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A SINGLE-CRYSTAL ESR STUDY ON A TETRAHEDRALLY COORDINATED VANADIUM(IV) COMPOUND: TETRAMESITYLVANADIUM(IV)

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Summary

A single-crystal ESR study on tetramesitylvanadium(IV) diluted in the corresponding Ti^{IV} compound is reported. The complete g tensor and metal hyperfine coupling tensor was obtained and the directions of their principal axes within the molecular frame were determined. In the x, y plane the principal axes of the g and the ^{51}V hyperfine tensor are not coincident, indicating a distortion of the elongated VC_4 tetrahedron by low-symmetry ligand-field components. Interpretation of the tensor parameters by means of a D_{2d} ligand-field model gives values for the effective spin-orbit coupling constant, the hyperfine parameters P and K and for the dd ligand-field transitions. Analysis of the anisotropy of the metal hyperfine interaction shows that the unpaired electron resides primarily on the vanadium atom in the B_1 state, mainly composed of $3d_{x^2-y^2}$ character. Hyperfine interactions with ligand protons are small and only poorly resolved in the spectra recorded at $T = 4.2$ K.

Introduction

ESR methods have been widely used to obtain detailed information about the structure, bonding properties and electron distributions in transition metal complexes [1,2]. Most detailed results in this respect can be derived from ESR studies on diamagnetically diluted single crystals. In organometallic chemistry such studies are very restricted due to the high chemical reactivity usually found for these compounds and due to the fact that suitable host compounds necessary for the diamagnetic dilution are available only in rare cases. In this paper we report a single-crystal ESR study on tetramesitylvanadium(IV) which was diamagnetically diluted by the corresponding titanium complex. In this compound vanadium is surrounded tetrahedrally by the four mesityl ligands [3]. Whereas $3d^1$ oxovanadium(IV) complexes have been studied to a large extent by ESR, to our knowledge only two tetrahedrally coordinated organovanadium(IV) complexes, $V(\eta^5-C_5H_5)_2S_5$ [4] and $V(\eta^5-C_5H_4CH_3)_2Cl_2$ [5], have been treated by the single-crystal ESR technique. Generally, tetrahedral complexes containing vanadium(IV) are rather uncommon. While solution ESR studies have been made on some tetrahedral complexes containing V—C σ bonds [$V(CH_2C_6H_5)_4$ [6] and V(1-norb)$_4$ [7]], until now no single-crystal ESR data have been reported on tetrahedral V^{IV} compounds containing only V—C σ bonds.

Experimental

Preparation of compounds and single crystals

V(mesityl)$_4$ was obtained as described earlier via LiV(mesityl)$_4$ [8,9]. Ti(mesityl)$_4$ was prepared analoguously [10].

Suitable single-crystals containing ca. 0.1% V(mesityl)$_4$ in the crystal lattice of Ti(mesityl)$_4$ were grown from benzene solution by slow evaporation of the solvent in the dark. All operations were carried out under an inert atmosphere.

ESR measurements

The single-crystal ESR spectra were recorded in the X band ($\nu \approx 9.3$ GHz) at room temperature using an E-112 spectrometer (Varian, USA). In addition, some of the crystal spectra were investigated at $T = 4.2$ K. DPPH was used as g marker.

The rhombohedrally shaped crystals were stuck onto small polystyrene angles having orthogonal edges. In order to derive the principal values of the g and A^V tensors the angular dependence of the ESR spectrum was studied. Spectra were recorded in 10° or 5° intervals, depending on the complexity of the spectra. The direction of the tensor components g_z and A_z^V was easily shown to be identical with the normal to the largest, well developed crystal plane.

To obtain the complete tensors of the spin Hamiltonian the angular dependences were analyzed by second-order perturbation treatment [1,2]. The crystals can be studied in the air because of the relatively chemical inertness of V(mesityl)$_4$ and Ti(mesityl)$_4$ [3,8], but must be kept under an inert atmosphere between the measurements.

