Preparation and X-Ray Crystal Structure of the Triply Hydrazide-bridged Complex $[NH_2Me_2]_2[\{VCl_3\}_2(\mu\text{-}NNMe_2)_3]$: a Species derived from the Disproportionation of $SiMe_3NHNMe_2$

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The reaction of $[VCl_3(PMePh_2)_2]$ or $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with $SiMe_3NHNMe_2$ produces the first triply hydrazide-bridged complex, identified by X-ray crystallography as $[NH_2Me_2]_2[\{VCl_3\}_2(\mu\text{-}NNMe_2)_3]$ in which the cations are formed by cleavage of the hydrazine and the bridge in the anion comprises two hydrazide(2^-) residues and one isodiazene residue.

The discovery that the enzyme nitrogenase can be based on vanadium, rather than molybdenum,[1] has led to a renewed interest in the dinitrogen chemistry of vanadium complexes.

Protonation of dinitrogen complexes of vanadium gives ammonia: from the mononuclear complex anion *trans*-$[V(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]^-$ **1** [reaction (1)][2] and from the binuclear complex $[\{V(C_6H_4NMe_2)_2(C_5H_5N)\}_2(\mu\text{-}N_2)]$ **2** [reaction (2)].[3]

$$\mathbf{1} + 3H^+ \rightarrow 3/2N_2 + NH_3 \qquad (1)$$

$$\mathbf{2} + 2H^+ \rightarrow 2/3NH_3 + 2/3N_2 \qquad (2)$$

It is very likely that metal-bound diazenide or hydrazide species are intermediates in these reactions, as has been established for related reactions of dinitrogen complexes of molybdenum and tungsten.[4] We have therefore sought routes to such hydrazides and report here the formation of the first triply hydrazide-bridged complex from the reaction of vanadium(III) compounds and $SiMe_3NHNMe_2$. The reaction involves the formal disproportionation shown in reaction (3).

$$2Me_2NNH_2 \rightarrow Me_2N{=}N + NHMe_2 + NH_3 \qquad (3)$$

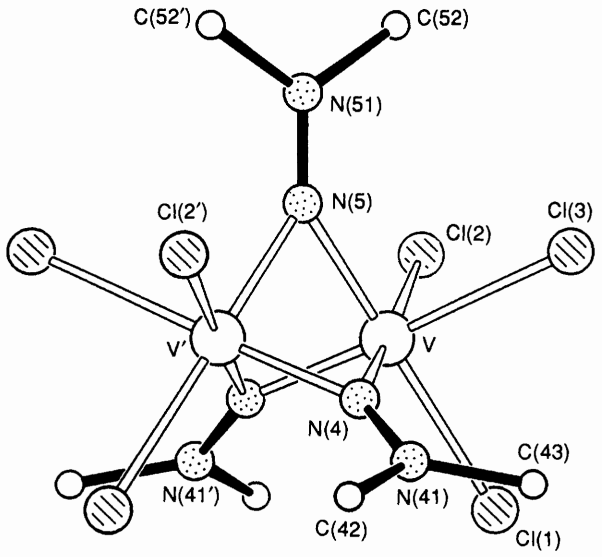

Fig. 1 View of $[\{VCl_3\}_2(\mu\text{-}NNMe_2)_3]^{2-}$

The isolated triply hydrazide-bridged complex $[NH_2Me_2]_2[\{VCl_3\}_2(\mu\text{-}NNMe_2)_3]$, contains products associated with the formal disproportionation and the ammonia produced in the reaction has been detected quantitatively in solution.

The reaction of $[VCl_3(PMePh_2)_2]$ or $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with 5 equiv. of $SiMe_3NHNMe_2$ in MeCN rapidly gives a brown solution. After removing all the volatiles *in vacuo*, slow crystallisation of the residue from CH_2Cl_2–Et_2O gave brown plates of the product, identified by X-ray crystallography as $[NH_2Me_2]_2[\{VCl_3\}_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$.†

The structure of the binuclear anion is shown in Fig. 1, and consists of two face-sharing octahedra, related by a crystallographic twofold symmetry axis that passes through N(51), N(5) and the midpoint of V–V′.

On the periphery of the ion each vanadium atom is coordinated by three chloro-groups [mean $r_{V\text{-}Cl}$ = 2.468(14) Å]. The two vanadium atoms are connected by three Me_2NN residues, and the short V–V separation [$r_{V\text{-}V}$ = 2.300(13) Å] is consistent with the presence of a metal–metal bond. Clearly, all three bridging ligands cannot be hydrazido(2^-)-species since the vanadium atoms would then be in too high a formal oxidation state to allow any vanadium–vanadium bond formation. Interestingly, not all the Me_2NN ligands are equivalent; one of the residues appears to have a shorter N–N distance [r_{NN} = 1.28(6) Å] than the other two [r_{NN} = 1.36(3) Å]. This is consistent with the bridge comprising two hydrazide(2^-), and one isodiazene ligands. Thus, both vanadium centres are formally V^{IV}, permitting a vanadium–vanadium single bond.

