Electron Spin Resonance Spectra of Trigonal-prismatic Bis[pentane-2,4-dione benzoylhydrazonato(2—)]vanadium(IV) and Bis[4-phenylbutane-2,4-dione benzoylhydrazonato(2—)]vanadium(IV)

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The e.s.r. spectra of the trigonal-prismatic title complexes have been recorded. The spectra show axial symmetry and are characterised by $g_{\|} = 2.00$ and $g_{\perp} = 1.956$ and $g_{\|} = 2.00$ and $g_{\perp} = 1.971$ respectively. Analysis of the values of the hyperfine coupling to vanadium, namely $A_{\|} = 22$ G and $A_{\perp} = 138$ G, indicates that the unpaired electron is mainly (92 and 95%) in a metal d_{z^2} orbital. On addition of acids the complexes decompose to $[VO]^{2+}$ ions.

OF the known vanadium(IV) complexes, the vast majority are vanadyl ($[VO]^{2+}$) derivatives. The remainder have either approximately tetrahedral stereochemistry,[1] involving amine or alkoxide ligands, or have approximately trigonal-prismatic symmetry. Recently bis[pentane-2,4-dione benzoylhydrazonato(2—)]vanadium(IV), $[V(pdbh)_2]$, has been prepared, and its crystal structure shows that the vanadium(IV) ion is at the centre of a distorted trigonal prism comprising two triangles each having as their vertices one nitrogen and two oxygen atoms (Figure 1).[2] Particularly interesting are the values of the metal–ligand, ligand–ligand, and bite distances, *a*, *s*, and *b* respectively. These parameters

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[1] G. F. Kokoszka, H. C. Allen, and G. Gordon, *Inorg. Chem.*, 1966, **5**, 91; C. E. Holloway, F. E. Mabbs, and W. R. Smail, *J. Chem. Soc.* (*A*), 1968, 2980; O. Piovesana and C. Furlani, *Chem. Comm.*, 1971, 256; D. C. Bradley, R. H. Moss, and K. D. Sales, *ibid.*, 1969, 1255; J. L. Petersen and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 6416, 6422.

[2] A. A. Diamantis, M. R. Snow, and J. A. Vanza, *J.C.S. Chem. Comm.*, 1976, 264.

have been recently recognised[3,4] as the most important features characterising the trigonal-prismatic (t.p.) and the trigonal-antiprismatic (t.a.p.) (octahedral) structures. From them, a further parameter, the twist angle ϕ (Figure 2), may be calculated; $\phi = 0°$ for t.p. and $60°$ for t.a.p. structures. Since the complex [V(pdbh)$_2$] has $\phi = 9°$, the structure is much closer to a trigonal prism than to a trigonal antiprism, a fact which is quite unusual with oxygen- and nitrogen-based ligands. Until now, V^{IV} has only been found in a t.p. structure when surrounded by very covalent ligands such as sulphur in various dithiolene complexes.[5,6] The reason for the stability of the t.p. symmetry has been attributed[7] to the short bite distance, b, of the ligands and to the low value of s/a, thus allowing the presence of interligand bonding forces which are stronger than those present in normal octahedral complexes. Furthermore, a good overlap between the ligand orbitals and the metal d_{z^2} orbital is achieved.

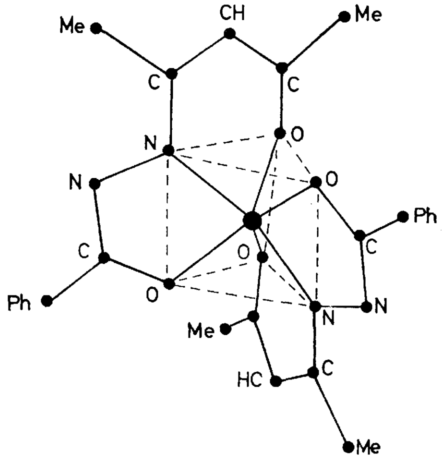

FIGURE 1 The structure of bis[pentane-2,4-dione benzoylhydrazonato(2−)]vanadium(IV)

Because electron spin resonance spectroscopy is a very sensitive tool for studying changes in structure and ligand environment, we have made e.s.r. measurements on both [V(pdbh)$_2$] and the 4-phenylbutane-2,4-dione derivative, [V(pbdbh)$_2$], in benzene with a view to comparing these molecules with other vanadium(IV) complexes. The colour of the complex [V(pdbh)$_2$] is unusual, being purple in the solid and in acetone solution, although [V(pbdbh)$_2$] is green.