Experimental results

The crystallographic structure of V(mesityl)$_4$ has been determined by Glowiak et al. [3]. V(mesityl)$_4$ gives monoclinic crystals, space group $P2_1/c$, with four molecules in the unit cell. The structure is illustrated in Fig. 1, and Table 1 gives a number of distances and angles of importance for the interpretation of the ESR spectra. Although the overall symmetry of the compound is C_1, the central part of the molecule has nearly D_{2d} symmetry (elongated tetra-

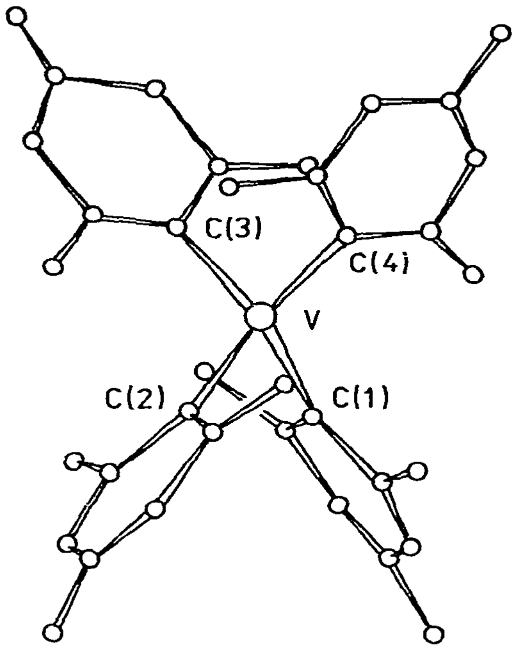

Fig. 1. Molecular Structure of V(mesityl)$_4$ [3].

hedral). The structure of Ti(mesityl)$_4$ used as diamagnetic host is not known. However, from the symmetry of the tensor parameters of the spin-Hamiltonian derived for V/Ti(mesityl)$_4$ we conclude that the geometry of the Ti(mesityl)$_4$ molecules is very similar to that of the vanadium complex.

The ESR spectra of V(mesityl)$_4$ show the typical eight-line hyperfine structure pattern due to the interaction of the unpaired electron with the ^{51}V nucleus (nuclear spin $I = 7/2$, natural abundance = 99.8%). In general, single-crystal ESR spectra show the signals of two magnetically non-equivalent molecules. However, the difference between the relatively positions of the two sites in the unit cell is found to be small. The signals of the two sites coincide when the magnetic field is parallel to the direction of the maximum ^{51}V hfs splitting and the direction of the minimum g value. This direction is be attributed to that of the z components of both tensors, as follows from symmetry considerations

TABLE 1

BOND DISTANCES AND ANGLES IN V(mesityl)$_4$ [3]

Distances	(pm)	Angles	(°)
V—C(1)	209.5	C(1)—V—C(2)	97.67
V—C(2)	207.1	C(1)—V—C(3)	117.81
V—C(3)	207.3	C(1)—V—C(4)	115.66
V—C(4)	207.5	C(2)—V—C(3)	114.45
		C(2)—V—C(4)	116.16
		C(3)—V—C(4)	96.41

