

Vanadium complexes of the $\text{N}(\text{CH}_2\text{CH}_2\text{S})_3^{3-}$ ligand with co-ligands relevant to nitrogen fixation processes

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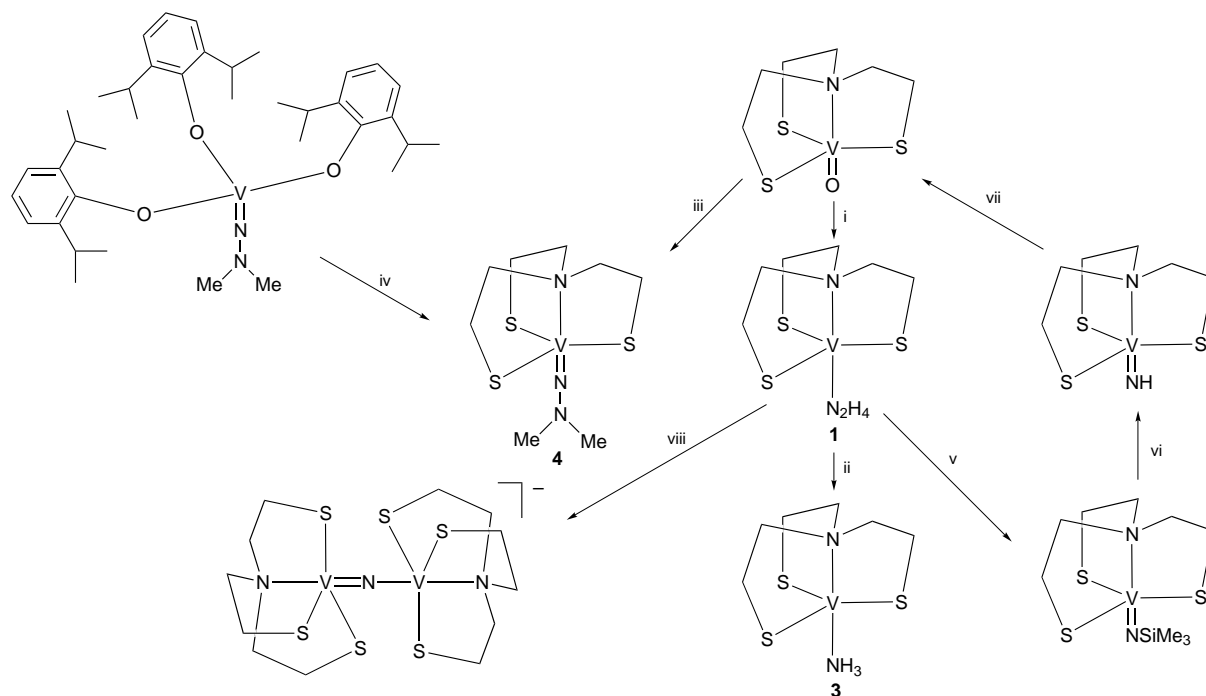
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Vanadium(III) and vanadium(V) complexes of the tris(2-thiolatoethyl)amine ligand L^{3-} containing hydrazine, hydrazide, imide, ammine, cyanide and isocyanide ligands are synthesised; the complexes $[\text{V}(\text{NH}_3)\text{L}]$ and $[\text{V}(\text{NNMe}_2)\text{L}]$ have been structurally characterised.

The cofactor of molybdenum nitrogenase contains an MoFe_7S_9 cluster with the Mo atom ligated by one nitrogen, three sulfurs and two oxygens¹ and it is thought that the vanadium atom in the analogous vanadium nitrogenase² is in a similar environment, as is possibly one of the iron atoms in the third 'iron-only' nitrogenase.³ The chemistry of V, Mo and Fe centres which carry three sulfurs (plus other ligands) (MS_3 sites) is therefore of great importance in understanding the mode of action of these enzymes. In particular, reduction of N_2 to NH_3 might involve intermediate species N_2H_m and NH_n ($m = 0-4$, $n = 0-3$) bound at MS_3 sites.⁴ Here we report use of the ligand $\text{N}(\text{CH}_2\text{CH}_2\text{S})_3^{3-}$ [L^{3-}] to generate a range of complexes of N_2H_m and NH_n and related ligands at MS_3 sites, particularly for vanadium, where there is very limited chemistry of reduced nitrogen species at this metal in a sulfur-donor environment.^{4,5} Key reactions to generate the vanadium series are shown in Scheme 1. All compounds described in this paper have been characterised by microanalysis and magnetic and spectroscopic data.

