DALTON

Syntheses and structural characterizations of novel tungsten and molybdenum complexes of fullerene $[M(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)]\cdot 2C_6H_6\cdot C_5H_{12}$ (M = W or Mo, phen = 1,10-phenanthroline, dbm = dibutyl maleate)

Kaluo Tang, Shijun Zheng, Xianglin Jin,* Hui Zeng, Zhennan Gu, Xihuang Zhou and Youqi Tang

Institute of Physical Chemistry, Peking University, Beijing 100871, P.R. China

Novel tungsten and molybdenum complexes of fullerene $[M(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)]\cdot C_6H_6\cdot C_5H_{12}$ (M = W **1** or Mo **2**; dbm = dibutyl maleate; phen = 1,10-phenanthroline) have been synthesized by heating a solution of C_{60} with $[M(CO)_4(phen)]$ and dbm in toluene followed by chromatography over silica gel. They have been characterized by chemical analysis, IR, UV/VIS, ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction analysis. The complexes are isomorphous. The metal atom co-ordination is distorted octahedral with the two CO groups and phen in the equatorial plane and the metal binds in an η^2 fashion to C–C bonds of C_{60} and dbm. Both complexes are remarkably stable in air and have unusually good solubility.

Since the report on the crystal structure of the first organometallic complex of fullerene $[Pt(\eta^2\text{-}C_{60})(PPh_3)_2]\cdot C_4H_8O$[1] several other fullerene complexes have been synthesized and characterized by X-ray diffraction. However, among them most of the metals were in Group VIII, such as Pt,[2] Ir,[3] Pd[4] and Rh.[5] Only a few molybdenum or tungsten complexes of C_{60} have been reported, such as $[Mo(\eta^2\text{-}C_{60})(\eta\text{-}C_5H_4R)_2]$ (R = H or Bu^n),[6] $[\{M(CO)_3(dppe)_2\}_x(\eta^2\text{-}C_{60})]$ [M = Mo or W, x = 1–3, dppe = 1,2-bis(diphenylphosphino)ethane],[7] $[\{Mo(CO)_3(ddh)\}_2C_{60}]\cdot 2.5C_6H_6$ and $[\{Mo(CO)_2(PPh_3)_2(ddh)\}_2C_{60}]$ (ddh = biacetyl dihydrazone).[8] However, there is no report on the crystal structure of a molybdenum complex of fullerene.

The key problems to the growth of single crystals of complexes of fullerenes are the instability of their solutions and low solubility. We have synthesized four air-stable organometallic C_{60} derivatives of molybdenum(0) and tungsten(0) with nitrogen-containing ligands $[M(\eta^2\text{-}C_{60})(CO)_3(L\text{–}L)]$ [M = Mo or W, L–L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)].[9] They are only sparingly soluble in chlorobenzene and *o*-dichlorobenzene. Crystals suitable for X-ray diffraction have not been obtained. However, when one carbonyl group of $[M(\eta^2\text{-}C_{60})(CO)_3(phen)]$ was displaced by dibutyl maleate (dbm), as was expected, the resulting complexes have good solubilities in a number of organic solvents, even much better than C_{60} itself. Here we report the syntheses and structural characterizations of these novel tungsten and molybdenum complexes **1** and **2**. Since the two compounds are isostructural, only the crystal structure of the tungsten complex is discussed in this paper.

Experimental

Fullerene C_{60} (99.9%) was prepared by the arc-heating graphite technique,[10] recrystallization and column chromatography. Its purity was determined by field desorption mass spectrometry and HPLC. All reactions of the complexes were carried out under a nitrogen atmosphere. The complexes $[M(CO)_4(phen)]$ (M = Mo or W) were prepared according to the literature.[11]

Infrared spectra were recorded from KBr pellets with a Perkin-Elmer 983G spectrometer. Only the most significant frequencies are given. The UV/VIS electronic spectra were recorded on a PU 1221 spectrophotometer, ^{1}H and ^{13}C NMR spectra in solution on a Bruker ARX-400 spectrometer.

