

Trinuclear Species in Vanadium(II) Chemistry

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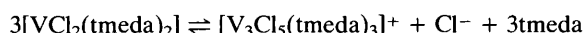
The *triangulo*-{V₃Cl₃} unit is shown to form easily in solutions from mononuclear vanadium(II) compounds such as [VCl₂(tmeda)₂] and structural studies show that this unit is contained in a trigonal bipyramidal arrangement with either chloride ions or methoxide ions at the apices, as in [V₃Cl₃(μ₃-Cl)₂(tmeda)₃]⁺, [V₃Cl₃(μ₃-OMe)₂(tmeda)₃]⁺ and [V₃Cl₃(μ₃-OMe)₂(depe)₃]⁺.

There has been considerable interest of late in the synthesis of simple, mononuclear compounds of vanadium(II) to explore its chemistry, in particular in its reactions with dinitrogen.¹ We have developed²⁻⁴ simple syntheses for [V(H₂O)₆]²⁺ and compounds derived from it, and [VCl₂(tmeda)₂] (tmeda = tetramethylethylenediamine), first described by Gambarotta,⁵ has proved very useful in developing V^{II} organometallic chemistry. However, our attempts to produce vanadium(II) diiodides have been less than entirely successful, generally giving unexpected results.

For example, we found that [VCl₂(tmeda)₂], or [V₂Cl₃(thf)₆][AlCl₂Et₂]⁶ and tmeda, reacts with Me₃SiI in boiling thf to yield a turquoise precipitate (25% yield) not of the expected [VI₂(tmeda)₂] but of tri-μ-chloro-di-μ₃-chloro-tris(tetramethylethylenediaminevanadium) iodide, [V₃Cl₅(tmeda)₃]⁺I⁻, **1** whose structure was shown by X-ray analysis. The trinuclear cation has already been characterised in other salts.⁷ Subsequently we showed that the blue solution of [VCl₂(tmeda)₂] in thf at room temperature immediately turned turquoise upon addition of Na[BPh₄]. On cooling this solution to -20 °C, blue crystals of [VCl₂(tmeda)₂] developed. Upon warming again to room temperature the crystals dissolved, giving on layering with hexane, turquoise crystals of [V₃Cl₅(tmeda)₃][BPh₄], **2**, (55% yield), whose structure was characterised by X-ray analysis (Fig. 1).[‡] This structure contains a cation identical to that in [V₃Cl₅(tmeda)₃]⁺I⁻, but in this case the X-ray data allowed a better structure resolution.

We have also shown that turquoise [V₃Cl₅(tmeda)₃][BPh₄] reacts with tmeda and chloride ion (but not with either,

separately) in thf to yield blue [VCl₂(tmeda)₂]. Evidently a facile equilibrium exists:



Further, upon attempting the synthesis of [VI₂(tmeda)₂] by reaction of VCl₂(EtOH)₂⁸ with KI and tmeda in MeOH/thf, the product we finally isolated proved to be cocrystallised [V₃(μ-Cl)₃(μ₃-OMe)₂(tmeda)₃]I⁻ and [V₃Cl₄(OMe)(tmeda)₃]I⁻, as shown by X-ray structure analysis (Fig. 2).[§] Thus the V₃Cl₃ unit seems to be present in VCl₂(EtOH)₂ and to survive the reactions we imposed upon it. In addition, we have shown by mass spectrometry and microanalysis that the cation in the salt obtained from the reaction of **2** with depe [bis(diethylphosphino)ethane] in methanol is [V₃(μ-Cl)₃(μ₃-OMe)₂(depe)₃]⁺, and the known [VCl₂(depe)₂]⁴ is obtained with an excess of depe.

Consequently, we have persuasive evidence that the *triangulo*-{V₃Cl₃} moiety with either chloride ions or methoxide ions in the axial positions has considerable stability in V^{II} chemistry, and that it may form frequently and spontaneously. For example, careful heating of [V(MeOH)₆Cl₂]^{6,8} shows a weight loss corresponding to the formation of VCl₂(MeOH)₂, which may be formulated as [V₃Cl₅(MeOH)₆]Cl. The many reported complexes VX₂L₂ (X = halide, L = monodentate ligand) may, in fact, be trinuclear. Further, [VCl₂(tmeda)₂], on heating *in vacuo* or in a thermal gravimetric analysis (TGA) experiment under N₂, loses weight at 180 °C, corresponding to the formation of VCl₂(tmeda), and the

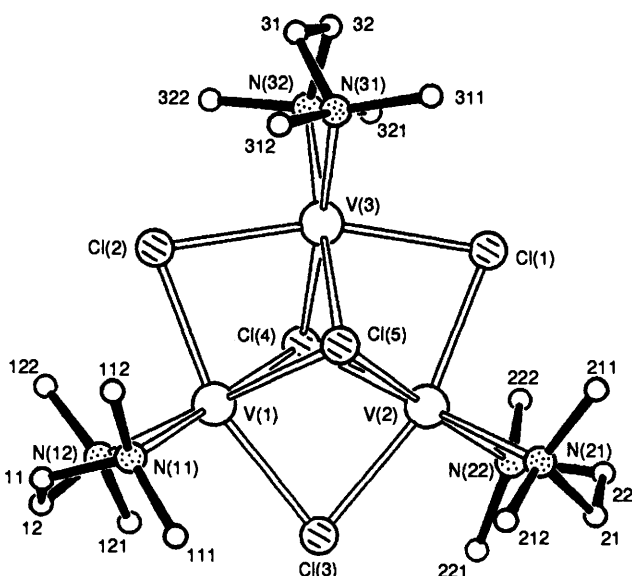


Fig. 1 Structure of the cation in [V₃Cl₅(tmeda)₃][BPh₄], showing the atom numbering scheme (carbon atoms are labelled with their number only). Principal mean dimensions: V...V 3.142(7), V-Cl_{eq} 2.500(4), V-Cl_{cap} 2.519(6), V-N 2.214(2) Å; Cl_{eq}-V-Cl_{eq} 162.1(2), V-Cl_{eq}-V 77.8(1)°.

