X-ray Crystallographic Characterization of Potassium Pentaphenyl[60]fullerene

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(Received May 12, 2005; CL-050634)

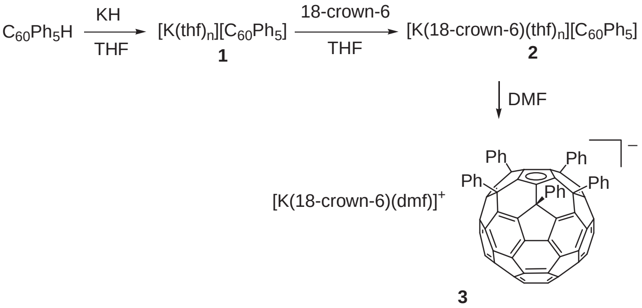
X-ray crystal structures of three differently solvated forms of potassium pentaphenyl[60]fullerene, $K(C_{60}Ph_5)(thf)_3$, $[K(thf)_6][C_{60}Ph_5]$, and $[K(18\text{-crown-}6)(dmf)][C_{60}Ph_5]$, indicate that the potassium cation and the fullerene cyclopentadienide become separated easily by cation solvation, and suggest that a solvent-separated ion pair is responsible for the formation of bilayer vesicles upon dissolution of $KC_{60}Ph_5$ in water.

Pentaphenyl[60]fullerene $C_{60}Ph_5H$[1] is an interesting hydrocarbon in that its anion ($KC_{60}Ph_5$) can be dissolved in water,[2] and forms bilayer vesicles.[3] Vesicles are fundamental structures in biology and are composed of lipid or related organic molecules that have a common structure feature—a hydrophilic polar head connected to long hydrophobic side chains. The side chains are generally composed of hydrocarbons, and the molecular shape of vesicle-forming molecules is rod-like so that the molecules self-assemble to form bilayer membrane. It is, therefore, surprising that $KC_{60}Ph_5$, lacking all structural features of conventional vesicle forming compounds, forms vesicles in water. No molecular level information has so far been available either for the mechanism of the vesicle formation or even for the vesicle structure that has so far been determined by an atomic force microscopic[2] and a laser light scattering studies.[3] To gain insight into the fullerene vesicles, we first need the information on the molecular structure of its component, $KC_{60}Ph_5$, especially, on the location of the potassium cation with respect to the cyclopentadienide of the $C_{60}Ph_5$ anion.[4] We report here three X-ray crystal structures of differently solvated $KC_{60}Ph_5$, which suggest that the complex exists in a solvent-separated, polar form in water.

Crystals of $KC_{60}Ph_5$ solvated by water molecules have so far been unobtainable, but those of the potassium complex solvated by THF and 18-crown-6 ether/DMF are now obtained and analyzed by X-ray crystallography, providing information on what we would expect to occur for $KC_{60}Ph_5$ in water. The THF-solvated crystals $[K(thf)_n][C_{60}Ph_5]$ (**1**) were obtained as dark-reddish brown powder in quantitative yield by deprotonating $C_{60}Ph_5H$ with potassium hydride (Scheme 1). The compound was spectroscopically identical with the sample previously prepared by using potassium *tert*-butoxide as a base.[1] The ^1H and ^{13}C NMR spectra show a C_{5v} symmetric signal pattern.

Slow diffusion of hexane to a THF solution of **1** afforded crystals suitable for X-ray crystallographic analysis,[5] and the ORTEP drawing is shown in Figure 1. A monoclinic unit cell was found to contain two $K(C_{60}Ph_5)(thf)_3$ (**1a**), two $[K(thf)_6][C_{60}Ph_5]$ (**1b**), and fourteen THF molecules, and thus to provide information on two different solvation states.

In **1a** (Figure 1a), the potassium cation K1 is located on the periphery of the cavity formed by the five phenyl groups, coordinated by three THF molecules on the upper side, and, on the bottom side, sandwiched by two of the five phenyl groups by cation–π interactions. K1 is bonded to each phenyl group with one very short K1–C bond (3.127(10) and 3.140(9) Å) and two longer ones (3.328(10)–3.419(10) Å). The values of the two short inter-atomic distances are much smaller than those in known potassium–arene complexes (3.230(8)[6a] and 3.29 Å[6b]). The distance between K1 and the centroid of the cyclopentadienide is 4.39 Å—too long to have direct interaction with each other (as opposed to typically a 2.5–3.0 Å distance in potassium cyclopentadienides).[4]



Scheme 1.

