetric titrations of vanadium(IV) chloride with various bases have shown the presence of hexachlorovanadates(IV) in a range of chlorinated solvents.[37-39] Other titrations gave evidence for the pentachloro-, heptachloro-, and octachlorovanadate(IV) ions which have not yet been isolated.[40] Fowles and Walton[41] first prepared the diethylammonium and triethylammonium salts of the hexachlorovanadate(IV) ion by the reaction of either vanadium(IV) chloride or its ethyl cyanide adduct with the ethylammonium salt in chloroform. Kilty and Nicholls[42]

epared the pyridinium, quinolinium, isoquinolinium, and sium salts of the hexachlorovanadate(IV) ion by the reaction of thionyl chloride with the corresponding tetrachloro(oxo)vanadate(IV) salt at room temperature.

$$M_2VOCl_4 + SOCl_2 \longrightarrow M_2VCl_6 + SO_2$$

All the salts except the cesium hexachlorovanadate(IV) ssolve in acetonitrile to give red solutions. Two peaks ve been observed in the solution and reflectance spectra. e peak at 15,000 cm^{-1} is believed to be the $^2T_{2g} \rightarrow {}^2E_g$ nsition. This peak is somewhat broad and asymmetric. e more intense peak around 21,000 cm^{-1} is a charge trans- band and accounts for the dark red color.

Anionic d^1 Transition Element Alkoxides

Recently several examples of d^1 anionic alkoxides e been prepared. Wentworth and Brubaker[9,10] first pred the pentachloroalkoxoniobate(IV) complex; the alkoxide methoxo, ethoxo, or isopropoxo, while the cation was ally a large protonated organic base. The complexes e prepared by the addition of the appropriate base to a tion of niobium(V) chloride in alcohol which had been ced electrolytically to niobium(IV). The color of the lexes was found to depend on the cation used.

Funk, et al.[43] first prepared pyridinium tetrachlorothoxomolybdate(V) by the treatment of $Mo(OCH_3)_2Cl_3 \cdot 3CH_3OH$ pyridinium chloride in methanol. McClung, et al.[12]

repared and investigated various other salts of the methoxide
omplex as well as the ethoxide and isopropoxide complexes.
hese complexes were prepared by a method somewhat different
rom Funk's. Molybdenum(V) chloride was dissolved in alcohol
195^{0}K and allowed to warm to room temperature. An excess
the cation was then added to the green solutions to give
e crystalline products.

Funk and Naumann[44] first prepared the pyridinium and
iethylammonium salts of the tetrachlorodimethoxotungstate(V)
n. Rillema, et al.[14] have recently prepared other examples
the tetrachlorodialkoxotungstate(IV) complex as well as
her salts of the dimethoxo complex. They also reported
e first examples of the pentachloroalkoxotungstate(V) ion.
ese complexes decompose in the solid state to give the
trachloro(oxo)tungstate(V) ion. The decomposition is

$$(R_4N)W(OR')Cl_5 \longrightarrow (R_4N)WOCl_4 + R'Cl$$

test when R and R' are methyl. The decomposition is
wer as either R' or R becomes larger. An apparently
en coordinate species, tetramethylammonium hexachloro-
oxotungstate(V), was also isolated from an HCl saturated
anol solution in which tungsten(V) chloride was dissolved.

Giggenbach and Brubaker[13] reported preparing a series
titanium(III) mixed chloride-alcoholates. More recently
same authors reported the preparation of two other
anium(III) chloride-methanolates[16], $[C_5H_6N]_2TiCl_5(CH_3OH)$
$[C_5H_6N]TiCl_4(CH_3OH)_2$, which are similar to the tungsten(V)

and molybdenum(V) alkoxides discussed earlier.

No anionic alkoxide complexes have been reported in the case of zirconium(III), hafnium(III), tantalum(IV), or chromium(V).

C. The Application of Electron Spin Resonance to Transition Metal Complexes

Several comprehensive reviews on the early development of electron spin resonance are given in previous theses from this department and will not be duplicated.[45-48]

Various recent books and reviews adequately cover the basic fundamentals of electron spin resonance. Low's[49] book is extremely useful although it covers only the esr of solids. Slichter[50] presents the theoretical development of esr in the solid state and Pake's[51] book is also a good reference. Anderson's[52] review gives various experimental applications of esr. Carrington and Lonquet-Higgens[53] have a thorough article covering the applications of esr to transition metal complexes and Robertson's[54] review also covers the applications of esr to transition metal complexes.

Several other more recent sources are available. Kuska and Rogers[5] certainly offer the most complete review of electron spin resonance studies of first row transition element complexes available at this time. Their chapter from "Radical Ions" is an extremely useful source as a complete review of the literature as well as a concise statement of the basic theories of covalent bonding parameters. Several

other chapters in "Radical Ions" also deal with inorganic systems.[55,56]

D. Electron Spin Resonance Studies of d^1 Transition Element Alkoxides

Only one example exists of an esr study of vanadium(IV) alkoxides. Kokoszka, et al.[57] investigated the tetrakis-(t-butoxo)vanadate(IV) complex. The spectra were measured in the temperature range of 295 to 77°K. The measurements were made on pure $V(OR)_4$, 1-2% $V(OR)_4$ in $Ti(OR)_4$, and 1-2% $V(OR)_4$ in CS_2 and the spectra were approximately the same in all samples. The electron spin resonance parameters for this compound are given in Table I.

Table I. Magnetic parameters for $V(OR)_4$*

Liquid Spectrum (295°K)	
$\langle g \rangle = 1.964 \pm 0.005$	$\langle a \rangle = 64.0 \pm 2.0$
Polycrystalline Spectra (77°K)	
$g = 1.940 \pm 0.005$	$A = 125 \pm 5.0$
$g = 1.984 \pm 0.005$	$A = 36 \pm 4.0$

*Hyperfine splittings are given in 10^{-4} cm^{-1}.

Rasmussen, et al.[11] investigated the solution and frozen solution (glasses) spectra of $Nb(OCH_3)Cl_5^=$. Both the isotropic g values and hyperfine splittings due to the ^{93}Nb (100% I = 9/2) nucleus were observed. The results

were interpreted in terms of an approximate molecular orbital approach to the bonding which takes into account the effect of charge-transfer states. The esr parameters and molecular orbital parameters obtained for this complex are listed in Table II. Because of the broad lines and lack of sufficient optical data, an accurate calculation of the molecular orbital parameters could not be made.

Table II. Esr and Molecular Orbital Parameters for $Nb(OCH_3)Cl_5^{=}$.

Liquid Spectrum	
$\langle g \rangle = 1.869 \pm .002$	$\langle a \rangle = 178 \pm 3$ gauss
Frozen Solution Spectrum	
$g_{\parallel} = 1.923 \pm .008$	$A_{\parallel} = 248 \pm 6$ gauss
$g_{\perp} = 1.842 \pm .010$	$A_{\perp} = 144 \pm 10$ gauss
Molecular Orbital Parameters	
$N^2_{\pi_2} = .62$	$N^2_{\sigma_2} \approx .45$
$N^2_{\pi_2} \approx .6$	

The electron spin resonance data which were reported for alcohol solutions of tetrachlorodialkoxomolybdates(V) now appear to be in error. The species being studied were probably the oxyion species and other hydrolysis products. The tetrachlorodialkoxomolybdates(V) are stabilized in alcoholic solutions which contain small amounts of HCl. The decomposition probably involves mechanisms such as:

$$Mo(OR)_2Cl_4^- + ROH \rightleftharpoons Mo(OR)_3Cl_3^- + HCl$$

$$Mo(OR)Cl_3^- \xrightarrow{fast} MoO(OR)Cl_3^- + ROR$$

$$HCl + MoO(OR)Cl_3^- \rightleftharpoons MoOCl_4^- + ROH$$

$$MoOCl_4^- + HCl \rightleftharpoons MoOCl_5^{-2} + H^+ .$$

This would explain the stabilizing effect of HCl as well as the esr being essentially the same as molybdenum oxochlorides which have been studied. Rillema and Brubaker[58] have re-investigated the esr spectra of solutions of tetrachloro-dialkoxomolybdates(V).

Rillema[59] studied the solution and frozen solution spectra of various pentachloroalkoxotungstates(V) as well as various tetrachlorodialkoxotungstates(V). The broad lines and lack of known constants (i.e. spin orbit coupling constants, overlap terms, etc.) for tungsten(V) made the calculation of accurate molecular orbital parameters impossible.

Giggenbach and Brubaker[16] have recently reported the esr spectra for a number of titanium(III) chloride-methanolates. Although very accurate g values could be obtained, no metal hyperfine structure was observed in any of the spectra and hence molecular orbital calculations could not be made for these complexes.

THEORETICAL

A. The Spin Hamiltonian

An unpaired electron in a transition metal complex interacts with its environment in several ways which are sensitive to study by electron spin resonance. These interactions are normally described in the form of spin Hamiltonian of the general form:

$$\mathcal{H} = \beta[g_z S_z H_z + g_x S_x H_x + g_y S_y H_y] + [A_z S_z I_z + A_x S_x I_x + A_y S_y I_y] + \sum_L [A_z^L S_z I_z^L + A_x^L S_x I_x^L + A_y^L S_y I_y^L] \quad (1)$$

where g_x, g_y, and g_z are the spectroscopic splitting factors, β is the Bohr magneton (0.92731×10^{-20} erg/Gauss), H_x, H_y, and H_z are the components of the magnetic field along the x, y, and z direction, and S_x, S_y, and S_z are the components of the electronic spin operator along the x, y, and z magnetic field axis respectively. I_x^L, I_y^L, and I_z^L are the ligand nuclear spins in the x, y, and z directions. A_x, A_y, and A_z are the metal hyperfine interaction constants and A_x^L, A_y^L, and A_z^L are the ligand hyperfine interaction constants. I_x, I_y, and I_z are the components of the metal nuclear spin along the respective axes.

For those cases in which the complex possesses axial symmetry, $x = y = \perp$ and $z = \parallel$ to give the more familiar form of the spin Hamiltonian.

$$\mathcal{H} = \beta[g_{\parallel}S_zH_z + g_{\perp}(S_xH_x + S_yH_y)] + [A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y)] + [\sum_L [A^LS_zI_z^L + A^L(S_xI_x^L + S_yI_y^L)]] \quad (2)$$

The first term in brackets in equation 2 is commonly referred to as the zeeman portion of the spin Hamiltonian. The second term is the metal hyperfine portion of the spin Hamiltonian. The third term is the ligand hyperfine, or super-hyperfine, portion of the spin Hamiltonian and it may be disregarded if no ligand hyperfine splittings are observed in the electron spin resonance spectrum. The principal information gained from the esr spectrum is the evaluation of the various g and A values of the spin Hamiltonian.

B. Molecular Orbital Theory

Various theories have been proposed and used to explain bonding in inorganic complexes. The first such theory was called Valence Bond Theory, VBT, and assumed that the ligands were groups which in some way donated electron pairs to metals, thus forming the so-called coordinate link. This theory enjoyed great and almost exclusive popularity in the 1930's and 1940's but was supplemented during the 1950's by Ligand Field Theory, LFT, LFT was developed between 1930

and 1940 by physicists, mainly, J. H. Van Vleck. The Ligand Field Theory that we employ today evolved from a purely electrostatic theory called Crystal Field Theory, CFT, which treats the metal and the ligands as pure point charges or point dipoles. At the opposite extreme, Molecular Orbital Theory, MOT, treats the metal-ligand interaction in terms of molecular orbitals formed by overlap of metal and ligand atomic orbitals. These various theories are covered in several books and reviews.[60,64] Molecular Orbital Theory has been extremely valuable in interpreting cases where there is a strong metal-ligand interaction (covalency).

Molecular Orbital Theory starts with the premise that metal and ligand orbitals will overlap to some degree whenever symmetry permits. It thus includes the electrostatic situation (no overlap) as one extreme, maximal overlap as the other extreme, and all intermediate degrees of overlap in its scope. The first task in working out the molecular orbital treatment for a particular type of complex is to find out which orbital overlaps are and are not possible because of the inherent symmetry requirements of the problem. This can be done elegantly and systematically by the use of group theory principles.

If one considers octahedral complexes, it is quite easy to obtain the pertinent molecular orbitals involved in

sigma (σ) and pi (π)-bonding. It is easy then to extend this treatment to complexes with lower symmetry.

In complexes involving transition metals one needs to only consider those metal orbitals which are valence orbitals, $3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, 4s, $4p_x$, and $4p_y$, and $4p_z$. It can be shown easily that the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals transform as the E_g representation in O_h symmetry. Also the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals transform as the T_{2g} representation, the 4s orbital transforms as the totally symmetric A_{1g} representation and the $4p_x$, $4p_y$, and $4p_z$ orbitals transform as the T_{1u} representation. Our task then is to construct ligand orbitals which have symmetries such that they can overlap with these metal orbitals to form either sigma or pi bonds. These ligand symmetry orbitals will be a linear combination of atomic ligand orbitals, LCAO, so that the bonding theory we are using is commonly called, LCAO-MO theory.

One first needs to obtain six ligand symmetry-orbitals to form six sigma-bonds with the metal orbitals. It is known from symmetry considerations that the $3d_{x^2-y^2}$, $3d_{z^2}$, 4s, $4p_x$, $4p_y$, and $4p_z$ metal orbitals lie along the x, y, z axes toward the ligand so the ligand sigma orbitals will be constructed to transform as E_g, A_{1g}, and T_{1u} representations. In this case, the six ligand symmetry-orbitals denoted 1 through 6, will be made from the six sp_z hybrid orbitals directed along the x, y, and z coordinates toward the metal. (A local right-handed coordinate system

where the σ-bond is the z axis has been taken on each on each ligand.) These six LCAO orbitals are given below.

$$\phi^{L}_{1\sigma} = \frac{1}{6}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) \qquad (A_{1g}) \qquad (3)$$

$$\phi^{L}_{2\sigma} = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \qquad (E_g) \qquad (4)$$

$$\phi^{L}_{3\sigma} = \frac{1}{12}(-\sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_5 + 2\sigma_6) \qquad (E_g) \qquad (5)$$

$$\phi^{L}_{4\sigma} = \frac{1}{\sqrt{2}}(\sigma_5 - \sigma_6) \qquad (T_{1u}) \qquad (6)$$

$$\phi^{L}_{5\sigma} = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3) \qquad (T_{1u}) \qquad (7)$$

$$\phi^{L}_{6\sigma} = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4) \qquad (T_{1u}) \qquad (8)$$

Where σ_1 and σ_3 lie along the + and - x axis, σ_2 and σ_4 along the + and - y axis, and σ_5 and σ_6 along the + and - z axis respectively. Now these six symmetry orbitals can overlap with the respective metal orbitals to form a sigma-bonding orbital (positive overlap) or a sigma-antibonding orbital (negative overlap). These molecular orbitals are commonly written as

$$\psi^{b} = N(\phi_m + \lambda\phi^{L}) \qquad (9)$$

$$\psi^{*} = N(\phi_m - \lambda\phi^{L}) \qquad (10)$$

where ϕ_m is the metal atomic orbital, ϕ^{L} is the ligand symmetry orbital, N is the normalization constant, and λ is the coefficient for the symmetry orbital. The separation between these two orbitals can be calculated. However, the separation is proportional to the amount of overlap and a

rough calculation of the overlap will give a good estimation of the separation. A molecular orbital diagram for an octahedral complex where no π-bonding has been considered is shown in Figure 1. The t_{2g} (d_{xz}, d_{yz}, and d_{xy} of the metal) orbitals are nonbonding. The asterick denotes an antibonding orbital which always lies higher in energy than its corresponding bonding orbital.

If the ligands have π-orbitals, filled or unfilled, it is necessary to consider their interaction with t_{2g} d orbitals on the metal. The simplest case occurs in the event that each ligand has a pair of p orbitals mutually perpendicular. Thus one has twelve linear combinations of atomic orbitals to consider. It can be shown that these twelve atomic orbitals transform as T_{1g}, T_{2g}, T_{1u}, and T_{2u} representations. Those atomic orbitals in the classes T_{1g} and T_{2u} will remain rigorously nonbonding. This is for the simple reason that the metal does not possess any orbitals of these symmetries with which they could interact. The T_{1u} set could interact with the metal p orbitals, which are themselves a set with T_{1u} symmetry and in a quantitative discussion it would be necessary to make allowances for this. However, in a qualitative treatment it may be assumed that since the metal p orbitals are already required for sigma-bonding and no π-bonding will take place involving the T_{1u} orbitals. This leaves only the t_{2g} set of symmetry orbitals to overlap with the metal t_{2g} d orbitals.

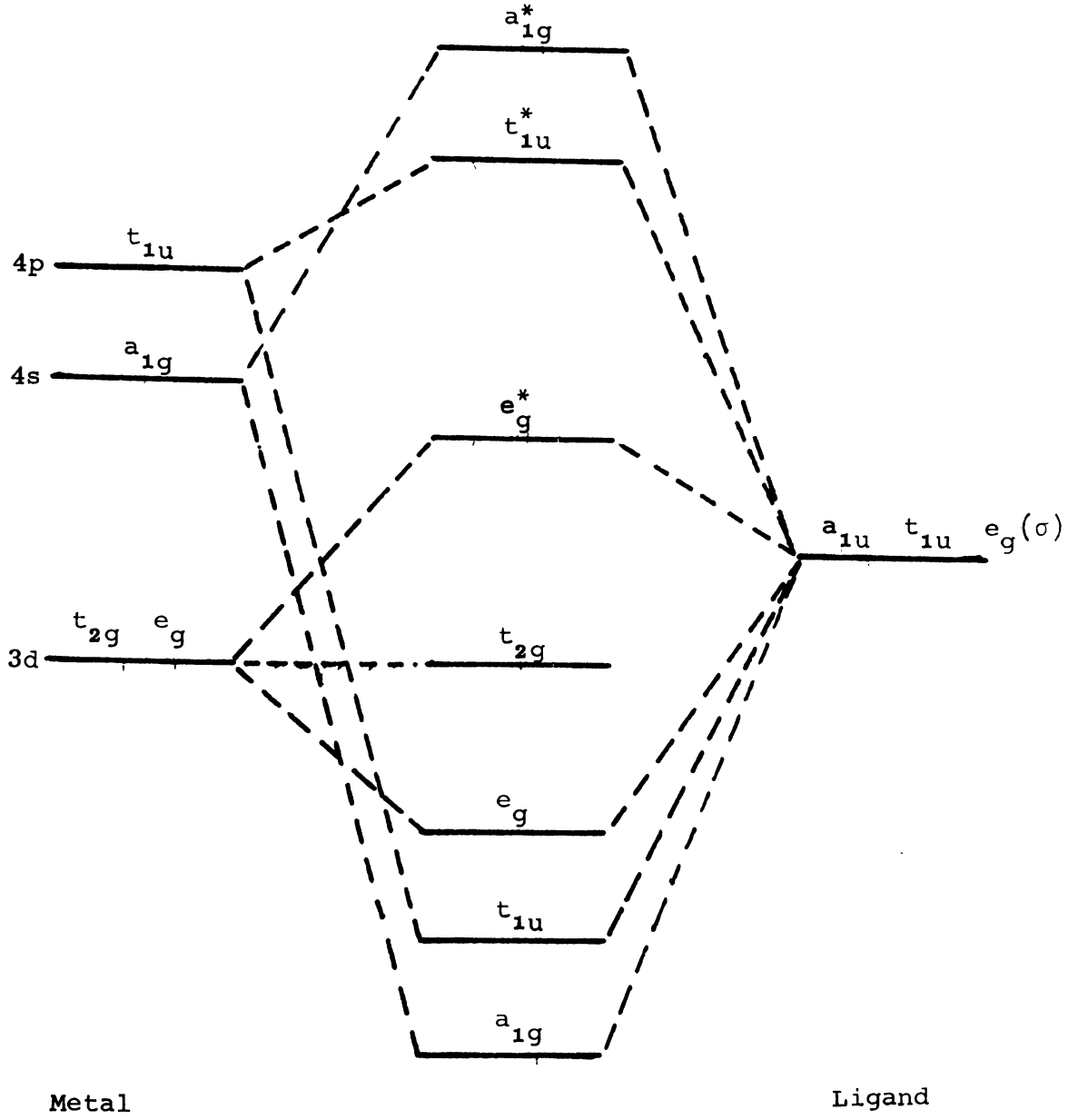


Figure 1. Molecular orbital diagram for an octahedral complex with no π-bonding.