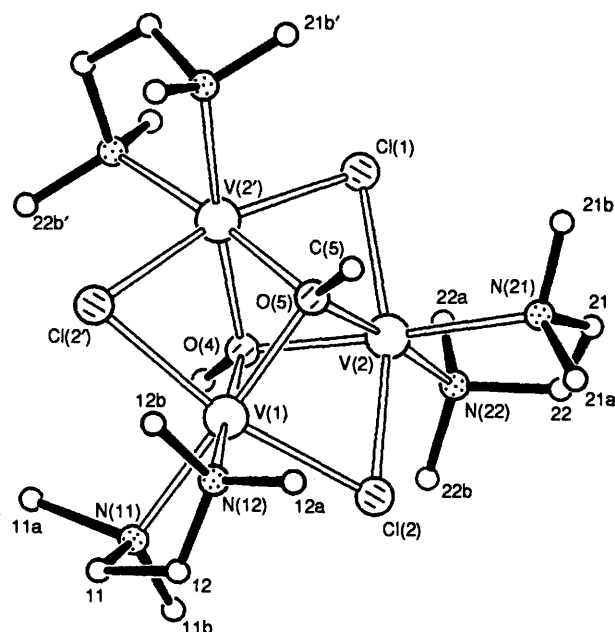


Fig. 2 Structure of the cation of the principal component of the co-crystals: [V₃Cl₃(OMe)₂(tmeda)₃]I⁻ (occupying ca. 83% of the sites) and [V₃Cl₄(OMe)(tmeda)₃]I⁻·MeOH (occupying 17% of the sites). Principal mean dimensions: V...V 3.002(4), V-Cl 2.496(7), V-O 2.136(5), V-N 2.270(11) Å; Cl-V-Cl 166.0(1), V-Cl-V 73.9(3)°. In the minor component, the methoxy group of O(5)-C(5) is replaced by a chloride ligand.

residue has the appropriate C, H, and N analyses. These, again, correspond to $[\text{V}_3\text{Cl}_5(\text{tmeda})_3]\text{Cl}$.

Gambarotta has reported that reactions of $[\text{VCl}_2(\text{tmeda})_2]$ with NaNPh_2 and with $[\text{VCl}_3(\text{thf})_3]$ yield $[\text{V}_3\text{Cl}_5(\text{tmeda})_3]^+$, a cation once described⁷ as being produced in a disproportionation reaction. Our data show that this is evidently not the case, and that the trinuclear unit, rather than being the one-off product of an unusual reaction, is of general occurrence in vanadium(II) chemistry.

Finally, it should be noted that $[\text{V}_3\text{Cl}_5(\text{tmeda})_3]\text{I}$ and $[\text{VI}_2(\text{tmeda})_2]$, and any other similar pairs of compounds containing $\text{V}_3\text{Cl}_5\text{I}$ or VI_2 , respectively, have the same C, H, and N contents, to the second decimal place. This is because the formula weights of $\text{V}_6\text{Cl}_{10}\text{I}_2$ {from $2[\text{V}_3\text{Cl}_5(\text{tmeda})_3]\text{I}$ } and V_3I_6 {from $3[\text{VI}_2(\text{tmeda})_2]$ } are equal. This coincidence emphasises the problems which can arise if too much reliance is placed upon C, H, and N analyses alone.

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Footnotes

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‡ Crystallographic data for $[\text{V}_3\text{Cl}_5(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)_3][\text{BPh}_4]$ $\text{C}_{42}\text{H}_{68}\text{BCl}_5\text{N}_6\text{V}_3$, $M = 998.04$, clear green, thick plate, monoclinic,

space group $P2_1/n$ (No. 14), $a = 19.619(1)$, $b = 21.566(2)$, $c = 12.050(1)$ Å, $\beta = 99.25(1)^\circ$, $V = 5032.3(7)$ Å³, $Z = 4$, $D_c = 1.317$ g cm⁻³, $F(000) = 2084$, $\mu = 8.3$ cm⁻¹, $\lambda = \text{Mo-K}\alpha$ (mean) 0.71069 Å. § Crystallographic data for the co-crystals of: $[\text{V}_3\text{Cl}_5(\text{OMe})_2(\text{tmeda})_3]\text{I}$ (ca. 83% occupancy) and $[\text{V}_3\text{Cl}_4(\text{OMe})(\text{tmeda})_3]\text{I}\cdot\text{MeOH}$ (17% occupancy). $\text{C}_{20}\text{H}_{54}\text{Cl}_3\text{N}_6\text{O}_2\text{V}_3\text{I}$ (major), $\text{C}_{19}\text{H}_{51}\text{Cl}_4\text{N}_6\text{OV}_3\text{I}$, CH_4O (minor) $M = 796.8$, 833.2 . Very dark, long, square prisms, orthorhombic, space group $P m n b$ (equiv. to no. 62), $a = 13.633(1)$, $b = 14.454(2)$, $c = 17.963(3)$ Å, $V = 3539.7$ Å³, $Z = 4$, $D_c = 1.495$ g cm⁻³, $F(000) = 1632$ [83% (major) + 17% (minor)], $\mu(\text{Mo-K}\alpha) = 18.8$ cm⁻¹ [83% (major) + 17% (minor)], $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å.

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

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