

A Mononuclear Vanadium(III) Thiolate Complex: Synthesis, Structure, and Properties of $[V\{S-2,4,6-Pri_3C_6H_2\}_3(thf)_2]$

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A mononuclear trigonal bipyramidal vanadium(III) complex, $[V(tipt)_3(thf)_2]$ (tipt = 2,4,6-tri-isopropylbenzenethiolate; thf = tetrahydrofuran), has been prepared and characterized by X-ray crystallography and magnetic susceptibility, u.v.-visible and infrared spectroscopic, and electrochemical measurements.

Intense interest in discrete transition metal thiolate complexes in recent years has led to the isolation and characterization of a large number of such species.^{1,2} Despite this activity, there are no examples of structurally characterized mononuclear thiolate complexes of vanadium(III). Vanadium(IV) thiolate species with terminal oxo or sulphido ligands have been described recently.³ Our interest in vanadium co-ordination chemistry, particularly in the +2 and +3 oxidation levels, also stems from the recent discovery⁴ of naturally occurring vanadium-containing nitrogenases in which the vanadium atoms are in a sulphur-rich environment.⁵ The thiolate ligand chosen for this study, 2,4,6-tri-isopropylbenzenethiolate (tipt), is sterically encumbered so as to prevent bridge formation. Furthermore, since the steric bulk of tipt ligands will allow only three or four of them to crowd around a metal centre, there is ample room for co-ordination of a small molecule. Aryl thiolates with substituents in the 2- and 6-positions have been used to prepare mononuclear complexes of Ti^{III} ,⁶ Mo^{II} ,⁷ Mo^{IV} ,^{7,8} Mo^V ,⁸ W^{II} ,⁷ Mn^{III} ,⁹ Tc^{III} ,¹⁰ Re^V ,¹¹ Fe^{III} ,¹² Ru^{IV} ,¹³ Os^{IV} ,¹³ Co^{II} ,¹⁴ Co^{III} ,⁹ and Cu^I .^{14a} Herein are reported the synthesis, structure, and some properties of $[V(tipt)_3(thf)_2]$ (**1**), the first example of a mononuclear vanadium thiolate species with potentially labile ligands in the axial co-ordination positions.

Compound (**1**) was prepared in the following manner: a

dark green-brown solution containing $VCl_3 \cdot 3thf$ ¹⁵ (0.514 g, 1.38 mmol), $Li(tipt)^{\dagger}$ (1.000 g, 4.126 mmol) and n-heptane (10 ml) was stirred for 10 h, then filtered. The orange solid which was removed was washed with 5 ml portions of n-heptane and toluene. Evaporation of the combined filtrates to 10 ml, followed by cooling at $-35^{\circ}C$ overnight and filtration, afforded the pure complex (**1**) (0.387 g, 31%).[‡] Dark orange plate-like crystals suitable for X-ray diffraction studies§ were grown by slow cooling of a solution in n-heptane.

[†] The protonated form, $Htipt$, was prepared according to ref. 7 and $Li(tipt)$ was generated by addition of n-butyl-lithium in hexane.

[‡] Found: C, 71.05; H, 9.6. $C_{53}H_{85}O_2S_3V$ requires C, 70.6; H, 9.5%.

[§] *Crystal data:* Compound (**1**) crystallizes in the monoclinic system, with space group $P2_1/c$, with $a = 20.327(3)$, $b = 17.530(3)$, $c = 16.023(2)$ Å, $\beta = 112.68(1)^{\circ}$, $V = 5268(3)$ Å³, $D_c = 1.136$ g cm⁻³, $Z = 4$. With use of 6873 unique data out to $2\theta = 45^{\circ}$, on a single crystal X-ray diffractometer, the structure was solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms, to an R index of 0.046 ($R_w = 0.055$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

