Table IV. Values for the Angles (θ) the Distances (r)[a] and the Calculated Geometric Factors for a Dodecahedral Ethylenediamine-Lanthanide Complex[b]

NH proton	θ, deg	r, Å	$10^3(3\cos^2\theta - 1)/r^3$	CH proton	θ, deg	r, Å	$10^3(3\cos^2\theta - 1)/r^3$
1	35	3.2	+30.91	1	70	3.8	−11.83
2	40	3.2	+23.22	2	66	4.7	−5.32
3	128	3.2	+4.18	3	93	3.6	−21.24
4	120	3.2	−7.63	4	93	4.5	−10.87
Av			+12.67				−12.32

[a] The metal-nitrogen distance is assumed to be 2.8 Å. Variations of ±0.5 Å do not significantly affect the ratio of the NH_2 to CH_2 proton shifts. [b] The plane determined by the metal ion and both nitrogens of the ethylenediamine contains the principal molecular axis.[23]

Thus it appears that for the ethylenediamine complexes of the lanthanide ions in acetonitrile solution a contact mechanism is the dominant factor in the proton shifts of the lighter members of the series, cerium-dysprosium, while a pseudocontact mechanism predominates in the heavy members of the series, holmium-ytterbium. A pseudocontact shift is apparently present for the lighter lanthanides as reflected by the $\Delta H_0/g_L(g_L - 1)J(J + 1)$ ratios for the NH_2 protons; however, the magnitude of this shift is not sufficient to distort the sinusoidal curve obtained for the CH_2 proton shifts as a function of atomic number (Figure 2). The apparent increase in the magnitude of the pseudocontact shift at holmium may result from the lanthanide contraction. The effect of the contraction is twofold. It could cause a distortion of the geometry in such a manner as to increase the anisotropy of the g tensor giving rise to a larger pseudocontact shift for the heavier and smaller members of the lanthanide series. In addition the geometric factor could be significantly altered due to a change in coordination geometry. For example, ethylenediamine may preferentially span sites in the square face of a square antiprism for the lighter lanthanides producing pseudocontact shifts of the same sign for the NH_2 and CH_2 protons. As the radii of the ions get smaller, the preferred coordination geometry could change such that the ethylenediamine molecule spans two sites in a triangular face (Table III). Of course several other geometrical possibilities exist which could cause such a change as a function of ionic radii.

Registry No. $[Ce(en)_4](ClO_4)_3$, 37523-48-1; $[Pr(en)_4](ClO_4)_3$, 22622-15-7; $[Nd(en)_4](ClO_4)_3$, 22622-16-8; $[Sm(en)_4](ClO_4)_3$, 37448-65-0; $[Eu(en)_4](ClO_4)_3$, 37474-08-1; $[Gd(en)_4](ClO_4)_3$, 37448-63-8; $[Tb(en)_4](ClO_4)_3$, 37474-06-9; $[Dy(en)_4](ClO_4)_3$, 37474-05-8; $[Ho(en)_4](ClO_4)_3$, 37474-04-7; $[Er(en)_4](ClO_4)_3$, 37448-99-0; $[Tm(en)_4](ClO_4)_3$, 37448-59-2; $[Yb(en)_4](ClO_4)_3$, 37474-02-5.

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Electron Spin Resonance and Electronic Structures of Vanadyl Bis(maleonitriledithiolene) and Vanadium Tris(maleonitriledithiolene)

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The electron spin resonance spectra of magnetically dilute vanadyl bis(maleonitriledithiolene) and of vanadium tris(maleonitriledithiolene) oriented in single crystals of diamagnetic hosts have been analyzed. The data are interpreted in terms of molecular orbital descriptions of the electronic structures of the complexes. A reassignment of the ground state of vanadium tris(maleonitriledithiolene) is proposed.

Introduction

Recently, there has been considerable interest in complexes in which a transition metal is coordinated by sulfur.[1] Insofar as the complexes exhibit low-energy d-d transitions, the thioorganic chelating groups can be classified as "weak field" ligands in the crystal field sense. On the other hand, the complexes are often very stable and can undergo a series of one-electron-transfer reactions. Two models have been proposed to explain the properties. Gray and his collaborators[2] preferred a more ionic model in which a metal cation stabilizes a sulfur ligand radical system, while Davison and his collaborators[3] have suggested extensive mixing between the metal d orbitals and the ligand π system. It is clearly of interest to probe the electronic structures of these complexes in more detail. Apart from the interest from the viewpoint of inorganic chemistry, there is the possibility that coordination of transition metals by sulfur may be important in systems of biological significance, for example, in non-heme iron proteins.

Complexes which have doublet ground states are particularly amenable to study by electron spin resonance, (esr), although the assignment of a ground state on the basis of esr data may not be a trivial operation, particularly if there is a high degree of covalent bonding. In the great majority of cases studied the esr data have been obtained from samples in fluid solutions and in rigid glasses and in the latter situation often indicate axial symmetry in the complex, although the true symmetry is strictly lower. It seemed desirable to study the anisotropies in more detail, and in this paper we present data for two oriented complexes, vanadyl bis(maleonitriledithiolene), $VO(mnt)_2^{2-}$, and vanadium tris(maleonitriledithiolene), $V(mnt)_3^{2-}$. The anisotropies of the g ten-

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(1) J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).

(2) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, 86, 4594 (1964).

(3) A. Davison, N. Edelstein, and R. H. Holm, *J. Amer. Chem. Soc.*, 85, 3049 (1963).

Table I

(a) Principal Values and Axes for the g and ^{51}V Hyperfine Tensors for $VO(mnt)_2(MeP(Ph)_3)_2$ in $TiO(C_2O_4)_2(MePPh_3)_2$

	X	Y	Z
$g_1 = 1.9809$	0.8971	0.2300	0.3772
$g_2 = 1.9877$	0.0236	−0.8775	0.4791
$g_3 = 1.9455$	−0.4412	0.4209	0.7926
$A_1 = 48.1 \times 10^{-4}$ cm^{-1}	0.8983	0.3180	0.3033
$A_2 = 38.1 \times 10^{-4}$ cm^{-1}	0.1258	−0.8474	0.5159
$A_3 = 145.1 \times 10^{-4}$ cm^{-1}	−0.4210	0.4252	0.8012

(b) The g and ^{51}V Hyperfine Values of $VO(mnt)_2(MeP(Ph)_3)_2$ in Solution and Frozen Glass

		Solvent	Temp, °K
$\langle g \rangle = 1.9840 \pm 0.0005$	$\langle A \rangle = (71.6 \pm 0.5) \times 10^{-4}$ cm^{-1}	$CHCl_3$	~300
$g_\perp = 1.986 \pm 0.001$	$A_\perp = (43 \pm 3) \times 10^{-4}$ cm^{-1}	1:1 CH_2Cl_2-DMF	~140
$g_\parallel = 1.973 \pm 0.001$	$A_\parallel = (135 \pm 3) \times 10^{-4}$ cm^{-1}		

sors and the metal hyperfine splittings are determined and discussed using molecular orbital (MO) theory.

Experimental Section

Triphenylmethylphosphonium titanyl oxalate, $TiO(C_2O_4)_2(CH_3P(C_6H_5)_3)_2$, was found to be a suitable host for $VO(mnt)_2^{2-}$. Initially we had hoped to use $TiO(mnt)_2(MePPh_3)_2$, but this proved too unstable and in any case had not been prepared when we started this work. Solutions of $TiO(C_2O_4)_2(MePPh_3)_2$ containing up to 3 mol % of $VO(mnt)_2$ were evaporated fairly fast by passing a stream of nitrogen over them. The vanadyl complex appeared to decompose when attempts were made to grow crystals more slowly. The method used gave crystals which did not have well-defined faces, but they showed weak extinctions under a polarizing microscope and the esr measurements showed that they were indeed single crystals. In the final stages of the evaporation the crystals generally formed a surface film of the vanadyl complex; this was always removed before esr spectra were recorded.

