

Organometallic Clusters Containing Oxygen Atoms: $(\eta\text{-C}_5\text{H}_5)_5(\text{O})\text{V}_6(\mu_3\text{-O})_8$ and $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})$, Two Further Derivatives of Octahedral $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$

Frank Bottomley,* Daniel F. Drummond, Daniel E. Paez, and Peter S. White

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

Oxidation of $(\eta\text{-C}_5\text{H}_5)_2\text{V}$ with $\text{C}_5\text{H}_5\text{NO}$ in toluene gives $(\eta\text{-C}_5\text{H}_5)_4\text{V}_4(\mu_3\text{-O})_4$ and $(\eta\text{-C}_5\text{H}_5)_5(\text{O})\text{V}_6(\mu_3\text{-O})_8$ (**1**) whereas oxidation with Me_3NO gives $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})_2\text{V}(\eta\text{-C}_5\text{H}_5)(\text{NMe}_3)_2$ and $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})$ (**2**); the structures of (**1**) and (**2**) have been established by X-ray crystallography.

Organometallic clusters containing oxygen atoms are a new class of compounds possessing both the solution properties of organic compounds and the physical properties (*e.g.* magnetic behaviour) of metal oxides in the solid state. Such clusters may be regarded as models for catalytically active metal oxides. We have previously reported the vanadium clusters $(\eta\text{-C}_5\text{H}_5)_5\text{V}_5(\mu_3\text{-O})_6$,^{1,2} $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$,³ and two dimeric derivatives of the latter, $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})_2\text{V}(\eta\text{-C}_5\text{H}_5)(\text{NMe}_3)_2$ and $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})_2\text{V}_4(\eta\text{-C}_5\text{H}_5)_4$.³ During attempts to obtain the parent $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$ in crystalline form we have prepared two further derivatives of it, a monomer, $(\eta\text{-C}_5\text{H}_5)_5(\text{O})\text{V}_6(\mu_3\text{-O})_8$ (**1**) and a dimer $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})$ (**2**) as well as a third basic cluster, $(\eta\text{-C}_5\text{H}_5)_4\text{V}_4(\mu_3\text{-O})_4$.

Oxidation of $(\eta\text{-C}_5\text{H}_5)_2\text{V}$ with $\text{C}_5\text{H}_5\text{NO}$ in toluene gives, on removal of the solvent, a mixture of products of which by far the most abundant are $(\eta\text{-C}_5\text{H}_5)_4\text{V}_4(\mu_3\text{-O})_4$ and $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$ judging by the mass spectrum. Sublimation of the mixture *in vacuo* at 275°C gives essentially pure $(\eta\text{-C}_5\text{H}_5)_4\text{V}_4(\mu_3\text{-O})_4$, but not yet in a crystalline form suitable for X-ray diffraction. This cluster is paramagnetic [μ_{eff} , (corr.) 1.72 μ_{B} , at 25°C, independent of field strength] though it contains an even number (8) of cluster electrons.⁴ The e.s.r. spectrum shows a very broad signal at $g = 1.96$.

When the initial toluene solution is set aside (*in vacuo*) for several weeks it deposits neither $(\eta\text{-C}_5\text{H}_5)_4\text{V}_4(\mu_3\text{-O})_4$ nor $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$ but crystals of a derivative of the latter, $(\eta\text{-C}_5\text{H}_5)_5(\text{O})\text{V}_6(\mu_3\text{-O})_8$ (**1**) as determined by X-ray diffraction.† As can be seen from Figure 1, (**1**) is derived from $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$ by replacement of one $\eta\text{-C}_5\text{H}_5$ ring by an oxygen atom. The V–O distance [1.600(8) Å] and $\nu(\text{V}=\text{O})$ frequency (959 vs cm^{-1}) of the terminal V=O unit indicate the presence of a double bond.⁵ The $\text{V}_6(\mu_3\text{-O})_8$ core of (**1**) is little distorted from idealised O_h symmetry. The V–V distances range from 2.923(3) to 2.954(3) Å with an average of 2.940(3) Å. Although the range is rather large there is no pattern of distortion. The V–($\mu_3\text{-O}$) distances to the axial V atom *trans* to the V=O group are, at an average of 1.950(8) Å (range 1.940–1.956 Å), marginally longer than those to the other five vanadium atoms [average 1.940(8) Å, range 1.917–1.952 Å]. There is no difference between the average

V–($\mu_3\text{-O}$) distance of the V=O group and those of the four equatorial vanadium atoms. As would be expected for a species with an odd number of cluster electrons, seven, (**1**) is paramagnetic [μ_{eff} , (corr.) 2.51 μ_{B} at 25°C]. There is a weak dependence on the field, indicating an antiferromagnetic contribution to the magnetic moment.

