Vanadium Thiolate Chemistry: Preparation and Structures of $[NMe_4]Na[VO(SCH_2CH_2S)_2]\cdot 2EtOH$ and $[Ph_4P]_2[V_2(SCH_2CH_2S)_4]$

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Reaction of $VO(acac)_2$ (Hacac = pentane-1,4-dione) or VCl_3 with ethanolic solutions containing excess of sodium ethane-1,2-dithiolate (Na_2edt) yields deep green and deep red solutions, respectively, from which the complexes $[NMe_4]Na[VO(edt)_2]\cdot 2EtOH$ (**1**) and $[Ph_4P]_2[V_2(edt)_4]$ (**2**) have been isolated and structurally characterized; e.s.r. data for (**1**) are included.

Vanadium has been known to be an essential trace metal in nature since 1911 when it was detected[1] in large amounts in the blood of seasquirts, a class of the tunicates. Since then this metal has been identified as essential to growth in a myriad of other living systems including green plants, seaweeds, marine microalgae, and higher animals,[2-6] but to date there is no conclusive evidence for the presence of tightly bound vanadium in a naturally occurring metallobiomolecule.

These facts have, however, been sufficient to prompt us to initiate an investigation of the co-ordination chemistry of vanadium with a variety of organic thiolates, based on (i) the near-ubiquitous occurrence of the thiolate function (RS^-) of the cysteine amino acid as a metal-binding group in metallobiomolecules, and (ii) the lack of well characterized vanadium-thiolate complexes, excluding the dithiocarbamates and related sulphur-containing ligands[7-9] which cannot be considered electronic analogues of the cysteine thiolate function. Preliminary experimentation has been with the bidentate ethane-1,2-dithiolate ligand which is not in itself an ideal substitute for the monodentate cysteine thiolate group but which has nevertheless provided the first successes of our programme.

We herein report the preparation and structures of $[NMe_4]Na[VO(edt)_2]\cdot 2EtOH$ (**1**) and $[Ph_4P]_2[V_2(edt)_4]$ (**2**) (edt = ethane-1,2-dithiolate), containing vanadium(IV) and vanadium(III), respectively, and representing the first structurally characterized examples of vanadium-thiolate complexes.

All manipulations were carried out under a dinitrogen atmosphere employing standard inert-atmosphere apparatus. $VO(acac)_2$ (Hacac = pentane-1,4-dione) was dissolved in an ethanolic solution of four equivalents of Na_2edt to yield a deep green solution. Addition of excess of NMe_4Cl slowly deposited green prisms of (**1**) suitable for *X*-ray studies. The material can be recrystallized from warm dimethylformamide (DMF)–MeCN as large, thin plates.

Crystal data: $C_{12}H_{32}NNaO_3S_4V$, M = 440.58, monoclinic,

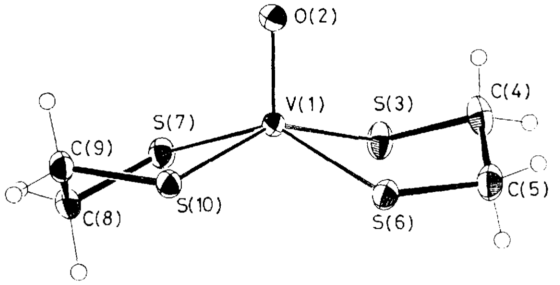

Figure 1. The structure of the $[VO(SCH_2CH_2S)_2]^{2-}$ anion of (**1**); non-hydrogen atoms are depicted as 50% probability ellipsoids. Selected bond lengths (Å) and angles (°) are: V(1)–O(2) 1.625(2), V(1)–S(3) 2.375(1), V(1)–S(6) 2.377(1), V(1)–S(7) 2.371(1), V(1)–S(10) 2.388(1); O(2)–V(1)–S(3,6,7,10) 104.03(8), 110.36(8), 106.92(8), 104.06(8) respectively, S(3)–V(1)–S(6) 84.82(4), S(3)–V(1)–S(7) 85.98(4), S(6)–V(1)–S(10) 85.03, S(7)–V(1)–S(10) 86.39(4).

space group $P2_1/n$, $Z = 4$, $a = 21.312(5)$, $b = 10.906(2)$, $c = 9.381(1)$ Å, $\beta = 92.77(1)°$, $U = 2177.86$ Å^3, $T = -159$ °C, crystal dimensions 0.23 × 0.21 × 0.18 mm; 2557 unique reflections with $F \geqslant 2.33\sigma(F)$ were refined to conventional values of $R = 3.46$ and $R_w = 4.25\%$.†

Anhydrous VCl_3 was dissolved in an ethanolic solution of three equivalents of Na_2edt to produce a deep red solution; red-black microcrystals were precipitated on addition of Ph_4PBr. Recrystallisation from warm DMF–MeCN–Et_2O gave black prisms of (**2**) suitable for *X*-ray studies.

Crystal data: $C_{56}H_{56}P_2S_8V_2$, $M = 1149.36$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 18.371(6)$, $b = 9.724(3)$, $c = 29.966(10)$Å, $\beta = 98.76(1)°$, $U = 5290.48$ Å^3, $T = -158$ °C, crystal dimensions 0.18 × 0.18 × 0.22 mm; 5574 unique reflections with $F \geqslant 2.33\sigma(F)$ were refined to conventional values of $R = 5.56$ and $R_w = 5.60\%$.†

The structure of the anion of (**1**) is shown in Figure 1. The vanadium atom is in a square pyramidal co-ordination environment, the basal positions being occupied by sulphur atoms S(3,6,7,10) of two bidentate ethanedithiolate ligands, and the oxygen atom occupying the apex. The molecule thus possesses idealised C_{2v} symmetry. The V(1)–O(2) distance [1.625(2) Å] is consistent with the presence of a vanadium–oxygen double bond (*i.e.*, the vanadyl $V{=}O^{2+}$ moiety) but is slightly longer than that normally found in this geometry ($\leqslant 1.60$ Å) in the absence of a sixth ligand *trans* to the oxygen.[10] This is reflected in the V=O stretching vibration which occurs at 928 cm^{-1}, nearer the lower end of the usual range associated with this group (950 ± 50 cm^{-1}).[9,10] The vanadium atom lies 0.668 Å above the basal plane of four sulphurs. In addition, the sodium atom makes close contacts with two solvent oxygen atoms (Na–O, 2.326, 2.402 Å) and the vanadyl oxygens from two adjacent V=O units (Na–O, 2.440, 2.455 Å).

