The Crystal Structures of Higher Fullerenes

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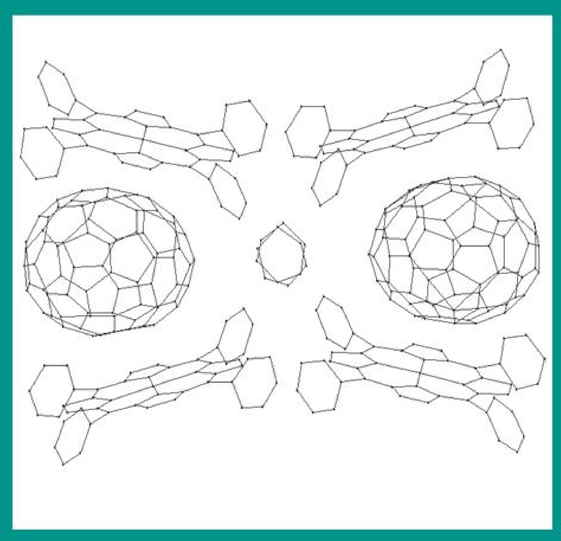
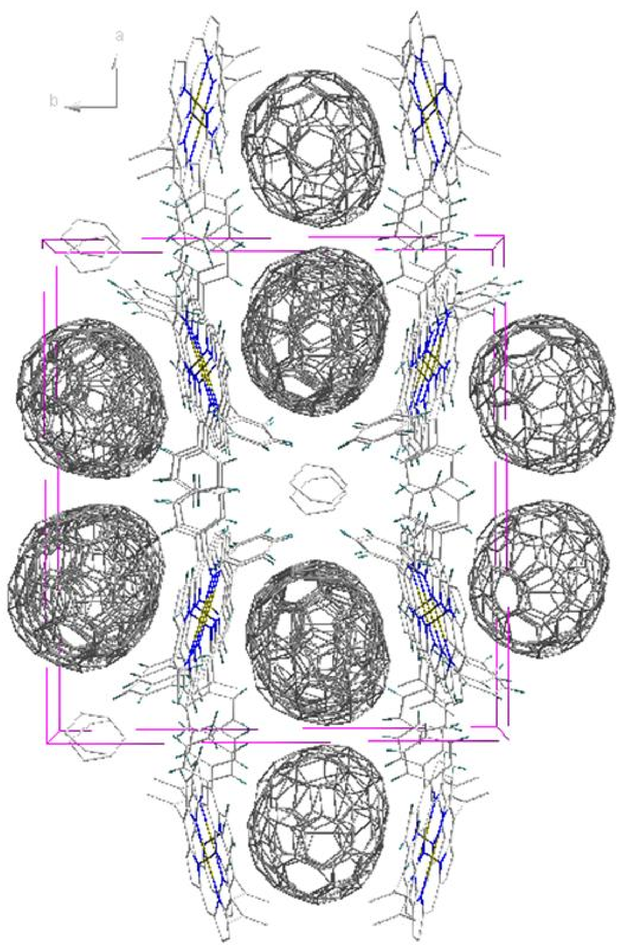
Introduction

The non-planar "aromatic" π-system is the most conspicuous feature common to fullerenes. The exact bond lengths and distribution of electron density in the molecule obtained from X-ray analysis provide a key to understanding its unique properties. The crystal structures of most abundant C_{60} and C_{70} fullerenes are thoroughly investigated, however, there are no reliable crystal data on individual isomers of higher fullerenes. Fullerene molecules tend to form disordered structures. This is a consequence of their quasi-spherical shape, thus, detailed analysis of single-crystal X-ray data has been performed just in a few cases [1,2]. Special co-crystallization agents can fix the fullerene molecule in the crystal, thus, helping to solve the problem of disorder. The interaction between co-crystallization agent and fullerene molecule increases the energetic barrier of fullerene rotation. Usually the selectivity of co-crystallization agents to fullerenes is high. As a consequence, the compound which forms crystals of good quality with C_{60} rarely forms ones with C_{70}, or other higher fullerenes.

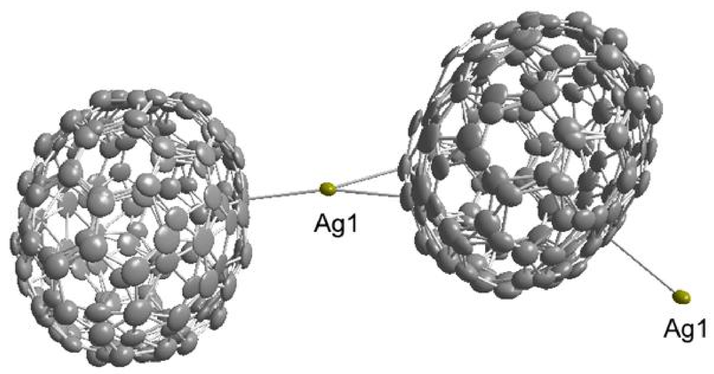


Here we present a series of co-crystal structures of higher fullerenes with silver-tetraphenylporphine (AgTPP) and copper-tetraphenylporphine (CuTPP). Due to the relatively strong interaction between AgTPP, CuTPP and fullerene, the disorder in fullerene molecules is minimized. The ordering in these compounds is sufficient to confirm the structure of the fullerene and can give information about the presence of stereo- or structural isomers in the sample. Moreover, the metal-TPP forms co-crystals with different fullerene cages. The crystal structures have the same morphology, in which the fullerene cage forms a sandwich complex with two AgTPP fragments as shown on the picture. A benzene molecule is incorporated in the voids between two fullerenes and two porphine fragments. Changing the fullerene-cage size leads only to changes in distance between porphine rings, no additional rotation of AgTPP fragments was observed. The pronounced adaptability of AgTPP to the shape of fullerene cages makes this compound a universal co-crystallising agent, useful for preparing single crystals of new fullerenes including endohedral ones.

