

Single-Crystal Electron Paramagnetic Resonance Study of a Trigonal Vanadium Tris(dithiolate) Complex

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The electron paramagnetic resonance spectrum of $V(mnt)_3^{2-}$ doped in single crystals of the isomorphous $[(C_6H_5)_4As]_2Mo(mnt)_3$ lattice has been measured. The spectrum is fit by an axially symmetric spin Hamiltonian with $g_{\parallel} = 2.000$, $g_{\perp} = 1.974$, $A_{\parallel} = 10$ G, and $A_{\perp} = 100$ G with the two A components having opposite sign. The parallel components of both g and A lie very close to the direction of the approximate threefold axis of $Mo(mnt)_3^{2-}$. These parameters are readily interpreted in terms of a 2A_1 ground state in D_3 symmetry. The orbital bearing the unpaired electron is shown to have a substantial metal d_{z^2} character, although the covalency is quite high. Orbital mixing coefficients are derived from the g and A values and it is shown that the g value is potentially a function of θ , the polar angle which describes the degree of compression of a trigonal structure. Finally, in light of these results the epr results on other trigonal tris(dithiolate) complexes are reconsidered.

Introduction

The chemistry of tris(1,2-dithiolate) complexes reveals an interesting range of novel behavior.²⁻⁴ Thus, these complexes engage in chemically and electrochemically reversible electron-transfer reactions leading to the accessibility of a number of formal oxidation states. In the more highly oxidized species the unusual trigonal-prismatic coordination is found,^{5,6} whereas the highly reduced species possess near octahedral structures.^{7,8} Intermediate states of oxidation are found to have structures between the octahedral and trigonal-prismatic limits.⁸⁻¹⁰ Various studies of the electronic structural factors responsible for the change in geometry with oxidation state have not led to a clear understanding of the structural trend.

One of the techniques which can supply important information in this respect is electron paramagnetic resonance (epr) spectroscopy. For example, in the bis(dithiolate) complexes, single-crystal and solution epr studies were very valuable in discerning the electronic ground states and in estimating the degree of delocalization.^{11,12} Initial studies of the tris complexes using epr were carried out by Davison, *et al.*,^{13,14} on various ions including the tris(maleonitriledithiolate) complex of vanadium, $V(mnt)_3^{2-}$. Davison, *et al.*, found from their frozen glass studies that this ion showed axially symmetric g and A tensors. This result is especially

interesting since in its bis $N(CH_3)_4^+$ salt⁹ this ion only possesses C_2 symmetry. Also of great interest is the conclusion^{13,14} that the values for g and A could not be accommodated with a ground state containing metal $3d^1$ configuration, when a near octahedral structure is assumed. In an attempt to more definitely identify the effective symmetry, to locate the molecular orientation of the g and A tensors, and to probe the electronic structure of this ion and related ions, we have carried out single-crystal epr studies of the $V(mnt)_3^{2-}$ ion doped in $[(C_6H_5)_4As]_2Mo(mnt)_3$. Our results show that this complex ion indeed has axial symmetry about its approximate threefold axis. Furthermore, despite earlier claims to the contrary,^{13,14} the orbitally nondegenerate ground state is most appropriately described as 2A_1 (roughly $3d^1$ metal). Moreover, using equations which relate g and A values to the bonding characteristics of the ion, we point out that these parameters depend critically on the detailed nature of the six-coordinate polyhedron of the particular ion. Taking this latter effect into account allows a consistent explanation of the epr properties of all trigonal tris(dithiolate) complexes.

Experimental Section and Treatment of Data

The unit cell of $[(C_6H_5)_4As]_2V(mnt)_3$ was determined by X-ray crystallography using $Mo K\alpha$ radiation. The dilute single crystals used in this study were grown from acetone-2-propanol solution with the ratio of vanadium to the molybdenum complex being 1:100. The faces of the dilute single crystal were identified by optical goniometry. A Varian 4500 X-band spectrometer was used to measure the epr. The field sweep was calibrated by means of a nmr gaussmeter and frequency counter. Diphenylpicrylhydrazyl served as a g marker to determine the klystron frequency.

The epr spectra were taken at 15° intervals about each of the three orthogonal crystal axes. Diagonalization¹⁵ of the observed g tensor led to a clearly axially symmetric tensor with g_{max} being in the direction of the pseudo C_3 axis and $g_{min} = g_{\perp}$ being perpendicular to this component. The principal axes of the tensor revealed that both g_{max} and g_{min} very nearly appear in the spectra found upon rotation about the b axis. That these were indeed maxima and minima was then further confirmed by using 5, 10, and 15° wedges. In no cases could larger or smaller values be found for g . Totally analogous procedures were used for A .

Results and Discussion

Geometrical Results and Considerations. The complex $[(C_6H_5)_4As]_2V(mnt)_3$ crystallizes in the space group $Pbcn$ with $a = 18.78$ (3) Å, $b = 15.60$ (2) Å, and $c = 18.32$ (3) Å and is thus closely isomorphous to $[(C_6H_5)_4As]_2Mo(mnt)_3$,

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(13) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 86, 2799 (1964).

