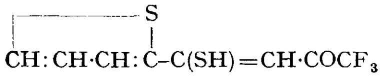
A Monothio-β-diketone Complex of Oxovanadium(IV)

By R. A. BOZIS and B. JACK MCCORMICK*
(*Department of Chemistry, West Virginia University, Morgantown, West Virginia* 26506)

LIVINGSTONE and his co-workers have prepared and characterized complexes derived from ligands of the type RC(SH) = CHCOR′ with a wide variety of metal ions.[1,2] Notably absent from these studies are complexes of oxovanadium(IV), although it has been pointed out that attempts to isolate VO^{2+} complexes were unsuccessful.[1] Further, it has been found that vanadium(IV) oxide sulphate reacts with



$CH{:}CH{\cdot}CH{:}C{-}C(SH){=}CH{\cdot}COCF_3$

to provide μ-dioxo-bridged dimers.[3]

We report the preparation of the first oxovanadium(IV) monothio-β-diketone complex. The olive-brown compound $VO[RC(S){=}CH{\cdot}COR]_2$ (R = Ph) has been prepared by treating an ethanolic solution of the ligand with $VOSO_42H_2O$ in the presence of a weak base such as acetate or carbonate. In the absence of base the complex does not form. The ligand was prepared by a modification of Livingstone's method.[4]

Elemental analyses and molecular weight determinations confirm the formulation $VO(C_{15}H_{11}OS)_2$. The room-temperature magnetic moment of 1·74 B.M. corresponds closely to the expected spin-only value for one unpaired electron. The compound is insoluble in water, but is soluble in most organic solvents. In some solvents such as benzene the complex decomposes slowly, even in the absence of air; however, the compound appears to be stable in the solid state for an indefinite period of time.

The i.r. spectrum of the complex is indicative of a tetragonal pyramidal structure in which both the oxygen and the sulphur atoms from the ligands are co-ordinated. Some characteristic i.r. bands (Table) match closely those reported by Livingstone[1,5] for complexes of this ligand with other metals in which both oxygen and sulphur atoms are co-ordinated. The V = O stretching frequency is located at 992 cm.$^{-1}$.

Infrared data

Band position (cm.$^{-1}$)	Assignment
1592w	Phenyl
1525s	C$\overset{\cdots}{-}$C
1490m	Phenyl
1465s	C$\overset{\cdots}{-}$O
1425s	C$\overset{\cdots}{-}$O + C–H
1267s	C$\overset{\cdots}{-}$S
830m	C$\overset{\cdots}{-}$S + C–H
450w	V–O
390w	V–S

The sixth co-ordination position *trans* to the V = O oxygen atom appears to be open for co-ordination by a sixth ligand, as judged by the fact that the V=O stretching frequency is lowered by some 40 cm.$^{-1}$ when the complex is treated with pyridine. In this respect the complex is very similar to VO(acetylacetonate)$_2$.[6] Significant solvent shifts are also observed in the electronic spectrum.

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[5] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Austral. J. Chem.*, 1965, **18**, 673.

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