Crystal structure of C_{76} with Ag-tetraphenylporphine

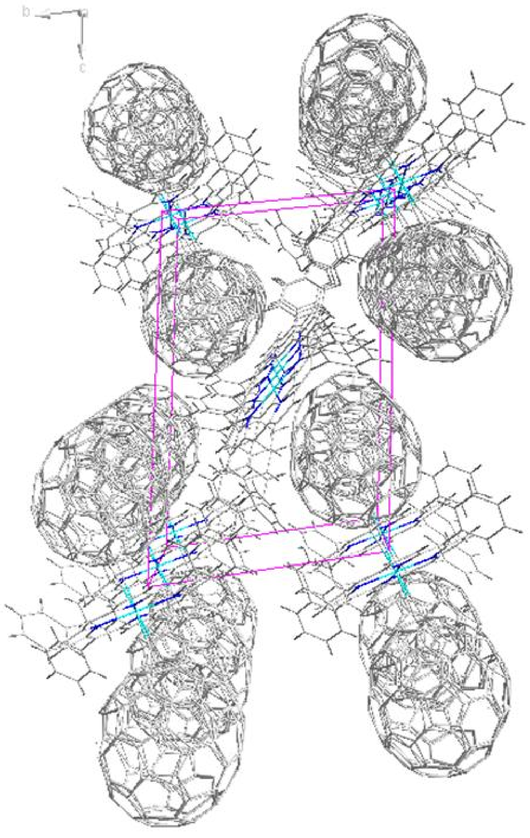


Formula	$C_{76} \cdot AgN_4C_{44}H_{28} \cdot C_6H_6$
Temperature / K	100
Wavelength / pm	71.073
Space group	C2
a / pm	2533.7
b / pm	2317.6
c / pm	1210.1
α / °	90.0
β / °	90.9
γ / °	90.0
Cell volume / nm³	7104.5
Z	4
Refinement	Full-matrix least-squares on F² (Jana2000)
Residuals (obs.) / %	Robs= 7.4, Rw,obs=5.9
Residuals (all) / %	Rall= 12.1, Rw,all=6.3
Refinement Fullerene	TLS

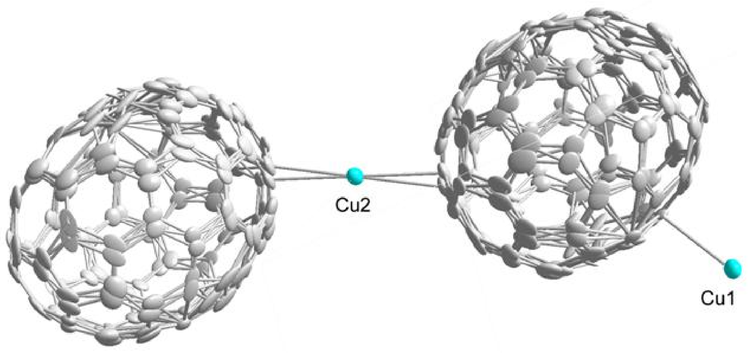


Ag1 - C 2.865 Å
Ag1 - C 2.768 Å
Ag1 - C 2.613 Å

Crystal structure of C_{78} with Cu-tetraphenylporphine



Formula	$C_{78} \cdot CuN_4C_{44}H_{28} \cdot C_6H_6$
Temperature / K	100
Wavelength / pm	71.073
Space group	P-1
a / pm	1201.4
b / pm	1420.0
c / pm	2168.7
α / °	80.2
β / °	78.5
γ / °	77.1
Cell volume / nm³	3502.9
Z	3
Refinement	Full-matrix least-squares on F² (SHELXL)
Residuals (obs.) / %	R1= 8.9 ,wR2=25.7
Residuals (all) / %	R1= 10.2 ,wR2=27.3
Refinement Fullerene	Individually anisotropic



Cu1 - C 2.969 Å
Cu2 - C 2.854 Å
Cu2 - C 2.851 Å

Results and Conclusion

Structures: Two new complexes of higher fullerenes were obtained. A tunnel system of fullerenes is observed in both structures. In C_{76}·AgTPP·Benzene two stereo isomeres of C_{76} are fixed by AgTPP, while in C_{78}·CuTPP·Benzene the C_{78} cage is found just in two of the three possible orientations. „Fixing" the fullerene moleculs with AgTPP and CuTPP decreases disorder. This enables one to analyse and describe the structure using full matrix least squares on F². The fullerene molecules can be individually refinded in anisotropic mode in SHELXL or using the TLS-method in JANA2000.

References

[1] M. Panthofer, D. Shopova, M. Jansen, Zeitschrift für anorganische und allgemeine Chemie, **2005**, 631 (8), 1387-1390

[2] A. Reich, M. Panthofer, H. Modrow, et al., J. of the Americian Chemical Society, **2004**, 126 (44), 14428-14434