TABLE 1

E.s.r. parameters for vanadium(IV) complexes of trigonal prismatic structure

Complex	$g_{\parallel}$	$g_{\perp}$	$g_{av.}$	$g_{iso.}$	$A_{\parallel}$	$A_{\perp}$	$A_{av.}$	$A_{iso.}$	α^2	κ	Ref.
					10^4 cm^{-1}						
[V(pdbh)$_2$]	2.000	1.956	1.970	1.972	20.5	−126	−77	84.6	0.92	0.42	This work
[V(pbdbh)$_2$]	2.000	1.971	1.980	1.977	20.5	−127	−77	84.6	0.95	0.43	This work
[AsPh$_4$]$_2$[V(mnt)$_3$]	2.000	1.974	1.982	1.980	9	−92	−63.3	63.5	0.65	0.32	6

RESULTS AND DISCUSSION

E.S.R. Spectra.—The e.s.r. X-band spectrum of a frozen solution of [V(pdbh)$_2$] at 77 K showed well resolved features separated by 138 G, but in the middle of the spectrum the resolution was poor due to considerable overlap of lines.* At Q-band frequencies the resolution was better (Figure 3) and the spectrum showed clear axial symmetry, although the line shape was rather unusual because of the large linewidths and large values of $A_{\perp}$ and small values of $A_{\parallel}$. From an analysis of the spectrum the parameters in Table 1 were deduced.

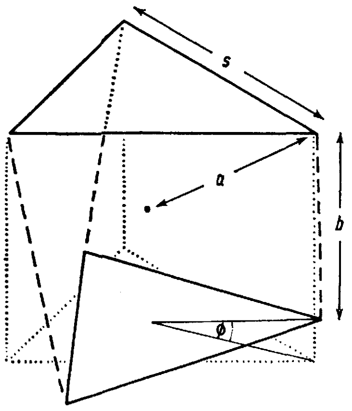

FIGURE 2 Critical dimensions of a trigonal prism

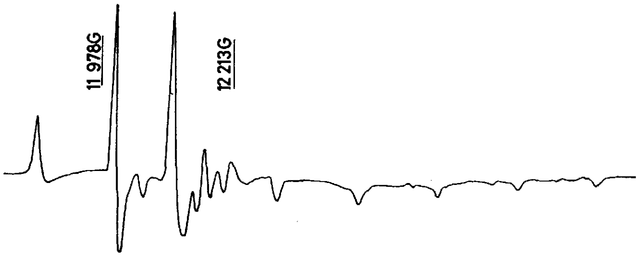

FIGURE 3 Q-Band spectrum of [V(pdbh)$_2$] at 77 K

At room temperature, eight well resolved lines were observed having a small coupling (84.6 G), but with no superhyperfine structure. The spectra were analysed and spin-Hamiltonian parameters corrected to second order. The analysis was checked by computer simulation.

The averaged and isotropic g values were in good

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* Throughout this paper: 1 G = 10^{-4} T.

[3] D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561.

[4] A. Avdeef and J. P. Fackler, *Inorg. Chem.*, 1975, **14**, 2002.

[5] H. L. Kwik and E. I. Stiefel, *Inorg. Chem.*, 1973, **12**, 2337.

[6] R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 1967, **6**, 1844.

[7] R. Hoffmann, J. M. Howell, and A. R. Rossi, *J. Amer. Chem. Soc.*, 1976, **98**, 2484.

agreement, but satisfactory averaging of the vanadium hyperfine tensor could only be achieved by assuming that $A_{\parallel}$ was positive and $A_{\perp}$ was negative, *i.e.* averaging to -77 G. Even so the agreement was not perfect. The most striking characteristic of the results is the low value of the isotropic hyperfine coupling. This value is quite unusual for vanadium(IV) complexes. Furthermore the relative values of the g tensor ($g_{\parallel}$ *ca.* 2 and $g_{\perp} < 2$) suggested that the complex did not have the $b_2(d_{xy})$ ground state usually associated with vanadium(IV) complexes. The general similarity of our parameters to those of Kwik and Stiefel[5] for $[V(mnt)_3]^{2-}$ (mnt = maleonitriledithiolate), and the known similarity in structure (both being close to trigonal prismatic, D_3), strongly implies an $a_1(d_{z^2})$ ground state.

In D_3 symmetry the metal d orbitals transform as A_1, E_a, and E_b. The ligands can form six σ orbitals with the metal e_b (d_{xz}, d_{yz}) orbitals, six π_h orbitals having both σ and π character with the metal a_1 (d_{z^2}) orbital, and 12 π_v orbitals with the metal e_a (d_{xy}, $d_{x^2-y^2}$) orbitals. We can write the molecular orbitals (1)—(3) where L are symmetry-adapted linear combinations of ligand orbitals and α, β, and β' and α_L, β_L, and β_L' are the orbital coefficients of the metal and ligand atoms respectively. Further descriptions of these molecular orbitals will be given later in this paper.

