Re-examination of the Electron Spin Resonance Spectrum of Trigonal-prismatic Bis[pentane-2,4-dione benzoylhydrazonato(2−)]vanadium(IV)

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The e.s.r. spectrum of the title complex has been reinterpreted in terms of completely anisotropic *g* and hyperfine tensors. Analysis of these tensors indicates that the unpaired electron occupies an orbital which is *ca.* 88% metal 3*d* in character (78% d_{z^2}, 10% $d_{x^2-y^2}$) and 2% metal 4*s*. Except for the anisotropy of the 3*d* contribution, this is virtually identical to the corresponding orbital in $[V(mnt)_3]^{2-}$ (mnt = maleonitriledithiolate).

AN electron spin resonance spectrum has been reported recently for the trigonal-prismatic complex, bis[pentane-2,4-dione benzoylhydrazonato(2−)]vanadium(IV), $[V(pdbh)_2]$.[1] The spectrum was interpreted in terms of axial *g* and hyperfine tensors and it was concluded that the electron occupies an orbital which is primarily vanadium $3d_{z^2}$ in character.

In an idealized trigonal-prismatic complex of D_3 symmetry, the simple fact that an e.s.r. spectrum is observable at room temperature would require an a_1 (d_{z^2}) ground state since d_{xy}, $d_{x^2-y^2}$ and d_{xz}, d_{yz} belong to the e_a and e_b representations, respectively. However, D_3 is not a good approximation to the symmetry of $[V(pdbh)_2]$ which has a non-crystallographic C_2 axis.[2] Thus symmetry arguments and the appearance of a room-temperature spectrum do not necessarily lead to the conclusion that the ground state is d_{z^2}.

The compound $[V(pdbh)_2]$ may be compared with tris(maleonitriledithiolato)vanadium(IV), $[V(mnt)_3]^{2-}$. Studies of $[V(mnt)_3]^{2-}$ in dilute single crystals of $[As(C_6H_5)_4]_2[Mo(mnt)_3]$ showed that the symmetry is D_3 to a good approximation and that, as expected, the electron resides in an orbital which is largely metal d_{z^2} in character.[3] The *g* and hyperfine tensors were axial. Another study of $[V(mnt)_3]^{2-}$ in dilute single crystals of $[P(C_6H_5)_4]_2[Mo(mnt)_3]$, however, found completely anisotropic *g* and hyperfine tensors.[4] Packing forces in this case apparently lead to a reduction in symmetry from D_3 to C_2. The unpaired electron occupies an orbital which is still largely d_{z^2} in character but with significant admixture of other metal 3*d* orbitals.

In the case of $[V(pdbh)_2]$, the lower symmetry suggested that the hyperfine interaction might also be completely anisotropic and that a re-examination might be worthwhile. Furthermore, several inconsistencies remain in the original work[1] on this species: (a) the reported isotropic coupling was in disagreement with that found in preliminary work;[2] (b) the average hyperfine coupling, $(a_{\parallel} + 2a_{\perp})/3$, was in poor agreement with either value of the isotropic coupling; and (c) the qualitative shape of the reported frozen-solution spectrum seemed inconsistent with the interpretation given. We have repeated the spectrum of $[V(pdbh)_2]$ and report here a reinterpretation which removes the inconsistencies and sheds further light on the nature of the orbital containing the unpaired electron.

RESULTS AND DISCUSSION

Interpretation of E.S.R. Spectra.—The room-temperature isotropic e.s.r. spectrum of $[V(pdbh)_2]$ in 1 : 1 toluene–dichloromethane consists of the usual eight hyperfine lines resulting from coupling of the unpaired electron to the ^{51}V nucleus. The spectrum was analysed to second order to give the values of $\langle g \rangle$ and $\langle a \rangle$ listed in Table 1. The spectrum of the same solution, frozen at *ca.* 120 K, is shown in Figure 1. Two series of features are easily distinguished, corresponding to hyperfine components of *ca.* 13.9 and 5.9 mT.

