

## Synthesis and X-Ray Crystal Structure Analysis of a Novel $\mu_4$ -Oxo Undeca-osmium Carbonyl Cluster $[\text{Os}_{11}(\mu_4\text{-O})_3(\text{CO})_{30}]$

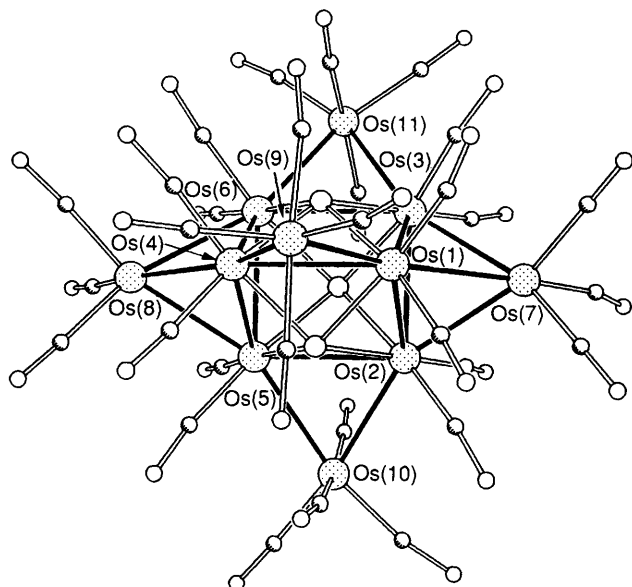
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The first example of an osmium cluster containing  $\mu_4$ -oxo groups,  $[\text{Os}_{11}(\mu_4\text{-O})_3(\text{CO})_{30}]$  **1**, has been obtained from the vacuum pyrolysis of  $[\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-OH})]$ , and has been shown by X-ray crystallography to contain a tri-edge bridged, bicapped trigonal prismatic metal core.

Over the past two decades the method of vacuum pyrolysis of triosmium clusters has been widely used to synthesize high nuclearity carbonyl clusters of osmium *via* the formation and recombination of reactive fragments.<sup>1-4</sup> Using this synthetic approach, clusters of up to and including 20 osmium atoms have been prepared and characterized.<sup>5,6</sup> These latter high nuclearity clusters are of considerable interest as model systems for the industrially important processes of chemisorption and catalysis at metal surfaces.<sup>7</sup>

The vacuum pyrolysis of the hydroxy bridged species  $[\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-OH})]$  at a temperature of 240 °C for 18 h and an initial pressure of  $10^{-3}$  Torr (1 Torr = 133.3 Pa) yielded, in addition to the known binary clusters of nuclearity 4 to 17, the previously unknown neutral green cluster  $[\text{Os}_{11}(\mu_4\text{-O})_3(\text{CO})_{30}]$  **1**.<sup>†</sup> The stoichiometry of **1** was initially deduced from liquid secondary ion mass spectrometry (LSIMS) and has been

