Electron Spin Resonance Studies on Quadrivalent Vanadium Compounds

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Summary A survey of quadrivalent vanadium compounds has been made, and e.s.r. studies have brought to light a novel type of isomerism in $V(S_2CNEt_2)_4$.

PREVIOUS e.s.r. studies on vanadium(IV) compounds have mainly involved oxovanadium species[1] but recent work on vanadium tetra-t-butoxide[2] and vanadium tetradiethylamide[3] has shown that spectra may be obtained on 'tetrahedral' VL_4 compounds and prompts this report of our studies on quadricovalent vanadium compounds ($L = OR$, NR_2, and S_2CNR_2).

We have confirmed substantially the results on monomeric $V(OBu^t)_4$[2] and $V(NEt_2)_4$[3] and similarly found for $V(NMe_2)_4$[4] in frozen methylcyclohexane ($-150°$) a resolved spectrum ($g_{\parallel} = 1{\cdot}955 \pm 0{\cdot}004$; $g_{\perp} = 1{\cdot}985 \pm 0{\cdot}004$) with ^{51}V hyperfine splitting ($A_{\parallel} = 135$; $A_{\perp} = 29{\cdot}7$ gauss) which is indicative of distortion to D_{2d} symmetry with $|x^2 - y^2\rangle$ ground state.

Solid vanadium tetramethoxide gave a very broad signal ($g = 1{\cdot}955 \pm 0{\cdot}005$) at room temperature with no hyperfine structure. Broad signals were also given in solution (methylcyclohexane or benzene; $g = 1{\cdot}94 \pm 0{\cdot}01$) but no hyperfine structure appeared even at low temperatures ($-150°$). This behaviour is consistent with that expected for the trimeric species with distortion from regular octahedral symmetry[5] and line broadening due to magnetic dipole interactions.

Solid vanadium tetraethoxide also gave a strong very broad signal at room temperature ($g = 1{\cdot}945 - 0{\cdot}01$) with no hyperfine structure and the line-width increased with rise in temperature (*e.g.* 500 gauss at 0°, 800 gauss at 50°). Solutions in benzene ($g = 1{\cdot}952 \pm 0{\cdot}005$; $A = 78{\cdot}0$ gauss) methylcyclohexane ($g = 1{\cdot}953 \pm 0{\cdot}005$; $A = 79{\cdot}1$ gauss), or carbon disulphide ($g = 1{\cdot}951 \pm 0{\cdot}005$; $A = 78{\cdot}6$ gauss) each gave broad signals with partial resolution of the eight line ^{51}V hyperfine interaction. Lowering the temperature caused loss of hyperfine structure and it was not possible to resolve anisotropic components down to $-170°$ although narrowing of the line-width occurred (400 gauss at $-20°$, 200 gauss at $-170°$). These results are consistent with magnetic dipole interactions in the bridged dimeric structure $V_2(OEt)_8$ where the vanadium is five-co-ordinated.[5]

The possibility that tetrakis-*NN*-dialkyldithiocarbamates $V(S_2CNR_2)_4$ may contain eight-co-ordinated vanadium[5,6] led us to investigate the methyl and ethyl derivatives. At room temperature, solid $V(S_2CNEt_2)_4$ gave a broad signal ($g = 1{\cdot}981 \pm 0{\cdot}006$) whilst a benzene solution initially gave a resolved eight-line spectrum I ($g = 1{\cdot}975 \pm 0{\cdot}004$; $A = 72{\cdot}5$ gauss) which slowly decreased in intensity in favour of a new spectrum *II* ($g = 1{\cdot}977 \pm 0{\cdot}004$; $A = 91{\cdot}6$ gauss). Similar behaviour was found for solutions in carbon disulphide, methylene dichloride, or chloroform. Experiments showed that species *I* and *II* reach an equilibrium depending on solvent and temperature. Increased temperature favours species *II*, whereas *I* may be obtained by recrystallization. Frozen solutions (benzene at -100 to $-150°$) of *II* gave partial resolution of anisotropic components ($A_{\parallel}$, 155 ± 5; $A_{\perp}$, 55 ± 5 gauss) consistent with the presence of either a distorted tetrahedral configuration (D_{2d}) arising from vanadium bonded to four unidentate ligands, or a dodecahedral (local D_{2d}) tetrachelated configuration. In *I* the vanadium may be eight-co-ordinated (tetrachelated) or six-co-ordinated (*cis* or *trans*-bis-unidentate bis-chelated) but i.r. spectra suggest the presence of a tetrachelated species. Thus freshly prepared *I* (Nujol mull) had a strong broad band at 995 cm.$^{-1}$ indicative of bidentate dithiocarbamato-groups (S···C···S stretching) whereas an aged sample gave strong sharp bands at 1006 and 953 cm.$^{-1}$ due to unidentate ligands.[7] Repeated recrystallization of the aged sample caused the disappearance of the bands at 1006 and 953 cm.$^{-1}$ and the reappearance of the broad band at 995 cm.$^{-1}$ due to species *I*. Fresh solutions of *I* in benzene or methylene dichloride had the broad band at 995 cm.$^{-1}$, but new sharper bands at 1003 and 960 cm.$^{-1}$ slowly appeared as *II* was reversibly formed. The electronic spectra showed for *II* a broad band at 10,800 cm.$^{-1}$, in the region expected for distorted tetrahedral $\mathrm{V^{IV}}$ complexes,[5] absent for *I*. Clearly, further structural work on *I* and *II* is required (*X*-ray studies are in progress) but it is evident that $\mathrm{V(S_2CNEt_2)_4}$ is exhibiting a novel form of isomerism. The solid methyl derivative $\mathrm{V(S_2CNMe_2)_4}$ gave at room temperature a single absorption ($g = 1{\cdot}979 \pm 0{\cdot}005$) with a narrower line-width than $\mathrm{V(S_2CNEt_2)_4}$. The low solubility of $\mathrm{V(S_2CNMe_2)_4}$ precluded solution i.r. spectra but a weak e.s.r. signal (1 : 1, benzene–carbon disulphide solution) showed ^{51}V hyperfine structure ($g = 1{\cdot}973 \pm 0{\cdot}004$; $\mathrm{A} = 89$ gauss) reminiscent of species *II* of $\mathrm{V(S_2CNEt_2)_4}$ although it was not possible either to resolve the anisotropic component at low temperature ($-170°$) or to demonstrate the presence of two species.

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