Preparations

Complex 1. Dibutyl maleate (0.34 cm^3, 1.5 mmol) was added to a solution of $[W(CO)_4(phen)]$ (238 mg, 0.5 mmol) in toluene (10 cm^3) and refluxed for 19 h. This solution (1.5 cm^3, 0.076 mmol) was added to a solution of C_{60} (55 mg, 0.076 mmol) in toluene (22 cm^3). The mixture was refluxed for 36 h, then concentrated. The resulting dark green solution was separated by column chromatography (silica gel) using benzene–acetone (12 : 1) as eluent. The main chromatographic band was collected, the solvents were removed and the residue dried *in vacuo* to give a dark green powder (34 mg, 33%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a benzene solution {Found: C, 75.30; H, 3.36; N, 1.60. Calc. for $[W(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)\cdot 2C_6H_6\cdot C_5H_{12}$: C, 76.98; H, 3.67; N, 1.76%}. IR: $\tilde{\nu}_{max}$/cm^{-1} 1963s, 1895s [ν(C≡O)]; 1684s [ν(C=O)]; 1422m, 1162s, 575w, 525s [$\nu(C_{60})$]; 471w {ν[W–(η^2-C=C)]}; 366w [ν(W–N)]. UV (C_6H_6): λ_{max}/nm 433. ^{1}H NMR (solvent $CDCl_3$, standard $SiMe_4$): δ 0.9 (t, 6 H, $CH_2CH_2CH_2CH_3$, 1.3 (m, 4 H, $CH_2CH_2CH_2CH_3$), 1.6 (m, 4 H, $CH_2CH_2CH_2CH_3$), 3.9 (br, 2 H, =CH), 4.1 (t, 4 H, $OCOCH_2$-$CH_2CH_2CH_3$), 7.5 (m, m, 2 H, H^{3,8} of phen), 8.0 (d, 2 H, H^{5,6} of phen), 8.2 (m, 2 H, H^{4,7} of phen) and 8.9 (dd, 2 H, H^{2,9} of phen). ^{13}C NMR (solvent $CDCl_3$ + CS_3): δ 14 (s, CH_2CH_2-CH_2CH_3), 19 (s, $CH_2CH_2CH_2CH_3$), 30 ($CH_2CH_2CH_2CH_3$), 64 (s, $OCOCH_2CH_2CH_2CH_3$), 77 (dd, C=C of C_{60} and dbm), 122–154 (s, 22 signals in which 6 phen, 16 C_{60} signals) and 173 (s, C=O).

Complex 2. Dibutyl maleate (0.5 cm^3, 2.2 mmol) was added to a solution of $[Mo(CO)_4(phen)]$ (260 mg, 0.67 mmol) in toluene (12 cm^3) and refluxed for 17 h. This solution (1.3 cm^3, 0.07 mmol) was added to a solution of C_{60} (36 mg, 0.05 mmol) in toluene (15 cm^3). The mixture was heated with stirring for 1.5 h, then concentrated to 5 cm^3. The resulting dark green solution was separated by column chromatography (silica gel) using benzene–acetone (10 : 1) as eluent. The main chromatographic band was collected, the solvents were removed and the residue dried *in vacuo* to give a dark green powder (20 mg, 31%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a benzene solution {Found: C, 80.58; H, 2.16; N, 2.06. Calc. for $[Mo(\eta^2\text{-}C_{60})(CO)_2(phen)$-$(dbm)]$: C, 80.49; H, 2.20; N, 2.18%}. IR: ν_{max}/cm^{-1} 1964s, 1901s [ν(C≡O)]; 1690s [ν(C=O)]; 1421m, 1164s, 573w, 525s [$\nu(C_{60})$]; 425w {ν[Mo–(η^2-C=C)]}, 360w [ν(Mo–N)]. UV (C_6H_6): λ_{max}/nm 440. ^{1}H NMR: (solvent $CDCl_3$, standard $SiMe_4$): δ 0.9 (t, 6 H, $CH_2CH_2CH_2CH_3$), 1.3 (m, 4 H, $CH_2CH_2CH_2CH_3$), 1.5 (m, 4 H, $CH_2CH_2CH_2CH_3$), 3.8 (br, 2 H, =CH), 4.1 (t, 4 H, $OCOCH_2CH_2CH_2CH_3$), 7.8 (m, m, 2 H, H^{3,8} of phen), 7.9