$V(mnt)_3^{2-}$ was incorporated into single crystals of its molybdenum homolog by the following procedure. $Mo(mnt)_3(PPh_4)_2$ (0.70 g) and $V(mnt)_3(PPh_4)_2$ (0.04 g) were dissolved in 20 ml of acetone, and the solution was filtered. Ethanol (15 ml) was added, and after a few minutes crystals began to form. At this stage acetone (10 ml) was added, and the solution was heated to boiling and then allowed to stand for up to 5 days at 0°. The well-formed crystals obtained were filtered off, washed with ethanol and then ether, and dried in air.

Room-temperature esr spectra were recorded at 10° intervals during rotation about three perpendicular axes. The crystals were mounted on a two-circle goniometer made of Teflon, similar to that described by Roberts and Derbyshire.[4] A Varian X-band spectrometer with 100-kHz magnetic field modulation was used. The magnetic field was calibrated with a Varian F-8 Fluxmeter in conjunction with an Advance TC1A 1-MHz frequency counter and TCD 40 frequency divider. Diphenylpicrylhydrazyl ($g = 2.0036$) was used as a g marker.

The esr spectra of the vanadyl complex were also remeasured for solutions, at room temperature in chloroform, and at 140°K in a one-to-one mixture of methylene chloride and dimethylformamide. The results are included in Table I. Analogous data for the vanadium compound, obtained by Davison *et al.*,[5] are included in Table II.

Results

Spectra were analyzed having the usual spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} \tag{1}$$

where we have omitted a quadrupole coupling term which is expected to be small, shifting line positions by considerably less than the line widths. The orientation dependence of the spectrum of a system described by this Hamiltonian with axially symmetric and parallel g and hyperfine tensors has long been known. Bleaney's treatment[6] can be extended to include the case having tensors of orthorhombic symmetry. The result correct to second order in perturbation theory, for $S = {}^1/_2$, is that the line positions are given by

$$H_0 = H_{m_I} + Km_I + \left\{ \frac{g_z^2A_z^2g_B^2B^2}{g_K^2K^2} + \frac{g_x^2A_x^2g_yA_y^2}{g_B^2B^2} - \frac{g_z^2A_z^2(g_K^2K^2 - g_B^2B^2)(g_B^2B^2 - g_x^2A_x^2)(g_B^2B^2 - g_y^2A_y^2)}{g_K^2K^2g_B^2B^2(g_z^2A_z^2 - g_B^2B^2)} \right\} \times \left\{ \frac{I(I+1) - m_I^2}{4g_K^2H_0} \right\} + \left\{ \frac{(g_z^2A_z^2 - g_K^2K^2) \times (g_K^2K^2 - g_B^2B^2)}{g_K^2K^2} - \frac{(g_z^2A_z^2 - g_K^2K^2)(g_B^2B^2 - g_x^2A_x^2)(g_B^2B^2 - g_y^2A_y^2)}{g_K^2K^2(g_z^2A_z^2 - g_B^2B^2)} \right\} \times \left\{ \frac{m_I^2}{2g_K^2H_0} \right\} \tag{2}$$

where H_0, H_{m_I}, K, B, A_x, A_y, and A_z are in units of magnetic field. H_0 is defined by

$$h\nu = g_K \beta H_0 \tag{3}$$

for a Klystron frequency, ν, and H_{m_I} is the resonance field of the m_Ith hyperfine line. Also

$$B = \left\{ A_x^2 g_x^4 \cos^2 \phi + A_y^2 g_y^4 \sin^2 \phi \right\}^{1/2} / g_B^2 \tag{4}$$

$$K = \left\{ B^2 g_B^4 \sin^2 \theta + A_z^2 g_z^4 \cos^2 \theta \right\}^{1/2} / g_K^2$$

$$g_B = \left\{ g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi \right\}^{1/2}$$

$$g_K = \left\{ g_B^2 \sin^2 \theta + g_z^2 \cos^2 \theta \right\}^{1/2}$$

with A_i, g_j the principal elements of the tensors and θ and ϕ the usual polar angles.

Equation 2 reduces to Bleaney's expression,[6] omitting quadrupole and fine-structure terms, when axial symmetry is admitted, *i.e.*, $A_x = A_y$ and $g_x = g_y$, and when the appropriate conversion from units of magnetic field to units of energy is made. Other workers[7] have derived more complete expressions for the nonaxial case and their results reduce to ours for $S = {}^1/_2$.

Equation 2 without the small correction terms was used to obtain first-order approximation of the g^2 tensor elements, whereas elements of the K^2 tensor could be obtained without approximation. The resulting first-order principal values and directions of the g tensor were then used to compute the small correction terms in the complete form of eq 2 for each orientation. Refined principal values and directions of the g tensor were obtained and the cycle was repeated until further changes were outside the limit of experimental error.

The crystals containing $VO(mnt)_2^{2-}$ did not have well-defined external faces and only showed weak extinction under the polarizing microscope. Accordingly, measurements were referred to a completely arbitrary set of axes; using the two-circle goniometer automatically ensures that these axes are orthogonal. The crystals showed spectra from two sites, but only one of these was analyzed. There was never any difficulty in tracking the chosen site. Results for the tensors are shown in Table I.

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(4) G. Roberts and W. Derbyshire, *J. Sci. Instrum.*, **38**, 511 (1961).

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

(6) B. Bleaney, *Phil. Mag.*, **42**, 441 (1951).

(7) G. H. Azarbayejani, *Phys. Lett. A*, **25**, 767 (1967); R. M. Golding, "Applied Wave Mechanics," Van Nostrand, London, 1969, Appendix 6.

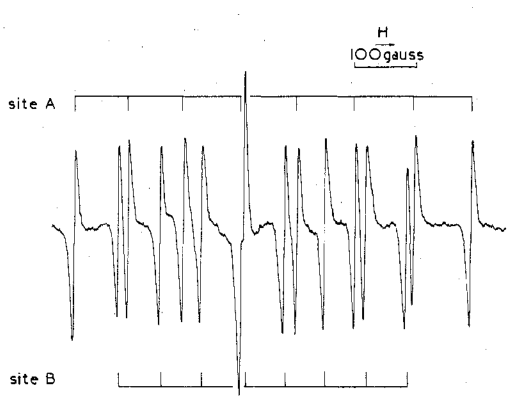

Figure 1. The epr spectrum of $V(mnt)_3(PPh_4)_2$ in a $Mo(mnt)_3(PPh_4)_2$ host lattice. Rotation about the *b* axis (*XZ* plane) is 20° from *X*.

Table II

(a) Principal Values and Axes for the *g* and ^{51}V Hyperfine Tensors for $V(mnt)_3(PPh_4)_2$ in $Mo(mnt)_3(PPh_4)_2$

		X	*Y*	*Z*
Site a	$g_1 = 1.9746$	1.000	0.0	0.0
	$g_2 = 1.9896$	0.0	0.8985	−0.4390
	$g_3 = 1.9769$	0.0	0.4390	0.8985
	$A_1 = 75.2 \times 10^{-4}\ cm^{-1}$	0.9931	0.0354	−0.1118
	$A_2 = 10.2 \times 10^{-4}\ cm^{-1}$	−0.0815	0.8940	−0.4406
	$A_3 = 91.3 \times 10^{-4}\ cm^{-1}$	0.0844	0.4467	0.8907
Site b	$g_1 = 1.9745$	1.000	0.0	0.0
	$g_2 = 1.9898$	0.0	0.8956	0.4448
	$g_3 = 1.9768$	0.0	−0.4448	0.8956
	$A_1 = 75.2 \times 10^{-4}\ cm^{-1}$	0.9919	0.0386	0.1210
	$A_2 = 8.6 \times 10^{-4}\ cm^{-1}$	0.0888	0.8922	0.4429
	$A_3 = 91.7 \times 10^{-4}\ cm^{-1}$	0.0908	−0.4501	0.8884

(b) The *g* and ^{51}V Hyperfine Values for $V(mnt)_3^{2-}$ in Solution and Frozen Glass[a]

		Solvent	Temp, °K
$\langle g \rangle = 1.980 \pm 0.001$	$\langle A \rangle = 58.6 \pm 0.5 \times 10^{-4}\ cm^{-1}$	1:1 $CHCl_3$-DMF	~300
$g_1 = 1.974 \pm 0.005$	$A_1 = 92 \pm 2 \times 10^{-4}\ cm^{-1}$	1:1 $CHCl_3$-DMF	~100

[a] Results taken from ref 5.

