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Crystallographic characterization of Kr@C_{60} in (0.09Kr@C_{60}/0.91C_{60})·{Ni^{II}(OEP)}·2C_6H_6

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A sample of C_{60} containing *ca.* 9% Kr@C_{60} has been used to form crystalline (0.09Kr@C_{60}/0.91C_{60})·{Ni^{II}(OEP)}·2C_6H_6 whose X-ray crystal structure reveals that the Kr atom is centered within the carbon cage and does not produce a detectable change in the size of the fullerene.

Fullerene cages are known to be able to enclose a variety of atoms in their interior space.[1] The atoms that have been found within fullerenes include relatively inert noble gas atoms,[2] ordinarily highly reactive atoms like nitrogen, which are protected by the presence of the cage,[3] and metal atoms, which transfer charge to the fullerene carbons.[4] Fullerenes with noble gas on the inside offer opportunities to examine the effects of van der Waals systems forces on the carbon cages. The ^{3}He NMR spectroscopy of fullerenes and chemically modified fullerenes containing entrapped helium atoms has proven to produce useful information in regard to the electronic and geometric structures of these molecules. However, the purification of endohedrals with noble gases on the inside is challenging. Generally, only minute quantities of purified endohedrals like Kr@C_{60} have been separated, and this separation was accomplished only after using tedious sequential HPLC separations.[5] Here we report the first crystallographic study of an endohedral fullerene with a noble gas atom trapped inside. This has been accomplished using a partially purified sample of Kr@C_{60}, mixed with empty C_{60}, in a 1:10 ratio.

A sample of 34 mg of C_{60} containing about 0.3% Kr@C_{60} was obtained by a high pressure/high temperature procedure, in which C_{60} in the presence of potassium cyanide as a catalyst was heated at 600–650 °C under 3200 bar of Kr.[6,7] Separation by HPLC utilizing toluene/hexane mixtures as eluents and a variety of different columns produced 0.8 mg of C_{60} that contained about 12% Kr@C_{60}.[7] Fig. 1 shows the HPLC trace (part A, 4.6 × 250 mm, 0.5 mL min^{-1} toluene, 50 °C) and the corresponding TOF MS spectrum (part B) for this material. The lack of a strong interaction between the krypton atom and the fullerene cage is shown by the small shift in the HPLC, with a separation factor of only about 1.09, as well as optical spectroscopy data.[6]

Co-crystallization of fullerenes and endohedral fullerenes with porphyrins, particularly metallo-octaethyporphyrin (M^{II}OEP), has been shown to be an effective means of obtaining samples with enough orientational order in the fullerene portion to be suitable for single crystal X-ray diffraction.[8–12] Consequently, we chose to co-crystallize the endohedral sample with {Ni^{II}(OEP)}, since we had determined the structure of C_{60}·{Ni^{II}(OEP)}·2C_6H_6 **1**† and found it to have a fully ordered C_{60} molecule that could be freely refined and gave an excellent crystallographic structure. Within that structure the closest and next closest approach of the fullerene carbons atoms to the nickel atom in the porphyrin are 3.0023(12) and 3.2042(13) Å. Consequently the fullerene is not coordinated to the nickel atom (crystals of C_{60}·{Ni^{II}(OEP)}·2C_6H_6 are isomorphic with those of C_{60}·{Cu^{II}(OEP)}·2C_6H_6 whose structure had been reported previously.[13]). Black crystals of (0.09Kr@C_{60}/0.91C_{60})·{Ni^{II}(OEP)}·2C_6H_6 **2** were obtained by the diffusion of a solution of an enriched sample of Kr@C_{60} in benzene into a solution of {Ni^{II}(OEP)} in benzene.†

Fig. 2 shows a perspective drawing of the entire assembly of four molecules in the crystal. The krypton atom is found at the

