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Synthesis and X-ray structure of the osmium carbonyl anion $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{20}]^-$

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Abstract

The reaction of $[HOs_3(CO)_{11}]^-$ with $[Os_3(CO)_{10}(MeCN)_2]$ in acetone gives the green-blue anion $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{20}]^-$ (1) amongst several other products; this anion has been structurally characterised by a single crystal X-ray study of its Bu_4P^+ salt.

Previous workers in our group have shown that treatment of the anion $[HOs_3(CO)_{11}]^-$ with $[Os_5(CO)_{16}]$ [1], $[Os_6(CO)_{18}]$ [2–4] or $[Os_7(CO)_{21}]$ [1] leads to the CO_2-linked anions $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_5(CO)_{15}]^-$, $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{17}]^-$ or $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_7(CO)_{20}]^-$, respectively. The presence of the CO_2-linkage was confirmed by a single crystal analysis of PPN^+ salt of $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{17}]^-$. Here we report the synthesis of the anion $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{20}]^-$ (1) which contains a planar Os_6 moiety linked to the same $[HOs_3(CO)_{10}]$ unit from the reaction of the hydrido-anion $[HOs_3(CO)_{11}]^-$ with trinuclear cluster $[Os_3(CO)_{10}(MeCN)_2]$ in acetone.

Treatment of the anion $[HOs_3(CO)_{10}]^-$ with 2 equivalents of $[Os_3(CO)_{10}(MeCN)_2]$ in acetone under dinitrogen leads to the initial formation of a dark red solution which upon subsequent stirring of reaction mixture in air for 24 h changes to dark green. Separation by chromatography on silica yields the green-blue nona-osmium anion which has been characterised as its Bu_4P^+ and PPN^+ salts. Figure 1 shows the structure of this anion established from a single crystal X-ray diffraction analysis, and some important bond parameters are included *. As observed previously for the nona-osmium derivatives mentioned above the complex is not a *closo*-osmium cluster but consists of an Os_3 unit linked via a CO_2-bridge to a planar Os_6 unit. This CO_2-bridging group forms a virtually planar symmetrical ring [maximum derivation 0.06 Å] described by atoms Os(7)–Os(8)–O(64)–C(64)–O(65). The strong band observed in the IR spectrum at ca. 1258 cm^{-1} (KBr) is consistent with this symmetrical arrangment. The Os–Os distances within the Os_6 planar unit are similar to those observed for other related Os_6 planar units, e.g. as in $[Os_6(CO)_{20}P(OMe)_3]$ [5] apart from those associated with Os(6). The dihedral angle between the planar ring and the Os_6 raft plane is 45.6°. The Os_3 unit has a

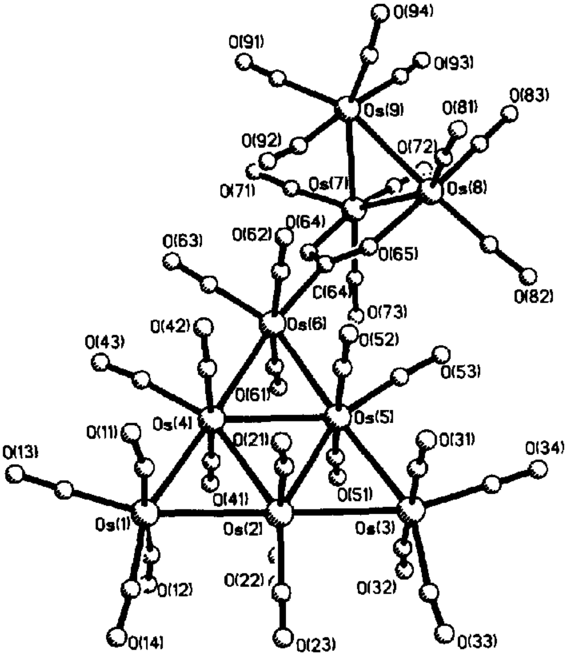

Fig. 1. The molecular structure of $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{20}]^-$ (1) showing the atom numbering scheme. Bond lengths: Os(1)–Os(2), 2.888(2); Os(1)–Os(4), 2.822(3); Os(2)–Os(3), 2.864(3); Os(2)–Os(4), 2.839(3); Os(2)–Os(5), 2.855(3); Os(3)–Os(5), 2.857(3); Os(4)–Os(5), 2.815(2); Os(4)–Os(6), 2.941(3); Os(5)–Os(6), 2.881(3); Os(7)–Os(8), 2.896(3); Os(7)–Os(9), 2.864(3); Os(8)–Os(9), 2.876(3); Os(6)–C(64), 2.09(5); Os(7)–O(64), 2.15(3); Os(8)–O(65), 2.18(3); C(64)–O(64), 1.29(6); C(64)–O(65), 1.21(5) Å. Bond angles: Os(2)–Os(1)–Os(4), 59.6(1); Os(1)–Os(2)–Os(3), 178.2(1); Os(1)–Os(2)–Os(4), 59.0(1); Os(1)–Os(2)–Os(5), 118.3(1); Os(3)–Os(2)–Os(4), 119.2(1); Os(3)–Os(2)–Os(5), 59.9(1); Os(4)–Os(2)–Os(5), 59.3(1); Os(2)–Os(3)–Os(5), 59.9(1); Os(1)–Os(4)–Os(2), 61.3(1); Os(1)–Os(4)–Os(5), 122.0(1); Os(1)–Os(4)–Os(6), 177.7(1); Os(2)–Os(4)–Os(5), 60.7(1); Os(2)–Os(4)–Os(6), 120.6(1); Os(5)–Os(4)–Os(6), 60.0(1); Os(2)–Os(5)–Os(3), 60.2(1); Os(2)–Os(5)–Os(4), 60.1(1); Os(3)–Os(5)–Os(4), 120.3(1); Os(2)–Os(5)–Os(6), 122.2(1); Os(3)–Os(5)–Os(6), 176.8(1); Os(4)–Os(5)–Os(6), 62.2(1); Os(4)–Os(6)–Os(5), 57.8(1); Os(8)–Os(7)–Os(9), 59.9(1); Os(7)–Os(8)–Os(9), 59.5(1); Os(7)–Os(9)–Os(8), 60.6(1); Os(4)–Os(6)–C(64), 171(1); Os(6)–C(64)–O(64), 115(3); Os(6)–C(64)–O(65), 121(4); O(64)–C(64)–O(65), 124(4); Os(8)–Os(7)–O(64), 80.4(6); Os(7)–Os(8)–O(65), 81.0(8)°.