The ligand symmetry orbitals which overlap with the metal d_{xz} orbital can be constructed as

$$\phi^{L}_{\pi_2} = \frac{1}{2}\left(p_y\,(1) + p_z\,(5) + p_x\,(3) + p_y\,(6)\right) \qquad (11)$$

where the numbering system is the same as used in the sigma-bonding case. Two similar symmetry orbitals can be written which overlap with the metal d_{xy} and d_{yz} orbitals. Again a set of bonding and antibonding orbitals are formed to give the MO diagram in Figure 2.

Now that the molecular orbital diagram has been developed for an octahedral complex, it is easy to obtain the molecular orbitals necessary for the discussion of other complexes of lower symmetry derived from octahedral symmetry. In the case of the vanadium alkoxide complexes discussed in this work, the symmetry is C_{4v}. From a correlation table such as that given by Cotton[65], the degenerate sets of symmetry orbitals in O_h symmetry can become nondegenerate in the lower C_{4v} symmetry. For example, the t_{2g} antibonding π-orbitals in O_h symmetry become b_2 and e antibonding π-orbitals in C_{4v} symmetry. Therefore the molecular orbital diagram for a complex with C_{4v} symmetry appears to be somewhat more complicated than the basic O_h case but is easy to understand if this approach is used. (Figure 3).

It cannot be shown from group theory which of the two orbitals b_2 or e is lower in energy. Similarly, it cannot be shown which of the two orbitals, a_1 or b_1

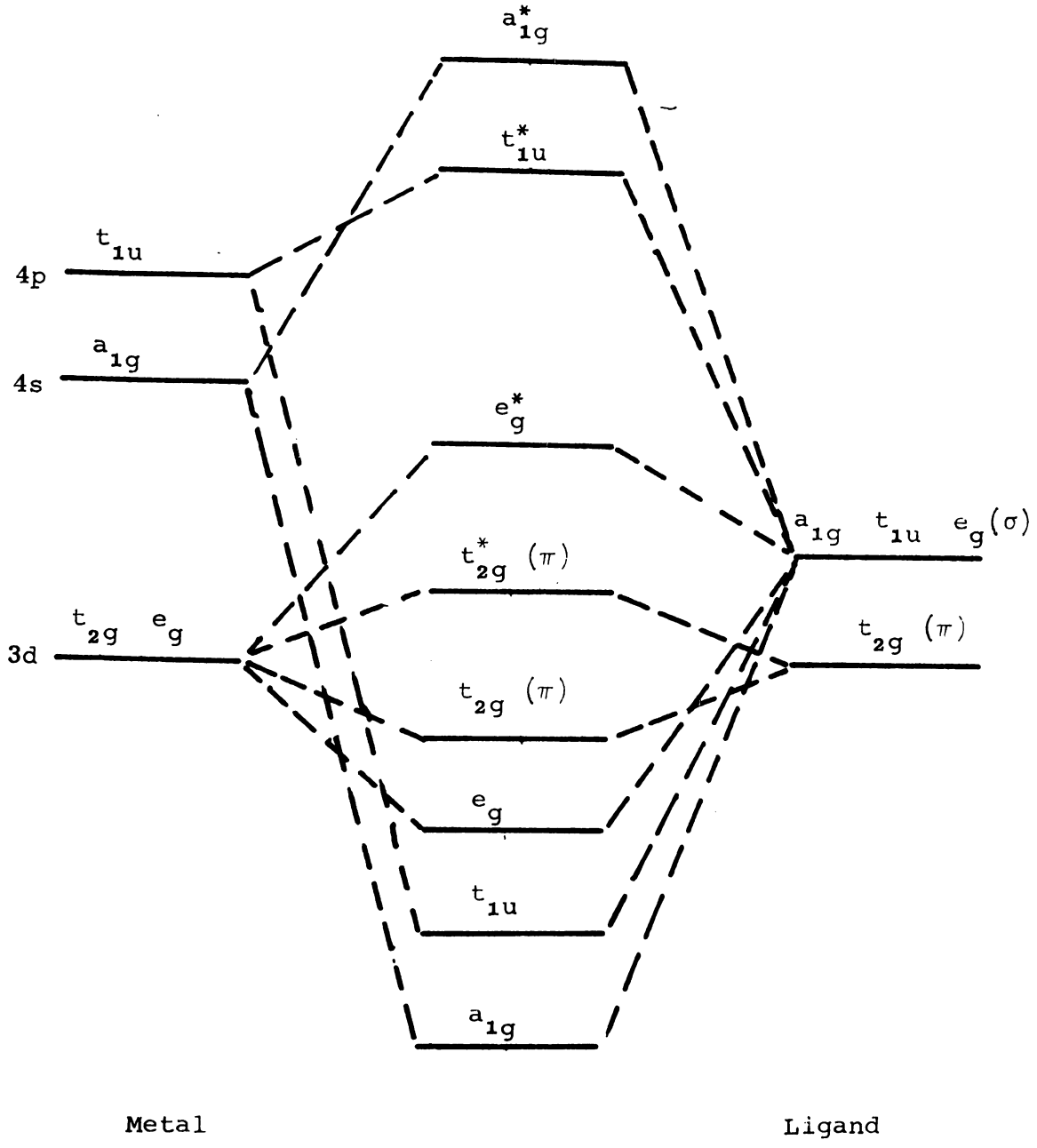


Figure 2. Molecular orbital diagram for an octahedral complex with π-bonding.

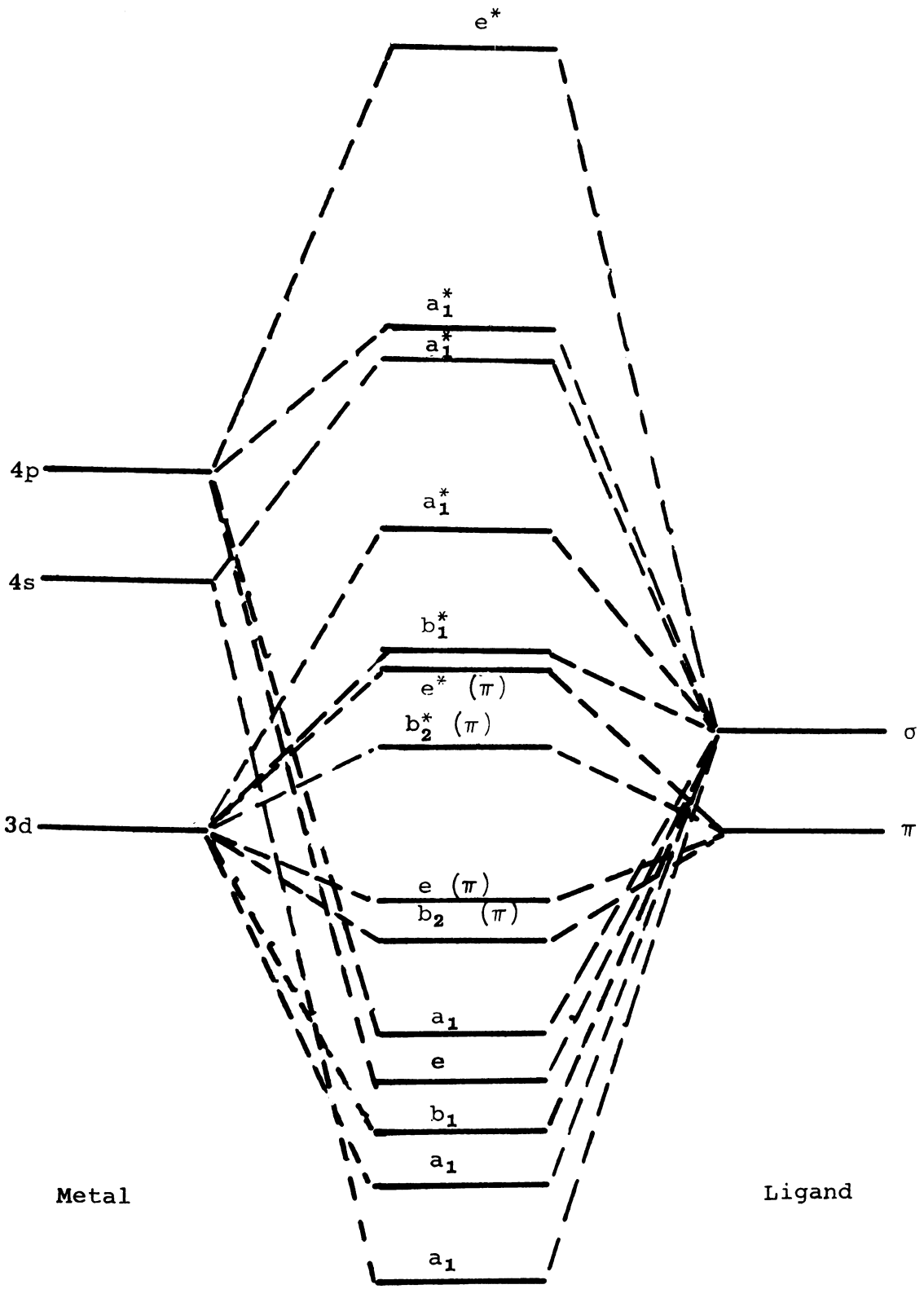


Figure 3. Molecular orbital diagram for a complex with C_{4v} symmetry and π-bonding.

arising from the e_g orbitals is lower in energy. However, either intuitive arguments or crystal field theory will show that the b_2 orbitals lies at a lower energy than the e orbital and the b_1 orbital lies at a lower energy than the a_1 orbital. The determination of the separation of the levels must come from the ultraviolet-visible spectrum of the complex.

Now if one fills in the orbitals with the available electrons, there are 12 electrons from the 6 ligand sp_z hybrid orbitals and 6 electrons from the 3 p orbitals which form bonds with the t_{2g} metal orbitals for a total of 18 electrons. The molecular orbitals are filled up to the lowest lying π-antibonding orbital so that in a d^1 case, the unpaired electron is in the b_2 antibonding molecular orbital. The first two excited states are e and b_1 so that the molecular orbitals necessary for the discussion of the bonding in a d^1 case are the b_2, e, and b_1. These molecular orbitals may be written similarly to those given above (Equation 10).

$$|B_2\rangle^* = N_{\pi_2}(d_{xy} - \lambda_{\pi_2}\ \phi^L_{\pi_2}) \tag{12}$$

$$|B_1\rangle^* = N_{\sigma_2}(d_{x^2-y^2} - \lambda_{\sigma_2}\ \phi^L_{\sigma_2}) \tag{13}$$

$$|E\ \rangle^* = N_{\pi_1}(d_{xz} \text{ or } d_{yz} - \lambda^e_{\pi_1}\ \phi^e_{\pi_1} - \lambda^a_{\pi_1}\ \phi^a_{\pi_1} \tag{14}$$

where

$$\phi^L_{\pi_2} = \frac{1}{2}(p_x(1) + p_y(2) + p_y(3) + p_x(4)) \tag{15}$$

$$\phi^{L}_{\sigma_2} = \frac{1}{2}(\sigma(1) + \sigma(2) + \sigma(3) + \sigma(4)) \qquad (16)$$

$$\phi^{e}_{\pi_1} = \frac{1}{\sqrt{2}}(p_y(1) + p_x(3)) \qquad (17)$$

$$\phi^{a}_{\pi_1} = \frac{1}{\sqrt{2}}(p_x(5) + p_y(6)) \qquad (18)$$

and $\lambda^{e}_{\pi_1}$ and $\lambda^{a}_{\pi_1}$ are the $|E\rangle^*$ molecular orbital coefficients for the equatorial and axial ligands respectively. The ligand orbital of the chlorine and oxygen involved in π-bonds are pure p orbitals while the ligand orbitals involved in σ-bonding are sp_z hybrids. In the actual calculation of the molecular orbitals, it is convenient to assume $\lambda^{a}_{\pi_1} = \lambda^{e}_{\pi_1}$ so that $\phi^{e}_{\pi_1} + \phi^{a}_{\pi_1} = \phi^{L}_{\pi_1}$.

C. The Theory of Obtaining Molecular Orbital Parameters from ESR g and A Values

For a free electron the $\langle g \rangle$ value is 2.0023; however, in transition metal complexes, spin-orbit interaction mixes some excited state into the ground state. The actual $\langle g \rangle$ value is given by the expression

$$g = 2.0023\ (\delta_{ij} - \zeta \Lambda_{ij}) \qquad (19)$$

where δ_{ij} is the Kronecker delta, ζ is the spin orbit coupling constant, and Λ_{ij} is defined by

$$\Lambda_{ij} = \sum_{n \neq 0} \langle \psi_0 | \hat{L}_i | \psi_n \rangle \langle \psi_n | \hat{L}_j | \psi_0 \rangle / (E_n - E_o)^{66} \qquad (20)$$

where $\hat{L}$ is the angular momentum operator, and $(E_n - E_o)$ is the energy between the ground and n^{th} excited state.

Owen[67] found that by using optical and magnetic data the value for the spin-orbit coupling constant in equation 12 was smaller by 20-30% than the free ion value. This decrease was interpreted in terms of covalent bonding between the metal and the ligand which forces some unpaired electron density onto the ligand.

Murao[68] attributed the lowering of the spin-orbit coupling constant to screening by the additional 3d electron density produced by the mixing of 3d chlorine wave functions into bonding orbitals. Several alternate procedures for considering screening effects have also been proposed.[8, 69, 70] Several investigators[69-71] have recently amended Owen's early theory to include charge transfer and ligand spin-orbit coupling contributions.

The complexes considered in this investigation have C_{4v} symmetry (Figure 4) and form coplanar bonds between the metal and each of four equatorial chlorine ligands. The alkoxide ligand is attached axially along the positive z axis. The fifth chlorine lies along the negative z axis.

The $V(OR)Cl_5^{=}$ ion has one unpaired electron (d^1) so the ground state is $^2B_2$. (See molecular orbital section.) The molecular orbitals which are necessary for this discussion are the ground state and the first two excited states and are given by equations 12, 13, and 14.

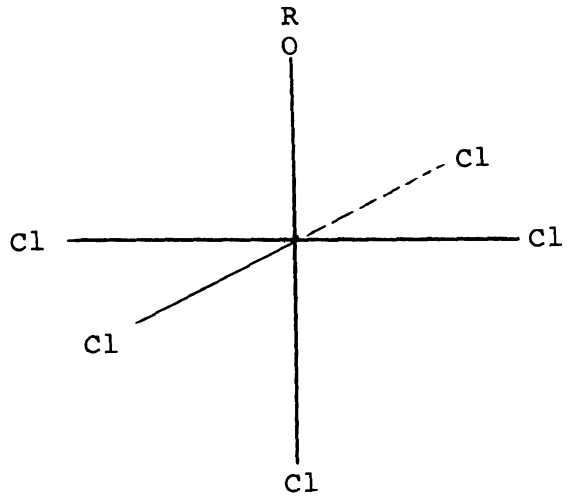


Figure 4. Symmetry of pentachloroalkoxovanadate(IV) complexes.

The experimental g and A values can be related to the molecular orbital coefficients by:

$$g_{\parallel} - 2.0023 = \frac{-8\zeta N_{\pi_2}^2 N_{\sigma_2}^2}{\Delta(b_2 - b_1)} \left[1 - \frac{1}{2}(\lambda_{\pi_2}\lambda_{\sigma_2})T(n) - 2\lambda_{\sigma_2}S_{b_1} - 2\lambda_{\pi_2}S_{b_2}\right] \quad (21)$$

$$g_{\perp} - 2.0023 = \frac{-2\zeta N_{\pi_2}^2 N_{\pi_1}^2}{\Delta(b_2 - e)} \left[1 - 1\sqrt{2}(\lambda_{\pi_1}^{e}\lambda_{\pi_2}) - 2\lambda_{\pi_2}S_{b_2} - \sqrt{2}\,\lambda_{\pi_1}^{e}S_{b_2} - \lambda_{\pi_1}^{a}S_{e}\right] \quad (22)$$

$$A_{\parallel} - \langle a \rangle = \frac{-4N_{\pi_2}^2 P}{7} - \frac{8\zeta N_{\pi_2}^2 N_{\sigma_2}^2 P}{\Delta(b_2 - b_1)} - \frac{6\zeta N_{\pi_2}^2 N_{\pi_1}^2 P}{7\Delta(b_2 - e)} \quad (23)$$

where S_{b_1}, S_{b_2}, and S_e are the metal-ligand overlap

integrals. T(n) is defined by Kivelson and Lee[72] as:

$$T(n) = n - (\tfrac{1}{3})^{\frac{1}{2}}(1 - n^2)^{\frac{1}{2}} R \int_0^{\infty} r^2 R_{31}(r) \frac{d}{dr} [R_{30}(r)] dr \quad (24)$$

where R is the vanadium-ligand distance and $R_{31}(r)$ and $R_{30}(r)$ are the normalized radial 3p and 3s functions respectively. $P = 2.0023\ g_N \beta_e \beta_N \langle r^{-3} \rangle$ avg., where β_e and β_N are the Bohr and nuclear magnetons, respectively, and g_N is the nuclear g factor. N_{π_2} and λ_{π_2} are related by the normalization requirement.

$$N^2_{\pi_2} = [1 - 4\lambda_{\pi_2} S_{b_2} + \lambda^2_{\pi_2}]^{-1} \quad (25)$$

This procedure can be extended to permit calculation of the spin density in the p_π orbitals of the equatorial chlorides and involves use of Mulliken's populational analysis which assumes the electron density is proportional to the square of the molecular orbital coefficient.[73] Several authors[1,2] have found excellent agreement between spin densities calculated in this manner and those calculated from ligand hyperfind splitting values.

$$\text{Unpaired electron density in each ligand } 3p_\pi \text{ orbital} = \frac{\lambda^2_{\pi_2} N^2_{\pi_2} - N^2_{\pi_2} \lambda_{\pi_2} S_{b_2}}{4} \quad (26)$$

EXPERIMENTAL

A. Materials

Vanadium Tetrachloride.-- Vanadium tetrachloride was prepared by elemental synthesis. Vanadium metal powder was obtained from Alfa Inorganics, Inc. (m2N8). The reaction took place in a tube furnace at 390° and the gaseous VCl_4 was condensed in a water condenser and subsequently collected in an ice bath. The use of the water condenser allowed the reaction to proceed much more rapidly than if a direct connection had been made to the ice bath. The crude vanadium tetrachloride was stored under chlorine in the absence of light until just before use. The VCl_4 was then distilled at atmospheric pressure under chlorine and degassed. (Calcd: V, 26.43; Found: V, 26.14.)

Tetraalkylammonium Chlorides.-- Tetramethylammonium chloride was obtained from Eastman Organic Chemicals and dried at 110° before use. Tetraethylammonium chloride was also obtained from Eastman Organic Chemicals and dried at 80° before use.

Pyridine.-- Reagent grade pyridine was stored over sodium hydroxide. Prior to use, the pyridine was allowed

to reflux over finely crushed barium oxide and was distilled.

Phenol.-- Reagent grade phenol was sublimed twice at room temperature.

Hydrogen Chloride, Chlorine, and Nitrogen.-- Anhydrous hydrogen chloride was obtained from Matheson Chemical Company and passed through concentrated sulfuric acid before use.

Chlorine was obtained from Matheson Chemical Company and was used without additional purification.

