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# Reactions of substituted hydrazines with vanadium(III) compounds: crystal structures of $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$, $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMe_2)_2]$ and $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMePh)_2]$†

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Reaction of $Me_3SiNHNMe_2$ with $[VCl_3(PMePh_2)_2]$ or $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) gave the triply hydrazide-bridged complex $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ **1** the crystal structure of which has been determined. Cyclic voltammetry shows **1** to have $E_{\frac{1}{2}}^{ox} = 0.30$ V (reversible at −35 °C) and $E_2^{ox} = 1.35$ V (*vs.* ferrocene-ferrocenium). Cation exchange gave $[PPh_4]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ and reaction with $Li(SC_6H_2Pr^i_3\text{-}2,4,6)$ gave $[NH_2Me_2]_2[\{V(SC_6H_2Pr^i_3\text{-}2,4,6)_3\}_2(\mu\text{-}NNMe_2)_2]$. Treatment of $[V(OC_6H_3Pr^i_2\text{-}2,6)_4Li(thf)]$ with $NH_2NMe_2$ gave the low-melting compound $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMe_2)_2]$, shown by a structure determination to be essentially trigonal bipyramidal, with axial hydrazine ligands. The analogue $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMePh)_2]$ has also been prepared and shown to have a similar structure.

In the reduction of dinitrogen by the enzyme nitrogenase derivatives of hydrazine such as hydrazide(2−) or hydrazidium(1−) are considered to be metal-bound intermediates.[1,2] The discovery that nitrogenase from *Azotobacter* contains vanadium and that this nitrogenase produces, besides ammonia, about 0.5% $N_2H_4$ per converted $N_2$ during the catalytic cycle[3] has prompted investigation of hydrazine and hydrazide complexes of vanadium in order to gain knowledge of likely intermediate species in the conversion of $N_2$ into $NH_3$ at vanadium, assuming that this is the metal in vanadium nitrogenase at which the binding and reduction of dinitrogen occurs. Hydrazine and hydrazide complexes of vanadium such as $[VCl_3(NH_2NMe_2)_2]$[4] and $[VCl_2(NNMePh)(NH_2NMePh)_2]Cl$[5] have been described as well as dinitrogen complexes such as *trans*-$[V(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$[6] and $[\{V(C_6H_4CH_2NMe_2\text{-}2)_2(C_5H_5N)\}_2(\mu\text{-}N_2)]$[7] which give ammonia on protonation.[8]

Previously, we have reported[9] briefly the reaction of $Me_3SiNHNMe_2$ with $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) which gives the complex $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ and here we describe the structure and reactions of this compound in detail, together with the preparation, properties and structural characterisation of the hydrazine complexes $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMe_2)_2]$ and $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMePh)_2]$.

## Results and Discussion

### Preparation, structure and reactions of $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ 1

The reaction of $[VCl_3(PMePh_2)_2]$ or, more conveniently, $[VCl_3(thf)_3]$ with an excess of $Me_3SiNHNMe_2$ in MeCN rapidly gives a brown solution. After removal of solvent, slow recrystallisation of the residue from $CH_2Cl_2$–$Et_2O$ gave brown, air-sensitive plates, the crystal structure of which, described below, showed them to be of the complex $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$ **1**, the first example of a triply hydrazide-bridged complex. Compound **1** is soluble in MeCN, $CH_2Cl_2$ and MeOH. The reaction between $[VCl_3(PMePh_2)_2]$ or $[VCl_3(thf)_3]$ and $Me_3SiNHNMe_2$ can be considered to be derived from the formal disproportionation reaction (1). In accord with this suggestion, the $Me_2N{=}N$ and

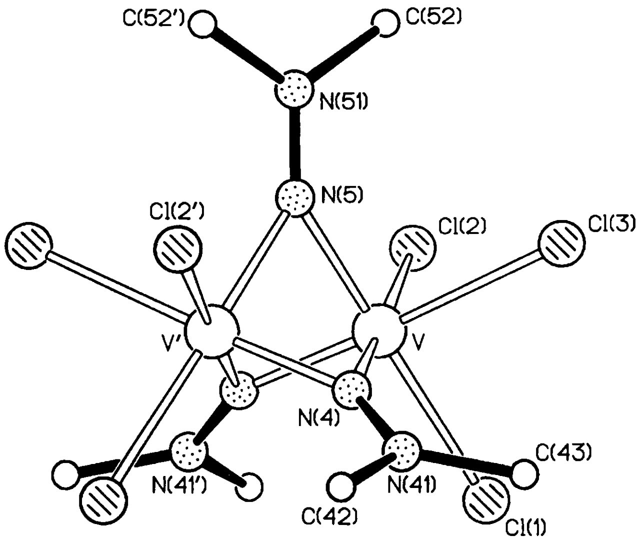

**Fig. 1** Crystal structure of the anion $[(VCl_3)_2(\mu\text{-}NNMe_2)_3]^{2-}$ of compound **1**. A two-fold symmetry axis passing through N(51) and N(5) relates the two halves of this dimeric anion

$$2Me_2NNH_2 \longrightarrow Me_2N{=}N + NHMe_2 + NH_3 \quad (1)$$

$NHMe_2$ fragments are incorporated in compound **1** and $NH_3$ was detected in solution during its preparation (Experimental section).

The structure of the anion of compound **1** is shown in Fig. 1, and bond dimensions are in Table 1. In spite of the relatively high *R* factors for this analysis (see Experimental section), we are confident of the principal features of this structure; the precision of the molecular dimensions, however, is not as high as we normally like to report. The anion consists of two face-sharing '$VCl_3N_3$' octahedra. On the periphery of the molecule

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T$^{-1}$.