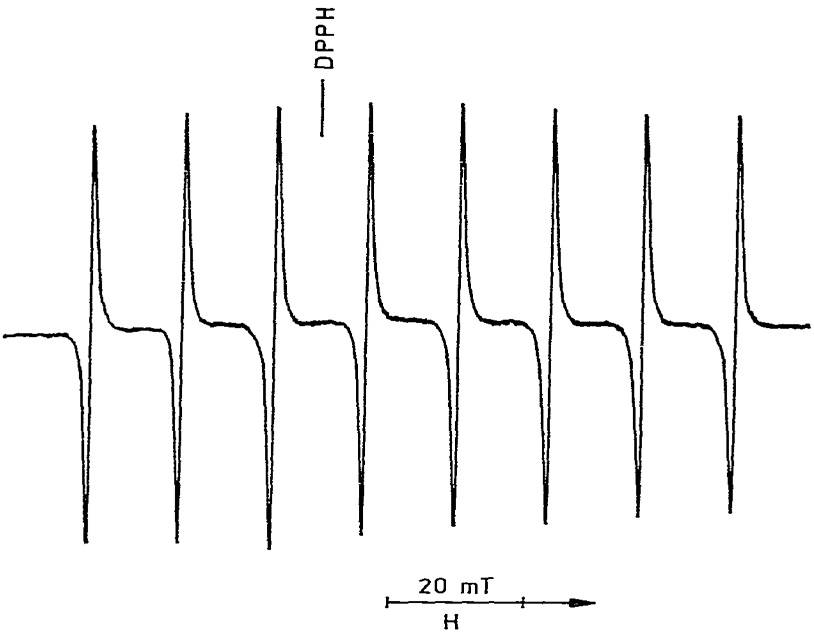

Fig. 2. X band single-crystal ESR spectrum of V/Ti(mesityl)$_4$. The magnetic field is located parallel to g_z, A_z^V; $T = 295$ K.

(see later). The ESR spectrum obtained for H||z is shown in Fig. 2. Figure 3 gives the angular variation of the g value and ^{51}V hfs upon rotation about an axis which is perpendicular to the z components of the g and the A^V tensor. Figure 4 shows the angular dependence of g and A^V given by rotation around the axis being identical with the direction of A_z (g_z). From the latter angular dependence it is evident that the principal axes of g and A^V do not coincide in the x, y plane of the tensors.

The ESR spectra can be described by a rhombic-symmetric spin-Hamiltonian (eq. 1):

$$\hat{H}_{sp} = \beta_e \vec{H}\tilde{g}\hat{\vec{S}} + \hat{\vec{S}}\tilde{A}^V\hat{\vec{I}}^V + \hat{\vec{I}}^V\tilde{Q}^V\hat{\vec{I}}^V + \sum_i \hat{\vec{S}}\tilde{A}^{H_i}\hat{\vec{I}}^{H_i}, \tag{1}$$

where β_e is the Bohr magneton, H the magnetic field applied, $\hat{S}$ the electron spin operator, $\hat{I}^V$ and $\hat{I}^{H_i}$ the nuclear spin operators of vanadium and the protons, and $\tilde{g}$, $\tilde{A}^V$, $\tilde{A}^H$, $\tilde{Q}^V$ are the g, the corresponding hyperfine interaction and the quadrupole interaction tensors, respectively. The parameters of eq. 1 derived from the angular dependence of the ESR spectra are summarized in Table 2; Figure 5 shows the orientation of the principal axes of the g tensor with respect to those of the A^V tensor.

The nuclear quadrupole interaction has not been analyzed in detail. However, from the analysis of the angular dependence of the ESR spectra it is evident that (a) the magnitude of this interaction is larger than that usually observed for VO^{2+} transition metal complexes and (b) that the principal axes of the quadrupole tensor Q^V certaintly do not coincide with those of the hyper-

