The Crystal Structure and Vibrational Absorption Spectrum of Tris(diethyldithiophosphato)vanadium(III)

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Summary Crystal structure and vibrational absorption spectral data are presented for the title compound, which is the first one reported containing the [$V^{III}S_6$] chromophore.

FEW compounds of vanadium(III) with sulphur-containing ligands are known, presumably because of their instability. However, reaction of $VOSO_4,5H_2O$ or VCl_3 with a mixture of P_2S_5 and EtOH under reflux gives, instead of VO dtp_2[1] [$dtp^- = S_2P(OEt)_2^-$], V dtp_3 as hexagonal orange-red plates, sufficiently stable for physical measurements. Since this appears to be the first V^{III} compound containing the chromophore [$V^{III}S_6$], we report its structure and electronic properties.

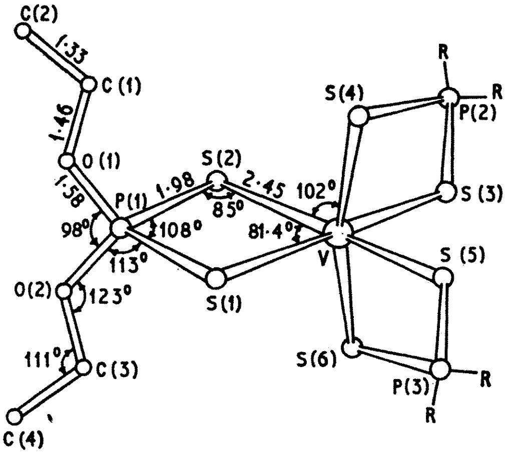

FIGURE 1. *A perspective drawing of an isolated tris(diethyldithiophosphato)vanadium(III) molecule. One complete* [$S_2P(OEt)_2$]$^-$ *ligand is shown on the left, while in the other two* dtp^- *ligands* R *stands for the* (OEt) *group. The bond lengths and angles are referred to average values.*

From ethanol, V dtp_3 crystallizes in the monoclinic space group $C2/c$, with $a = 8{\cdot}644 \pm 0{\cdot}005$, $b = 18{\cdot}487 \pm 0{\cdot}008$, $c = 17{\cdot}688 \pm 0{\cdot}007$ Å, $\beta = 93° \pm 0{\cdot}1$; $V = 2823$ Å^3; $M = 606{\cdot}6$; $D_m = 1{\cdot}415$ g./cm.^{3} (by flotation); $D_c = 1{\cdot}427$ g./cm.^{3}; $Z = 4$. The intensities of 1124 independent non-zero reflections were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the *a* (6 layers) and *b* (4 layers) axes. The crystal structure was solved by conventional Patterson and Fourier methods and refined by the block diagonal approximation least-squares method. The non-hydrogen atoms were refined with anisotropic temperature factors to $R = 0{\cdot}077$. Hydrogen atom positions and temperature factors were not refined. The structure of an isolated molecule, showing the principal intramolecular distances and angles is shown in Figure 1. All distances and angles are mean values.

The vanadium atom is crystallographically required to occupy one of the four-fold special positions (O, y, 1/4) of the space group, and the crystallographically required two-fold symmetry axis of the molecule passes through the vanadium atom and bisects one of the metal–chelate rings. The six sulphur atoms are virtually equidistant from the vanadium and form a slightly distorted octahedron. The average V–S bond length is $2{\cdot}45 \pm 0{\cdot}02$ Å and the average S–V–S angle is 81° 4′. The latter compares with an angle of 81° 42′ found in the corresponding nickel(II) complex.[2]

In toluene solution, the compound shows only two bands, at 13·2 and 18·5 kK, assignable to the $^3T_{2g} \longleftarrow {}^3T_{1g}(F)$ and $^3T_{1g}(P) \longleftarrow {}^3T_{1g}(F)$ transitions, respectively, of the [$V^{III}S_6$] (O_h) chromophore. However, a crystal spectrum shows that these two bands are further split, the components of which may be assigned, assuming C_3 symmetry, as in the Table (the actual site symmetry of the molecule is even lower, C_2, but no three-fold splitting was observed). It is noteworthy that a third *d–d* band, at 26·4 kK, assignable to the rarely observed[3] two-electron transition, is clearly observed. That this tentative assignment is reasonable may be seen from a weak-field calculation using an O_h crystal field. This gives, for $10Dq = 14{\cdot}0$, $B = 0{\cdot}42$ kK ($\beta = 0{\cdot}49$), values of $E(^3T_{2g}) = 13{\cdot}1$, $E(^3T_{1g}) = 18{\cdot}5$, and $E(^3A_{2g}) = 27{\cdot}1$ kK, in good agreement with the experimental results. The optical electronegativity of dtp^- is 2·6, similar to, but slightly lower than, that found (2·7) for other compounds with this ligand.[4]

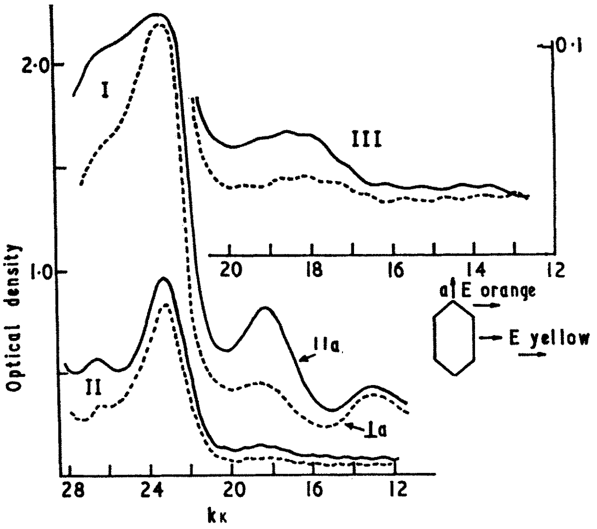

FIGURE 2. I. *Crystal spectrum of* V dtp_3; II. *Crystal spectrum of* V dtp_3/In dtp_3; III. *As for* II. *Absorption scale* 0—0·1 (*arbitrary origin*).

On dilution in the corresponding indium compound In dtp_3, the [$V^{III}S_6$] chromophore of the otherwise unstable compound is stabilised and the electronic spectrum, at room temperature, shows further bands which may be attributed to vibrational progressions (see Figure 2). The structure present in the first two *d–d* bands occurs with an interval of 800 ± 50 cm.$^{-1}$. This frequency appears to be too large to be that due to a mode [ν (V–S) or δ (S–V–S)] of the chromophore, but is in the range expected for a P–S or P–O stretching vibration[5] (allowing for differences in frequency brought about by changes in the extent of π-bonding on chelation). It is thus possible that the electronic transitions are allowed by vibrations within the ligands rather than by metal–sulphur vibrations.

TABLE

Energy (kK)	*Assignment* C_3	O_h
13·0	$^3A \longleftarrow {}^3A$	$^3T_{2g} \longleftarrow {}^3T_{1g}(F)$
13·3	$^3E \longleftarrow {}^3A$	
18·3	$^3A \longleftarrow {}^3A$	$^3T_{1g}(P) \longleftarrow {}^3T_{1g}(F)$
18·5	$^3E \longleftarrow {}^3A$	
23·3	Charge transfer	
26·4	$^3A \longleftarrow {}^3A$	$^3A_{2g} \longleftarrow {}^3T_{1g}(F)$

While solution spectra of the propyl derivative are similar, preliminary data suggest that dilution in the analogous indium(III) compound gives rise to the presence of more complex species.

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