Solutions of (**1**) in dimethyl sulphoxide at room temperature display an isotropic eight-line e.s.r. spectrum with $g_{iso} = 1.979$, consistent with a d^1 species, with hyperfine coupling $A_{iso} = 75 \times 10^{-4}$ cm^{-1} due to the ^{51}V ($I = 7/2$) nucleus. In frozen solution at 77 K an anisotropic spectrum is obtained with $g_{\parallel} = 1.981$ ($A_{\parallel} = 133 \times 10^{-4}$ cm^{-1}) and $g_{\perp} = 1.984$ ($A_{\perp} = 42 \times 10^{-4}$ cm^{-1}).‡ The similarity between $g_{\parallel}$ and $g_{\perp}$ and the relatively small values of $A_{\parallel}$ and $A_{\perp}$ when compared with those for, *e.g.*, $VO(acac)_2$[11] [$g_{\parallel} = 1.943$ (± 0.005); $A_{\parallel} = 167$ (± 3) $\times 10^{-4}$ cm^{-1}; $g_{\perp} = 1.980$ (± 0.001); $A_{\perp} = 61$ (± 2) $\times 10^{-4}$ cm^{-1}] suggest significant π interactions in (**1**) between the sulphur lone pairs and the metal d orbitals leading to increased delocalisation of the vanadium d electron and increased electron density at the vanadium atom in comparison with $VO(acac)_2$. This we suggest is also the primary cause of the increased V=O bond distance in (**1**) and its correspondingly lowered stretching frequency.

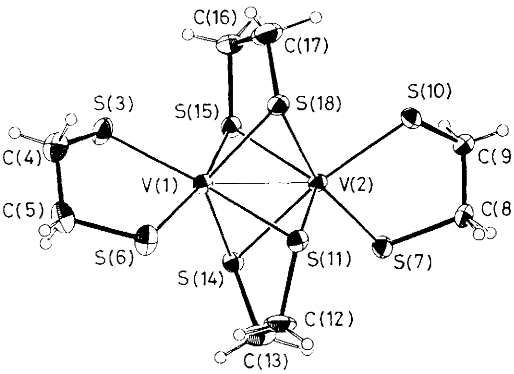

Figure 2. The structure of the $[V_2(SCH_2CH_2S)_4]^{2-}$ anion of (**2**); non-hydrogen atoms are depicted as 50% probability ellipsoids. Selected bond lengths (Å) and angles (°) are: V(1)–V(2) 2.600(2), V(1)–S(3) 2.389(2), V(1)–S(6) 2.381(2), V(2)–S(7) 2.385(2), V(2)–S(10) 2.370(2), V(1)–S(11) 2.514(2), V(1)–S(14) 2.394(2), V(1)–S(15) 2.514(2), V(1)–S(18) 2.385(2), V(2)–S(11) 2.401(2), V(2)–S(14) 2.497(2), V(2)–S(15) 2.408(2), V(2)–S(18) 2.491(2); S(14)–V(1)–S(15) 71.1(1), S(11)–V(1)–S(15) 112.1(1), S(3)–V(1)–S(15) 82.2(1), S(3)–V(1)–S(6) 84.2(1), S(6)–V(1)–S(11) 82.5(1).

The structure of the anion of (**2**) is depicted in Figure 2. Two dithiolate groups provide four μ_2-sulphur atoms S(11,14,15,18) to yield a quadruply bridged vanadium(III) dimer [mean $V{-}S_{br.} = 2.45(5)$ Å] Each V–S–V bridge is, however, significantly asymmetric [*e g.*, V(1)–S(11) = 2.514(2), V(2)–S(11) = 2.401(2) Å and V(1)–S(14) = 2.394(2), V(2)–S(14) = 2.497(2) Å] a situation also found (to a greater extent) in $[M_2(edt)_4]^{2-}$ ($M = Mn^{III}$, Fe^{III})[12,13] which, however, do not possess the same overall structure. Each vanadium is additionally co-ordinated by a terminal dithiolate group. The orientations of these V(1)–S(3)–S(6) and V(2)–S(7)–S(10) planes are staggered (dihedral angle = 102.0°) which affords a molecule of idealised D_2 symmetry, none of whose elements are crystallographically imposed. An alternative and convenient way of describing the structure of (**2**) is as two staggered and interlocking distorted square-planar VS_4 units, V(1)–S(3,6,11,15) and V(2)–S(7,10,14,18). Finally, each vanadium atom is six-co-ordinate (excluding the probable presence of direct metal–metal bonding), but the distortions from both octahedral and trigonal prismatic geometry are so severe that the co-ordination is best described as square prismatic (cubic) with two vacant sites, corresponding to a total of four terminal positions in the dimer.

The two complexes described herein represent the first products in our systematic investigation of vanadium thiolate chemistry with various metal oxidation states and types of thiolate ligand. We consider them to presage a rich new area of vanadium co-ordination chemistry.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallography Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Quoted *g* values are corrected for second-order shifts.

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