

Syntheses, structures and properties of novel molybdenum and tungsten complexes of fullerenes

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Synthesis and characterization of several fullerene-based organometallic complexes containing Mo and W is reported.

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Since the report on the crystal structure of the first organometallic complex of fullerene ($\eta^2\text{-C}_{60}$)Pt(*PPH*₃)₂ · C₄H₈O [1], several other complexes have been synthesized and characterized by *x*-ray diffraction method. However, among them most metals are in the group VIII, such as Pt, Ir, Pd, Rh etc. Only a few molybdenum or tungsten complexes of C₆₀ are described in the literature, such as [M($\eta^2\text{-C}_{60}$)(CO)₃(dppb)] (*M* = Mo, W) [2], [M($\eta^2\text{-C}_{60}$)(CO)₃(dppe)] (*M* = Mo, W) [3], [Mo($\eta^2\text{-C}_{70}$)(CO)₃(dppe)] [3] etc. with phosphorous-containing ligands.

The key problems in growing single crystals of fullerene-based complexes are the instability of their solution and the low solubility. We have synthesized four air-table organometallic C₆₀ derivatives of molybdenum (0) and tungsten (0) with nitrogen-containing ligands ($\eta^2\text{-C}_{60}$)M(CO)₃LL (*M* = Mo, W, LL = 2, 2'-bipyridine or 1, 10-phenanthroline) [4]. They are only slightly soluble in chlorobenzene and *o*-dichlorobenzene. No crystals suitable for *X*-ray diffraction studies were obtained. However, when one carbonyl group of ($\eta^2\text{-C}_{60}$)M(CO)₃(*o*-phen) was displaced by dibutyl fumarate (dbf), the resulting complexes had good solubility in a number of organic solvents, even much better than C₆₀ itself. Here we report syntheses, crystal structures and properties of the novel molybdenum and tungsten complexes of C₆₀ and C₇₀.

A series of Mo/W complexes of fullerenes ($\eta^2\text{-C}_x$)[M(CO)₂(*o*-phen)(dbf)]_{*n*} (*x* = 60 or 70, *M* = Mo or W, *n* = 1, 2, 3, phen = 1, 10-phenanthroline) have been synthesized by heating a solution of fullerene (C₆₀ or C₇₀) with [M(CO)₂(*o*-phen)(dbf)]₂ in toluene followed by column chromatography over silica gel. They are remarkably stable in air and have unusually good solubility. The complexes were characterized by chemical analysis, IR, UV/vis, ¹H and ¹³C NMR spectroscopy and single crystal *X*-ray diffraction analysis [5,6].

The *X*-ray structure analysis indicates that molybdenum and tungsten complexes of C₆₀ are isomorphous compounds, ($\eta^2\text{-C}_{60}$)M(CO)₂(*o*-phen)(dbf) · 2C₆H₆ · C₅H₁₂ (*M* = Mo (**1**) or W (**2**)). The molecular structure of unsolvated complexes is shown in Fig. 1 [5].

In the molecules of complexes (**1**) and (**2**), the Mo or W atom coordination is distorted octahedrally with the two CO

groups *cis* to each other, but each *trans* to a nitrogen atom of *o*-phenanthroline. The metal (*M*) atom, two CO groups and *o*-phen are in the equatorial plane. They are coplanar within 0.050 Å. The *M* atom binds in an η^2 fashion to the C–C bond [C(1)–C(2)] between two six-member rings of C₆₀. The distances of W–C(1) and W–C(2) are almost equal (2.30(2), 2.30(3) Å). The *M* atom binds also in an η^2 fashion to the C–C bond [C(85)–C(91)] of dibutyl fumarate (W–C(85) 2.28(3) Å and W–C(91) 2.29(3) Å). The two C–C bonds (C(1)–C(2) and C(85)–C(91)) are almost orthogonal and each alkene ligand eclipses a N–M–CO vector (av. 171.4°). The coordination about metal atom closely resembles that observed in the molybdenum complex of methyl acrylate ($\eta^2\text{-CH}_2 = \text{CHCOOMe}$)₂Mo(CO)₂(bipy) (**3**), the structure of which has been determined by us. Actually, we prepared complex (**3**) as an electronic model for the corresponding C₆₀ compound [7].