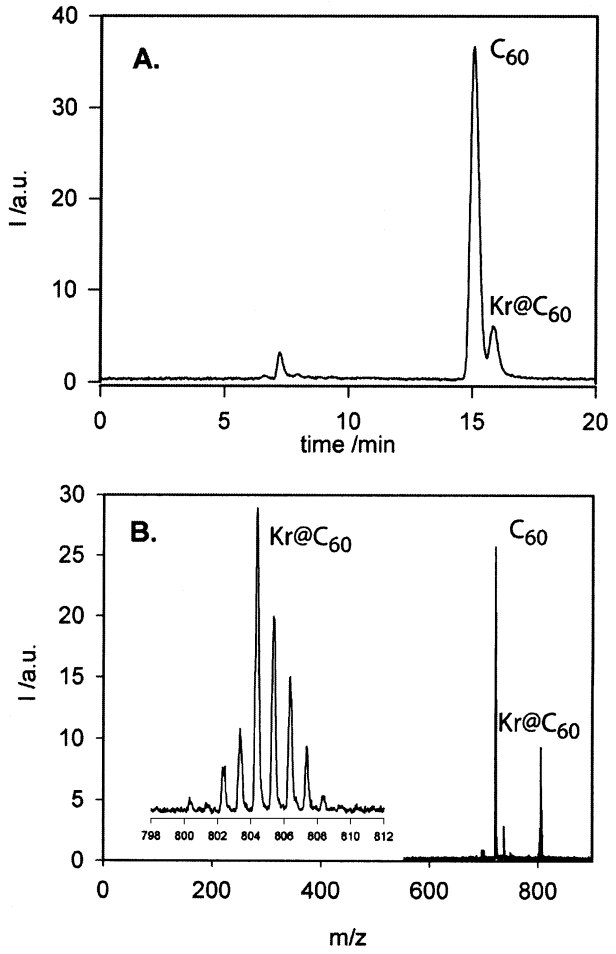

Fig. 1 A. HPLC chart of 12% Kr@C_{60}/C_{60}, after two separations on a preparative Cosmosil Buckyprep column 4.6 × 250 mm, 0.5 ml min^{-1} toluene, 50 °C. Both peaks are clearly separated. B. TOF-MS of the same sample, inset is the experimental isotopic distribution for Kr@C_{60}.

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center of the fullerene cage. In contrast in $C_{60}\cdot\{Ni^{II}(OEP)\}\cdot 2C_6H_6$, the fullerene cage is empty and there is no residual electron density at the center of the fullerene cage. In refining the $(0.09Kr@C_{60}/0.91C_{60})\cdot\{Ni^{II}(OEP)\}\cdot 2C_6H_6$ structure, the occupancy of the krypton atom was allowed to vary and the structure refines best with an occupancy 0.09. With this occupancy, the equivalent isotropic thermal parameter for the krypton atom was 0.023(1) Å^2 which is similar to those (range, 0.021(1)–0.033(1) Å^2) of the fullerene carbon atoms. The average Kr···C separation is 3.540(3) Å. For comparison, the sum of the van der Waals radii for carbon (1.70 Å) and krypton (2.02 Å) is 3.72 Å, so the krypton atom is tightly confined within the C_{60} cage. Clearly since co-crystallization of $Kr@C_{60}$ and C_{60} occurs, the endohedral molecules can occupy the same space as undoped C_{60}. Careful comparison of this structure with that of the undoped parent, $C_{60}\cdot\{Ni^{II}(OEP)\}\cdot 2C_6H_6$, reveals no detectible changes in the positions of the carbon atoms of the fullerene cage.