The symmetry behavior of the spectra of the crystals containing $V(mnt)_3^{2-}$ was consistent with monoclinic symmetry: in a general orientation there was a twofold site splitting while for one plane and the plane perpendicular to that plane the site splitting vanished. Thus there was no difficulty in identifying the *b* axis, the unique axis. The other two reference axes were chosen to coincide with external features of the crystals, though it was not clear whether these were *a* and *c** or *a** and *c*. We refer to our reference axes as *X*, *Y*, and *Z*, with $Y \equiv b$. A spectrum with the magnetic field lying in a plane perpendicular to *b* is shown in Figure 1. The analysis of the spectra was straightforward, and the results are shown in Table II.

Theory

Metal-Dithiolene Complexes. To attempt an interpretation we limit the model to the interaction of the valence orbitals of the metal (3d, 4s, 4p) with (a) the π system of the S_2C_2 fragment and (b) the 3s and 3p hybrids of sulfur in the S_2C_2 plane available for overlap with the metal. In each S_2C_2 system there are two hybrids (σ_s) directed toward the metal atom and two (n_s) pointing away from the metal. The π system comprises two π and two π^* orbitals, all of which are considered higher in energy than the σ_s and n_s orbitals. Each

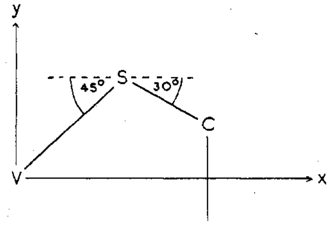

Figure 2. The axis system for construction of hybrid orbitals about S_1.

neutral S_2C_2 fragment, considering only these orbitals, contributes a total of 12 electrons.

To assess the effects of metal-ligand covalency from the spin-Hamiltonian parameters it is useful to have some estimate of the various coefficients in the orbitals of the 'non-interacting' dithiolene fragment. The coefficients of the in-plane hybrids are determined by (a) the geometry of the M-S-C bonding, (b) assuming that the third hybrid lying along the S-C bond has exact sp^2 character, and (c) orthonormality conditions. The orthonormal hybrids about S_1 referred to the axis system in Figure 2 are

$$\begin{aligned} n_1 &= C_n|3s\rangle - C_n'|3p_x\rangle + C_n''|3p_y\rangle \\ \sigma_1 &= C_\sigma|3s\rangle - C_\sigma'|3p_x\rangle - C_\sigma''|3p_y\rangle \end{aligned} \tag{5}$$

where $C_n = 0.7406$, $C_n' = 0.2431$, and $C_n'' = 0.6264$ and $C_\sigma = 0.3437$, $C_\sigma' = 0.6640$, and $C_\sigma'' = 0.6640$.

The π- and π^*-orbital coefficients are estimated from a Huckel calculation. The diagonal terms for $S(3p_z)$ and $C(2p_z)$[8] were −94.0 and −86.0 respectively, and the off-diagonal S_1C_1 and C_1C_2 elements were estimated[9] as 10.06 and 24.13, respectively, in units of $10^3\ cm^{-1}$. The coefficients and energies are given below.

	$S_1(3p_z)$	$C_1(2p_z)$	$C_2(2p_z)$	$S_2(3p_z)$	Energy × 10^{-3}, cm^{-1}
π^*	0.1952	−0.6796	0.6796	−0.1952	−59.0
π^*	0.6375	−0.3060	−0.3060	0.6375	−89.0
π	0.6796	0.1952	−0.1952	−0.6796	−96.9
π	0.3060	0.6375	0.6375	0.3060	−115.0

The Vanadyl Complex. We follow the standard procedure[10] by forming molecular orbitals through overlap of the metal 3d orbitals with appropriate symmetry-adapted ligand orbitals. It is useful to have a qualitative level scheme and we refer to that shown in Figure 3 derived from the following arguments.

The complex has C_{2v} point group symmetry. Symmetry-adapted combinations of the in-plane hybrids and out-of-plane π, π^* orbitals on both dithiolene ligands are formed. In order of increasing energy the π orbitals are arranged as four pairs of degenerate levels a_1b_1, a_2b_2, $a_1^*b_1^*$, $a_2^*b_2^*$. The metal d orbitals are placed between the $a_1^*b_1^*$ and $a_2^*b_2^*$ levels and since they retain predominantly metal d character,[11] they are assumed to have the same ordering as predicted by crystal field (CF) theory. The oxygen $2p_x$, p_y (b_1, b_2) orbitals are placed between the a_1b_1 and a_2b_2 pairs of the dithiolene π system. The s-p hybrid orbitals on the oxygen and sulfur atoms are placed lower in energy than the dithiolene π system.

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(8) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964.

(9) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(10) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31, 35 (1958).

(11) N. M. Atherton, J. Locke, and J. A. McCleverty, *Chem. Ind. (London)*, 1300 (1965).

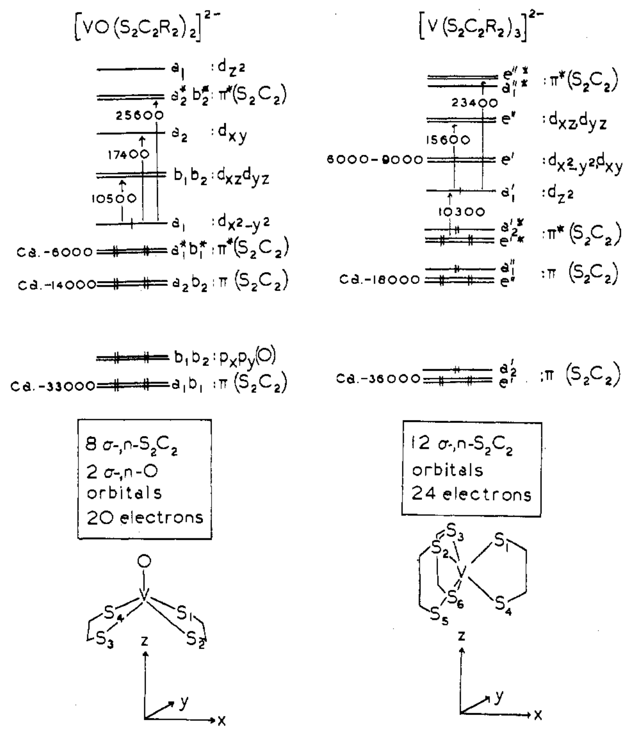

Figure 3. The energy level diagrams for the vanadyl bis(dithiolene) and vanadium tris(dithiolene) dianions.

In this framework $VO(S_2C_2R_2)_2{}^{2-}$ is a 37-electron system and has a $(a_1{}^*)^2(b_1{}^*)^2(d_{x^2-y^2})^1$ ground-state configuration.

The important one-electron MO's are

$$
\begin{aligned}
|a_1'\rangle &= \gamma[c_1|d_{z^2}\rangle - c_2|d_{x^2-y^2}\rangle] - \gamma'|\sigma_{A1}(O)\rangle - \gamma''|\sigma_{A1}(S)\rangle \\
|a_2\rangle &= \alpha_2|d_{xy}\rangle - \alpha_2'|\sigma_{A2}(S)\rangle \\
|b_1\rangle &= \beta_1|d_{xz}\rangle - \beta_1'|2p_x(O)\rangle - \beta_1''|\pi^*{}_{B1}(S)\rangle \\
|b_2\rangle &= \beta_2|d_{yz}\rangle - \beta_2'|2p_y(O)\rangle - \beta_2''|\pi_{B2}(S)\rangle \\
|a_1\rangle &= \alpha_1[c_1|d_{x^2-y^2}\rangle + c_2|d_{z^2}\rangle + c_s|4s\rangle] - \alpha_1'|n_{A1}(S)\rangle
\end{aligned}
\tag{6}
$$

in descending order of energy.