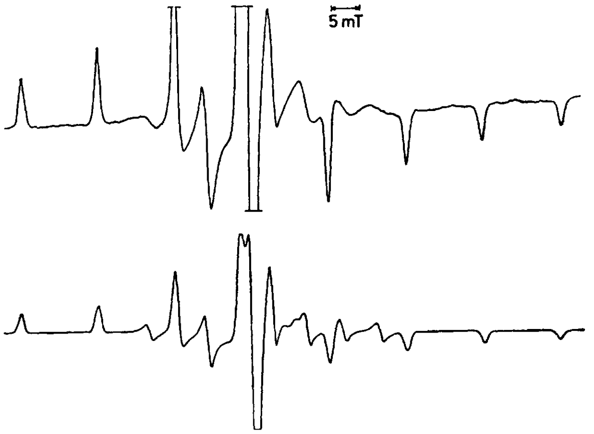

FIGURE 1 *X*-Band e.s.r. spectrum of $[V(pdbh)_2]$ in C_7H_8–CH_2Cl_2 at *ca.* 120 K: (upper) experimental spectrum; (lower) computer-simulated spectrum (parameters from Table 1)

Although only two series of features were observed in the frozen-solution spectrum, assignment to an axial hyperfine tensor was unsatisfactory in two respects: (i) agreement between the observed isotropic coupling, $\langle a \rangle$, and the average coupling, $(a_{\parallel} + 2a_{\perp})/3$, was poor for all possible assignments of $a_{\parallel}$ and $a_{\perp}$ to the observed spacings; and (ii) agreement between computer-simulated spectra and the experimental spectrum was poor for all assignments.

If we assume that the hyperfine tensor is anisotropic, the missing third hyperfine component must be small since no features are resolved. Using $\langle a \rangle$ and $\langle g \rangle$ to determine a_3 and g_3, we then arrive at the values given in Table 1. It is necessary that a_1, a_2, and a_3 all have the same sign as $\langle a \rangle$, which we assume is negative. The spectrum, computer simulated with these parameters,[5] is shown in Figure 1. Agreement with the experimental spectrum is satisfactory although the features corresponding to a_2 in the experimental spectrum are somewhat broader than in the simulation.

The Nature of the Orbital containing the Unpaired Electron.—The magnitude of the e.s.r. hyperfine tensor components suggests that the unpaired electron occupies an orbital which is largely vanadium 3*d* in character. These parameters, together with the *g* tensor, can be used to construct a detailed description of the orbital occupied by the unpaired electron.

TABLE 1

Electron spin resonance parameters

i	$a_i/10^{-4}\text{cm}^{-1}$	g_i
1	—126.6	1.957
2	—54.8	1.983
3	—13.7	1.979
Isotropic	—65.0	1.973

Under C_2 symmetry (with the x-axis equivalent to the C_2 axis), d_{z^2}, $d_{x^2-y^2}$, and d_{yz} belong to the a representation while d_{xy} and d_{xz} transform as b. We can immediately reject combinations of b symmetry since any d_{xy}, d_{xz} combination would give an axial hyperfine tensor (neglecting small spin–orbit coupling contributions).[5] Thus the ground-state orbital is described in general by equation (1) where small additional contributions might

$$|a\rangle_0 = \alpha_1[c_1|z^2\rangle + c_2|x^2\text{-}y^2\rangle + c_3|yz\rangle] + \ldots \quad (1)$$

be expected from vanadium 4*s* and $4p_x$ orbitals as well as from appropriate ligand orbitals.

If we neglect the small spin–orbit coupling corrections, the experimental dipolar tensor components are given by equation (2). A theoretical dipolar hyperfine tensor

$$b_i = a_i - \langle a \rangle \quad (2)$$

can be computed from the *d*-orbital constructions choosing the coefficients c_1, c_2, and c_3 to fit the ratios of the experimental tensor components.[5,6] The fit is not unique, however, and we obtain two families of hybrid orbitals, the compositions of which are shown in Figure 2. In all cases, the diagonal dipolar tensor is given by equation (3). Comparison with experiment gives $P\alpha_1^2 =$