Pure nitrogen was obtained by passing Matheson prepurified nitrogen through a three foot BTS[74] column and subsequently through calcium chloride and barium oxide drying towers.

Solvents.-- Methanol, ethanol, and isopropanol were dried by reaction with magnesium and were subsequently distilled. Cyclohexanol, n-propanol, n-butanol, and n-octanol were reagent grade and were used without additional purification.

Acetonitrile was caused to reflux over phosphorus pentoxide and distilled under a nitrogen stream. This process was repeated at least three times and the solvent was then stored over Linde-4A molecular sieves.

Methylene chloride and carbon tetrachloride were allowed to reflux continuously over calcium hydride and distilled as needed.

Chloroform was distilled twice from phosphorus pentoxide and stored over Linde-4A molecular sieves in the absence of light.

Nitromethane was distilled from calcium chloride and passed over a two foot column of Dowex 1-X8 resin in the acid form, which had been previously dried with anhydrous ethanol.

Ethyl ether was distilled from solid sodium and stored over fresh sodium wire.

Thionyl chloride was reagent grade and used without additional purification.

B. Analytical Methods

Vanadium Analysis and Oxidation State Determination[75].-- Weighed samples of a vanadium complex were dissolved in dilute sulfuric acid and the solution was heated to boiling and allowed to cool to 60-80°. The solution was then titrated with standard $KMnO_4$. Sulfur dioxide gas was then passed through the cooled solution for five minutes followed by nitrogen for 20 minutes. The solution was then retitrated with standard $KMnO_4$. If the results of the two titrations agreed, the oxidation state was confirmed as +4. The second titration proved to be more reproducible and those values are reported.

Chloride Analysis.-- Weighed samples of the vanadium complexes in Schlenk-tubes were cooled to 77°K. Dilute

sulfuric acid was then added to a sample and the mixture was warmed slowly to room temperature. This procedure prevents the loss of hydrogen chloride. Such losses may occur if the samples are dissolved directly in water or dilute sulfuric acid at room temperature. Chloride was determined by potentiometric titration of aliquots of the resulting solution with standard silver nitrate.

Gravimetric chloride determinations were made on several of the less stable complexes. The silver nitrate solution was added directly to the sample in a cooled Schlenk-tube. This procedure eliminated the possibility of loss of hydrogen chloride but was very time consuming.

Carbon, Hydrogen, and Nitrogen Analyses.-- The analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan which reported, "The compounds hydrolyze very easily."

Pyridine Analysis.-- Solutions of pyridine up to 1.7×10^{-4} M in 0.05 N sulfuric acid have been found to obey Beer's Law at 255 mμ.[76] Samples were dissolved in aqueous solutions of sulfuric acid of known concentration. The solutions were diluted to one liter with sufficient sulfuric acid and water so that the final concentration was 0.05 N in H_2SO_4. The pyridine concentration was determined spectrophotometrically at 255 mμ. ($\epsilon = 5.32 \times 10^3$ l. mole^{-1} cm^{-1}.)[13]

C. General Experimental Procedure

All reactions, transfers, weighings, etc. were carried out in either an inert atmosphere (dry N_2) or in a vacuum, mainly by use of Schlenk-tube methods. Filtrations and washings were all performed by the application of pressure or by suction. All drying was *in vacuo* and compounds were stored under nitrogen in the absence of light.

D. Preparation of Compounds

Tetramethylammonium Hexachlorovanadate(IV).-- Tetramethylammonium chloride (5.0 g) was dissolved in approximately 50 ml of thionyl chloride. A solution consisting of 3 ml of freshly distilled vanadium tetrachloride in 20 ml of thionyl chloride was added and the solution stirred vigorously during the addition. A red-black precipitate formed immediately. The precipitate was extremely fine and difficult to filter. The filtration took several days. The product was washed twice with 100 ml of carbon tetrachloride and once with ethyl ether and was dried under vacuum.

Anal. Calcd for $VCl_6C_8H_{14}N_2$: V, 12.3; Cl, 51.65; C, 23.31; H, 5.87; N, 6.80. Found: V, 12.34; Cl, 51.65 (gravimetric), 51.20 (potentiometric); Cl, 23.01; H, 5.68; N, 6.68. Oxidation Number: 4.07.

Tetraethylammonium Hexachlorovanadate(IV).-- Tetraethylammonium chloride (9.0 g) was dissolved in approximately 40 ml of thionyl chloride. A solution consisting of 3 ml of freshly-distilled vanadium tetrachloride in 20 ml of thionyl chloride was added and the solution was stirred vigorously during the addition. A red-black oil formed in the reaction flask. Dry carbon tetrachloride was added slowly until a crystalline precipitate was observed. The precipitate was filtered under nitrogen, washed twice with carbon tetrachloride, and with dry ether, then dried under vacuum.

Anal. Calcd for $VCl_6C_{16}H_{40}N_2$: V, 9.72; Cl, 40.60; C, 36.64; H, 7.69. Found: V, 9.51; Cl, 40.47; C, 36.31; H, 7.83. Oxidation Number: 4.11.

Pyridinium Hexachlorovanadate(IV).-- Pyridinium chloride (5.0 g) was dissolved in 50 ml of chloroform. A solution consisting of 3 ml of freshly-distilled vanadium tetrachloride in 20 ml of a 5% solution of thionyl chloride in chloroform was added and the solution was stirred vigorously during the addition. A dark red precipitate formed immediately. The mixture was stirred for one hour, filtered under nitrogen, washed with 100 ml of chloroform and dried under vacuum. This complex had been prepared by Kilty and Nicholls.[42]

Anal. Calcd for $VCl_6C_{10}H_{12}N_2$: Cl, 50.19. Found: Cl, 49.92 (gravimetric).

Tetramethylammonium Pentachloromethoxovanadate(IV).--Tetramethylammonium hexachlorovanadate(IV) (2.7 g) was dispersed in a solution of 20% acetonitrile in ether. The slurry was stirred for two hours to break up any lumps in the starting material so that the reaction could proceed smoothly. (The reaction also takes place in methylene chloride or nitromethane.) One equivalent of methanol was added while the mixture was stirred. The reaction proceeded immediately with the formation of a golden product. Hydrogen chloride could be detected above the reaction flask. The product was stirred one hour, filtered under nitrogen, washed with warm acetonitrile and ether, and dried under a vacuum.

Anal. Calcd for $VCl_5C_9H_{27}N_2O$: V, 12.50; Cl, 43.50; C, 26.50; H, 6.68. Found: V, 12.60; Cl, 43.56; C, 26.44; H, 6.78. Oxidation Number: 4.07.

Tetramethylammonium Pentachloroethoxovanadate(IV).--This complex was prepared in the same manner as the above methoxo complex.

Anal. Calcd for $VCl_5C_{10}H_{29}N_2O$: V, 12.09; Cl, 42.06; C, 28.47; H, 6.94. Found: V, 12.20; Cl, 42.03; C, 28.56; H, 6.98. Oxidation Number: 4.00.

Tetramethylammonium Pentachloro(n-propoxo)vanadate(IV).--This complex was prepared in the same manner as the above methoxo complex except the tetramethylammonium hexachlorovanadate(IV) was dispersed in a 50% acetonitrile-ether solution.

Anal. Calcd for $VCl_5C_{11}H_{31}N_2O$: V, 11.70; Cl, 40.71. Found: V, 11.69; Cl, 40.67.

Tetramethylammonium Pentachloro(n-butoxo)vandate(IV).--This complex was prepared in the same manner as the above methoxo-complex except the tetramethylammonium hexachlorovanadate(IV) was dispersed in acetonitrile.

Anal. Calcd for $VCl_5C_{12}H_{33}N_2O$: V, 11.33; Cl, 39.44. Found: V, 11.22; Cl, 39.21.

Tetraethylammonium Pentachloromethoxovanadate(IV).--This complex and subsequent complexes were prepared in the same manner as the corresponding tetramethylammonium complexes.

Anal. Calcd for $VCl_5C_{17}H_{43}N_2O$: V, 9.81; Cl, 34.12. Found: V, 9.81; Cl, 34.10. Oxidation Number: 4.17.

Tetraethylammonium Pentachloroethoxovanadate(IV).--

Anal. Calcd for $VCl_5C_{18}H_{45}N_2O$: V, 9.55; Cl, 33.22. Found: V, 9.70; Cl, 33.41.

Tetraethylammonium Pentachloro(n-propoxo)vanadate(IV).--

Anal. Calcd for $VCl_5C_{19}H_{47}N_2O$: V, 9.30; Cl, 32.26. Found: V, 9.20; Cl, 32.17.

Pyridinium Pentachloromethoxovanadate(IV).--

Anal. Calcd for $VCl_5C_{11}H_{15}N_2O$: V, 12.15; Cl, 42.26; $C_5H_6N^+$, 38.19. Found: V, 12.16; Cl, 42.30; $C_5H_6N^+$, 38.61.

Attempts to Prepare Other Monoalkoxides.-- Attempts to prepare the tetraethylammonium pentachloro(n-butoxo)-vanadate(IV) as well as various other monoalkoxides were unsuccessful. Even in refluxing acetonitrile, cyclohexanol, isopropanol, t-butanol, and n-octanol do not react with the hexachlorovanadate(IV) ion to any appreciable extent. One assumes that steric factors play an important role here.

No attempt was made to prepare other monoalkoxides starting with sodium or potassium alkoxides. There is no obvious method available to separate the product from the NaCl or KCl.

Phenol reacts extremely rapidly with the hexachlorovanadate(IV) ion in acetonitrile. However, no stoichiometric compound could be isolated.

Attempts to Prepare Complexes Containing the Tetrachlorodialkoxovanadate(IV) Ion.-- Considerable time was spent trying to prepare dialkoxo compounds. Two basic methods were tried and will be discussed.

Green solutions were obtained if the hexachlorovanadate(IV) salts were dissolved in alcohols. When the solutions were evaporated to dryness, only salts containing the tetrachloro(oxo)vanadate(IV) ion could be obtained. Variations of temperature of the reaction and in the concentration of the reactants had no effect on the product. The addition of HCl gas during the reaction did not eliminate or slow down the decomposition. Although the

hexachlorovanadate(IV) salts dissolved slowly in n-propyl and n-butyl alcohol, the decomposition seemed to be as rapid.

If two or more equivalents of alcohol were added to a slurry of the hexachlorovanadate(IV) salts in ether or ether-acetonitrile mixtures, the isolated product appears to be the monoalkoxo species. However, a series of preparations that used 1, 2, 3, or 4 equivalents of methanol per vanadium was carried out. An infrared spectrum was obtained for each product and these are shown in part in Figure 5. The spectra show a decrease in the intensity of the peak at 1050 cm^{-1} normally assigned to the presence of a methoxide ligand in going from 1 to 4 equivalents.[76] There is also an increase in the intensity of the peak at 1000 cm^{-1} normally associated with the presence of a vanadyl unit. Figure 6 shows the infrared spectrum of pure $[(CH_3)_4N]_2$-$V(OCH_3)Cl_5$ and a completely hydrolyzed sample. Experiments with various other solvents such as nitromethane, chloroform, and ether gave similar results.

Attempts to prepare the dialkoxide complexes by the reaction of sodium or lithium alkoxide with the hexachlorovanadate(IV) salts were not made. There is no reason to believe these would be any more successful than the two methods described.

The decomposition must involve a reaction of a higher alkoxide species formed in solution and not a decomposition of the monoalkoxide. The mechanism is probably similar to

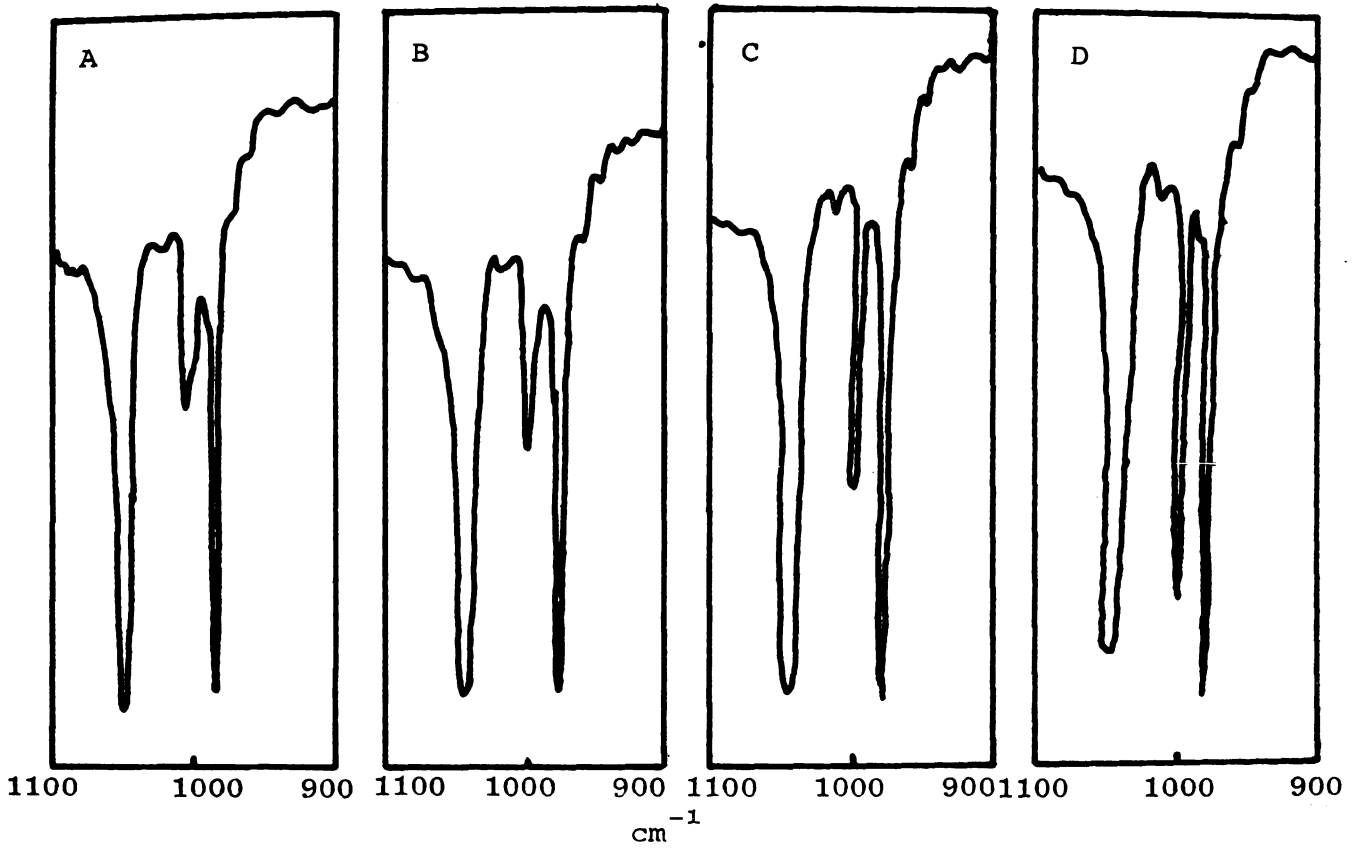


Figure 5. Infrared spectra (1100-900 cm^{-1}) for $[(CH_3)_4N]_2VCl_6$ with:
A. 1 Equivalent of CH_3OH added. B. 2 Equivalents of CH_3OH added.
C. 3 Equivalents of CH_3OH added. D. 4 Equivalents of CH_3OH added.

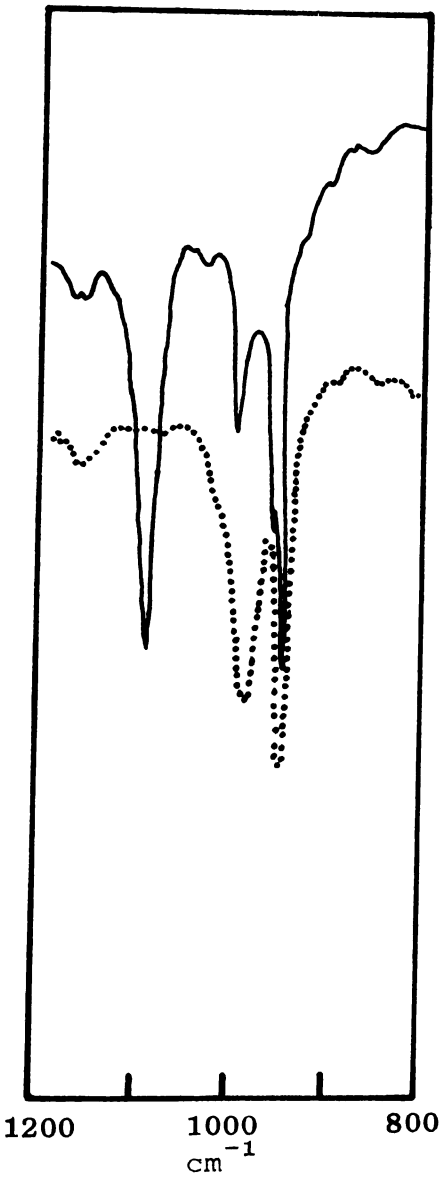


Figure 6. Infrared spectrum of pure $[(CH_3)_4N]_2V(OCH_3)Cl_5$ (800-1200 cm^{-1}) (———).
Infrared spectrum of hydrolyzed $[(CH_3)_4N]_2V(OCH_3)Cl_5$ (800-1200 cm^{-1}) (-----).

that proposed for the decomposition of the molybdenum dialkoxides.

$$VCl_6^{=} + CH_3OH \rightleftharpoons V(OR)Cl_5^{=} + HCl$$

$$V(OR)Cl_5^{=} + CH_3OH \rightleftharpoons V(OR)_2Cl_4^{=} + HCl$$

$$V(OR)_2Cl_4^{=} \xrightarrow{\text{fast}} VOCl_4^{=} + ROR.$$

E. Magnetic Moment Measurements

Magnetic susceptibilities were measured by the Gouy method by use of methods similar to those described by Vander Vennen.[77] The major difference was that the apparatus was constructed in order to allow a constant stream of helium to pass over the sample tube. This prevented water from condensing on the sample tube at low temperatures and also protected the sample from hydrolysis.

The calculation of the magnetic moment was made by the use of the equation:[78]

$$10^6 \chi = f' \times \frac{\beta}{W_s} \qquad (27)$$

where χ is the gram-susceptibility of the sample; f' is the force exerted on the sample alone, i.e., the measured force corrected for the force experienced by the tube alone; W_s is the weight of the sample in grams; and β is the tube constant.

In practice the constant β must be determined for a particular tube by use of a material of known susceptibility.

In this work, $Hg[Co(SCN)_4]$ was used: its susceptibility is 16.44×10^6 cgs units.[79]

The molar susceptibility, χ_m, of the sample is obtained by multiplying the gram-susceptibility by the molecular weight. The susceptibility of the metal ion, χ'_m, is obtained by correcting the molar susceptibility for any diamagnetic species present. Pascal's constants[74] were used to estimate the diamagnetism of the ligands and cations.

In normal paramagnetic substances χ'_m is related to the absolute temperature as

$$\chi'_m = \frac{C}{T} \qquad \text{(Curie Law)} \qquad (28)$$

or

$$\chi'_m = \frac{C}{(T + \theta)} \qquad \text{(Curie-Weiss Law)} \qquad (29)$$

For the latter case a plot of $1/\chi'_m$ against T allows evaluation of θ from the intercept.

The magnetic moment μ of the sample may be calculated from the molar susceptibility by

$$\mu = 2.84 \ (T \times \chi'_m)^{1/2} \qquad (30)$$

The low temperature studies were performed by using a specially constructed Dewar flask similar to that described by Vander Vennen.[77] The magnetic moment was measured at room temperature and at 77^0K. In those cases where a large change occurred, the moment at 195^0K was also determined.