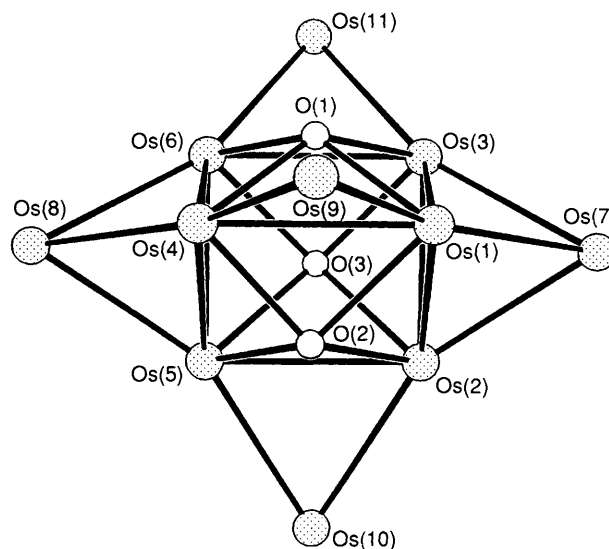


**Fig. 1** Molecular structure of  $[\text{Os}_{11}(\mu_4\text{-O})_3(\text{CO})_{30}]$  **1**. Principle bond lengths (Å): Os(1)–Os(2) 2.870(3), Os(1)–Os(3) 2.852(3), Os(1)–Os(4) 2.912(3), Os(1)–Os(7) 2.782(4), Os(1)–Os(9) 2.809(4), Os(2)–Os(3) 2.839(3), Os(2)–Os(5) 2.891(3), Os(2)–Os(7) 2.781(4), Os(2)–Os(10) 2.810(3), Os(3)–Os(6) 2.939(3), Os(3)–Os(7) 2.788(4), Os(3)–Os(11) 2.808(3), Os(4)–Os(5) 2.864(3), Os(4)–Os(6) 2.824(3), Os(4)–Os(8) 2.781(3), Os(4)–Os(9) 2.802(3), Os(5)–Os(6) 2.843(3), Os(5)–Os(8) 2.782(3), Os(5)–Os(10) 2.814(3), Os(6)–Os(8) 2.772(3), Os(6)–Os(11) 2.799(3), O(1)–Os(1) 2.17(3), O(1)–Os(3) 2.18(3), O(1)–Os(4) 2.16(4), O(1)–Os(6) 2.14(3), O(2)–Os(1) 2.25(3), O(2)–Os(2) 2.15(3), O(2)–Os(4) 2.19(3), O(2)–Os(5) 2.10(3), O(3)–Os(2) 2.15(3), O(3)–Os(3) 2.14(3), O(3)–Os(5) 2.20(3), O(3)–Os(6) 2.18(3).

<sup>†</sup> *Spectroscopic data for 1*: IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu/\text{cm}^{-1}$  2096vs, 2037m, 2021m, 1979w, 1945w; IR (KBr disk) no absorption due to  $\nu(\text{O-H})$  observed; positive ion LSIMS, most abundant isotope for  $[\text{Os}_{11}(\mu_4\text{-O})_3(\text{CO})_{30}]$ ,  $m/z$  2983 (simulated 2982).  $\{^1\text{H}\}^{13}\text{C}$  NMR ( $\text{C}_2\text{D}_2\text{Cl}_4$ )  $\delta$  176.6 (12 CO), 175.1 (6 CO), 170.3 (6 CO), 169.1 (6 CO).

confirmed by a single crystal X-ray structural analysis (Fig. 1).<sup>‡</sup>

The molecular structure of **1** consists of a trigonal prism of osmium atoms which is capped on the two trigonal faces by  $\text{Os}(\text{CO})_3$  fragments and has three  $\text{Os}(\text{CO})_4$  units bridging the square edges of the prism. In addition there are three  $\mu_4$ -oxo atoms<sup>§</sup> which cap the square faces of the trigonal prism (Fig. 2), lying approximately 2.17 Å from the osmium atoms which define the square face and at a distance of 0.70 Å above these faces. The angles subtended at the  $\mu_4$ -oxo groups for *cis*-osmium atoms range from 81(1)–86(1)°, whereas those for *trans*-osmium atoms lie within the range 140(2)–141(1)°. Hence from the observed coordination geometry of the  $\mu_4$ -oxo groups it can be concluded that these oxygen atoms possess a lone pair of electrons that point away from the cluster core. The  $\mu_4$ -oxo moiety exhibits a similar coordination geometry as that found in the mixed-metal cluster<sup>8</sup>  $[\text{Fe}_2\text{Ru}_3(\text{CO})_{14}(\mu_4\text{-O})]^{2-}$ , where the oxygen atom sits above the square  $\text{Fe}_2\text{Ru}_2$  plane by 0.90 Å. It is likely that this difference in the displacement of the oxygen atom from the square face is due mainly to the longer metal–metal bonds in **1**. It has been shown by extended Hückel molecular orbital calculations for



**Fig. 2** The  $\text{Os}_{11}$  framework in **1** depicting the  $\mu_4$ -oxo groups which cap the square faces of the trigonal prism

<sup>‡</sup> *Crystal data for  $[\text{Os}_{11}(\mu_4\text{-O})_3(\text{CO})_{30}]$  **1***:  $[\text{C}_{30}\text{O}_{33}\text{Os}_{11}]$ , monoclinic, space group  $P2_1/n$ ,  $a = 11.736(3)$ ,  $b = 21.775(5)$ ,  $c = 19.388(7)$  Å,  $\beta = 99.57(3)^\circ$ ,  $M = 2980.51$ ,  $U = 4885.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 4.052$  g cm<sup>-3</sup>,  $F(000) = 5120$ ,  $R = 0.0729$  for 3841 reflections with  $F_o > 3\sigma(F_o)$  corrected for absorption [ $\mu(\text{Mo-K}\alpha) = 285.7$  cm<sup>-1</sup>]. 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.