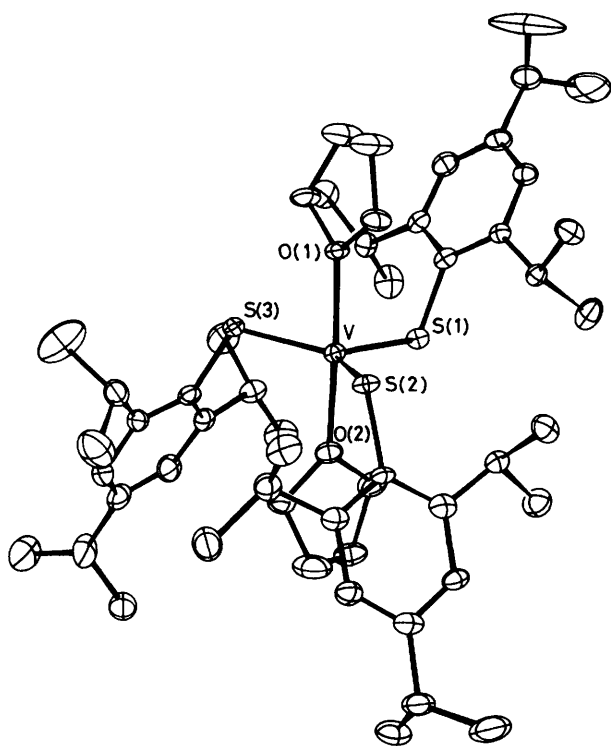


Figure 1. Structure of $[V(\text{tipt})_3(\text{thf})_2]$ showing the 30% probability thermal ellipsoids and atom-labelling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (\AA) and angles ($^\circ$) are as follows: V-S(1) 2.308(1), V-S(2) 2.334(1), V-S(3) 2.320(1), V-O(1) 2.123(2), V-O(2) 2.109(2), S(1)-V-S(2) 116.11(3), S(1)-V-S(3) 116.33(3), S(2)-V-S(3) 127.30(3), S(1)-V-O(1) 93.76(6), S(2)-V-O(1) 87.57(5), S(3)-V-O(1) 84.21(5), S(1)-V-O(2) 89.00(6), S(2)-V-O(2) 92.71(6), S(3)-V-O(2) 93.07(6), O(2)-V-O(1) 176.78(8).

The structure of (1) (Figure 1) is that of a mononuclear, distorted trigonal bipyramidal V^{III} complex with tipt groups occupying the equatorial positions and THF molecules filling the axial sites. The monomeric nature of (1) is in distinct contrast to that of the V^{III} complex of edt ($\text{edt} = \text{-SCH}_2\text{CH}_2\text{S}^-$), $[\text{V}_2(\text{edt})_4]^{2-}$, which is dimeric and contains a metal-metal single bond.¹⁶ Similar trigonal bipyramidal structures have been described for $[\text{Mo}(\text{tipt})_3(\text{CO})_2]^-$ (2),⁷ $[\text{Mo}(\text{NNPh})(\text{tipt})_3(\text{MeCN})]$ (3),⁷ and $[\text{Tc}(\text{tmbt})_3(\text{MeCN})_2]^{10}$ ($\text{tmbt} = 2,3,5,6\text{-tetramethylbenzenethiolate}$). The average V-S bond length in (1) (2.321 \AA) is similar to the average Mo-S bond distances in (2) (2.330 \AA) and (3) (2.320 \AA). The average V-SPh bond distance in $[\text{VS}(\text{SPh})_4]^{2-}$ (2.391 \AA)¹⁷ is significantly longer than that of (1), presumably owing to the electronic demands of the vanadium-sulphido double bond in the former. Distortion from an idealized trigonal bipyramidal structure is evident from inspection of the S-V-S angles given in the Figure caption. The same type of distortion was observed for (2) and (3). The disposition of the phenyl rings with respect to the equatorial plane is the same for all three of these trithiolate species, with two on one side and one on the other. The largest S-M-S angle in each case is between tipt ligands which are on the same side of the equatorial plane. Thus, not surprisingly, steric repulsion between tipt ligands appears to be responsible for the deviation from trigonal bipyramidal geometry. Trigonal bipyramidal geometry for V^{III} has been observed previously in species such as $\text{VBr}_3(\text{NMe}_3)_2$ and $\text{VBr}_3(\alpha\text{-pic})_2$ ($\alpha\text{-pic} = \alpha\text{-picoline}$).¹⁷⁻¹⁹

The magnetic susceptibility of (1) in $[\text{H}_8]\text{toluene}$ solution as determined by n.m.r. is 2.60 μ_{B} , consistent with values for

other five-coordinate V^{III} complexes.¹⁸ Several distinct charge-transfer bands are observed in the u.v.-visible spectrum, along with d-d transitions at 561 and 1010 nm. In analogy to assignments made for $\text{VBr}_3(\text{NMe}_3)_2$,¹⁷ these absorptions may arise from ${}^3\text{E}'$, ${}^3\text{A}_2' \leftarrow {}^3\text{A}_2'$ and ${}^1\text{E}' \leftarrow {}^3\text{A}_2'$ transitions, respectively. The i.r. spectrum of (1) displays absorption maxima at 420 and 351 cm^{-1} , tentatively assigned to V-S stretching. Complexes with the formula VX_3L_2 (X = Cl or Br; L = NMe_3 or $\alpha\text{-pic}$) have V-X vibrations in the range 320-422 cm^{-1} .^{17,18} Of particular interest was the accessibility of lower oxidation states in the vanadium trithiolate system. Cyclic voltammetry of (1) in THF displays a reduction wave ($E_{\text{pc}} = -1.62$ V) and re-oxidation wave ($E_{\text{pa}} = -1.15$ V, vs. Ag/Ag^+).

Thus a novel mononuclear trigonal bipyramidal V^{III} thiolate complex has been prepared and structurally characterized. Spectroscopic studies suggest that the solid-state structure is maintained in solution. Electrochemical measurements demonstrate the availability of a lower oxidation level. Studies of the reactivity of (1) and further reduced species are under way.

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