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## FOR MORE INFORMATION

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## The Structure of Ba@C<sub>74</sub>

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*For the first time, the structure of a monometallofullerene has been analyzed using single crystal synchrotron diffraction on microcrystals of Ba@C<sub>74</sub>·Co(OEP)·2C<sub>6</sub>H<sub>6</sub> (where Co(OEP) is cobalt(II)-octaethylporphyrin) at 100 K. This monometallofullerene exhibits a high degree of localization of its endohedral metal ion, with just two split positions for barium and two orientations for the C<sub>74</sub> cage. The crystal structure consists of complex units (Ba@C<sub>74</sub>)[Co(OEP)]<sub>2</sub>(Ba@C<sub>74</sub>) arranged in a distorted, primitive hexagonal packing. Despite the disorder still present, we have derived a consistent and conclusive structure model for the title compound by employing a combination of x-ray diffraction, x-ray absorption near-edge structure (XANES) spectroscopy, and quantum chemical calculations.*

Since the discovery of fullerenes, information about the molecular and electronic structure of this new family of carbon allotropes, which include "endohedral" metallofullerenes (those with metal atoms inside the fullerene cage) and fullerene compounds, has been essential for understanding their physical and chemical properties. To acquire such information, the availability of precise crystal structure data is a crucial prerequisite.

In ongoing research efforts, we have developed a method that allows a high-yield synthesis of small and mid-sized endohedral fullerenes consisting of divalent metals that follow M@C<sub>m</sub> (where m = 60, 70, 72, 74, 76; M = Ca, Sr, Ba, Eu). In this method, we inductively heat graphite and the corresponding metal inside a radiofrequency field to temperatures of up to 3000 K (**Figure 1**), and then isolate individual species from the raw soot extracts using multi-step high-performance liquid chromatography (HPLC).

By employing micro-crystal synchrotron diffraction techniques, computational chemistry, and XANES spectroscopy in a synergistic manner, we were able to determine the structure of Ba@C<sub>74</sub>



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as a co-crystallate with Co-octaethylporphyrin (Co(OEP)) and C<sub>6</sub>H<sub>6</sub> (benzene).

The crystal structure of Ba@C<sub>74</sub>·Co(OEP)·2C<sub>6</sub>H<sub>6</sub> consists of complex units (Ba@C<sub>74</sub>)[Co(OEP)]<sub>2</sub>(Ba@C<sub>74</sub>) exhibiting a back-to-back orientation of two Co(OEP) molecules, each coordinating one Ba@C<sub>74</sub> molecule (**Figure 2**). The overall structure may be regarded as a distorted, primitive hexagonal packing of these complex units. Yet, the fullerene substructure is

disordered, with two orientations for the C<sub>74</sub> cage and two positions for the barium atom. Thus, four different barium-to-C<sub>74</sub> coordination schemes have to be discussed. Out of those, two are similar to those found from the results of the quantum-chemical investigations. Yet, the shortest Ba-C distances do not correspond to the central 6:6 bond of a pyracylene unit located at one of the three pockets of the cloverleaf-shaped C<sub>74</sub> molecule, but to its vicinity.

As stated above, computational investigations on  $\text{Ba}@C_{74}$  show that the local minimum structure of  $\text{Ba}@C_{74}$  corresponds to a 3-fold degenerate arrangement with barium located in one of the three pockets of  $C_{74}$ , coordinating to the central 6:6 pyracylene bond. Remarkably, the molecular structure of the neutral  $C_{74}$  cage in  $\text{Ba}@C_{74}$  differs only slightly from the molecular structure of a  $C_{74}^{2-}$  dianion (both determined using the density-functional theory in local-density approximation). Those differences are highly localized in the central 6:6 bond of the pyracylene units.

This discrepancy between the re-

sults of the experimental and the computational investigations is clearly due to the intermolecular interactions present in the co-crystallite. On one hand, those  $\text{Co(OEP)}-\text{Ba}@C_{74}$  configurations that result in a large contact surface between the two molecules allow attractive  $\pi-\pi$  and dispersion interactions. On the other hand, configurations where the pyracylene unit at the pocket of  $\text{Ba}@C_{74}$  is pointed towards the Co-atom of the  $\text{Co(OEP)}$  molecule allow stabilization via multipole-multipole interactions. The competition between these two different intermolecular interactions triggers the orientational disorder

of the  $C_{74}$  cage. Furthermore, molecular dynamics simulations reveal a nearly flat potential hypersurface around the local minima positions within the pocket of the cloverleaf-shaped molecule. This suggests an easy displacement of the Ba atom near a minimum that is produced by a direct interaction between the  $\text{Ba}^{2+}$  cation and the  $\text{Co(OEP)}$  molecule. Thus, the positional disorder of the barium atom is a consequence of the orientational disorder of the  $C_{74}$  cage, which is due to the competition of  $\pi-\pi$  and electrostatic interactions.



Figure 1. The radio-frequency furnace for endohedral fullerene synthesis in action.

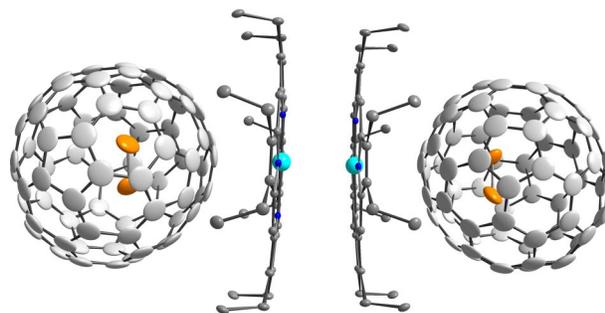


Figure 2. A  $(\text{Ba}@C_{74})[\text{Co(OEP)}]_2(\text{Ba}@C_{74})$  unit in  $\text{Ba}@C_{74}\cdot\text{Co(OEP)}\cdot 2C_6H_6$  (for clarity, only one fullerene orientation is given).