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Syntheses and X-ray crystal structures of dumbbell-shaped bis-fullerene tungsten and molybdenum complexes

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Received (in Cambridge, UK) 22nd January 2002, Accepted 21st February 2002
First published as an Advance Article on the web 12th March 2002

In the first neutral bis-fullerene complexes with tungsten(0) and molybdenum(0) $[M(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]$ [M = W and Mo, dbcbipy = 4,4′-di(butyl carboxyl)-2,2′-bipyridine] synthesized in solution, the metal atom coordination is distorted octahedral with two CO groups and the bipy group of dbcbipy in the equatorial plane and the metal atom binding in an η^2-fashion to C–C bonds of two C_{60} at axial orientation to give a dumbbell shaped molecule.

The study on transition metal complexes of fullerenes attracts wide interest not only for their interesting structures but also for their potential use as new materials with unique properties. A considerable number of transition metal complexes of fullerenes have been reported.[1] However, among them, most of the metal atoms directly coordinate to a single fullerene in an η^2-manner. The interest in fullerene polymers and complexes composed of a metal and a few fullerenes has been increasing. A dumbbell shaped C_{60} dimer C_{120} has been synthesized by a solid-state mechanochemical reaction and structurally characterized by X-ray diffraction.[2] Huang and Freiser synthesized a bis-C_{60} metal adduct ion $Ni(C_{60})_2^+$ in the gas phase and observed it in a Fourier transform mass spectrometer.[3] Zimmerman and Hercules found that bis- and tris-fullerene/metal adduct ions can be formed with silver, gold, rhodium and palladium by argon-ion bombardment of the fullerenes deposited on a metal substrate, with the use of a TOF-SIM spectrometer.[4] Nakajima's group reported the multiple dumbbell structures of vanadium–C_{60} clusters $V_n(C_{60})_m^+$ [(n,m) = (1,1), (1,2), (2,3), (3,4), (4,4) and (5,5)] by the use of laser vaporization and time-of flight mass spectrometry.[5] All these results, in which the metal ions are naked and metal/fullerene adducts were detected in gas phase by mass spectrometry, led to the suggestion that the bis-fullerene metal ″dumbbell″ complexes are analogous to the metallocenes or bis-benzene complexes, and that C_{60} acts as an η^6-ligand.[5] However, to date, there is no report on discrete bis-fullerene/metal complexes isolated by solution chemical techniques and structurally characterized by X-ray structural analysis. Here we describe the synthesis of the first neutral bis-fullerene complexes with tungsten(0) and molybdenum(0) in solution and determined their single crystal structures by X-ray diffraction. This shows that the metal atom directly coordinates to both fullerenes in an η^2-fashion and the two C_{60} are in axial orientation which leads to the molecule adopting a dumbbell shape.

We have previously reported the syntheses and X-ray structures of molybdenum(0) and tungsten(0) complexes of fullerenes $[M(\eta^2\text{-}C_n)(CO)_2(phen)(dbm)]$ (M = Mo or W, n = 60 or 70, phen = 1,10-phenanthroline, dbm = dibutyl maleate).[6–8] These complexes are stable in air and have unusually good solubility. The ligand dibutyl maleate, which has long alkyl groups, increases the solubility of the complexes greatly. We also found that the ligand dbm can be replaced by another C_{60} to form bis-C_{60} complexes $[M(\eta^2\text{-}C_{60})_2(CO)_2(phen)]$. However, the key problem of the latter complexes was their poor solubility, making it difficult to grow single crystals. We modified the ligands by adding substituents, such as 4,7-diphenyl-1,10-phenanthroline (dpphen) and 4,4′-di(butyl carboxyl)-2,2′-bipyridine (dbcbipy) to increase the solubility. When the ligand phen is replaced by dbcbipy, which has long alkyl groups, the resulting complexes $[M(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]$ had good solubility in a number of organic solvents. Here we report the syntheses and structural characterizations of these novel tungsten and molybdenum complexes. Since the two compounds are isostructural, only the crystal structure of the tungsten complex is discussed here.

