Synthesis and Structure of $[V_3S_2O_3(S_2CNEt_2)_3]^-$: a Trinuclear Vanadium Cluster with Bridging Vanadyl Groups

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$[V_3S_2O_3(S_2CNEt_2)_3]^-$ is prepared and shown to comprise an $\{(Et_2NCS_2)VO(\mu_2\text{-}S)_2VO(S_2CNEt_2)\}$ component, the two oxo-groups of which are bound *cis* to the oxo-group of a $VO(S_2CNEt_2)$ moiety to form a novel trinuclear vanadium cluster.

The coordination chemistry of vanadium bound to sulfur and/or sulfur-donor ligands has attracted increased attention in recent years,[1] owing to its relevance to various chemical, industrial and biological systems, such as removal of vanadium impurities from the heavier crude oils,[2] vanadium–sulfur electrical conductors,[3] and vanadium nitrogenase.[4,5] However, the structural information available in this area is much more limited than that for Mo/S and W/S systems. Here, we report the synthesis of $[NEt_4][V_3S_2O_3(S_2CNEt_2)_3]\cdot1.5H_2O$ **1**, the anion of which represents a novel trinuclear vanadium(IV) cluster involving μ_2-vanadyl oxo-groups.

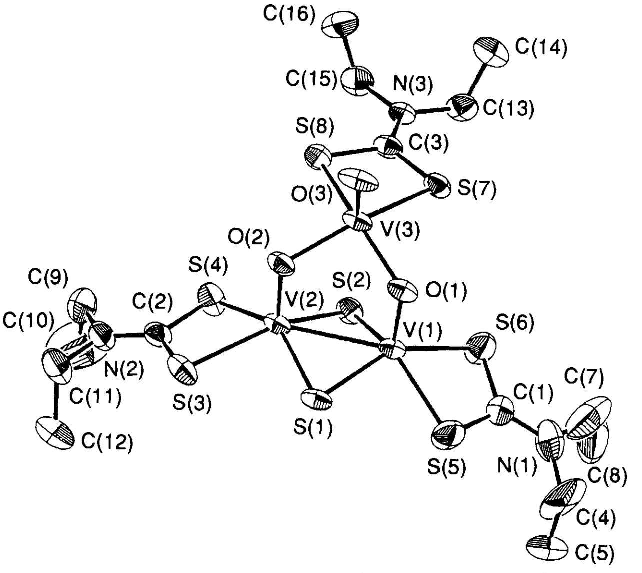

Fig. 1 Structure of the anion of $[NEt_4][V_3O_3S_2(S_2CNEt_2)_3]\cdot1.5H_2O$. Selected interatomic distances: V(1)···V(2) 2.715(3), V(1)–O(1) 1.684(8), V(1)–S(1) 2.263(4), V(1)–S(2) 2.228(4), V(1)–S(5) 2.424(4), V(1)–S(6) 2.451(4), V(2)–O(2) 1.665(7), V(2)–S(1) 2.257(4), V(2)–S(2) 2.246(4), V(2)–S(3) 2.422(4), V(2)–S(4) 2.430(4), V(3)–O(1) 1.999(8), V(3)–O(2) 2.008(8), V(3)–O(3) 1.587(8), V(3)–S(7) 2.417(4), V(3)–S(8) 2.429(4) Å.

1 was synthesised by reacting VCl_3, Li_2S, $[NEt_4]Br$ and $NaS_2CNEt_2\cdot3H_2O$ (1 : 2 : 1 : 1) in MeCN under an atmosphere of purified dinitrogen. The slurry was stirred overnight at room temp., the resultant dark red–brown solution was filtered and the filtrate allowed to stand at −20 °C for several days, after which air-sensitive black prismatic crystals formed. Elemental analyses consistent with the formulation $[NEt_4][V_3S_2O_3(S_2CNEt_2)_3]\cdot1.5H_2O$ were obtained and the crystals were suitable for investigation by X-ray crystallography.†

In the crystal unit cell there are eight molecules of **1**, which are related by the symmetry elements of the *C2/c* space group. The molecular structure of the anion (Fig. 1) contains a