**Table 1** Molecular dimensions (bond lengths in Å, angles in °) in $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]\cdot4CH_2Cl_2$ **1** with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| (*a*) About the V atom | | | |
| V–V′ | 2.300(13) | V–N(4) | 1.871(26) |
| V–Cl(1) | 2.457(12) | V–N(4′) | 1.855(27) |
| V–Cl(2) | 2.496(11) | V–N(5) | 1.95(4) |
| V–Cl(3) | 2.451(12) | | |
| Cl(1)–V–Cl(2) | 88.6(4) | Cl(3)–V–N(4′) | 177.6(10) |
| Cl(1)–V–Cl(3) | 88.0(4) | N(4)–V–N(4′) | 87.6(11) |
| Cl(2)–V–Cl(3) | 86.6(4) | Cl(1)–V–N(5) | 178.6(4) |
| Cl(1)–V–N(4) | 92.7(9) | Cl(2)–V–N(5) | 92.5(7) |
| Cl(2)–V–N(4) | 178.7(10) | Cl(3)–V–N(5) | 91.2(7) |
| Cl(3)–V–N(4) | 93.6(9) | N(4)–V–N(5) | 86.2(11) |
| Cl(1)–V–N(4′) | 94.0(9) | N(4′)–V–N(5) | 86.7(11) |
| Cl(2)–V–N(4′) | 92.2(9) | | |
| (*b*) In the hydrazido/isodiazene ligands | | | |
| N(4)–N(41) | 1.36(3) | N(5)–N(51) | 1.28(6) |
| N(41)–C(42) | 1.46(4) | N(51)–C(52) | 1.50(4) |
| N(41)–C(43) | 1.45(4) | | |
| V–N(4)–V′ | 76.2(10) | V–N(5)–V′ | 72.2(18) |
| V–N(4)–N(41) | 141.8(22) | V–N(5)–N(51) | 143.9(9) |
| V′–N(4)–N(41) | 141.6(21) | | |
| N(4)–N(41)–C(42) | 122.5(28) | N(5)–N(51)–C(52) | 121.7(25) |
| N(4)–N(41)–C(43) | 121.5(28) | | |
| C(42)–N(41)–C(43) | 115.6(29) | C(52)–N(51)–C(52′) | 117(4) |
| (*c*) In the $[NH_2Me_2]^+$ cation | | | |
| N(8)–C(81) | 1.48(5) | C(81)–N(8)–C(82) | 118(4) |
| N(8)–C(82) | 1.32(5) | | |
| (*d*) In the dichloromethane molecules | | | |
| C(6)–Cl(61) | 1.70(4) | C(7)–Cl(71) | 1.68(4) |
| C(6)–Cl(62) | 1.74(4) | C(7)–Cl(72) | 1.69(4) |
| Cl(61)–C(6)–Cl(62) | 111.5(23) | Cl(71)–C(7)–Cl(72) | 113.1(26) |
| (*e*) In the hydrogen bonds | | | |
| H(6a) · · · Cl(3) | 2.67 | H(8a) · · · Cl(1) | 2.55 |
| H(6b) · · · Cl(1″) | 2.81 | H(8a) · · · Cl(2) | 2.77 |
| H(7a) · · · Cl(3) | 2.69 | H(8a) · · · Cl(3) | 2.55 |
| H(7b) · · · Cl(2′) | 2.73 | H(8b) · · · Cl(2‴) | 2.48 |
| Cl(3) · · · H(6a)–C(6) | 151.6 | Cl(3) · · · H(8a)–N(8) | 132.9 |
| Cl(1″) · · · H(6b)–C(6) | 163.9 | Cl(2‴) · · · H(8b)–N(8) | 149.3 |
| Cl(3) · · · H(7a)–C(7) | 137.4 | Cl(1) · · · H(8a) · · · Cl(2) | 81.1 |
| Cl(2′) · · · H(7b)–C(7) | 162.6 | Cl(1) · · · H(8a) · · · Cl(3) | 84.0 |
| Cl(1) · · · H(8a)–N(8) | 135.5 | Cl(2) · · · H(8a) · · · Cl(3) | 79.2 |
| Cl(2) · · · H(8a)–N(8) | 123.6 | | |

Primes denote symmetry-related atoms: ′ $\frac{1}{4} - x, y, \frac{1}{4} - z$; ″ $x, y - 1, z$; ‴ $\frac{1}{2} - x, -y, \frac{1}{2} - z$.

each vanadium is co-ordinated by three chloro-groups [$2.45 \leqslant r$(V–Cl) $\leqslant 2.50$]. The two vanadium atoms are connected by three bridging $NNMe_2$ residues.

The V–V distance is 2.300(13) Å. This distance is longer than a normal triple bond (V≡V), which is in the range 2.1–2.2 Å, as for example in the complex $[V_2\{C_6H_3(OMe)_2\text{-}2,6\}_4]$[10,11] and is therefore more consistent with a double (V=V) or single bond (V–V); V=V distances are usually the order of 2.4 Å, as in $[V_2Zn_2H_4(BH_4)_2(PMePh_2)_4]$,[12] and V–V distances are of the order of 2.6–2.8 Å, *e.g.* 2.8 Å in $[(MeCS_2)_2V(\mu\text{-}\eta^2\text{-}S_2)_2\text{-}V(S_2CMe)_2]$[13] and 2.6 Å in $[(\eta^5\text{-}C_5H_4Pr^i)V(\mu\text{-}\eta^1\text{-}S_2)(\mu\text{-}S)_2V(\eta^5\text{-}C_5H_4Pr^i)]$.[14] It should be noted, however, that the diamagnetic complex $[\{V(OC_6H_4OMe\text{-}2)\}_2(\mu\text{-}NN{=}CH\text{-}SiMe_3)_2]$ has a V–V distance of 2.498(1) Å, but it is not considered to have, necessarily, a bonding interaction between the two $V^{IV}$ atoms, but rather the short V–V distance is suggested to be imposed by the ligand framework. Evidence cited in favour of this view is the relatively easy cleavage of the dinuclear framework and the theoretical demonstration that a V–V distance of 2.4 Å can be non-bonding.[15] The V–V distance in complex **1** at 2.300(13) Å might be simply a consequence of the three bridges holding the two metals close together, but if so it is remarkably short and in other triply bridged systems, *e.g.* $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu\text{-}F)_3]BF_4$ [*r*(WW) = 3.216(3) Å][16] and $[\{MoH_2(PMePh_2)_3\}_2(\mu\text{-}F)_3]BF_4$ [*r*(MoMo) = 3.256(2) Å],[17] the metal–metal distances are too large to permit any bonding, despite the metals being bridged by three small atoms.

If all three bridging groups in compound **1** were hydrazide(2−) ligands (*i.e.* $Me_2NN^{2-}$) this would require each V atom to be in the +5 oxidation state. Clearly this is too high a formal oxidation state to allow any vanadium–vanadium bond. In order for there to be a metal–metal interaction, the vanadium centres must have a formal oxidation state of +4 or lower. This could be achieved were one of the $NNMe_2$ ligands to adopt the isodiazene form.[18] There is some indication that this might be the case. While the two symmetry-related $Me_2NN$ residues have a N–N distance of 1.36(3) Å (Table 1), consistent with a classical hydrazide(2−) ligand,[1,2] the third residue might be somewhat shorter [1.28(6) Å]; however, the large errors in these distances make this argument unreliable. Nevertheless, the hydrazide ligands could form a delocalised system, of which the 'single isodiazene' structure would be one canonical form; both vanadium centres would then be formally $V^{IV}$, permitting a vanadium–vanadium single bond. The observed V–V distance of 2.3 Å might seem short for a single bond, but this could result from the strain caused by the octahedral geometry around each vanadium atom, and the requirements of the bridging ligands.

Based on either the $V^{V}$–$V^{V}$ non-bonding or the $V^{IV}$–$V^{IV}$ metal–metal bonded formalisms above complex **1** will be diamagnetic, as is demonstrated by its $^1H$ NMR spectrum at room temperature (δ 7.25–7.85, br, NH; 0.0, s, NMe; 2.5, br s, bridging $Me_2NN$), and its $^{51}V$ NMR spectrum (s at δ −707). Only one resonance is seen for the $Me_2NN$ groups, even at temperatures down to −60 °C, which would be consistent with the $V^{V}$–$V^{V}$ non-bonding formulation, but also with the $V^{IV}$–$V^{IV}$ metal–metal bonded formalism with the hydrazide groups being equivalent due to delocalisation or a fast exchange process.

An additional important observation is the ability of compound **1** to undergo a one-electron oxidation. If we assume that this is metal-centred, then the $V^{IV}$–$V^{IV}$ metal–metal bonded structure is favoured; alternatively the electron could be removed from a ligand-based orbital under either formalism. At the present time we cannot distinguish these possibilities, but on balance we favour the $V^{IV}$–$V^{IV}$ metal–metal bonded formalism.

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

The $[NH_2Me_2]^+$ cation in compound **1** may be exchanged upon treatment with $[PPh_4]Br$ in MeOH to give dark brown $[PPh_4]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ **2**.