Configuration interaction of the $a_1(d_{x^2-y^2})^1$ ground state with the excited state $a_1(d_{z^2})^1$ allows admixture of d_{z^2} into the ground level. For similar reasons a much smaller but direct admixture of 4s must also be considered. We define $c_1{}^2 + c_2{}^2 \simeq 1$ and $c_s{}^2 \ll 1$.

The important symmetry-adapted basis orbitals for the ligands are

$$
\begin{aligned}
|n_{A1}(S)\rangle &= \frac{c_n}{2}(s_1 + s_2 + s_3 + s_4) + \frac{c_n'}{2}(-x_1 - x_2 + x_3 + x_4) + \frac{c_n''}{2}(y_1 - y_2 - y_3 + y_4) \\
|\sigma_{A2}(S)\rangle &= \frac{c_\sigma}{2}(s_1 - s_2 + s_3 - s_4) + \frac{c_\sigma'}{2}(-x_1 + x_2 + x_3 - x_4) + \frac{c_\sigma''}{2}(-y_1 - y_2 + y_3 + y_4) \\
|\pi^*{}_{B1}(S)\rangle &= \frac{c_{\pi_1}}{2}(z_1 + z_2 - z_3 - z_4) + \frac{c_{\pi_1}'}{2}(\pi_1 + \pi_2 - \pi_3 - \pi_4) \\
|\pi_{B2}(S)\rangle &= \frac{c_{\pi_2}}{2}(z_1 - z_2 - z_3 + z_4) + \frac{c_{\pi_2}}{2}(\pi_1 - \pi_2 - \pi_3 + \pi_4)
\end{aligned}
\tag{7}
$$

z and π refer to $3p_z(S)$ and $2p_z(C)$, respectively.

The two dithiolene systems are not expected to be exactly coplanar; the vanadium atom would be raised relative to the basal plane of the four sulfur atoms. This would result in the presence of a small component of $\pi_{a_1}{}^*(S)$ in the a_1 ground level. We assume that the admixture coefficient would be much less than α_1' and neglect it. Estimates of the various coefficients C_n, etc., have already been made in (5).

In seeking expressions for the spin-Hamiltonian parameters we shall restrict ourselves to contributions from spin densities on atoms within the first coordination sphere and in the first instance (see Discussion) excited states involving the levels between $a_1{}^*b_1{}^*$ and $a_2{}^*b_2{}^*$. We neglect cross terms involving metal-ligand overlap,[12] orbital angular momentum contributions from s orbitals on different centers,[13] *g*-shift contributions from spin density on centers whose spin-orbit coupling constant is less than that of vanadium, and overlap terms in normalization relations, *i.e.*, $\alpha_1{}^2 + \alpha_1'{}^2 = 1$.

The *g* values now become

$$g_i = g_e + \Delta g_i \quad (i = x, y, z;\ g_e = 2.0023) \tag{8}$$

where

$$
\begin{aligned}
\Delta g_x &= -2\langle a_1|L_x|b_2\rangle\langle b_2|\lambda(r)L_x|a_1\rangle(\Delta E_{yz})^{-1} = \\
&\quad \frac{-2}{\Delta E_{yz}}[(c_1{}^2 + 2\sqrt{3}c_1c_2 + 3c_2{}^2)\alpha_1{}^2\beta_2{}^2\lambda_v - (c_1 + \sqrt{3}c_2)\alpha_1\alpha_1'\beta_2\beta_2'c_n''c_{\pi_2}(\lambda_v + \lambda_s) + \alpha_1'^2\beta_2'^2c_n''^2 \times c_{\pi_2}{}^2\lambda_s] \\
\Delta g_y &= -2\langle a_1|L_y|b_1\rangle\langle b_1|\lambda(r)L_y|a_1\rangle(\Delta E_{xz})^{-1} = \frac{-2}{\Delta E_{xz}} \times \\
&\quad [(c_1{}^2 - 2\sqrt{3}c_1c_2 + 3c_2{}^2)\alpha_1{}^2\beta_1{}^2\lambda_v - (c_1 - 3c_2)\alpha_1 \times \alpha_1'\beta_1\beta_1'c_n'c_{\pi_1}(\lambda_v + \lambda_s) + \alpha_1'^2\beta_1'^2c_n'^2c_{\pi_1}{}^2\lambda_s] \\
\Delta g_z &= -2\langle a_1|L_z|a_2\rangle\langle a_2|\lambda(r)L_z|a_1\rangle(\Delta E_{xy})^{-1} = \frac{-2}{E_{xy}}[4c_1{}^2 \times \\
&\quad \alpha_1{}^2\alpha_2{}^2\lambda_v + 2c_1\alpha_1\alpha_1'\alpha_2\alpha_2'(c_\sigma'c_n'' + c_n'c_\sigma'')(\lambda_v + \lambda_s) + \alpha_1'^2\alpha_2'^2(c_\sigma'c_n'' + c_n'c_\sigma'')^2\lambda_s]
\end{aligned}
\tag{9}
$$

where ΔE_{yz}, etc., refer to the energy differences between the states in question, and λ_v, λ_s are the spin-orbit coupling constants for vanadium and sulfur, respectively. In general, Δg_x, for example, will be the sum of many terms similar to that derived, each one corresponding to some level containing d_{yz}. The sign of each contribution depends upon whether the level lies above (negative) or below (positive) the ground level.

The principal metal hyperfine values are given by

$$A_i = A_{iso} + a_i \quad (i = x, y, z) \tag{10}$$

where

$$
\begin{aligned}
A_{iso} &= -P\kappa\alpha_1{}^2 + \tfrac{1}{3}P(\Delta g_x + \Delta g_y + \Delta g_z) + A_{4s}\alpha_1{}^2c_s{}^2 \\
a_x &= -P[\tfrac{2}{7}\alpha_1{}^2(-c_1{}^2 + 2\sqrt{3}c_1c_2 + c_2{}^2) - \tfrac{2}{3}\Delta g_x + \tfrac{1}{3}\Delta g_y + \tfrac{1}{3}\Delta g_z - \tfrac{2}{7}u_{xx}] \\
a_y &= -P[\tfrac{2}{7}\alpha_1{}^2(-c_1{}^2 - 2\sqrt{3}c_1c_2 + c_2{}^2) - \tfrac{2}{3}\Delta g_y + \tfrac{1}{3}\Delta g_z + \tfrac{1}{3}\Delta g_x - \tfrac{2}{7}u_{yy}] \\
a_z &= -P[\tfrac{2}{7}\alpha_1{}^2(2c_1{}^2 - 2c_2{}^2) - \tfrac{2}{3}\Delta g_z + \tfrac{1}{3}\Delta g_x + \tfrac{1}{3}\Delta g_y - \tfrac{2}{7}u_{zz}]
\end{aligned}
\tag{11}
$$

in the usual notation following Abragam and Pryce[14] where

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(12) R. Lacroix and G. Emch, *Helv. Phys. Acta*, 35, 592 (1962).

(13) A. J. Stone, *Proc. Roy. Soc., Ser. A*, 271, 424 (1963).

$$u_{xx} = +[\frac{\sqrt{3}}{4}\frac{c_2}{c_1} + \cdots]\Delta g_z - [\frac{3}{4} + \sqrt{3}\frac{c_2}{c_1} + \cdots]\Delta g_y$$

$$u_{yy} = -[\frac{3}{4}\frac{c_2}{c_1} + \cdots]\Delta g_z - [\frac{3}{4} - \sqrt{3}\frac{c_2}{c_1} + \cdots]\Delta g_x \qquad (12)$$

$$u_{zz} = +[\frac{3}{4} - \sqrt{3}\frac{c_2}{c_1} + \cdots]\Delta g_x + [\frac{3}{4} + \sqrt{3}\frac{c_2}{c_1} + \cdots]\Delta g_y$$

Several smaller additional terms whose magnitude would be within experimental error of measurement are omitted.