The reactions of $M(CO)_4(dbcbipy)$ (M = W or Mo) [prepared by the reaction of $M(CO)_6$ and 4,4′-dibutyl carboxyl-2,2′-bipyridine (dbcbipy)[9] (in 1 : 1 molar ratio) in toluene], with two equivalents of C_{60} in boiling xylene (for W) or toluene (for Mo) under a nitrogen atmosphere for 3 h gave the dark green neutral complexes $[W(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]$ **1** or $[Mo(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]$ **2** after chromatographic work-up on silica gel (toluene as eluent): yield 24% for **1** and 26% for **2**. Crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a carbon disulfide solution. Complex **1** [Found: C, 83.50; H, 1.23; N, 1.40. Calc. for $C_{142}H_{24}N_2O_6W$ (unsolvated): C, 83.70; H, 1.19; N, 1.37%]. UV-vis (C_6H_6): λ_{max}/nm 435. IR (KBr): 1962s, 1898vs [$\nu(C\equiv O)$]; 1730s [$\nu(C=O)$]; 1424m, 1184m, 578w, 526s [$\nu(C_{60})$]; 1621w [ν(bipy)]; 491vw {$\nu[W\text{–}(\eta^2\text{-}C=C)]$} cm^{-1}.

Complex **2** [Found: C, 87.39; H, 1.27; N, 1.49. Calc. for $C_{142}H_{24}N_2O_6Mo$ (unsolvated): C, 87.48; H, 1.24; N, 1.44%]. UV-vis (C_6H_6): λ_{max}/nm 440. IR (KBr): 1962vs, 1900vs [$\nu(C\equiv O)$]; 1730s [$\nu(C=O)$]; 1422m, 1184m, 577w, 525s [$\nu(C_{60})$]; 1619w [ν(bipy)]; 487w {$\nu[W\text{–}(\eta^2\text{-}C=C)]$} cm^{-1}.

The X-ray crystal structure analyses of complex **1** and **2** revealed their unique and aesthetically pleasing dumbbell-shaped molecular structures.† The components of complexes **1** and **2** in the crystals are $[W(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]\cdot C_5H_{12}\cdot 3CS_2$ and $[Mo(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]\cdot C_5H_{12}\cdot 4CS_2\cdot H_2O$, respectively. The molecular structure of unsolvated **1** is shown in Fig. 1; selected bond lengths and angles are reported in Fig. 1; the perspective view of the packing in **1** is shown in Fig. 2.

The crystals of **1** and **2** are apt to lose the solvent molecules CS_2 and C_5H_{12} because of their low boiling point. In the molecule of complex **1**, the metal atom, two CO groups and the bipy group of the ligand dbcbipy are in the equatorial plane and are coplanar to within 0.099 Å. The W atom binds in an η^2 fashion to the C105–C106 and C201–C202 bonds between two six-membered rings of both C_{60}. The W–C105, W–C106, W–C201 and W–C202 distances are 2.31(2), 2.26(2), 2.23(1) and 2.33(2) Å, respectively. The mean W–C distance is 2.28 Å, which is close to those in $[W(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)]$ [2.30(2) and 2.30(3) Å][6] and in $[Mo(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)]$ [2.31(2) and 2.32(3) Å].[7] The two M–C distances of one C–C bond to the metal are almost equal in these single-C_{60} complexes; while one is shorter than the other M–C distance in the bis-C_{60} complex. The two C_{60} ligands in **1** are *trans* to each other with axial orientation and *cis* to CO groups. The two C–C bonds [C105–C106 and C201–C202] are almost mutually orthogonal (95.3°) and each eclipses an N–W–CO vector (average 171.4°). In the two C_{60} ligands of **1**, the average C–C bond length at 6 : 6 ring junctions (1.387 Å) is shorter than the average C–C bond length at 6 : 5 ring junctions (1.431 Å). However, the average bond length of C105–C106 and C201–

