

MS18 O1

Supramolecular Chemistry of Crown Ethers Marina S. Fonari *Institute of Applied Physics, Academy of Sciences of R. Moldova, Chisinau, Moldova;*
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Keywords: molecular co-crystals; hydrogen bondings in organic crystals; pharmaceutical relevance

The interest to the crown ethers and their complexes stems not only from the fact that these studies provide unlimited exploration of structural assembly but also from the chemical and biological potential of these compounds. The relative simplicity of the appropriate model systems allows for specific interactions to be isolated and studied. Verification of unusual properties in synthetic receptor systems and the general extensibility of the chemistry can give inside into the biological implications for such chemical interactions [1]. This contribution will aim to show some recent examples of crown ether hydrogen-bonded interactions with small biologically important molecules, 2,4-dithiouracil (DTU), novel thiosemicarbazide and dihydropyrimidine-2,4-(1H,3H)-dione derivatives, aromatic pharmaceutical acids (PABA, salicylic and mefenamic acids). DTU or thiosemicarbazide derivatives, being coupled with O-containing crown ethers, result in anhydrous or hydrated *molecular complexes* of 1:1 or 1:2 stoichiometry where the components are assembled in *molecular capsules, chains* (for DTU) [2], *layers* or *grids* (if the thiosemicarbazide molecule possesses additional H-bonding center for self-association, viz., -COOH, -NH₂ groups). The functionalized (oxime, N→O, sulfoxide) pyrimidine derivatives, being coupled with diaza-18-crown-6, revealed different modes of deprotonation (terminal oxime or sulfoxide functionalities or NH of pyrimidine ring) that results in proton-transfer complexes organised in 2D or 3D networks via charge-assisted hydrogen bonds [3]. Anhydrous or hydrated proton-transfer complexes were obtained by Aspirin, salicylic, mefenamic or *p*-aminobenzoic [4] acids coupling with 6-, 12-, 14-, 15- and 18-membered N,O- or N-containing macrocycles. In all complexes cations and anions are associated *via* (H₂N⁺)NH⁺⋯O(COO⁻) charge-assisted hydrogen bonds. The number of carboxylic anions in the complex equals to the number of N-protonated binding sites in the cyclic molecule. Water molecules show the important glue function to balance the number of proton-donor and proton-acceptor sites mediating the supramolecular reagents. The T-shape arrangement of the SA or MF anions neighboring in the crystal is the only stable synthon that preserves in the complexes as a part of the self-assembling of the corresponding pure forms.

[1] G.W. Gokel, W.M. Leevy and M.E. Weber, *Chem. Rev.* 2004, 104, 2723.

[2] Wen-Jwu Wang, Ed.V. Ganin, M.S. Fonari, Yu.A. Simonov, G. Bocelli, *Org. & Biomol. Chem.*, 2005, 3, 3054.

[3] M.S. Fonari, Yu.A. Simonov, Yu.M. Chumakov, G. Bocelli, Ed.V. Ganin, A.A. Yavolovskii *Supramolecular Chemistry* 2004, V.16 (1) pp 23-30

[4] B. Moulton, B.S. Luisi, M.S. Fonari, S.S. Basok, Ed.V. Ganin, V.Ch. Kravtsov *New J. Chem.* (accepted).

MS18 O2

Design of Bistable Non-Covalent Networks for Guest Inclusion Alessia Bacchi, Mauro Carcelli, Tiziana Chiodo, Giancarlo Pelizzi *Dipartimento di Chimica GIAF, University of Parma, Italy.*
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Keywords: crystal engineering, inclusion compounds, host-guest structures

