Multimetallic Binding to Fullerenes: $C_{60}\{Ir_2Cl_2(1,5\text{-}COD)_2\}_2$. A Novel Coordination Mode to Fullerenes

Merja Rasinkangas, Tuula T. Pakkanen,
Tapani A. Pakkanen,* Markku Ahlgrén, and Juha Rouvinen

Department of Chemistry, University of Joensuu
P.O. Box 111, SF-80101 Joensuu, Finland

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Chemistry of metal fullerene complexes has emerged as a new area in organometallic chemistry. Since the report of the first such complex $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})\cdot C_4H_8O$,[1] several other complexes have been synthesized and characterized.[2] A common feature in all of these complexes is the similar binding mode of the metal to the external surface of the fullerene cage. The metal binds in an η^2 fashion to the carbon–carbon bond between two six-membered rings. The metals are typically Pt and Ir, ligated with phosphine, chloride, and carbonyl groups. Some of these complexes are multiple addition products where the metal centers are on the opposite sides of the C_{60} frame.

Here we report the synthesis and crystallographic characterization of the first multimetallic addition product of C_{60}, where two metals connected to each other coordinate to the same six-membered ring of C_{60}.

The new fullerene complex was obtained by mixing solutions of C_{60} and $Ir_2Cl_2(1,5\text{-}COD)_2$ in benzene (or toluene) in a 1:1 mole ratio at room temperature. A brown precipitate formed and was separated by decantation. The air-stable product was found to be only slightly soluble in benzene (or toluene) on heating and was characterized with IR spectroscopy and chemical analysis.[3] Crystals of good quality were grown by slow diffusion of C_{60} and $Ir_2Cl_2(1,5\text{-}COD)_2$ benzene solutions together. The black rectangular plates crystallized in several weeks.

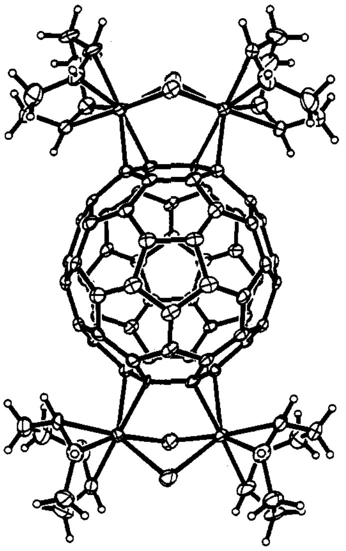

Figure 1. Perspective view of $C_{60}\{Ir_2Cl_2(1,5\text{-}COD)_2\}_2\cdot 2C_6H_6$, with 50% thermal contours. The solvent molecules have been omitted for clarity.

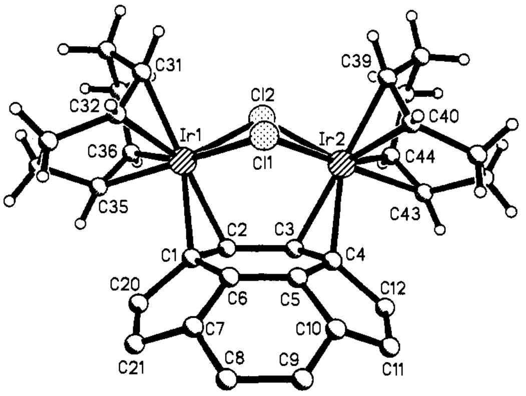

Figure 2. Detailed view of the coordination arrangement of the Ir_2Cl_2 moiety. Important interatomic distances (angstroms) and angles (deg): Ir1–C1, 2.231(6); Ir1–C2, 2.211(6); Ir2–C3, 2.201(7); Ir2–C4, 2.225(7); Ir1–Cl1, 2.398(3); Ir1–Cl2, 2.552(2); Ir1–C31, 2.140(7); Ir1–C32, 2.145(7); C1–C2, 1.491(10); C2–C3, 1.502(9); C3–C4, 1.454(12); C1–C6, 1.496(11); C5–C6, 1.384(10); C1–Ir1–C2 39.2(2); Cl1–Ir1–Cl2, 79.6(1).

The structure of $C_{60}\{Ir_2Cl_2(1,5\text{-}COD)_2\}_2$ is shown in Figure 1.[4] Two $Ir_2Cl_2(1,5\text{-}COD)_2$ groups bind to the opposite ends of the C_{60} frame, giving a C_{2h} point group symmetry for the molecule. Two trapped benzene solvent molecules are also found in the structure with no short contacts to the complex. The detailed geometry of the $Ir_2Cl_2(1,5\text{-}COD)_2$ binding site to C_{60} is shown in Figure 2. The complexation of the $Ir_2Cl_2(1,5\text{-}COD)_2$ takes place without any leaving groups. In complexation the iridium moiety opens up for binding with distortion of its original geometry. The two iridiums bind to two adjacent 6:6 ring fusions. The coordination sphere of iridium remains otherwise unaltered, except that the two chloride bridges and the two 1,5-COD η^2-bound ligands are bent away from C_{60}. The coordination geometry of C_{60} is similar to that of the monometallic complexes. The distance between the two iridium atoms is 346.5 pm, which is close to the typical range of metal distances in polymetallic complexes.

The complexation reaction between C_{60} and $Ir_2Cl_2(1,5\text{-}COD)_2$ can be rationalized as an addition reaction of an unsaturated iridium complex. The binding of the Ir_2Cl_2 unit to the two carbon–carbon bonds in the same six-membered ring shows that neighboring 6:6 ring junctions can also be activated in metal complexation. This result suggests that fullerene complexes with extended polynuclear metal systems bound to the surface of C_{60} can be synthesized.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen positions and drawings showing the atomic numbering scheme (8 pages); listing of observed and calculated structure factors (29 pages). Ordering information is given on any masthead page.

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(3) $C_{60}\{Ir_2Cl_2(1,5\text{-}COD)_2\}_2\cdot 2C_6H_6$ elemental analysis: C (calcd) 56.3, (found) 55.6; H (calcd) 2.7, (found) 2.6. IR absorptions in KBr: 2944 (s), 2918 (sh), 2910 (s), 2880 (s), 2831 (s), 1478 (m), 1460 (m), 1428 (m), 1387 (m), 1328 (s), 1300 (w), 1259 (w), 1245 (w), 1190 (m), 1177 (m), 1161 (m), 1088 (w), 1028 (m), 1008 (m), 838 (m), 787 (m), 733 (m), 701 (m), 679 (s), 585 (w), 527 (s), 518 (w), 509 (w), 480 (m) cm^{-1}.

(4) Black rectangular plates of $C_{60}\{Ir_2Cl_2(1,5\text{-}COD)_2\}_2\cdot 2C_6H_6$ form in the triclinic space group $P\bar{1}$ with $a = 10.249(3)$, $b = 11.516(3)$, and $c = 15.996(4)$ Å; $\alpha = 69.09(2)°$, $\beta = 78.16(2)°$, $\gamma = 80.53(2)°$; and $V = 1717.6(9)$ Å^3 at 298 K with $Z = 1$, d(calcd) = 2.147 g/cm^3. Refinement of 5521 reflections yielded $R = 0.0323$, $R_W = 0.0324$.

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