A New Type of Decaosmium Cluster Geometry: the Synthesis and *X*-Ray Structure Analysis of $Os_{10}(S)_2(CO)_{23}$

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Pyrolysis of $Os_3(CO)_{12}$ with elemental sulphur gives a range of clusters including $Os_3(S)_2(CO)_9$, $Os_5S(CO)_{15}$, $Os_6(CO)_{18}$, $Os_7(S)_2(CO)_{20}$, and $Os_{10}(S)_2(CO)_{23}$ (**1**); *X*-ray analysis shows that (**1**) has a new type of Os_{10} metal core geometry.

The first decaosmium cluster species $[Os_{10}C(CO)_{24}]^{2-}$ was isolated from the pyrolysis reactions of $Os_3(CO)_{12}$ and of its pyridine derivative.[1] The dianion has the tetracapped octahedral geometry predicted from skeletal electron counting procedures,[2] and the carbido-centred geometry has proved to be very stable.[3] More recently reaction of $Os_3(CO)_{12}$ under reflux in isobutyl alcohol has given small amounts of a hydrido dianion $[H_4Os_{10}(CO)_{24}]^{2-}$ which has the same tetracapped octahedral metal core arrangement but without the central carbido atom.[4] We now report that pyrolysis of $Os_3(CO)_{12}$ in the presence of elemental sulphur also gives a decaosmium species (**1**) together with the known

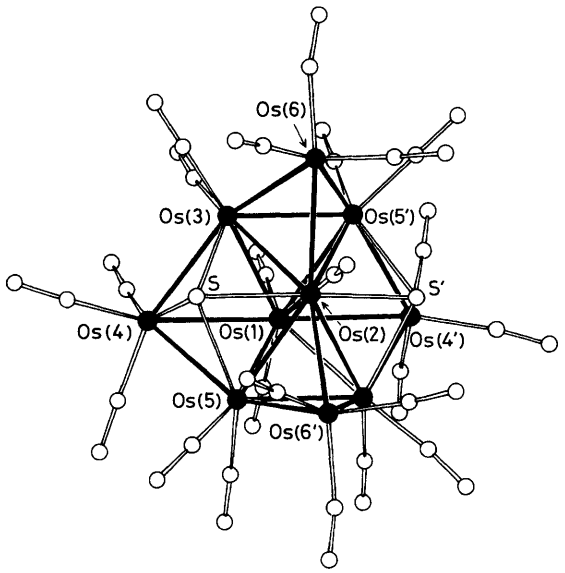

Figure 1. The structure of the $Os_{10}(S)_2(CO)_{23}$ molecule (**1**). The Os–Os bond lengths (Å) are: 1-2 2.771, 1-3 2.780, 1-4 2.864, 1-5 2.803, 2-3 2.716, 2-5 2.719, 2-6 2.818, 3-4 2.827, 3-6 2.761, 4-5 2.809, 5-6′ 2.718; maximum e.s.d.'s are 0.003. Other important bond lengths (Å) are: Os(2)–S 2.352(10), Os(3)–S 2.401(8), Os(4)–S 2.439(10), Os(5)–S 2.455(9).

cluster species $Os_3S(CO)_9$,[5] $Os_5S(CO)_{15}$,[6] $Os_6(CO)_{18}$,[7] and $Os_7(S)_2(CO)_{20}$,[8] which were identified by their i.r. spectra.[†] The relative yields of the products can be varied by altering the pyrolysis temperature; for example, on raising it from 200 to 260 °C the yield of (**1**) is increased at the expense of the lower nuclearity clusters.

Fast atom bombardment mass spectroscopy shows a molecular ion at m/z 2682, which together with the X-ray analysis,[‡] and i.r. spectroscopy establishes that (**1**) is $Os_{10}(S)_2(CO)_{23}$ with the molecular structure of exact C_2 symmetry shown in Figure 1. The metal core geometry may be described as two square pyramidal units fused to two trigonal bipyramids, so that they have an edge Os(1)–Os(2) in common. Two μ_4-sulphur atoms bridge the square bases of the pyramids, and the S atoms may be regarded as donating 4e to cluster bonding. The molecule (**1**) has a total of 134 cluster valence electrons which is the number expected from application of the fused polyhedral approach to skeletal electron counting.[9]