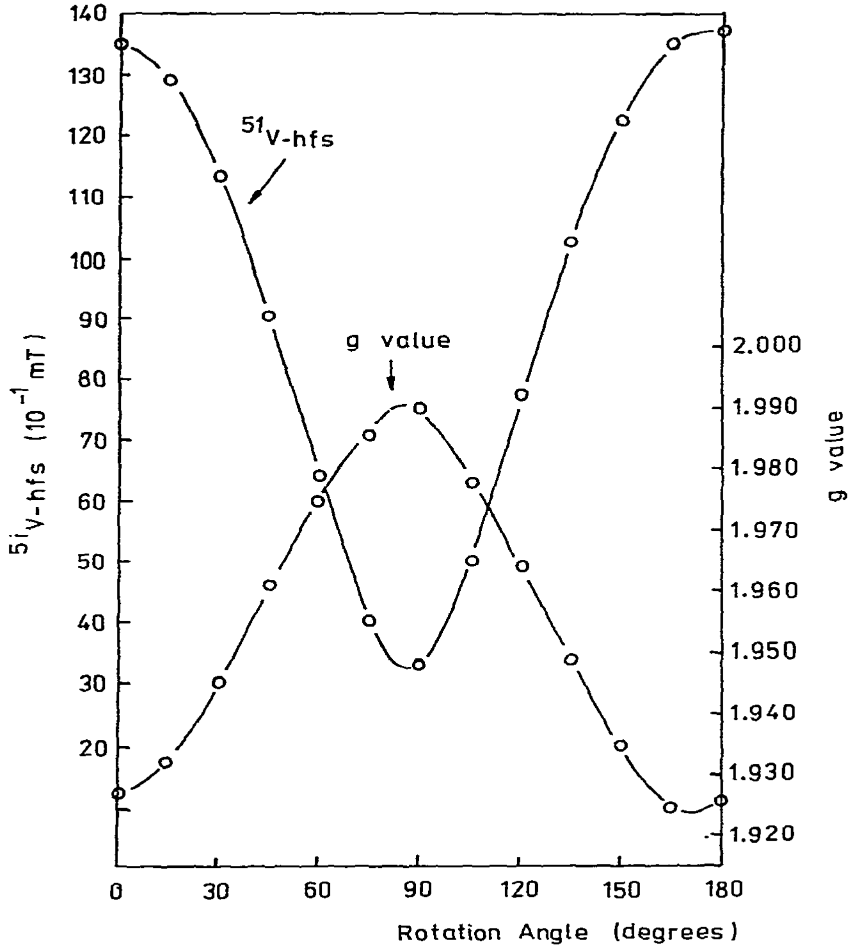

Fig. 3. Angular variation of the g value and the ^{51}V hfs upon rotation of the crystal about an axis which is perpendicular to the z components of g and A^{V}.

TABLE 2

ESR PARAMETERS [a] FOR V/Ti(mesityl)$_4$ (HYPERFINE COUPLING CONSTANTS ARE GIVEN IN 10^{-4} cm^{-1})

g		A^{V}	
g_x	1.984	A_x	26.9
g_y	1.994	A_y	39.5
g_z	1.925	A_z	123.6
g_{av}	1.968	A_{av}	63.3
g_0 [b]	1.972	a_0 [b]	57.5
α [c] = (22 ± 5)°			

[a] Experimental error: g_x, g_y ± 0.002; g_z ± 0.001; A_x, A_y ± 1.0; A_z ± 0.5. [b] Liquid-solution ESR data [24]. [c] Angle between g_x and A_x.

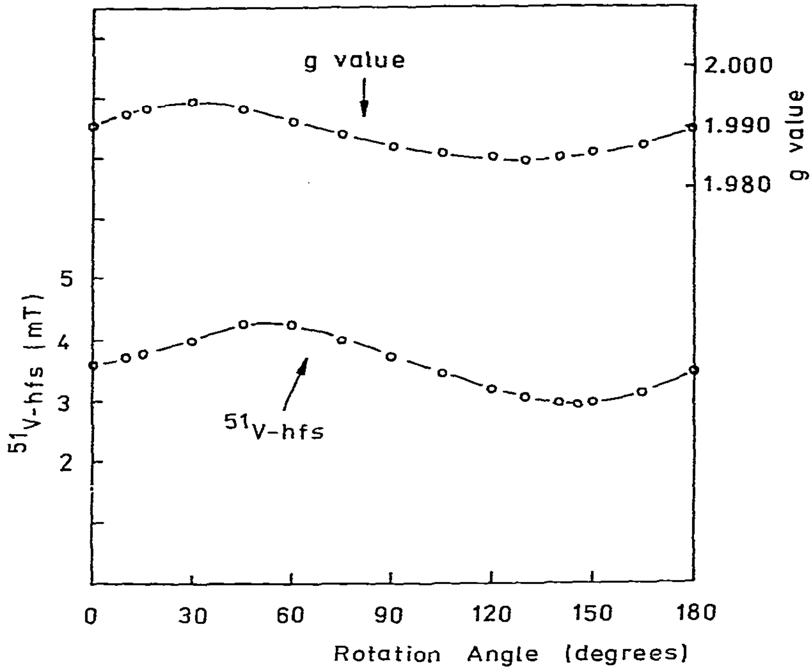

Fig. 4. Angular dependence of g and A^V in the x, y plane.

fine structure tensor A^V. Nevertheless, the magnitude does not exceed $2 \times 10^{-4}\ \mathrm{cm}^{-1}$.