Treatment of compound **1** with an excess of $Li(SC_6H_2Pr^i{}_3\text{-}2,4,6)$ in $CH_2Cl_2$ results in metathesis of the chloride ligands and loss of one $NNMe_2$ group to give diamagnetic $[NH_2Me_2]_2[\{V(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3\}_2(\mu\text{-}NNMe_2)_2]\cdot CH_2Cl_2$ **3** which shows the characteristic resonances for the $SC_6H_2Pr^i{}_3$-2,4,6 ligand in its $^1H$ NMR spectrum (Experimental section). Presumably **3** is, like **1**, a $V^{IV}$–$V^{IV}$ metal–metal bonded dimer, but with only two $NNMe_2$ bridges. The $NNMe_2$ residue that has been lost might well be the isodiazene ligand.

The cyclic voltammogram of complex **1** in $CH_2Cl_2$ exhibits two oxidations, $E_1^{ox}$ = +0.30 V and $E_2^{ox}$ = +1.35 V, the first of which is reversible at −35 °C (Fig. 3). At higher temperatures even this first oxidation is irreversible. Reduction of **1** could not provide any information because of complications due to the presence of $Me_2NH_2^+$. Thus, only the reduction of $Me_2NH_2^+$ to $Me_2NH$ and $H_2$ at $E_{red}$ = −1.5 V is observed. The cyclic voltammogram of the $[PPh_4]^+$ salt **2** was studied, but no reduction was observed down to −1.85 V. In addition the oxidation processes were complicated by the oxidation of the $[PPh_4]^+$ cation.

The question arises as to how complex **1** is formed. A possible mechanism is shown in Scheme 1, assuming the $V^{IV}$–$V^{IV}$ metal–bonded structure. A $Me_2NN^{2-}$ fragment derived from $Me_3SiNHNMe_2$ (presumably the $SiMe_3$ residue is lost by hydrolysis) bridges between two vanadium(III) centres (**A**). This is followed by the formation of a second hydrazide bridge to lead to the formation of **B**, overall charge 4−. A one-electron reduction from each metal centre to one of the hydrazide ligands with concomitant protonation by solvent gives **C** together with 1 mole equivalent of both $Me_2NH$ and $NH_3$. The metal centres in **C** are therefore oxidised to $V^{IV}$. Addition of a further $Me_2NN^{2-}$ fragment subsequently results in the formation of **D**. A one-electron reduction of each metal centre gives a vanadium(III) dimer, **E**, and rearrangement of one of the hydrazido(2−)-bridges to a neutral isodiazene compound. **F** is formed by addition of a $Me_2NN^{2-}$ fragment. A second one-electron reduction from the metal centres to one of the hydrazido(2−)-bridges gives the vanadium(IV) dimer **G**, $NH_3$ and $Me_2NH$. The product **1** is formed by addition of a final $Me_2NN^{2-}$ group to the bridging position. Consistent with this proposal, the ammonia produced in the reaction has been detected quantitatively *in situ* (80–90%, see Experimental section). Although the sequence of reactions shown in Scheme 1 leads to a ready rationalisation of the observed products, its validity can only be established from more detailed mechanistic studies. In particular, the order in which we have presented the various elements of this reaction, bridge formation, nitrogen–nitrogen cleavage and intramolecular processes, is to some extent arbitrary and other permutations of this scheme can be envisaged.

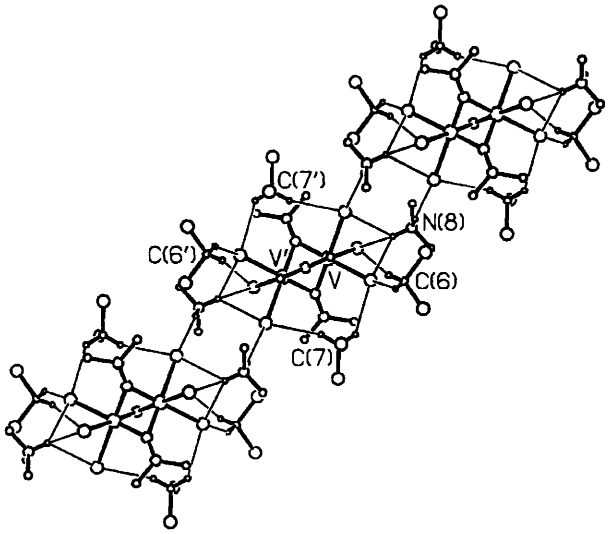


**Fig. 2** The hydrogen bonding in the crystal structure of $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$ **1**. The hydrogen atoms (in idealised positions) in the cations and solvent molecules are shown, with the proposed hydrogen bonds shown

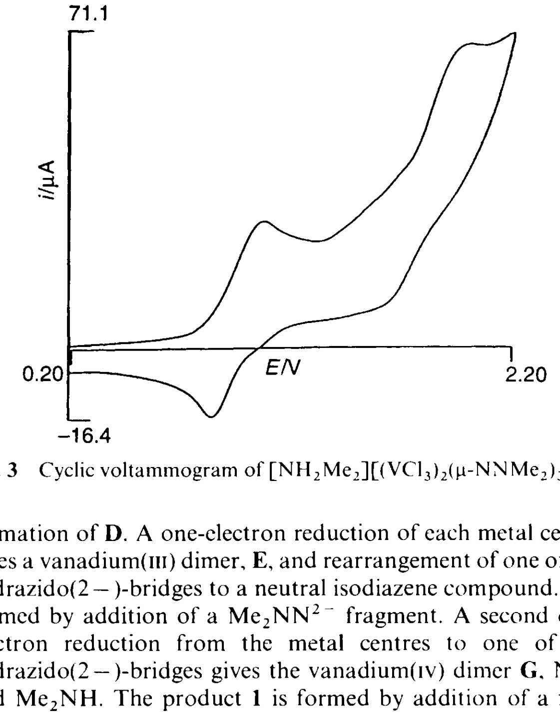
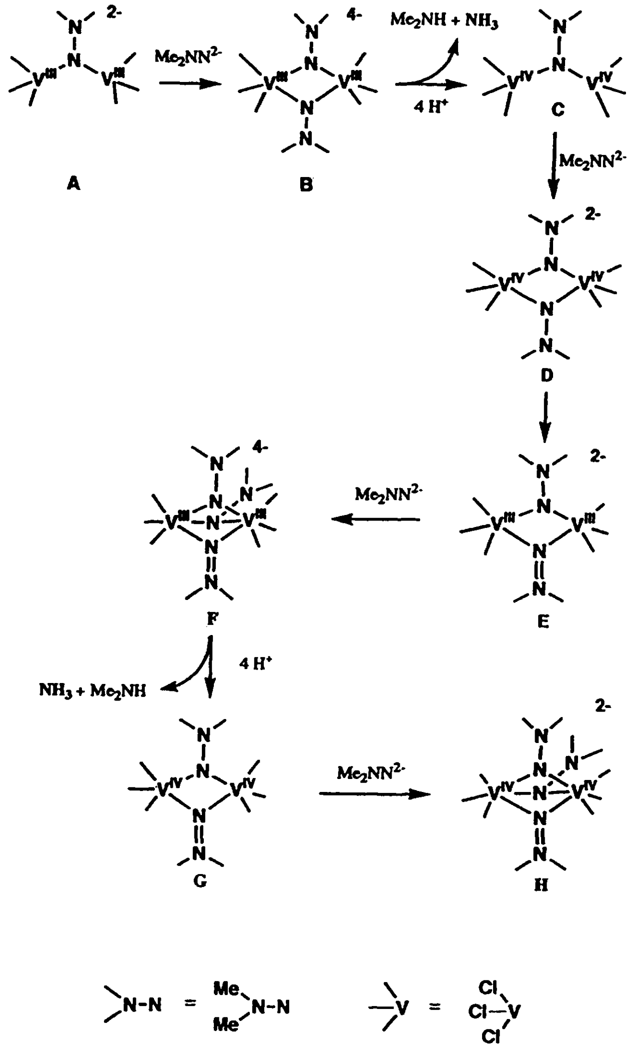