$$|\psi(a_1)\rangle = \alpha d_{z^2} + \alpha_L L(a_1) \qquad (1)$$

$$|\psi(e_a)\rangle = \beta'(d_{xy}, d_{x^2-y^2}) + \beta_L' L(e_a) \qquad (2)$$

$$|\psi(e_b)\rangle = \beta(d_{xz}, d_{yz}) + \beta_L L(e_b) \qquad (3)$$

The hyperfine parameters have been given by McGarvey[8] and reduce to (4) and (5) for the case of $\Delta E \gg \lambda$ where α is the orbital coefficient defined above and κ is the isotropic contact term. Assuming for $^{51}V^{4+}$ that $P = 172 \times 10^{-4}$ cm^{-1},[9] we find that $\alpha^2 = 0.92$ and $\kappa = 0.42$. The choice of value of the parameter P is difficult and depends on the effective charge of the metal. If the usual value of 128×10^{-4} cm^{-1} (for V^{2+}) is taken, then $\alpha^2 = 1.36$ and is clearly impossible. We are thus forced to use a larger value for P which makes $\alpha^2 < 1$. It follows that the bonding in the complex is very ionic and this may arise because of the difficulty of electron charge transfer in a molecule whose stereochemistry prevents efficient overlap of ligand and metal orbitals. The low value of κ arises from mixing of a small amount of an s orbital which transforms as a_1. The crystal field will mix $|\psi(d_{z^2})\rangle$ and $|4s\rangle$ and therefore the ground-state orbital becomes $|\psi(a_1)\rangle = \gamma[\psi(d_{z^2})] + \gamma'[\psi(4s)]$. Since the Fermi-contact interaction is quite large and positive for the $4s$ orbital a small change in γ' can produce a relatively large change in κ.

$$A_{\parallel} = [-\kappa + \tfrac{4}{7}\alpha^2 - \tfrac{1}{7}(g_{\perp} - 2.002\,3)]P \qquad (4)$$

$$A_{\perp} = [-\kappa - \tfrac{2}{7}\alpha^2 + \tfrac{15}{14}(g_{\perp} - 2.002\,3)]P \qquad (5)$$

The same analysis has been performed on $[V(pbdbh)_2]$. The e.s.r. spectrum shows the same hyperfine couplings as $[V(pdbh)_2]$. The only difference is a shift towards lower field of $g_{\perp}$ and a consequent small increase in α^2 and κ. This indicates a lower delocalisation of the unpaired electron on to the ligands, probably due to the increased withdrawing power of the phenyl substituent. Nevertheless, the difference is very small and we can affirm that the two complexes have the same structure. More interesting is the comparison[5] with the e.s.r. parameters of $[AsPh_4]_2[V(mnt)_3]$. In this complex both α^2 and κ are smaller (see Table 2) because the more covalent sulphur ligands allow a stronger overlap between the metal d_{z^2} and the ligand orbitals, and also the d_{z^2}–$4s$ mixing may make a more substantial contribution than in our complexes. In Table 2 the crystal parameters of some trigonal-prismatic vanadium(IV) complexes are reported. It is interesting to note that this symmetry is very sensitive to the distance and nature of the ligands. In the case of sulphur ligands it has been noted[6] that the particularly short interligand distance of 3.07 Å is the optimum to allow the formation of interdonor-atom bonding forces which help the stabilisation of the t.p. structure. This was shown to be true from $[AsPh_4]_2[V(mnt)_3]$ where all the ligands are sulphur but a lengthening of the a, b, and s distances causes a distortion from a perfect t.p. structure.[10] In our case, we have about the same distortion but our ligands are nearer to the metal than the sulphur ligands because they are smaller and less covalent. This short distance can allow the stabilisation of a pseudo-trigonal-prismatic structure with ligands such as oxygen and nitrogen also.

TABLE 2

Dimensions of some vanadium(IV) trigonal-prismatic complexes

Complex	a/Å	b/Å	s/Å	ϕ/°	b/a	s/a	Ref.
$[V(pdbh)_2]$	1.99	2.44	2.68	24	1.22	1.34	2
$[V(S_2C_2Ph_2)_3]$	2.34	3.06	3.07	3	1.31	1.31	*
$[AsPh_4]_2[V(mnt)_3]$	2.39	3.14	3.24	28	1.31	1.35	*
$[NMe_4]_2[V(mnt)_3]$	2.36	3.13	3.31	44.5	1.33	1.40	10

* E. I. Steifel and G. F. Brown, *Inorg. Chem.*, 1972, **11**, 434.

There is no possibility of the complex having approximately octahedral symmetry because this would require a d_{xy} ground state with $g_{\parallel} < g_{\perp} < 2$ and $|A_{\parallel}| > |A_{\perp}|$. Furthermore, the colour of the complex in solution is the same as in the solid, suggesting that the stereochemistry is the same in both cases.

