

Preparation and Characterization of $[V_3Cl_5(tmeda)_3][V(NPh_2)_4]$ (*tmeda* = *N,N,N',N'*-tetramethylethylenediamine): a V^{II} – V^{III} Mixed Valence Complex

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Reaction of *trans*- $[VCl_2(tmeda)_2]$ (*tmeda* = *N,N,N',N'*-tetramethylethylenediamine) with an excess of $NaNPh_2$ led to the formation of the V^{II} – V^{III} mixed-valence species $[V_3Cl_5(tmeda)_3][V(NPh_2)_4]$, through an unusual disproportionation reaction.

Interest in the chemistry of divalent vanadium has been stimulated by several diverse features shown by this versatile metal. They include: dinitrogen activation/fixation,¹ the formation of vanadium–vanadium multiple bonds,² a rich organometallic chemistry,³ and the puzzling role played by vanadium (probably low-valent) in several metallo-proteins.⁴

However, apart from considerable development of the cyclopentadienyl and related systems,³ the chemistry of divalent vanadium remains limited.⁵ Undoubtedly a lack of suitable starting materials has been the limiting factor for the development of the chemistry of this oxidation state. Binuclear, ionic $[V_2Cl_3L_6]_2[M_2Cl_6]$ ($M = Zn,$ ⁶ $Al,$ ⁷ $Co,$ ⁷ and Fe ⁷)

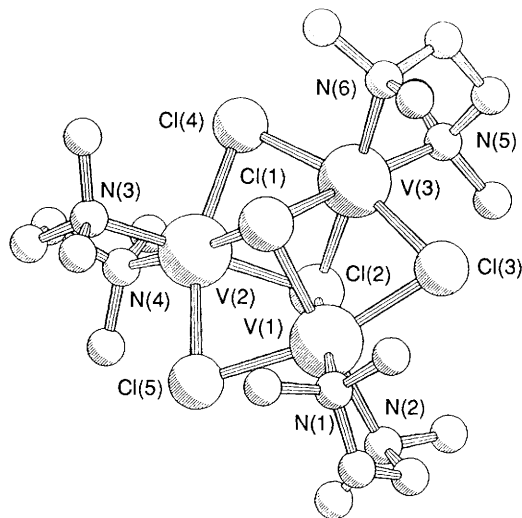
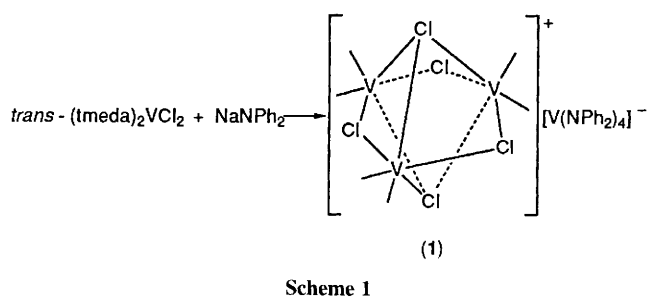


Figure 1. PLUTO plot of $[\text{V}_3\text{Cl}_5(\text{tmeda})_3]^+$. Selected bond distances (Å) and angles ($^\circ$): V(1)–Cl(1) 2.499(4), V(1)–Cl(2) 2.522(4), V(1)–Cl(3) 2.480(4), V(1)–Cl(5) 2.495(4), V(1)–N(1) 2.211(9), V(1)–N(2) 2.209(9), Cl(1)–V(1)–Cl(2) 87.9(1), Cl(1)–V(1)–Cl(3) 83.8(1), Cl(1)–V(1)–Cl(5) 84.3(1), V(1)–Cl(1)–V(2) 78.0(1), V(1)–Cl(2)–V(2) 76.9(1), N(1)–V(1)–N(2) 82.9(3), V(1) \cdots V(2) 3.142(3).

species have been obtained by reaction of $[\text{VCl}_3(\text{thf})_3]$ (thf = tetrahydrofuran) with a number of reducing agents. The binuclear nature of these complexes is especially attractive, in the absence of a direct V–V bond, for studying the factors which favour polynuclear aggregation in both the solid state and solution (nature of the ligand, magnetic interaction between the two metals). On the other hand, the robust hetero-bimetallic nature of these complexes, preserved during several ligand-replacement reactions,⁸ is hampering their utilization as starting materials to study the chemical reactivity of V^{II} .

We have recently prepared a class of *cis*- and *trans*-monomeric and octahedral $[\text{VCl}_2(\text{amine})_4]$ complexes.⁹ These complexes are versatile and readily available starting materials for the preparation of a variety of V^{II} compounds *via* simple ligand-replacement reactions.

