

# The crystal structure of the molybdenum complex of [70]fullerene $\text{Mo}(\eta^2\text{-C}_{70})(\text{CO})_2(\text{phen})(\text{dbm}) \cdot 2\text{C}_3\text{H}_8\text{O} \cdot 2.5\text{H}_2\text{O}$ (phen = 1,10-phenanthroline, dbm = dibutyl maleate)

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The molybdenum complex of  $\text{C}_{70}$ ,  $[\text{Mo}(\eta^2\text{-C}_{70})(\text{CO})_2(\text{phen})(\text{dbm})]$  (**1**) (phen = 1,10-phenanthroline, dbm = dibutyl maleate) has been synthesised by heating a solution of  $\text{C}_{70}$  with  $[\text{Mo}(\text{CO})_2(\text{phen})(\text{dbm})_2]$  in toluene followed by chromatography over silica gel and the crystal structure has been determined.

**Keywords:**  $\text{C}_{70}$ ; molybdenum complex; crystal structure

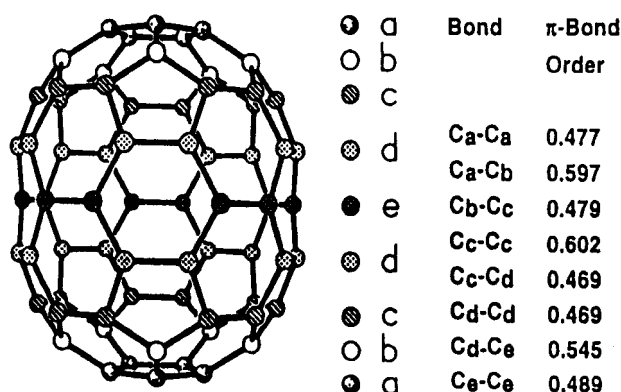
Since the availability of macroscopic quantities of fullerenes, great efforts have been made in the investigation of the reactions of transition metal complexes with  $\text{C}_{60}$  and a number of metal-fullerene[60] complexes have been prepared and characterised by X-ray diffraction<sup>1</sup>. However, up to now, only a few crystal structures of metal- $\text{C}_{70}$  complexes have been reported, such as those of Ir<sup>2,3</sup>, Ru<sup>4</sup>, Pt<sup>5</sup>, Pd<sup>6</sup>, Mo<sup>7</sup>, etc. In these complexes the phosphorus-containing ligands, such as  $\text{PPh}_3$ ,  $\text{PPhMe}_2$ , and dppe (1,2-diphenylphosphinoethane), are used to coordinate with metal atoms and stabilise the complexes. We have previously synthesised the molybdenum and tungsten complexes of  $\text{C}_{60}$   $[(\eta^2\text{-C}_{60})\text{M}(\text{CO})_2(\text{phen})(\text{dbm})]$  (M = Mo, W)<sup>8</sup> by using the nitrogen-containing ligand, 1,10-phenanthroline, which enables the strong interaction between metal atoms and fullerenes and the resulting complexes are remarkably stable in the air. Recently, with the similar methods, we obtained the molybdenum complex of  $\text{C}_{70}$ ,  $[(\eta^2\text{-C}_{70})\text{Mo}(\text{CO})_2(\text{phen})(\text{dbm})]$  (**1**) and it has showed different characteristics from  $\text{C}_{70}$  in both its chemical and physical properties. For example, the redox behaviour of complex (**1**) is different from free  $\text{C}_{70}$ . The presence of the Mo fragment in complex (**1**) induces a cathodic shift (0.10V) of the first two  $\text{C}_{70}$ -centered one-electron reductions followed by a single two-electron reduction with respect to free  $\text{C}_{70}$ .<sup>9</sup> It has also been found that the complex (**1**) performs better optical limiting behaviour than  $\text{C}_{70}$ .<sup>10</sup> By the method of slow diffusion of pentane and isopropyl alcohol into a dichloromethane

solution, we obtained single crystals of complex (**1**) suitable for X-ray diffraction analysis and collected the diffraction data at low temperature ( $-100^\circ\text{C}$ ) on a Rigaku R-AXIS RAPID imaging plate diffractometer. Here we report the crystal structure detail of the molybdenum complex of  $\text{C}_{70}$  (**1**).

