

MS24.P21*Acta Cryst.* (2011) **A67**, C364**Solvent induced polymorphism and pseudopolymorphism among fullerene C₆₀ organic adducts**Aidar Gubaidullin, Alina Saifina, *Laboratory of Diffraction Methods, A.E. Arbuzov Institute of Organic and Physical Chemistry of RAS, Kazan (Russian Federation)*. E-mail: aidar@iope.ru

Polymorphism, despite the wide popularity and the practical importance, still comprises uncertainty and a set of riddles. In general it is impossible to predict the possibility of polymorphism for a given compound. The same is true for the pseudo-polymorphs involving polymorphic forms and solvate of compounds with different stoichiometry. Of special interest is less common type of polymorphism caused by the change of solvent type, rather than by temperature variation. Quite rare such polymorphic transitions are reversible.

We have studied these phenomena for such important class of compounds as organic adducts of fullerene. At the same time the crystal structure of such compounds is studied insufficiently.

Herewith a detailed results on the molecular, supramolecular and crystal structures of the series of new mono-, bis- and hexa-adducts of the methanofullerenes and pyrrolidino-fullerenes are presented. The supramolecular structures of these compounds are determined mainly by the interplay of fullerene...fullerene interactions and C-H...O hydrogen bonds. In spite of the presence of large substituents in the molecules and solvate molecules in the crystals, which hinder such interactions, the fullerene fragments are closely packed with different fullerene environments - honeycomb structures, zigzag-chains, dimers, columns and layers. It was shown that the supramolecular structure of the fullerene C₆₀ organic adducts in the crystals can be designed via the solvent alteration.

A mechanism of formation of various polymorphic and pseudopolymorphic forms upon the solvent variation has been studied for the methanofullerene with the thiophene substituents (61-bis-(3-thiophenemethylcarboxy)methano-[60]-fullerene). It was established that the replacement of aromatic solvent by the nonaromatic one reversibly induces the formation of different polymorphic and pseudopolymorphic forms and thus provides the possibility of reversible regulation of the supramolecular structure type in the crystals. Polymorphic and pseudopolymorphic transitions are characterized by the XRD and DSC methods. Moreover the small-angle X-ray research proved the formation of stable associates of the methanofullerene molecules with the thiophene substituents in the toluene solution upon medium concentrations.

We have demonstrated that a deeper understanding of the crystal polymorphism in such a complicated system as functionally substituted fullerenes can be gained by combining the complementary information obtained from thermodynamic, single-crystal, powder and small-angle data.

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Keywords: polymorphism, fullerene_derivative, X-ray_diffraction

MS24.P22*Acta Cryst.* (2011) **A67**, C364**Entropies of polymorphic crystals from diffraction data**Anders Ø. Madsen, Nanna Wahlberg, Piotr Krzysztof Ciochon, Sine Larsen, *Department of Chemistry, Faculty of Science, University of Copenhagen, (Denmark)*. E-mail: madsen@chem.ku.dk

A central goal of crystal structure prediction is to assess the

relative stabilities of proposed structures. This is normally done by calculation of crystal energies or enthalpies (H). However it is well known that differences in entropies (S) can be sufficiently large to alter the order of stability of polymorphs with temperature (T), as expressed by the Gibbs equation $G = H - TS$.

Differences in solid state entropies of polymorphic compounds can be obtained by analysis of the anisotropic displacement parameters derived from X-ray or neutron diffraction experiments [1,2,3,4]. This approach paves the way for understanding how molecular vibrations contribute to the stabilities of crystals. We provide examples where the approach has been applied to the polymorphs of pyrazinamide [5] and the epimeric xylitol and ribitol systems [2,3], compare the experimental results to periodic DFT calculations [6] and discuss the merits and limitations of the approach as a tool for crystal engineering.

We provide examples where the approach has been successfully applied to polymorphic [5] and epimeric [2,3] systems, compare the experimental results to periodic DFT calculations [6] and discuss the merits and limitations of the approach as a tool for crystal engineering.

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MS24.P23*Acta Cryst.* (2011) **A67**, C364**Magneto-structural transformations in coordination polymers upon gas sorption**Guillermo Minguez Espallargas, Mónica Giménez-Marqués, Eugenio Coronado, *Instituto de Ciencia Molecular, Universidad de Valencia, Paterna (Spain)*. E-mail: guillermo.minguez@uv.es

Tunable molecular magnets are attracting increasing attention in the field of crystal engineering because of their potential application as switches or sensors. Magnetic properties can be modified by a variety of external stimuli such as temperature, pressure, redox, light excitation, or gas adsorption. The physisorption of guest molecules in porous materials provoke subtle changes which affect the magnetic properties [1]. In addition, although less common, the structural changes can also be caused by the removal/addition of ligands from the framework itself, which modify the metal coordination environment [2].

Here we present a new approach in which the magneto-structural transformation takes place upon chemisorption of a gas which is incorporated into the framework. This remarkable concerted rearrangement of covalent bonds occurs in a single-crystal-to-single-crystal manner, thus providing direct structural evidence of the cleavage and formation of covalent bonds as a result of the sorption process. The structural changes that take place in the solid state affects significantly the magnetic properties of the materials, switching from strong antiferromagnets to ferromagnets upon gas sorption. In addition, the gas molecules can be partially removed, yielding a new material which is a weak antiferromagnet.

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