Table 1 Crystal data and details of refinement of complex **1**

Empirical formula	$C_{103}H_{52}N_2O_6W$
M	1597.3
Colour	Dark green
Crystal size/mm	0.80 × 0.50 × 0.15
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	14.860(7)
b/Å	19.083(12)
c/Å	13.826(8)
α/°	110.74(5)
β/°	92.29(5)
γ/°	110.22(4)
U/Å^3	3381(4)
Z	2
D_c/g cm^{-3}	1.691
F(000)	1612
μ/mm^{-1}	1.950
2θ range/°	4.0–50.0
Index ranges	$0 < h < 17$, $-22 < k < 21$, $-16 < l < 16$
Minimum, maximum transmission *	0.6236, 1.000
No. unique reflections	11 911
R_{int}	0.0357
No. observed reflections, $F > 6\sigma(F)$	8226
Data-to-parameters ratio	15.1 : 1
ρ_{min}, ρ_{max}/e Å^{-3}	−2.64, 2.21
Maximum and mean shift to error ratio	0.738, 0.019
Weighting scheme parameter *g* in $w = 1/[\sigma^2(F) + gF^2]$	0.0047
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.087
$R' = [\Sigma w(\|F_o\| - F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.091
Goodness of fit	1.39

* Semiempirical absorption correction.

(d, 2 H, H^{5,6} of phen), 8.4 (m, 2 H, H^{4,7} of phen) and 9.0 (dd, 2 H, H^{2,9} of phen). ^{13}C NMR (solvent $CDCl_3 + CS_2$): δ 13 (s, $CH_2CH_2CH_2CH_3$), 19 (s, $CH_2CH_2CH_2CH_3$), 30 (s, $CH_2CH_2CH_2CH_3$), 63 (s, $OCOCH_2CH_2CH_2CH_3$), 77 (dd, C=C of C_{60} and dbm), 124–157 (s, 22 signals in which 6 phen, 16 C_{60} signals) and 171 (s, C=O).

Crystallography

Single crystals of complex **1** were mounted inside a glass capillary and sealed with solvent. Data were recorded at ambient temperature (296 K) on a Rigaku AFC6S automated four-circle diffractometer using Mo-Kα radiation (λ = 0.71073 Å) and 2θ–ω scans. During data collection three standard reflections were remeasured every 150 and no significant fluctuations in their intensities were observed. All calculations were carried out on a MicroVax II computer using the SHELXTL PLUS[12] system of programs. Crystal data and details of the structure solution and refinement are presented in Table 1. After the initial atomic coordinates of the heavy atom (W) had been derived by direct methods, the remaining non-hydrogen atoms were located from a series of least-squares refinement cycles followed by Fourier-difference maps. The structure was solved in the centrosymmetric space group $P\bar{1}$, but the mean $|E^2 - 1| = 0.661$ (expected 0.968 for centrosymmetric and 0.736 for non-centrosymmetric) indicated that thermal vibration of the atoms in the crystal is large at ambient temperature. It was found in the refinement that the bond lengths and angles of two CO groups and phen were reasonable and the bond distances of C_{60}, dbm and C_5H_{12} covered a wide range. Thirty bond distances in C_{60}, five in dbm and five in C_5H_{12} were restrained to a reasonable range. An attempt to refine in a non-centrosymmetric space group *P*1 and to constrain centrosymmetric atomic coordinates of the heavy atom, CO and phen with free variables was unsuccessful. The atoms of the heavy atom, CO groups and phen were refined with anisotropic thermal parameters and the atoms of C_{60}, dbm and C_5H_{12} with isotropic thermal parameters. No hydrogen atoms were included in the refinement.