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a fact which had been surmised previously⁷ from X-ray powder patterns. Due to the rather strict isomorphism we assume henceforth that in the isomorphous mixed crystal $V(mnt)_3^{2-}$ occupies the same sites as $Mo(mnt)_3^{2-}$ and has a similar orientation within these sites.

A representative epr spectrum of the $[(C_6H_5)_4As]_2V(mnt)_3-[(C_6H_5)_4As]_2Mo(mnt)_3$ mixed crystal is shown in Figure 1. The two sets of hyperfine lines $[I(^{51}V) = 7/2]$ are due to the existence of two sets of molecules whose orientation with respect to the magnetic field is not equivalent. The behavior of the two sets of lines was virtually symmetrical with respect to the ab plane. The crystal structure of the host¹⁰ reveals the arrangement of anions shown in Figure 2. It is clear from the figure that the threefold axis of each pair of molecules is related to the threefold axis of the remaining pair by a glide plane perpendicular to c . Thus, the epr results are in agreement with the assumption that $V(mnt)_3^{2-}$ ions occupy $Mo(mnt)_3^{2-}$ sites with similar orientation.

The X-ray structure of the host shows the $Mo(mnt)_3^{2-}$ anion to contain two approximately parallel roughly equilateral triangles of S atoms with Mo midway between these triangles. The triangles are twisted by $\phi = 28^\circ$ from the trigonal prism ($\phi = 0^\circ$) and the compression ratio¹⁶ $s/h = 1.09$ compared to 1.00 for the known trigonal prisms and 1.22 for the octahedron. The molecule is thus near midway between trigonal-prismatic and octahedral limits. While strictly speaking the molecule only contains C_2 symmetry, the deviations from D_3 symmetry are small, and the D_3 point group is assumed in the discussion which follows. This assumption is clearly justified by the experimental results (*vide infra*). The direction angles of the approximate C_3 axis for one set of molecules (the others are mirror images and behave in all respects equivalently) with respect to the crystallographic a , b , and c axes are $\alpha = 70^\circ$, $\beta = 90^\circ$, and $\gamma = 20^\circ$.

Spin-Hamiltonian Parameters. The epr of $V(mnt)_3^{2-}$ in single crystal can be fit by the axially symmetric spin Hamiltonian¹¹

$$\mathcal{H} = g_{\parallel}\beta_e H_z S_z + g_{\perp}\beta_e [H_x S_x + H_y S_y] + A_{\parallel} I_z S_z + A_{\perp} [I_x S_x + I_y S_y]$$

with the values for g_{\parallel} , g_{\perp} , A_{\parallel} , and A_{\perp} shown in Table I. The averaged g and A values are in excellent agreement with the isotropic $\langle g \rangle$ and $\langle A \rangle$ found in $CHCl_3$ -DMF solution.¹⁴ The treatment of the experimental results revealed that the $V(mnt)_3^{2-}$ ion has effective axial symmetry and that the parallel components of the g and A tensors are nearly coincident with each other and with the C_3 molecular axis. One orientation of the corresponding perpendicular component is then in the direction of the crystallographic b axis (the molecular C_2). Thus, g_{\max} , A_{\max} , g_{\min} , and A_{\min} all very nearly appear in the ac net (rotation about b) and the angular variation of this net is shown in Figure 3. The directional agreement with the molecular C_3 axis is immediately apparent from the plot as well as from the direction angles shown in Table I.

At this point it is appropriate to compare our results with the experimental findings of Davison, *et al.*¹³ Based on solution and frozen solution studies Davison assigned $A_{\parallel} = 100$ G and $A_{\perp} = 45$ G with $g_{\parallel} = 1.974$. Due to the discrepancy between our results and those of Davison, *et al.*, we reexamined the frozen glass spectrum of $V(mnt)_3^{2-}$ in

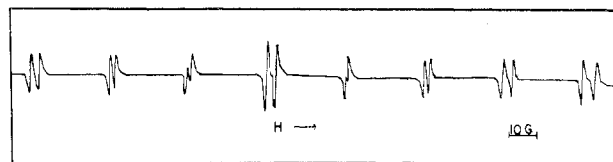


Figure 1. A spectrum of the $[(C_6H_5)_4As]_2V(mnt)_3-[(C_6H_5)_4As]_2Mo(mnt)_3$ mixed single crystal.

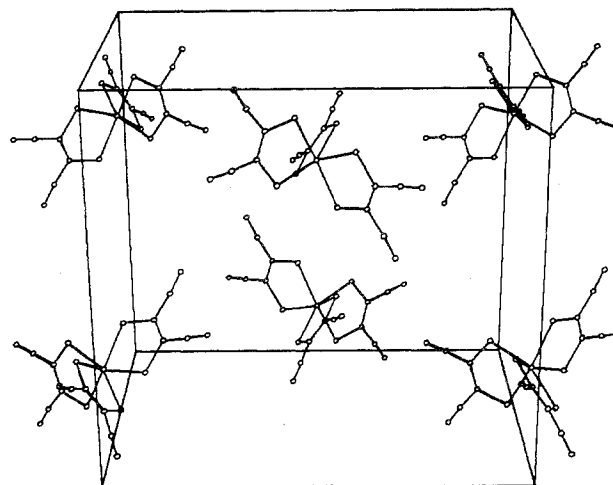


Figure 2. Distribution of the anions in the $[(C_6H_5)_4As]_2Mo(mnt)_3$ unit cell. (The c axis is horizontal, a is vertical, while b is going into the paper. The crystallographically required molecular C_2 axis is parallel to b .)