In this paper we describe the result of the usual disproportionation reaction of *trans*- $[\text{VCl}_2(\text{tmeda})_2]$ (tmeda = *N,N,N',N'*-tetramethylethylenediamine) with Ph_2NNa (Scheme 1). The reaction proceeded rapidly in thf, forming brown-reddish solutions from which olive-green crystals of $[\text{V}_3\text{Cl}_5(\text{tmeda})_3][\text{V}(\text{NPh}_2)_4]$ (**1**) were isolated in 31% yield upon filtration, concentration, and addition of small amounts

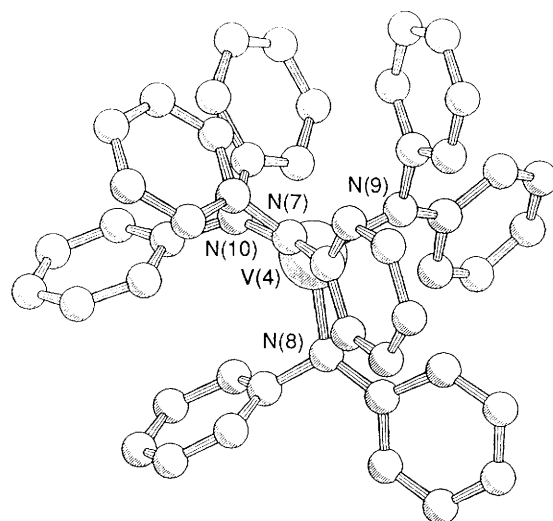


Figure 2. PLUTO plot of $[\text{V}(\text{NPh}_2)_4]^-$. Selected bond distances (Å) and angles ($^\circ$): V(4)–N(7) 1.978(9), V(4)–N(8) 1.996(7), V(4)–N(9) 1.974(8), V(4)–N(10) 2.009(9), N(7)–V(4)–N(8) 114.3(4), N(7)–V(4)–N(9) 109.9(4), N(7)–V(4)–N(10) 105.2(4), N(9)–V(4)–N(10) 112.9(4).

of toluene. The utilization of larger amounts of Ph_2NNa did not modify the result of the reaction.[†]

The structure of (**1**) has been determined by X-ray analysis.[‡] Unfortunately, the crystals scattered very weakly and repeated attempts to obtain better quality crystals were unsuccessful. In one case it was possible to obtain a data set sufficient to solve the structure. The unit cell contains two independent fragments, identified as a singly charged cation and anion. The first moiety, the cation, is a $[\text{V}_3\text{Cl}_5(\text{tmeda})_3]$ unit (Figure 1). The molecular core of this unit is defined by three vanadium atoms with three bridging chlorine atoms in the same plane, the remaining two η^3 -chlorine atoms being symmetrically placed above and below the molecular plane. Each of three molecules of tmeda chelates one of the three equivalent vanadium atoms, imposing a slightly distorted octahedral co-ordination geometry on each metal centre. The V–Cl distances, formed by the apical and equatorial chlorine atoms, are comparable in spite of the different bonding to vanadium (μ vs. η^3). The bond lengths are quite long [ranging from 2.480(4) to 2.531(4) Å] but compare well with those found⁶ in the dinuclear, cationic $[\text{V}_2\text{Cl}_6]^{2+}$ and in the neutral, monomeric *trans*- $[\text{VCl}_2(\text{tmeda})_2]$,⁹ *trans*- $[\text{VCl}_2(\text{pyridine})_4]$,⁵ⁱ and *trans*- $[\text{VCl}_2(\text{dmpe})_2]$ ^{5b} (dmpe = bisdimethylphosphinoethane) species. No special features were observed for the

[†] A thf solution (150 ml) of neat Ph_2NH (16 mmol) was treated with NaH (16 mmol). The mixture was stirred and warmed for 30 min. The addition of *trans*- $[\text{VCl}_2(\text{tmeda})_2]$ (7.8 mmol) to the resulting mixture caused a colour change to deep-red. Stirring was continued for 14 h. The solvent was removed *in vacuo* and the solid residue recrystallized from toluene (40 ml)–thf (10 ml). Olive-green crystals of (**1**) separated upon cooling at -30°C (yield 0.61 mmol, 31%). Satisfactory elemental analyses were obtained.

[‡] Crystal data for (**1**): $\text{C}_{66}\text{H}_{88}\text{Cl}_5\text{N}_{10}\text{V}_4$, $M = 1402.52$, orthorhombic, $Pbca$, $a = 20.624(5)$, $b = 22.978(6)$, $c = 28.839(4)$ Å, $V = 13667(5)$ Å³, $Z = 8$, $D_c = 1.363$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 7.6$ cm⁻¹, $\lambda = 0.71073$ Å, crystal dimension (mm) $0.10 \times 0.12 \times 0.20$, $R_F = 0.117$, $R_w = 0.067$, GoF = 1.356 for 5364 reflections with $I \geq 1.5\sigma(I)$ collected at 138 K on an Enraf-Nonius CAD4 diffractometer. 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.

three co-ordinated molecules of tmeda, except for the long V–N distances (av. V–N 2.209 Å). The V···V non-bonding distance [av. V···V 3.133(3) Å] is slightly longer than that observed in the [V₂Cl₃L₆]⁺ species [V···V 2.993(1) Å] and rules out the presence of V–V bonds.

The second, anionic fragment (Figure 2) is mononuclear with vanadium placed in the centre of a near-regular tetrahedron, the small observed distortion probably being an effect of the steric congestion due to the eight phenyl rings. The trigonal planar geometry of each nitrogen atom may indicate a significant extent of V–N π-bonding, although the V–N distances are normal [av. V–N 1.980(8) Å].

The formation of complex (1), obviously a VII–VIII mixed-valence species, is interesting. The partial oxidation possibly occurs via a disproportionation reaction and formation of some unknown low-valent vanadium species, because no traces of metallic vanadium were detected. However, attempts to isolate other complexes have so far failed.

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