**Fig. 3** Cyclic voltammogram of $[NH_2Me_2][(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ **1**

## Preparation and structure of $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3(NH_2NMe_2)_2]$ 4 and $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3(NH_2NMePh)_2]$ 5

Reaction of $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_4Li(thf)]$[18] {generated in solution from $[VCl_3(thf)_3]$ and $Li(OC_6H_3Pr^i{}_2\text{-}2,6)$} with $NH_2NMe_2$ in hexane gave pink-red crystals at −30 °C which are low melting and consequently the crystal structure determination of this compound was carried out at −100 °C. This showed it to be the hydrazine adduct $[V(OC_6H_3Pr^i{}_2$-



**Scheme 1** Proposed pathway for the formation of $[NH_2Me_2]_2$-$[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ **1**

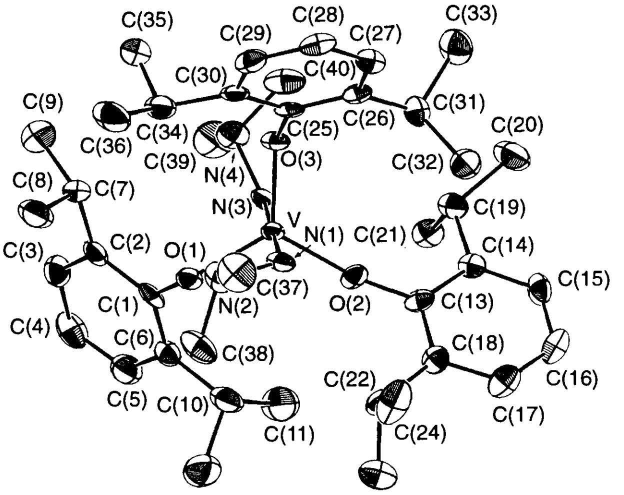


**Fig. 4** Crystal structure of $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMe_2)_2]$ **4**

2,6)$_3$(NH$_2$NMe$_2$)$_2$] **4** as presented in Fig. 4. Bond dimensions are in Table 2. Compound **4** has essentially trigonal-bipyramidal geometry about the vanadium with the phenoxide ligands in the girdle and the axial hydrazine ligands co-ordinated end-on by the $NH_2$ groups. The V–O distances [average 1.876(4) Å] are close to those of the terminal V–O phenoxide distances [1.839(2) and 1.820(2) Å] in the starting material $[V(OC_6H_3Pr^i_2\text{-}2,6)_4Li(thf)]$.[19] The bulky $C_6H_3Pr^i_2$-2,6 substituents are arranged in the 'two-up, one-down' configuration with respect to the trigonal plane, as is commonly seen in analogous thiolate complexes, such as $[V(SC_6H_2Pr^i_3\text{-}2,4,6)_3(thf)_2]$.[20] This arrangement minimises steric pressure between the aromatic groups. The *trans*-hydrazine groups have N–N distances of 1.461(7) and 1.453(9) Å, in the range normally associated with N–N single bonds {*e.g.* 1.455(5) and 1.440(19) Å in $[VCl_2(H_2NNMePh)_2(NNMePh)]Cl$[4] and 1.434(6) Å in $[V(salen)(NH_2NHPh)_2]I$}. [H$_2$salen = *N,N*-bis(salicylidene)ethane-1,2-diamine].[21] They are bound end-on through the $NH_2$ groups to the V atom with the N(1)–V–N(3) angle 178.8(2)°. The V–N(1)–N(2) and V–N(3)–N(4) angles are 121.0(5) and 122.7(4)° respectively, as expected for essentially tetrahedral, sp$^3$-hybridised orbitals at N(1) and N(3). In keeping with the formulation as a bis(hydrazine) complex of vanadium(III), compound **4** is paramagnetic with $\mu_{eff} = 2.69\ \mu_B$.

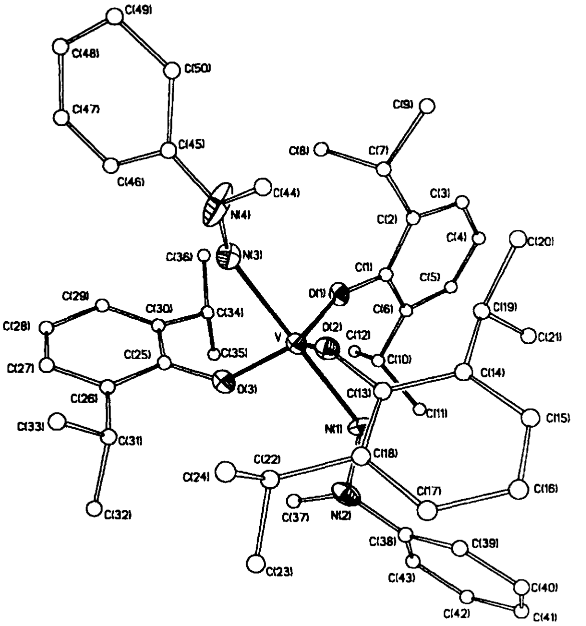


**Fig. 5** Crystal structure of $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMePh)_2]$ **5**

The analogue of **4**, $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMePh)_2]$ **5**, was prepared as deep red crystals by an identical route to **4** and its crystal structure was determined at −93 °C (Fig. 5). Bond dimensions are in Table 3. Complex **5** has a very similar structure and the same trigonal-bipyramidal geometry as **4** with end-on, apical $NH_2NMePh$ groups [N–N 1.427(10) and 1.356(10) Å V–N(1)–N(2) and V–N(3)–N(4) 126.0(6) and 135.0(7)°]. The unusually short N–N distance and enlarged V–N–N angle involving N(3) may result from inversion of configuration about N(4); the estimated standard deviations (e.s.d.s) of the thermal parameters and coordinates of that atom and of some of the phenyl C atoms suggest that there is disorder over the two tetrahedral orientations about N(4). Whereas the conformation about N(2) is the normal umbrella type, with N(2) 0.43 Å out of the plane of N(1), C(37) and C(38), the arrangement about N(4) appears more planar with that atom calculated to be 0.13 Å out of the corresponding plane of N(3), C(44) and C(45). In complex **4** there is no indication of disorder. Thus there is little difference in physical properties between **4** and **5** on passing from $H_2NNMe_2$ to $H_2NNMePh$ as ligand, although the higher melting point of **5** allows a more complete characterisation (Experimental section).

