Synthesis and Characterization of Thiovanadyl ($V{=}S^{2+}$) Complexes

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Summary The existence of the thiovanadyl ion, $V{=}S^{2+}$, has been established by reaction of V=O(salen) and V=O(acen) [H_2salen = *NN'*-ethylenebis(salicylideneamine), H_2acen = *NN'*-ethylenebis(acetylacetonylideneamine)] with B_2S_3 to form the thiovanadyl compounds, infrared and e s r spectroscopy indicate that the V=S bond has greater covalency but is weaker than its vanadyl analogues

The vanadyl ion ($V{=}O^{2+}$) has been described as probably the most stable diatomic ion known,[1] its characteristic deep blue colour is ubiquitous in vanadium chemistry

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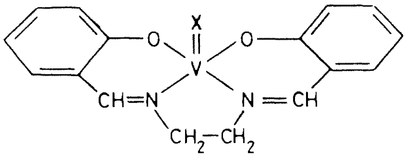
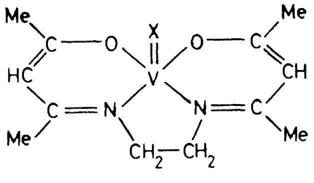
Although the sulphur analogues of a number of transition metal oxoanions have been known for many years (*e.g.* MoS_4^{2-}, WS_4^{2-}, VS_4^{3-}, and ReS_4^{-}),[2] the lack of evidence for the thiovanadyl ion ($V{=}S^{2+}$) has attracted the attention of several research groups, but without success.[3] We now report the synthesis of two complexes of the thiovanadyl ion, formed by reaction of V=O(salen)[4] (**1**) or V=O(acen)[5] (**2**) [H_2salen = *NN′*-ethylenebis(salicylideneamine); H_2acen = *NN′*-ethylenebis(acetylacetonylideneamine)] with the powerful oxophile B_2S_3, and the changes in properties resulting from replacement of oxygen by sulphur in these compounds.



(1) X = O
(3) X = S



(2) X = O
(4) X = S

TABLE. E.s.r. parameters[a]

Compound	⟨*g*⟩	$g_{\parallel}$	$g_{\perp}$	⟨*a*⟩	$a_{\parallel}$	$a_{\perp}$
V=O(salen)	1·974	1·957	1·982	−98·76	−174·6	−63·1
V=S(salen)	1·964	1·957	1·964	−89·67	−155·9	−60·2
V=O(acen)	1·977	1·963	1·982	−99·12	−171·9	−63·1
V=S(acen)	1·965	1·961	1·969	−89·61	−157·5	−55·9

[a] See text for conditions; *a* values in Gauss.

Reaction of CH_2Cl_2 solutions of (**1**) or (**2**) with equimolar amounts of solid B_2S_3, with rigorous exclusion of oxygen and moisture, led to colour changes [(**1**), emerald green to brown after 48 h at reflux; (**2**), deep blue to red-orange after 24 h stirring at 25 °C], and addition of hexane to the resulting filtrates gave deep magenta crystals of V=S(salen) (**3**) or V=S(acen) (**4**) in 67 and 46% yields, respectively.‡ Both solids are relatively stable to atmospheric attack (no visible change after several weeks' exposure), but their solutions are considerably more reactive and revert (as determined by i.r. or u.v.–visible spectroscopy) to vanadyl starting materials [$t_{\frac{1}{2}}$ seconds for (**3**), minutes for (**4**)] upon exposure to the atmosphere.

The i.r. spectra of (**3**) and (**4**) showed the absence of the V=O stretch of the starting materials [989 and 982 cm^{-1} for (**1**), 980 cm^{-1} for (**2**)] and the appearance of new, medium to strong intensity bands at 543 (**3**) and 556 cm^{-1} (**4**), which we assign to ν (V=S). A reduced-mass calculation, which assumes identical force constants for the V=O and V=S bonds, predicts the V=S stretching frequency to lie in the 780—770 cm^{-1} region. This assumption is of doubtful accuracy, for Muller[6] has shown that W=O and W=S stretching force constants for $OWSe_3^{2-}$ and $SWSe_3^{2-}$ are 6·66 and 3·47 mdyn Å^{-1},§ respectively. A similar change of force constant in going from V=O to V=S leads to a calculated ν (V=S) of 551 cm^{-1}, in excellent agreement with our observations.

E.s.r. spectra of (**3**) and (**4**) were recorded at *X*-band frequencies in CH_2Cl_2–toluene (60:40) solutions at 0 and −160 °C; both samples exhibit 8-line isotropic solution spectra and axially symmetric frozen solution spectra. The measured e.s.r. parameters are presented in the Table, along with those measured for the starting vanadyl complexes under the same conditions. Both ⟨*g*⟩ and ⟨*a*⟩ decrease in magnitude on substitution of oxygen by sulphur; this is consistent with a lower charge density on the metal and greater covalency in the V=S bond.[7]

While this work was in progress Wasson, Hall, and Hatfield reported the results of their calculations on the stabilities and properties of $V{=}X^{2+}$ (X = S, Se, Te) species.[8] Our experimental results for the thiovanadyl compounds are in close agreement with their predictions of decreased metal-ligand *d-p* σ- and π-bonding (reflected in the lower V=S stretching force constant) and decreased charge on the metal in going from V=O to V=S (as shown by the e.s.r. data).[7]

We thank the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(*Received* 17*th July* 1979; *Com.* 770.)

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‡ Both new compounds gave satisfactory elemental analyses (V, S, C, H, N).

§ 1 mdyn Å^{-1} = 10^2 N m^{-1}.

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[2] K. Schmidt and A. Müller, *Co-ordination Chem. Rev.*, 1974, **14**, 115, and references therein.

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[6] K. Schmidt and A. Müller, *Spectrochim. Acta*, 1972, **28A**, 1829; A. Müller, K. Schmidt, and U. Zindt, *ibid.*, 1976, **32A**, 901.

[7] Further details will be presented elsewhere.

[8] J. R. Wasson, J. Hall, and W. E. Hatfield, *Transition Metal Chem.*, 1978, **3**, 195.