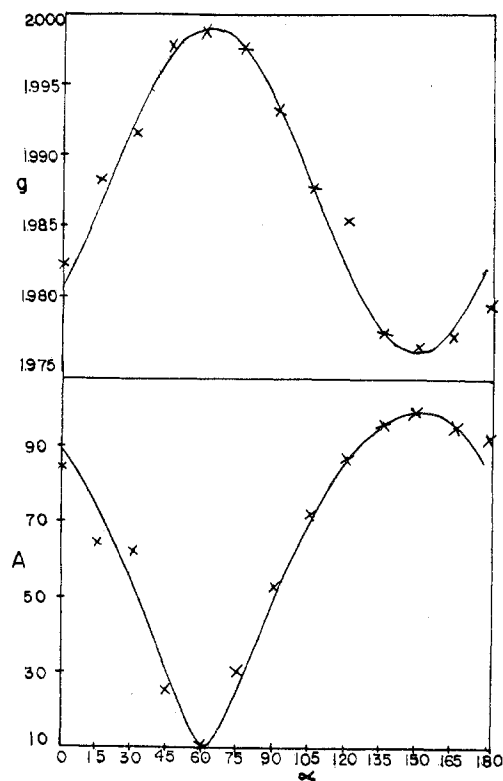


Figure 3. A plot of the angular variation of g and A in the ac net as a function of α , the angle between the a axis and the magnetic field. The points represent experimental data while the plots are best fits to the functions $g^2 = g_{\max}^2 \cos^2 \alpha + g_{\min}^2 \sin^2 \alpha$ and $g^2 A^2 = g_{\max}^2 A_{\min}^2 \cos^2 \alpha + g_{\min}^2 A_{\max}^2 \sin^2 \alpha$.

$CHCl_3$ -DMF at 77°K. Interestingly, the spectrum showed that only the larger components of A and the corresponding g could be measured unambiguously. The smaller compo-

(16) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 11, 434 (1972).

Table I. g and A Values and Direction Angles^b of g , A , and the Molecular C_3

	g_{\parallel}	g_{\perp}	$\langle g \rangle$	$\langle g \rangle$ solution ^a	A_{\parallel}	A_{\perp}	$\langle A \rangle$	$\langle A \rangle$ solution ^a	C_3 direction
Value	2.000 ± 0.001	1.974 ± 0.001	1.982 ± 0.002	1.980 ± 0.001	10 ± 1 G	-100 ± 2 G	-63.3 ± 2 G	63.5 ± 0.5 G	
					(9.2 × 10 ⁻⁴ cm ⁻¹)	(-91 × 10 ⁻⁴ cm ⁻¹)	(-57.7 × 10 ⁻⁴ cm ⁻¹)		
α	64 ± 2°	24 ± 2°			65 ± 2°	24 ± 2°			70
β	90 ± 2°	90 ± 2°			90 ± 2°	90 ± 2°			90
γ	25 ± 2°	66 ± 2°			25 ± 2°	66 ± 2°			20

^a CHCl₃-DMF (1:1 v/v) solvent. ^b α , β , and γ are the angles of the principal tensor axis with a , b , and c , respectively.

nents could not easily be discerned and it thus seems likely that these were deduced by comparison with the solution results with the assumption that A_{\parallel} and A_{\perp} have the same sign. The value for the larger component of A thus obtained corresponds, however, to the *perpendicular* component which we have found from the single-crystal study. In view of the fact that assignments by single-crystal epr involve much less ambiguity than randomly oriented frozen glass studies, we conclude that the frozen glass spectrum was incorrectly assigned in the previous study. In light of the present results the 100-G component of the frozen glass spectrum must be associated with the perpendicular component. In order for this assignment to agree with the solution $\langle A \rangle$ value, it must be assumed that A_{\parallel} and A_{\perp} have opposite signs. While this is theoretically quite reasonable, it has to our knowledge only rarely been observed previously for V(IV) complexes.¹⁷⁻¹⁹ The reason for this occurrence is easy to ascertain. The isotropic part of the hyperfine splittings has always made a dominant contribution to the overall splitting and thus determined its sign. In the present case, the isotropic hyperfine splitting [$\langle A \rangle = 63.3$ G (58.6 × 10⁻⁴ cm⁻¹)] is one of the smallest yet observed for V(IV) complexes and thus the anisotropic components (which enter A_{\parallel} and A_{\perp} with opposite sign) contribute substantially to the splitting and determine the signs of A_{\parallel} and A_{\perp} .