In the ion pair **1b** (Figure 1b), the potassium cation K2 is surrounded by six THF molecules, and is located far from the pentaphenyl cone. The distance between K2 and the centroid of the cyclopentadienyl anion is 8.87 Å. The potassium cation has therefore little interaction with $C_{60}Ph_5$ anion, leaving it "naked". Among potassium cyclopentadienides reported in the literature, the naked one has so far been known to form only in the presence of strongly solvating crown ether ($[K(15\text{-crown-}5)_2]^+[C_5Me_5]^-$).[7]

Potassium solvation with 18-crown-6 afforded a well defined, very polar structure. Addition of a solution of 18-crown-6 in THF to the solution of **1** afforded a crown ether complex $[K(18\text{-crown-}6)(thf)_n][C_{60}Ph_5]$ (**2**), which was isolated by addition of toluene as black microcrystals in 87% yield (Scheme 1).[8] The ^1H and ^{13}C NMR spectra displayed signals due to the C_{5v} symmetric fullerene molecule and the 18-crown-6 ligand in a 1:1 ratio.

Single crystals suitable for an X-ray analysis were grown by slow diffusion from a three layered solution of DMF, toluene, and hexane. The X-ray grade crystals obtained now contains one molecule each of 18-crown-6 and DMF. Figure 2 shows the molecular structure of $[K(18\text{-crown-}6)(dmf)][C_{60}Ph_5]$ (**3**).[9] The potassium cation is surrounded by the 18-crown-6 and one DMF molecules and is located just above the conical cavity. The potassium cation is coordinated nearly symmetrically by the six oxygen atoms of 18-crown-6 ether (2.776(7)–2.861(7) Å) (cf. 2.901 Å for K–O distance in $[K(18\text{-crown-}6)](C_5H_5)]$,[10] and also by the DMF oxygen atom (2.592(10) Å). The K/crown ether complex is held in position above the cavity through hydro-

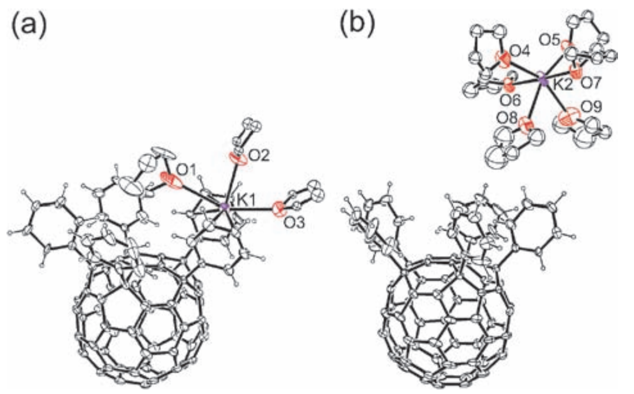


Figure 1. ORTEP drawing of two crystallographically independent ion pairs of $[K(thf)_n][C_{60}Ph_5]$ **1**. Thermal ellipsoids are 20% probability level. (a) $K(C_{60}Ph_5)(thf)_3$ (**1a**). (b) $[K(thf)_6][C_{60}Ph_5]$ (**1b**).