F. Spectroscopic Measurements

The infrared spectra of the complexes were obtained by use of Nujol mulls and a Unicam Model SP-200 spectrophotometer (5000 cm^{-1} to 650 cm^{-1}) and a Beckman IR-7 spectrophotometer (700 cm^{-1} to 200 cm^{-1}). The visible and ultraviolet spectra were obtained by use of a Unicam Model SP-800 spectrophotometer and a Cary Model 14 spectrophotometer. The visible and ultraviolet spectra were determined in either methylene chloride or acetonitrile by preparing the complexes in solution. Great care was taken in handling the solutions and in filling the cells to prevent hydrolysis. Reflectance spectra were determined by means of a Bausch and Lomb Spectronic 600 spectrometer with diffuse reflectance attachment.

X-Band electron spin resonance spectra were determined for the pure solids and solutions at $100^{0}K$ and room temperature. The spectra were determined at frequencies from 9.2 to 9.5 KHz by using a Varian-4502-04 spectrometer and were recorded on an X-Y recorder with the X-axis proportional to the magnetic field strength. A Hall probe was used as a field sensor. First derivative curves were recorded. The hyperfine splittings were measured by means of a Hewlett-Packard 524C Frequency counter which was checked against aqueous $VOSO_4$ ($A = 116.13 \pm 0.2$ gauss between fourth and fifth lines)[48] and aqueous $K_3[Cr(CN)_5NO]$ ($A^N = 5.265 \pm .05$ gauss).[48]

Peak separations were measured by markers, corresponding to measured proton frequencies, placed as near each peak as conveniently possible. The magnetic field in gauss was calculated from the following equation:

$$H \text{ in gauss} = 2.3487465 \times \nu_1 \times 10^{-4} \qquad (31)$$

where ν_1 is the frequency of the proton resonance at the magnetic field in question. Peak separations, in gauss, were converted to frequencies by the following equation:

$$A(cm^{-1}) = 4.668597 \times 10^{-7} \times g \times A(\text{gauss}) \qquad (32)$$

where g is the g value for the set of lines being considered.

Values of g were determined from the measured klystron frequency and the field strength. The klystron frequency was determined by means of a TS-148/UP U.S. Navy Spectrum Analyzer which operates on the wave meter principle. The analyzer is calibrated directly in megacycles and the instrument does not lose accuracy at low klystron powers. Although the accuracy is reported to be ±2 mc, the precision of the measurements are reported to be ±0.5 mc.[48] Thus for a series of measurements this method proves to be quite satisfactory. Pitch in KCl ($g = 2.0028$) and aqueous $K_3[Cr(CN)_5N]$ ($g = 1.9945$) were used as standards to check the accuracy of the measured g values.

Most of the low temperature experiments were conducted employing a Varian V-4547 variable temperature Dewar with liquid nitrogen as coolant.

G. Determination of g and A values from ESR Spectra

During this research, it was necessary to determine g and A values as accurately as possible. Any differences in the spectra of successive complexes was expected to be small. Thus random errors in g and A had to be eliminated.

The isotropic g and A values were determined from the solution spectra at room temperature. The anisotropic terms $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ were determined from the frozen solution (glasses) spectra at either 77^0K or 100^0K.

Since the hyperfine splittings were on the order of 100 gauss, the high field approximation could not be applied. The perturbation of the Zeeman transitions resulting from the hyperfine interactions was corrected by means of the following equations:

$$h\nu = g\beta H_0 \tag{33}$$

for isotropic g

$$H_0 = H_m + \langle a \rangle m_I + \frac{\langle a \rangle^2}{2H_m}[I(I+1) - m_I^2] \tag{34}$$

for $g_{\parallel}$

$$H_0 = H_m + A_{\parallel} m_I + \frac{A_{\parallel}^2}{2H_m}[I(I+1) - m_I^2] \tag{35}$$

for $g_{\perp}$

$$H_0 = H_m + A_{\perp} m_I + \frac{A_{\parallel}^2 + A_{\perp}^2}{4H_m}[I(I+1) - m_I^2] \tag{36}$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I, ν is the

klystron frequency and $\langle a \rangle$, $A_{\parallel}$, and $A_{\perp}$ are the hyperfine aplitting constants. The corrections are necessarily re-iterative and were carried out by desk calculator. Normally three iterations were sufficient. The hyperfine splitting constants were determined from the positions of the 4^{th} and 5^{th}, 3^{rd} and 6^{th}, 2^{nd} and 7^{th}, and 1^{st} and 8^{th} lines where resolution permitted. For example, if the 4^{th} and 5^{th} lines are considered for g isotropic, one obtains:

$$H_0 = H_{4,5} + \frac{31A^2}{4H_{4,5}} \qquad (37)$$

where $H_{4,5}$ is the midpoint between the 4^{th} and 5^{th} lines. Similar equations can be written for the other 3 pairs of lines.

The values obtained for H_0 from each spectrum (3 or 4 separate values depending on the resolution) were averaged to obtain the final value of H_0 that was used to calculate g in the following equation:

$$g = 0.714489\ \nu^k/H_0 \qquad (38)$$

where ν^k is the klystron frequency.

The A values reported are the averaged A values obtained by considering either three or four pairs of lines.

The estimated errors in the measurements of g, A, $g_{\parallel}$, $A_{\parallel}$, $g_{\perp}$ and $A_{\perp}$ are given in Table III.

Table III. Estimated errors in esr parameters*

g	$\pm$ 0.0004	A	$\pm$ 0.2
$g_{\parallel}$	$\pm$ 0.0002	$A_{\parallel}$	$\pm$ 0.1
$g_{\perp}$	$\pm$ 0.0005	$A_{\perp}$	$\pm$ 0.3

*Hyperfine values given in 10^{-4} cm^{-1}.

RESULTS AND DISCUSSION

A. Preparation of Complexes

During the course of this research, two new salts of the hexachlorovanadate(IV) ion as well as various salts of a new class of complexes, the pentachloroalkoxovanadates(IV), were prepared.

The tetramethylammonium and tetraethylammonium hexachlorovanadate(IV) complexes were prepared by a method somewhat different from that used previously for hexachlorovanadate(IV) salts. Kilty and Nicholls[42] prepared four such salts by the reaction of thionyl chloride on various oxotetrachlorovanadate(IV) salts. Fowles and Walton[41] prepared several salts in chloroform starting with bis(acetonitrile)tetrachlorovanadate(IV). The method employed here was a combination of these two methods. Thionyl chloride is a very good chlorinating reagent and has the added advantage of eliminating hydrolysis of the complexes. Thus the hexachlorovanadate(IV) salts which were to be used as starting materials for the preparation of the alkoxo complexes could be prepared in high purity.

The pentachloroalkoxovanadates(IV) were prepared by a method not yet used in the preparation of alkoxo complexes.

Almost all examples of alkoxo complexes or compounds were prepared in anhydrous alcohols. As discussed above, this method gave only vanadyl species when employed during this research. The hexachlorovanadate(IV) complexes were known to be soluble and stable in acetonitrile. It was hoped that the hexachlorovanadate(IV) salts would be more stable toward decomposition than the species which forms in alcohols (probably $V(OR)_2Cl_4^=$) and that the acetonitrile would also help to stabilize any product (acetonitrile is a less polar solvent than alcohols and it was felt that the polar alcohol solvents probably contributed to the lability of the vanadium species). This method proved to be successful as well as similar preparations employing nitromethane and methylene chloride as solvents.

The tetramethylammonium complexes seemed to be more stable than the tetraethylammonium complexes. The pyridinium salts of the hexachlorovanadate(IV) ion and the pentachloromethoxovanadate(IV) ion were extremely labile toward hydrolysis and could not be completely characterized.

B. Magnetic Moments

The magnetic moments of the new complexes were determined at room temperature and in some cases at 77^0K and 195^0K. The results are given in Table IV. Both the hexachlorovanadate(IV) and pentachloroalkoxovanadate(IV) complexes exhibit Curie-Weiss paramagnetism. The magnetic moments of the alkoxo complexes show little temperature

Table IV. Magnetic moments of vanadium(IV) complexes.

		295°K	195°K	77°K
$[(CH_3)_4N]_2VCl_6$	I*	1.73	1.53	1.32
$[(CH_3)_4N]_2V(OCH_3)Cl_5$	II	1.79		1.76
$[(CH_3)_4N]_2V(OC_2H_5)Cl_5$	III	1.79		1.76
$[(CH_3)_4N]_2V(OC_3H_7)Cl_5$	IV	1.77		1.72
$[(CH_3)_4N]_2V(OC_4H_9)Cl_5$	V	1.79		1.74
$[(C_2H_5)_4N]_2VCl_6$	VI	1.74	1.57	1.32
$[(C_2H_5)_4N]_2V(OCH_3)Cl_5$	VII	1.78		1.75
$[(C_2H_5)_4N]_2V(OC_2H_5)Cl_5$	VIII	1.77		1.72
$[(C_2H_5)_4N]_2V(OC_3H_7)Cl_5$	IX	1.75		1.72
$[C_5H_6N]_2VCl_6$	X	1.73		
$[C_5H_6N)_2V(OCH_3)Cl_5$	XI	1.77		

*In succeeding tables these compounds will be referred to by number only.

dependence and their Weiss constants are therefore small. The magnetic moments of the hexachlorovanadate(IV) complexes show a strong temperature dependence. In the determination of the Weiss constant, θ, for the hexachlorovanadates(IV), the three points do not define a curve accurately enough to estimate the value of θ. However, by analogy to previously studied vanadyl complexes, only two points for the alkoxo complexes allow an estimation of the Weiss constant.[80] This is the case if the magnetic moments change only slightly with temperature.

The shoulder on the $^2T_{2g} \longrightarrow {}^2E_g$ transition observed in the ultraviolet spectra of the hexachlorovanadate(IV) complexes corresponds to removal of the degeneracy of the ground state by axial distortion to give tetragonal symmetry. Thus it is possible to employ the calculations outlined by Figgis[82] to obtain k (a measure of the delocalization of the $3d^1$ electron onto the ligand), Δ (the separation between the orbital levels of the $^2T_{2g}$ created by axial distortion of the ligand field), and ν (which is Δ/ζ where ζ is the spin orbit coupling constant). The values obtained by this treatment are given in Table V and are quite similar to those obtained by Machin and Murray.[81] The value of 160-170 cm^{-1} for the spin orbit coupling constant indicates that the formal charge on the vanadium in the hexachlorovanadate(IV) complexes is approximately +2.[83]

Table V. Magnetic properties of vanadium(IV) complexes

	(θ^0K)	ζ(cm^{-1})	K	ν	Δ(cm^{-1})
I		160-170	0.8-0.85	2	320-340
II	-6				
III	-6				
IV	-4				
V	-7				
VI		160-170	0.8-0.85	2	320-340
VII	-3				
VIII	-4				
IX	-2				

C. Optical Spectra

The optical spectra in solution and the reflectance spectra of the complexes were determined and the results are given in Tables VI and VII. The solution spectra were determined in either acetonitrile or methylene chloride. Traces of representative solution spectra as well as plots of representative reflectance spectra are given in Figures 7 to 10.

The distorted peak at approximately 15.5 x 10^3 cm^{-1} for the hexachlorovanadate(IV) complexes is the $^2T_{2g} \rightarrow {}^2E_g$ transition. The other two maxima are charge transfer bands. The two maxima at approximately 13.5 x 10^3 cm^{-1} and

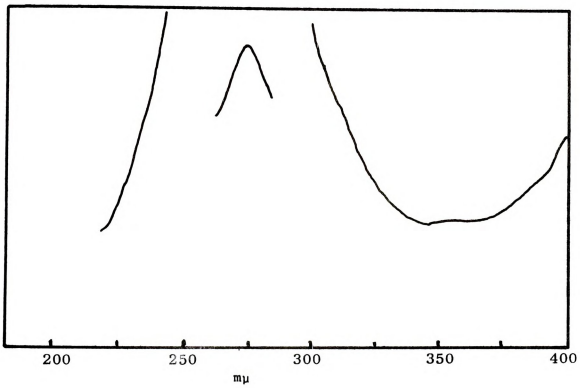
Table VI. Optical spectroscopic features of the tetramethylammonium complexes.

Complex	(CH_3CN) Electronic absorptions maxima x 10^{-3} cm^{-1} (ϵ in parentheses)	Electronic absorptions reflectance maxima x 10^{-3} cm^{-1}
I	13.8 (sh)[a]	15.2
	15.3 (70)	19.4
	21.2 (330)	22.5
	37.5	22.5
II	13.5 (3.0)	13.3
	14.5 (3.4)	15.5 (vw)[a]
	26.1 (1250)	28.6
	~ 41.0	
III	13.5 (2.3)	13.4
	14.5 (2.6)	15.5 (vw)
	26.1 (1070)	26.0
	~ 41.0	
IV	13.4 (2.1)	13.6
	14.8 (2.3)	15.4 (vw)
	26.1 (1070)	26.0
	~ 40.0	
V	13.5 (2.0)	13.7
	14.4 (2.0)	15.5 (vw)
	26.1 (1030)	26.0
	~ 40.0	

[a] sh = shoulder; vw = very weak.

Table VII. Optical spectroscopic features of tetraethylammonium complexes.

Complex	CH_3CN Electronic absorptions maxima x 10^{-3} cm^{-1} (ϵ in parentheses)	CH_2Cl_2	Electronic absorptions reflectance maxima x 10^{-3} cm^{-1}
VI	15.4		15.2, 15.5
	21.2		17.8
	37.3		20.6
	~ 41.0		22.8
VII	13.7	14.3 (8.0)	13.8
	14.9	26.0 (2000)	15.5 (vw)
	26.0		
	~ 37.9	~ 40.0	27.0
VIII	13.3	14.4 (9.7)	14.1
	15.0	26.2 (1420)	15.5 (vw)
	25.9	~ 40.0	28.5 (vw)
	37.8		
IX	13.5	14.5 (9.5)	14.3
	14.9	26.3 (1490)	15.5 (vw)
	25.9	~ 40.0	28.5
	~ 37.8		



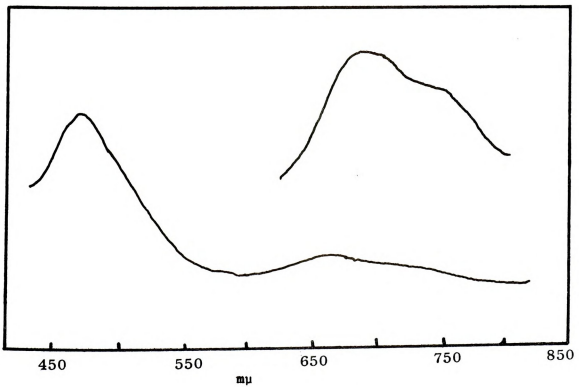
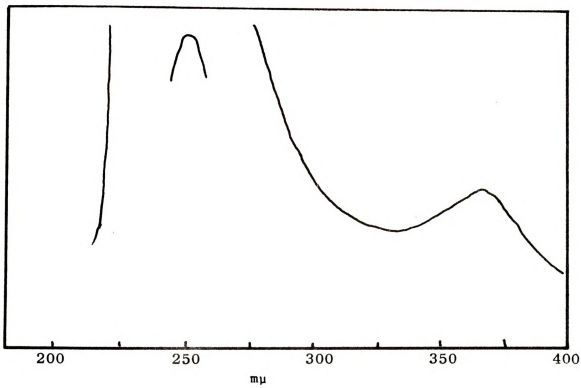


Figure 7. Solution spectrum of $[(CH_3)_4N]_2VCl_6$.



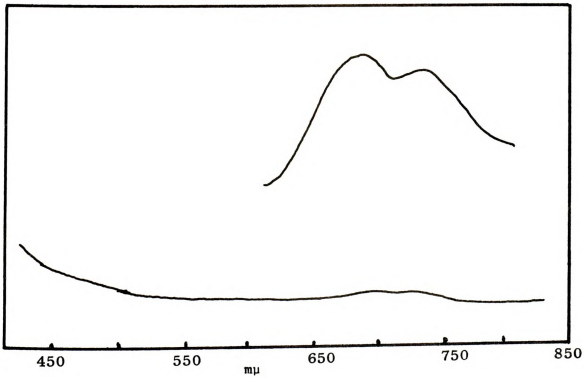


Figure 8. Solution spectrum of $[(CH_3)_4N]_2V(OCH_3)Cl_5$.

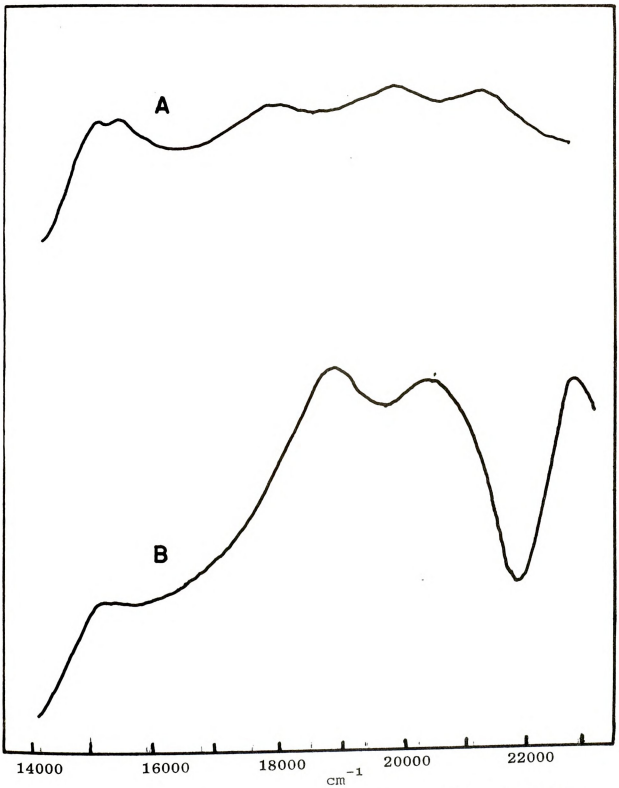


Figure 9. A. Reflectance spectrum of $[(C_2H_5)_4N]_2VCl_6$.

B. Reflectance spectrum of $[(CH_3)_4N]_2VCl_6$

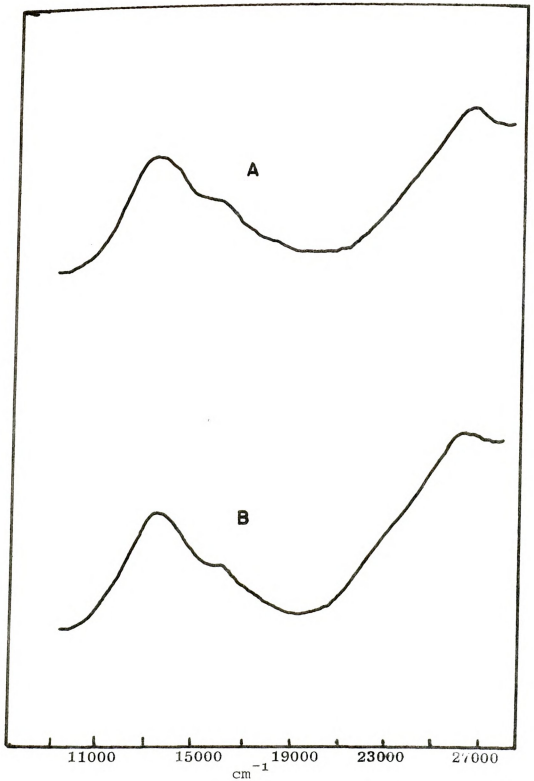


Figure 10. A. Reflectance spectrum of $[(CH_3)_4N]_2V(OCH_3)Cl_5$.
B. Reflectance spectrum of $[(CH_3(_4N]_2V(OC_2H_5)Cl_5$.

14.5×10^3 cm^{-1} for the alkoxo complexes are probably the $^2B_2 \longrightarrow {}^2E$ and the $^2B_2 \longrightarrow {}^2B_1$ transitions respectively (see the molecular orbital diagram for C_{4v} complexes, page 21). The two maxima, approximately 26.0×10^3 cm^{-1} and 40.0×10^3 cm^{-1}, are charge transfer bands. The reflectance spectra and solution spectra agree well in most cases and thus indicate that the species in solution is the same species as in the solid.