The Vanadium Tris Complex. We adopt a similar procedure to that of the vanadyl complex in the case of the vanadium tris complex. The structure of the complex has been shown to have distorted D_{3h} symmetry (Figure 4).[15] One C_2 axis (x), about which ligands 2 and 3 twist to form a propeller arrangement, is retained.

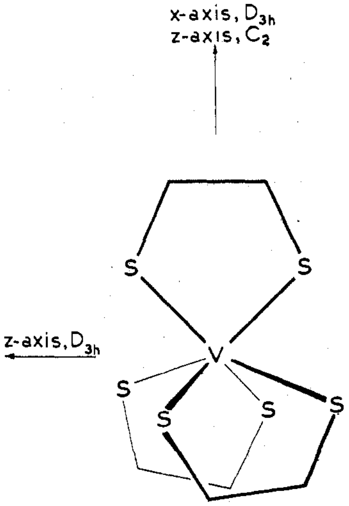

Figure 4. The structure of the vanadium tris(dithiolene) dianion.

The π orbitals of the three S_2C_2 fragments form four triply degenerate levels—$a_2'e'$, $a_1''e''$, $a_2'^*e'^*$, and $a_1''^*e''^*$—in order of ascending energy. The metal d orbitals are assumed to lie between the $a_2'^*e'^*$ and $a_1''^*e''^*$ levels; their ordering being that predicted by CF theory. As in the vanadyl complex the σ(S) and n(S) orbitals are placed lower in energy than the π orbitals. The complex is treated as a 43-electron system in which the ground state is $(a_2'^*)^2(e'^*)^4(d_{z^2})^1$.

Departure from the D_{3h} point group symmetry in the manner described allows admixture of d_{yz}, $d_{x^2-y^2}$ with d_{z^2} and this is particularly reflected in the anisotropy of the hyperfine tensor.

Using the axis system shown in Figure 3 the important one-electron MO's are

$$|e_a''\rangle = \alpha_3[c_1|d_{yz}\rangle - c_2|d_{z^2}\rangle] - \alpha_3'|\sigma_{E_a}''\rangle - \alpha_3''|\pi_{E_a}''\rangle$$

$$|e_b''\rangle = \beta_3|d_{xz}\rangle - \beta_3'|\sigma_{E_b}''\rangle - \beta_3''|\pi_{E_b}''\rangle$$

$$|e_a'\rangle = \alpha_2|d_{x^2-y^2}\rangle - \alpha_2'|\sigma_{E_a}'\rangle - \alpha_2''|\pi_{E_a}'\rangle \qquad (13)$$

$$|e_b'\rangle = \beta_2|d_{xy}\rangle - \beta_2'|\sigma_{E_b}'\rangle - \beta_2''|\pi_{E_b}'\rangle$$

$$|a_1'\rangle = [\alpha_1 c_1|d_{z^2}\rangle + c_2|d_{yz}\rangle + c_3|d_{x^2-y^2}\rangle + c_s|4s\rangle] - \alpha_1'|\sigma_{A_1}'\rangle$$

in descending order of energy.

Combinations involving n(S) have been omitted since they have very little overlap with the metal d orbitals. We define $c_1^2 + c_2^2 \simeq 1$ since preliminary investigation shows $c_3 c_s \ll 1$.

The important symmetry-adapted σ and π orbitals of the three dithiolene ligands are

$$|\sigma_{A_1}'\rangle = \frac{c_\sigma}{\sqrt{6}}(s_1 + s_2 + s_3 + s_4 + s_5 + s_6) + \frac{c_\sigma'}{2\sqrt{6}}(-2x_1 + x_2 + x_3 - 2x_4 + x_5 + x_6) + \frac{c_\sigma'}{2\sqrt{2}}(y_2 - y_3 + y_5 - y_6) + \frac{c_\sigma''}{\sqrt{6}}(-z_1 - z_2 - z_3 + z_4 + z_5 + z_6)$$

$$|\sigma_{A_2}'\rangle = \frac{c_\sigma}{\sqrt{6}}(s_1 + s_2 + s_3 - s_4 - s_5 - s_6) + \frac{c_\sigma'}{2\sqrt{6}}(-2x_1 + x_2 + x_3 + 2x_4 - x_5 - x_6) + \frac{c_\sigma'}{2\sqrt{2}}(y_2 - y_3 - y_5 + y_6) + \frac{c_\sigma''}{\sqrt{6}}(-z_1 - z_2 - z_3 - z_4 - z_5 - z_6)$$

$$|\sigma_{E_a}'\rangle = \frac{c_\sigma}{2\sqrt{3}}(2s_1 - s_2 - s_3 + 2s_4 - s_5 - s_6) + \frac{c_\sigma'}{4\sqrt{3}} \times (-4x_1 - x_2 - x_3 - 4x_4 - x_5 - x_6) + \frac{c_\sigma'}{4}(-y_2 + y_3 - y_5 + y_6) + \frac{c_\sigma''}{2\sqrt{3}}(-2z_1 + z_2 + z_3 + 2z_4 - z_5 - z_6)$$

$$|\sigma_{E_b}'\rangle = \frac{c_\sigma}{2}(s_2 - s_3 + s_5 - s_6) + \frac{c_\sigma'}{4}(x_2 - x_3 + x_5 - x_6) + \frac{\sqrt{3}c_\sigma'}{4}(y_2 + y_3 + y_5 + y_6) + \frac{c_\sigma''}{2}(-z_2 + z_3 + z_5 - z_6)$$

$$|\sigma_{E_a}''\rangle = \frac{c_\sigma}{2}(-s_2 + s_3 + s_5 - s_6) + \frac{c_\sigma'}{4}(-x_2 + x_3 + x_5 - x_6) + \frac{\sqrt{3}c_\sigma'}{4}(-y_2 - y_3 + y_5 + y_6) + \frac{c_\sigma''}{2}(z_2 - z_3 + z_5 - z_6)$$

$$|\sigma_{E_b}''\rangle = \frac{c_\sigma}{2\sqrt{3}}(2s_1 - s_2 - s_3 - 2s_4 + s_5 + s_6) + \frac{c_\sigma'}{4\sqrt{3}} \times (-4x_1 - x_2 - x_3 + 4x_4 + x_5 + x_6) + \frac{c_\sigma'}{4}(-y_2 + y_3 + y_5 - y_6) + \frac{c_\sigma''}{2\sqrt{3}}(-2z_1 + z_2 + z_3 + 2z_4 - z_5 - z_6)$$

$$|\pi_{A_1}''\rangle = \frac{c_\pi}{2\sqrt{2}}(x_2 - x_3 - x_5 - x_6) + \frac{c_\pi}{2\sqrt{6}}(2y_1 - y_2 - y_3 - 2y_4 + y_5 + y_6) + \frac{c_\pi'}{\sqrt{6}}(\pi_1 + \pi_2 + \pi_3 - \pi_4 - \pi_5 - \pi_6)$$

$$|\pi_{A_2}'\rangle = \frac{c_\pi}{2\sqrt{2}}(x_2 - x_3 + x_5 - x_6) + \frac{c_\pi}{2\sqrt{6}}(2y_1 - y_2 - y_3 + 2y_4 - y_5 - y_6) + \frac{c_\pi'}{\sqrt{6}}(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5 + \pi_6)$$

$$|\pi_{E_a}'\rangle = \frac{\sqrt{3}c_\pi}{4}(-x_2 - x_3 - x_5 - x_6) + \frac{1}{4}c_\pi(y_2 - y_3 + y_5 - y_6) + \frac{c_\pi'}{2}(-\pi_2 + \pi_3 - \pi_5 + \pi_6)$$

$$|\pi_{E_b}'\rangle = \frac{c_\pi}{4}(-x_2 + x_3 - x_5 + x_6) + \frac{c_\pi}{4\sqrt{3}}(4y_1 + y_2 + y_3 + 4y_4 + y_5 + y_6) + \frac{c_\pi'}{2\sqrt{3}}(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6)$$

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(14) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, 218, 553 (1953).