$$b = |\pm 0.533 \mp 0.090 \mp 0.443| P\alpha_1^2 \quad (3)$$

115×10^{-4} cm^{-1}. Theoretical values of P range from 128×10^{-4} to 172×10^{-4} cm^{-1},[7-9] so that $\alpha_1^2 = 0.90$—0.67. One family of orbitals, shown in Figure 2(*a*), corresponds to the upper signs of equation (3) and thus to a positive value of $\langle a \rangle$. A positive isotropic coupling would require a 4*s* contribution to the ground-state orbital of the order of 10% (see below). Although 4*s* admixture is not symmetry forbidden, such a large contribution seems unlikely and this family of hybrids is rejected. The other family, shown in Figure 2(*b*), leads to the lower signs of equation (3) and is consistent with the expected negative value of $\langle a \rangle$. It should be emphasized that each family of hybrid orbitals in fact corresponds to an orbital of constant shape but with different orientations of the principal axes in the molecular co-ordinate system. Since we have no experimental information on the orientation of the hyperfine tensor axes relative to the molecular axes, we cannot make a unique choice of hybrid composition based on the evidence of the hyperfine tensor alone.

We can, however, use the qualitative results of crystal-field and molecular-orbital theory treatments to make some plausible suggestions. Molecular-orbital (m.o.) theory calculations[10-12] on D_3 trigonal-prismatic transition-metal complexes show that the *d* orbitals increase in energy in the order: $d_{z^2} < d_{xy}, d_{x^2-y^2} \ll d_{xz}, d_{yz}$. Crystal-field theory[12-14] is somewhat ambivalent about the relative energies of d_{z^2} and the d_{xy}, $d_{x^2-y^2}$ degenerate pair; the order and spacing of these levels is very dependent on the choice of parameters. It seems reasonable to assume, however, that the d_{xz} and d_{yz} orbitals will be at high energy and that the ground

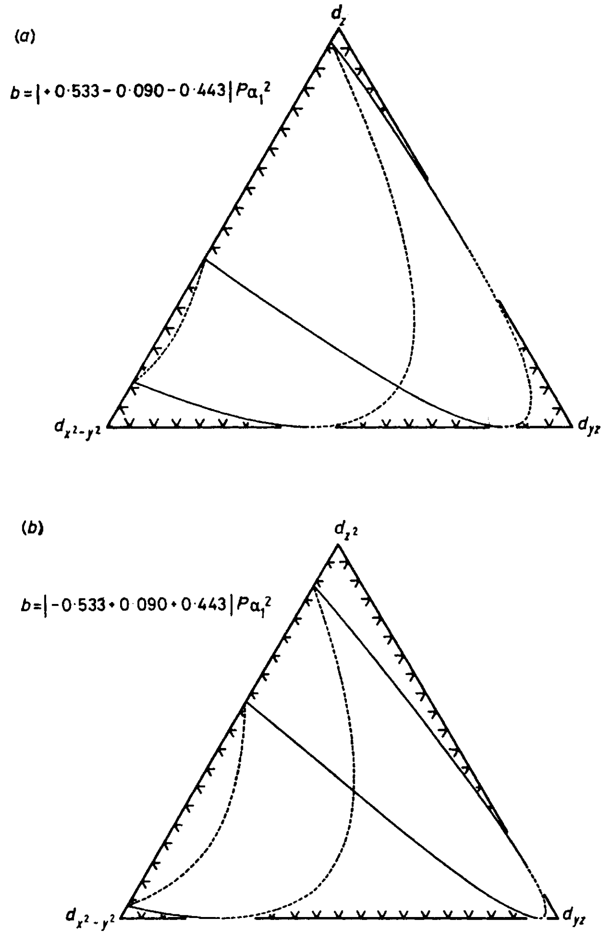

FIGURE 2 Hybrid orbital compositions which give dipolar hyperfine tensors matching experimental results. The solid and dashed portions of the curves correspond to hybrids with $c_1/c_2 > 0$ and $c_1/c_2 < 0$ respectively

state will be primarily d_{z^2} with some admixture of $d_{x^2-y^2}$. With this assumption, we have only three possible hybrid combinations consisting of *ca.* 89%, 57%, or 4% d_{z^2} character and 11%, 43%, or 96% $d_{x^2-y^2}$ character, respectively. Of these three possible hybrids, the first matches theoretical expectations quite well; however all three possibilities were analysed in more detail using equations given by Evans *et al.*[6] to approximately include the effects of spin-orbit coupling. The results are given in Table 2.