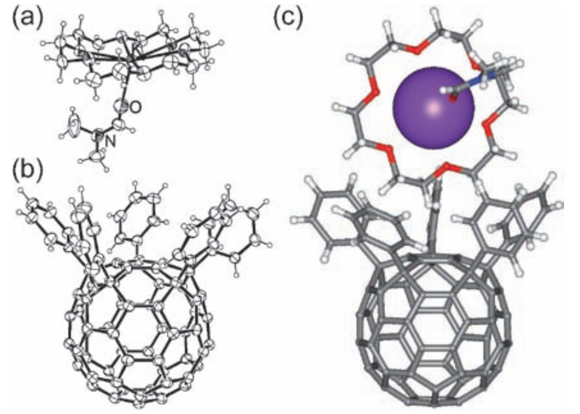


Figure 2. Crystal structure of **3**. (a) ORTEP drawing of cationic part of **3**. (b) Anionic part of **3**. Thermal ellipsoids are 30% probability level. (c) Stick and CPK (potassium ion) model of **3**.

gen–π interaction between the phenyl groups and the methylene hydrogen atoms of the crown ether. The distance between the potassium cation to the centroid of the cyclopentadienide is 7.16 Å, making the anion completely free from interaction with the cation.

In summary, we have determined three structures of solvated $KC_{60}Ph_5$ and found that the complex exists always as a solvent-separated ion pair. We ascribe this unique property of the $C_{60}Ph_5$ anion to the high stability of the anion: The cyclopentadienide moiety in $C_{60}Ph_5$ is endohedrally homoconjugated[11] with the bottom 50π-system, and hence its anionic charge is reduced than that in the parent C_5H_5 anion. Water being much more polar than THF and crown ether examined in the present study, we expect that the potassium cation of $KC_{60}Ph_5$ in water would be separated completely from the fullerene moiety as in **1b** and **3**, and that the cyclopentadienide moiety would be stabilized by water molecule(s) through hydrogen bonding. The formation of a highly polarized structure must, therefore, be the decisive factor that allows the extremely hydrophobic fullerene molecule be dissolved in water. Though the $C_{60}Ph_5$ molecule appears to differ very much from the ordinary lipid molecules, the molecular shape of the ion pair such as **3** has a polar top and a hydrophobic bottom that, taken together, would assist formation of bilayer membrane through two-dimensional self-assembly of the fullerene molecules.[3] Further studies on this and related polar fullerene molecules would provide useful insights for the mechanism of the bucky ball vesicle formation and for designing of nonlipid membrane-forming materials.

We thank Dr. H. Isobe for fruitful discussion, Frontier Carbon Corporation for generous supply of [60]fullerene, and the 21st Century COE Program for Frontiers in Fundamental Chemistry for partial financial support.

References and Notes

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5 Crystal data for **1**: $C_{114}H_{74}K_1O_6$, monoclinic, $C2/c$, $a = 23.7630(16)$ Å, $b = 14.5970(18)$ Å, $c = 44.188(3)$ Å, $\alpha = 90°$, $\beta = 98.892(4)°$, $\gamma = 90°$, $Z = 8$, $V = 15143(2)$ Å^3, $D_{calcd} = 1.385$ g/cm^3, $T = 143$ K, $R = 0.134$, $wR = 0.336$ ($I > 2\sigma(I)$). CCDC No. 271686.

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8 NMR data for **3**: ^{1}H NMR (400 MHz, DMF-d_7) δ 3.61 (s, 24H, 18-crown-6), 7.13–7.20 (m, 15H, C_6H_5), 7.91–7.96 (m, 10H, C_6H_5). ^{13}C NMR (100 MHz, DMF-d_7) δ 62.11 (5C), 70.80 (12C, 18-crown-6), 126.68 (5C), 128.34 (5C), 128.45 (10C), 128.91 (10C), 143.00 (10C), 145.50 (5C), 146.31 (5C), 147.07 (10C), 148.93 (10C), 149.06 (5C), 159.41 (10C).

9 Crystal data for **3**: $C_{105}H_{56}K_1N_1O_7$, monoclinic, $P2_1$, $a = 13.8230(9)$ Å, $b = 17.7550(14)$ Å, $c = 14.3440(9)$ Å, $\alpha = 90°$, $\beta = 91.011(4)°$, $\gamma = 90°$, $Z = 4$, $V = 3519.9(4)$ Å^3, $D_{calcd} = 1.397$ g/cm^3, $T = 153$ K, $R = 0.105$, $wR = 0.247$ ($I > 2\sigma(I)$). CCDC No. 271685.

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Published on the web (Advance View) June 26, 2005; DOI 10.1246/cl.2005.1078