DOI: 10.1039/b200793b

C202 (1.483 Å), which are coordinated to the metal, is longer than the other bond lengths at 6:6 ring junctions and even longer than the bond lengths at 6:5 ring junctions. A similar situation also occurred in the dumbbell-shaped dimer C_{120}, which is composed of two C_{60} cages sharing a cyclobutane ring at 6:6 ring junctions, and the intra-cage C–C bond lengths [1.581(7) Å] are elongated.[2] In forming complexes **1** and **2**, the nitrogen-containing ligand 4,4′-di(butyl carboxyl)-2,2′-bipyridine (dbcbipy) plays an important role in leading to a strong electronic interaction between the metal atom and C_{60}, and the resulting complexes are remarkably stable in air. The bipy group of the dbcbipy ligand and two CO groups are in the equatorial plane and the low steric demands of these ligands enable the displacement of C_{60} from axial orientation. We have observed that the complex $[Mo(CO)_4(PPh_3)_2]$ with bulky hindered phosphine ligand does not react with C_{60}. The ligand dbcbipy has long alkyl groups, which increase the solubility of the fullerene complexes greatly, making them easy to characterise and use in applications. We expect that these new complexes **1** and **2** have special properties, the investigation of which is in process and efforts will be continued to explore their application.

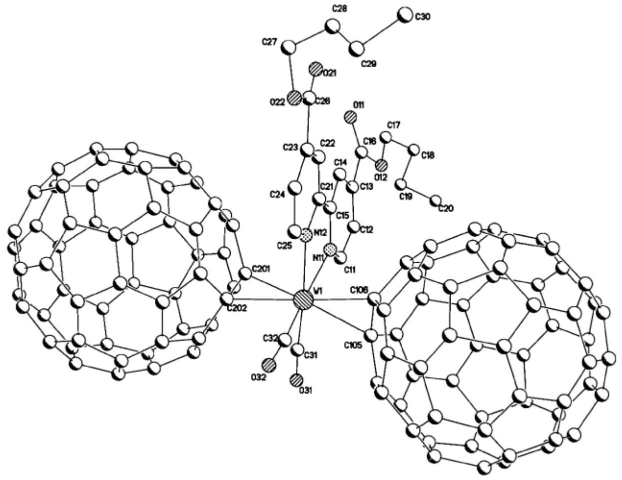

Fig. 1 Perspective view of the structure of $[W(\eta^2\text{-}C_{60})_2(CO)_2(dbcbipy)]$ **1**. Important distances and angles: W1–C31 1.916(15), W1–C32 1.934(17), W1–N12 2.215(12), W1–N11 2.247(12), W1–C106 2.257(15), W1–C105 2.311(15), W1–C201 2.234(13), W1–C202 2.326(15); C31–W1–C32 85.0(6), C31–W1–N12 173.2(5), C32–W1–N12 99.2(6), C31–W1–C201 86.8(5), C32–W1–C201 109.5(6), N12–W1–C201 86.8(5), C31–W1–N11 103.4(5), C32–W1–N11 170.2(6), N12–W1–N11 72.8(4), C201–W1–N11 76.3(5), C31–W1–C106 108.1(6), C32–W1–C106 90.6(6), N12–W1–C106 77.3(5), C201–W1–C106 156.3(6), N11–W1–C106 82.2(5), C31–W1–C202 87.3(5), C32–W1–C202 70.9(5), N12–W1–C202 89.1(5), C201–W1–C202 38.8(5), N11–W1–C202 113.9(4), C106–W1–C202 155.1(5), C31–W1–C105 71.3(6), C32–W1–C105 90.3(6), N12–W1–C105 113.7(5), C201–W1–C105 149.3(5), N11–W1–C105 87.9(5), C106–W1–C105 36.9(5), C202–W1–C105 152.9(5).

