Organometallic Oxides: Preparation of $[\{(\eta\text{-}C_5Me_5)NbCl_2\}_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)]$ and Its Reduction to the Diamagnetic Trinuclear Clusters $[\{(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)\}_3]^+$ and $[\{(\eta\text{-}C_5Me_5)Nb\}_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3]^+$

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Oxidation of $[(\eta\text{-}C_5Me_5)_2NbCl_2]$ with O_2 in the presence of H_2O gave $[\{(\eta\text{-}C_5Me_5)NbCl_2\}_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)]$ **1** and polymeric $[Nb_2Cl_2O_4(thf)_3]_x$ (thf = tetrahydrofuran); reduction of **1** with Zn–ZnO gave diamagnetic $[\{(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)\}_3][\{(\eta\text{-}C_5Me_5)Nb\}_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3][Zn_4Cl_{10}]$, the structure of which was determined by X-ray diffraction.

Cyclopentadienyl oxides of vanadium can be prepared by oxidation of $(\eta\text{-}C_5R_5)_2V$. Examples are $[\{(\eta\text{-}C_5H_5)V\}_5(\mu_3\text{-}O)_6]$[1] and $[\{(\eta\text{-}C_5Me_5)V\}_4(\mu_2\text{-}O)_6]$.[2] Analogous reactions are not possible with niobium, because $(\eta\text{-}C_5R_5)_2Nb$ complexes are not available. We have therefore prepared cyclopentadienyl oxides of niobium by reduction of high valent cyclopentadienylniobium oxo chlorides, prepared by various routes.[3–6] We report here the preparation and structure of a new cyclopentadienyl oxide of Nb^V, $[\{(\eta\text{-}C_5Me_5)NbCl_2\}_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)]$ and its reduction to two remarkable trinuclear cations, $[\{(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)\}_3]^+$ and $[\{(\eta\text{-}C_5Me_5)Nb\}_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3]^+$, the charge being balanced by a novel anion, $[\{ZnCl\}_4(\mu\text{-}Cl)_6]^{2-}$ which has an adamantane-like structure.

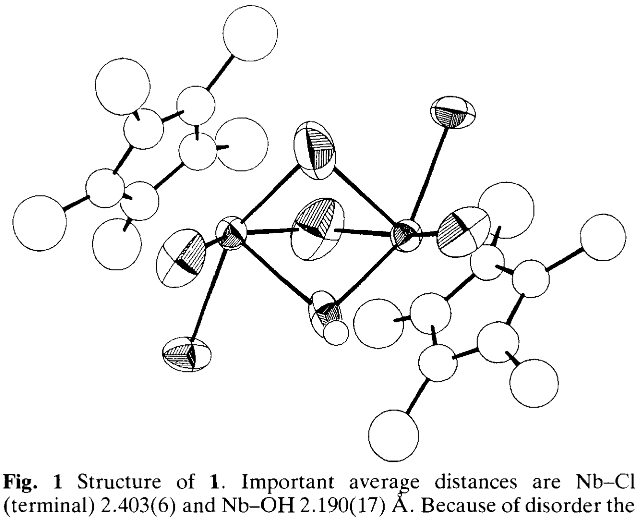

Fig. 1 Structure of **1**. Important average distances are Nb–Cl (terminal) 2.403(6) and Nb–OH 2.190(17) Å. Because of disorder the Nb–O–Nb and Nb–Cl–Nb distances are not reliable.

Oxidation of a tetrahydrofuran (thf) solution of $[(\eta\text{-}C_5Me_5)_2NbCl_2]$[7] with O_2 in the presence of H_2O gave a mixture of the orange $[\{(\eta\text{-}C_5Me_5)NbCl_2)\}_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)]$ **1** and a purple compound formulated as $[Nb_2Cl_2O_4(thf)_3]$ **2**. The latter was initially more soluble in toluene than **1**, allowing separation, but **2** slowly precipitated from solution to give an insoluble material with a molecular weight in excess of 2800. The yields of **1** and **2** were *ca.* 50%, **2** being favoured by rigorously anhydrous conditions. The structure of **1** is shown in Fig. 1.† It is similar to $[\{(\eta\text{-}C_5H_4SiMe_3)NbCl_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}O)]$.[6]