<sup>§</sup> The assignment of these atoms as oxygen was based on the observed geometry about these atoms, elemental analysis (found: C, 11.87%, calculated for  $\text{Os}_{11}\text{O}_{33}\text{C}_{30}$ : C, 12.09%) and the lack of a signal attributable to carbide atoms in the  $\{^1\text{H}\}^{13}\text{C}$  NMR spectrum ( $\delta$  200–500).

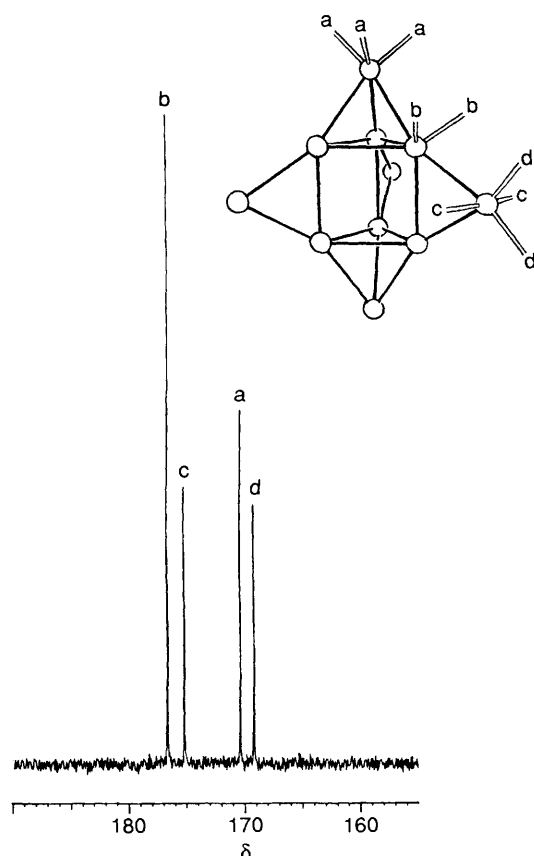


Fig. 3  $\{^1\text{H}\}^{13}\text{C}$  NMR spectrum of  $[\text{Os}_{11}(\mu_4\text{-O})_3(\text{CO})_{30}]$  ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 298 K). The tentative assignment of the resonances is based on their chemical shifts and relative intensities.

square pyramidal  $\text{M}_5\text{E}$  clusters,<sup>9</sup> that displacement of the heteroatom (when  $\text{E} = \text{S}, \text{O}$ ) from the basal plane of the cluster avoids an unfavourable non-bonding interaction between the filled heteroatom  $p_z$  orbital and the filled metal  $d-\pi$  orbitals of the same symmetry. In the sulfido cluster<sup>10</sup>  $[\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})]$ , this displacement of the heteroatom is also observed, where the sulfur atom lies out of the  $\text{Os}_4$  basal plane by 1.26 Å. This is the first example of a  $\mu_4$ -oxo group coordinating to an osmium cluster, in contrast the coordination of a  $\mu_3$ -oxo moiety to  $\text{Os}_6$  raft clusters is known,<sup>11,12</sup> in the latter case the  $\mu_4$ -oxo group lies 1.21 Å above the  $\text{Os}_3$  plane.

The  $\{^1\text{H}\}^{13}\text{C}$  NMR spectrum of the cluster ( $^{13}\text{C}$ -enriched) recorded at 298 K displays four signals of relative intensity 12:6:6:6 (Fig. 3) as expected for the molecule possessing  $C_{3v}$  symmetry with no exchange between the axial and equatorial carbonyl ligands of the bridging  $\text{Os}(\text{CO})_4$  groups. Even on heating the sample to 393 K no broadening or coalescence of resonances attributable to the axial and equatorial carbonyls of this latter group could be observed.

The cluster in the natural oxidation state has an overall electron count of 160 which is in contrast with the count of 156 predicted from the polyhedral skeletal electron pair theory for condensed polyhedra.<sup>13</sup> Preliminary cyclovoltammetric studies of **1** have revealed a rich electrochemistry, which may be due in part to the redox capabilities of the  $\mu_4$ -oxo groups in addition to the increased density of accessible oxidation states for large clusters.<sup>14</sup>

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