Other products from the reaction of hydrazines with vanadium complexes have been reported, in particular $[VCl_3(NH_2NMe_2)_2]$ has been prepared. It was not structurally characterised, but it was suggested that this compound contained side-on hydrazines.[4] Although the steric properties of the $OC_6H_3Pr^i_2$-2,6 ligands in **4** and **5** might well force terminal ligation of their hydrazide groups, their structures

**Table 2** Intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMe_2)_2]\cdot 0.5C_6H_{14}$ **4**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| V–O(1) | 1.878(4) | V–O(2) | 1.881(5) | C(13)–C(14) | 1.405(8) | C(13)–C(18) | 1.409(10) |
| V–O(3) | 1.868(4) | V–N(1) | 2.196(6) | C(14)–C(15) | 1.384(12) | C(14)–C(19) | 1.528(11) |
| V–N(3) | 2.192(6) | O(1)–C(1) | 1.351(8) | C(15)–C(16) | 1.381(11) | C(16)–C(17) | 1.367(9) |
| O(2)–C(13) | 1.355(10) | O(3)–C(25) | 1.362(8) | C(17)–C(18) | 1.389(12) | C(18)–C(22) | 1.528(9) |
| N(1)–N(2) | 1.461(7) | N(2)–C(37) | 1.460(10) | C(19)–C(20) | 1.524(10) | C(19)–C(21) | 1.530(10) |
| N(2)–C(38) | 1.466(9) | N(3)–N(4) | 1.453(9) | C(22)–C(23) | 1.517(11) | C(22)–C(24) | 1.536(11) |
| N(4)–C(39) | 1.443(11) | N(4)–C(40) | 1.453(9) | C(25)–C(26) | 1.401(10) | C(25)–C(30) | 1.420(10) |
| C(1)–C(2) | 1.410(12) | C(1)–C(6) | 1.399(10) | C(26)–C(27) | 1.389(9) | C(26)–C(31) | 1.521(10) |
| C(2)–C(3) | 1.362(11) | C(2)–C(7) | 1.523(10) | C(27)–C(28) | 1.386(10) | C(28)–C(29) | 1.374(11) |
| C(3)–C(4) | 1.400(11) | C(4)–C(5) | 1.348(13) | C(29)–C(30) | 1.375(10) | C(30)–C(34) | 1.523(11) |
| C(5)–C(6) | 1.387(11) | C(6)–C(10) | 1.495(13) | C(31)–C(32) | 1.524(12) | C(31)–C(33) | 1.527(9) |
| C(7)–C(8) | 1.537(10) | C(7)–C(9) | 1.490(13) | C(34)–C(35) | 1.494(12) | C(34)–C(36) | 1.526(10) |
| C(10)–C(11) | 1.541(11) | C(10)–C(12) | 1.527(10) | C(41)–C(42) | 1.45(4) | C(42)–C(43) | 1.27(3) |
| | | | | | | | |
| O(1)–V–O(2) | 117.6(2) | O(1)–V–O(3) | 121.7(2) | C(11)–C(10)–C(12) | 110.2(7) | O(2)–C(13)–C(14) | 118.8(6) |
| O(1)–V–N(1) | 92.8(2) | O(1)–V–N(3) | 87.2(2) | O(2)–C(13)–C(18) | 121.1(5) | C(14)–C(13)–C(18) | 120.1(7) |
| O(2)–V–O(3) | 120.4(2) | O(2)–V–N(1) | 94.5(2) | C(13)–C(14)–C(15) | 118.2(7) | C(13)–C(14)–C(19) | 119.8(7) |
| O(2)–V–N(3) | 86.6(2) | O(3)–V–N(1) | 87.2(2) | C(15)–C(14)–C(19) | 121.9(6) | C(14)–C(15)–C(16) | 122.3(6) |
| O(3)–V–N(3) | 91.7(2) | N(1)–V–N(3) | 178.8(2) | C(15)–C(16)–C(17) | 118.7(8) | C(16)–C(17)–C(18) | 122.1(7) |
| V–O(1)–C(1) | 133.1(4) | V–O(2)–C(13) | 159.4(4) | C(13)–C(18)–C(17) | 118.5(6) | C(13)–C(18)–C(22) | 122.6(7) |
| V–O(3)–C(25) | 134.5(4) | V–N(1)–N(2) | 121.0(5) | C(17)–C(18)–C(22) | 118.8(7) | C(14)–C(19)–C(20) | 114.2(7) |
| N(1)–N(2)–C(37) | 108.9(6) | N(1)–N(2)–C(38) | 107.5(5) | C(14)–C(19)–C(21) | 109.9(5) | C(20)–C(19)–C(21) | 108.8(5) |
| C(37)–N(2)–C(38) | 108.9(6) | V–N(3)–N(4) | 122.7(4) | C(18)–C(22)–C(23) | 112.4(6) | C(18)–C(22)–C(24) | 109.9(6) |
| N(3)–N(4)–C(39) | 107.9(6) | N(3)–N(4)–C(40) | 107.3(6) | C(23)–C(22)–C(24) | 109.7(6) | O(3)–C(25)–C(26) | 119.9(6) |
| C(39)–N(4)–C(40) | 110.0(5) | O(1)–C(1)–C(2) | 118.8(6) | O(3)–C(25)–C(30) | 119.8(6) | C(26)–C(25)–C(30) | 120.3(6) |
| O(1)–C(1)–C(6) | 120.5(7) | C(2)–C(1)–C(6) | 120.7(7) | C(25)–C(26)–C(27) | 119.0(6) | C(25)–C(26)–C(31) | 121.6(6) |
| C(1)–C(2)–C(3) | 118.1(7) | C(1)–C(2)–C(7) | 120.1(6) | C(27)–C(26)–C(31) | 119.3(7) | C(26)–C(27)–C(28) | 120.8(7) |
| C(3)–C(2)–C(7) | 121.7(8) | C(2)–C(3)–C(4) | 121.7(8) | C(27)–C(28)–C(29) | 119.7(6) | C(28)–C(29)–C(30) | 122.1(7) |
| C(3)–C(4)–C(5) | 119.4(7) | C(4)–C(5)–C(6) | 121.8(7) | C(25)–C(30)–C(29) | 118.2(7) | C(25)–C(30)–C(34) | 119.3(6) |
| C(1)–C(6)–C(5) | 118.3(8) | C(1)–C(6)–C(10) | 122.1(7) | C(29)–C(30)–C(34) | 122.3(6) | C(26)–C(31)–C(32) | 111.7(6) |
| C(5)–C(6)–C(10) | 119.5(6) | C(2)–C(7)–C(8) | 109.7(5) | C(26)–C(31)–C(33) | 111.0(6) | C(32)–C(31)–C(33) | 111.5(6) |
| C(2)–C(7)–C(9) | 114.3(6) | C(8)–C(7)–C(9) | 110.6(7) | C(30)–C(34)–C(35) | 110.1(5) | C(30)–C(34)–C(36) | 112.6(7) |
| C(6)–C(10)–C(11) | 111.7(7) | C(6)–C(10)–C(12) | 112.4(7) | C(35)–C(34)–C(36) | 111.3(7) | C(41)–C(42)–C(43) | 127(3) |

raise the possibility that $[VCl_3(NH_2NMe_2)_2]$ also has terminal, apical hydrazine ligands. Most of the NH hydrogen atoms in **4** and **5** could not be detected in the structure determination, but they are clearly present from the geometrical considerations above and all lie buried within the molecule; none forms a normal hydrogen bond but all have short H • • • C contacts with the neighbouring phenoxide ligands. These hydrogen atoms show characteristic N–H absorptions in the IR spectra of **4** and **5** (Experimental section). As expected from the paramagnetism of **4** and **5**, their $^1H$ NMR spectra are broad, but some resonances can be assigned, in particular a weak broad resonance at δ 3.0 (relative to $SiMe_4$) is assigned to $NMe_2$ in **4** {*cf. ca.* δ 2.5 for $[VCl_3(NH_2NMe_2)_2]$[4]}.

## Conclusion

We have demonstrated two reactions of substituted hydrazines at vanadium(III) centres, simple adduct formation at a sterically congested site to give $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMe_2)_2]$ **4** and $[V(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_2NMePh)_2]$ **5** and at a less congested site formation of the novel triply bridged hydrazide unit in $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ **1**. The reactions of **4** and **5** will be discussed at a later date. So far the triple bridge of **1** appears to be moderately robust, but metathesis of the chloride ligands by thiolate leads to loss of one $NNMe_2$ bridging ligand.

