Coordination and Oxidation of Vanadium(II) by 1,2-Bis(2-sulfidophenylsulfanyl)ethane(2−) (S_4): the Structures of [V(S_4)tmeda], the First Example of Vanadium(II)–Sulfide Coordination, and of [V_3(μ-O)$_2$(S_2)$_4$(tmeda)$_2$] (S_2 = 1,2-benzenedithiolate(2−))

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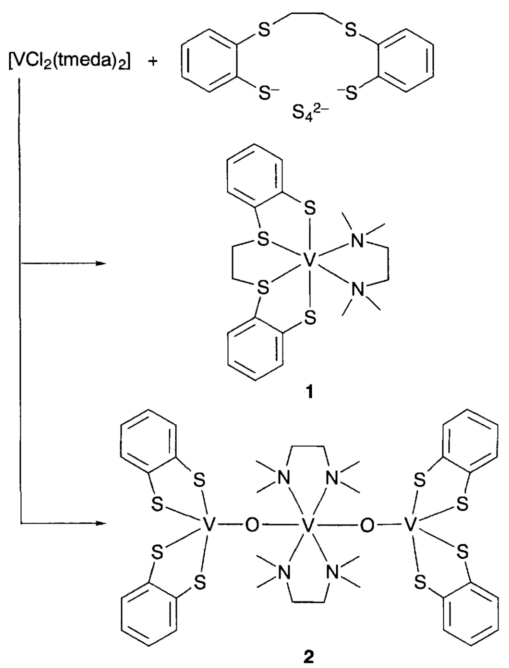
[VCl_2(tmeda)] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) reacts with the tetradentate sulfur ligand 1,2-bis(2-sulfidophenylsulfanyl)ethane(2−) (S_4) to form [V(S_4)tmeda] with S_4 acting as a thiolato and sulfide donor; the trinuclear, linear, oxo-bridged complex [V_3(μ-O)$_2$(S_2)$_4$(tmeda)$_2$] [S_2 = 1,2-benzenedithiolate(2−)] is formed as a byproduct.

Recent interest in the chemistry of divalent vanadium has been stimulated by its ability to activate and fix N_2. Several ill-defined bulk systems containing V^{II} and oxygen donors such as catecholate, hydroxide, α,ω-dicarboxylates with or without additional reducing agents convert dinitrogen into ammonia and/or hydrazine.[1] Further, a few V^{II} complexes with bridging dinitrogen, and stabilized by *N*-functionalised and σ-*C* bonded ligands have been characterised, some of which react with protic agents to yield ammonia.[2] On the other hand, sulfur is involved in the vanadium environment of vanadium nitrogenase, the cofactor of which, in its reduced form, contains V^{II} coordinated to S^{2-} (and possibly also to histidine and homocitrate).[3] We have therefore started a programme to synthesise divalent vanadium complexes in biologically more relevant coordination spheres by employing the tetradentate sulfur ligand 1,2-bis(2-sulfidophenylsulfanyl)ethane(2−) (S_4). Many Group VI and VIII transition metal complexes with this ligand have been characterised and several of these compounds have been addressed as model compounds for the active sites in nitrogenases and oxidoreductases.[4]

So far, only two V^{II} thiolato complexes have been structurally characterised, in which pyridine-2-thiolate acts as a bidentate ligand, and it has been suggested that the pyridine nitrogen is essential for complex formation and stability.[5] We now show that sulfide functions stabilize V^{II} in a mixed thiolato/sulfide ligand set. The chemistry of sulfide complexes of vanadium is scarcely developed; a few V^{III} complexes with alkylsulfides, and the structure of a V^{IV} complex stabilised by crown thioether complexation have been reported.[6]

[V(S_4)tmeda] **1** is, to the best of our knowledge, the first vanadium complex ligated by thiolato and sulfide donor functions and, furthermore, the first V^{II} sulfide complex. Compound **1** is formed by treatment of [VCl_2(tmeda)$_2$] with Na_2(S_4) in THF at ambient temperatures (Scheme 1). The compound precipitates as a red solid in moderate yields (20–30%) after stirring the reaction mixture for 12 h, filtration and cooling to 4 °C. The IR spectrum shows two intense bands at 380 [ν(VS)$_{as}$] and 309 cm^{-1} [ν(VS)$_{s}$]. CV and coulometry of **1** in CH_2Cl_2 exhibit a reversible, kinetically hampered oxidation/reduction step (−0.31/−0.44 V; relative to SCE). Single crystals of **1**·thf suitable for X-ray structure analysis† were obtained by recrystallisation of **1** from THF. The molecular structure of **1** is shown in Fig. 1. The hexa-coordinated vanadium lies in the centre of a slightly distorted octahedron, with vanadium, the two amine and the two sulfide functions forming the plane. The thiolato groups are located in *trans* positions and shifted away from tmeda [S(1)–V–S(4) = 165.42(5)°]. The structure parameters of the [V(tmeda)] moiety fit well with the data of other V^{II} tmeda complexes.[7] The V–S(thiolato) bond lengths [2.476(2) and 2.485(2) Å] are slightly shorter than in the complexes formed between V^{II} and pyridine-2-thiolate (av. 2.546 Å). Despite the different sulfur donor types, all of the V–S bond distances are about the same (av. 2.479 Å), probably as a result of electron delocalisation mediated through the phenyl rings, and a rather high affinity of the sulfide towards a relatively electron-rich, and therefore soft V^{II} centre, leading to comparatively short *d*[V–S(sulfide)].