Treatment of $[\text{VO}(\text{L})]^{6-}$ with four equivalents of anhydrous hydrazine in acetonitrile removes the oxide ligand to give an almost quantitative yield of the complex $[\text{V}(\text{NH}_2\text{NH}_2)\text{L}]$ **1** as an insoluble yellow powder. When **1** is heated in suspension in tetrahydrofuran a decomposition/disproportionation reaction takes place giving a dark green, poorly soluble precipitate of composition VL **2** and a yellow solution from which $[\text{V}(\text{NH}_3)\text{L}]$ **3** crystallises on cooling. The structure of **3** is shown in Fig. 1.† The geometry around the V atom is trigonal bipyramidal with the S atoms in equatorial positions and N(4)–V–N(5) almost linear. The V–N(4) bond distance [2.155(8) Å] in **3** is considerably shorter than the corresponding distance in $[\text{VO}(\text{L})]^{6-}$ [2.291(6) Å], presumably reflecting the high *trans*-influence of the oxide ligand of $[\text{VO}(\text{L})]$ relative to the NH_3 ligand in **3**. Individual molecules of **3** are held in chains by hydrogen bonds between the three hydrogen atoms of the ammine ligand and the S atoms of neighbouring molecules.

The formation of **1** probably involves a hydrazide intermediate such as $[\text{V}(\text{NNH}_2)\text{L}]$, since treatment of $[\text{VO}(\text{L})]$ with $\text{Me}_3\text{SiNHNMe}_2$ gives diamagnetic $[\text{V}(\text{NNMe}_2)\text{L}]$ **4**, whose X-ray structure is shown in Fig. 2.† As far as we are aware, this is the first hydrazide of vanadium with sulfur-donor co-ligands. Compound **4** can also be prepared from $[\text{V}(\text{OC}_2\text{H}_3\text{Pr}_2-2,6)_3(\text{NNMe}_2)]$.⁷ The V–NNMe₂ distance in **4** is shorter than the



Scheme 1 Reagents and conditions: i, 4 equiv. N_2H_4 , MeCN, 20 °C; ii, thf, 60 °C; iii, $\text{Me}_3\text{SiNHNMe}_2$, CH_2Cl_2 , 20 °C; iv, 1.5 equiv. H_3L , hexane, 20 °C; v, excess N_3SiMe_3 , MeCN, 80 °C; vi, MeCN– H_2O , 20 °C; vii, NMe₄OH, MeOH, 60 °C, 10 min, then HCl–Et₂O; viii, NEt_4Cl , MeCN, 80 °C, then excess NaN_3 , MeCN, 80 °C

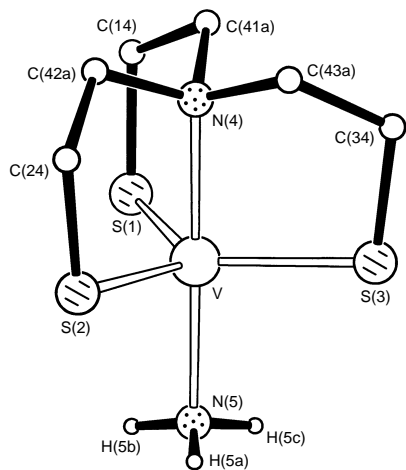


Fig. 1 The molecular structure of **3**. There is disorder of the three C(4*n*) atoms (*n* = 1–3); the principal component, with *ca.* 80% occupancy, C(4*na*) is shown here. Selected bond lengths (Å) and angles (°): V–N(5) 2.154(7), V–N(4) 2.155(8), V–S(1) 2.283(3), V–S(2) 2.285(3), V–S(3) 2.301(3); N(5)–V–N(4) 178.7(3), N(5)–V–S(av.) 93.9(5), N(4)–V–S(av.) 86.1(2).

V–NH₃ distance in **3**, and the V–NS₃ distance is correspondingly longer in **4** [2.214(3) Å], approaching that in [VO(L)]. The N–N distance of the hydrazide ligand [1.305(5) Å] is in the range generally found in hydrazide complexes of the early transition metals^{8,9} and in the only structurally characterised hydrazide complexes of vanadium, [V(C₅H₅)₂{NN(SiMe₃)₂}] [1.369(9) Å],¹⁰ the anion [VCl₂(NH₂NMePh)₂(NNMePh)][–] [1.295(17) Å]¹¹ and [(C₉H₁₈N₂)₂(OSiMe₃)₂V(μ-O)VO(O-SiMe₃)₂] [1.285(3) and 1.245(4) Å].⁹ However, whilst there is no doubt of the nature of the NNMe₂ ligand in **4**, it is unusual in that the N–C distances appear to be unequal [1.401(15), 1.502(15) Å] and N(3) lies some 0.21 Å out of the plane formed by N(2), C(7) and C(8) (Fig. 2). This phenomenon is under further investigation.