## Experimental

All operations were carried out under a dry dinitrogen or argon atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. Infrared spectra were recorded on a Perkin-Elmer 882 instrument in Nujol mulls or in solution, NMR spectra on a JEOL GSX-270 instrument. Analyses were by Mr. C. J. Macdonald of this Laboratory, using a Perkin-Elmer 2400 CHN elemental analyser. Magnetic moment determinations in the solid state used a Faraday balance, those in solution used the NMR method of Evans and James.[22]

The compounds 1,1-dimethylhydrazine, 1-methyl-1-phenylhydrazine, trimethylsilyl chloride, and $HOC_6H_3Pr^i_2\text{-}2,6$ were obtained from Aldrich Chemical Co., tetraphenylphosphonium bromide from Lancaster Synthesis Ltd. The compounds $[VCl_3(thf)_3]$, $[VCl_3(PMePh_2)_2]$,[23] 1,1-dimethyl-2-trimethylsilylhydrazine, 1-methyl-1-phenyl-2-trimethylsilylhydrazine[24] and $HSC_6H_2Pr^i_3\text{-}2,4,6$[25] were prepared by literature methods.

### Preparation of $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$ 1

**Method 1.** The compound $[VCl_3(PMePh_2)_2]$ (0.69 g, 1.24 mmol) was dissolved in MeCN (20 $cm^3$). The solution turned from red-purple to green. 1,1-Dimethylsilylhydrazine (6.19 mmol, 0.82 g) was added. The solution turned dark reddish brown and was stirred at room temperature for 2.5 h. The solvent was pumped off *in vacuo* and the dark brown solid stirred in hexane for 3 h. The suspension was filtered to give a brown shiny solid. It was recrystallised from $CH_2Cl_2$ (10 $cm^3$)–hexane (20 $cm^3$) giving dark thin *plate crystals* which were filtered off and dried *in vacuo* (20%). They contain 4 $CH_2Cl_2$ of crystallisation (Found: C, 19.5; H, 5.1; N, 12.1. $C_{14}H_{42}Cl_{14}N_8V_2$ requires C, 18.3; H, 4.6; N, 12.2%). IR: ν(VCl) 496; ν(NH) 2420 $cm^{-1}$. UV/VIS (in $CH_2Cl_2$): $\lambda_{max}$ 434 nm, ε 26 237 $dm^3$ $mol^{-1}$ $cm^{-1}$. NMR ($CDCl_3$): $^1H$, δ 0.0 (s, NMe), 2.5 (s, br, $NMe_2$) and 7.25–7.85 (br, NH; $^{51}V$, δ − 707 (s).

**Method 2.** This method gives the $CH_2Cl_2$-free complex. The compound $[VCl_3(thf)_3]$ (0.322 g, 0.86 mmol) was dissolved in MeCN (30 $cm^3$) and $Me_3SiNHNMe_2$ (0.57 $cm^3$, 4.31 mmol) was added to the green solution. The solution turned dark brown and was stirred at room temperature for 2 h. It was filtered, then the filtrate was evaporated. The shiny brown *solid* was stirred in hexane for a few hours then filtered off (55%). Aliquots of the reaction solution were tested for ammonia after extraction with $H_2SO_4$, using the indophenol test.[1] Yields were

**Table 3** Intramolecular distances (Å) and angles (°) with e.s.d.s parentheses for $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3(NH_2NMePh)_2]$ **5**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| V–O(1) | 1.858(5) | V–O(2) | 1.860(6) | C(17)–C(18) | 1.406(12) | C(18)–C(22) | 1.508(13) |
| V–O(3) | 1.864(6) | V–N(1) | 2.204(7) | C(19)–C(20) | 1.549(14) | C(19)–C(21) | 1.484(14) |
| V–N(3) | 2.217(8) | O(1)–C(1) | 1.354(9) | C(22)–C(23) | 1.512(14) | C(22)–C(24) | 1.562(14) |
| O(2)–C(13) | 1.361(11) | O(3)–C(25) | 1.379(10) | C(25)–C(26) | 1.416(14) | C(25)–C(30) | 1.401(14) |
| N(1)–N(2) | 1.427(10) | N(2)–C(37) | 1.446(15) | C(26)–C(27) | 1.41(2) | C(26)–C(31) | 1.46(2) |
| N(2)–C(38) | 1.463(12) | N(3)–N(4) | 1.356(10) | C(27)–C(28) | 1.34(2) | C(28)–C(29) | 1.46(2) |
| N(4)–C(44) | 1.28(2) | N(4)–C(45) | 1.387(15) | C(29)–C(30) | 1.401(15) | C(30)–C(34) | 1.479(14) |
| C(1)–C(2) | 1.399(12) | C(1)–C(6) | 1.450(12) | C(31)–C(32) | 1.56(2) | C(31)–C(33) | 1.53(2) |
| C(2)–C(3) | 1.45(2) | C(2)–C(7) | 1.498(15) | C(34)–C(35) | 1.56(2) | C(34)–C(36) | 1.59(2) |
| C(3)–C(4) | 1.33(2) | C(4)–C(5) | 1.355(15) | C(38)–C(39) | 1.400(13) | C(38)–C(43) | 1.352(13) |
| C(5)–C(6) | 1.412(13) | C(6)–C(10) | 1.459(13) | C(39)–C(40) | 1.357(14) | C(40)–C(41) | 1.38(2) |
| C(7)–C(8) | 1.55(2) | C(7)–C(9) | 1.51(2) | C(41)–C(42) | 1.35(2) | C(42)–C(43) | 1.37(2) |
| C(10)–C(11) | 1.548(14) | C(10)–C(12) | 1.519(14) | C(45)–C(46) | 1.388(15) | C(45)–C(50) | 1.44(2) |
| C(13)–C(14) | 1.415(13) | C(13)–C(18) | 1.408(13) | C(46)–C(47) | 1.36(2) | C(47)–C(48) | 1.34(2) |
| C(14)–C(15) | 1.414(12) | C(14)–C(19) | 1.517(12) | C(48)–C(49) | 1.38(2) | C(49)–C(50) | 1.41(2) |
| C(15)–C(16) | 1.393(14) | C(16)–C(17) | 1.414(14) | | | | |
| O(1)–V–O(2) | 119.6(3) | O(1)–V–O(3) | 115.2(3) | C(15)–C(16)–C(17) | 119.7(9) | C(16)–C(17)–C(18) | 119.9(10) |
| O(1)–V–N(1) | 91.9(3) | O(1)–V–N(3) | 89.5(3) | C(13)–C(18)–C(17) | 120.3(9) | C(13)–C(18)–C(22) | 120.5(8) |
| O(2)–V–O(3) | 125.1(3) | O(2)–V–N(1) | 86.7(3) | C(17)–C(18)–C(22) | 119.1(9) | C(14)–C(19)–C(20) | 110.9(8) |
| O(2)–V–N(3) | 90.9(3) | O(3)–V–N(1) | 95.2(3) | C(14)–C(19)–C(21) | 114.5(9) | C(20)–C(19)–C(21) | 110.6(9) |
| O(3)–V–N(3) | 86.0(3) | N(1)–V–N(3) | 177.6(3) | C(18)–C(22)–C(23) | 112.8(9) | C(18)–C(22)–C(24) | 110.9(7) |
| V–O(1)–C(1) | 158.1(6) | V–O(2)–C(13) | 136.5(5) | C(23)–C(22)–C(24) | 110.3(8) | O(3)–C(25)–C(30) | 120.2(9) |
| V–O(3)–C(25) | 135.1(5) | V–N(1)–N(2) | 126.0(6) | C(26)–C(25)–C(30) | 121.9(9) | C(25)–C(26)–C(27) | 116.3(12) |
| N(1)–N(2)–C(37) | 107.9(10) | N(1)–N(2)–C(38) | 110.7(8) | C(25)–C(26)–C(31) | 123.6(10) | C(27)–C(26)–C(31) | 120.1(10) |
| C(37)–N(2)–C(38) | 115.4(8) | V–N(3)–N(4) | 135.0(7) | C(26)–C(27)–C(28) | 122.7(12) | C(27)–C(28)–C(29) | 121.7(12) |
| N(3)–N(4)–C(44) | 124.6(11) | N(3)–N(4)–C(45) | 119.5(10) | C(28)–C(29)–C(30) | 116.0(12) | C(25)–C(30)–C(29) | 121.1(10) |
| C(44)–N(4)–C(45) | 113.1(10) | O(1)–C(1)–C(2) | 117.4(7) | C(25)–C(30)–C(34) | 120.6(10) | C(29)–C(30)–C(34) | 118.1(11) |
| O(1)–C(1)–C(6) | 119.8(7) | C(2)–C(1)–C(6) | 122.6(8) | C(26)–C(31)–C(32) | 109.3(10) | C(26)–C(31)–C(33) | 114.4(12) |
| C(1)–C(2)–C(3) | 116.4(10) | C(1)–C(2)–C(7) | 121.5(9) | C(32)–C(31)–C(33) | 114.1(11) | C(30)–C(34)–C(35) | 112.2(10) |
| C(3)–C(2)–C(7) | 121.7(10) | C(2)–C(3)–C(4) | 122.2(10) | C(30)–C(34)–C(36) | 114.0(13) | C(35)–C(34)–C(36) | 106.7(13) |
| C(3)–C(4)–C(5) | 119.6(9) | C(4)–C(5)–C(6) | 125.2(10) | C(39)–C(38)–C(43) | 117.4(10) | N(2)–C(38)–C(39) | 118.5(8) |
| C(5)–C(6)–C(1) | 113.9(9) | C(1)–C(6)–C(10) | 123.6(8) | N(2)–C(38)–C(43) | 124.1(9) | C(38)–C(39)–C(40) | 122.1(10) |
| C(5)–C(6)–C(10) | 122.2(9) | C(2)–C(7)–C(8) | 108.7(9) | C(39)–C(40)–C(41) | 119.5(11) | C(40)–C(41)–C(42) | 117.8(11) |
| C(2)–C(7)–C(9) | 117.7(11) | C(8)–C(7)–C(9) | 109.3(10) | C(41)–C(42)–C(43) | 122.9(12) | C(42)–C(43)–C(38) | 120.1(11) |
| C(6)–C(10)–C(11) | 111.4(9) | C(6)–C(10)–C(12) | 112.1(9) | C(46)–C(45)–C(50) | 113.1(11) | N(4)–C(45)–C(46) | 121.4(10) |
| C(11)–C(10)–C(12) | 107.1(8) | O(2)–C(13)–C(14) | 119.6(9) | N(4)–C(45)–C(50) | 125.5(10) | C(45)–C(46)–C(47) | 123.6(12) |
| O(2)–C(13)–C(18) | 120.2(8) | C(14)–C(13)–C(18) | 120.0(9) | C(46)–C(47)–C(48) | 121.9(15) | C(47)–C(48)–C(49) | 120.2(15) |
| C(13)–C(14)–C(19) | 122.3(8) | C(15)–C(14)–C(19) | 118.7(8) | C(48)–C(49)–C(50) | 118.0(12) | C(49)–C(50)–C(45) | 122.9(12) |
| C(13)–C(14)–C(15) | 119.0(9) | C(14)–C(15)–C(16) | 121.1(9) | | | | |

