

An Octanuclear Iridium Carbonyl Cluster Based on Two Equivalent Tetrahedral Units. Synthesis and X-Ray Characterization of Bis(tetraphenylphosphonium) Hexa- μ -carbonylhexasdecacarbonyl-ditetrahedro-octairidate(2-)

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Summary The reaction of $\text{Ir}_4(\text{CO})_{12}$ with KOH in 1,2-dimethoxyethane, under nitrogen, yields the $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ anion, which has been shown by X-ray crystallography to contain an iridium double cluster based on two symmetry-equivalent tetrahedral subunits.

REDUCTION of $\text{Ir}_4(\text{CO})_{12}$ by alkaline agents in methanolic solution was reported in 1975¹ to give rise to a number of tetra-, hexa-, and octa-nuclear iridium carbonyl anions which were formulated only on the basis of elemental analysis and spectroscopic data. In the reinvestigation of these compounds we have recently reported the X-ray characterization of the $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ anion.² We report here the synthesis and the X-ray structure determination of $[\text{PPh}_4]_2[\text{Ir}_8(\text{CO})_{22}]$, which is the first octanuclear iridium cluster to be characterized by X-ray diffraction.

The $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ anion was prepared by stirring $\text{Ir}_4(\text{CO})_{12}$ (2.32 g) in 1,2-dimethoxyethane (50 ml) with powdered KOH (3 g) at room temperature under nitrogen, until all the $\text{Ir}_4(\text{CO})_{12}$ had reacted and a red solution had been formed (ca. 48 h). The solution was filtered and evaporated to dryness *in vacuo*, and the residue was treated with 10% aqueous KBr, to give $\text{K}_2[\text{Ir}_8(\text{CO})_{22}]$ as a red

powder. Crystals of $[\text{PPh}_4]_2[\text{Ir}_8(\text{CO})_{22}]$ suitable for X-ray analysis were obtained by slow diffusion of a saturated solution of PPh_4Cl in propan-2-ol into a tetrahydrofuran (THF) solution of $\text{K}_2[\text{Ir}_8(\text{CO})_{22}]$. Pure $[\text{PPh}_4]_2[\text{Ir}_8(\text{CO})_{22}]$ in THF solution has an i.r. spectrum (ν_{CO} bands at 2070vw, 2040m, 2020vs, 1970m,br, and 1820m cm^{-1}) which is quite different from that previously reported for a species formulated as $[\text{Et}_4\text{N}]_2[\text{Ir}_8(\text{CO})_{22}]$ by Malatesta and his co-workers. We think that their product is probably an isomer of the one we are reporting now, since we observed, for instance, that the alkaline reduction of $\text{Ir}_4(\text{CO})_{12}$ yields different red products depending on the reaction conditions. The molecular geometry of $[\text{PPh}_4]_2[\text{Ir}_8(\text{CO})_{22}]$ has been established by a single-crystal X-ray diffraction study.

Crystal data: $\text{C}_{70}\text{H}_{40}\text{Ir}_8\text{O}_{22}\text{P}_2$, $M = 2832.8$, dark-red, air- and light-sensitive triclinic prisms, space group $P\bar{1}$ (after refinement), $a = 14.564(4)$, $b = 12.341(4)$, $c = 13.282(6)$ Å, $\alpha = 90.53(4)$, $\beta = 116.31(4)$, $\gamma = 114.81(4)^\circ$, $U = 1886$ Å³, $Z = 1$, $D_c = 2.49$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 150.3$ cm^{-1} . Intensity data were collected on a BASIC diffractometer with graphite-monochromated Mo-K α radiation in the 2θ range 6–50°. The structure was solved by conventional Patterson and Fourier methods using 4613 reflections

corrected for absorption and decay, having $I \geq 3\sigma(I)$. In the block-matrix least-squares refinement, anisotropic thermal factors were assigned to all the atoms of the anion, while the phenyl rings of the cation were constrained to D_{6h} geometry. The current conventional R value is 0.042.† The structure of the $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ anion, of crystallographic C_{2h}^- symmetry, is shown in the Figure. It is based on a