According to the molecular structure [3], several protons come close enough to the vanadium nucleus (≈300 ppm) to give rise to a superhyperfine interaction (shfs) represented by the last term of the spin-Hamiltonian (eq. 1). The additional splitting caused by this shfs interaction could not, however, be detected at room temperature, obviously due to the large linewidth ($\Delta H_{pp} \approx$

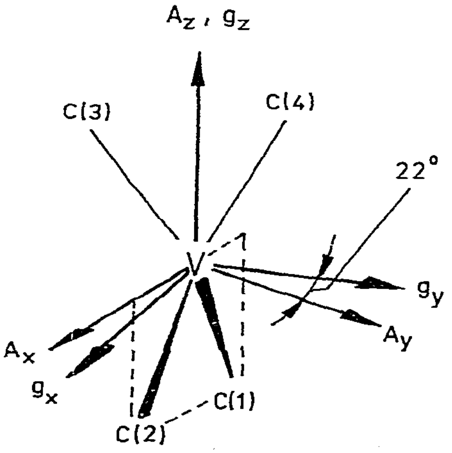

Fig. 5. Orientation of principal axes of the g and the ^{51}V hfs tensor.

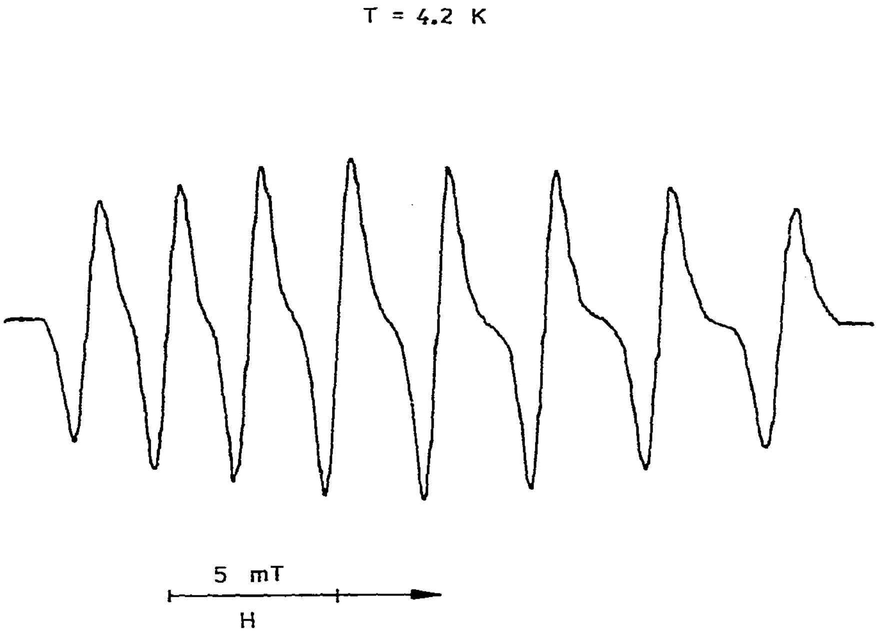

Fig. 6. Representative X band single-crystal ESR spectrum of V/Ti(mesityl)$_4$ recorded at $T = 4.2$ K.