As we have previously reported, oxidation of $(\eta\text{-C}_5\text{H}_5)_2\text{V}$ with Me_3NO in toluene over 24 h gives $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})_2\text{V}(\eta\text{-C}_5\text{H}_5)(\text{NMe}_3)_2$.³ When the reaction is conducted for 72 h the product is $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})$ (**2**), whose structure was determined by X-ray diffraction.† As is seen from Figure 2, (**2**) is a relative of both $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$ and (**1**), being composed of two $(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8$ units linked by an oxygen atom [V–($\mu_2\text{-O}$) 1.764(9) and 1.773(9) Å, V–O–V 141.3(6)°]. The equatorial V–V distances in the two $\text{V}_6(\mu_3\text{-O})_8$ units average 2.911(3) Å (range 2.882–2.924 Å) and are marginally longer than the V–V distances to the vanadium atoms *trans* to the oxo bridge [2.887(4) Å, range

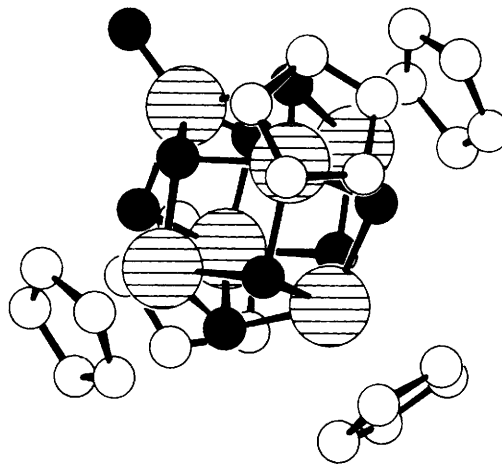


Figure 1. The molecular structure of $(\eta\text{-C}_5\text{H}_5)_5(\text{O})\text{V}_6(\mu_3\text{-O})_8$, (**1**).

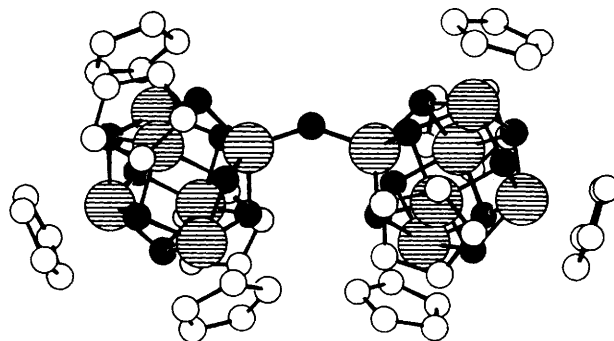


Figure 2. The molecular structure of $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O})$, (**2**).

† Crystal data: For (**1**), $\text{C}_{25}\text{H}_{25}\text{O}_9\text{V}_6$: $M = 775.14$, monoclinic, space group $P2_1/c$, $a = 16.760(3)$, $b = 16.500(2)$, $c = 9.750(1)$ Å, $\beta = 99.38(1)^\circ$, $Z = 4$, Mo- K_α radiation, $\lambda = 0.71073$ Å, 2009 observed [$I > 3\sigma(I)$] reflexions out of 3471 possible ($2\theta < 45^\circ$), final $R = 0.066$ and $R_w = 0.068$ for 236 parameters. Empirical absorption correction ($\mu = 1.98 \text{ mm}^{-1}$). For (**2**), $\{(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8\}_2(\mu\text{-O}) \cdot 3/2(\text{PhMe})$: $M = 1672.50$, monoclinic, space group $P2_1/n$, $a = 16.032(2)$, $b = 20.396(4)$, $c = 19.664(4)$ Å, $\beta = 99.05(1)^\circ$, $Z = 4$, Mo- K_α radiation, $\lambda = 0.71073$ Å, 4943 observed [$I > 2.5\sigma(I)$] reflexions out of possible 8254 ($2\theta < 45^\circ$), final $R = 0.083$ and $R_w = 0.103$ for 507 parameters. No absorption correction ($\mu = 1.69 \text{ mm}^{-1}$). Both data sets were collected on a Nonius CAD4 diffractometer at 20°C. 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.

2.873—2.898 Å]. The V—V distances to the vanadium atoms in the bridge are however shorter [average 2.877(3) Å, range 2.862—2.889 Å], and the V—O distances to these vanadium atoms [average 1.885(9) Å, range 1.874—1.898 Å] are also shorter than the other V—O distances [average 1.952(10) Å, range 1.927—1.972 Å]. Cluster (2) has 8 cluster electrons in each of the $(\eta\text{-C}_5\text{H}_5)_5\text{V}_6(\mu_3\text{-O})_8$ units. It is paramagnetic with $\mu_{\text{eff.}}(\text{corr.})$ 2.10 μ_{B} at 25 °C. The moment is field-independent but the value is subject to large errors because of the solvent molecules in the crystal lattice.

We are still seeking an explanation for the lability of one $(\eta\text{-C}_5\text{H}_5)$ ring in $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$ in contrast to other $\{(\eta\text{-C}_5\text{H}_5)\text{M}\}_m(\mu_3\text{-O})_n$ clusters. Since $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6(\mu_3\text{-O})_8$ is thermally stable and the solvents used in the preparations are non-co-ordinating, the explanation must lie in the electronic structure of the cluster.

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References

- 1 F. Bottomley and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1981, 28.
 - 2 F. Bottomley, D. E. Paez, and P. S. White, *J. Am. Chem. Soc.*, 1982, **104**, 5651.
 - 3 F., Bottomley, D. E. Paez, and P. S. White, *J. Am. Chem. Soc.*, 1985, **107**, 7226.
 - 4 F. Bottomley and F. Grein, *Inorg. Chem.*, 1982, **21**, 4170.
 - 5 K. Wiegardt, U. Bossek, K. Volckmar, W. Swiridoff, and J. Weiss, *Inorg. Chem.*, 1984, **23**, 1387.
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