The molecular structure of molybdenum complex of C₇₀ ($\eta^2\text{-C}_{70}$)Mo(CO)₂(*o*-phen)(dbf) · 2C₃H₈O · 2.5H₂O (**4**) is shown in Fig. 2 [6]. The Mo atom binds in an η^2 fashion to the Ca–Cb bond of C₇₀ (C(1)–C(2)) and the distances of Mo–C(1) and Mo–C(2) bonds are very close (2.29 and 2.28 Å). The typical distances can also be found in other molybdenum complexes of fullerenes. For example, the distances of Mo–C(1) and Mo–C(2) are 2.31 and 2.32 Å in the complex (**1**), 2.33 and 2.31 Å in [Mo($\eta^2\text{-C}_{60}$)(CO)₃(dppb)] [2], 2.31 and 2.31 Å in [Mo($\eta^2\text{-C}_{60}$)(CO)₃(dppe)] [3], 2.29 and 2.28 Å in [Mo($\eta^2\text{-C}_{70}$)(CO)₃(dppe)] [3]. The crystal structure analysis indicates that the molecular configuration of complex (**4**) is similar to that of Mo–C₆₀ complex (**1**).

The electrochemical behaviour of these complexes has been studied in dichloromethane solution, and EPR spectra of electrogenerated monoanions have also been studied [8,9]. Electrochemistry of complexes (**1**) and (**2**) shows that they undergo four sequential reduction processes. As with free C₆₀, the first three electrons add reversibly (even if the relevant potentials are shifted *ca.* 0.15 V toward negative values), whereas the fourth reduction features chemical irreversibility [8]. Comparison with the redox behaviour of C₇₀-analog reveals significant differences, namely complex (**4**) exhibits two reversible one-electron reductions followed by a single two-electron reduction, all of these reductions being centred

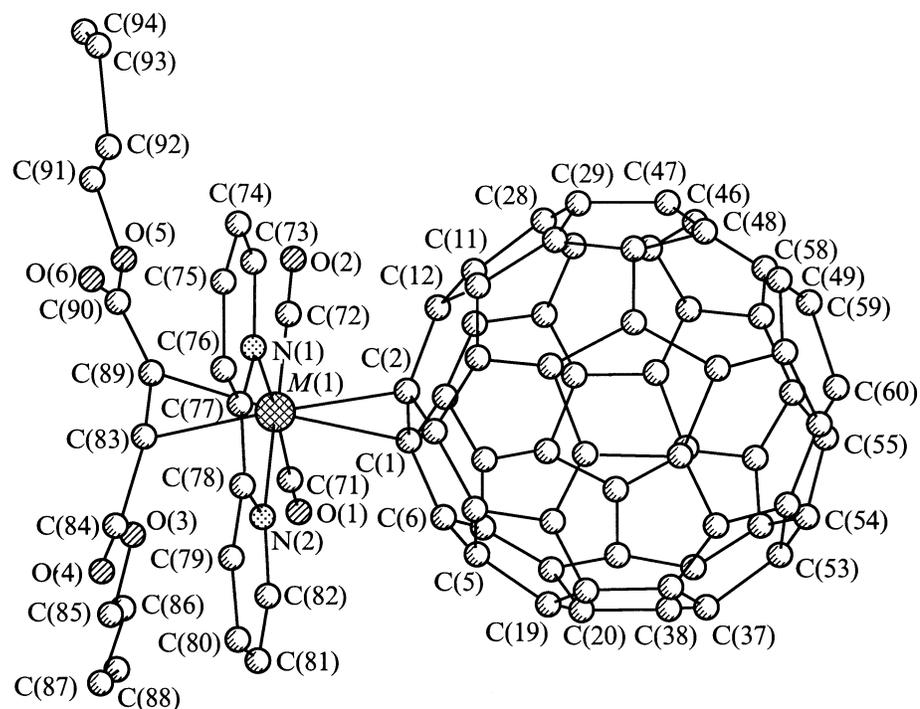


Figure 1. Perspective view of the structure of $[M(\eta^2-C_{60})(CO)_2(phen)(dbf)]$ ($M = Mo, W$).

