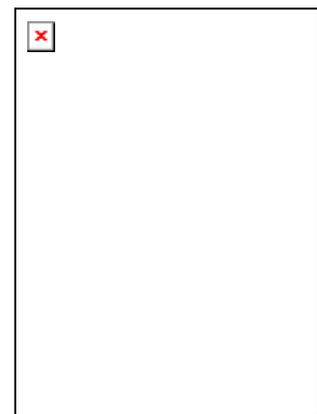


**COMBINED SYNCHROTRON X-RAY AND NEUTRON  
DIFFRACTION STUDY OF Ba<sub>4</sub>C<sub>60</sub> SUPERCONDUCTOR**

I. Margiolaki E. Aslanis S. Margadonna K. Prassides  
PG Pigeonholes, University of Sussex CPES, Chichester Building, Falmer  
BRIGHTON EAST SUSSEX BN1 9QJ UK

Selected members of the alkali-earth fullerenes family display superconductivity. In the present study, the crystal structure of Ba<sub>4</sub>C<sub>60</sub> is studied in detail by combined Rietveld refinement of synchrotron X-ray and neutron powder diffraction data at 5 and 295 K. We find that the Ba<sup>2+</sup> ions, which occupy two crystallographically inequivalent sites, are severely sterically crowded. The observed shortest Ba-C contacts imply hybridisation between Ba 5d states and C<sub>60</sub> t<sub>1g</sub> states. This is also consistent with the temperature dependence of the lattice constants between 5 and 320 K (Figure 1), which clearly indicates a highly anisotropic orthorhombic structure with negligible thermal expansivity along the c axis. The molecular structure of the C<sub>60</sub><sup>8-</sup> anion prominently deviates from icosahedral symmetry with a large distortion mainly along the short c-axis of the unit cell. We discuss the observed structure of the C<sub>60</sub><sup>8-</sup> anion in terms both of electronic effects due to the Jahn-Teller distortion and crystal effects arising from the Ba-C interaction. We note that the superconducting behaviour of alkaline earth fullerenes can be



partially attributed to the hybridization effect, and the enhanced deviation from spherical symmetry found here is consistent with this idea. Normal-state susceptibility measurements (1) and LDA calculations (2) show that the density-of-states at the Fermi level is about half that of the A<sub>3</sub>C<sub>60</sub> compounds, suggesting broader bands, despite the similarities in band filling. References: 1. C. M. Brown et al, Phys. Rev. Lett. 83, 2258 (1999). 2. K. Umemoto et al, Phys. Rev. B 61, 14204 (2000).

**Keywords: FULLERENE,  
SUPERCONDUCTIVITY,  
DIFFRACTION**

**A STUDENT INVESTIGATION OF SULFA DRUG/CARBOXYLIC  
ACID MOLECULAR RECOGNITION BY COCRYSTALLIZATION**

D.A. Adsmund<sup>1</sup> M.A. Whitener<sup>2</sup> P.J. Squattrito<sup>3</sup>  
<sup>1</sup>Ferris State University Physical Sciences Department ASC 3009, 820  
Campus Drive BIG RAPIDS MICHIGAN 49307 USA <sup>2</sup>Department of  
Chemistry and Biochemistry, Montclair State University, Upper Montclair,  
New Jersey 07043, USA <sup>3</sup>Department of Chemistry, Central Michigan  
University, Mount Pleasant, Michigan 48859, USA

During the past three years, students in the second semester of organic chemistry at Ferris State University have been introduced to the field of solid-state chemistry through a 6-week research project investigating the molecular recognition properties of 9 different sulfa drugs. The amidine and sulfonamide functional groups seen in sulfa drugs are complementary to carboxylic acids and might be expected to form bidentate hydrogen-bonded complexes with them. To test this, crystals were grown by slow evaporation of solutions, each containing a sulfa drug and a carboxylic acid compound. The formation of sulfa drug/carboxylic acid cocrystals was indicative of preferential binding between the sulfa drug and the acid molecules while formation of separate acid and sulfa drug crystals was indicative of preferential binding between like molecules. The crystals were analyzed by solution NMR to determine their identity and stoichiometry and were analyzed by solid-state FTIR to gain information on the nature of the specific binding interaction. Single crystal X-ray diffraction, carried out on select representative cocrystals, revealed the complete hydrogen-bond patterns of the cocrystals. The initial study showed that the presence of the amidine group is a necessary but not sufficient condition for a sulfa drug:acid binding. Further studies showed that removal of the sulfonyl portion of the drug molecule greatly increased the affinity of the amidine site for carboxylic acids.