Compared with  $\text{C}_{60}$ , which has only one type of carbon atom and two types of C–C bonds, there are five types of carbon atoms and eight types of C–C bonds in  $\text{C}_{70}$  (Fig. 1).<sup>1</sup> The results of theoretical calculation demonstrate that Ca–Cb and Cc–Cc bonds are expected to be the more active ones. On the other hand, it has been proved that the regiochemistry of  $\text{C}_{70}$  is driven by the degree of pyramidalization rather than

**Table 1.** Selected bond lengths (Å) and angles (°) for complex (**1**)

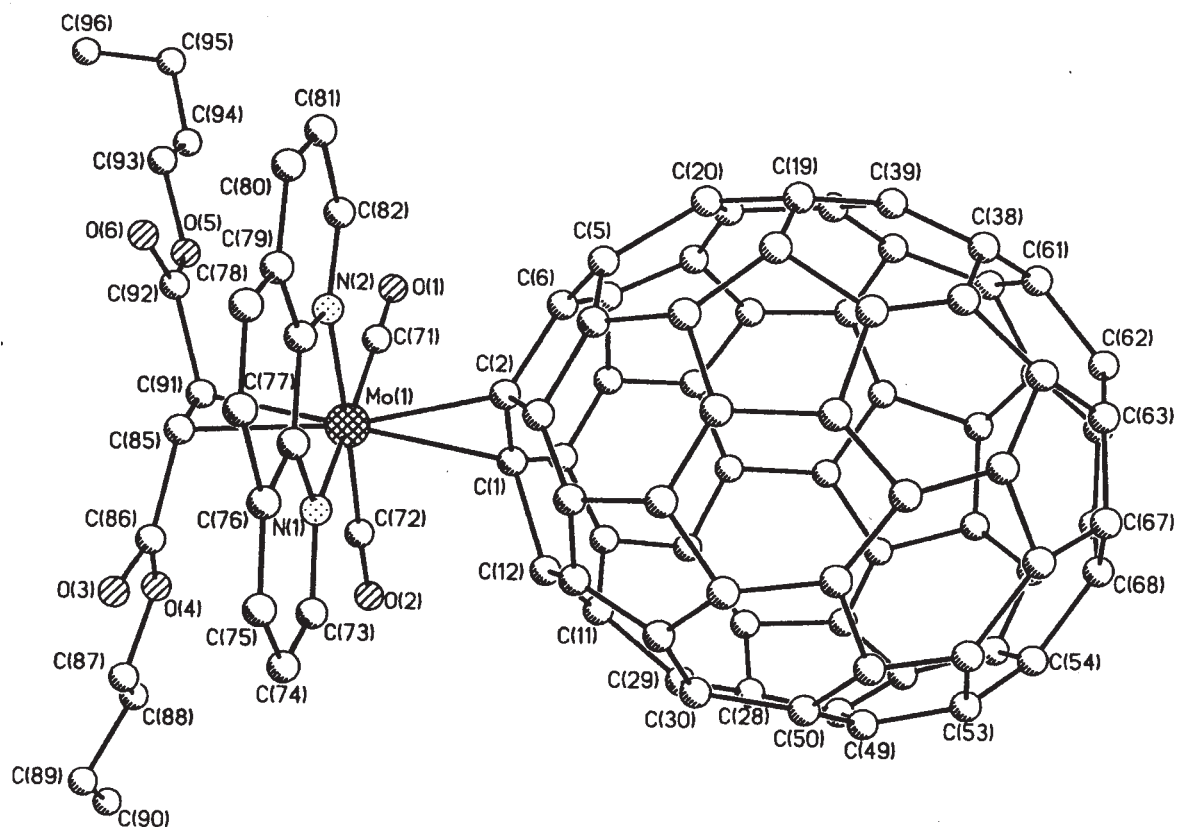
Mo(1)–C(71)	2.001(10)
Mo(1)–C(72)	1.970(10)
Mo(1)–N(1)	2.216(9)
Mo(1)–N(2)	2.233(9)
Mo(1)–C(1)	2.294(12)
Mo(1)–C(2)	2.281(12)
Mo(1)–C(85)	2.256(9)
Mo(1)–C(91)	2.350(12)