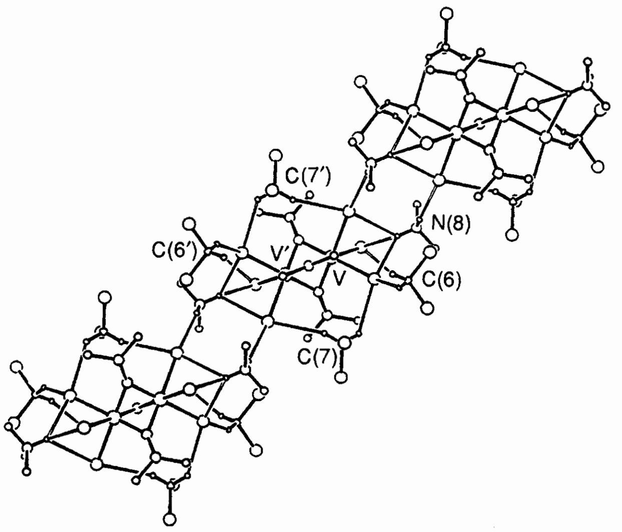

Fig. 2 The hydrogen bonding in the crystal structure of $[NH_2Me_2]_2[\{VCl_3\}_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$. The hydrogen atoms (in idealised positions) in the cations and solvent molecules are shown, with the proposed hydrogen bonds as the hollow bonds.

As expected from this description, the complex is diamagnetic and exhibits signals in the ^1H NMR spectrum attributable to $[NH_2Me_2]^+$ [δ 7.25–7.85, broad (N*H*); δ 0.0, singlet (N*Me*)] and the bridging Me_2NN [δ 2.5, broad singlet (N*Me*$_2$)]; and the ^{51}V NMR spectrum a singlet at δ −707.‡

Cyclic voltammetry of the complex (CH_2Cl_2, $[NBu^n_4]BF_4$ = 0.1 mol dm^{-3}) exhibits two oxidations, the first of which is reversible at −35 °C, $E_{\frac{1}{2}}^{ox}$ = 0.30 V, E_2^{ox} = 1.35 V (*vs.* ferrocene/ferrocinium). No reduction of the analogous $[PPh_4]^+$ salt is observed down to −1.85 V.

Finally, extensive hydrogen bonding is evident in the crystal lattice as shown in Fig. 2. One proton in $[NH_2Me_2]^+$ is hydrogen bonded to the three chloro-groups bound to a single vanadium, and this cation bridges to another anion by hydrogen bonding of the other amine proton to a chloro-ligand on the adjacent anion. In addition two molecules of CH_2Cl_2 [of C(7) and C(7′)] are hydrogen bonded between chloro-groups across the bridge of each anion, and a further two molecules [of C(6) and C(6′)] are hydrogen bonded between chloro-ligands linking anions along the twofold symmetry axes, *i.e.* the direction of viewing.

Work is continuing to define the reaction products with other hydrazines and to replace the peripheral chloro-ligands with sulfur donor ligands.

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† *Crystal structure analysis* of $[NH_2Me_2]_2[\{VCl_3\}_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$, *Crystal data*: $2C_2H_8N\cdot C_6H_{18}Cl_6N_6V_2\cdot 4CH_2Cl_2$, M = 920.8. Monoclinic, space group $F2/d$ (equivalent to no. 15), a = 24.041(7), b = 8.859(2), c = 38.086(9) Å. β = 100.15(2)°, V = 7984.5 Å^3. Z = 8, D_c = 1.532 g cm^{-3}. $F(000)$ = 3728, μ(Mo-Kα) = 14.2 cm^{-1}. λ(Mo-K$\bar{\alpha}$) = 0.71069 Å.

Very thin plate, moisture-sensitive crystals, typical of the whole sample were mounted in capillaries: brief photographic examination; Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for cell parameters (from 25 reflections, θ = 6–8°, each centred in four orientations) and diffraction intensities (θ_{max} = 20°). Intensity data corrected for Lorentz-polarisation effects, crystal deterioration (*ca.* 45%) and absorption. 1862 Unique reflections, generally weak [only 612 with $I > 2\sigma(I)$] in SHELX system[5] for structure determination (from automated Patterson routines in SHELXS).[6] Refinement to R = 0.181 and R_g = 0.155 for 956 reflections [$I > \sigma(I)$] weighted $w = (\sigma_F^2 + 0.00289F^2)^{-1}$. V and Cl atoms refined with anisotropic thermal parameters, N and C atoms isotropically. H atoms included in calculated positions riding on parent C or N atoms.

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

‡ ^1H NMR shifts *vs.* tetramethylsilane; ^{51}V NMR signals *vs.* $[VOCl_3]$.