(15) E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, 89, 3353 (1967).

$$|\pi_{\mathrm{E_a}}{}''\rangle = \frac{1}{4}c_\pi(-x_2 + x_3 + x_5 - x_6) + \frac{1}{4\sqrt{3}}c_\pi(4y_1 + y_2 + y_3 - 4y_4 - y_5 - y_6) + \frac{c_\pi{}'}{2\sqrt{3}}(2\pi_1 - \pi_2 - \pi_3 - 2\pi_4 + \pi_5 + \pi_6)$$

$$|\pi_{\mathrm{E_b}}{}''\rangle = \frac{\sqrt{3}}{4}c_\pi(x_2 + x_3 - x_5 - x_6) + \frac{1}{4}c_\pi(-y_2 + y_3 + y_5 - y_6) + \frac{c_\pi{}'}{2}(\pi_2 - \pi_3 - \pi_5 + \pi_6) \qquad (14)$$

Departure from strict D_{3h} symmetry in the manner described (c_2 axis $\equiv x$ axis in D_{3h}) allows admixture between orbitals having the same irreducible representation in the C_2 point group, *i.e.*

A: $\mathrm{A_1}'$, $\mathrm{A_1}''$, E$'$, E$''$

B: $\mathrm{A_2}'$, $\mathrm{A_2}''$, E$'$, E$''$

We assume such admixture to be small enough to be neglected in the one-electron orbitals used to seek expressions for g shifts and hyperfine splitting (hfs), but we include direct admixture of other d orbitals transforming as the A irreducible representation in C_2 symmetry.

The various coefficients, c_σ, etc., take the same values as in the vanadyl complex and are given explicitly in (5). We adopt the same approximations as for the vanadyl complex in seeking expressions for the principal g and hyperfine values. The g-shift expressions are

$$\Delta g_x = \frac{-2}{\Delta E_{yz}}\left[(3 + 2\sqrt{3}c_1c_3)\alpha_1{}^2\alpha_3{}^2\lambda_\mathrm{v} - \left(\frac{\sqrt{3} + c_1c_3}{\sqrt{2}}\right) \times \alpha_1\alpha_1{}'\alpha_3\alpha_3{}''c_\sigma{}'c_\pi(\lambda_\mathrm{v} + \lambda_\mathrm{s}) + \frac{1}{2}\alpha_1{}'^2\alpha_3{}''^2c_\sigma{}'^2c_\pi{}^2\lambda_\mathrm{s}\right] - \frac{2}{\Delta E_{x^2-y^2}}[c_2{}^2\alpha_1{}^2\alpha_2{}^2\lambda_\mathrm{v}]$$

$$\Delta g_y = \frac{-2}{\Delta E_{xz}}\left[(3c_1{}^2 - 2\sqrt{3}c_1c_3)\alpha_1{}^2\beta_3{}^2\lambda_\mathrm{v} - \left(\frac{\sqrt{3}c_1 - c_3}{2}\right) \times \alpha_1\alpha_1{}'\beta_3\beta_3{}''c_\sigma{}''c_\pi(\lambda_\mathrm{v} + \lambda_\mathrm{s}) + \frac{1}{2}\alpha_1{}'^2\beta_3{}''^2c_\sigma{}''^2c_\pi{}^2\lambda_\mathrm{s}\right] - \frac{2}{\Delta E_{xy}}[c_2{}^2\alpha_1{}^2\beta_2{}^2\lambda_\mathrm{v}] \qquad (15)$$

$$g_z = \frac{-2}{\Delta E_{x^2-y^2}}[4c_3{}^2\alpha_1{}^2\beta_2{}^2\lambda_\mathrm{v}] - \frac{2}{\Delta E_{xz}}[c_2{}^2\alpha_1{}^2\beta_3{}^2\lambda_\mathrm{v}] + \frac{2}{\Delta E_{\mathrm{A_2}'(\pi^*)}}[c_\pi{}^2c_\sigma{}'^2\alpha_1{}'^2\lambda_\mathrm{s}]$$

where the energy differences ΔE_{yz}, etc., are defined with reference to Figure 3 and are also defined as positive.

The isotropic and anisotropic parts of the principal hyperfine values are

$$A_\mathrm{iso} = -P\kappa\alpha_1{}^2 + \frac{1}{3}P(\Delta g_x + \Delta g_y + \Delta g_z) + A_{4\mathrm{s}}\alpha_1{}^2c_\mathrm{s}{}^2$$

$$a_x = -P\left[\frac{2}{7}\alpha_1{}^2(c_1{}^2 + 2c_2{}^2 - c_3{}^2 + 2\sqrt{3}c_1c_3) - \frac{2}{3}\Delta g_x + \frac{1}{3}\Delta g_y + \frac{1}{3}\Delta g_z - \frac{2}{7}u_{xx}\right]$$

$$a_y = -P\left[\frac{2}{7}\alpha_1{}^2(c_1{}^2 - c_2{}^2 - c_3{}^3 - 2\sqrt{3}c_1c_3) - \frac{2}{3}\Delta g_y + \frac{1}{3}\Delta g_z + \frac{1}{3}\Delta g_x - \frac{2}{7}u_{yy}\right] \qquad (16)$$

$$a_z = -P\left[\frac{2}{7}\alpha_1{}^2(-2c_1{}^2 - c_2{}^2 + 2c_3{}^2) - \frac{2}{3}\Delta g_z + \frac{1}{3}\Delta g_x + \frac{1}{3}\Delta g_y - \frac{2}{7}u_{zz}\right]$$

where, after many approximations

$$u_{xx} \simeq \left\{\frac{1}{4} + \frac{1}{\sqrt{3}}\left(\frac{c_3}{c_1}\right) - \frac{1}{2}\left(\frac{c_2}{c_1}\right)\left(\frac{c_3}{c_1}\right)\right\}\Delta g_y - \left\{\frac{\sqrt{3}}{8}\left(\frac{c_1}{c_3}\right)\left(\frac{c_2}{c_3}\right) - \frac{1}{8}\left(\frac{c_2}{c_3}\right)^2\right\}\Delta g_z$$

$$u_{yy} \simeq \left\{\frac{1}{4} - \frac{5\sqrt{3}}{12}c_1c_3 - \frac{1}{2}c_2{}^2\right\}\Delta g_x + \left\{\frac{1}{2}\left(\frac{c_2}{c_1}\right) \times \left(\frac{c_3}{c_1}\right)\right\}\Delta g_y + \left\{\frac{1}{8}\left(\frac{c_2}{c_3}\right)^2 + \frac{\sqrt{3}}{8}\left(\frac{c_1}{c_3}\right)\left(\frac{c_2}{c_3}\right)\right\}\Delta g_z \qquad (17)$$

$$u_{zz} \simeq -\left\{\frac{1}{4} - \frac{5\sqrt{3}}{12}c_1c_3 - \frac{1}{2}c_2{}^2\right\}\Delta g_x - \left\{\frac{1}{4} + \frac{1}{\sqrt{3}}\left(\frac{c_3}{c_1}\right)\right\} \times \Delta g_y - \left\{\frac{1}{4}\left(\frac{c_2}{c_3}\right)^2\right\}\Delta g_z$$

Choice of Parameters. Some discussion regarding the choice of parameter values is required before use can be made of expressions 9-12 and 15-17.