CCDC reference number 186/638.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

W–N(1)	2.246(12)	W–N(2)	2.184(11)
W–C(71)	2.010(16)	W–C(72)	1.974(15)
W–C(1)	2.304(26)	W–C(2)	2.300(19)
W–C(85)	2.279(26)	W–C(91)	2.285(26)
O(1)–C(71)	1.111(21)	O(2)–C(72)	1.166(19)
C(1)–C(2)	1.429(30)	C(85)–C(91)	1.368(28)
N(1)–W–N(2)	73.7(5)	N(1)–W–C(71)	171.4(5)
N(2)–W–C(71)	97.8(5)	N(1)–W–C(72)	97.7(6)
N(2)–W–C(72)	171.4(6)	C(71)–W–C(72)	90.8(6)
N(1)–W–C(1)	111.7(6)	N(2)–W–C(1)	90.9(6)
C(71)–W–C(1)	68.8(7)	C(72)–W–C(1)	92.0(7)
N(1)–W–C(2)	76.2(6)	N(2)–W–C(2)	87.5(5)
C(71)–W–C(2)	105.0(7)	C(72)–W–C(2)	90.1(6)
C(1)–W–C(2)	36.2(8)	N(1)–W–C(85)	95.4(7)
N(2)–W–C(85)	108.3(6)	C(71)–W–C(85)	86.2(8)
C(72)–W–C(85)	72.4(7)	C(1)–W–C(85)	150.6(7)
C(2)–W–C(85)	159.6(8)	N(1)–W–C(91)	84.7(7)
N(2)–W–C(91)	73.4(6)	C(71)–W–C(91)	91.9(7)
C(72)–W–C(91)	106.7(7)	C(1)–W–C(91)	153.6(9)
C(2)–W–C(91)	156.2(6)	C(85)–W–C(91)	34.9(7)
W–C(71)–O(1)	177.5(14)	W–C(72)–O(2)	178.1(13)

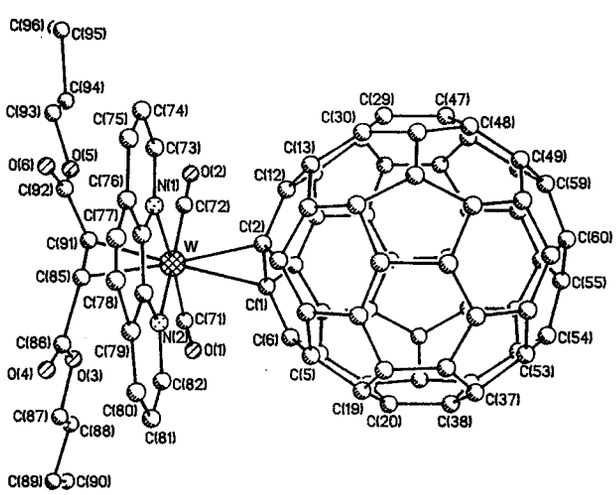

Fig. 1 Perspective view of the structure of $[W(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)]$ **1**

Results and Discussion

The crystal structure analysis indicates that complexes **1** and **2** are isomorphous, $[M(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)]\cdot 2C_6H_6\cdot C_5H_{12}$ [M = W **1** or Mo **2**]. The molecular structure of unsolvated **1** is shown in Fig. 1; selected bond lengths and angles are reported in Table 2.

Although the quality of the X-ray data is not very good, the main structural features obtained from the crystal structure determination are consistent with the other results such as chemical analysis, IR, UV/VIS, ^{1}H and ^{13}C NMR spectra. In the molecules of complex **1** the W atom co-ordination is distorted octahedral with the two CO groups *cis* to each other, but each *trans* to a nitrogen atom of phenanthroline. The metal atom, two CO groups and phen are in the equatorial plane, coplanar to within 0.050 Å. The W atom binds in an η^2 fashion to the [C(1)–C(2) bond between two six-membered rings of C_{60}. The distances W–C(1) and W–C(2) are almost equal [2.30(2), 2.30(3) Å]. The W atom binds also in an η^2 fashion to the C(85)–C(91) bond of dibutyl maleate [W–C(85) 2.28(3) and W–C(91) 2.29(3) Å]. The two C–C bonds [C(1)–C(2) and