Energy Levels for D_3 Ions. Before we discuss more detailed interpretations of the spin-Hamiltonian parameters, we look at the general problem of the electronic structure of an ion with D_3 symmetry. We first choose to look at the d-orbital splitting for a 3d¹ ion. Under D_3 symmetry the five 3d levels split into three sets, one belonging to a_1 symmetry and two belonging to e symmetry. The linear combinations are

$$d(e_b)_1 = [bd_{-2} - ad_1]$$

$$d(e_b)_2 = [bd_2 - ad_{-1}]$$

$$d(e_a)_1 = [ad_{-2} + bd_1]$$

$$d(e_a)_2 = [ad_2 + bd_{-1}]$$

$$d(a_1) = d_0$$

The subscripts used for the two e 's are merely labels as the two sets of linear combinations are not distinct as far as symmetry is concerned. For octahedral symmetry $a^2 = 2/3$, $b^2 = 1/3$ and a_1 and e_a are components of the lower energy t_{2g} levels. For trigonal-prismatic coordination $a^2 = 1$ and $b^2 = 0$ and e_a and e_b become distinct by symmetry as e' and e'' , respectively. Since the geometry of $V(mnt)_3^{2-}$ is between these limits, values of a and b are not immediately obvious.

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(19) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

Simple crystal-field considerations predict the energy ordering $e_b \gg e_a > a_1$ for the trigonal-prismatic species while for complexes with near octahedral structures either a_1 or e_a can be the lowest level. The spin-Hamiltonian parameters allow for an unequivocal assignment of the ground state. Thus, the anisotropy of the g tensor is such that g_{\parallel} is close to the free electron value while g_{\perp} deviates substantially from 2.0023. Furthermore, the parallel component of the hyperfine tensor, A_{\parallel} , is numerically much smaller than the perpendicular component A_{\perp} . These facts are totally consistent with the unpaired electron being in a nondegenerate molecular orbital which is substantially d_{z^2} on the metal ion. The ground-state configuration for the $V(mnt)_3^{2-}$ ion is thus described as 2A_1 . The epr results which these most closely resemble are those of McGarvey²⁰ on $Ti(CH_3COCHCOCH_3)_3$, also a tris(bidentate) trigonal, 3d¹ complex. It is thus unnecessary to invoke^{13,14} any unusual electronic configuration to explain the experimental parameters.

Since the earlier results^{13,14} are based on the incorrect assignment ($A_{\parallel} = 100$ G), the postulation of a ligand molecular orbital as the bearer of the unpaired electron is no longer necessary. This previous conclusion, not surprisingly, led to serious difficulties in achieving a consistent interpretation of all the available data on this and other complexes.^{14,21}

The crystal-field and symmetry considerations discussed above are sufficient for qualitative understanding of the data. Any quantitative treatment immediately reveals that a pure crystal-field treatment using free ion values greatly overestimates the anisotropic hyperfine coupling and the g shift. Clearly, a reduction of these free ion parameters is required and we choose to do this by recognizing the molecular orbital nature of the crystal-field levels discussed above. These levels then become

$$\Psi(e_b)_1 = \alpha d(e_b)_1 + \alpha_L L(e_b)_1$$

$$\Psi(e_b)_2 = \alpha d(e_b)_2 + \alpha_L L(e_b)_2$$

$$\Psi(e_a)_1 = \beta' d(e_a)_1 + \beta'_L L(e_a)_1$$

$$\Psi(e_a)_2 = \beta' d(e_a)_2 + \beta'_L L(e_a)_2$$

$$\Psi(a_1) = \beta d_0 + \beta_L L(a_1)$$

where the L are symmetry-adapted linear combinations of ligand orbitals, α , β' , and β are metal orbital coefficients, while α_L , β'_L , and β_L are ligand coefficients. The a_1 and e_a levels are both predominantly π -type levels and for simplicity we assume henceforth that $\beta = \beta'$ (which is only rigorously true in the octahedral limit). The e_b level is on the other hand a predominantly σ -type level. Thus, β becomes a measure of the π bonding in the complex while α is a measure of the σ bonding. We note however, that σ and π bonding are not separable by symmetry in D_3 . Nevertheless, qualita-

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(21) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 1956 (1966).

tive and quantitative²¹ consideration of overlap as well as extrapolation to the octahedral limit leads to the distribution of the σ and π bonding in the indicated manner. We use these levels in considerations which follow.

Hyperfine Coupling. To discuss the hyperfine parameters we use the equations of Ray²² as corrected by McGarvey.²⁰ In the present case ΔE values are much greater than λ and hence the equations reduce to²³

$$A_{\parallel} = -K + {}^4/7\beta^2 P - {}^1/7(g_{\perp} - 2.0023)P$$

$$A_{\perp} = -K - {}^2/7\beta^2 P - {}^{13}/14(g_{\perp} - 2.0023)P$$

Here K represents the isotropic component,²⁰ the second term represents the dipole-dipole term from the electron residing in the $\psi(a_1)$ ground state orbital. β is the mixing coefficient defined above. The last term accounts for the small mixing of other d orbitals into the ground state. $P = 2.0023g_n\beta_n\beta_e(1/r^3)$ and the values for P have been tabulated by McGarvey²⁴ using $\langle 1/r^3 \rangle$ values obtained from Watson and Freeman's Hartree-Fock calculations.²⁵ For V^{4+} , $P = 172 \times 10^{-4} \text{ cm}^{-1}$ (for 5V). Since A_{\parallel} , A_{\perp} , and g_{\perp} are known from experiment, β^2 and K are the two unknown parameters in these two equations. It is found that

$$\beta^2 = 0.65$$

$$K = 55.2 \times 10^{-4} \text{ cm}^{-1}$$

K in turn is related to χ , the spin density at the nucleus,²³ and χ is then calculated to be -1.75 au .

