Synthesis and Structural Characterisation of a Novel Paramagnetic Trigonal Bipyramidal Cluster, $(\eta^5\text{-}C_5H_5)_5V_5O_6$

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Summary The reaction of N_2O with $(\eta^5\text{-}C_5H_5)_2V$ gives $(\eta^5\text{-}C_5H_5)_5V_5O_6$, whose structure, determined by *X*-ray crystallography, shows a trigonal bipyramid of five V atoms, each capped by a $(\eta^5\text{-}C_5H_5)$ ring, with oxygen atoms bridging each of the six faces of the trigonal bipyramid.

We report the preparation and structural characterisation of $(\eta^5\text{-}C_5H_5)_5V_5O_6$, which provides a link between the very rare homonuclear metal carbonyl clusters having a trigonal bipyramidal architecture[1] and the equally rare cyclopentadienyl-oxo clusters of the early transition metals.[2] This synthesis is part of our continuing investigation of the controlled mild oxidation of organometallic complexes which can be attained by the use of dinitrogen oxide (N_2O).[3,4]

Toluene solutions of Cp_2V (Cp = $\eta^5\text{-}C_5H_5$) absorbed N_2O at −78 °C, the solution changing colour from purple–blue to wine-red. On standing for several hours, or on warming to room temperature N_2 was evolved, the solution became darker and deposited black crystals of $Cp_5V_5O_6$. We presume that the wine-red solution contains a $Cp_2V\text{–}N_2O$ complex, but have so far been unable to isolate this.

$Cp_5V_5O_6$ gave no e.s.r. signal at room temperature and showed only an extremely broad signal centred at $g = 1{\cdot}972$ at 77 K (toluene solution), but had a bulk magnetic moment of 2·84 BM per $Cp_5V_5O_6$ unit at 20 °C, corresponding to two unpaired electrons per cluster.

Crystal data: $C_{25}H_{25}O_6V_5$, $M = 676{\cdot}2$; monoclinic, $P2_1/c$, $a = 9{\cdot}825(4)$, $b = 15{\cdot}584(9)$, $c = 19{\cdot}592(8)$ Å, $\beta = 123{\cdot}83(3)°$; $Z(C_{25}H_{25}O_6V_5) = 4$. $R = 0{\cdot}069$, $R_w = 0{\cdot}086$, for 2180 observed reflections.†

The compound has a trigonal bipyramidal arrangement of V atoms, each V being capped by a Cp ring, with V–Cp-(equatorial) 1·973; V–Cp(axial) 1·997 Å. The O atoms lie an average of 1·128 Å (range 1·11—1·14 Å) above each of the six faces of the trigonal bipyramid, displaced 0·29 Å from the face centre towards the axial V atoms (see the Figure). The three-co-ordinate O atoms and capping Cp ring are similar to those in $Cp_6Ti_6O_8$.[2]

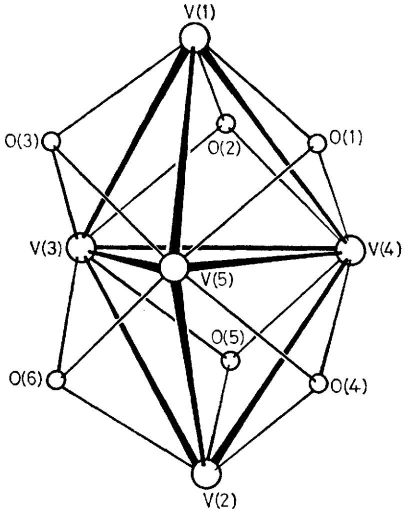

Figure. The V_5O_6 cluster of $Cp_5V_5O_6$.

If each O atom is considered as contributing 4 electrons to the cluster then $Cp_5V_5O_6$ has 74 electrons to be used for V–Cp bonding and in the V_5O_6 cluster. The other known trigonal bipyramidal clusters, $[Ni_5(CO)_{12}]^{2-}$ [1] and $[M_2Ni_3(CO)_{16}]^{2-}$ [5] (M = Cr, Mo, W) have, using the same counting procedure, 76 electrons. Dahl and co-workers have proposed a molecular orbital description for the carbonyl

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

clusters in which the highest occupied molecular orbital is of degenerate e symmetry, and is antibonding with respect to the interaction between the equatorial and the axial metal atoms. The diamagnetism of $[Ni_5(CO)_{12}]^{2-}$ and $[M_2Ni_3(CO)_{16}]^{2-}$ and the considerably longer Ni(axial)–Ni(equat.) distance {0·45 Å in $[Ni_5(CO)_{12}]^{2-}$} compared to the Ni(equat.)–Ni(equat.) distance (the latter being appropriate to a Ni–Ni single bond) were thus explained.

Although extension of the carbonyl model to $Cp_5V_5O_6$ must include the vanadium and the oxygen atoms in the cluster bonding, it is noteworthy that the Dahl model predicts that $Cp_5V_5O_6$ (74 electrons) will have two unpaired electrons, as is observed. The average V(equat.)–V(equat.) distance [2·740(2) Å] is only marginally shorter than the average V(axial)–V(equat.) distance [2·752(2) Å]. However, all V–V distances are very long compared to the V–V single bond (2·46 Å) in $Cp_2V_2(CO)_5$,[6] though much shorter than the V–V distance (3·13 Å) in the $V_{10}O_{28}^{6-}$ [7] ion where VO_6 octahedra are joined together. The V–O bonds on the other hand are in the range to be expected for a V–O single bond: V–O(axial) 1·861(6), V–O(equat.) 1·992(6) Å. If the electrons required for the V–O and V–Cp bonding are subtracted, only 8 electrons remain for V–V bonding. Hence, compared to the electron rich $[Ni_5(CO)_{12}]^{2-}$, a much more open cluster is to be expected. Nevertheless, the removal of two electrons from the M(axial)–M(equat.) antibonding orbitals clearly equalises the M(axial)–M(equat.) and M(equat.)–M(equat.) bonding.

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