Scheme 1

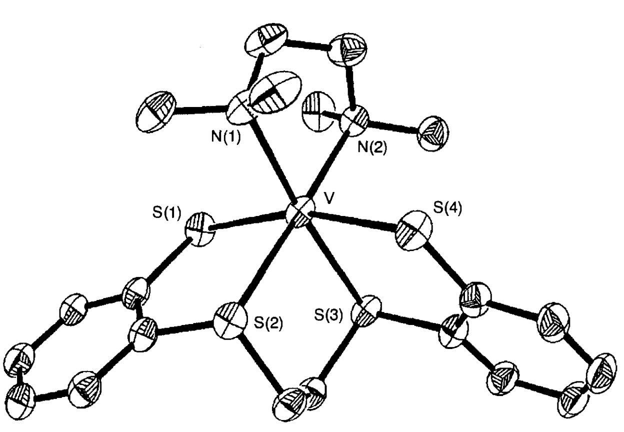


Fig. 1 ORTEP plot (50% probability ellipsoids) of [V(S_4)tmeda], **1**. Selected bond distances (Å) and angles (°): V–N(1) 2.243(4), V–N(2) 2.235(4), V–S(1) 2.476(2), V–S(2) 2.477(2), V–S(3) 2.479(2), V–S(4) 2.485(2), N(1)–V–N(2) 82.2(1), S(1)–V–S(4) 165.42(5), S(1)–V–S(2) 83.14(6), S(2)–V–S(3) 86.72(5), S(3)–V–S(4) 83.06(6), S(1)–V–N(1) 96.7(1), S(2)–V–N(1) 97.3, S(3)–V–N(1) 175.1(1), S(4)–V–N(1) 94.4(1).

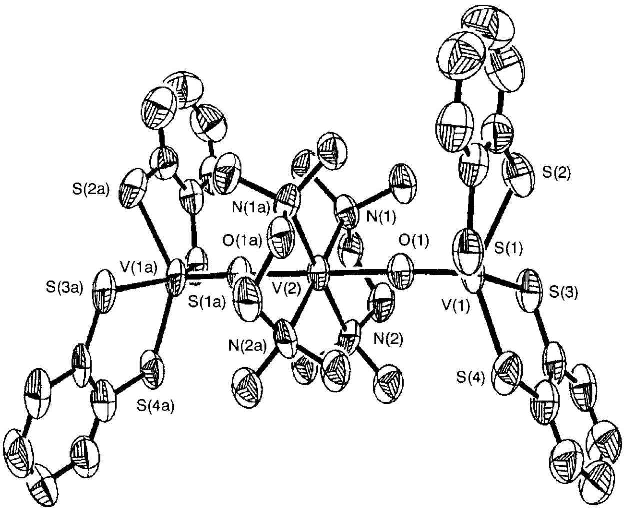


Fig. 2 ORTEP plot (50% probability ellipsoids) of $[V_3(\mu\text{-}O)_2(S_2)_4(tmeda)_2]$, **2**. Selected bond distances (Å) and angles (°): V(1)–O(1) 1.668(6), V(2)–O(1) 2.001(6), V(1)–S(1) 2.377(3), V(1)–S(2) 2.344(3), V(1)–S(3) 2.367(3), V(1)–S(4) 2.343(3), V(2)–N(1) 2.275(7), V(2)–N(2) 2.253(7), V(1)–O(1)–V(2) 177.9(4), S(1)–V(1)–S(2) 83.6(1), S(1)–V(1)–S(4) 83.9(1), S(2)–V(1)–S(3) 84.0(1), O(1)–V(1)–S(1) 105.5(2), O(1)–V(1)–S(2) 112.1(2), O(1)–V(1)–S(3) 105.0(2), O(1)–V(1)–S(4) 113.2(2), N(1)–V(2)–N(2) 81.2(3), O(1)–V(2)–O(1a) 180.