Bonding.—The molecular orbitals involved in the bonding of trigonal-prismatic dithiolene complexes are

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[8] B. R. McGarvey, in 'Electron Spin Resonance of Metal Complexes,' ed. T. F. Yen, Hilger, London, 1969, p. 1 (equation 14 in this paper has an incorrect sign); *J. Phys. Chem.*, 1967, **71**, 55; A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 31.

[9] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135; P. F. Bramman, T. Lund, J. B, Raynor, and C. J. Willis, *J.C.S. Dalton*, 1975, 45.

[10] E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 3353.

now well understood.[7,11] The presence of sulphur ligands permits extensive covalency in all the molecular orbitals. Figure 4 shows the molecular orbitals in D_3 symmetry for MS_6 and MO_4N_2 type complexes. The ligand orbitals on oxygen and nitrogen will all be stabilised relative to those for sulphur. The main change is that the set of four e_a ligand orbitals (which are delocalised over the S–C–C–S π framework in dithiolenes) are now more widely spaced than on sulphur, and have much less interaction with the metal orbitals of the same symmetry. The effect is to make $1e_a$, $2e_a$, and $3e_a$ more ligand-like and $4e_a$ more metal-like. With oxygen and nitrogen ligands the ligand a_1 orbital (effectively an sp^2 hybrid orientated at 120° to the π bond) interacts well with the metal $3d_{z^2}$ and $4s$ orbitals to give a $3a_1$ molecular orbital which is mainly metal-like. Its bonding has both σ and π character with sulphur ligands, but has almost no π character with oxygen and nitrogen ligands because of the smaller size of the ligand orbitals. The $3a_1$ orbital has even more metal character with oxygen and nitrogen ligands than with sulphur ligands because of the lower energy of the parent ligand orbitals. The e_b ligand orbitals exhibit much the same behaviour with oxygen and nitrogen as with sulphur since they are effectively sp^2 hybrids pointing towards the metal and forming strong σ bonds with the metal d_{xz} and d_{yz} orbitals. The remaining a_2-ligand orbital is non-bonding on the ligands and has lower energy than the $3a_1$ molecular orbital in both cases.

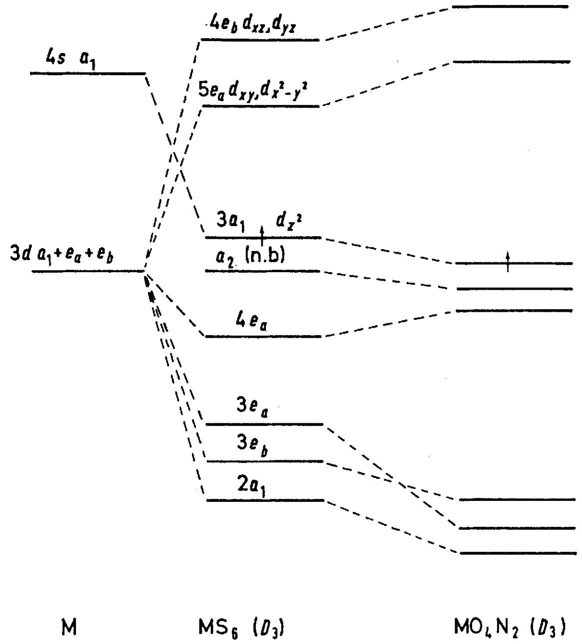

FIGURE 4 The relative energies of the molecular orbital energy levels of interest in metal dithiolene complexes as (MS_6) and [V(pdbh)$_2$] (MO_4N_2) in D_3 symmetry (twisted trigonal prism). n.b. = Non-bonding

Reaction with Strong Electron Acceptors.—The lone pair of electrons on the nitrogen atom not involved in co-ordination to the vanadium may, subject to steric hindrance, be sufficiently basic to interact with suitable Lewis acids or solvents with a large acceptor number (as described by Mayer *et al.*[12]). We have recorded the e.s.r. spectrum of [V(pdbh)$_2$] or [V(pbdbh)$_2$] in the pure (acid) solvent, or of the solvent added to a solution of the complex in acetone. In the case of oxalic acid, acetic acid, or water there was no effect, but with formic, trifluoroacetic, and methylsulphuric acids there was an immediate change in the colour of the solution to yellow. The e.s.r. spectrum changed completely and exhibited axial symmetry with $g_{\parallel} < g_{\perp}$ and $A_{\parallel} > A_{\perp}$. The spin-Hamiltonian parameters are very similar to that of $[VO]^{2+}$ in the same solvent, and we conclude that decomposition takes place in the presence of strong, but not weak, Lewis acids.

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[11] R. Huisman, R. de Jonge, C. Haas, and F. Jellinek, *J. Solid State Chem.*, 1971, **3**, 56.

[12] U. Mayer, V. Gutmann, and W. Gerger, *Monatsh.*, 1975, **106**, 1235.