Novel nitride and imide complexes have been obtained from **1** as shown in Scheme 1. The dimer NBu₄[LV(μ-CN)V], the salt NEt₄[VCl(L)] and the adducts [V(NCMe)L] and

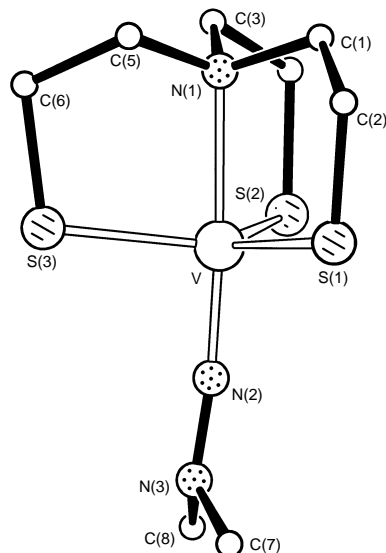


Fig. 2 The molecular structure of **4**. Selected bond lengths (Å) and angles (°): V–N(1) 2.214(3), V–N(2) 1.681(3), N(1)–C(1) 1.514(9), V–S(1) 2.261(3), V–S(2) 2.273(3), V–S(3) 2.255(2), N(2)–N(3) 1.305(5), N(3)–C(7) 1.401(15), N(3)–C(8) 1.502(15); N(1)–V–N(2) 176.6(2), V–N(2)–N(3) 173.9(4), N(1)–V–S(av.) 84.4(3), N(2)–V–S(av.) 95.6(14)°.

[V(CNBut⁺)L] have also been obtained from reaction of **3** with NBu₄CN, NEt₄Cl, MeCN and CNBu⁺ respectively.

The characterisation of this set of nitrogen-donor ligands at a VS₃ site lends further credence to the idea that fixation of N₂ could occur at the vanadium site of vanadium nitrogenase,^{2,4,5} and we intend to probe this further by study of the interconversion of the various NR (NR = N₂H₄, NH₃, NH, etc.) ligands in these compounds.

We have also prepared [Fe(NH₂NH₂)L] and a very insoluble compound formulated as Mo(NH₂NH₂)L which appears to be polymeric; their properties will be described at a later date.

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Footnotes

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† *Crystal structure analyses: crystal data:* **3**: C₆H₁₅N₂S₃V, *M* = 262.3, orthorhombic, space group P2₁2₁2₁ (no. 19), *a* = 8.0612(6), *b* = 16.6065(13), *c* = 8.5004(12) Å, *U* = 1137.9(2) Å³, *Z* = 4, *D_c* = 1.531 g cm^{–3}, *F*(000) = 544, μ(Mo–Kα) = 13.3 cm^{–1}, *T* = 293 K, λ(Mo–Kα) = 0.710 69 Å. Crystals are yellow, translucent plates. One, *ca.* 0.40 × 0.08 × 0.05 mm mounted on a glass fibre; photographic examination; Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for accurate cell parameters (25 reflections, θ = 10–11°, each centred in four orientations) and diffraction intensities (1175 unique reflections to θ_{max} = 25°, 729 ‘observed’ with *I* > 2σ). Structure determined by automated Patterson routines;¹² refined (on *F_o²*) by full-matrix least-squares methods¹³ to *wR*₂ = 0.093 and *R*₁ = 0.085 for 1170 reflections weighted *w* = σ(*F_o²*)^{–2}.

4: C₈H₁₈N₃S₃V, *M* = 303.4, monoclinic, space group P2₁ (no. 4), *a* = 7.494(1), *b* = 11.649(2), *c* = 7.584(2) Å, β = 92.03(1)°, *U* = 661.5(2) Å³, *Z* = 2, *D_c* = 1.523 g cm^{–3}, *F*(000) = 316, μ(Mo–Kα) = 12.0 cm^{–1}, *T* = 300 K, λ(Mo–Kα) = 0.710 69 Å. Crystals are red, rectangular prisms. One, *ca.* 0.5 × 0.3 × 0.2 mm, sealed in a glass capillary under dinitrogen; Kuma KM-4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (25 reflections, θ = 8.5–13°, each centred in four orientations) and for measurement of diffraction intensities (1218 unique reflections to θ_{max} = 25°; 1118 were ‘observed’ with *I* > 2σ). Structure determined by direct methods;¹² refinement on *F²* by full-matrix least-squares methods¹³ to *wR*₂ = 0.089 and *R*₁ = 0.032 for the ‘observed’ reflections weighted *w* = {σ²(*F²*) + (0.0458*P*)² + 0.56*P*}^{–1}, with *P* = (*F_o²* + 2*F_c²*)/3. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/487.

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