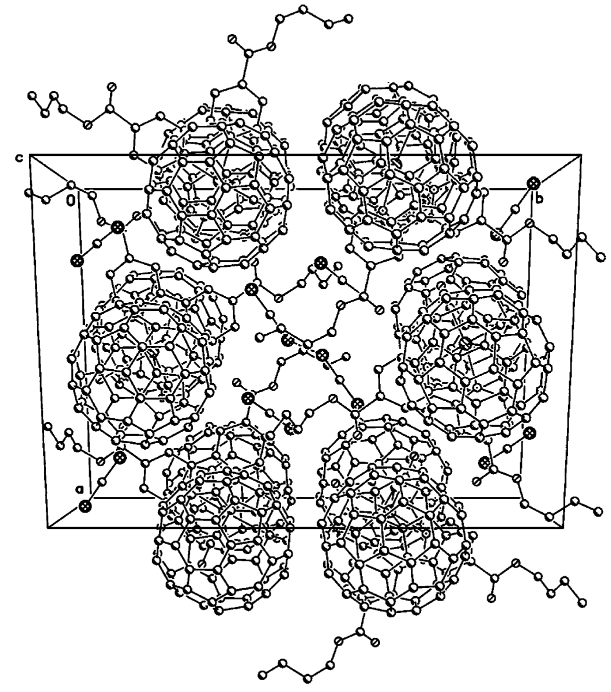

Fig. 2 Perspective view of the packing in complex **1**.

This work was supported by NNSF of China (Grant No. 29873001).

Notes and references

† Crystal data were collected on a Rigaku R-AXIS RAPID Image Plate diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 40 mA. Crystal size: 0.30 × 0.20 × 0.05 mm for **1**, 0.60 × 0.40 × 0.15 mm for **2**. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program. The structures were solved by direct method and successive difference map (SHELXS-97) and refined by full-matrix least-squares on F^2 using all unique data (SHELXL-97). *Crystal data* for **1**: $C_{142}H_{24}N_2O_6W{\cdot}C_5H_{12}{\cdot}3CS_2$, M_r = 2338.02, monoclinic, $P2_1/a$, a = 18.402(4), b = 24.291(5), c = 21.414(4) Å, β = 112.48(3)°, V = 8845(3) Å^3, D_c = 1.756 Mg m^{-3}, Z = 4, T = 123(2) K, μ(Mo-Kα) = 1.527 mm^{-1}, F(000) = 4672. 53881 reflections collected, θ range 2.12–25.00°, 15139 unique reflections (R_{int} = 0.1276), final R indices [$I > 2\sigma(I)$], R_1 = 0.0850, wR_2 = 0.1443; 731 parameters (W, S anisotropic, C isotropic); there are three large unknown difference Fourier peaks (1.76, 1.69 e Å^{-3} near the W atom and 1.55 e Å^{-3} near C_5H_{12} solvent molecules, respectively). CCDC reference number: 176773. *Crystal data* for 2: $C_{142}H_{24}N_2O_6Mo{\cdot}C_5H_{12}{\cdot}4CS_2{\cdot}H_2O$, M_r = 2344.25, monoclinic, $P2_1/a$, a = 18.598(4), b = 24.550(5), c = 21.429(4) Å, β = 112.36(3)°, V = 9048(3) Å^3, D_c = 1.721 Mg m^{-3}, Z = 4, T = 123(2) K, μ(Mo-Kα) = 0.410 mm^{-1}, F(000) = 4736. 56408 reflections collected, θ range 1.95–25.00°, 15526 unique reflections (R_{int} = 0.0623), final R indices [$I > 2\sigma(I)$], R_1 = 0.0983, wR_2 = 0.2705; 1448 parameters (Mo, S anisotropic, C anisotropic except the three C in one alkyl chain and the C in the solvent molecule C_5H_{12} and two of four CS_2); there are eight large unknown Fourier-difference peaks (3.16, 3.01, 2.78, 2.69, 2.03, 1.46, 1.39, 1.35 e Å^{-3}) near solvent molecules. The bond distances C18–C19 and C19–C20 were restrained to a reasonable range. CCDC reference number 176774. See http://www.rsc.org/suppdata/cc/b2/b200793b/ for crystallographic data in CIF or other electronic format.

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