in the range 80–90% (Found: C, 20.4; H, 6.2; N, 19.6. $C_{10}H_{34}Cl_6N_8V_2$ requires C, 20.7; H, 5.9; N, 19.3%).

### Preparation of $[PPh_4]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ 2

Compound **1** (0.273 g, 0.47 mmol) was dissolved in MeOH (30 cm$^3$), $[PPh_4]Br$ (0.60 g, 1.43 mmol) was added and the brown solution stirred at room temperature for 5 h. The solvent was removed *in vacuo* and the resulting dark brown *solid* stirred in hexane for 2 h, then filtered and dried *in vacuo* (40%) (Found: C, 53.4; H, 4.8; N, 7.7. $C_{66}H_{58}Cl_6N_6P_2V_2$ requires C, 55.5; H, 5.0; N, 7.2%). $^1H$ NMR ($CD_2Cl_2$): δ 7.80–8.00 (m, 20 H, aromatic) and 1.40 (s, 18 H, $NMe_2$).

### Reaction of compound 1 with $Li(SC_6H_2Pr^i{}_3\text{-}2,4,6)$

To a red-brown solution of compound **1** (0.23 g, 0.41 mmol) in dichloromethane (50 cm$^3$) was added $Li(SC_6H_2Pr^i{}_3\text{-}2,4,6)$ (0.6 g, 3.26 mmol) and the mixture was stirred for 3 d followed by heating under reflux for 6 h. The brown-green solution was filtered and the solvent removed *in vacuo*. The oily residue was redissolved in hexane (10 cm$^3$), filtered and the filtrate held at −30 °C for 2 d. A dark microcrystalline *solid* precipitated which was filtered off and dried *in vacuo* (**3**). It appears to contain one $CH_2Cl_2$ of crystallisation. Yield 0.2 g (Found: C, 66.2; H, 9.7; N, 4.3; S, 9.1. $C_{99}H_{168}N_6S_6V_2$ requires C, 65.8; H, 9.4; N, 4.7; S, 10.6%). $^1H$ NMR ($CD_2Cl_2$): δ 1.22 (d, CH) 1.25 (d, CH); 2.28, 2.72, 3.14 (s, $NCH_3$), 2.85 and 3.46 (m, CH) and 7.00 (s, br, aromatic).

### Reaction of $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_4Li(thf)]$ with $NH_2NMe_2$

To a slurry of $[VCl_3(thf)_3]$ (0.47 g, 1.25 mmol) in hexane (30 cm$^3$) was added $Li(OC_6H_3Pr^i{}_2\text{-}2,6)$ (0.93 g, 5.00 mmol). After the reaction mixture was stirred for 12 h the green solution was filtered, concentrated to *ca.* 15 cm$^3$ and treated with $NH_2NMe_2$ (0.30 g, 5.00 mmol), to produce a pink-red solution. The mixture was stirred for 5 min and allowed to stand overnight at −30 °C. Red prismatic crystals separated. X-Ray-quality *crystals* of $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3(NH_2NMe_2)_2]$ **4** were obtained after recrystallisation from hexane solution at −30 °C. Yield 0.3 g, 32%. Their air-sensitivity and low melting point prevented an accurate elemental analysis of the crystals but a magnetic moment could be obtained by the Evans method ($\mu_{eff}$ = 2.69 $\mu_B$). $^1H$ NMR ($[^2H_8]$thf): δ 1.58, 1.85 (doublets, $CH_3$), 2.30 (s, $NCH_3$), 3.0 (s, br, $NCH_3$), 3.22–3.32 (m, CH) and 6.71–7.07 (m, aromatic): IR (Nujol): 3256 and 1588 cm$^{-1}$ [ν(N–H)].

