

**The Crystal and Molecular Structure of Bis(1-methyl-1-phenylhydrazine)dichloro-  
{1-methyl-1-phenylhydrazido(2-)}vanadium(v) Chloride, a Complex containing Two  
Side-on-co-ordinated Hydrazine Molecules**

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The complex  $[\text{VCl}_2(\text{H}_2\text{NNMePh})_2(\text{NNMePh})]\text{Cl}$  shows simultaneous co-ordination of side-on hydrazine and end-on hydrazide (2-), and forms a tetranuclear structure *via* an extensive array of hydrogen bonds.

We have been interested<sup>1-4</sup> in the chemistry of dinitrogen residues bound to transition elements for the light they might throw on intermediates involved in nitrogen fixation processes. Vanadium is now known to be a vital constituent of one kind of nitrogenase,<sup>5</sup> and dinitrogen is reduced by vanadium(II) in alkaline media.<sup>6</sup> However, dinitrogen or

hydrazine derivatives of vanadium have not been characterized. For these reasons, we have investigated the reactions of  $[\text{VCl}_3(\text{MeCN})_3]$  with hydrazines, and report here the structural analysis of the very air-sensitive red crystals obtained from its reaction with  $\text{MePhNNH}_2$ .

The crystals have a formula corresponding to

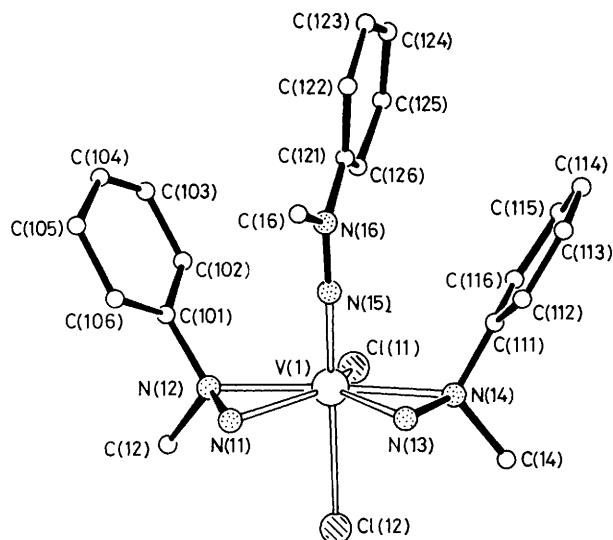


Figure 1. Structure of an individual cationic unit  $[\text{VCl}_2(\text{NH}_2\text{-NMePh})_2(\text{NNMePh})]^+$ .

$[\text{VCl}_2(\text{H}_2\text{NNMePh})_2(\text{NNMePh})]\text{Cl}$  (confirmed by subsequent chemical analysis). The complex crystallises in the triclinic system, with eight  $[\text{VCl}_2(\text{H}_2\text{NNMePh})_2(\text{NNMePh})]^+$  cations in the unit cell in two symmetry-related groups of four.<sup>†</sup>

The structure is best understood by consideration of the co-ordination about the vanadium (Figure 1) and then of the way the four independent complexes are bound together (Figures 2 and 3). The co-ordination about vanadium exhibits a pseudo-mirror-plane in a pentagonal bipyramidal arrangement. Of the two co-ordinated chlorines, the longer V-Cl separation [2.478(10) Å] is *trans* to the linear NNMePh moiety in the axial position. This lengthening reflects its *trans*-influence. The other V-Cl separation [2.321(2) Å] is not affected by a *trans*-ligand. The axial hydrazine residue has geometry and distances characteristic<sup>7</sup> of complexes with