We want to design flexible dynamic frameworks that can create pores to include small guest molecules[1]. These dynamic pores come from a sort of "bistability" of the soft apohost framework, capable to convert from a closed to an open phase in response to guest molecules[2,3]. The dynamic reorganization between the apohost and the solvate phases requires two conditions: (i) a low cost structural rearrangement between the two states, (ii) a easily accessible migration path for the outgoing and incoming guest molecules. The host diol molecules must switch reversibly from a situation where they interact with themselves (self-mediated network, SMN) to another one where they interact with the guests (guest-mediated network, GMN). Recently we have characterised hybrid organic-inorganic crystalline matrices able to reversibly rearrange their crystal three-dimensional structure as a response to the inclusion/release of small guest molecules (G) via solid-gas processes[5,6] (Figure 1). Inorganic wheel-and axle *trans*-[M(LOH)₂X₂] (M = Pd, Pt; LOH = α -(4-pyridyl)benzhydrol; X = Cl, I, CH₃COOH, CH₃) may convert from the self-mediated network of the apohost, sustained by OH⋯X hydrogen bonds, to a guest-mediated network, based on OH⋯guest hydrogen bonds[7,8]. In all these cases the apohost is completely converted into the corresponding crystalline solvate forms by exposure to vapours of guest, and conversely it is quantitatively recovered from the solvate by gentle heating, without observing any transient amorphous phase during the transition.

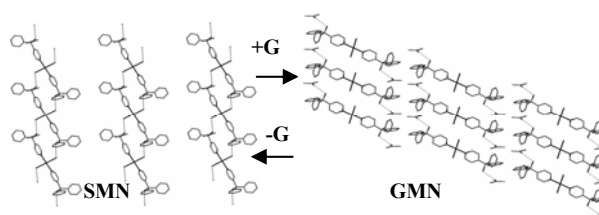


Figure 1

In this work we show that the condition for the formation of a bistable network is the existence of a remarkable steric encumbrance around the carbinol groups. The release of the steric tensions consents the formation of different OH...X networks, without any clathrating properties, as in Zn(LOH)₂X₂ (X = Cl, Br) puckered networks, and in Pd(LOH)₂X₂ (LOH3 = α -(4-pyridyl)ethanol; X = Cl, Br, I) quadrangular planar networks.

[1] J. L. Atwood, L. J. Barbour, A. Jerga, B. L. Schottel, *Science*, 2002, 298, 1000.

[2] L. R. Nassimbeni, *CrystEngComm*, 2003, 5, 200.

[3] S. Kitagawa, K. Uemura, *Chem. Soc. Rev.*, 2005, 34, 109. [4]

A. Bacchi, E. Bosetti, M. Carcelli, *CrystEngComm*, 2005, 7, 527.

[5] A. Bacchi, E. Bosetti, M. Carcelli, P. Pelagatti, D. Rogolino, G. Pelizzi, *Inorganic Chemistry*, 2005, 44, 431.

[6] M. R. Caira, A. Jacobs, L. R. Nassimbeni, F. Toda, *CrystEngComm*, 2003, 5, 150.

[7] I. Csoregh, T. Brehmer, S.I. Nitsche, W. Seichter, E. Weber, *J. Inclusion. Phen. Macr. Chem.*, 2003, 47, 113

MS18 O3

Predicting and Engineering Inclusion Frameworks
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Keywords: organic inclusion compounds, crystal structure prediction, computer modelling solids

Inclusion compounds have attracted the interest of materials chemists for the last fifty years or so, with one of the main reasons being their numerous potential applications. However, since they were first discovered in 1810 (eg. choleic acid discovered by H. Davy), inclusion compounds have been obtained mainly by serendipity. Amongst these compounds we also find organic inclusion solvates: crystal structures in which the main component is an organic molecule forming a well-defined hydrogen bonded network that serves as a host to the solvent molecule. In many instances, inclusion solvates tend to be isostructural: while the host structure is always maintained, a great variety of solvent molecules can serve as guest. This is the case of sulfathiazole, a drug well known for its numerous solvates. Prediction of this type of behavior for molecules of pharmaceutical interests would be of great importance, since in many cases solvates tend to be avoided, whenever possible, in drug formulation. In this context we describe, for the first time, a way of anticipating possible and likely inclusion frameworks *ab initio*, using only a knowledge of the molecular connectivity of the host. We suggest that crystal structure prediction calculations, combined with voids analysis in putative crystal structures of high energy and low density, as a way of identifying possible inclusion frameworks. We present preliminary results for some well known inclusion systems and drug molecules with inclusion properties.

