

Synthesis and X-Ray Crystal Structure of the Cluster Cation $[\text{Os}_4(\mu_2\text{-H})_3(\text{CO})_{12}(\text{NCMe})_2]^+$: an Example of an Unsupported Butterfly Os_4 Geometry

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The cation $[\text{Os}_4(\mu_2\text{-H})_3(\text{CO})_{12}(\text{NCMe})_2]^+$ has been obtained by electrochemical and chemical (with NOX , $\text{X} = \text{BF}_4$ or PF_6) oxidation of $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ in acetonitrile; the four Os atoms define a 'butterfly' configuration with all the CO and MeCN ligands bonded in a terminal fashion.

A wide variety of geometries has been observed for the metal skeleton in osmium cluster carbonyls,¹ but all of the tetranuclear 'butterfly' complexes observed to date have some atom

or group of atoms bridging the 'wing-tip' metals. The unsupported 'butterfly' configuration in which no bridging unit occurs has been observed, but only in heteronuclear metal

systems.² In this communication we report the synthesis and structure of the salt $[\text{Os}_4(\mu_2\text{-H})_3(\text{CO})_{12}(\text{NCMe})_2][\text{BF}_4]$ which is the first example of an unsupported butterfly arrangement of osmium atoms. This complex is significant also because it is one of a very few cationic cluster complexes, and, as such, has considerable potential for reaction with mononuclear and cluster anions to produce larger clusters. Other osmium cluster compounds with labile acetonitrile ligands are found to be reactive under mild conditions.³ Such reactivity may also apply to the title complex.

The tetranuclear hydride anion $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ reacts with NOX ($\text{X} = \text{BF}_4, \text{PF}_6$) in MeCN to give the salt $[\text{Os}_4(\mu_2\text{-H})_3(\text{CO})_{12}(\text{NCMe})_2][\text{X}]$ in ca. 35% yield. The fluoroborate complex was recrystallized from dichloromethane to form yellow block-shaped crystals. In CH_2Cl_2 the cluster cation exhibits i.r. carbonyl absorptions at 2113(w), 2091(ms), 2070(s), 2016(s), and 2001(sh) cm^{-1} . The ^1H n.m.r. spectrum at 30 °C in CD_2Cl_2 shows two singlet resonances at 27.27 τ and 28.28 τ of relative intensity 1 : 2, which may be assigned to the hydride ligands, and a sharp singlet at 7.27 τ due to the co-ordinated acetonitrile ligands. Significantly, on addition of one drop of CD_3CN this latter singlet disappears (1 h) and is replaced by a new signal at 8.04 τ due to free acetonitrile. This observation confirms the lability of the co-ordinated MeCN ligands. The structure was established by a single-crystal X-ray analysis.

Crystal data: $[\text{C}_{16}\text{H}_9\text{N}_2\text{O}_{12}\text{Os}_4][\text{BF}_4]$, $M = 1268.86$, monoclinic, space group $P2_1/c$, $a = 17.555(7)$, $b = 9.252(4)$, $c = 17.767(8)$ Å, $\beta = 108.93(3)^\circ$, $U = 2729.6$ Å³, $Z = 4$, $D_c = 3.087$ g cm^{-3} , $F(000) = 2239$, graphite-monochromated Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 186.3$ cm^{-1} . The diffracted intensities were measured to $2\theta_{\text{max}} = 50^\circ$ on a Syntex $P2_1$ diffractometer and were corrected for absorption. 3454 reflections [$F > 3\sigma(F)$] were used to solve (direct methods and Fourier difference techniques) the structure which was refined by blocked-cascade least squares (Os, O, and acetonitrile N, C atoms anisotropic; B, F, carbonyl C isotropic; methyl H common isotropic) to $R = 0.049$ and $R_w = 0.051$.†

The structure of the cation is shown in Figure 1 which includes some important bond parameters. The two Os_3 triangles are joined by the $\text{Os}(2)\text{--Os}(3)$ 'hinge' bond, and the dihedral angle between the $\text{Os}(1)\text{Os}(2)\text{Os}(3)$ and $\text{Os}(2)\text{Os}(3)\text{Os}(4)$ planes is $112.2(1)^\circ$. This angle is considerably more obtuse than the value of 97.70° for the same angle in $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}(\text{OH})]^+$ where the two 'wing-tip' Os atoms are supported by the bridging hydroxy-ligand.⁴ The distances between the non-bonded 'wing-tip' osmiums reflect this with a value of 3.537(2) Å for the hydroxy-bridged complex and 4.338(2) Å for the title compound. These two cationic clusters are similar to the neutral species $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^0$ and $[\text{Os}_4(\text{CO})_{12}(\text{HC}:\text{CH})]^0$ in that all are sixty-two electron systems, which recent theory predicts to prefer the observed butterfly configuration.⁷

The two 'wing-tip' Os atoms, $\text{Os}(1)$ and $\text{Os}(4)$, are each bonded to an axial acetonitrile group which is orientated away from the centre of the cluster. Each 'wing-tip' Os atom is also co-ordinated to one axial and two equatorial carbonyl groups; the 'hinge' metal atoms each have three terminal carbonyls associated with them. The Os–Os bonds may be split into three different groups. The $\text{Os}(1)\text{--Os}(3)$ and $\text{Os}(2)\text{--Os}(4)$ distances are similar to the Os–Os unbridged, single bonds in $[\text{Os}_4\text{H}_3(\text{CO})_{12}\text{I}]$.⁵ The $\text{Os}(2)\text{--Os}(3)$ bond is similar in