### Reaction of $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3Li(thf)]$ with $NH_2NMePh$

The reaction was carried out under the same conditions and in the same molar ratios as used for $NH_2NMe_2$, to give red, thermally stable, X-ray-quality *crystals* of $[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3(NH_2NMePh)_2]$ **5** in 40% yield (Found: C, 72.6; H, 8.6; N, 6.8. $C_{50}H_{71}N_4O_3V$ requires C, 72.6; H, 8.7; N, 6.8%). $^1H$ NMR ($C_6{}^2H_6$): δ 1.1 (d, $CH_3$), 2.9, 3.9, 4.4 (br, $CH_3$), 6.8–7.4 (m, aromatic) and 10.6 (br, NH). IR (Nujol): 3280 and 1588 cm$^{-1}$ [ν(N–H)].

## Cyclic voltammetry

The cyclic voltammetry of $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$ was studied under dinitrogen in $CH_2Cl_2$ and MeCN at temperatures between −30 and −40 °C in a glove-box (electrolyte 0.1 mol dm$^{-3}$ $[NBu^n{}_4]BF_4$. The working electrode was a platinum wire or vitreous carbon rod, the secondary electrode was tungsten and the reference electrode, silver. Cyclic voltammograms were recorded on a EG&G instrument, model 273 potentiostat-waveform generator controlled by an IBM/PC AT computer with a Hewlett-Packard HP 7470A plotter and Philips type PM 8043 auxiliary X–Y chart recorder.

## Crystallography

**$[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]\cdot 4CH_2Cl_2$ 1.** *Crystal data.* $C_{10}H_{34}Cl_6N_8V_2\cdot 4CH_2Cl_2$, $M = 920.8$, monoclinic, space group $F2/d$ (equivalent to no. 15), $a = 24.041(7)$, $b = 8.859(2)$, $c = 38.086(9)$ Å, $\beta = 100.15(2)°$, $U = 7984.5$ Å$^3$, $Z = 8$, $D_c = 1.532$ g cm$^{-3}$, $F(000) = 3728$, $\mu$(Mo-K$\alpha$) = 14.2 cm$^{-1}$, $\lambda$(Mo-K$\alpha$) = 0.710 69 Å.

Very thin plate crystals of this moisture-sensitive sample were mounted under dinitrogen in capillaries. Eventually a crystal (*ca.* 0.02 × 0.30 × 0.60 mm) was found which appeared single and stable. After brief photographic examination the crystal was mounted on the Enraf-Nonius CAD4 diffractometer (with monochromatic radiation) for determination of cell parameters (from the settings of 25 reflections having $\theta = 6\text{–}8°$, each centred in four orientations) and measurement of diffraction intensities (to $\theta_{max} = 20°$).

The intensity data were corrected for Lorentz-polarisation effects, crystal deterioration (the intensities of monitor reflections decreased by 45% during the data collection) and absorption (from crystal measurement). 1862 Unique reflections (generally rather weak, only 612 with $I > 2\sigma_I$) were entered into the SHELX program system,[26] where the complex anion structure was eventually recognised from the automated Patterson routines in SHELXS[27] in the non-centrosymmetric space group $Fd$ (equivalent to $Cc$, no. 9). Successive iterations of refinement and difference-map calculations revealed the atoms of the cations and solvent molecules.

After transfer to $F2/d$, refinement (on $F$) was continued to $R = 0.181$ and $R_g = 0.155$[25] for 956 reflections (those having $I > \sigma_I$) weighted $w = (\sigma_F{}^2 + 0.002\,89F^2)^{-1}$. The V and Cl atoms were refined with anisotropic thermal parameters but not very satisfactorily; the V atom has a 'non-positive-definite' thermal ellipsoid. The N and C atoms were refined isotropically. Hydrogen atoms were included in calculated positions, the methyl groups in staggered orientations, riding on those of the parent C or N atoms. In a final difference map, the principal peak (*ca.* 1.6 e Å$^{-3}$) was close to the midpoint of the V–V bond: there were no other peaks of significance.

Scattering factor curves were taken from ref. 28. Computer programs used in this analysis have been noted above and in Table 4 of ref. 29, and were run on a DEC MicroVAX II computer in the Nitrogen Fixation Laboratory.

**$[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3(NH_2NMe_2)_2]\cdot 0.5C_6H_{14}$ 4.** *Crystal data.* $C_{40}H_{67}N_4O_3V\cdot 0.5C_6H_{14}$, $M = 702.9$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.957(5)$, $b = 12.759(7)$, $c = 15.762(6)$ Å, $\alpha = 70.22(4)$, $\beta = 81.27(3)$, $\gamma = 83.29(4)°$, $U = 2231$ Å$^3$, $Z = 2$, $D_c = 1.11$ g cm$^{-3}$, $F(000) = 814$, $\mu$(Mo-K$\alpha$) = 2.5 cm$^{-1}$, $T = 173$ K, $\lambda = 0.710\,69$ Å.

In a similar analysis to that above, accurate cell dimensions of a crystal, 0.3 × 0.2 × 0.2 mm, were refined from the goniometer settings of 25 reflections having $7 < \theta < 10°$. Diffraction intensities were measured to $\theta_{max} = 23°$. No decay or absorption correction was applied. Of 6188 unique reflections, 3945 significant reflections $[|F^2| > 2\sigma(F^2)]$ were used in the analysis.

Structure solution was by standard heavy-atom methods[27] and refinement (on $F$) by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms using Enraf-Nonius MoLEN programs.[30] Hydrogen atoms were included in idealised positions and refinement concluded with $R = 0.072$ and $R' = 0.041$,[30] $S = 1.9$, for the observed data, weighted $w = \sigma^{-2}(F)$. There is a molecule of hexane solvate lying across an inversion centre.

**$[V(OC_6H_3Pr^i{}_2\text{-}2,6)_3(NH_2NMePh)_2]$ 5.** *Crystal data.* $C_{50}H_{71}N_4O_3V$, $M = 827.05$, orthorhombic, space group $Pbn2_1$ (equivalent to no. 33), $a = 13.938(8)$, $b = 19.419(16)$, $c = 17.914(9)$ Å, $U = 4848(6)$ Å$^3$, $Z = 4$, $D_c = 1.133$ g cm$^{-3}$, $D_m = 1.128$ g cm$^{-3}$, $F(000) = 1784$, $T = 180.0(2)$ K, $\mu$(Mo-K$\alpha$) = 2.5 cm$^{-1}$.

Crystals are deep red and were cut down for use. One, *ca.* 0.5 × 0.4 × 0.4 mm, was sealed in a glass capillary. Intensities were measured on a Kuma KM4 four-circle diffractometer, for $\theta$ 2–23°, in the $\omega$–$2\theta$ scanning mode. There was no crystal deterioration. Of 12488 reflections measured ($4 < 2\sigma < 56°$), the 2926 unique 'observed' data with $I > 3\sigma_I$ were used in the analysis.

The structure was determined by the Patterson method and refined (on $F^2$) by full-matrix least-squares methods with the program SHELXL 93.[31] Hydrogen atoms of methylene and methyl groups were included in idealised positions; the hydrogen atoms on N(1) were located from a difference map and refined, whilst those on N(3) were included in calculated positions. Absorption corrections using DIFABS[32] were applied. At the conclusion of refinement, $R_1$ and $wR_2$[31] values were 0.052 and 0.131 for the 'observed' data weighted $w = [\sigma^2 + (0.0840P)^2 + 6.41P]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. The final difference map showed a general background between −0.22 and 0.34 e Å$^{-3}$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.* 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/56.

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