For complexes in which the oxidation state is formally V(IV) and in which delocalization throughout the ligand system might occur, the true occupancy of the metal valence orbitals is expected to be $\mathrm{d^3s^xp^y}$ where $1 \leqslant x + y \leqslant 2$.[16,17] We therefore choose the value λ_v = 160 cm^{-1} [18] consistent with a $\mathrm{d^3s^1}$ or $\mathrm{d^3s^2}$ configuration. The d-orbital wavefunction for configurations d^{n-2} and $\mathrm{d}^{n-2}\mathrm{s}^2$ have been shown to be very similar.[19] We therefore feel justified in using the value $P = 128 \times 10^{-4}$ cm^{-1} [20] calculated from Freeman and Watson's value[21] of $\langle r^{-3}\rangle$ for the configuration $\mathrm{d^3}$. The value of λ_s = 382 cm^{-1} is that given by Morton, *et al.*[22]

The isotropic component of the ^{51}V hyperfine interaction should incorporate three contributions, the largest of these arising from excited-state admixture with the ground state through configuration interaction (the κ term) and direct s admixture into the ground state (the A_s term). Both κ[23] and A_s[5] are expected to be positive so that these terms are in competition. A second-order contribution[14] arising from the joint effect of electron spin-orbit (**L**·**S**) and nuclear spin-orbit (**L**·**I**) terms of the Hamiltonian is included, its sign being dependent on that of the isotropic g shift. The value A_s = 0.15 cm^{-1} has been calculated from an expression[24] modified by Trees[25] for the configuration $\mathrm{d^3s^1}$, using configuration energies. Estimates for the value of κ have been made for vanadium[27-29] in several different environments. We choose the value 0.85 estimated for $\mathrm{VO(H_2O)_5{}^{2+}}$ and $\mathrm{VOCl_5}$[29] where nearly C_{4v} symmetry precludes direct admixture of the 4s orbital into the ground level.

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(16) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962). These authors obtain $\mathrm{3d^{2.9}4s^{0.5}4p^{0.6}}$ for $[\mathrm{VO(H_2O)_5}]^{2+}$.

(17) M. Zerner and M. Gouterman, *Inorg. Chem.*, **5**, 1699 (1966).

(18) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

(19) R. E. Watson, *Phys. Rev.*, **119**, 1934 (1960).

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

(21) A. J. Freeman and R. E. Watson, "Magnetism," Vol. IIA, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1965, p 167.

(22) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Nat. Phys. Lab. (U. K.), Rep.*, No. B.P.R. 13 (1962). See also D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(23) V. Heine, *Phys. Rev.*, **107**, 1002 (1957).

(24) S. Goudschmidt, *Phys. Rev.*, **43**, 636 (1933).

(25) R. Trees, *Phys. Rev.*, **92**, 308 (1953).

(26) C. E. Moore, *Nat. Bur. Stand. (U. S.), Circ.*, No. 467 (1949).

(27) D. E. O'Reilly, *J. Chem. Phys.*, **29**, 1188 (1958).

(28) R. M. Golding, *Mol. Phys.*, **5**, 369 (1962).

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

Table III. Molecular Orbital Coefficients for VO(mnt)$_2^{2-}$ [a]

Orbital	[Metal coeff]^2	[S$_2$C$_2$ σ,n coeff]^2	[S$_2$C$_2$ π,π^* coeff]^2	[O$_{p_xp_y}$ coeff]^2
a$_2$ (d$_{xy}$)	0.75[c]	0.25[c]		
b$_1$ (d$_{xz}$)	0.89		0.06	(0.05)[b]
b$_2$ (d$_{yz}$)	0.90		0.05	
a$_1$ (d$_{x^2-y^2}$)	0.89	0.11		
a$_1$ (π^*)				
b$_1$ (π^*)	0.06		0.94	
a$_2$ (π)				
b$_2$ (π)	0.05		0.95	

[a] Ground level: $|a_1\rangle = 0.934|3d_{x^2-y^2}\rangle + 0.0374|3d_{z^2}\rangle + 0.122 \cdot |4s\rangle - 0.332|n_{a_1}(S)\rangle$. [b] Value has been estimated as explained in the Discussion. [c] If $\Delta E_{a_2'(\sigma)}$ is $\gg$34,000 cm^{-1}, $\alpha_2'^2$ is *ca.* 0.72; if $\Delta E_{a_2'(\sigma)}$ is *ca.* 20,000 cm^{-1}, $\alpha_2'^2$ is *ca.* 0.80.

Table IV. MO Coefficients for V(mnt)$_3^{2-}$ [a]

Orbital	[Metal coeff]^2	[S$_2$C$_2$ σ,n coeff]^2	[S$_2$C$_2$ π,π^* coeff]^2
e$_a''$ (d$_{yz}$)	0.52, 0.69[b]	0.48, 0[b]	0, 0.31[b]
e$_b''$ (d$_{xz}$)	0.48, 0.66[b]	0.52, 0[b]	0, 0.34[b]
e$_a'$ (d$_{x^2-y^2}$)	0.97, 0.90[b]		
e$_b'$ (d$_{xy}$)			
a$_1'$ (d$_{z^2}$)	0.97	0.03	

[a] Ground level: $|a_1'\rangle = 0.748|3d_{z^2}\rangle \pm 0.557|3d_{yz}\rangle - 0.265 \cdot |3d_{x^2-y^2}\rangle + 0.170|4s\rangle - 0.176|n_{a_1}'(S)\rangle$. [b] In each case the first figure indicates the solution for exclusive σ bonding and the latter that for exclusive π bonding.

The relative energies of the important levels in the diagrams (Figure 3) are obtained by making reasonable assignments of low-lying bands in the visible absorption spectra. The assignments are made on the basis of expected extinction coefficients and comparison with accepted assignments in analogous complexes.

In VO(mnt)$_2^{2-}$ [11,30] we make the following assignments.

	Type	ΔE, cm^{-1}	ϵ
$(a_1^*b_1^*)^4(d_{x^2-y^2})^1 \rightarrow (a_1^*b_1^*)^4(d_{xz}, d_{yz})^1$	d–d	20,500	170
$(a_1^*b_1^*)^4(d_{x^2-y^2})^1 \rightarrow (a_1^*b_1^*)^4(d_{xy})^1$	d–d	17,400	350
$(a_1^*b_1^*)^4(d_{x^2-y^2})^1 \rightarrow (a_1^*b_1^*)^4(a_2^*b_2^*)^1$	d–π^*	25,600	8200

The first two bands follow the usual assignment for similar vanadyl complexes.[16] Similarly, for V(mnt)$_3^{2-}$ [30,31] the assignments are as follows.

	Type	ΔE, cm^{-1}	ϵ
$(a_2'^*e'^*)^6(d_{z^2})^1 \rightarrow (a_2'^*e'^*)^5(d_{z^2})^2$	d–π^*/d	10,300	2800
$(a_2'^*e'^*)^6(d_{z^2})^1 \rightarrow (a_2'^*e'^*)^6(d_{xz}, d_{yz})^1$	d–π^*/d	15,600	2100
$(a_2'^*e'^*)^6(d_{z^2})^1 \rightarrow (a_2'^*e'^*)^6(a_1''^*, e''^*)^1$	d–π^*	23,400	6600

The second band in the tris complex is assigned by comparison with Ti(acac)$_3^-$.[30,32] The $(a_z'^*e'^*)^6(d_{z^2})^1 \rightarrow (a_2'^*e'^*)^6(d_{x^2-y^2}, d_{xy})^1$ is not expected to be as small as 1000–4000 cm^{-1}, as in Ti(acac)$_3^-$. The typical epr line width for V(mnt)$_3^{2-}$ in a dilute crystal is much smaller than in Ti(acac)$_3^-$. We estimate this transition to lie in the range 6000–9000 cm^{-1}. The remaining levels in both diagrams are then approximately located according to the energetics of the S$_2$C$_2$ π system discussed earlier.

Discussion

The Vanadyl Complex. In-plane anisotropy of the principal g and ^{51}V hyperfine values has been observed for vanadium(IV) in TiO$_2$ [33,34] and SnO$_2$ [35] host lattices. Using the arguments of Kikuchi and Chen[35] and McGarvey,[36] c_1 and c_2 are expected to have the same sign, thereby reducing the charge density along the x axis. On this basis we assign the in-plane ($\perp$) ^{51}V hyperfine value having the *larger anisotropic magnitude* to be in the x direction, *i.e.*, $1 \equiv x$, $2 \equiv y$, $3 \equiv z$ in Table I.