The tetraethylammonium pentachloroalkoxovanadates(IV) were too unstable in acetonitrile to permit determination of molar absorptivities. The difference between the solution spectra in acetonitrile and methylene chloride is probably due to solvent effects. In methylene chloride the $^2B_2 \longrightarrow {}^2E$ and $^2B_2 \longrightarrow {}^2B_1$ transitions may be superposed.

D. Infrared Spectra

The infrared spectrum for each of the complexes was determined in Nujol mulls and the results are given in Table VIII. Traces of representative spectra as well as plots of representative far infrared spectra are shown in Figures 11 through 19. The peaks marked with an asterisk in Table VIII are those normally associated with the C-O stretch in alkoxo complexes. The peaks around 250 cm^{-1} are metal-chlorine vibrations. The peaks at approximately 600 cm^{-1} observed in the tetramethylammonium alkoxo complexes are in the correct region to be the metal-oxygen stretch but

Table VIII. Infrared spectroscopic features of vanadium(IV) complexes.

Complex	Infrared absorption maxima, cm^{-1}									
I	1490	1290		996,990		465	295			
II	1490	1290	1090*	996,990	605	458	240			
III	1490	1290	1085*,1050*	990	600	468	240			
IV	1490	1300	1060*	920	705,575	462 390,380	240			
V	1490	1300	1090*,1010*	970	700	460				
VI	1195		1019	805	412,405	385,380,370				
VII	1195	1080*	1010	805	420	390				
VIII	1195	1090*,1040*	1010	805	425	390		230		
IX	1195	1050*	1010	805	425	390,370		240		
X	1630	1600	1525	1475	1335	1240	1195	1160		
IX	1630	1600	1525	1475	1335	1240	1195	1160	1050*	

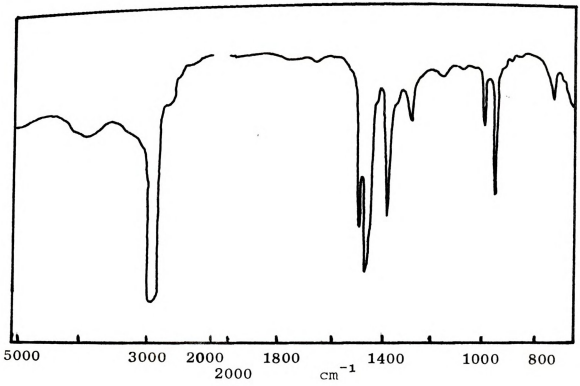


Figure 11. Infrared spectrum of $[(CH_3)_4N]_2VCl_6$.

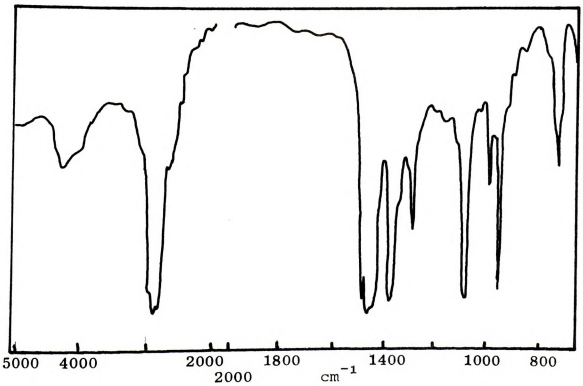


Figure 12. Infrared spectrum of $[(CH_3)_4N]_2V(OCH_3)Cl_5$.

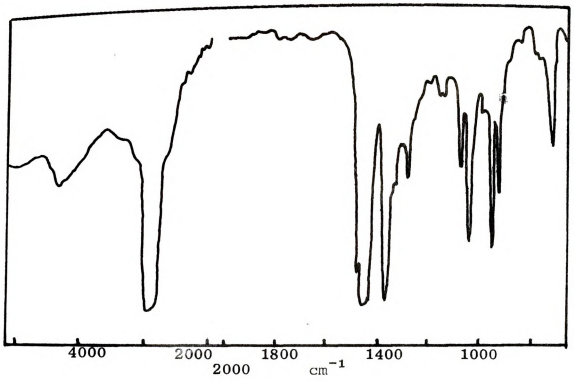


Figure 13. Infrared spectrum of $[(CH_3)_4N]_2V(OC_2H_5)Cl_5$.

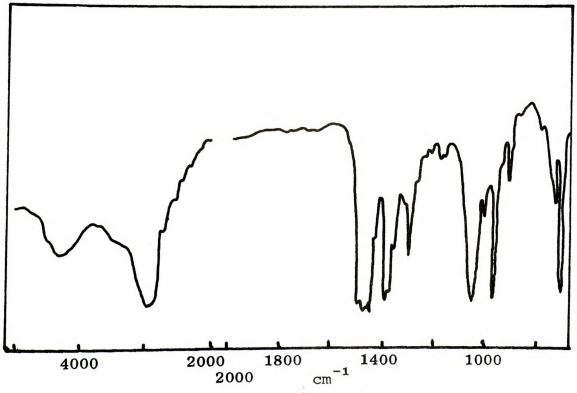


Figure 14. Infrared spectrum of $[(CH_3)_4N]_2V(O\text{-}\underline{n}C_3H_7)Cl_5$.

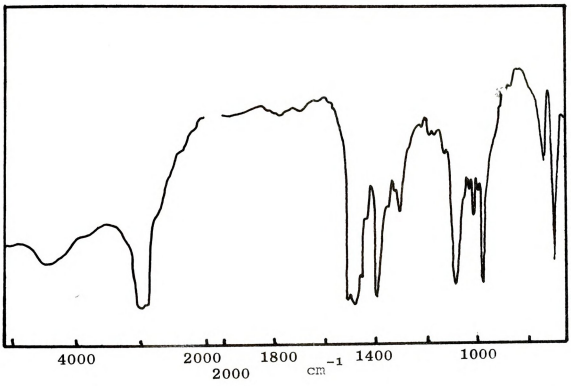


Figure 15. Infrared spectrum of $[(CH_3)_4N]_2V(O\text{-}\underline{n}C_4H_9)Cl_5$.

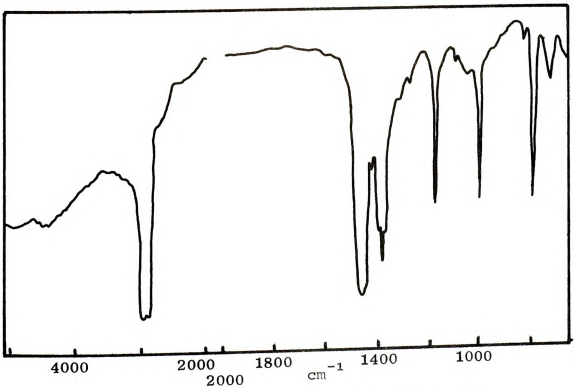


Figure 16. Infrared spectrum of $[(C_2H_5)_4N]_2VCl_6$.

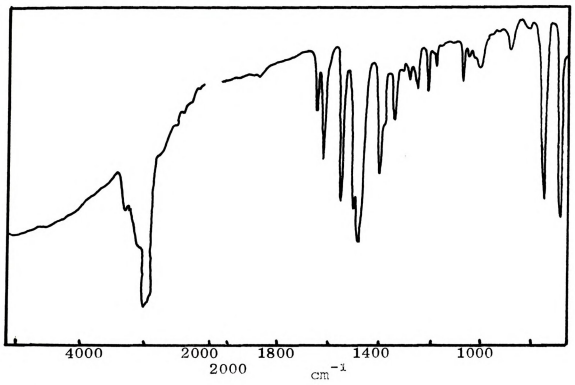


Figure 17. Infrared spectrum of $(C_5H_6N)_2VCl_6$.

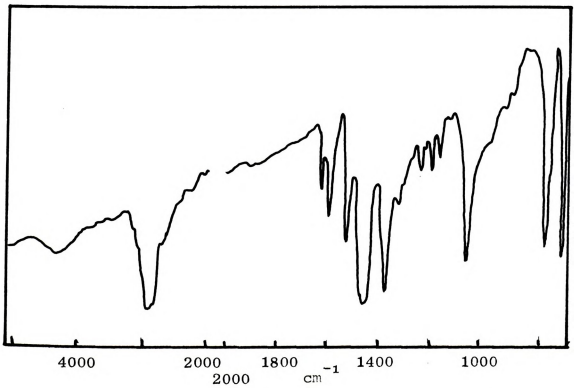


Figure 18. Infrared spectrum of $(C_5H_6N)_2V(OCH_3)Cl_5$.

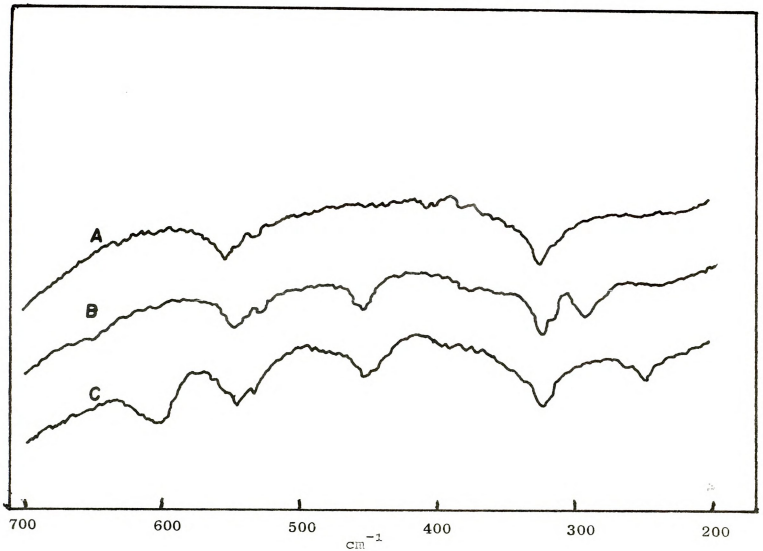


Figure 19. A. Far infrared spectrum of Nujol. B. Far infrared spectrum of $[(CH_3)_4N]_2VCl_6$ in Nujol. C. Far infrared spectrum of $[(CH_3)_4N]_2V(OCH_3)Cl_5$ in Nujol.

no corresponding peaks were observed in the tetraethylammonium complexes.

E. Electron Spin Resonance Spectra

The esr spectra were determined for solutions and solids at room temperature and at 100°K (glasses) for each of the complexes. Acetonitrile was used as a solvent for both the tetramethylammonium and the tetraethylammonium complexes while nitromethane was also used as a solvent for the tetraethylammonium complexes. The results are shown in Tables IX and X and traces of representative spectra are given in Figures 20 through 24. Figure 25 shows a superposition of the esr spectra of $[(CH_3)_4N]_2V(OCH_3)Cl_5$ and $[(CH_3)_4N]_2V(O\text{-}n\text{-}C_3H_7)Cl_5$ where the differences in $A_{||}$ and $A_{\perp}$ are small but very evident.

No esr signal could be detected for the hexachlorovanadate(IV) complexes in either the solid state of in thionyl chloride solutions at 295°K or 77°K. In fact the metal hyperfine structure of the alkoxo complexes could be observed in diluted powders of the pentachloroalkoxovanadates(IV) in the hexachlorovanadates(IV) at room temperature. Thus the hexachlorovanadates(IV) acted as a diamagnetic host but these spectra were not investigated further.

Vanadium metal hyperfine was observed in both the solution and frozen solution spectra but no chlorine superhyperfine structure was observed. The solution spectra consisted of 8 lines ($I = \frac{7}{2}$) while the frozen solution spectra could be resolved into parallel and perpendicular components.

Table IX. Esr parameters for tetramethylammonium complexes*

Complex	g_{solid}	$\langle g \rangle$	A	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$A_{\perp}$	g_{calc}	A_{calc}
II	1.949	1.9688	97.4	1.9478	168.9	1.9794	66.6	1.9689	100.7
III	1.950	1.9696	97.1	1.9510	167.5	1.9788	65.0	1.9710	99.2
IV	1.946	1.9698	97.0	1.9516	166.3	1.9736	64.6	1.9696	98.5
V	1.946	1.9681	96.8	1.9519	166.2	1.9796	64.5	1.9702	93.4

*Hyperfine splittings are given in 10^{-4} cm^{-1}.

Table X. Esr parameters for tetraethylammonium complexes*

Complex	g_{solid}	$\langle g \rangle$	A	$g_{\parallel}$	$A_{\parallel}$	$g_{\perp}$	$A_{\perp}$	g_{calc}	A_{calc}
				In CH_3CN					
VII	1.946	1.9697	97.6	1.9493	172.0	1.9777	65.1	1.9666	101.1
VIII	1.945	1.9696	96.8	1.9498	169.2	1.9767	64.7	1.9677	100.3
IX	1.945	1.9696	96.7	1.9498	167.8	1.9777	63.8	1.9684	98.5
				In CH_3NO_2					
VII	1.946	1.9685	97.5	1.9414	172.7	1.9741	66.0	1.9518	101.6
VIII	1.945	1.9689	97.4	1.9416	172.2	1.9737	65.4	1.9632	101.0
IX	1.945	1.9687	97.2	1.9407	171.6	1.9734	65.1	1.9625	100.6

*Hyperfine splittings are given in 10^{-4} cm^{-1}.

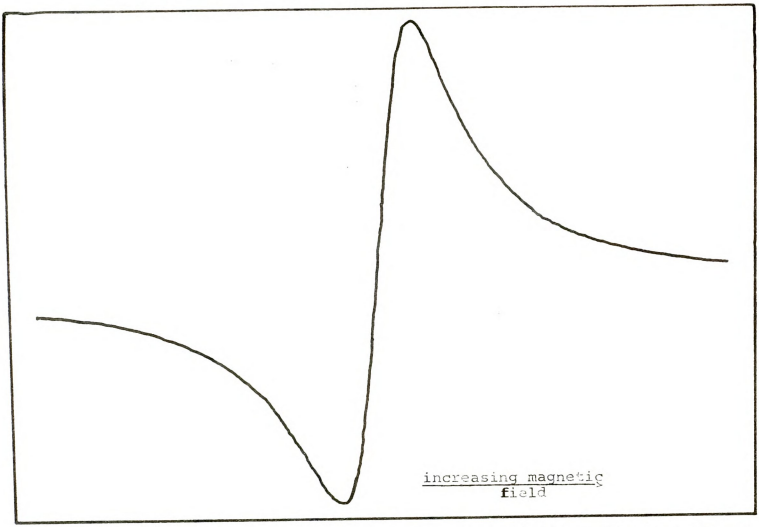


Figure 20. Electron spin resonance spectrum of solid $[(CH_3)_4N]_2V(OCH_3)Cl_3$ at 300°K.

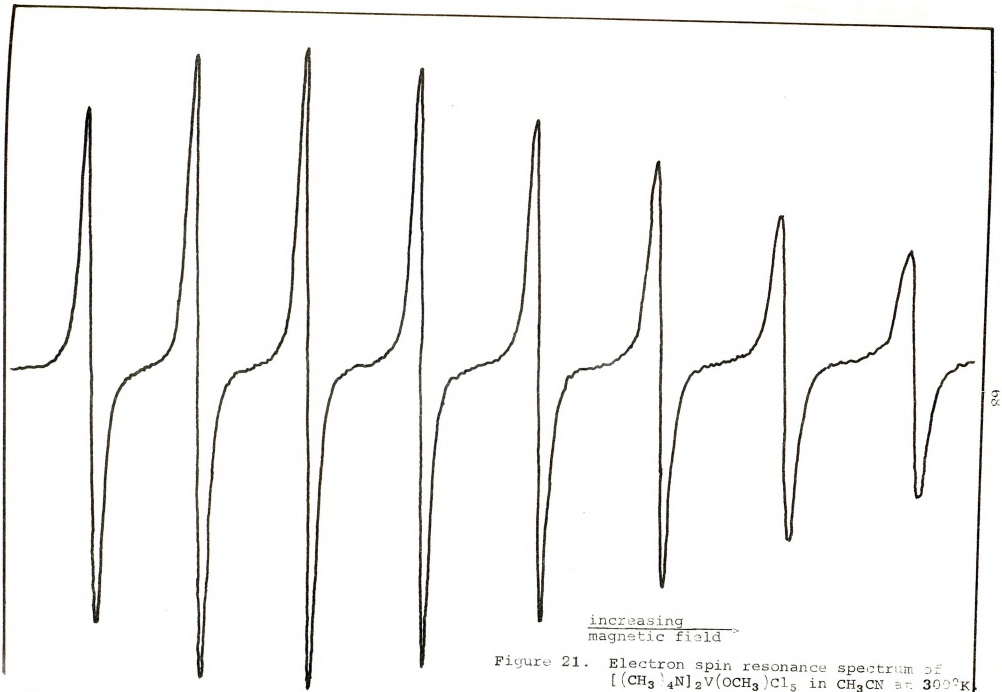


Figure 21. Electron spin resonance spectrum of $[(CH_3)_4N]_2V(OCH_3)Cl_5$ in CH_3CN at 300°K.