Only a few other compounds with krypton atoms trapped by van der Waals interactions have been studied by crystallography. The crystal structure of krypton trapped in zeolite A reveals that there are three different sites that the krypton atoms occupy.[14] In the smaller sodalite cage, the krypton atom is 3.87(2) Å away from three framework oxygen atoms and 3.39 Å from the closest sodium ion. Tetra-*tert*-butyltetrahedrane forms a clathrate with krypton with a hexagonal arrangement of krypton atoms in which each occupies octahedral holes between six *tert*-butyl groups of six different tetra-*tert*-butyltetrahedrane molecules.[15]

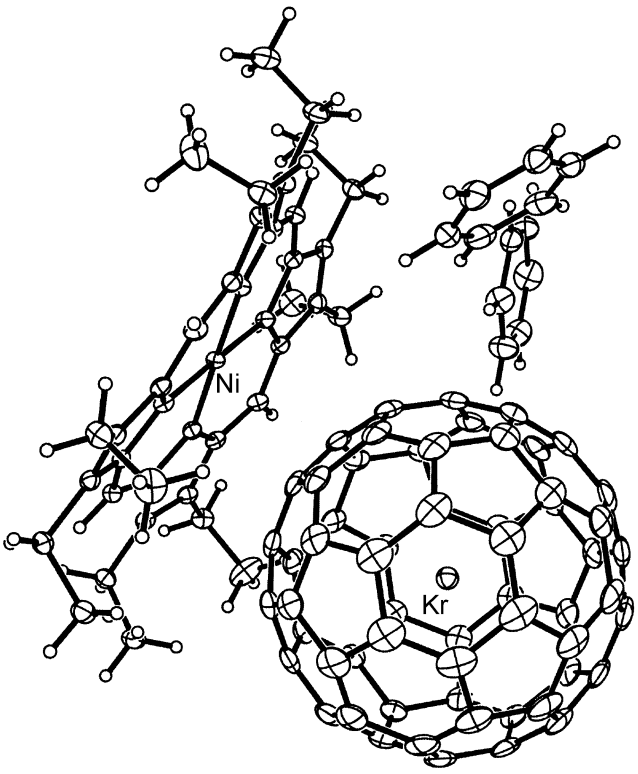

Fig. 2 A perspective view of the structure of $(0.09Kr@C_{60}/0.91C_{60})\cdot\{Ni^{II}(OEP)\}\cdot 2C_6H_6$ **2**. The atoms are shown with 50% thermal ellipsoids.

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Notes and references

† *Crystal data*: for **1**: black prisms of of $C_{60}\cdot NiC_{36}H_{44}N_4\cdot 2C_6H_6$ that were obtained by diffusion of a benzene solution of C_{60} into a benzene solution of Ni^{II}(OEP) form in the triclinic space group *P*1 with a = 14.1318(8), b = 14.3851(9), c = 17.2064(12) Å, α = 87.583(4), β = 75.762(4), γ = 75.615(5)° at 92(2) K with Z = 2 with the use of graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Refinement of 19789 reflections and 1026 parameters yielded *wR*2 = 0.107 for all data and a conventional R_1 = 0.039 based on 16575 reflections with $I > 2\sigma(I)$. The largest peak and hole in the final difference map are 0.44 and −0.39 e Å^{-3}.

For **2**: black prisms of $(0.085Kr@C_{60}/0.915C_{60})\cdot NiC_{36}H_{44}N_4\cdot 2C_6H_6$ that were obtained by diffusion of a benzene solution of $0.085Kr@C_{60}/0.915C_{60}$ into a benzene solution of Ni^{II}(OEP) form in the triclinic space group *P*1 with a = 14.120(2), b = 14.373(2), c = 17.212(3) Å, α = 87.608(4), β = 75.795(7), γ = 75.628(7)° at 92(2) K with Z = 2 with the use of graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation on a crystal of dimensions 0.30 × 0.12 × 0.08 mm. Refinement of 14829 reflections and 1036 parameters yielded *wR*2 = 0.075 for all data and a conventional R_1 = 0.046 based on 10641 reflections with $I > 2\sigma(I)$. The largest peak and hole in the final difference map are 0.45 and −0.58 e Å^{-3}.

CCDC reference numbers 182460 and 182461. See http://www.rsc.org/suppdata/cc/b2/b202925c/ for crystallographic data in CIF or other electronic format.

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