**Keywords: MOLECULAR RECOGNITION, CARBOXYLIC ACID,  
SULFONAMIDE**

**STRUCTURE OF ISOMER II OF THE ENDOHEDRAL FULLERENE  
ER<sub>2</sub>@C<sub>82</sub>**

M. M. Olmstead<sup>1</sup> A. L. Balch<sup>1</sup> H. M. Lee<sup>1</sup> H. C. Dorn<sup>2</sup> S. Stevenson<sup>3</sup>  
<sup>1</sup>University of California Department of Chemistry One Shields Ave. DAVIS  
CA 95616 USA  
<sup>2</sup>Virginia Polytechnic Institute, Blacksburg, VA 2406 <sup>3</sup>Luna Nanomaterials,  
Blacksburg, VA 2406

Three different isomers of ErC<sub>82</sub> have been separated by chromatography as byproducts of the synthesis of Er<sub>3</sub>N@C<sub>80</sub>. Nine possible isomers of C<sub>82</sub> obey the isolated pentagon rule. Recently we found that one of these products, called Isomer I, has C<sub>s</sub> (82:6) symmetry, and the two Er's are preferentially disposed around the interior in a circle that is close to a single ring of ten 6-membered rings. One set of two Er's has a prominent (35%) occupancy and a non-bonded distance of 3.641(3) Å. Each of the remaining eight isomers presents a different interior to the two Er's. However, only two of these isomers possess contiguous 6-membered rings that span the entire circumference of the fullerene. These are one of the two C<sub>3v</sub> (82:8) isomers and the C<sub>2v</sub> (82:9) isomer. The crystal structure of a second isomer, the co-crystal, Er<sub>2</sub>C<sub>82</sub>·Ni(OEP)·2 benzene, was determined. In addition to the identification of the isomer, one of those with C<sub>3v</sub> symmetry, the structure shows a positioning of the Er's into two groups with multiple sites. The fullerene portion has three rings of ten 6-membered rings. Although the disorder is extensive, the results agree with the wide separation of the two Er's seen in isomer I.

**Keywords: FULLERENE ENDOHEDRAL ERBIUM**

**ON POLYMORPHISM OF SOME HYDRATED CERIUM SULFATES**

B. M. Casari V. Langer  
Department of Inorganic Chemistry University of Goteborg GOTEBOG 412  
96 SWEDEN

Cerium sulfates are, due to their redox chemistry, raising an interest as valuable oxidation tools in organic chemistry. Tetravalent ceric salts are highly hydrolysed in aqueous solutions and hydrated basic salts tend to form readily. Simple trivalent salts can be prepared by dissolving the oxide, or a more reactive precursor, in an appropriate acid. Upon crystallization a wide variety of hydrated species can be a result. However, in aqueous solutions Ce(IV) is metastable with regard to the oxidation of water and mixed Ce(III)-Ce(IV) solutions tend to occur. The crystal structures of two polymorphic cerium disulfate tetrahydrates, Ce(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> and a novel form of dicerium trisulfate tetrahydrate, Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub> has been determined. The two Ce(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> polymorphs are forming bright yellow crystals of different morphology. In both cases the cerium(IV) coordinate to four sulfate and four water oxygens but the two coordination polyhedra are slightly different. These structures are built up by layers of Ce(SO<sub>4</sub>)<sub>2</sub> components, held together by water sulfate hydrogen bonds. The main difference between these closely related polymorphs is the different stacking of the cerium(IV) layers. The Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub> structure extends through edge and corner sharing between cerium and sulfur polyhedra. In this infinite three-dimensional network the nine and ten-vertex cerium polyhedra are forming channels and the cerium coordinating water molecules are mainly directed towards these channels. This structure is related to a polymorphic structure (1) already known. These polymorphs have similar packing features but exhibits different cerium coordination geometry. (1) Dareigne A. et al., Bull. de la Soc. Fr. de Mineralogie et Crystallographie, 95 (1972) 269-280.

**Keywords: POLYMORPHISM, CERIUM SULPHATE HYDRATES,  
SINGLE CRYSTAL X-RAY DIFFRACTION**