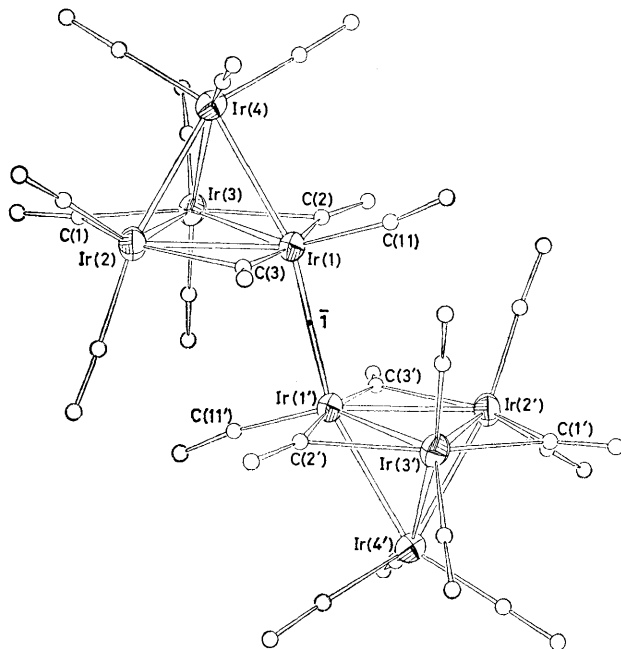


FIGURE. ORTEP view of $[\text{Ir}_8(\text{CO})_{22}]^{2-}$. Metal-metal bond lengths are: Ir(1)–Ir(2) 2.751(1), Ir(1)–Ir(3) 2.743(1), Ir(1)–Ir(4) 2.763(1), Ir(2)–Ir(3) 2.719(1), Ir(2)–Ir(4) 2.722(1), Ir(3)–Ir(4) 2.723(1), Ir(1)–Ir(1') 2.857(1) Å.

metal skeleton consisting of two inversion-related iridium tetrahedra, linked by a non-bridged Ir–Ir single bond 2.857(1) Å long. The whole anion displays an overall idealized C_{2h}^- symmetry, the mirror plane being defined by atoms Ir(1), Ir(4), Ir(1'), and Ir(4'). Its structure may be derived either from the dimerization of two hypothetical $[\text{Ir}_4(\text{CO})_{11}]^-$ paramagnetic units, or from the replacement of a carbonyl group of $\text{Ir}_4(\text{CO})_{12}$ with an $[\text{Ir}_4(\text{CO})_{11}]^{2-}$ substituent. In the latter view, the role of the two symmetry-equivalent tetrahedral subunits is interchangeable, each of them behaving as a substituent to the other. Significant structural features within each

subunit are: (i) the carbonyl ligands [which in $\text{Ir}_4(\text{CO})_{12}$ are all terminal³] follow the partially bridged pattern of $\text{Co}_4(\text{CO})_{12}$ ⁴ and $\text{Rh}_4(\text{CO})_{12}$ ⁵; (ii) the triply edge-bridged metal triangle includes the iridium atom which has undergone substitution; (iii) with respect to the plane of this triangle the substituent is in an axial configuration; (iv) the two bridging carbonyls connecting non-equivalent iridium atoms are markedly asymmetric, with shorter contacts to the substituted metal atom. Interestingly, all these stereochemical features were also found in the structures of $[\text{Ir}_4(\text{CO})_{10}\text{H}_2]^{2-}$,⁶ and $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$,⁷ the only other tetrahedral anionic derivatives of $\text{Ir}_4(\text{CO})_{12}$ for which an X-ray investigation has been reported.

Bond parameters within each tetrahedral fragment are normal: av. Ir–Ir 2.737, av. Ir–C (terminal) 1.880, av. Ir(1)–C(2) and Ir(1)–C(3) 1.998, av. Ir(2)–C(3) and Ir(3)–C(2) 2.313, av. Ir(2)–C(1) and Ir(3)–C(1) 2.084, av. C–O (terminal) 1.120, av. C–O (bridge) 1.152 Å; av. angle Ir–C–O (terminal) 176.2°; angle Ir(4)–Ir(1)–Ir(1') 161.4(1)°. Typical e.s.d.s are Ir–Ir 0.001, Ir–C 0.015, C–O 0.02 Å. The three intra-tetrahedral metal–metal bonds involving the substituted Ir(1) atom are slightly but significantly longer than the other three (mean 2.752 and 2.721 Å respectively), and the Ir(1)–C(11) bond length [1.847(14) Å] is the shortest metal–carbonyl interaction of the cluster. This trend is in keeping with a partial residual localization of the anionic negative charge on the substituted metal atom, which would also justify the unusual lengthening of the Ir(1)–Ir(1') bond {2.857(1) Å compared, for instance, with the unbridged Ir–Ir bond length of 2.717 Å in $[\text{Ir}(\text{NO})_2\text{PPh}_3]_2$ ⁸. In this respect, however, a possible mutual *trans*-influence within the *quasi*-linear Ir(4)–Ir(1)–Ir(1')–Ir(4') catenation should also be considered, whereas non-bonding repulsions between the two tetrahedral units seem not to be relevant [shortest C...C and O...O contacts 3.095(13) and 3.011(21) Å, respectively]. $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ provides the first example of a double cluster in which the two subunits are connected only by a simple metal–metal bond {in $[\text{Rh}_{12}(\text{CO})_{36}]^{2-}$ the inter-octahedral Rh–Rh bond is reinforced by two carbonyl bridges⁹. As a result, the $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ anion is particularly reactive towards the cleavage of this bond, and for instance, reaction with PPh_3 , FeCl_3 , H_2 , and I_2 , gives the known $\text{Ir}_4(\text{CO})_{12-x}(\text{PPh}_3)_x$ ($x = 1, 2, \text{ or } 3$),¹⁰ $\text{Ir}_4(\text{CO})_{12}$,³ and $[\text{Ir}_4(\text{CO})_{11}\text{X}]^-$ ($\text{X} = \text{H}^+$ or I^-), respectively.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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