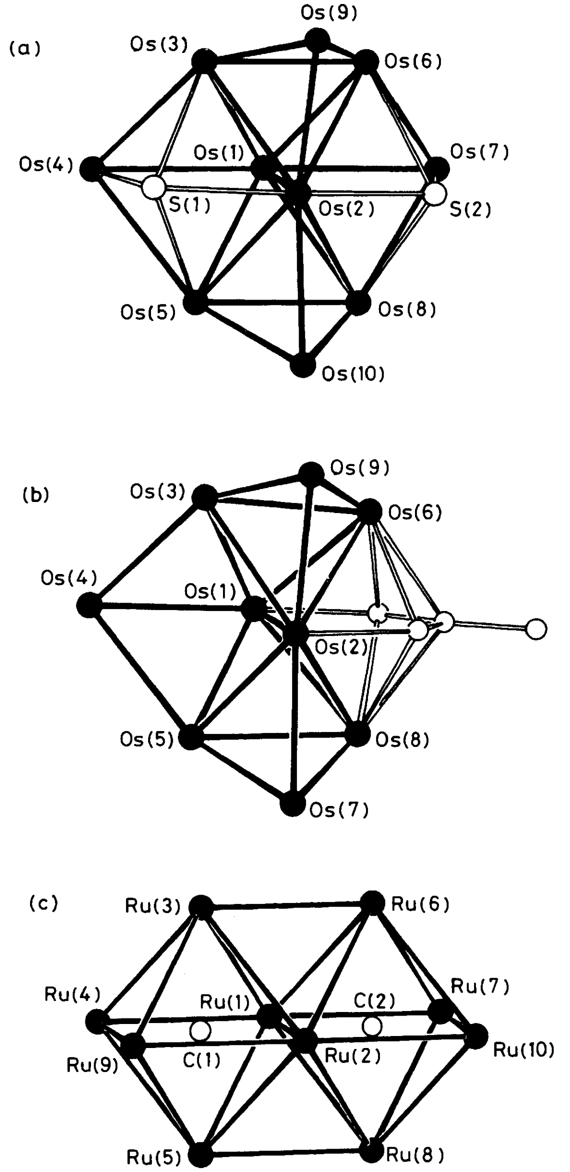

Figure 2. (a) The structure of the $Os_{10}(S)_2$ core in (**1**) (renumbered from Figure 1). (b) The structure of the Os_9(CHCMeCH) core in (**2**; R = Me) (ref. 10). (c) The structure of the $Ru_{10}(C)_2$ core in (**3**) (ref. 11).

It is interesting that the metal core in (**1**) [Figure 2(a)] may be directly related to the Os_9 core observed[10] in the anions $[Os_9(CO)_{21}(CHCRCH)]^-$ (R = Me or Et) (**2**) [Figure 2(b)] by the removal of one osmium atom, Os(4′), thus converting one of the square pyramidal units of (**1**) into the 'butterfly' type of unit found accommodating the organo-ligand in (**2**). Surprisingly the Os_{10} core of (**1**) is also readily related to the edge-linked bi-octahedral Ru_{10} core observed recently[11] in $[Ru_{10}(C)_2(CO)_{24}]^{2-}$ (**3**). The metal core of (**3**) [Figure 2(c)] may be generated from that of (**1**) by removing one apex from each trigonal bipyramid and using these two metal atoms to replace the two sulphur atoms thus converting the square pyramids into metal octahedra.

[†] ν(CO), CH_2Cl_2, $Os_6(CO)_{18}$ 2016w, 2077s, 2063vs, 2040s, 2032sh, 2005w; hexane, $Os_3(S)_2(CO)_9$ 2080s, 2060s, 2019s, 2014m; $Os_5S(CO)_{15}$ 2065vs, 2061sh, 2049w, 2041s, 2019w, 2008w, 1999w; $Os_7(S)_2(CO)_{20}$ 2127w, 2107m, 2081s, 2068w, 2058vs, 2048m, 2035w, 2025sh, 2022s, 2012w, 1996w, 1983w, 1960w, 1950w; $Os_{10}(S)_2(CO)_{23}$ 2079m, 2074vs, 2067s, 2037m, 2019m, 2010w cm^{-1}.

[‡] *Crystal data* for $Os_{10}(S)_2(CO)_{23}$ (**1**): $C_{23}O_{23}Os_{10}S_2$; $M = 2\,610.4$, monoclinic, space group $C2/c$, $a = 19.977(3)$, $b = 10.585(2)$, $c = 20.887(3)$ Å, $\beta = 119.03°$, $U = 3\,861.8$ Å^3, $F(000) = 4\,456$, $Z = 4$, $D_c = 4.49$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 316.7 cm^{-1}. Current R value 0.042 for 1365 reflections with $I \geqslant 3\sigma(I)$ corrected for absorption.

The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

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