O(1)–C(71)	1.135(9)
O(2)–C(72)	1.159(10)
C(71)–Mo(1)–C(72)	90.4(3)
C(72)–Mo(1)–N(1)	98.8(4)
C(71)–Mo(1)–N(1)	170.5(4)
C(72)–Mo(1)–N(2)	173.2(4)
C(71)–Mo(1)–N(2)	96.4(4)
N(1)–Mo(1)–N(2)	74.4(4)
C(72)–Mo(1)–C(85)	94.3(4)
C(71)–Mo(1)–C(85)	103.0(4)
N(1)–Mo(1)–C(85)	78.4(4)
N(2)–Mo(1)–C(85)	83.9(4)
C(72)–Mo(1)–C(2)	106.1(5)
C(71)–Mo(1)–C(2)	87.8(5)
N(1)–Mo(1)–C(2)	87.7(5)
N(2)–Mo(1)–C(2)	74.5(5)
C(85)–Mo(1)–C(2)	156.9(4)
C(72)–Mo(1)–C(1)	74.3(5)
C(71)–Mo(1)–C(1)	86.0(5)
N(1)–Mo(1)–C(1)	94.5(5)
N(2)–Mo(1)–C(1)	106.4(4)
C(85)–Mo(1)–C(1)	165.7(7)
C(2)–Mo(1)–C(1)	31.9(4)
C(72)–Mo(1)–C(91)	86.2(5)
C(71)–Mo(1)–C(91)	72.9(4)
N(1)–Mo(1)–C(91)	109.5(4)
N(2)–Mo(1)–C(91)	95.5(5)
C(85)–Mo(1)–C(91)	31.3(4)
C(2)–Mo(1)–C(91)	157.4(8)
C(1)–Mo(1)–C(91)	151.2(4)