The complexation reaction between $[VCl_2(tmeda)_2]$ and $Na_2(S_4)$ is accompanied by a redox reaction between these two components (Scheme 1), leading to the trinuclear $[V_3(\mu\text{-}O)_2(S_2)_4(tmeda)_2]$ **2**. In the course of this reaction, the ligand S_4 is reductively cleaved to form S_2 and ethylene. Concomitantly, O^{2-} is incorporated, possibly from traces of water, rather than from solvent decomposition. Yields are *ca.* 30%. Compound **2** is not formed in very rigorously dried THF; and it is the only isolated product in wet THF. Black crystals of **2** grew when storing the mother liquor obtained after removal of **1** at 2 °C for a month. The X-ray structural analysis of **2**‡ (Fig. 2) reveals that the compound, in addition the two coordinated tmeda ligands, contains two defined molecules of tmeda of crystallisation, along with further disordered solvent molecules.§ In the central $V(tmeda)_2$ unit, formally with V^{II}, the d(V–N) are again in the usual range. The two terminal vanadium atoms, formally V^V, carry four thiolato donors with d(V–S) (av. 2.376 Å) in the expected range for thiolates binding to vanadyl centres.[8] Vanadium is displaced from the best plane formed by the four thiolates by 0.76 Å towards the bridging oxygen. The V=O double bond [1.668(6) Å] is longer than usually observed for non-bridging vanadyl oxygens (1.58 Å). This lengthening of the double bond corresponds to a rather low ν(V=O) = 884 cm^{-1}. The V–O bond lengths in the $V_2\mu$–O bridges [1.668(6) and 2.001(6) Å] are comparable to the double and single bond lengths in oxo-bridged V^{IV} complexes.[9] On this basis, **2** may also be considered a $(V^{IV})_3$ rather than a mixed valence $(V^V)_2(V^{II})$ complex.

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Footnotes

† *Crystal data* for **1**·thf. $C_{24}H_{36}N_2OS_4V$; M = 547.73, dark-red prisms (0.5 × 0.5 × 0.15 mm), sensitive to loss of solvent, triclinic, space group $P\bar{1}$, a = 9.305(4), b = 12.627(5), c = 12.83(8) Å, α = 116.95(3), β = 93.56(5), γ = 96.03(4)°, V = 1324.3 Å^3, Z = 2, D_c = 1.374 g cm^{-3}, μ(Mo-Kα) = 0.71 mm^{-1}. Data collection was carried out on a Hilger & Watts diffractometer (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, T = 153 K) in the 2θ scan mode, θ range 1.8–27.6°, 7867 reflections measured, 6038 independent, 4507 with $I > 2\sigma(I)$ considered as observed. Solution by direct methods (SHELX-86), refinement with SHELXL-93, 329 refined parameters, $R1$ = 0.0719, w$R2$ = 0.1893, non-hydrogen atoms refined anisotropically, hydrogen atoms calculated into ideal positions and included in the final FMLS refinement.

‡ *Crystal data* for **2**·(tmeda)$_2$·(solvent$_n$):§ $C_{73}H_{80}N_8O_2S_8V_3$; M = 1506.08, black blocks (0.4 × 0.4 × 0.4 mm), sensitive to loss of solvent, rhombohedral, space group R-3c, a = 26.825(8), b = 26.825(8), c = 57.90(2) Å, V = 36080 Å^3, Z = 18, D_c = 1.248 g cm^{-3}, μ(Cu-Kα) 5.14 mm^{-1}. Data collection was carried out on an Enraf-Nonius CAD4 diffractometer (Cu-Kα radiation, λ = 1.54178 Å, graphite monochromator, T = 173 K) in the 2θ scan mode, θ range 2.44–57.03°, 16287 reflections measured, 5426 independent, 3723 with $I > 2\sigma(I)$ considered as observed. Solution by direct methods (SHELX-86), refinement with SHELXL-93, 489 refined parameters, $R1$ = 0.1015, w$R2$ = 0.2296, non-hydrogen atoms were refined anisotropically (except of the unassigned solvent carbons), hydrogen atoms calculated at ideal positions and included in the final FMLS refinement.

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

§ In addition, there is residual electron density due to erratically disordered solvent (THF) and/or additional tmeda molecules. No suitable model for the assignment and disorder was found. The residual electron density was therefore modelled as carbon with constant isotropic temperature factors (0.1) and free site occupancy parameters, amounting to an equivalent of 25 carbons. Despite these disorder problems, the molecular structure of **2**·(tmeda)$_2$ was well determined.

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