We note first that the value of K and therefore χ does not significantly depend on the choice of P (i.e., oxidation state). Clearly the value observed for χ is smaller than that for most $V(\text{IV})$ complexes but it is definitely of roughly the same magnitude and more significantly of the same sign. Thus, this calculation shows χ to be quite in line with previous results and it is clear that an unusual ground state (e.g., $d^0 1^1$ as opposed to $1^0 d^1$) is no longer required to understand the results.

The smallness of the χ value [the average for $V(\text{IV})$ complexes is about -2.5 au] can be understood in terms of the two mechanisms which give rise to this effect.²⁵ Thus, unpaired electron density must be produced at the nucleus and this requires a net spin density in s orbitals. In D_3 symmetry this can arise by either direct s-d mixing (both transform as a_1) or by spin polarization of inner s levels (mostly 2s) by the unpaired electron residing in a 3d level. The former effect produces positive contributions to χ while the latter effect produces a net negative contribution. The vast majority of first row transition metal ions shows χ to be negative and in fact of roughly constant value. Thus, the latter effect dominates the contribution. In the highly covalent $V(\text{mnt})_3^{2-}$, on the other hand, the d-s mixing may be a somewhat more substantial contribution than usual and this may reduce the magnitude of the observed effect.

In addition to the smallness of the isotropic contribution, the anisotropic components are also small compared to other $V(\text{IV})$ complexes (both vanadyl and nonvanadyl).¹⁸ This is a consequence of covalent bonding which in the present treatment manifests itself in giving $\beta^2 = 0.65$ ($\beta = 0.81$) which

is again one of the smallest known values for $V(\text{IV})$ species.²⁶ We feel, however, that this is not unexpected for sulfur donor complexes in relatively high metal oxidation states and it is clearly comparable in magnitude to values estimated¹² for other metal complexes of 1,2-dithiolate ligands. It is also quite comparable to the value of $\beta^2 = 0.59$ estimated for $\text{Ti}(\text{acac})_3$,²⁰ the only other d^1 tris(chelate) studied in detail. Thus, the result indicates substantial delocalization of the electron in the a_1 level. This would seem to indicate that the metal d_{z^2} overlaps strongly with some ligand orbitals and the most likely candidate for this would seem to be the lone pair orbital on S which is not involved in σ bonding. (This orbital has been designated π_h in previous studies^{21,27}). Then, occupation of the a_1 orbital by one electron in the "in between" structure is of interest since in the oxidized forms [e.g., $V(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3^-$], known to be trigonal prismatic,⁹ it is empty. This orbital is antibonding in nature and its bonding counterpart has been suggested as a stabilizing factor for the trigonal prism. The present observation thus lends credence to the notion that the $d_{z^2}-\pi_h$ interaction may be an important contributor to the stability of the trigonal prism in the oxidized forms. The occupancy of the a_1 antibonding level may be an important factor in causing the in-between structure to obtain in $V(\text{mnt})_3^{2-}$.

g Values. In the limit when $\Delta E \gg \lambda$ the equations for g^{24} reduce to the following.

$$g_{\parallel} = g_e$$

$$g_{\perp} = g_e - 6\lambda \left[\frac{\alpha^2 \beta^2 a^2}{\Delta E_b} + \frac{\beta^4 b^2}{\Delta E_a} \right]$$

The quantities α and β are the metal orbital coefficients in the LCAO's defined above. λ is the spin-orbit coupling constant [250 cm^{-1} for $V(\text{IV})$]²⁸ and ΔE_a and ΔE_b are the energy differences between the ground state and e_a and e_b , respectively. In the present case, we emphatically cannot make the assumption that $a^2 = 2/3$ and $b^2 = 1/3$ made by McGarvey²⁰ for $\text{Ti}(\text{CH}_3\text{COCHCH}_3)_3$. Since the structure of the $V(\text{mnt})_3^{2-}$ complex lies between the octahedral and trigonal-prismatic limits, it seems reasonable that values of a^2 (note that $b^2 = 1 - a^2$) would lie between the octahedral ($2/3$) and trigonal-prismatic (1.00) values. The question is, where? One approach to this problem involves inspection of the angular distributions of the two sets of e orbitals. In particular, we look at the maximum of e_b as a function of angle since $\psi(e_b)$ is a strongly σ -interacting level. For the octahedron $a^2 = 2/3$ and e_b has an angular maximum at $54^\circ 44'$ from the C_3 axis [this angle is the polar angle (henceforth θ) and corresponds to the angle between the C_3 axis and the M-L bond for the octahedron]. At the other extreme, the trigonal prism, the orbital maximum occurs at $\theta = 45^\circ$ (where $e_a = e''$ is made up of d_{xz} , d_{yz}). In the known tris(chelate) trigonal prism the polar angle = $\arctan(2/\sqrt{3}) = 49.11^\circ$.¹⁶ To estimate the value of a^2 for a given "in-between" complex, we assume that in general the angular maximum for the e_b