Reduction of **1** by zinc powder in the presence of zinc oxide occurred readily according to eqn. (1). The three products

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† *Crystal data* for **1**: $C_{20}H_{31}Cl_5Nb_2O_2$, $M = 666.5$, monclinic, *Cc*, $a = 8.7636(11)$, $b = 14.3936(18)$, $c = 20.254(5)$ Å, $\beta = 101.49(2)°$ $U = 2503.6(8)$ Å^3, $Z = 4$, $D_c = 1.77$ Mg m^{-3}, $\lambda = 0.71073$ Å, $F(000) = 1336$, $\mu = 14.2$ cm^{-1}. Final $R = 0.085$, $R_w = 0.098$ for 2716 independent reflections with $I > 2.5\sigma(I)$ to $2\theta < 50°$ on an Enraf-Nonius CAD4 ($\theta/2\theta$ mode). The Nb, Cl and O atoms were refined anisotropically, the C isotropically (160 parameters). There was disorder between the bridging Cl and O atoms. Hydrogen atoms were included as fixed contributors.

Crystal data for the salt $\{$**3**$\}\{$**4**$\}\{$**5**$\}\cdot 0.5Et_2O\cdot 0.5CH_2Cl_2$, $M = 2353.7$, orthorhombic, $P2_12_12_1$, $a = 15.996(1)$, $b = 19.539(1)$, $c = 28.0275(19)$ Å, $U = 8759.8(9)$ Å^3, $Z = 4$, $D_c = 1.72$ Mg m^{-3}, $F(000) = 4652$, $\mu = 2.39$ cm^{-1}. Final $R = 0.089$, $R_w = 0.088$ for 3571 independent reflections with $I > 2.0\sigma(I)$ to $2\theta < 50°$. The Nb, Cl and Zn atoms were refined anisotropically, all others isotropically (518 parameters). Hydrogen atoms were included as fixed contributors.

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

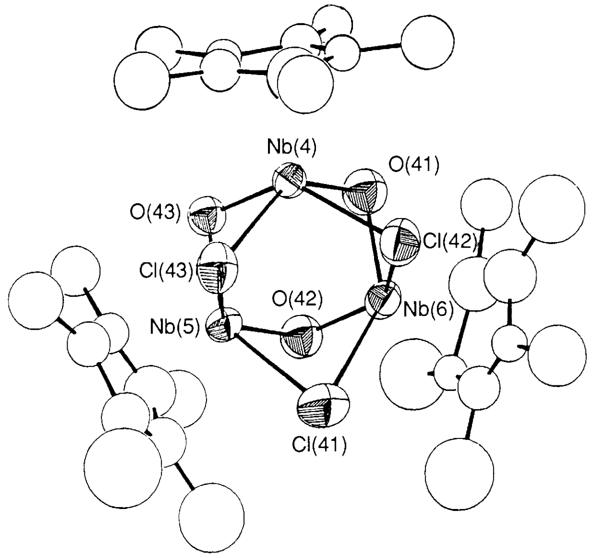

Fig. 2 Structure of **3**. Important average distances are Nb–Cl 2.538(11,23) and Nb–O 1.938(25,42) Å.

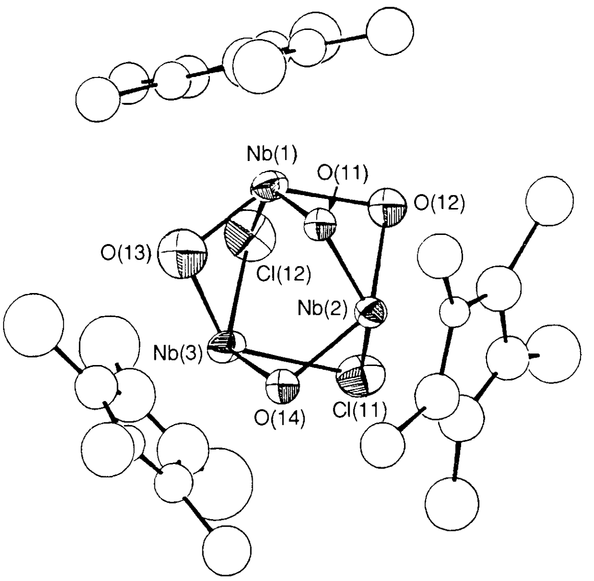

Fig. 3 Structure of **4**. Important average distances are Nb–Cl 2.530(10,26), Nb–O 1.920(20,24), Nb–(OH) 2.145(20) Å. The OH group is O(11).