Admixture of the d$_{xz}$, d$_{yz}$ functions into b$_1$, b$_2$ levels that are predominantly ligand in character may occur and we assume that this is significant only in (a) π or π^* S$_2$C$_2$ orbitals whose density is mainly on the sulfur atoms and (b) the p$_x$, p$_y$ orbitals of oxygen. To facilitate calculations we further assume that the oxygen p$_x$, p$_y$ levels contain *ca.* 5% d$_{xz}$, d$_{yz}$ character, respectively. Figures of this order are supported by theoretical studies[37] and esr evidence[16,29] from other square-planar vanadyl complexes where the in-plane π bonding is small. The a$_2'$(σ) level is rather arbitrarily set at 1000 cm^{-1} below the lowest π level of the S$_4$C$_4$ fragment. A fairly rigorous SCF calculation on [Fe(NO)(mnt)$_2$]$^{2-}$ [30] using a similar hybrid scheme shows that estimates of this order are quite reasonable.

Results of the calculations are shown in Table III. As expected the 3d$_{z^2}$, 4s contributions to the ground level are small. Consideration of the b$_1$(π^*) and b$_2$(π) levels in the calculation of the metal coefficients from the Δg_x, Δg_y expressions leads to a much larger proportion of metal character in the d$_{xz}$, d$_{yz}$ levels than has been previously estimated.[38] We believe this is more in keeping with the observed extinction coefficient of the (a$_1$)^1 → (b$_1$, b$_2$)^1 absorption.

The Vanadium Tris Complex. Early X-ray crystallographic evidence[31] has shown that the V(mnt)$_3$(PPh$_4$)$_2$ and Mo(mnt)$_3$(PPh$_4$)$_2$ structures are very similar. Since only limited data[15] are available, it has not been possible to assign the two in-plane principal values to the x and y molecular axes directly. We use the same reasoning as in the vanadyl case to show that the sign of c_3 is opposite to that of c_1. Then with the conditions laid down earlier a_y is expected to have the larger magnitude, *i.e.*, $1 \equiv x$, $2 \equiv z$, $3 \equiv y$ in Table II.

As in the vanadyl case, it is necessary to make some assumptions regarding coefficients in order to calculate those of interest. The e$'$ (d$_{x^2-y^2}$, d$_{xy}$) levels are not expected to experience as large an interaction with the ligand orbitals as the e$''$ (d$_{xz}$, d$_{yz}$). Their coefficients are expected to be close to unity and the basic quality of degeneracy is retained. To facilitate an overall solution we set $\alpha_2^2 = \beta_2^2$. We regard admixture of d$_{xz}$, d$_{yz}$ with $\sigma_{e''}$, $\pi_{e''}$ as significant, though small or negligible with $\pi^*_{e''}$ owing to the low density on sulfur in this orbital. Calculations have been carried out for two extreme cases: (i) d$_{xz}$, d$_{yz}$ interacting exclusively with $\sigma_{e''}$; (ii) d$_{xz}$, d$_{yz}$ interacting exclusively with $\pi_{e''}$. In addition we have estimated the positions of the e$'$ (d$_{x^2-y^2}$) and the $\sigma_{e''}$ to be *ca.* 7500 cm^{-1} above and *ca.* 37,000 cm^{-1} below the ground level. The latter difference is estimated as in the vanadyl case.

The results are shown in Table IV. The epr of V(mnt)$_3^{2-}$ in a magnetically dilute single crystal is consistent with a d^1 configuration in a distorted D_{3h} crystal field. The ground level is principally 3d metal in character; the largest compo-

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(30) C. J. Winscom, Ph.D. Thesis, University of Sheffield, 1968.

(31) J. A. McCleverty, J. Locke, and E. J. Wharton, *J. Chem. Soc. A*, 816 (1968).

(32) B. R. McGarvey, *J. Chem. Phys.*, **38**, 388 (1963).

(33) H. J. Geritsen and H. R. Lewis, *Phys. Rev.*, **119**, 1010 (1960).

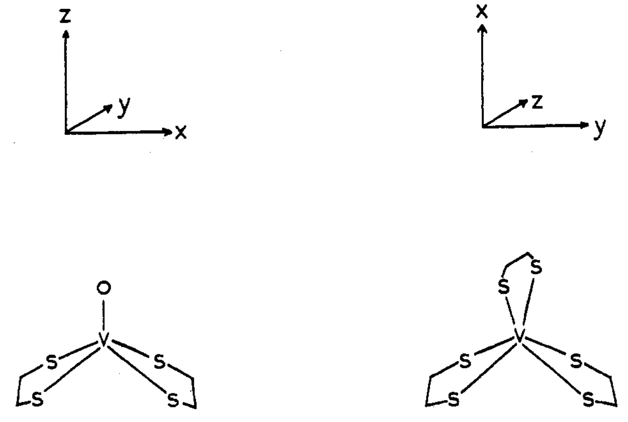
(34) E. Yamaka and R. G. Barnes, *Phys. Rev. A*, **135**, 144 (1964).

(35) C. Kikuchi and I. Chen, *J. Chem. Phys.*, **42**, 181 (1965).

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

(37) K. D. Carlson and C. Moser, *J. Chem. Phys.*, **44**, 3259 (1966).

(38) L. J. Boucher, E. C. Tynan, and T. F. Yen, "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Hilger, London, 1969, p 111.



$(\text{metal coeff.})^2$	d-function		d-function	$(\text{metal coeff.})^2$
0.89	d_{z2}	↔	d_{z2}	0.97
	d_{x2-y2}		d_{x2-y2}	0.90 - 0.97
0.75	d_{xy}	↔	d_{yz}	0.53 - 0.69
0.89	d_{yz}	↔	d_{xy}	0.90 - 0.97
0.90	d_{yz}	↔	d_{xz}	0.48 - 0.66

Figure 5. Changes in metal coefficients on replacement of O by $S_2C_2R_2$ in the vanadium complexes.

nent being d_{z^2} with substantial d_{yz} admixture. This contradicts the results of Davison, *et al.*,[5] who appear to have overlooked the possibility of a rather small $A_{\parallel}$. Our results show that the g tensor is indeed rather isotropic, but we find that this is mainly due to the large distortional pollution of the ground level. The isotropic part of the ^{51}V hyperfine splitting is somewhat lower than expected for other V(IV) complexes[29] and we attribute this to the allowed direct 4s admixture[20] into the ground level.

While our results are not consistent with the previous proposals by Davison, *et al.*,[5] for dianionic vanadium tris(dithiolenes), we do not disagree with their suggestions for the isoelectronic Cr, W, and Mo analogs. In the case of Mo, the anisotropic part of the $^{95}Mo^{97}Mo$ hyperfine splitting indicates that the ground level is only *ca.* 10-20% metal in character (based on literature estimates of P[20,39]) and the metal orbital involved is *not* d_{z^2}. This would seem to indicate that in any group of isoelectronic species the level ordering is rather sensitive to the metal. Moreover, the possibility of level reordering in $M(S_6C_6R_6)^{n-}$ of different ionic charge (n) yet of the same metal (M) should not be overlooked. This view is supported by the observations of McCleverty, *et al.*,[31] in trying to rationalize polarographic, spectral, and magnetic data for a large number of first-row dithiolene complexes.

It is interesting to compare the bis(dithiolene) with the tris(dithiolene) species viewed as the replacement of an oxygen in the former by another dithiolene ligand. By mapping the 3d functions in the VO axis system onto those of the tris complex (Figure 5) changes in the (metal coefficients)^2 may be discussed. Clearly, the most drastic change has occurred in the $d_{yz}(VO) \rightarrow d_{xz}(VS_6)$ level and is readily rationalized on the basis of increased ligand-metal d_{xz} overlap. More generally, the overall results indicate that in both cases the metal has more electron density than its formal oxidation state (IV) would imply, and markedly so in the tris complex.

Registry No. $[MeP(Ph)_3]_2VO(mnt)_2$, 36926-68-8; $[P(Ph)_4]_2V(mnt)_3$, 36965-91-0.

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(39) B. A. Goodman and J. B. Raynor, *J. Inorg. Nucl. Chem.*, **32**, 3411 (1970).