(26) Using values of P for V^{3+} and V^{2+} , values of β^2 of 0.76 and 0.88 are calculated, respectively. We prefer to use the P values for V^{4+} (the actual formal oxidation state) and to allow the orbital coefficients (α and β) to absorb all of the effects of covalency. While this certainly does not represent the real situation, we feel this approach is preferable to arbitrarily splitting up the reduction between reduced P values and β^2 .

(27) The π_h orbitals are in the plane of the SCCS ligand and can be viewed roughly as S sp^2 orbitals. In the trigonal prism these orbitals point upward along the C_3 axis and overlap considerably with the d_{z^2} metal orbital.²¹

(28) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions," Clarendon Press, Oxford, England, 1970.

(22) D. K. Ray, *Nuovo Cimento*, **21**, 1 (1961).

(23) B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).

(24) J. S. Griffith, "The Theory of Transition Metal Ions," University Press, Cambridge, England, 1961.

(25) A. J. Freeman and R. E. Watson in "Magnetism," G. T. Rado and H. Suhl, Eds., Academic Press, New York, N. Y., 1965, p 167.

functions coincides with the M-L direction.²⁹ The parameter a^2 is then shown³⁰ to be related to θ by the simple expression

$$a^2 = 1/(1 + 4 \cot^2 2\theta)$$

A plot of this function is shown in Figure 4. Thus, if the θ is known from the geometry of the complex [recall¹⁶ $\theta = \arctan(s/h)(2/\sqrt{3})$], then a^2 is calculable. In the present case $s/h = 1.09$, $\theta = 51.5^\circ$ and $a^2 = 0.82$. If we use the V^{4+} value for $\lambda = 250 \text{ cm}^{-1}$, the only unknowns remaining in the g equation are the excitation energies and the orbital mixing coefficient α (since β is known from the A calculations). The low-energy electronic absorption spectrum of $V(\text{mnt})_3^{2-}$ is complex⁷ and shows a number of bands below $30,000 \text{ cm}^{-1}$. While detailed assignments for the spectrum are not yet at hand, certain bands can be eliminated as responsible for the ΔE_a and ΔE_b transitions. In particular, we can eliminate those bands which are also found in the isomorphous $3d^0$, Ti^{4+} complex. It thus seems reasonable to assign the $10,850\text{-cm}^{-1}$ band to ΔE_a and the $23,400\text{-cm}^{-1}$ band to ΔE_b .³¹ Using these values we calculate a value for $\alpha^2 = 0.53$. This value indicates substantial covalency in M-L σ bond. Again this is in agreement with most bonding notions for complexes of this type.³²

(29) This assumption would maximize e_b overlap if the L, σ orbitals are pointing directly toward the metal. Since e_b is the largest σ -type interaction in these complexes, it seems likely that this would be roughly the case. As always, however, bent bonds cannot be eliminated and we simply make this assumption since it is the simplest and at least for an octahedral structure is rigorously true.

(30) The calculation involves taking the general expression for the metal angular functions in terms of the usual spherical harmonics and a^2 and determining its maximum with respect to polar coordinate θ . One can now solve for a^2 in terms of θ which is now the direction of the angular maximum.

(31) The low-energy electronic absorption spectrum of $V(\text{mnt})_3^{2-}$ has bands at $10,850$, $15,040$, $17,240$, $19,050$, $23,400$, and $26,500 \text{ cm}^{-1}$. The $15,000\text{-cm}^{-1}$ band is closely analogous to a transition which occurs in the $3d^0$, $Ti(\text{mnt})_3^{2-}$ ion and thus cannot be a "d-d" band of the type sought. The same argument arises for the $26,000\text{-cm}^{-1}$ band. We are thus left with the $10,850\text{-cm}^{-1}$ band which is reasonably assigned to the e_a excitation while the bands at $17,240$, $19,050$, and $23,400 \text{ cm}^{-1}$ all seem candidates for the ΔE_b transition. We choose the $23,400\text{-cm}^{-1}$ band based simply on the notion that the σ bonding and antibonding should be substantially larger than the predominantly π interactions which produce ΔE_a . The choice has some effect on α^2 . See text.

(32) It seems appropriate to mention the severe limitations under which we work and the approximations which are necessary to overcome them. We first consider the treatment for g . First, ligand interactions including spin-orbit coupling with ligand atoms have been totally neglected and these may be significant for S compounds (see, for example, ref 33). Second, the unknown effective charge of the central metal ion requires a guess as to the appropriate metal spin-orbit coupling constant. While intelligent estimates place metal charges at <2.0 , the precise values are certainly unknown and in fact are even poorly defined. Third, the values used for the excitation energies in the Δg expressions are uncertain since the rather complex absorption spectrum of the ion has not been assigned in detail.³¹ (The values used are only reasonable in light of preconceived notions as to the magnitudes of the interactions which give rise to the splittings.) Finally, due to the highly covalent nature of the bonding in these complexes formally charge-transfer interactions may have substantial "d-d" character and since these occur at fairly low energy in these intensely colored complexes their contributions to g should not be neglected.