1.0—1.2 mT) observed. Since electron spin-lattice interactions must be considered as essential for the room temperature linewidth in this tetrahedral complex [11—13], several ESR spectra were recorded at liquid helium temperature. A representative spectrum obtained at $T = 4.2$ K is shown in Fig. 6. It is to be seen that even at very low temperatures shfs interactions with protons are only poorly resolved. The shfs coupling constants do not exceed 2×10^{-4} cm^{-1}. This is in a good agreement with calculations based on the simple point dipole approximation [14].

Interpretation and discussion of the ESR data

A striking result found from the angular dependence of the ESR spectra is the non-coincidence of the principal axes of g and A^V in one plane. ESR studies on other systems for which non-coincidence of the principal axes of g and A has been observed to a large extent [15—19] have shown that this observation is mainly due to (a) a low symmetry of the molecules and (b) the presence of heavy ligator atoms possessing large spin-orbit coupling constants. In the system under study the observed effect must be attributed to the low overall symmetry (see Table 1). Ligand spin-orbit contributions are small ($\lambda(^{13}C) = 29$ cm^{-1}) and can be neglected.

The orientation of the principal axes of g and A^V in V(mesityl)$_4$ is shown in Fig. 5. Since the ESR parameters can be well understood in terms of an elongated tetrahedron, the z axis must be located parallel to the axis of elongation which is the bisector of the small C—V—C angles. An interchange of the z axis with x or y would result in another ground state which would not account for the ESR parameters.

The ESR parameters will now be interpreted using a D_{2d} ligand-field model. The electronic ground state is represented by $|B_1\rangle = |d_{x^2-y^2}\rangle$. The three excited states which are of importance for the calculation of the tensor components are: $|A_1\rangle = |d_{z^2}\rangle$, $|B_2\rangle = |d_{xy}\rangle$ and $|E\rangle = |d_{xz}, d_{yz}\rangle$, respectively. In the $|A_1\rangle$ state mixing with the vanadium $|4s\rangle$ function can occur, in the other states there is mixing with the corresponding $|4p\rangle$ functions because of the lack of an inversion centre. $|4s\rangle$ and $|4p\rangle$ contributions have been found to be small in complexes with related symmetries [4,5,20—22]. In addition they give only very small contributions to g and A^{V} if second-order perturbation theory is applied, and so will be neglected. The ligand-field model assumes that the principal axes of g and A^{V} are coincident, however, this approach can still be used for our purpose because non-coincidence occurs in the g tensor plane of smallest anisotropy. Applying the usual second-order perturbation treatment [1,2] the following expressions for the principal values of g and A^{V} are derived (eq. 2 and 3):

$$g_x = g_e - \frac{2\lambda}{\Delta E_{yz}}, \quad g_y = g_e - \frac{2\lambda}{\Delta E_{xz}}, \quad g_z = g_e - \frac{8\lambda}{\Delta E_{xy}} \tag{2}$$

and

$$\begin{aligned} A_x^{\mathrm{V}} &= -K + P[\tfrac{2}{7} + \tfrac{3}{14}(g_e - g_y) - (g_e - g_x)], \\ A_y^{\mathrm{V}} &= -K + P[\tfrac{2}{7} + \tfrac{3}{14}(g_e - g_x) - (g_e - g_y)], \\ A_z^{\mathrm{V}} &= -K + P[-\tfrac{4}{7} - \tfrac{3}{14}(g_e - g_y) - \tfrac{3}{14}(g_e - g_x) - (g_e - g_z)], \end{aligned} \tag{3}$$

where λ is the spin-orbit coupling constant for vanadium. ΔE_{xy}, ΔE_{xz} and ΔE_{yz} are the ligand-field transition energies $E(xy) - E(x^2 - y^2)$, $E(xz) - E(x^2 - y^2)$ and $E(yz) - E(x^2 - y^2)$, respectively; $P = g_e g_n \beta_e \beta_n \langle r^{-3}\rangle$ and $K = -g_e g_n \beta_e \beta_n \frac{2}{3} \chi$ [23]. By means of eq. 2 and 3 the parameters λ, ΔE_{xy}, ΔE_{xz}, ΔE_{yz}, P and K can be estimated. The following values are obtained: $P = 92 \times 10^{-4}$ cm^{-1}, $K = -60.3 \times 10^{-4}$ cm^{-1}, $\lambda = 125$ cm^{-1}, $\Delta E_{xy} = 12\,987$ cm^{-1}, $\Delta E_{yz} = 13\,890$ cm^{-1} and $\Delta E_{xz} = 31\,250$ cm^{-1}.