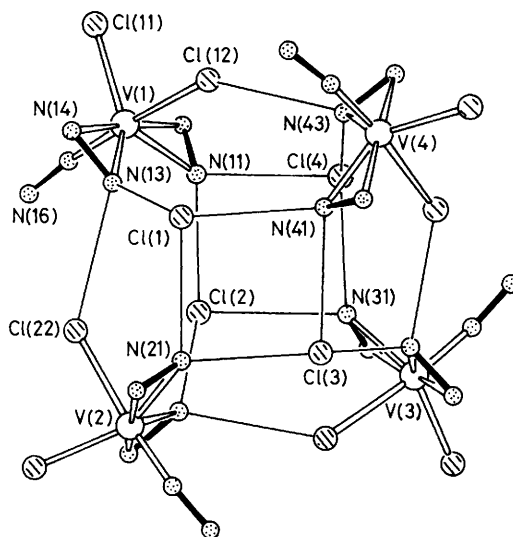


Figure 2. View of the tetranuclear assembly showing interaction with the chloride ions forming two squares of hydrogen bonding and the girdle of hydrogen bonds. The two squares are ca. 5.1 Å apart.

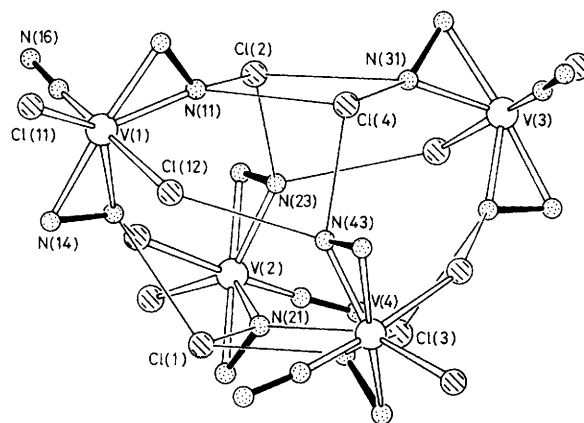


Figure 3. View of the tetranuclear assembly from about 90° to the view in Figure 2.

assigned hydrazido(2-)-ligands [V-N 1.696(24), N-N 1.295(17) Å;  $\angle\text{VNN} = 174.4(19)^\circ$ , co-ordination about *exo*-nitrogen planar, trigonal]. Thus, although the data do not permit the location of N-hydrogens, there cannot be any hydrogens on this residue, and the bond lengths exclude a formulation as *iso*-diazene.<sup>8</sup> Consequently, the other, side-on, residues must be hydrazines or *iso*-diazenes, and hydrazide(1-) is excluded for them.

The VNN triangles associated with these latter residues are isosceles, with N-N averaging at 1.455(5) and 1.440(19) Å (single bonds), and V-N all ca. 2.1 Å. In hydrazido(1-)-complexes of titanium,<sup>3</sup> whereas the N-N separation (1.41 Å) is likewise suggestive of an N-N single bond (*cf.* 1.47 Å in hydrazine itself),<sup>9</sup> the Ti-N separations are ca. 1.8 Å (involving Ti and the anionic nitrogen) and 2.1 Å (Ti and neutral nitrogen). This again suggests that the dinitrogen residues here are contained in a neutral hydrazine, and, consistent with this, the co-ordination about the NMePh nitrogen is roughly tetrahedral. The hydrazine formulation is confirmed by the pattern of hydrogen-bonding discussed below.