MS18 O4

Twinning in Clathrates-II Reiner Ramlau, Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany.
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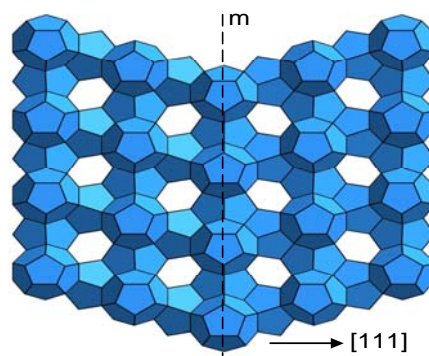
Keywords: clathrates, twinning, germanium

A new crystalline modification of elemental germanium, the guest-free germanium clathrate-II $\square_{24}\text{Ge}_{136}$, has been successfully prepared recently [1] through oxidation of Ge_9^{4-} Zintl anions in ionic liquids under ambient conditions. The new modification—shortly called clathrate-II germanium—(space group $Fd\bar{3}m$) is an open, covalently bonded 3D network of tetrahedrally coordinated Ge atoms forming pentagon-dodecahedral Ge_{20} and hexakaidecahedral Ge_{28} cages. Each unit cell contains 16 pentagon dodecahedra [5^{12}] and 8 hexakaidecahedra [$5^{12}6^4$]. (In a completely filled clathrate-II the 24 polyhedral cages would provide space for 24 guest positions.) Investigations by electron diffraction and

high-resolution transmission electron microscopy (HRTEM) revealed the strong tendency to both polysynthetic and cyclic twinning. Twinning has already been reported for the partly filled binary clathrate-II $\text{Na}_x\text{Si}_{136}$ ($x < 11$) [2].

The present study shows that an intrinsic structural feature, the approximate mirror symmetry of an extended structural entity, compels repeated twinning and may seriously compromise single-crystal growth. The mentioned entity is not only own to the elemental clathrate-II germanium but also to the host framework of all binary type-II clathrates. It is supposed that multiple twinning occurs also in clathrate-II hydrates [3] and dodecasil-3C [4], although this is seemingly not reported yet.

The twin law is comprehensively formulated as reflection twinning with a $\{111\}$ -type plane as the twin plane, intersecting the corners 0,0,0 of the cubic unit cell. The twin interface is identical with the twin plane. It is completely coherent and smooth. An atomic model of the interface is established (Figure). In this model the dodecahedra which are constituting the layer at the twin interface adopt perfect $\{111\}$ mirror symmetry and are, hence, slightly distorted with respect to those inside the twin components. (Which on their part are slightly distorted regular dodecahedra.) Model-based image simulation is in very good agreement with experimental HRTEM images of the twin interface.



[1] Guloy, A.M.; Ramlau, R.; Tang, Z.; Schnelle, W.; Baitinger, M.; Grin, Y. *Nature* 2006, 443, 320.

[2] Nistor, L.; van Tendeloo, G.; Amelinckx, S.; Cros, C. *Phys. Status Solidi* 1994, 146, 119.

[3] von Stackelberg, M.; Müller, H.R. *Z. Elektrochem.* 1954, 58, 25.

[4] Gies, H.; Liebau, F.; Gerke, H. *Angew. Chem.* 1982, 94, 214.

MS18 O5

Self-assembly of functionalized calixarenes.

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Keywords: calixarenes, self-assembly, X-ray structure

The calix[n]arenes are aromatic macromolecules that can engender a wide range of derivatives thanks to their easy and selective chemical modifications. An extremely wide range of solid-state studies have been undertaken on these