The Crystal Structure of $Os_4O_4(CO)_{12}$

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Summary The crystal structure of $Os_4O_4(CO)_{12}$ has been determined by *X*-ray diffraction and found to contain four equivalent osmium atoms arranged in the form of a cube with $Os(CO)_3$ groups alternating with O atoms at the corners.

THE isolation of an oxocarbonyl of osmium from the reaction of OsO_4 with CO at 150° and 200 atmospheres pressure was recently reported by Johnson *et al.*,[1] who established its formula as $Os_4O_4(CO)_{12}$ by mass spectroscopy. Subsequently Bradford and Nyholm found that the compound could be obtained in larger yields by carrying out the reaction at 175° with 128 atmospheres pressure.[2] The structure shown in Figure 1, an acid–base adduct of OsO_4 and $Os_3(CO)_{12}$, has been suggested for this compound.[3] In order to confirm or deny this suggestion an *X*-ray structure determination was undertaken.

Crystals of $Os_4O_4(CO)_{12}$ are tetragonal with $a = 14{\cdot}043(7)$, $c = 9{\cdot}825(5)$ Å,[4] $Z = 4$, space group $I4_1/amd$, requiring molecular symmetry $\bar{4}2m$. The structure, based on 450 diffractometer data corrected for absorption, was refined by least-squares with all atoms anisotropic to a current R factor of 7·8%. The structure is shown in Figure 2. It is best described as a cube skeleton with O atoms and $Os(CO)_3$ groups at alternate corners, analogous with the structures found for $[ZnO(OCH_3)]_4$[5] and $[PtCl(CH_3)_3]_4$.[6] Every non-carbonyl oxygen atom is co-ordinated to three osmium atoms and every osmium atom is octahedrally co-ordinated by three oxygen atoms and three terminal carbonyl groups. The compound is certainly not an acid–base adduct of OsO_4 and $Os_3(CO)_{12}$ as previously suggested, but may be regarded as a tetramer of the electron-deficient compound $O(CO)_3Os^{II}$.

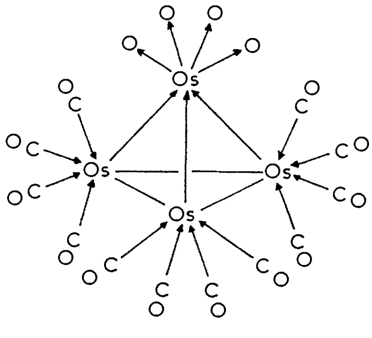

FIGURE 1. *Suggested structure of* $Os_4O_4(CO)_{12}$

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The cube skeleton is slightly distorted by a movement of the O atoms closer to its centre than the Os atoms. The molecule has $\bar{4}2m$ crystallographic symmetry, and in addition it has non-crystallographic three-fold axes along the body diagonals of the cube. The overall molecular symmetry is $\bar{4}3m$.

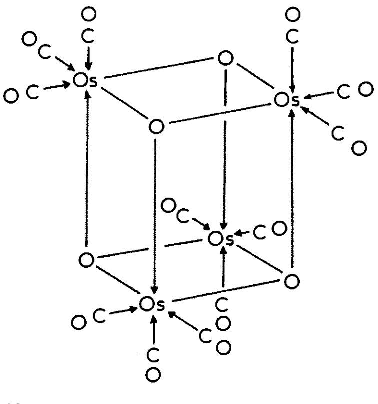

FIGURE 2. *Structure of* $Os_4O_4(CO)_{12}$

The Os–C distances, 1·91(4) and 1·92(4) Å are comparable with those found in $Os_3(CO)_{12}$,[7] 1·95 Å, while the two independent Os–Os distances, 3·253(4) and 3·190(4) Å, are considerably longer than the Os–Os bond distances of 2·88 Å in $Os_3(CO)_{12}$. This suggests that there is no metal–metal bonding in the oxocarbonyl. Both distances are also longer than the 3·05 Å reported[8] for the Os–Os distance in $[Os_2O_6(NO_2)_4]^{4-}$. The O–Os–O angles are 78(1) and 76(1)°, and the Os–O–Os angles are 100(1) and 103(1)°. The carbonyl groups are all linear within experimental error.

It is notable that the two independent Os–Os distances are highly significantly different (15 e.s.d.). The same distances were also found from photographic data taken with a different crystal. Such a difference might arise if the three bonds from Os to O were not equivalent, *i.e.* if the bonding were fixed in the configuration shown in Figure 2 with the oxygen atoms forming electron-exchange bonds with two osmium atoms, and forming a two-electron-donor bond with a third. However, there is no suggestion from the Os–O distances, 2·06(2) and 2·06(2) Å, that the Os–O bonds are not all equivalent, and it seems more likely that the difference in the Os–Os distances is due to crystal packing.

Some of the Weissenberg photographs of the compound show very weak streaks indicative of some slight stacking disorder. This disorder is being further investigated.

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[4] Figures in parentheses are the standard deviations in the least significant digits.

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