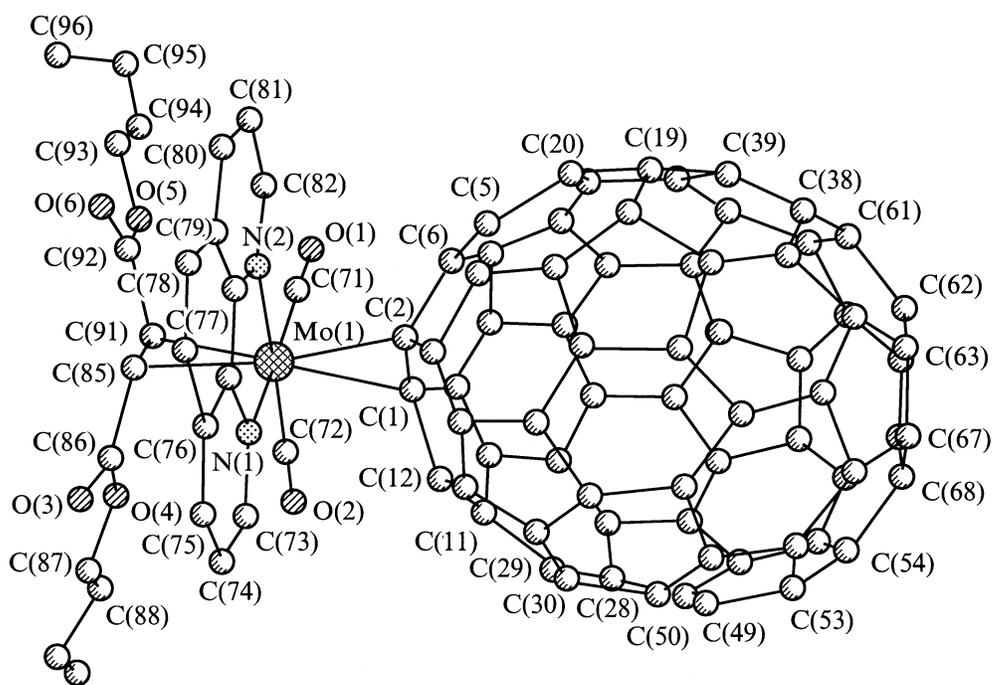


Figure 2. Perspective view of the structure of $[Mo(\eta^2-C_{70})(CO)_2(phen)(dbf)]$.

on the fullerene ligand. A further cathodic step centred on the metallic fragment is present, which, also in this case, causes framework destruction releasing the C₇₀ ligand. Under the same experimental conditions, the cathodic shift induced by appending the Mo(CO)₂(phen)(dbf) unit to C₇₀ is lower than for C₆₀ (0.10 V vs 15 V), thus suggesting that the extent to which the double bond conjugation is broken by the co-ordination to C₇₀ should be lower than with C₆₀ [9].

Optical limiting property of molybdenum complexes of fullerenes C₆₀ and C₇₀ have been investigated under irradiation of 10-ns laser pulse at 532 nm. The experimental results demonstrated that the complexes performed with better optical limiting behaviour than the parents C₆₀ or C₇₀. Each (η^2 -C₆₀)[Mo(CO)₂(phen)(dbf)] molecule's absorption was as much as 3 times that of a C₆₀ C₆₀ molecule [10], whereas each (η^2 -C₇₀)[Mo(CO)₂(phen)(dbf)] molecule absorbed as much as 1.7 times more than a C₇₀ molecule [11]. An explanation based on the enhanced triplet-state absorption caused by the intra-molecular charge transfer was predicted.

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