Trimeric Pentamethylcyclopentadienylvanadium Dioxide, $[(\eta\text{-C}_5\text{Me}_5)\text{V(O)}(\mu\text{-O})]_3$

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The preparation of $(\eta\text{-C}_5\text{Me}_5)\text{VO}_2$ from $(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2\text{(O)}$ and Ag_2CO_3 is reported; it has the trimeric structure $[(\eta\text{-C}_5\text{Me}_5)\text{V(O)}(\mu\text{-O})]_3$.

The recent preparation of $(\eta\text{-C}_5\text{Me}_5)\text{Re(O)}_3$[1,2] coupled with the much earlier discovery of $[(\eta\text{-C}_5\text{H}_5)\text{Mo(O)}_2]_2(\mu\text{-O})$[3] suggests that a series of cyclopentadienyl–metal–oxo complexes with the metal in its highest possible oxidation state may exist, *viz.* $[(\text{cp})\text{M}^{\text{IV}}\text{(O)}]_2(\mu\text{-O})$, $(\text{cp})\text{M}^{\text{V}}\text{(O)}_2$, $[(\text{cp})\text{M}^{\text{VI}}\text{(O)}_2]_2(\mu\text{-O})$, and $(\text{cp})\text{M}^{\text{VII}}\text{(O)}_3$, cp = $\eta\text{-C}_5\text{Me}_5$ or $\eta\text{-C}_5\text{H}_5$. Related complexes with the metal in less than the highest possible oxidation state are also known, *e.g.* $[(\text{cp})\text{M(O)}]_2(\mu\text{-O})_2$ (cp = $\eta\text{-C}_5\text{Me}_5$, M = Cr;[4] cp = $\eta\text{-C}_5\text{H}_5$, M = Mo[3,5]) and $[(\eta\text{-C}_5\text{Me}_5)\text{Re}(\mu\text{-O})_2]_3{}^{2+}$.[6] We have been seeking other members of these series of complexes, and report here the preparation of $(\eta\text{-C}_5\text{Me}_5)\text{VO}_2$, which has the trimeric structure $[(\eta\text{-C}_5\text{Me}_5)\text{V(O)}(\mu\text{-O})]_3$ shown in Figure 1.

When Ag_2CO_3 was added to green $(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2\text{(O)}$ in a 2:1 molar ratio in tetrahydrofuran as solvent CO_2 was evolved, AgCl was slowly precipitated, and brown $(\eta\text{-C}_5\text{Me}_5)\text{VO}_2$ was formed [reaction (1)]. The starting complex $(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2\text{(O)}$ was obtained either from the reaction between $(\eta\text{-C}_5\text{Me}_5)_2\text{VCl}_2$ and NO[7] or more easily, and in higher yield, from $(\eta\text{-C}_5\text{Me}_5)_2\text{V}$ and $\text{O}_2\text{–SOCl}_2$, the latter reaction being analogous to that used for the preparation of $(\eta\text{-C}_5\text{H}_5)\text{VCl}_2\text{(O)}$.[8]

$$3(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2\text{(O)} + 3\text{Ag}_2\text{CO}_3 \rightarrow [(\eta\text{-C}_5\text{Me}_5)\text{V(O)}(\mu\text{-O})]_3 + 6\text{AgCl} + 3\text{CO}_2 \quad (1)$$