**Figure 1** The idealized structure of  $\text{C}_{70}$

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.



**Figure 2** Perspective view of the structure of  $[\text{Mo}(\eta^2\text{-C}_{70})(\text{CO})_2(\text{phen})(\text{dbm})]$  (**1**)

bond length or bond order.<sup>11</sup> With a higher degree of pyramidalization of Ca–Cb bond at the poles, we believe that the Ca–Cb bond is the most active bond in the  $\text{C}_{70}$  molecule although its  $\pi$ -bond order is smaller than that of the Cc–Cc bond. Among the reactions of transition metal complexes with  $\text{C}_{70}$ , most additions occur at the Ca–Cb bond. Only in some cases, for example, in the osmylation of  $\text{C}_{70}$ ,<sup>12</sup> the isomers (addition products at Ca–Cb and Cc–Cc bonds) have been observed and the ratio is 2.1:1. By studying the  $^{31}\text{P}$  NMR spectrum,<sup>7</sup> Shapley also observed the existence of an addition product occurring at the Cc–Cc bond as the minor form.

The molecular structure of complex (**1**) is shown in Fig. 2 and selected bond lengths and angles are reported in Table 1. As expected, the Mo atom binds in an  $\eta^2$ -fashion to the Ca–Cb bond of  $\text{C}_{70}$  (C(1)–C(2)) and the distances of Mo–C(1) and the Mo–C(2) bonds are very close (2.294 Å and 2.281 Å). These distances are in the typical range found in other molybdenum complexes of fullerenes. For example, the distances of Mo–C(1) and Mo–C(2) are 2.312 Å and 2.323 Å in the complex  $[\text{Mo}(\eta^2\text{-C}_{60})(\text{CO})_2(\text{phen})(\text{dbm})]$  (**2**),<sup>13</sup> 2.32 and 2.313 Å in  $[\text{Mo}(\eta^2\text{-C}_{60})(\text{CO})_3(\text{dppb})]$ ,<sup>14</sup> 2.309 Å and 2.306 Å in  $[\text{Mo}(\eta^2\text{-C}_{60})(\text{CO})_3(\text{dippe})]$ ,<sup>7</sup> 2.290 Å and 2.278 Å in  $[\text{Mo}(\eta^2\text{-C}_{70})(\text{CO})_3(\text{dippe})]$ .<sup>7</sup> The crystal structure analysis indicates that the molecular configuration of complex (**1**) is similar to that of the Mo– $\text{C}_{60}$  complex (**2**). In the molecule of (**1**), the Mo atom co-ordination is distorted octahedral with the two CO groups *cis* to each other, but each is *trans* to a nitrogen atom of phen. The Mo atom, two CO groups and phen are in the equatorial plane, coplanar to within 0.04 Å, and in complex (**2**), it is also within 0.04 Å. The Mo atom also binds in an  $\eta^2$ -fashion to the C(85)–C(91) bond of dbm. The two C–C bonds [C(1)–C(2) and C(85)–C(91)] are almost mutually orthogonal and each alkene ligands eclipses a N–Mo–CO vector. It has been reported that in octahedral olefin com-

plexes, such an eclipsed orientation is more stable than the staggered one and the energy barrier between the two configurations is ca 7–10 kcal/mol.<sup>15</sup> The N–Mo–CO units are almost linear and the average angle is 171.9°, which is very close to that of complex (**2**), 170.3°. The bite angles of the phen ligand, N(1)–Mo–N(2), are almost identical in the two complexes, for (**1**) 74.4° and for (**2**) 74.7°.

**Table 2.** Crystal data and details of refinement of complex (**1**)

Empirical formula	$\text{C}_{102}\text{H}_{48}\text{MoN}_2\text{O}_{10.5}$
Formula weight	1566.47
Colour	Red Brown
Crystal description	Block
Crystal size/mm	$0.65 \times 0.18 \times 0.10$
Crystal system	Monoclinic
Space group	C2/c
$a/\text{Å}$	27.5026(12)
$b/\text{Å}$	28.1043(11)
$c/\text{Å}$	19.9666(8)
$\alpha/^\circ$	90
$\beta/^\circ$	122.195(1)
$\gamma/^\circ$	90
$V/\text{Å}^3$	13060.0(9)
Z	8
$D_c/\text{g cm}^{-3}$	1.592
$F(000)$	6408
$\mu/\text{mm}^{-1}$	0.282
$2\theta$ range/ $^\circ$	5.50–50.00
Index ranges	$0 \leq h \leq 32, 0 \leq k \leq 33, -23 \leq l \leq 20$
Max. and min transmission	1.2570 and 0.8232
Reflections collected / unique	84433/11459
Weighting scheme parameter	0.1791
$g$ in $w = 1/[\sigma^2(F_o^2) + (g \times P)^2]$	
$P = (F_o^2 + 2F_c^2) / 3$	
$R1 = \sum( F_o  -  F_c ) / \sum  F_o $	0.0953
$wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)]\}^{1/2}$	0.2543
Goodness of fit on $F^2$	0.912

The other important feature of the complexes (**1**) and (**2**) is that the ligand dbm, which has long alkyl groups, has increased the solubility of the complexes greatly. It has provided us with a good way to synthesise a series of new transition metal–fullerene complexes because the complexes could be the precursors for the further reactions. For example, if the dbm were replaced by another fullerene molecule, we could obtain the dumb-bell complexes with novel structures and properties. The work is in process.