Figures 2 and 3 show how four cationic units and four

<sup>†</sup> Crystal data:  $\text{C}_{21}\text{H}_{28}\text{Cl}_3\text{N}_6\text{V}$ ,  $M = 521.8$ , triclinic, space group  $P\bar{1}$ ,  $a = 16.883(3)$ ,  $b = 18.430(3)$ ,  $c = 21.994(5)$  Å,  $\alpha = 107.2(2)$ ,  $\beta = 103.0(2)$ ,  $\gamma = 100.7(2)^\circ$ ,  $U = 6132.7$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.130$  g cm<sup>-3</sup>,  $F(000) = 2160$ ,  $\mu(\text{Mo-K}\alpha) = 5.93$  cm<sup>-1</sup>. Hemisphere of data collected, all  $h$  positive, on a CAD-4 diffractometer, graphite monochromator, Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $1 \leq \theta \leq 19^\circ$ ,  $\omega/2\theta$  scan, scan speed 3.33°/min. Number of reflections 10316, 6360 with  $I \geq 3\sigma(I)$ . After Lorentz-polarisation correction, a linear correction was applied to offset a decay of 18.2% during data collection, followed by an empirical absorption correction. The structure was solved by Patterson and direct methods to derive 4 V and 12 Cl positions, followed by normal heavy-atom methods for the remaining atoms. Refinement by full-matrix least-squares of structure amplitudes to isotropic convergence gave  $R = 0.16$ , with phenyl H only in calculated positions ( $d_H = 1.0$  Å). Anisotropic refinement of non-H atoms, restricted by program and computer limitations, was done alternately in two parts; (a) V, Cl, N, and Me groups (52 atoms) and (b) V, Cl, and phenyl rings (86 atoms), with weighting scheme  $w = (23.208 - 0.5421 F + 0.0105 F^2)^{-1}$ . Final  $R = 0.107$ ,  $R_w = 0.158$ ,  $S = 1.098$ . Overall standard deviations of bond distances were limited by the restricted data set consequent upon heavy crystal decay. V-Cl distances,  $\sigma \sim 0.005$  Å; V-N distances,  $\sigma \sim 0.015$  Å; N-C and C-C distances,  $\sigma \sim 0.02$  Å. Mean phenyl bond distance = 1.36(5) Å. In the discussion all quoted distances and angles are the means taken over the four independent groups. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

chlorides are bound together to form a tetranuclear oligomer by hydrogen bonding. In this assembly, there are 16 hydrogen bonds, so that every N-hydrogen is involved, along with the four chlorides and the four axial chloro-ligands, in a hydrogen-bonding network. The spatial arrangement of the bonds and the N-Cl separations are all consistent with this complex of hydrogen bonding, even though the data set do not allow the location of individual hydrogen atoms. Only the chloro-ligands in the 'pentagonal' plane, which presumably are the least negative of the chloro-species present, do not take part in hydrogen bonding.

The sixteen hydrogen bonds are divided into three groups. There are two square arrangements involving chlorides, at the top and the bottom of the cluster (Figure 2), involving eight hydrogen bonds, e.g., N(11) ···· Cl(2) (N-H ···· Cl ca. 3.16 Å). There is a girdle of bonds in a sequence V-Cl ···· H-N-V-Cl ···· around the 'waist' of the cluster involving four hydrogen bonds, e.g., N(23) ···· Cl(22) (N-H ···· Cl ca. 3.31 Å). Finally, there are four 'vertical' bonds to the chlorides which act as internal braces for the cluster, e.g., N(23) ···· Cl(2) (N-H ···· Cl ca. 3.11 Å) (Figure 3).

This complex is only the second example of a side-on co-ordinated hydrazine which has been unequivocally proved. The first is [Mo(C<sub>5</sub>H<sub>5</sub>)(NO)I(NH<sub>2</sub>NHPh)][BF<sub>4</sub>],<sup>10</sup> but our vanadium complex accommodates two hydrazines side-on, rather than one, and is the first indication of a type of intermediate which might be involved in the reduction of N<sub>2</sub> by V<sup>2+</sup>. With examples from other transition metals there is now a precedent for side-on co-ordination of every intermediate in a supposed protonation sequence N<sub>2</sub>, N<sub>2</sub>H, NNH<sub>2</sub>, NHHNH<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>. It is the first example of an organohydrazine

and hydrazide(2-) in the same co-ordination sphere. Finally, it is an oligomeric structure which is based entirely on an extensive and co-operative array of hydrogen bonds. The significance of such interactions in hydrazine chemistry is being explored.

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