TABLE 2

Electron spin resonance/molecular orbital parameters

c_1^2	c_2^2	Assignment [a,b]	$P\alpha_1^2$/ 10^{-4} cm^{-1}	$\Delta E/\lambda\alpha_1^2$ [b,c]		
				xy	*xz*	*yz*
0.889	0.111	*x,y,z*	113	39	178	172
0.565	0.435	*x,z,y*	112	183	36	171
0.039	0.961	*z,x,y*	111	171	36	184

[a] Principal axes corresponding to a_1, a_2, a_3. [b] The assignments given are for $c_1/c_2 > 0$; for $c_1/c_2 < 0$, all *x* and *y* labels must be interchanged. Numerical values are negligibly affected by this interchange of label. [c] Energies of *d* orbitals relative to that of the ground level in units of the spin-orbit coupling parameter.

The components of the *g* tensor are given by equations (4a)—(4c). Substituting the values of c_1 and c_2 from Table 2 into equations (4), we obtain the values of $\Delta E/\lambda\alpha_1^2$ which are given in Table 2. We see that the

$$g_e - g_x = \frac{2\lambda(\sqrt{3}c_1 + c_2)^2\alpha_1^2}{\Delta E(yz)} \qquad (4a)$$

$$g_e - g_y = \frac{2\lambda(\sqrt{3}c_1 - c_2)^2\alpha_1^2}{\Delta E(xz)} \qquad (4b)$$

$$g_e - g_z = \frac{8\lambda c_2^2\alpha_1^2}{\Delta E(xy)} \qquad (4c)$$

hybrid orbital containing 88.9% d_{z^2} is again most consistent with the expected ordering of the *d* orbitals. Unfortunately, the strong charge-transfer bands in the spectrum of [V(pdbh)$_2$] extend into the visible and obscure any *d–d* bands which could have been used to estimate the energies of the orbitals.

Using the most commonly accepted value of *P*, 128 × 10^{-4} cm^{-1}, we obtain $\alpha_1^2 = 0.88$, suggesting that

$$\langle a\rangle = -K - P(g_0 - \langle g\rangle) \qquad (5)$$

ca. 12% of the orbital character is contributed by other metal and ligand orbitals. The isotropic coupling constant is given by equation (5). With the above value of *P*, $K = 61.3 \times 10^{-4}$ cm^{-1}. The parameter *K* is given in turn by equation (6). We choose $P\kappa$ to match the isotropic coupling in [VO(OH$_2$)$_5$]$^{2+}$ where a 4*s* contribution is symmetry forbidden and we assume $\alpha_1^2 = 1$; with $A_{4s} = 0.139$ cm^{-1} from Morton and Preston,[9] we obtain $c_s^2 = 0.016$. If the vanadium 4*p* contribution

$$K = P\kappa\alpha_1^2 - A_{4s}c_s^2 \qquad (6)$$

is of the order of a few percent, the ligand orbital contributions must amount to less than 10%.

A similar treatment of the e.s.r. parameters for [V(mnt)$_3$]$^{2-}$ of Kwik and Stiefel[3] gives $P\alpha_1^2 = 111 \times 10^{-4}$ cm^{-1}. With $P = 128 \times 10^{-4}$ cm^{-1}, we have $\alpha_1^2 = 0.87$. Similarly, the 4*s* contribution is found to be $c_s^2 = 0.019$. In other words, the vanadium 3*d* and 4*s* contributions to the orbital containing the unpaired electron are virtually the same in [V(pdbh)$_2$] and in [V(mnt)$_3$]$^{2-}$. Furthermore, the anisotropy observed in the case of [V(pdbh)$_2$] is comparable in magnitude to that found for [V(mnt)$_3$]$^{2-}$ where crystal packing forces lower symmetry.[4] Since the V–S bonds in [V(mnt)$_3$]$^{2-}$ are expected to be considerably more covalent than the V–O and V–N bonds in [V(pdbh)$_2$], this result is at first somewhat surprising. However, it must be recalled that the unpaired electron occupies an essentially non-bonding orbital which is largely metal in character and is thus independent, to a first approximation, of the covalent character of the bonding orbitals.

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