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[*] *Crystal data*. $C_{47}H_{37}O_{32}POs_9$, M 2856.5, monoclinic, space group $P2_1/n$ (non-standard setting $P2_1/c$ no. 14), a 15.621(3), b 18.152(4), c 23.497(5) Å, β 98.57(3)°, V 6588(2) Å, D_c 2.88 g cm^{-3}, $Z = 4$, $F(000) = 5096$, $\lambda(Mo\text{-}K_\alpha)$ 0.71069 Å, $\mu(Mo\text{-}K_\alpha)$ 174.16 cm^{-1}. Dark blue hexagonal platelet, crystal dimensions: 0.12×0.32×0.45 mm, $\mu R = 2.6$, 9514 data measured on a Nicolet R3mV four-circle diffractometer ($5.0 \leqslant 2\theta \leqslant 45.0°$, h, k, $\pm l$), corrected for absorption, 4229 independent observed reflections with $F > 4(\sigma F)$. The structure was solved by a combination of direct methods and difference Fourier techniques, and refined by full-matrix least-square analysis, with all Os, P and O atoms assigned anisotropic displacement parameters. The hydride atoms position was estimated by potential energy calculation [7] while no allowance has been made for hydrogen atoms of the $[Bu_4P]$ cation. The refinement converged at $R = 0.064$ and $R_w = 0.063$. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (UK). Any request should be accompanied by a full literature citation for this communication.

Table 1

Summary of spectroscopic data of the new compounds

Compound	IR (ν(CO), cm^{-1}, CH_2Cl_2)	^{1}H NMR $\delta(CD_2Cl_2)$	MS (m/e)
$[PPN][HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{20}]$	2106w, 2075s, 2068s, 2028s, 2019sh, 2009s, 1982m,br, 1946w	-10.3 (s, 1H, MH) 7.59 (m, 30H, PPN)	2594 (^{190}Os)
$[HOs_3(CO)_{10}(O_2CBr)]$	2115w, 2076vs, 2068s, 2027vs, 2015s, 2001w, 1991m, 1972vw, 1960vw	-14.3 (s, MH)	981 (^{192}Os)

geometry almost exactly similar to that observed in other related system $[HOs_3(CO)_{10} \cdot O_2C \cdot Os_6(CO)_{17}]^-$. The spectroscopic data (see Table 1) are also totally consistent with this formulation and structure.

The anion **1** is the major product of the reaction (ca. 60%). However, three products are also formed and may be separated by TLC. The first yellow band was found to correspond to the trinuclear cluster $[HOs_3(CO)_{10}(OH)]$ which is frequently an additional product of the coupling reactions described previously [1–3]. A second yellow product was found to be $[HOs_3(CO)_{10}(O_2CBr)]$ based on spectroscopic data (see Table 1), where the probable source of bromide is trace of impurity $[Bu_4P]Br$ introduced in preparation of $[Bu_4P][HOs_3(CO)_{11}]$. A final blue compound formed in very small amounts and insoluble in all common solvents has not been characterised. Treatment of **1** with acetonitrile at room temperature gives the known compounds $[Os_6(CO)_{20}(MeCN)]$ and $[Os_6(CO)_{19}(MeCN)_2]$ in good yields (ca. 30% and 50%, respectively) but the fate of the Os_3 unit has not been established.

The mechanism of formation of **1** has not been established. Our initial view was that the precursor material, $[Os_3(CO)_{10}(MeCN)_2]$, underwent reaction to produce a planar Os_6 derivative of the type $[Os_6(CO)_{20}(MeCN)]$. This seemed reasonable since we have shown previously [6] that $[Os_3(CO)_{10}(MeCN)_2]$ undergoes a catalytic coupling reaction in the presence of $PdCl_2$ to form such planar derivatives. However, the preformed planar cluster $[Os_6(CO)_{20}(MeCN)]$ failed to produce **1** when treated with the anion $[HOs_3(CO)_{11}]^-$ under the conditions of the experiment. Nor do we understand the formation of CO_2-bridge and the role of oxygen in this reaction. Just as in previous case the trinuclear cluster $[HOs_3(CO)_{10}(OH)]$ is observed as a product of the reaction, leading us to suspect that the coupling reaction occurs as a consequence of the nucleophilic addition of the anion $[HOs_3(CO)_{10}(O)]^-$ to a bonded CO ligand; we have however previously discounted this possibility but reexamination of this problem is currently underway.

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