The approximations involved for A value calculations are less numerous but equally disturbing. Thus, the value of $(1/r^2)$ used in the calculations is of necessity obtained from SCF calculations on the free ion. Clearly, this value must be reduced in the complex but the reduction is a complicated phenomenon both due to expansion of the orbital due to its extension to the ligands and also due to the overall charge donated to the central metal by the covalent bonding with the ligands. Thus, simply using the conventional orbital reduction factor (α^2 and β^2 are equivalent to $K_{\sigma\sigma}$ and $K_{\pi\pi}$ used previously²⁰) may not in fact represent a fully valid procedure. Nevertheless, due to the lack of a better treatment we have succumbed and done the things which in this footnote we disparage.

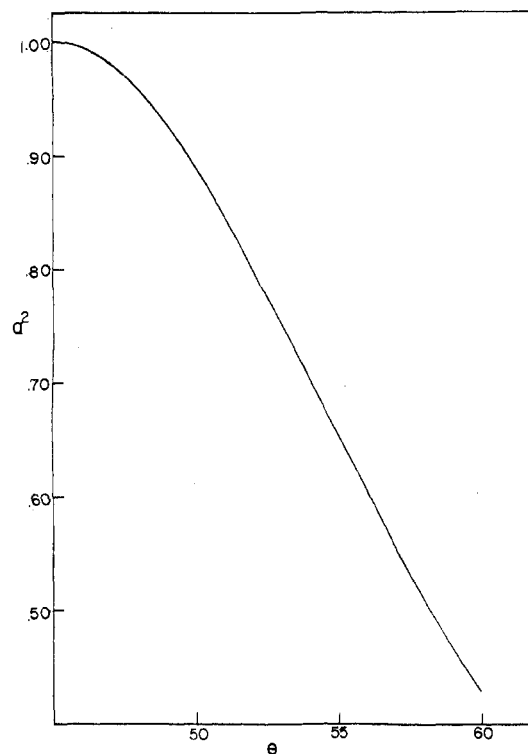


Figure 4. A plot of a^2 vs. $1/(1 + 4 \cot^2 2\theta)$.

We might at this point discuss what effect varying some of our input parameters can have on calculated values for β and α . We note first that using free ion values for P and λ gives us the smallest values for α^2 and β^2 (i.e., the greatest covalency).²⁴ Thus, if anything, the procedure we have used may overestimate the covalency, especially in the π levels (β^2 value). The effect of changing the excitation energy assignment should also be discussed. Thus, if the band at $17,240 \text{ cm}^{-1}$ is used for ΔE_b ,³¹ then α^2 is calculated to be 0.39 , indicating an orbital with greater than 50% ligand character. In any event the σ level in question is highly delocalized. The choice of excitation energy does not, however, effect the calculation of β^2 .

Finally, we would like to explicitly point out the potential effect of the detailed six-coordinate polyhedron on the value of g_{\perp} . As a structure approaches the trigonal-prismatic limit,¹⁶ a^2 approaches one while b^2 approaches zero. Changes in a^2 and b^2 effect the way in which ΔE_a and ΔE_b contribute to g and in the following section we recognize this effect and use it to discuss the epr parameters of other tris(dithiolate) complexes.

Related Complexes. Although $V(\text{mnt})_3^{2-}$ is the only tris(dithiolate) complex to be studied by single-crystal techniques, solution and/or frozen glass studies have been reported for $V(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3$,^{14,30} $\text{Cr}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3$,³⁴ $\text{Mo}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3$,³⁴ $\text{Mo}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3$,¹³ $\text{W}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3$,³⁴ $\text{Re}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_3$,²¹ and $\text{Re}(\text{S}_2\text{C}_7\text{H}_6)_3$.²¹ The striking feature of the epr of all of these complexes is the extremely small observed g tensor anisotropy. This observation is readily understood if each of the forementioned complexes is close to the trigonal-prismatic limit. In that case the trigonal g value equations reduce to

(33) B. B. Garrett, K. DeArmond, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965).