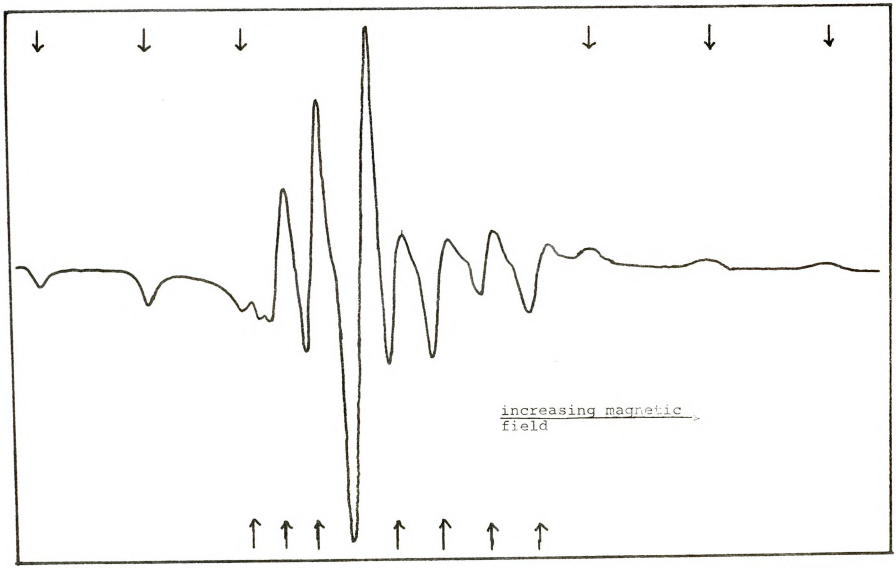


Figure 22. Electron spin resonance spectrum of $[(CH_3)_4N]_2V(OCH_3)Cl_5$ in CH_3CN at 100°K.
↓ indicates || line ↑ indicates ⊥ line

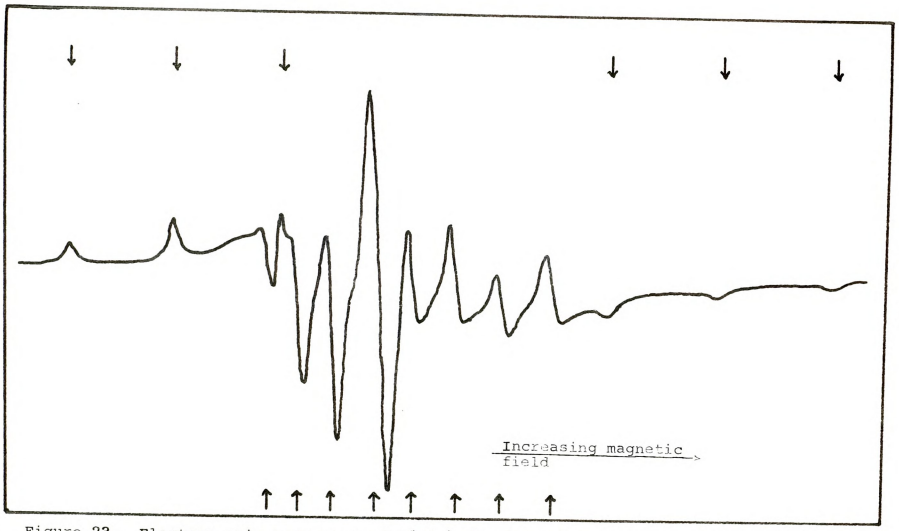


Figure 23. Electron spin resonance of $[(CH_3)_4N]_2V(OC_2H_5)Cl_5$ in CH_3CN at 100°K.
↓ indicates || line ↑ indicates ⊥ line

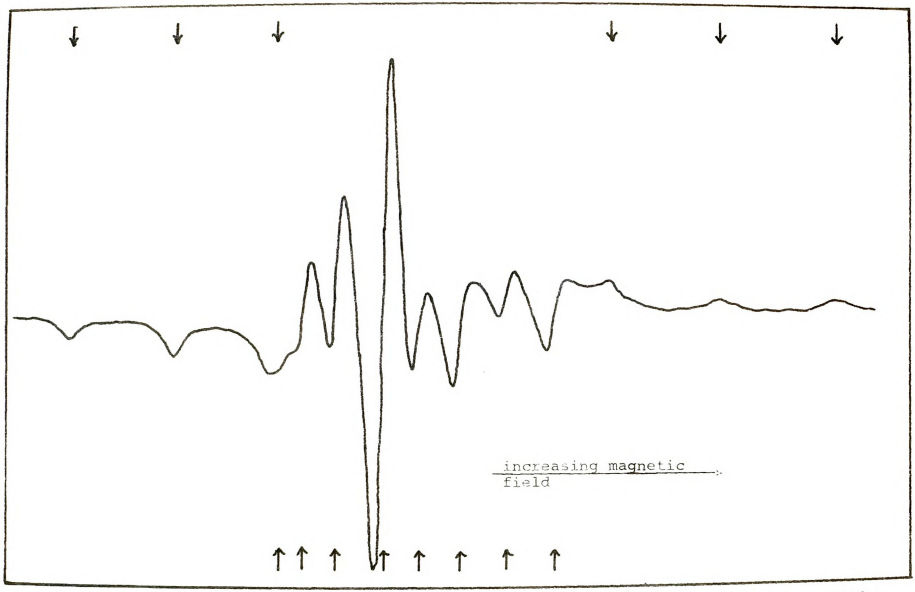


Figure 24. Electron spin resonance spectrum of $[(CH_3)_4N]_2V(O\text{-}n\underline{C}_3H_7)Cl_5$ in CH_3CN at 100°K.
↓ indicates || line ↑ indicates ⊥ line

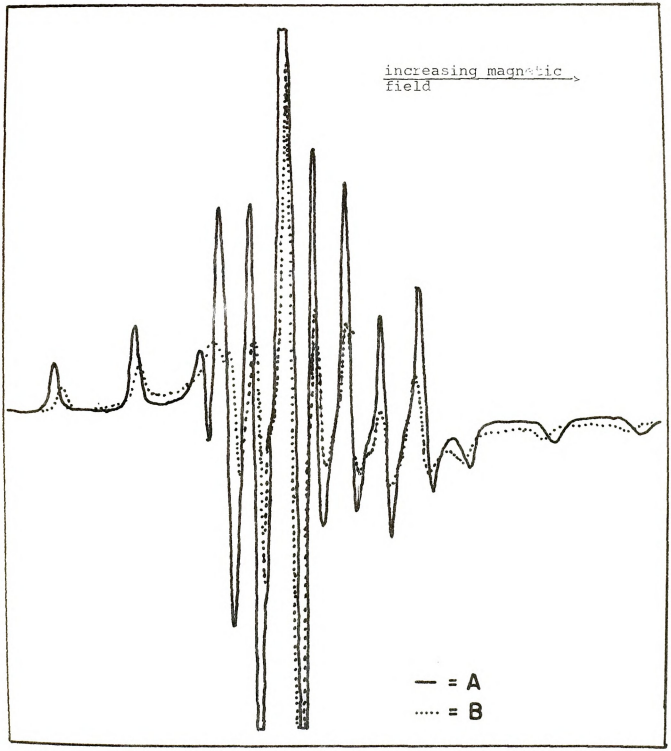


Figure 25. Electron spin resonance spectrum of $[(CH_3)_4N]_2V(OCH_3)Cl_5$ (A) at 100^0K and $[(CH_3(_4N]_2V(O\text{-}n\underline{C}_3H_7)Cl_5$ (B) at 100^0K superposed to show differences.

Various trends can be observed in the esr parameters in going from the tetramethylammonium pentachloromethoxovanadate(IV) to the pentachloro(n-butoxo)vanadate(IV). $A_{\parallel}$, $A_{\perp}$, and A all decrease through the series while $g_{\parallel}$ increases and $g_{\perp}$ seems to decrease. No trends are apparent in the isotropic $\langle g \rangle$ value. The tetraethylammonium salts show similar trends. The same trend is seen in CH_3CN and CH_3NO_2. Kuska[48] studied a series of vanadyl complexes and found an inverse relationship between $g_{\parallel}$ and and $A_{\parallel}$ similar to that observed here. Figure 26 shows a plot of $g_{\parallel}$ vs $A_{\parallel}$ for the tetramethylammonium alkoxo complexes.

F. Calculation of Molecular Orbital Parameters

The observed g and A values were used to calculate the coefficients in a simple molecular orbital scheme. The procedure was similar to that of Kuska and Rogers except contributions from charge transfer bonds were not included.[5]

In order to solve for $N^2_{\pi_2}$, $N^2_{\sigma_2}$, and $N^2_{\pi_1}$ in equations 21, 22, and 23 above, values must be obtained for ζ, P, T(n), S_{b_2}, S_{b_1}, and S_e. The values of ζ and P depend on the formal charge assigned to the vanadium atom. In calculations involving the VO^{++} unit, most authors feel the charge is reduced to approximately +2. It would seem reasonable then to assume the charge in the similar

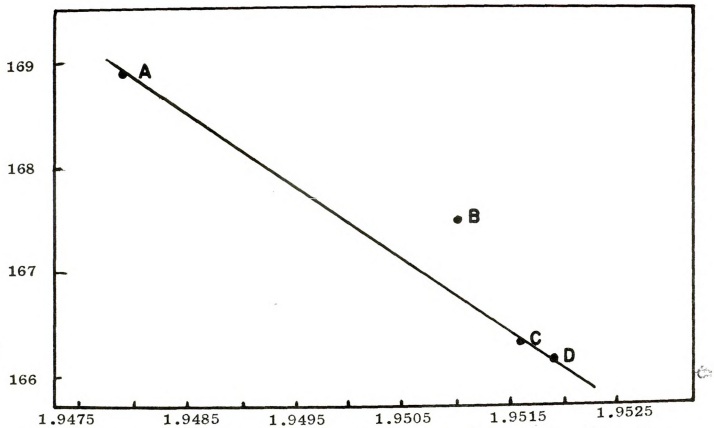


Figure 16. A plot of g vs A for $[(CH_3)_4N]_2V(OR)Cl_5$ (A in 10^{-4} cm^{-1}). A. R = $-OCH_3$. B. R = $-OC_2H_5$. C. R = $-OC_3H_7$. D. R = $-OC_4H_9$.

alkoxo group $V(OR)^{+++}$ is somewhat larger. While the formal charge does not have to be an integer, the value of +3 was used. Thus[4] P is 1.50×10^{-2} cm^{-1} and ζ was taken as 210 cm^{-1} from Dunn's[77] tables. T(n) depends on the ligand sigma orbital hybridization. In this case where the chlorine sigma bond is an sp hybrid, the value of T(n) was estimated as 0.25. The overlap terms S_{b_2}, S_{b_1}, and S_e were not determined but should be very near those values calculated by Gutowsky[3] for the tetrachloro(oxo)vanadate(IV) ion. Thus S_{b_2}, S_{b_1}, and S_e were taken as 0.099, 0.165, and 0.139 respectively. The assumption was made that little change occurs in these values in going from the methoxo to the n-butoxo complex. It was also assumed that $\lambda^a_{\pi_1} \cong \lambda^e_{\pi_1}$.

The values obtained by an iterative treatment of equations 21, 22, and 23 are given in Table XI. The calculations are strongly dependent on the trends in $A_{||}$, $g_{||}$, and $g_{\perp}$. A decrease is observed in $N^2_{\pi_2}$ and $N^2_{\sigma_2}$ as the alkoxo group becomes larger and an increase occurs in $N^2_{\pi_1}$. An increase in $N^2_{\pi_2}$ and $N^2_{\sigma_2}$ indicates that the $|B_2\rangle^*$ and $|B_1\rangle^*$ molecular orbitals become more covalent through the series. The increase in $N^2_{\pi_1}$ indicates the $|E\rangle^*$ molecular orbital becomes more ionic from the methoxo to the n-butoxo complex. Similar trends would result from a treatment of the data obtained from CH_3NO_2 solutions.

Thus it would appear that as the alkoxyl group becomes longer, electron density flows toward the metal in the bond involving the alkoxo group, the metal, and the axial chlorine. Also electron density flows from the metal to the equatorial chlorines in both sigma and pi bonds in the same series.

The unpaired electron density in the four equatorial $3p_{\pi}$ orbitals of chlorine is given by equation 25. The values of the spin densities are given in Table XI. The values vary as would be expected. The spin densities increase in going from the methoxo to the n-butoxo complex. Monoharan and Rogers[2] and Dalton, et al.[1] have found excellent agreement between the spin densities calculated in this manner and those calculated from ligand hyperfine splittings.

This work can be compared to the trends found in the molecular orbital parameters for $MoOX_5^=$ as $X = F^-$, Cl^-, or Br^-.[1,2] Table XII gives the coefficients found in a similar molecular orbital approach for these complexes. As the ligand X is changed from F^- to Cl^- to Br^-, the electron density on the halide becomes larger in those molecular orbitals involving the metal $d_{x^2-y^2}$ and the d_{xz} or d_{yx} orbitals. No trend is observed in the coefficients of the molecular orbital involving the $d_{x^2-y^2}$ metal orbital. As would be expected these changes are much larger than similar changes in the alkoxo series.

Table XI. Molecular orbital coefficients and spin densities for $V(OR)Cl_5^{-2}$ complexes.

Complex	$N^2_{\pi_2}$	$N^2_{\pi_1}$	$N^2_{\sigma_2}$	λ_{π_2}	$\%f_{\pi}$
II	0.947	0.882	0.794	0.506	4.87
III	0.934	0.910	0.767	0.529	5.31
IV	0.921	0.924	0.751	0.552	5.75
V	0.919	0.924	0.739	0.555	5.81
VII	0.982	0.914	0.811	0.438	3.64
VIII	0.961	0.949	0.767	0.481	4.41
IX	0.944	0.955	0.765	0.512	4.99

Table XII. Molecular orbital coefficients for $MoOX_5^{=1,2}$

X	N_{π_2}	N_{π_1}	N_{σ_2}
F^{-1}	0.956	0.960	0.891
Cl^{-1}	0.905	0.901	0.754
Br^{-1}	0.932	0.844	0.596

SUMMARY

The object of this research was to prepare and characterize a series of pentachloroalkoxovanadates(IV) and to study their esr spectra in detail. It was hoped that trends would be found in the esr parameters which could be related to the molecular orbital parameters. Little was known about trends in the molecular orbital coefficients until recently.[1] With the large number of electron spin resonance studies which have been made on transition metal complexes, it was necessary to understand these trends.

PART II

THE INVESTIGATION OF THE APPARENT THERMOCHROMISM OF SOME VANADIUM(III) COMPLEXES

INTRODUCTION AND HISTORICAL

A. Thermochromism

During the investigation of the vanadium(IV) complexes described in Part I of this thesis, two vanadium(III) complexes were prepared. One of these complexes, $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$, possessed the unusual property of changing color with temperature change. The second vanadium(III) complex which was prepared, $[(C_2H_5)_4N]VCl_4 \cdot 2CH_3CN$, did not apparently change color with temperature change. It was interesting that the tetraethylammonium bis(acetonitrile)tetrabromovanadate(III) complex appeared to be the same color at 77^0K as the tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III) complex at room temperature. Thus the effect of warming the tetrabromo complex was equivalent to substituting Cl^- for Br^- in the equatorial position in the coordination shell. For this reason, an attempt was made to prepare all the intermediate complexes containing Cl^- and Br^- with the hope that their properties might elucidate the thermochromic mechanism.

Thermochromism is defined as the reversible change in color of a compound when it is heated or cooled.[1,2] The thermochromic color change is distinguished by being

noticeable and sometimes occurring over a narrow temperature range. For inorganic complexes this transition in color may result from a change in the crystalline phase, change in ligand geometry, or to a change in the number of solvent molecules in the coordination sphere. For those complexes with a sharp transition, the thermochromic temperature may be changed by dispersing the compound into solid matrices such as paraffin waxes or oils.

Houston[3] first examined the property of thermochromism by heating solids on copper strips over a bunsen burner. Day's[1] review article adequately reviews most inorganic compounds which are known to be thermochromic.

Thermochromism is believed to be a general property of chromium(III) compounds. The continuous thermochromic transition is from red to violet to green as the temperature is raised. Poole[4] found that the color change which occurred in mixed oxides of chromium(III) with aluminum, lanthanum-gallium, lanthanum-gallium-aluminum, and yittrium-aluminum was a consequence of the lattice expansion which occurs when the sample is heated. Theoretical and electron spin resonance studies have shown that the chromium ion occupies octahedral or quasi-octahedral sites exclusively and that the color changes depend on the distance to the neighboring central ions.

The structure of the thermochromic complex Ag_2HgI_4 has been studied as a function of temperature by several

physical techniques.[5,7] It was found that variations in various physical properties could be correlated to thermochromic temperature changes.

No thermochromic complexes of vanadium(III) are known. A striking apparent thermochromism of liquid $VOCl_3$ is due to traces of water or even hydroxyl groups on the glass containers.[8] Dry $VOCl_3$ which contains traces of water is yellow, but at -70^0 is bright red. A solution of the compound in methylene chloride is orange, again due to traces of water, and is thermochromic due to the narrowing of a strong absorption band which extends into the visible region. There are no distinct bands in the ultraviolet but continuously increasing absorption. The absorbing species has not been identified, but it is possibly a mixture of partially hydrolyzed products.

Thermochromism in liquids is well known.[1] Most of these cases either involve simple equilibria between solvent molecules and ligand groups or a change in coordination number from 4 to 6.[9,10]

There are in general two broad classes of thermochromism. The first is a gradual deepening in color with rising temperature and occurs for a great many substances. The complexes investigated in this thesis would belong to this class. However, Day notes that this property is seldom reported.[1] The second is a drastic color change over a very limited temperature range. In the case of solids the temperature range may be dependent on the rate of heating.

Thermochromism in many inorganic complexes depends on the position of charge transfer bands. In many transition element complexes the wave-lengths of the first strong (charge transfer) bands vary in an interesting way with the nature of the ligands. For example, in the series of halide complexes, $[Co(NH_3)_5X]^{+2}$ the fluoride begins to absorb strongly in the far-ultraviolet at about the same place as the $[Co(NH_3)_6]^{+3}$ ion itself (50,000 cm^{-1}), but the chloride (45,000 cm^{-1}), bromide (37,000 cm^{-1}), and iodide (32,000 cm^{-1}) have strong bands at progressively longer wave-lengths and finally in the iodide these largely obscure the weaker d-d transitions.[11] Thus the strong absorption bands move to longer wave-lengths as the ligand becomes more easily oxidized. Many colorimetric analytical reagents used for detecting transition element ions are in fact ligands which form complexes having strong charge transfer bands.

B. Vanadium(III) Complexes

Vanadium(III) chemistry has been investigated quite extensively and vanadium(III) is known to form cationic, neutral, and anionic complexes. Nicholl's[12] review of vanadium chemistry covers these areas and only complexes of interest to this research will be discussed here.

Vanadium(III) halides react with donor molecules to form six-coordinate adducts. Examples of such complexes are given in Table I. Little is known concerning most of

these complexes except those compounds with nitriles as ligands, which may be prepared by causing the halide to reflux in the solvent. The alkyl cyanide complexes can also be prepared by the direct reaction of the nitriles with vanadium(IV) chloride.

Table I. Vanadium(III) nitrile adducts

$VCl_3 \cdot 3C_2H_5OH$	
$VCl_3 \cdot 3RCN$	R = CH_3-, C_2H_5-, C_3H_7-
$VBr_3 \cdot 3RCN$	R = CH_3-, C_2H_5-
$VCl_3 \cdot 3C_5H_5N$	

The diffuse reflectance spectra of $[VCl_3 \cdot 3CH_3CN]$ and the absorption spectrum of a solution of vanadium(III) chloride in acetonitrile are almost identical.[13,14] These compounds are non-electrolytes in the parent nitriles and are formulated, e.g., as $[VCl_3 \cdot CH_3CN]^0$. Two peaks are observed in the visible region for this complex. The maxima at 14,400 cm^{-1} has been assigned to the $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ transition and the shoulder around 21,000 cm^{-1} to the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition. The corresponding bromo-compound shows only the first ligand field peak while a strong charge transfer band obscures the second peak.

Both the tetraphenylarsonium and the tetraethylammonium salts of the octahedral bis(acetonitrile)tetrachlorovanadate(III) complex have been prepared.[15,16] The

tetraphenylarsonium complex shows two peaks in the visible spectrum at 13,500 cm^{-1} and 20,400 cm^{-1}. Several salts of the octahedral bis(acetonitrile)tetrabromovanadate(III) complex have also been isolated.[16] One mixed octahedral complex, tetraethylammonium bis(acetonitrile)bromotrichlorovanadate(III) has been prepared.[16] All these complexes lose acetonitrile when heated to 100^0 under vacuum to give tetrahedral vanadium(III) complexes. While the tetrahedral complexes have received some attention, little is known about the octahedral complexes.

EXPERIMENTAL

A. Materials

Tetraethylammonium hexachlorovanadate(IV).- The preparation of tetraethylammonium hexachlorovanadate(IV) is explained in Part I of this thesis.

Vanadium(III) chloride.[17]-- Vanadium(III) chloride was prepared by the reaction of sulfur monochloride (S_2Cl_2) with vanadium pentoxide. The vanadium pentoxide was obtained from K and K Laboratories and the sulfur monochloride was obtained from Eastman Organic Chemicals. Fine, pure V_2O_5 powder (18 g) and 40 ml of S_2Cl_2 were caused to reflux under anhydrous conditions for 8 hours (constant stirring). The excess S_2Cl_2, containing dissolved S, was decanted and the VCl_3 was washed 10 times with CS_2 to remove adhering sulfur. The product was then dried at 120^0 under vacuum. The yield was about 27 g.

Tetraethylammonium halides.- Tetraethylammonium chloride and tetraethylammonium bromide were obtained from Eastman Organic Chemicals and were dried at 80^0 before using.

Ethanethiol.- Ethanethiol was obtained from Eastman Organic Chemicals.

Hydrogen Bromide and Nitrogen.- Anhydrous hydrogen bromide was obtained from Matheson Chemical Company.

Pure nitrogen was obtained in the same manner as described in Part I of this thesis.

Solvents.- Acetonitrile and ethyl ether were purified in the same manner as described in Part I of this thesis.

B. Analytical Methods

All analyses were performed in the same manner as described in Part I of this thesis.

C. General Experimental Procedure

All experimental procedures were the same as described in Part I of this thesis.

