

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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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.

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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.

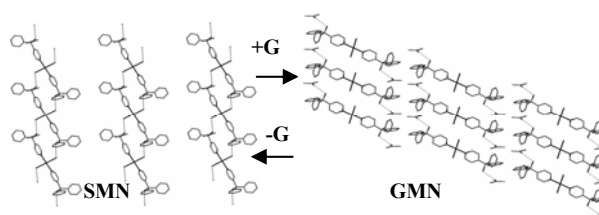


Figure 1

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 (LOH = α -(4-pyridyl)ethanol; X = Cl, Br, I) quadrangular planar networks.

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