The brown product, which had the empirical formula $(\text{C}_5\text{Me}_5)\text{VO}_2$,† was very soluble in toluene and was established to be the trimer $[(\eta\text{-C}_5\text{Me}_5)\text{V(O)}(\mu\text{-O})]_3$ by the following evidence. The molecular weight by osmometry in CH_2Cl_2 was 644 [calculated for $(\text{C}_5\text{Me}_5)_3\text{V}_3\text{O}_6$, 654] and the highest peak in the mass spectrum was at *m/z* 654 $[(\text{C}_5\text{Me}_5)_3\text{V}_3\text{O}_6{}^+]$ with an equally intense peak at 638 $[(\text{C}_5\text{Me}_5)_3\text{V}_3\text{O}_5{}^+]$. Other fragment ions of the trimer were apparent, but no peaks appeared in the region of the dimer (436) or monomer (218), nor were higher oligomers evident. The i.r. spectrum showed *two* intense absorption bands at 920 and 935 cm^{-1}, assigned to ν(V=O) of terminal V=O groups. Three ν(V=O) vibrations are expected for the trimer of C_s symmetry shown in Figure 1. These correspond to symmetric and antisymmetric vibrations of the two V=O groups related by the mirror plane and the vibration of the unique V=O group. The antisymmetric vibration would give rise to a band of very weak intensity because the net change in dipole will be very small and approximately parallel to the line connecting the equivalent vanadium atoms. The ^{1}H n.m.r. spectrum (in CDCl_3 solution) showed *two* resonances at δ 2.09 and 2.13, assigned to C_5Me_5, with an integrated intensity ratio of 2:1.

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† Found: C 55.2; H 6.9_5; V 23.1. $\text{C}_{10}\text{H}_{15}\text{O}_2\text{V}$ requires C 55.0; H 6.9; V 23.3_5%.

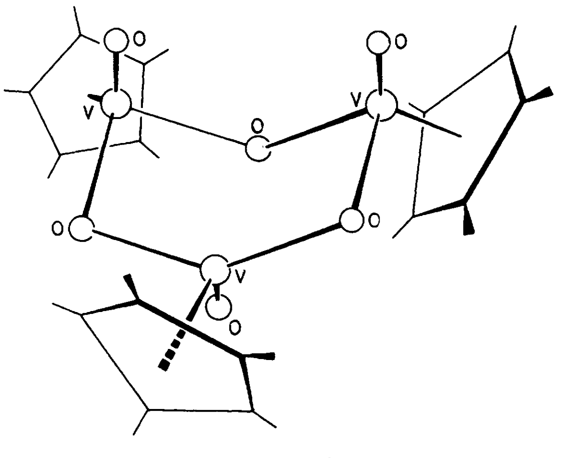

Figure 1. Proposed structure for $[(\eta\text{-}C_5Me_5)V(O)(\mu\text{-}O)]_3$.

The intensity ratio remained the same regardless of the temperature of measurement. The ^{51}V n.m.r. spectrum ($CDCl_3$ solution) showed *two* resonances at −530 and −547 p.p.m. relative to $VCl_3(O)$, also with an integrated intensity ratio of 2 : 1. Finally, the ^{13}C n.m.r. ($CDCl_3$ solution) showed *two* resonances at δ 124.8 and 125.8 (assigned to C_5Me_5) and *two* at δ 11.81 and 11.71 (assigned to C_5*Me*$_5$). In both cases the intensity ratios were 2 : 1.

The analytical and spectroscopic evidence can only be explained by the formulation of a cyclic trimer $[(\eta\text{-}C_5Me_5)\text{-}V(O)(\mu\text{-}O)]_3$ which has both terminal V=O and bridging V–O–V units. The spectra prove the uniqueness of one $(\eta\text{-}C_5Me_5)V(O)$ unit and the equivalence of the other two. This can only be achieved in a planar, a chair, or a boat conformation of the $[V(\mu\text{-}O)]_3$ ring by placing two of the C_5Me_5 ligands above and one below the plane of the three vanadium atoms, with the terminal oxygen atoms on the opposite side of the plane to the C_5Me_5 ligands. The relatively large differences in the ν(V=O) i.r. frequencies and in the ^{51}V n.m.r. signals, together with the steric bulk of the C_5Me_5 ligand, strongly suggest that the boat form depicted in Figure 1 is the correct structure.

Attempts to obtain crystals of $[(\eta\text{-}C_5Me_5)V(O)(\mu\text{-}O)]_3$ suitable for *X*-ray diffraction have been unsuccessful, but are continuing. Preliminary indications are that $(\eta\text{-}C_5H_5)VCl_2(O)$ or $(\eta^5\text{-}C_5H_4Me)VCl_2(O)$ react with Ag_2CO_3 to give an insoluble polymer. We are investigating the reactions of $[(\eta\text{-}C_5Me_5)V(O)(\mu\text{-}O)]_3$.

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