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Electron Spin Resonance of Dihalogeno Vanadium IV Complexes having different Ground States

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Direct reaction of excess of $SOCl_2$ with oxovanadium IV chelates dissolved in organic solvents yields six coordinate dichloro derivatives [1]. In a study of 20 complexes, all but one, VCl_2 (tripolonate)$_2$ showed e.s.r. spectra typical of an unpaired electron in a $d_{x^2-y^2}$ orbital, *i.e.* with $|A_z(^{51}V)| > |A_{x,y}(^{51}V)|$ and $g_z < g_{x,y}$. The X-band spectrum of VCl_2(tropolonate)$_2$ in $SOCl_2$/diethylacetamide was quite different (Fig. 1) and readily interpreted in terms of an approximately axially symmetrical tensor with $|A_z(^{51}V)| < |A_{x,y}(^{51}V)|$ and g_z *ca.* 2, $g_{x,y} < 2$. At Q-band frequencies, there was a clear separation of the perpendicular features. The experimental Spin Hamiltonian parameters are given in the Table along with for comparison those for VCl_2(acacen) (acacen = Schiff base of acetylacetone and ethylenediamine) and their oxovanadium IV parent complexes VO(tropolonate)$_2$ and VO(acacen). A similar reaction takes place with $SOBr_2$ yielding VBr_2(tropolonate)$_2$, the e.s.r. parameters of which were almost identical to those of the dichloro complex (Table I).

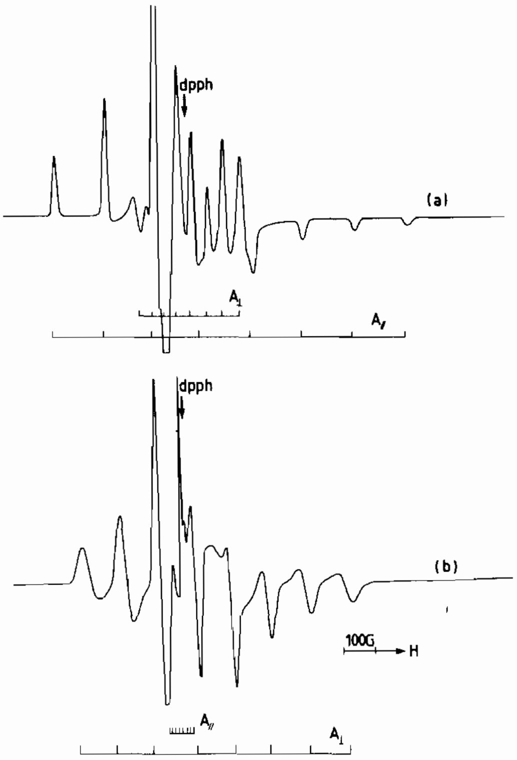

Fig. 1. E.s.r. spectrum of (a) VO(tropolonate)$_2$ in CH_2Cl_2 and (b) VCl_2(tropolonate)$_2$ in $SOCl_2$/diethylacetamide both at 77 K.

The derived parameters P and κ (which have their usual meaning) and a^2 and b^2 were calculated using the expressions derived from second-order perturbation theory by McGarvey [2] and reformulated by Evans *et al.* [3]. The unpaired electron is in an A_1 orbital (in approximately C_{2v} symmetry) having

TABLE I. Experimental and Calculated E.s.r. Parameters.

	VO(acacen)$_2$	VO(trop)$_2$	VCl_2(acacen)$_2$	VCl_2(trop)$_2$
A_x (cm^{-1})	−0.0055	−0.0050	−0.0045	−0.0110
A_y (cm^{-1})	−0.0055	−0.0040	−0.0045	−0.0102
A_z (cm^{-1})	−0.0164	−0.0155	−0.0144	−0.0009
A_{iso} (cm^{-1})^a	−0.0091	−0.0082	−0.0075	−0.0071
g_x	1.987	1.981	1.987	1.938
g_y	1.987	1.989	1.987	1.944
g_z	1.956	1.950	1.908	1.996
g_{iso}^{a}	1.978	1.972	1.961	1.959
a^2	0	0.001	0	0.997
b^2	1	0.999	1	0.003
P (cm^{-1})	0.0121	0.0122	0.0105	0.0105
K (cm^{-1})	0.7268	0.6397	0.7032	0.6563

^{a}Measured at −40 °C.

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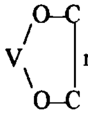
$$|\psi_o> = a|d_{z^2}> + b|d_{x^2-y^2}>$$

where

$$a^2 + b^2 = 1$$

The dihalogeno complexes all have significantly lower P values than the parent vanadyl complexes thus showing increased delocalisation of the unpaired electron. Most important, however is the change in ground state from A_1 comprising a mainly $d_{x^2-y^2}$ orbital for VCl_2(acacen) and other 'conventional' VCl_2^{2+} complexes to A_1 which is mainly d_{z^2} for VCl_2(tropolonate)$_2$ and VBr_2(tropolonate)$_2$. VCl_2(acacen) is known to be in the *trans* form, but VCl_2(tropolonate)$_2$ cannot be *trans* if the d_{z^2} orbital lies along the Halogen–V–Halogen bonds since the dibromo derivative has identical parameters and there was no evidence for chlorine or bromine hyperfine coupling. Chemical analysis showed that the ratio V:tropolone was 1:2. The complex was a non conductor in $CHCl_3$/$SOCl_2$ mixed solvent. The isolated complex was hydrolysed by water, the e.s.r. spectrum of the resulting solution being identical to the parent VO(tropolonate)$_2$. From these observations, we conclude that the complex is non-ionic and six coordinate, *viz.* VCl_2(tropolonate)$_2$ rather than [VCl(tropolonate)$_2$]-Cl or [V(tropolonate)$_2$] Cl_2.

We believe the VCl_2(tropolonate)$_2$ and VBr_2(tropolonate)$_2$ complexes must be strongly distorted from octahedral perhaps caused by the unique feature that they have a five membered  ring system in contrast to the six membered ring systems of the Schiff Base and other complexes studied. The only other six coordinate V(IV) complexes having an unpaired electron primarily in a d_{z^2} orbital are those with the $V(mnt)_3^{2-}$ anion, (mnt = maleonitriledithiolate) [4], and V(pdbh)$_2$ (pdbh = pentane-(or 4-phenylbutane) 2,4-dione benzoylhydrazonate) [5] which also have five membered ring systems incorporating the central metal atom.

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