The value estimated for P can be compared with the P values calculated [23] for various electronic configurations of vanadium. From this it is apparent that the effective nuclear charge on the vanadium is nearly + 1. The value of (—) K of -60.3×10^{-4} cm^{-1}, the isotropic part of the vanadium hyperfine interaction which is due to spin polarization, is close to the isotropic coupling constant, $a_{\mathrm{iso}}^{\mathrm{V}}$, derived from the liquid-solution ESR spectrum: $a_{\mathrm{iso}}^{\mathrm{V}} = -57.5 \times 10^{-4}$ cm^{-1} [24]. For a d^1 system the isotropic coupling constant is related to K by the expression $a_{\mathrm{iso}}^{\mathrm{V}} = -K + (g_{\mathrm{iso}} - g_e)P$ [23], therefore, the small difference between the values of $a_{\mathrm{iso}}^{\mathrm{V}}$ and K is not surprising because of the closeness of g_{iso} to the free-electron g value g_e.

The spin-orbit coupling constant of vanadium obtained from the eqs. 2 and 3 is reduced by approximately 50% if compared to that calculated by Dunn [25] for $\mathrm{V}^{4+}(d^1)$: $\lambda(\mathrm{V}^{4+}) = 255$ cm^{-1}. This reduction is attributed to screening effects and to some electron-spin delocalization over the mesityl ligands. Investigating the ESR spectrum of tetrakis-t-butoxyvanadium(IV), Kokoszka et al.

[21] obtained the relationship $\lambda \approx 1.45 \times 10^4 P$, based on the fact that both λ and P vary approximately as $\langle r^{-3} \rangle$ [26]. In our case a factor of 1.36×10^4 is obtained, close to that derived by Kokoszka et al..

From the experimental ESR parameters the "*dd*" transition energies ΔE_{xy}, ΔE_{xz} and ΔE_{yz} are estimated. The electronic spectrum of V(mesityl)$_4$ in benzene shows only one *dd* transition at 13 370 cm^{-1} [3]. Obviously, the transitions ΔE_{xy} and ΔE_{yz} contribute to the absorption band observed experimentally. The transition energy obtained for the ΔE_{xz} transition is certaintly too large. However, this is acceptable considering the simplicity of the ligand-field model used.

Some remarks should be made concerning the limits of the above-made D_{2d} symmetry ligand-field model. The real symmetry of V(mesityl)$_4$ as determined by X ray structural analysis [3] (see Table 1) is lower than D_{2d}. This is reflected by the non-coincidence of g and A^{V}. Deviations from D_{2d} symmetry are also reflected by the χ parameter calculated to be $\chi = -1.93$ a.u. which represents the polarization of the inner *s* electrons through an exchange interaction with the unpaired electron. The estimated χ value indicates a direct 4*s* orbital contribution to the ground state of the unpaired electron of about 1—2% [4] which is not possible for the D_{2d} model. Nevertheless, the smallness of this contribution justifies its neglect.

Finally, it should be noted that covalency effects are not considered directly in the ligand-field approach made. A molecular orbital model, however, has not been used because there are not enough experimental parameters (g and A values) to determine the MO parameter set unambiguously. From studies on complexes having a coordination geometry similar to that found for V(mesityl)$_4$ it is apparent that in the ground state the unpaired electron is essentially localized on the central metal atom; in the excited states, however, there may be ligand orbital contributions [4,5,20—22]. Possibly, the larger value for the ΔE_{xz} transition estimated can be regarded as a result of neglect of such contributions. A better explanation of the experimental parameters should be achieved by semi-empirical molecular orbital calculations, which are in progress.

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