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† *Crystal data*: $C_{23}H_{53}N_4S_8V_3O_{4.5}$, monoclinic, space group *C2/c*, $Z = 8$, $a = 26.550(3)$, $b = 15.953(2)$, $c = 23.394(3)$ Å, $\beta = 123.578(4)^0$, $V = 8255(3)$ Å^3, $D_c = 1.395$ g cm^{-3}, $F(000) = 3616$, Cu-Kα radiation, $\lambda = 1.5418$ Å, μ(Cu-Kα) = 96.75 cm^{-1}. The structure was solved by direct methods.[14] The non-hydrogen atoms were refined either anisotropically for the anion or isotropically for the $[NEt_4]^+$ cation and H_2O. Hydrogen atoms of S_2CNEt_2 ligands of the title compound were included in the structure factor calculation in idealized positions (C–H = 0.95 Å), and were assigned isotropic temperature factors but the hydrogen atoms of the $[NEt_4]^+$ cation and the H_2O molecule were not included because of the disorder of the 4-CH_2-carbon and the oxygen atom, respectively. The final cycle of full-matrix least-squares refinement was based on 3627 observed reflections $[I > 3.00\sigma(I)]$ and 379 variable parameters and converged with unweighted and weighted agreement factors $R = 0.073$, $R_w = 0.110$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.82 and −0.56 e Å^{-3}, respectively. A single crystal (0.35 × 0.30 × 0.58 mm) was mounted in a glass capillary which was flame-sealed under an atmosphere of dinitrogen. The diffraction data were collected on a Rigaku AFC5R diffractometer with graphite monochromator, using the $\omega/2\theta$ scan technique to a maximum 2θ value of 120.1°, Lorentz polarization and absorption corrections were applied to the data. All calculations were performed using the TEXSAN crystallographic software package.[15]

Diffraction data of the title complex were also recorded with Mo-Kα radiation, but the resolution was not significantly improved due to the disorders of the crystal structure.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

dimeric $V_2O_2(\mu_2\text{-}S)_2$ moiety, of which the vanadyl oxygens, O(1) and O(2), bond *cis* to another oxovanadium centre, V(3)=O(3), to form a $V_3O(\mu_2\text{-}O)_2(\mu_2\text{-}S)_2$ core. Each vanadium is ligated to a bidentate S_2CNEt_2 group and the anion approximates to C_s symmetry.

The anion of **1** represents the first example of *cis*-coordination of the one oxovanadium(IV) centre by two other such centres. The *cis*-bridges, V(1)–O(1)–V(3) and V(2)–O(2)–V(3), involve angles of 112.7(4) and 113.7(4)°, respectively and the V(1)···V(3) and V(2)···V(3) separations are 3.072(3) and 3.080(3) Å, respectively. *trans*-Coordination of one V=O group by another has been identified in, *e.g.* [(VO(salpn)] [(salpn = propane-1,2-diylbis(salicylideneaminato)][6] and $VO(SiP_2O_8)$[7] with V=O···V angles of 158.2 and 180°, respectively. The length of the V(3)–O(3) bond [1.587(8) Å] is typical of that for terminal oxovanadium(IV) groups[8] (see below). Coordination of O(1) and O(2) to V(3) involves V(3)–O bonds of a normal[8] length [1.999(8) and 2.008(8) Å, respectively] and leads to a significant lengthening of the two V=O bonds: V(1)–O(1) = 1.684(8); V(2)–O(2) = 1.665(7) Å. The IR spectrum of **1** in KBr includes strong absorptions at 971 and 844 cm^{-1}. The former is assigned to the V(3)–O(3) stretching frequency, comparable with the frequency of 970 cm^{-1} for $[VO(S_2CNEt_2)_2]$;[9] the latter is attributed to the stretching of V(1)–O(1) and V(2)–O(2), and occurs at a slightly lower value than the V–O stretching frequency of 854 cm^{-1} of [VO(salpn)][6] the V–O bond of which is *ca.* 0.03 Å shorter than V(1)–O(1) and V(2)–O(2).

The vanadium atoms [V(1) and V(2)] of the $V_2O_2(\mu_2\text{-}S)_2$ moiety are pyramidally coordinated by an oxygen atom at the apex and four sulfur atoms in the plane, two of which are the bridging sulfur atoms [S(1), S(2)] and two are sulfur atoms from a terminal bidentate S_2CNEt_2 ligand. V(1) is 0.66 Å out of the plane of S(1), S(2), S(5) and S(6) and V(2) is 0.64 Å out of the plane S(1), S(2), S(3) and S(4). This is the first structural characterisation of the $V_2Y_2(\mu_2\text{-}S)_2$ (Y=O,S) bridging arrangement although the corresponding molybdenum analogues, $Mo_2Y_2(\mu_2\text{-}S)_2$ are well known.[10] The V(1)–V(2) separation of 2.715(3) Å can be considered in the context provided by the V···V distance of 2.610(1) Å in $[(Pr^iC_5H_4)_2V_2S_4]$[11] and the Mo···Mo distance in $[Mo_2O_2S_2(S_2CNH_2)_2]\cdot 2MeCN$,[12] both of which are considered to involve a metal–metal bond.

The EPR (electron paramagnetic resonance) signal of powdered, crystalline **1** at 295 K manifests a spectrum similar to that of monooxovanadium(IV) centres such as in $[NMe_4]_2[VO(S_2C_2H_4)_2]$.[13] Thus, the paramagnetism of **1** appears to be associated with a single vanadium centre. Based on the composition and structure of **1**, the cluster is considered to be comprised of the three V^{IV} centres. The pair of d-electrons associated with V(1) and V(2) are considered to be spin-coupled by the V···V interaction over 2.715(3) Å and the EPR signal arises from the V(3) centre.

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