(34) J. H. Waters, R. William, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Amer. Chem. Soc.*, **86**, 4198 (1964).

$$g_{\parallel} = g_e$$

$$g_{\perp} = g_e - 6\lambda\alpha^2\beta^2/\Delta E_b$$

We note first that the contribution of the lower lying e_a level is no longer present since this level is now d_{xy}, x^2-y^2 and is therefore composed entirely of d_{+2} and d_{-2} which do not contribute to g through mixing by the spin-orbit coupling. Furthermore, ΔE_b is expected to be quite large in trigonal-prismatic complexes²¹ and α and β , representing covalency, are each expected to be considerably less than one. These factors may combine to make g quite close to g_e and thus produce the observed small anisotropy in g . These arguments rest of course upon the assumption that the ground state in all these complexes is 2A_1 . This is not an unreasonable conclusion and in fact seems to be the only way to fully understand the epr data. For the V complexes this requires a reversal of metal and ligand levels in going from the dianionic to the neutral species. In other words, the dianion has a roughly 1^2d^1 configuration while the neutral complex has a roughly d^{10} configuration. This type of reversal does not seem unusual as increasing positive charge will often stabilize metal levels more than ligand levels (*i.e.*, the metal will always bear a larger part of the net positive charge no matter where the electrons are removed from). Thus, the smallness of the g anisotropy is evident. More detailed descriptions of the bonding parameters for these complexes would require unequivocal assignments for A_{\parallel} and A_{\perp} values in each case. Furthermore, contribution to g from spin-orbit coupling on the ligands should be considered to understand the small g shifts in each case.

Finally, it is tempting to offer the measurement of g_{\perp} as a probe for the details of the six-coordinate polyhedron in these and related structures. Thus, should alternate and accurate ways for estimating α , β , λ , and $\langle 1/r^3 \rangle$ become avail-

able (either from experiment or theory) then g_{\perp} could represent a sensitive probe for the value of a^2 and hence for the degree of compression and twisting in trigonal tris(chelate) complexes.³⁵

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Registry No. [(C₆H₅)₄As]₂Mo(mnt)₃, 25595-41-9; [(C₆H₅)₄As]₂V(mnt)₃, 12114-37-3.

(35) After we submitted the current article, a paper appeared reporting a similar study [N. M. Atherton and C. J. Winscom, *Inorg. Chem.*, **12**, 283 (1973)]. These workers describe a single crystal study of [(C₆H₅)₄P]₂V(mnt)₃ doped in [(C₆H₅)₄P]₂Mo(mnt)₃. When averaged to axial symmetry, the g and A values found in their study agree well with ours. The small rhombic anisotropy of g and A which they resolve could be due to lower effective symmetry in their host lattice which was said to be monoclinic. Since the structure of the host is unknown in their case, the identification of g and A tensor components with molecular directions can only be tentative. In point of fact these authors seem unaware of the previous communication¹⁰ of the structure of [(C₆H₅)₄As]₂Mo(mnt)₃, the host which we used in the present study. In view of the probable similarity of structure of the two host lattices, it would seem that the V(mnt)₃²⁻ anion should occupy similar sites in both cases. In that case V(mnt)₃²⁻ should have approximate D_3 symmetry with a small rhombic asymmetry. Thus the assumption by Atherton and Winscom of D_{3h} symmetry for the initial calculations on V(mnt)₃²⁻ is at odds with the known structures of both V(mnt)₃²⁻ itself⁹ and the host, Mo(mnt)₃²⁻.¹⁰ This invalid assumption is not mitigated by the subsequent distortion to C_2 symmetry which does not recognize the true nature of the "in between" structures¹⁶ which these compounds adopt. In particular, the e_a-e_b mixing, which we fully discuss in the text, is not considered by Atherton and Winscom. Thus, while the experimental results are in gross agreement in the two studies, the interpretations differ markedly, due to the diverse assumptions of geometric and hence electronic structural parameters.

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A Crystal Field Approach To Pentagonal-Bipyramidal Seven-Coordinate Complexes. Electronic Structure of Heptacyanovanadate(III)

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Crystal field parameters for seven-coordinate pentagonal-bipyramidal complexes have been calculated using a point charge model. These are related to parameters dependent upon energy differences between adjacent metal orbitals. A comparison of the several sets of parameters is made for trigonal- and pentagonal-bipyramidal geometries. The electronic spectrum of the V(CN)₇⁴⁻ ion (symmetry D_{5h}) is interpreted within the context of a strong crystalline field. General trends for the spectra of seven-coordinate D_{5h} complexes are predicted and discussed.

Introduction

A single-crystal X-ray diffraction study of potassium heptacyanovanadate(III) dihydrate, K₄V(CN)₇·2H₂O, has shown the V(CN)₇⁴⁻ complex ion to be seven-coordinate with a pentagonal-bipyramidal structure (D_{5h} symmetry).¹ In addition, interest in seven-coordination has manifested itself in the recent appearance of many X-ray crystallographic studies² on compounds with this relatively neglected

coordination number. While the geometry of many of these has proven to be that of a capped octahedron (C_{3v} symmetry), the most regular of the possible geometries³ is pentagonal bipyramidal. For these reasons, and in anticipation of more heptacoordinate transition metal complexes of symmetry D_{5h} , a consideration of the electronic structure of pentagonal-bipyramidal complexes has been undertaken. The primary focus here will be on the V(CN)₇⁴⁻

(1) R. L. R. Towns and R. A. Levenson, *J. Amer. Chem. Soc.*, **94**, 4345 (1972).

(2) M. G. B. Drew, J. D. Wilkins, and A. P. Wolters, *J. Chem. Soc., Chem. Commun.*, 1278 (1972), and references cited therein.

(3) See E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967), for a description of possible seven-coordinate geometries.