[{(η-C_5Me_5)Nb(μ-Cl)(μ-O)}$_3$]$^+$ **3** [{(η-C_5Me_5)Nb}$_3$(μ-Cl)$_2$(μ-OH)(μ-O)$_3$]$^+$ **4** and [{ZnCl}$_4$(μ-Cl)$_6$]$^{2-}$ **5** crystallise as a salt. The structures of the components **3–5** are shown in Figs. 2–4 respectively.† Despite its complexity, the salt was isolated in 70% yield.

$$3[\{(\eta\text{-}C_5Me_5)NbCl_2\}_2(\mu\text{-}Cl)(\mu\text{-}OH)(\mu\text{-}O)] + 2Zn + 2ZnO \rightarrow [\{(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)\}_3][\{(\eta\text{-}C_5Me_5)Nb\}_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3][Zn_4Cl_{10}] + H_2O \quad (1)$$

The only difference between **3** and **4** is that one bridging Cl in **3** has been replaced by an OH ligand in **4**. There is a shortening of the Nb–Nb distance to 2.807(4) Å where this substitution occurs, from an average of 2.857(5,6) Å for all other Nb–Nb distances.‡ These distances are much shorter than the non-bonding distance of 3.245(1) Å in [{(η-C_5H_5)NbCl(μ-Cl)}$_3$(μ_3-OH)(μ_3-O)] and approach the 2.823(1) Å which represents a single Nb–Nb bond in the same compound.[3,8] The short Nb–Nb distances in **3** and **4**, and for the diamagnetism observed for the salt **3**$^+$ **4**$^+$ **5**$^{2-}$ are consistent with the molecular orbital description[9] of the electronic structure of [{(η-C_5Me_5)Re(μ-O)$_2$}$_3$]$^{2+}$.[10,11] The energy level diagram proposed for the {(η-C_5H_5)M(μ-A)(μ-B)}$_3$ species has, as its lowest energy cluster orbital, one of $1a_1$ symmetry which is strongly M–M bonding between all three metals.[9] This orbital is occupied by the two electrons of the Nb_3^{13+} core of **3** and **4**.

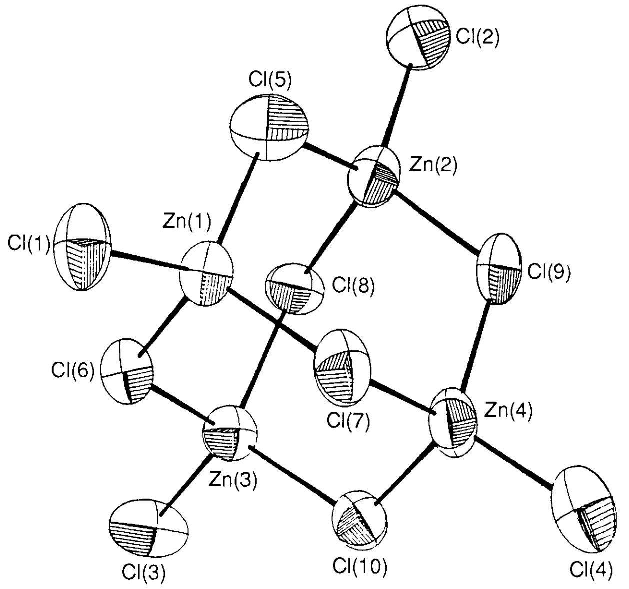

Fig. 4 Structure of **5**. Important distances are given in the text.

The [{ZnCl}$_4$(μ-Cl)$_6$]$^{2-}$ **5** anionic cluster has a novel adamantane-like structure (Fig. 4). The zinc is tetrahedrally coordinated, the terminal Zn–Cl distances averaging 2.181(12,14) and the bridging Zn–Cl 2.298(12,24) Å.

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‡ The first figure in brackets is the e.s.d., the second the maximum deviation from the mean.

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