C(85)–C(91)] are almost mutually orthogonal and each alkene ligand eclipses a N–W–CO vector (average 171.4°). The coordination about the metal atom closely resembles that observed in the molybdenum complex of methyl acrylate $[Mo(\eta^2\text{-}CH_2{=}CHCO_2Me)_2(CO)_2(bipy)]$ **3**, the structure of which has been determined by us. Actually, we prepared complex **3** as an electronic model for the corresponding C_{60} compound.[13]

In complexes **1**–**3**, the nitrogen-containing ligands, 1,10-phenanthroline or 2,2′-bipyridine, enable the strong interaction between the metal atom and C_{60} or electron-deficient alkenes, and the resulting complexes are remarkably stable in air. The low steric demands of these ligands enables the displacement from the axial orientation. We have observed that the complex $[Mo(CO)_4(PPh_3)_2]$ with the bulky hindered phosphine ligand reacts neither with C_{60} nor with methyl acrylate. The displacement of dibutyl maleate which has long alkyl groups increases the solubility of the fullerene complexes greatly. Both complexes **1** and **2** have unusually good solubility and stability in solution. They could be the precursors for further reactions. This suggests a new way to synthesize a series of new complexes of W or Mo with fullerenes.

Acknowledgements

We wish to express our gratitude for the financial support of this work by China's National Natural Science Foundation (Project No. 29393090).

References

1 P. J. Fagan, J. C. Calabrese and B. Malone, *Science*, 1991, **252**, 1160.
2 P. J. Fagan, J. C. Calabrese and B. Malone, *J. Am. Chem. Soc.*, 1991, **113**, 9408; *Acc. Chem. Res.*, 1992, **25**, 134.
3 A. L. Balch, V. J. Catalano and J. W. Lee, *Inorg. Chem.*, 1991, **30**, 3980; A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead and S. R. Parkin, *J. Am. Chem. Soc.*, 1991, **113**, 8953; A. L. Balch, J. W. Lee, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1992, **114**, 10984; A. L. Balch, J. W. Lee and M. M. Olmstead, *Angew. Chem.*, 1992, **31**, 1356; M. Rasinkangas, T. T. Pakkanen, T. A. Pakkanen, M. Ahlgren and J. Rouvinen, *J. Am. Chem. Soc.*, 1993, **115**, 4901; A. L. Balch, J. M. Lee, B. C. Noll and M. M. Olmstead, *Inorg. Chem.*, 1994, **33**, 5328; A. L. Balch, A. S. Ginwalla, J. W. Lee, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1994, **116**, 2227.
4 V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, S. V. Lindeman, I. A. Guzey and Y. T. Struchkov, *Organometallics*, 1993, **12**, 991.
5 A. L. Balch, J. W. Lee, B. C. Noll and M. M. Olmstead, *Inorg. Chem.*, 1993, **32**, 3577; Y. Ishii, H. Hoshi, Y. Hamada and M. Hidai, *Chem. Lett. Jpn.*, 1994, 801.
6 R. E. Douthwaite, M. L. H. Green, A. H. H. Stephens and J. F. C. Turner, *J. Chem. Soc., Chem. Commun.*, 1993, 1522.
7 J. R. Shapley, Y. Du, H.-F. Hsu and J. J. Way, *Proc. Electrochem. Soc.*, 1994, **24**, 1255; H.-F. Hsu and J. R. Shapley, *Proc. Electrochem. Soc.*, 1995, **10**, 1087.
8 M. Iglesias and A. Santos, *Inorg. Chim. Acta*, 1996, **248**, 67.
9 K. Tang, X. Jin, H. Zeng, H. Zhou, S. Zheng and Y. Tang, *The Abstracts of the 17th International Conference Organometallic Chemistry, Brisbane, 7–12 July*, 1996, p. 194.
10 W. Kratschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature* (*London*), 1990, **347**, 354.
11 M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.
12 G. M. Sheldrick, SHELXTL PLUS, Version 4.0, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.
13 X. Jin, K. Tang, H. Zeng, S. Zheng and Y. Tang, *Chemical Research in Chinese Universities*, in the press.

Received 13*th June* 1997; *Paper* 7/04145D