D. Preparation of Compounds

Tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III).- This complex could be prepared by two methods.

Method 1.

To a known amount of tetraethylammonium hexachlorovanadate(IV) in acetonitrile, one equivalent of ethanethiol was added. The color changed from red brown to yellow immediately. The mixture was stirred for 1 hour and filtered. The product was recrystallized several times from boiling acetonitrile and dried under vacuum.

Anal. Calcd for $VCl_4C_{12}H_{26}N_3$: V, 12.58; Cl, 35.01; C, 35.58; H, 6.47; N, 10.37. Found: V, 12.32; Cl, 35.41; C, 35.51; H, 6.47; N, 10.17.

Method 2.

A solution of vanadium trichloride in acetonitrile was treated with one equivalent of tetraethylammonium chloride. The green solution became bright blue on the addition of the tetraethylammonium chloride, and when cooled became violet. The complex precipitated as a yellow powder and was recrystallized twice from boiling acetonitrile. This complex has been prepared by Clark et al.[16] by the same Method 2 described.

Anal. Found: V, 12.38; Cl, 35.37.

Tetraethylammonium bis(acetonitrile)bromotrichlorovanadate(III).- One equivalent of tetraethylammonium bromide was added to a slurry of vanadium(III) chloride in warm acetonitrile. The mixture was heated and stirred for one hour and cooled. The yellow-orange product was recrystallized twice from boiling acetonitrile and dried under vacuum. This complex was previously prepared by Clark et al.[16] in the same manner as described here.

Anal. Calcd for $VBrCl_3C_{12}H_{26}N_3$: V, 11.33; Br, 17.78; Cl, 23.66; C, 32.05; H, 5.83; N, 9.35. Found: V, 11.17; Br, 17.99; Cl, 24.03; C, 31.91; H, 5.88; N, 9.30.

Tetraethylammonium bis(acetonitrile)dibromodichlorovanadate(III).- No pure material with this composition could be obtained but products whose composition were near this could be obtained by two methods.

Method 1.

If the bright red product whose composition was near that of tetraethylammonium bis(acetonitrile)tribromochlorovanadate(III) was washed well with warm acetonitrile, an orange product was obtained which gave an analysis near that expected for the dibromodichloro product.

Anal. Calcd for $VBr_2Cl_2C_{12}H_{26}N_3$: V, 10.31; Br, 32.35; Cl, 14.35. Found: V, 10.14; 10.27; Br, 32.08, 31.74; Cl, 13.71, 13.83.

Method 2.

If one equivalent of tetramethylammonium bis(acetonitrile)tetrabromovanadate(III) was mixed with one equivalent of tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III) in a small amount of acetonitrile, an orange product could be obtained. This product gave analyses similar to those above.

Tetraethylammonium bis(acetonitrile)tribromochlorovanadate(III).- No pure product with this composition could be obtained but a product whose composition was near this could be produced by bubbling anhydrous HBr into a slurry of tetraethylammonium hexachlorovanadate(IV) in acetonitrile.

After 10 minutes, the HBr gas flow was removed and ethyl ether added. A bright red precipitate was obtained which was filtered, washed with ether, and dried under vacuum.

Anal. Calcd for $VBr_3ClC_{12}H_{26}N_3$: V, 9.96; Br, 44.52; Cl, 6.53. Found: V, 9.37; Br, 43.97; Cl, 6.44.

Tetraethylammonium bis(acetonitrile)tetrabromovanadate(III).- If the red solid obtained above was dissolved in hot HBr saturated acetonitrile, large red-brown crystals of the product could be obtained. This complex has been prepared by Clark, et al.[16] by the addition of tetraethylammonium bromide to vanadium(III) bromide in acetonitrile.

Anal. Calcd for $VBr_4C_{12}H_{24}N_3$: V, 8.74; Br, 54.83; C, 24.72; H, 4.50; N, 7.21. Found: V, 8.75; Br, 55.01; C, 24.45; H, 4.46; N, 7.18.

E. Magnetic Moment Measurements

The magnetic moments of the complexes were determined in the same manner as described in Part I of this thesis.

F. Spectroscopic Measurements

The infrared spectra were obtained by use of Nujol mulls and a Perkin-Elmer Model 457 Spectrophotometer (4000 cm^{-1} to 250 cm^{-1}). The ultraviolet-visible spectra were obtained by use of Nujol mulls and a Unicam Model SP-800 spectrophotometer and a Cary Model 14 spectrophotometer. Both infrared and uv-visible spectra on the Cary

Model 14 spectrophotometer were obtained at 77°K and 195°K by means of a specially constructed cell (See Figure 1). The cell was constructed so that it could be used for either low temperature uv-visible absorption spectra, low temperature reflectance spectra, or low temperature infrared spectra depending on the cell windows employed. The sample was ground in Nujol and pressed between two plates (quartz for uv-visible or reflectance spectra and cesium iodide for infrared spectra). The plates were tightened between the two metal plates of the sample holder (A). The sample holder (A) is connected by a kovar seal to the Dewar. The lower half of the cell could be evacuated (B) to prevent condensation of moisture onto the cell windows or sample plates. The external cell windows (C) could be varied again according to the area of the spectrum being investigated. The cell base and Dewar portion of the cell are connected by an O-ring seal so that the cell may be disassembled easily.

The nuclear quadrupole resonance spectra were determined with the aid of Dr. E. Carlson, Department of Physics, Michigan State University, on a superregenerative spectrometer similar to that of Dean.[18] All frequencies were measured with a Hewlet-Packard frequency counter. A Princeton Applied Research lock-in amplifier was used for derivative detection.

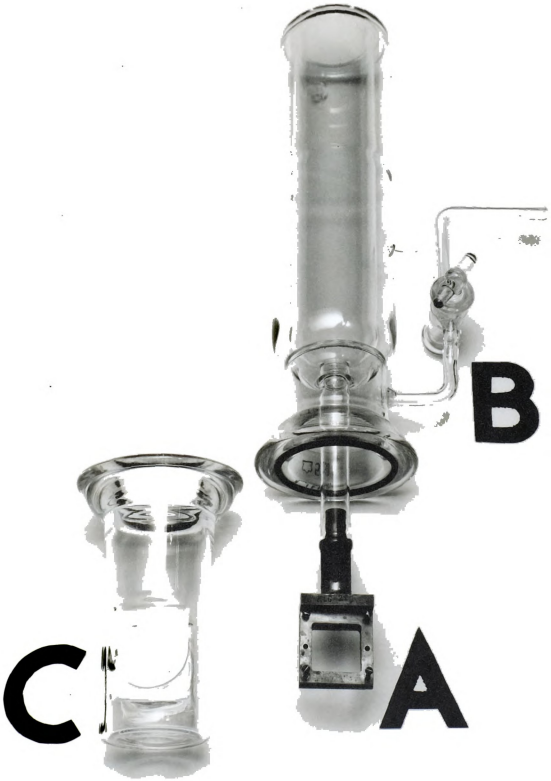


Figure 1. Low temperature cell for infrared and uv-visible spectra.

RESULTS AND DISCUSSION

A. Preparation of Compounds

During the preparation of the complexes described in this thesis, it became quite evident that the mixed halo complexes tend to disproportionate. For example, if one starts with vanadium(III) bromide and tetraethylammonium chloride in acetonitrile, the products isolated are tetraethylammonium bis(acetonitrile)tetrabromovanadate(III) and impure tetraethylammonium bis(acetonitrile)dibromodichlorovanadate(III). The reactions which occur in solution are probably:

$$VBr_3 + 3CH_3CN \rightleftharpoons VBr_3 \cdot 3CH_3CN$$

$$VBr_3 \cdot 3CH_3CN + (C_2H_5)_4NCl \rightleftharpoons [(C_2H_5)_4N]VBr_3Cl \cdot 2CH_3CN + CH_3CN$$

$$2[(C_2H_5)_4N]VBr_3Cl \cdot 2CH_3CN \rightleftharpoons [(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN + [(C_2H_5)_4N]VBr_2Cl_2 \cdot 2CH_3CN$$

Either the disproportionation is very rapid or the equilibrium lies far to the right for the complex with 3 $Br's^-$ and 1 Cl^-. The disproportionation is less apparent for the complex with 2$Cl's^-$ and 2$Br's^-$ and almost nonexistent for the complex with 3$Cl's^-$ and 1 Br^-. The disproportionation

process can become an advantage in preparing the mixed complexes.

For example, if HBr is bubbled into a slurry of the tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III) complex in acetonitrile at room temperature, apparently only three chlorides are replaced. If ethyl ether is added, the total solvent becomes much less polar and the disproportionation is stopped so that the complex with $3Br^-$'s and $1\ Cl^-$ can be isolated. Of course, this complex cannot be recrystallized in acetonitrile because it would then disproportionate. However, if small amounts of warm acetonitrile are added, it is possible to obtain the complex with $2Cl^-$'s and $2Br^-$'s because the disproportionation products differ greatly in solubility. The tetrabromo complex is much more soluble and is washed out while the dibromodichloro complex is less soluble and is left behind.

The fact that the uv-visible spectrum of each of these "impure" complexes is different and consists of one narrow band in the visible region tends to support the belief that the products are fairly pure.

B. Magnetic Moments

The magnetic moments for each of the complexes were determined at room temperature. The magnetic moments for the tetraethylammonium bis(acetonitrile)tetrachlorovanadate-(III) and tetraethylammonium bis(acetonitrile)tetrabromovanadate(III) were also determined at 195^0K and 77^0K. The results are listed in Table II.

Table II. Magnetic moments of vanadium(III) complexes

Complex	300°K	195°K	77°K
$[(CH_3CH_2)_4N]VBr_4 \cdot 2CH_3CN$	2.72	2.67	2.58
$[(CH_3CH_2)_4N]VBr_3Cl \cdot 2CH_3CN$	2.73		
$[(CH_3CH_2)_4N]VBr_2Cl_2 \cdot 2CH_3CN$	2.73		
$[(CH_3CH_2)_4N]VBrCl_3 \cdot 2CH_3CN$	2.75		
$[(CH_3CH_2)_4N]VCl_4 \cdot 2CH_3CN$	2.75	2.71	2.66

It was hoped that the magnetic behavior of the tetrabromo complex would be quite different from that of the tetrachloro complex--that is not the case. All the complexes exhibit temperature dependent paramagnetism with the moments being near that for a spin only d^2 system. The three points for the tetrabromo and tetrachloro complexes do not define a line well enough to allow an estimation of the Weiss Constants.

C. Infrared Spectra

Little or no differences were observed in the infrared spectra obtained at room temperature and the spectra obtained at 77°K for any of the complexes. Figures 2-7 show the spectra obtained for the complexes. The features of the infrared spectra are listed in Tables III and IV, along with possible assignments of the peaks. Tables V and VI give the vibrational modes and the description of the

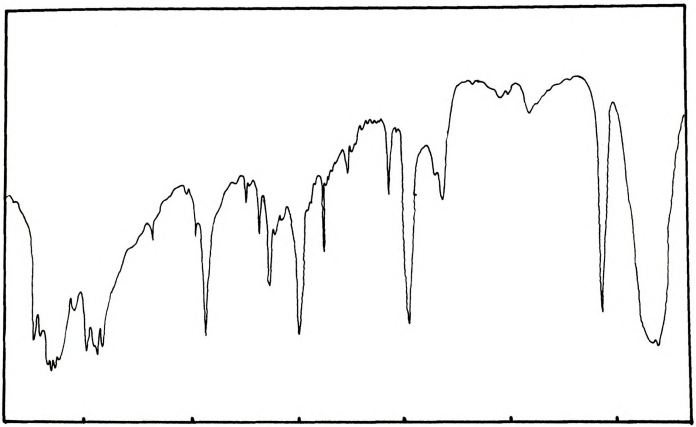


Figure 2. Infrared spectrum of $(C_2H_5)_4NVCl_4 \cdot 2CH_3CN$ (77°K).

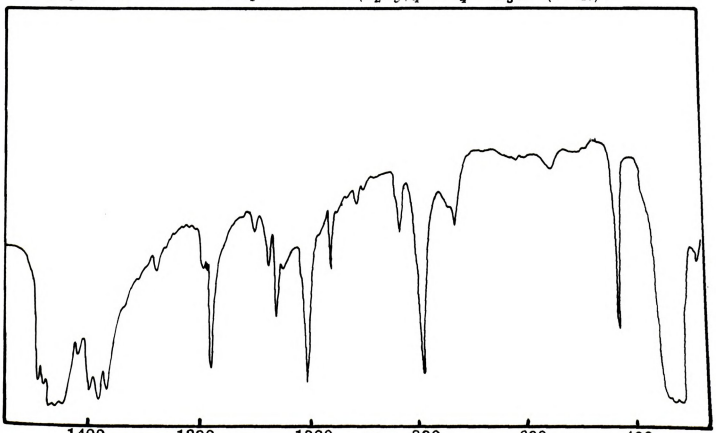


Figure 3. Infrared spectrum of $(C_2H_5)_4NVBrCl_3 \cdot 2CH_3CN$ (77°K).

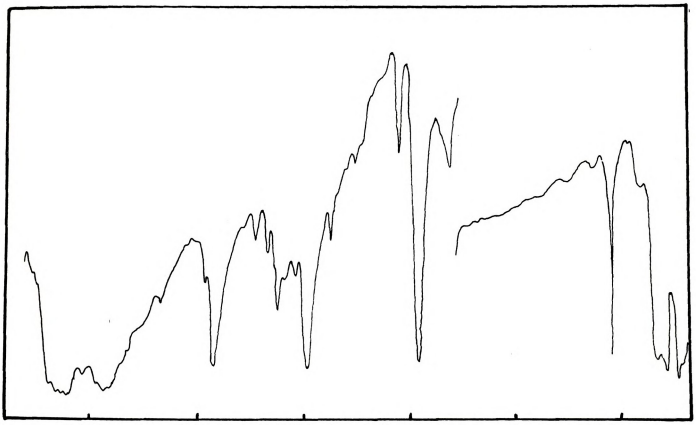


Figure 4. Infrared spectrum of $[(C_2H_5)_4N]VClBr_3 \cdot 2CH_3CN$ (77°K).

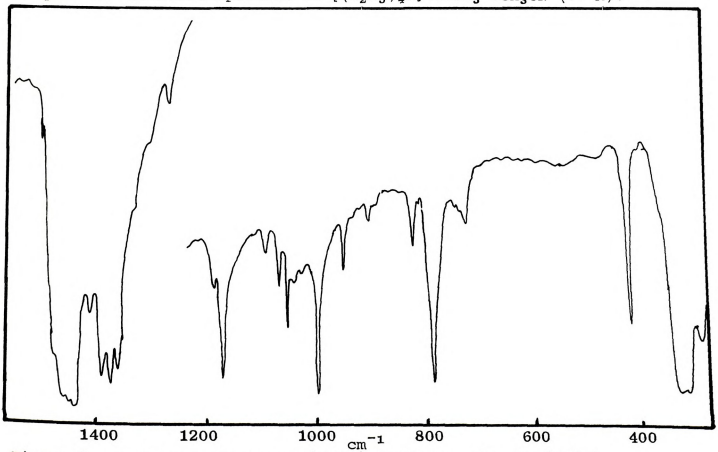


Figure 5. Infrared spectrum $[(C_2H_5)_4N]VCl_2Br_2 \cdot 2CH_3CN$ (77°K).

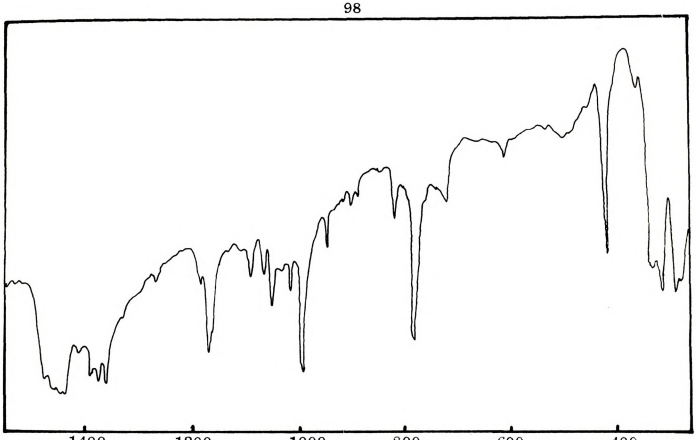


Figure 6. Infrared spectrum of $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$ (300^0K).

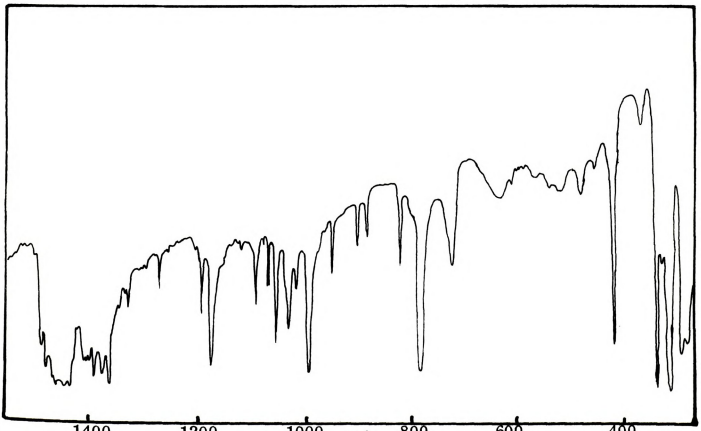


Figure 7. Infrared spectrum of $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$ (77^0K).

Table III. Features of the far infrared spectra of the vanadium(III) complexes

Complex		M-Cl	M-Br	M-N
$[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$	I		275·285	420
$[(C_2H_5)_4N]VBr_3Cl \cdot 2CH_3CN$	II	320	260·280(sh)	418
$[(C_2H_5)_4N]VBr_2Cl_2 \cdot 2CH_3CN$	III	330(broad)	270	418
$[(C_2H_5)_4N]VBrCl_3 \cdot 2CH_3CN$	IV	330(broad)	270(weak)	420
$[(C_2H_5)_4N]VCl_4 \cdot 2CH_3CN$	V	335(broad)		420

modes expected for tetraethylammonium chloride and acetonitrile respectively.

In a complex with D_{4h} symmetry, there should be two metal-ligand vibrations due to equatorial ligands. In this case the metal-bromine vibrations should lie lower in energy than the metal-chlorine vibrations. With this information and the changes in the far-infrared spectra from complex to complex, it is possible to assign most of the metal-ligand vibrations.

D. Nuclear Quadrupole Resonance Spectra

Nuclear quadrupole resonance has been used extensively to study phase transitions in inorganic solids. The transition points of R_2MX_6 type complexes, located by the temperature dependence of the NQR signal, are given in Table VII. At a transition point the resonance frequency may move to

Table IV. Features of infrared spectra of the vanadium(III) complexes

	I	II	III	IV	V[a]
	2740(vw)	--	2740(w)	2740(vw)	2740(vw)
$\nu_3 + \nu_7$	2405(w)	--	2400(w)	2415(vw)	2410(vw)
$\nu_3 + \nu_4$	2320(s)	2320	2320(m)	2325(m)	2330(w)
ν_2	2290(s)	2290(s)	2290(s)	2290(s)	2290(s)
$2\nu_4 + \nu_8$	2245(vw)	--	--	--	2245(vw)
	1490(vw)	--	--	1490(sh)	1490(sh)
	1470(vw)	--	1470(sh)	1470(sh)	--
ν_6	1390(w)	--	1390(m)	1390(m)	1395(m)
ν_3	1360(w)	--	1360(m)	1360(m)	1365(m)
	1190(m)	1190(sh)	1190(sh)	1190(sh)	1190(sh)
$(C_2H_5)_4N^+$	1175(s)	1170(s)	1170(s)	1170(s)	1170(s)
	1090(w)	1090(w)	1090(m)	1090(w)	1090(w)
	1065(w)	1070(w)	1070(m)	1070(w)	1070(m)
ν_7	1050(s)	1050(m)	1050(m)	1050(m)	1050(m)
	1030(w)	1030(vw)	--	--	--
$(C_2H_5)_4N^+$	995(s)	990(w)	1000(s)	1000(s)	1000(s)
ν_4	950(m)	950(s)	950(m)	950(m)	950(m)
	900(w)	900(w)	900(vw)	900(vw)	900(w)
	885(w)	885(w)	885(vw)	--	--
$2\nu_8$	820(m)	830(m)	840(m)	820(m)	820(m)
$(C_2H_5)_4N^+$	790(s)	780(s)	790(s)	790(s)	790(s)
	370(s)	--	--	--	--
	320(m)				

[a]Numbers refer to complexes in Table III.