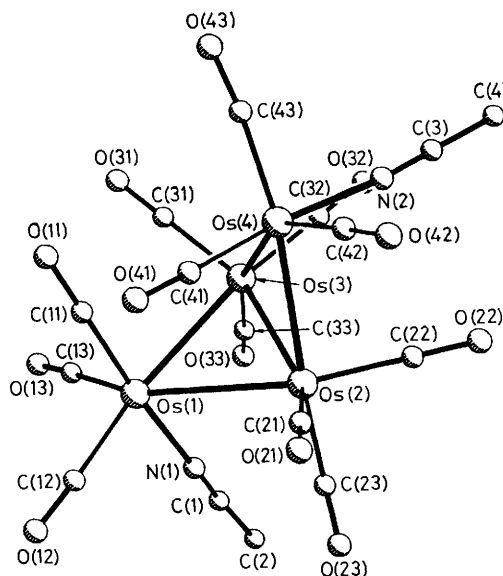
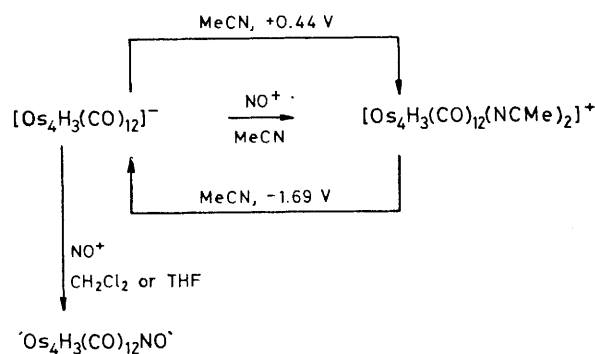


Figure 1. The structure of the $[\text{Os}_4(\mu_2\text{-H})_3(\text{CO})_{12}(\text{NCMe})_2]^+$ cation. Bond lengths: $\text{Os}(1)\text{--Os}(2)$, 3.130(1); $\text{Os}(1)\text{--Os}(3)$, 2.828(1); $\text{Os}(2)\text{--Os}(3)$, 2.937(1); $\text{Os}(2)\text{--Os}(4)$, 2.847(1); $\text{Os}(3)\text{--Os}(4)$, 3.145(1); $\text{Os}(1)\text{--N}(1)$, 2.10(2); $\text{Os}(4)\text{--N}(2)$, 2.13(1) Å. Bond angles: $\text{Os}(1)\text{--N}(1)\text{--C}(1)$, $169(2)^\circ$; $\text{Os}(4)\text{--N}(2)\text{--C}(3)$, $174(2)^\circ$.



Scheme 1

length to the hydrido-bridged 'hinge' bond in the iodide complex.⁵ The $\text{Os}(1)\text{--Os}(2)$ and $\text{Os}(3)\text{--Os}(4)$ bonds are similar in length to the two hydrido-bridged $\text{Os}(\text{hinge})\text{--Os}(\text{wing-tip})$ bonds in $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^0$.⁵ This suggests that the hydrides in this cation also bridge the three longer Os–Os edges and this is confirmed by the arrangement of the carbonyl ligands. The carbonyls adjacent to the three longer bonds bend away from these bonds with an average Os--Os--C angle of 109° owing to the steric influence of the hydrides. This assignment of the hydride positions is consistent with the ^1H n.m.r. spectrum in which the two hydrides bridging the $\text{Os}(1)\text{--Os}(2)$ and $\text{Os}(3)\text{--Os}(4)$ bonds are equivalent by a C_2 rotation and are distinct from the 'hinge'-bond bridging hydride to give the observed 2 : 1 intensity pattern. The fluoroborate counter-ion is not co-ordinated to the cluster.

Cyclic voltammetry of $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ in acetonitrile at a platinum microsphere shows an irreversible oxidation wave at $E = +0.44$ V vs. an Ag/AgNO_3 reference electrode, scan rate = 1 V/s, E_1 (ferrocene/ferrocinium) = +0.19 V. Controlled potential electrolysis of $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ at a platinum gauze at this potential gives $[\text{Os}_4\text{H}_3(\text{CO})_{12}(\text{NCMe})_2]^+$ in quantitative yield. Cyclic voltammetry of $[\text{Os}_4\text{H}_3(\text{CO})_{12}(\text{NCMe})_2]^+$ shows an irreversible reduction wave at $E = -1.69$ V; quantitative

† 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.

reduction of this product in acetonitrile leads to the reformation of the anion $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$. No other carbonyl-containing products could be detected by i.r. or e.s.r. spectroscopy in these redox processes. These electrochemical results indicate that in the chemical oxidation of $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$, NO^+ is simply acting as an electron transfer agent (see Scheme 1). However, in CH_2Cl_2 or tetrahydrofuran (THF) it has been found that NO^+ reacts with $[\text{Os}_4\text{H}_3(\text{CO})_{12}]^-$ to give a product which, on the basis of microanalytical and mass spectroscopic data, may be formulated as a nitrogen-containing Os_4 cluster.

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