Tetrakis(dithiocarboxylato)vanadium(IV)

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Summary The reaction of vanadyl salts with dithiocarboxylates $RCS_2^- = L$ results in cleavage of the V–O vanadyl bond and yields stable compounds of stoicheiometry VL_4 containing chelated RCS_2^- ligands, with a probable eight-co-ordinate vanadium atom.

FEW examples of V^{IV} complexes with sulphur-containing ligands are known and the factors determining the stoicheiometry and stereochemistry of these complexes appear not to be fully understood. Thus the $R_2NCS_2^-$ ion can form either "normal" $VO(R_2NCS_2)_2$[1] or eight co-ordinate $V(R_2NCS_2)_4$[2] complexes, depending on the reagents and solvents. Anionic vanadyl bis-1,2-dithiolenes have been characterised[3] while $S_2P(OEt)_2^-$ reduces VO^{2+} to V^{III}.[4] No other system of this type has been characterised.

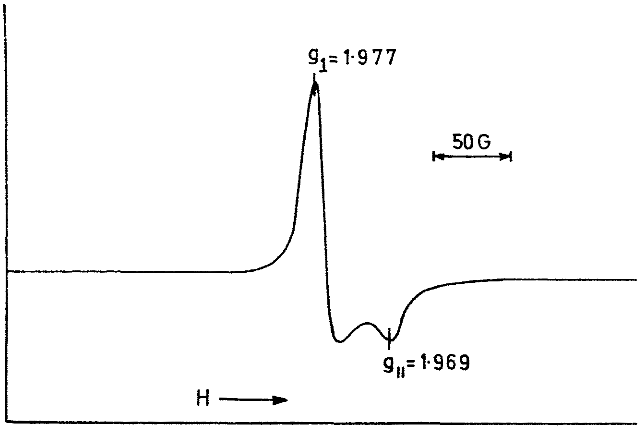

FIGURE. *E.s.r. room temperature powder spectrum of* $V(CH_3CSS)_4$

The behaviour of some dithiocarboxylates RCS_2^-, [R = Ph (dtb), $Me{\cdot}C_6H_4$ (dtt), Me (dta), and $PhCH_2$ (dtpa)] as ligands toward VO^{2+} has been investigated.

The peculiarity of these ligands is that they are able to destroy the vanadyl V–O bond present in vanadyl sulphate or chloride, in solvents such as water or ethanol, to give stable, oxygen-free compounds for which complete elemental analyses indicate the stoicheiometry $V(RCS_2)_4$. Magnetic measurements confirmed that the central metal ion had an oxidation state of +4. The magnetic moments were almost temperature independent and in the expected range ($1{\cdot}7$—$1{\cdot}8\ \mu_B$) for a $3d_1$ system. The e.s.r. spectra are also typical of V^{IV} (*vide infra*).

Various stereochemistries are possible for $V(RCS_2)_4$, depending on the number of sulphur *atoms* bonded to the metal and on the nature of the bonding. Bridging behaviour by the CS_2^- group is ruled out by molecular weight measurements in C_6H_6 and CH_2Cl_2 solutions, which indicate a monomeric composition, so the co-ordination number is determined by the mono- or bi-dentate nature of the CS_2^- group. I.r. spectra were used to decide whether or not the negative charge was localised on one of the two sulphur atoms in a CS_2^- group, as $\nu(CS_2)$ stretching modes for localised cases are expected at different wavelengths from that of the delocalised case. The simplest case is that of $V(dta)_4$. In the free acid, the symmetric and antisymmetric stretching frequencies of the CS_2 group fall at 581 and 1216 cm^{-1}, respectively.[5] On complex formation these bands disappear and are replaced by three new bands, one at 860 cm^{-1} and a doublet at 1150 and 1175 cm^{-1}. This is consistent with a delocalised negative charge, *i.e.* chelation. No "mixed" behaviour is apparent so all four ligands in $V(dta)_4$ are equivalent.

In $V(dtb)_4$, two bands can be assigned as mainly ν_s and ν_{as}, at 1015 and 1260 cm^{-1}, respectively, so again the four ligands are equivalent and the frequency values are consistent with chelation. These views are supported by comparison with the spectra of square planar Ni^{II} complexes with the same ligands, in which chelation was established by spectroscopic[6] and *X*-ray methods.[7] $V(dtpa)_4$ and $V(dtt)_4$ behave substantially in the same way.

Thus, in so far as i.r. spectra are sensitive to the effects above, a co-ordination number of eight can be assumed for the $V(RCS_2)_4$ complexes.

A preliminary e.s.r. investigation has been undertaken for these complexes. Their solution spectra in CH_2Cl_2 or C_6H_6 exhibit the typical eight line-hyperfine splitting (^{51}V, $I = 7/2$). Room-temperature powder spectra for $V(dta)_4$ and $V(dtt)_4$ show axially symmetric anisotropy: $g_\perp = 1{\cdot}977$, $g_\parallel = 1{\cdot}969$ and $g_\perp = 1{\cdot}981$, $g_\parallel = 1{\cdot}966$ respectively.

The choice of the eight-co-ordinate polyhedron for V^{IV} can be restricted, for different reasons, to that between two idealized structures: the square antiprismatic (D_{4d} symmetry) and the dodecahedral (D_{2d} symmetry).[8] Since in D_{4d} symmetry the lowest-lying metal orbital is d_{z^2} and in D_{2d} symmetry $d_{(x^2-y^2)}$, at least in the case of $V(dta)_4$ and $V(dtt)_4$ the e.s.r. spectra clearly indicate a D_{2d} symmetry.

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