Table V.[18] Infrared peaks of $(C_2H_5)_4NCl$.

1195	1019	805	467	425	392	350

Table VI.[19] Infrared peaks of CH_3CN.

Vibrational mode	Description[a]	Frequency[b] (liquid)[c]	Shift-ranges[c]
ν_8 (E)	C-C≡N bend.	380 (m)	380-420
$2\nu_8$ (A_1)	overtone	750 (m)	750-825
ν_4 (A_1)	C-C str.	920 (m)	924-980
ν_7 (E)	CH_3 rock.	1040 (s)	1038-1025
ν_3 (A_1)	CH_3 def.	1376 (s)	1374-1355
ν_6 (E)	CH_3 def.	1442 (s)	
$2\nu_4 + \nu_8$ (A_1)	comb.	2208 (vw)	2215-2285
ν_2 (A_1)	C≡N str.	2257 (m)	2266-2325
$\nu_3 + \nu_4$ (A_1)	comb.	2297 (m)	2300-2355
$\nu_3 + \nu_7$ (E)	comb.	2412 (vw)	
$\nu_2 + \nu_8$ (E)	comb.		
ν_1 (A_1)	C-H str.		
ν_5 (E)	C-H str.		
$\nu_2 + \nu_4$ (A_1)	comb.		

[a] bend. = bending mode; str. = stretching mode; rock. = rocking mode; def. = deformation mode; comb. = combination band.

[b] s = strong; m = medium; w = weak; v = very.

[c] Frequencies in cm^{-1}.

much higher or lower frequency or the resonance may disappear altogether.

Table VII. Transition points observed by NQR spectroscopy.

Compound	Transition Point (^{0}C)	Reference
K_2SeBr_6	-64,-52,-33	21
$(NH_4)_2TeBr_6$	-52	22
Rb_2TeI_6	-40,-16, 55	23
K_2SnI_6	-8.5	24
$(NH_4)_2PtBr_6$	0.5	23
K_2ReBr_6	-27,-16,-4	25,26
K_2ReI_6	166	26

A chlorine nuclear quadrupole resonance has been observed for VCl_3 at 9.40 MHz at room temperature.[27] In this investigation only the tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III) complex gave a resonance signal. Two signals were observed at 9.45 and 9.60 MHz which indicated two chlorine environments in the solid state. The observed spectrum is given in Figure 8.

If the signals which were observed at 77^{0}K were followed as the sample was warmed to room temperature only a decrease in intensity and a gradual shift of the two signals to (9.49 and 9.62 MHz) was observed. Since no major shift in the signal took place, there is probably no phase transition for

Figure 8. Cl nuclear quadrupole resonance spectrum of $(C_2H_5)_4NVCl_4 \cdot 2CH_3CN$ at 77°K. (Frequencies in MHz)

A = Cl signal for $2^{35}Cl$ atoms in crystalline environment A.

B = Cl signal for $2^{35}Cl$ atoms in crystalline environment B.

C = ^{37}Cl signal for two different environments.

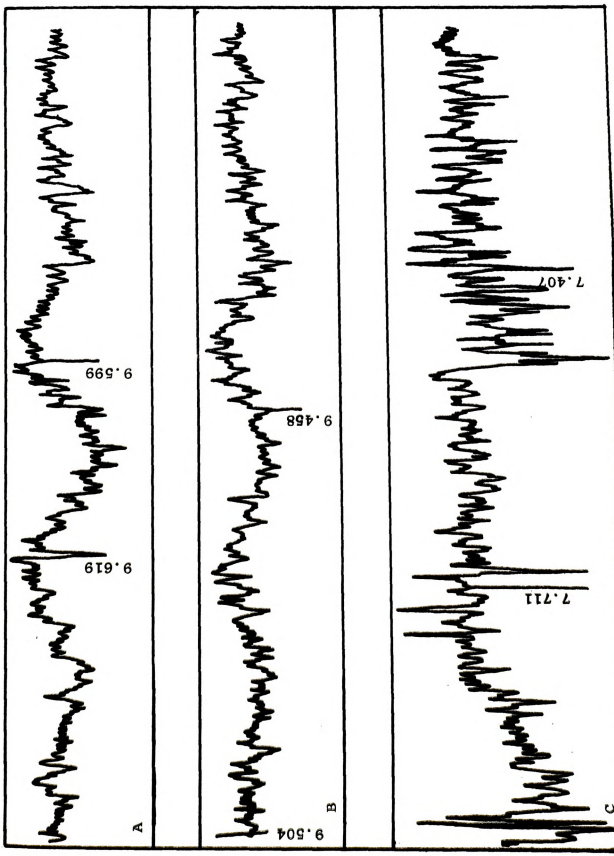


Figure 8.

tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III) between 77°K and room temperature.

E. Optical Spectra

The uv-visible spectrum of each of the complexes was determined as an absorption spectrum of the Nujol mull of the solid. The results are given in Table VIII and the spectra are shown in Figures 9-13. There is a trend in $^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$ transition from a lower to a higher energy in going from the tetraethylammonium bis(acetonitrile)-tetrabromovanadate(III) complex to the tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III) complex. The $^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ was observed only in the tetraethylammonium bis(acetonitrile)tetrachlorovanadate(III) complex because the broad shoulder in all the other complexes due to the low lying charge transfer band obscures the transition.

The smooth variation in color from the light yellow tetrachloro complex to the red-brown tetrabromo complex is due to the position of the first charge transfer band. A peak near 20,000 cm^{-1} will produce a red-brown color while no peaks in this area result in a light color depending on the position of the d-d transition. This color can be compared to the red-black hexachlorovanadate(IV) and golden pentachloroalkoxovanadate(IV) species investigated in Part I of this thesis.

Table VIII. Optical spectroscopic features of vanadium(III) complexes. (bands in cm^{-1})

Complex	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$	$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$
$(C_2H_5)_4NVBr_4 \cdot 2CH_3CN$	12,950	
$(C_2H_5)_4NVBr_3Cl \cdot 2CH_3CN$	13,200	
$(C_2H_5)_4NVBr_2Cl_2 \cdot 2CH_3CN$	13,420	
$(C_2H_5)_4NVBrCl_3 \cdot 2CH_3CN$	13,700	
$(C_2H_5)_4NVCl_4 \cdot 2CH_3CN$	13,900	20,800

Position of center of first charge transfer band	Color
20,200	red-brown
22,000	red
22,600	orange
23,800	yellow-orange
25,600	yellow

The charge transfer peak which produces the color change was investigated in some detail for tetrabromo and tetrachloro-complexes. The results of these spectra are shown in Table IX and representative spectra are given in Figure 14. As the temperature is lowered, the charge transfer band present in the tetrabromo complex shifts slightly to a higher energy and becomes narrower. This behavior is observed to a lesser extent for the tetrachloro complex. Thus while it would appear that the tetrabromo complex is

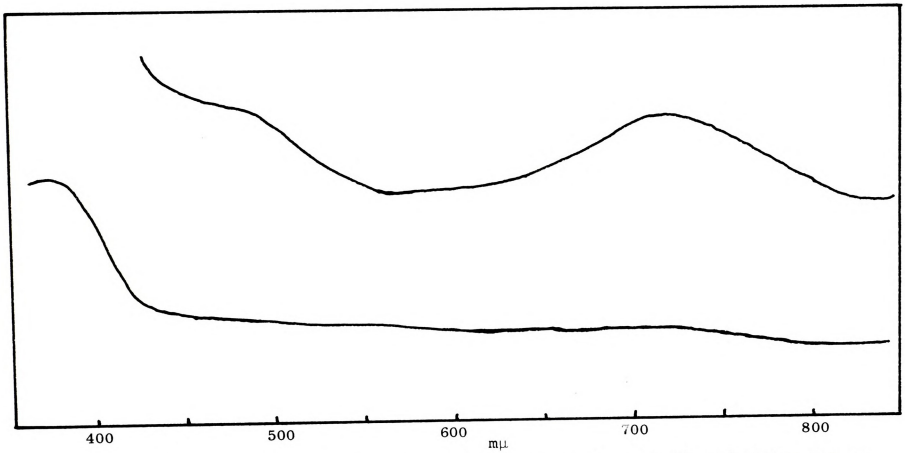


Figure 9. Ultraviolet-visible absorption spectrum of solid $[(C_2H_5)_4N]VCl_4 \cdot 2CH_3CN$ (300°K).

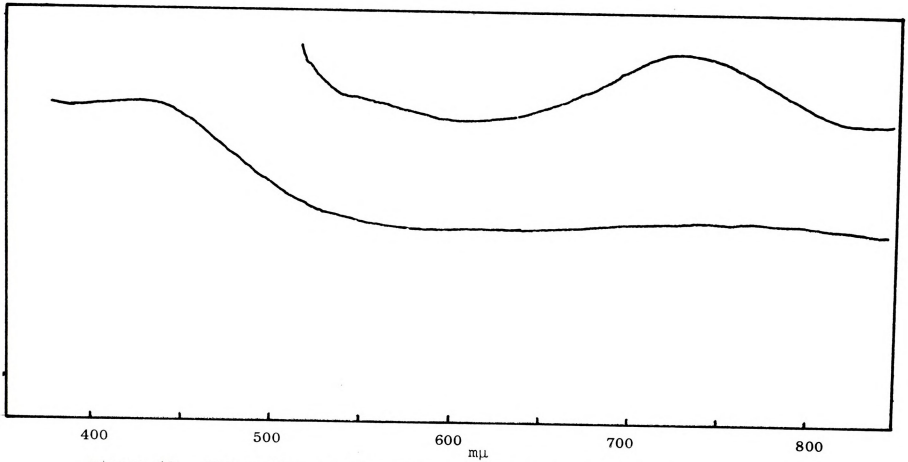


Figure 10. Ultraviolet-visible absorption spectrum of solid $[(C_2H_5)_4N]VBr_3Cl \cdot 2CH_3CN$ (300^0K).

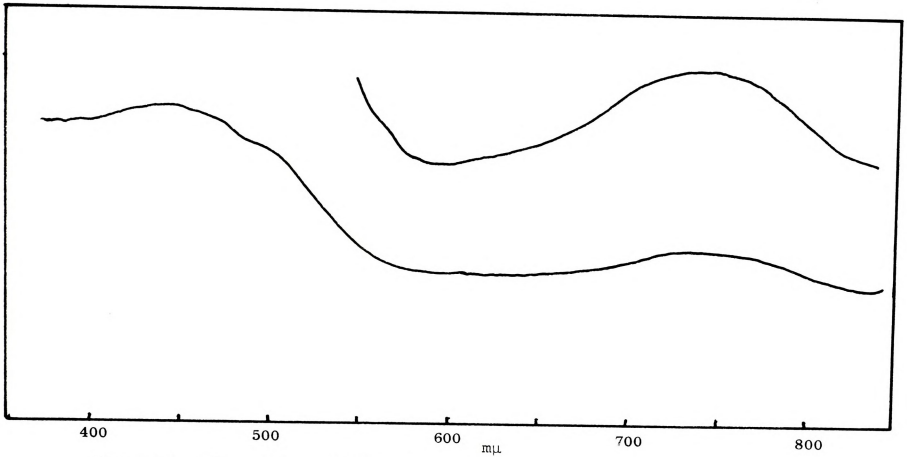


Figure 11. Ultraviolet-visible absorption spectrum of solid $[(C_2H_5)_4N]VBr_2Cl_2 \cdot 2CH_3CN$ (300^oK).

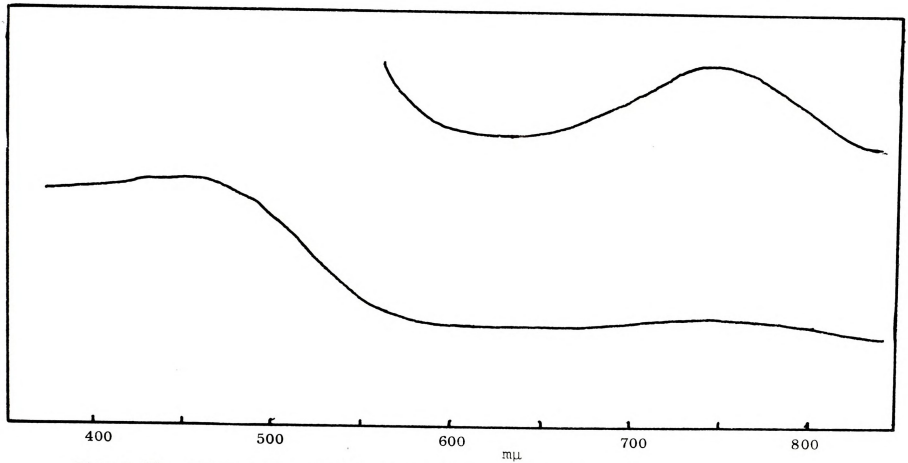


Figure 12 Ultraviolet-visible absorption spectrum of solid $[(C_2H_5)_4N]VBrCl_3 \cdot 2CH_3CN$ (300°K)

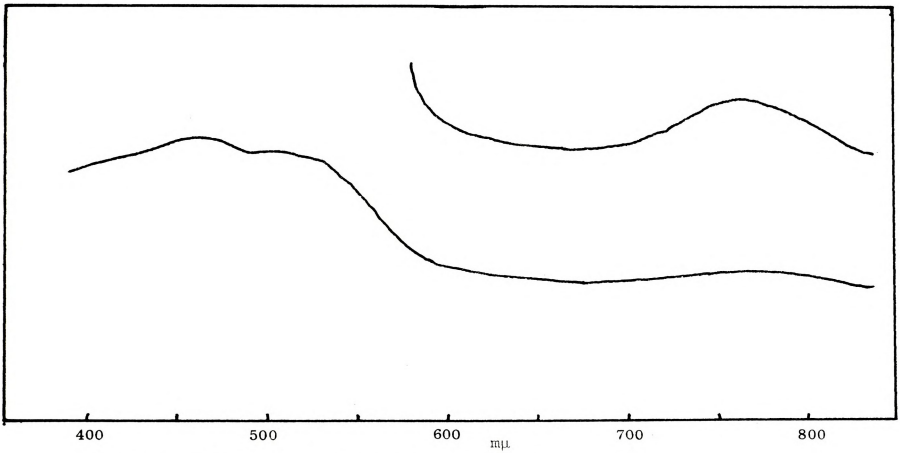


Figure 13. Ultraviolet-visible absorption spectrum of solid $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$ (300^0K).

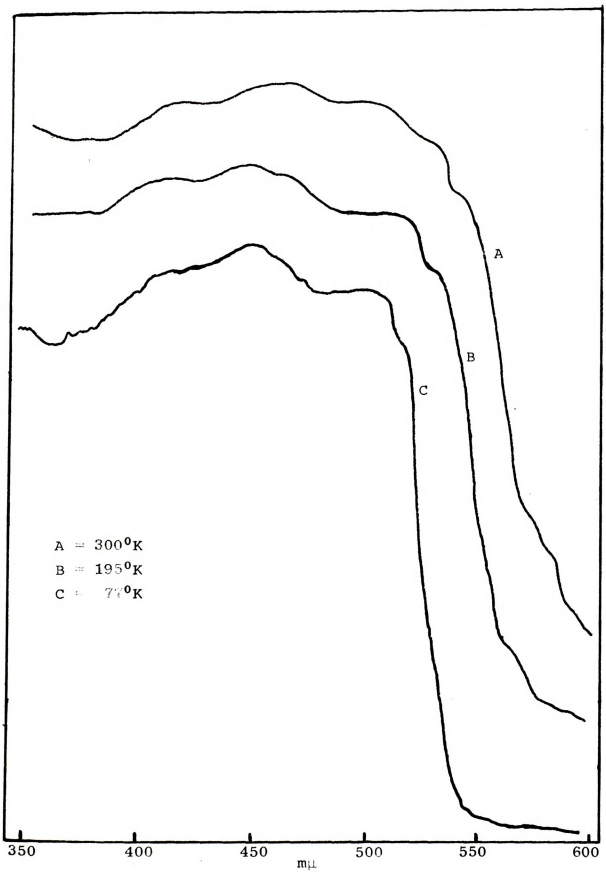


Figure 14. Ultraviolet-visible absorption spectrum of solid $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$.

thermochromic and the tetrachloro complex is not, the quality which produces the thermochromism is present in both of the complexes studied. The charge transfer band is located such that all the complexes with bromide ligands appear to be thermochromic while the tetrachloro complex is not.

Table IX. Spectroscopic features of first charge transfer band in $[(C_2H_5)_4N]VCl_4 \cdot 2CH_3CN$ and $[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$

Compound	Temperature	Peaks (10^3 cm^{-1})*
$[(C_2H_5)_4N]VCl_4 \cdot 2CH_3CN$	300^0K	25.6
	195^0K	25.7
	77^0K	25.8
$[(C_2H_5)_4N]VBr_4 \cdot 2CH_3CN$	300^0K	18.3,19.2,21.5,23.8
	195^0K	18.8,19.4,21.8,24.1
	77^0K	19.2,19.8,22.0,24.2

*Averaged from 4-6 spectra at each temperature.

The structure on the charge transfer band could result from the superposition of the $^3T_1(F) \longrightarrow {}^3A_2(F)$ ligand field transition as well as from the two spin forbidden ligand field transitions $^3T_1(F) \longrightarrow {}^1A_1(G)$ or $^3T_1(F) \longrightarrow {}^1T_2(G)$ band onto the charge transfer band.

No shift in the position of the $^3T_1(F) \longrightarrow {}^2T_1(F)$ transition was observed as the temperature was changed.

However these peaks are less intense and small changes might go undetected.

CONCLUSIONS

Table X lists all of those compounds given in Day's review[1] with thermochromic properties similar to the complexes investigated in this research. It would seem then that all thermochromic transitions actually should be listed in three classes:

(1) Those transitions which are gradual and involve a mechanism similar to that found for the vanadium(III) complexes investigated here.

(2) Those transitions which involve a change in the phase of the solid.

(3) Those transitions which take place in solution and involve equilibria.

It is felt that this investigation more clearly defines the phenomenon of thermochromism, and will encourage future thorough investigations of the theoretical implications of the color changes.

Table X. Compounds with thermochromic properties

Compound	Color change on heating[1]
$Cu_2Fe(CN)_6$	red —> dark red or black
Sb_2S_3	red —> dark red or black
FeO	red —> dark red or black
CuI_2	red —> dark red or black
HgS	red —> dark red or black
$PbCrO_4$	red —> dark red or black
PbO	red —> dark red or black
$K_2Cr_2O_7$	red —> dark red or black
As_2S_3	yellow —> orange red
$HgSO_4$	yellow —> orange red
$BaCrO_4$	yellow —> orange red
SnS_2	yellow —> orange red
Hg_2I_2	green —> yellow —> orange —> red
SnO_2	white —> green —> yellow —> orange
AgI	yellow —> red brown
Ag_2HgI_4	yellow —> orange
Cu_2HgI_4	red —> dark red
Tl_2HgI_4	orange —> red
	Color change on cooling[1]
HgS	red —> light red
SnS_2	yellow —> light yellow
$HgSO_4$	yellow —> green
PbI_2	orange —> yellow orange
$PbCrO_4$	yellow orange —> yellow green

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