## Experimental

*Preparation of [Mo( $\eta^2$ -C<sub>70</sub>)(CO)<sub>2</sub>(phen)(dbm)]:* [Mo(CO)<sub>2</sub>(phen)(dbm)<sub>2</sub>] (39mg, 0.05mmol) was added to a solution of C<sub>70</sub> (42mg, 0.05mmol) in benzene (25cm<sup>3</sup>). The mixture was heated under reflux for 1h, and then concentrated to 5cm<sup>3</sup>. The resulting red-brown solution was separated by column chromatography (silica gel) using toluene–acetone (12:1) as eluent. The main chromatographic band was collected. The solvents were removed and the residue dried to give a red brown powder (23mg, 32%). The crystals were obtained by slow diffusion of pentane and isopropyl alcohol into a dichloromethane solution.

Found: C 81.90, H 2.55, N 1.85; calcd. for complex (**1**) C<sub>96</sub>H<sub>28</sub>MoN<sub>2</sub>O<sub>6</sub>: C 82.29, H 2.01, N 2.00. IR:  $\nu_{\max}$  [cm<sup>-1</sup>] = 1957 (s), 1890 (s) [ $\nu$ C≡O]; 1684 (s) [ $\nu$ C=O]; 1427 (s), 1410 (s), 1159 (s), 1131 (m), 797 (w), 674 (w), 640 (w), 573 (w), 535 (w), 456 (w) [ $\nu$ C<sub>70</sub>]; 434 (w) [ $\nu$ (Mo- $\eta^2$ -C=C)]; 367 (w) [ $\nu$ Mo-N]. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  [nm]: 238. <sup>1</sup>H NMR:  $\delta_{\text{H}}$  (Solvent CDCl<sub>3</sub> + CS<sub>2</sub>, standard SiMe<sub>4</sub>): 0.9 (t, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.3 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.5 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.1 (t, 4H, O = C- $\overset{\text{H}}$ CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, s, 2H, = $\overset{\text{H}}$ CH), 7.8 (m, 2H, H<sup>3,8</sup> of phen), 7.9 (d, 2H, H<sup>5,6</sup> of phen), 8.4 (m, 2H, H<sup>4,7</sup> of phen), 9.0 (d, 2H, H<sup>2,9</sup> of phen). <sup>13</sup>C NMR:  $\delta_{\text{C}}$  (Solvent CDCl<sub>3</sub> + CS<sub>2</sub>): 14 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 20 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 64 (s, O = C- $\overset{\text{O}}$ CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 77 (dd, C=C of C<sub>70</sub> and dbm), 124–163 (s, 41 signals comprising 6 phen and 35 C<sub>70</sub> signals, 1 signal omitted), 172 (s, C = O).

*Crystal structure determination:* Single crystal X-ray diffraction data for complex [Mo( $\eta^2$ -C<sub>70</sub>)(CO)<sub>2</sub>(phen)(dbm)] • 2C<sub>3</sub>H<sub>8</sub>O • 2.5H<sub>2</sub>O was collected at 173K on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) operating at 50kV and 40mA. Indexing was performed from two oscillation images that were exposed for 5 min. The detector swing angle was 5.00° and the crystal-to-detector distance was 127.4 mm. Readout was performed in the 0.100 mm pixel mode. Absorption corrections were applied by correlation of symmetry-equivalent reflections using the ABSCOR program. The crystal data and details of the parameters associated with data collection are given in Table 2. All calculations were carried out on a PC Founder FP+5166 using the SHELX97 program. All structures were solved by direct methods and subsequent Fourier difference techniques and

refined anisotropically for all non-hydrogen atoms (except some atoms in the solvent molecules) by full-matrix least-squares calculations on F<sup>2</sup>. The hydrogen atoms were included in their calculated positions with geometrical constraint and refined in the riding model. The thermal vibration of the atoms in the crystal is large and it was found that in the refinement the bond lengths and angles of two CO groups and phen were reasonable and the bond distances of C<sub>70</sub>-dbm and (CH<sub>3</sub>)<sub>2</sub>CHOH covered a wide range. So 58 bond distances in C<sub>70</sub>, six in dbm and eight in (CH<sub>3</sub>)<sub>2</sub>CHOH were restrained to a reasonable range.

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