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The Phenomenon of Dynamic Cooperativity in the Solid State

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In continuation of our studies on single-crystal-to-single crystal transformations [1, 2] we report an example which nicely illustrates the cooperative behavior of molecules in the solid state. Crystals composed of neutral molecular rectangles were obtained as yellow acetone solvates **1**. During desolvation, significant conformational changes were observed. The molecular rectangles collapse to assume an "imploded" conformation with loss of the guest-templated aperture and shrinkage of the crystal volume by approximately 17% **2**. Upon exposure of **2** to acetonitrile vapor for several minutes, a color change from greenish-yellow to red was observed with no apparent fracturing of the individual crystals. Single crystal X-ray analysis shows that a third phase **3** is formed upon stoichiometric uptake of acetonitrile. The packing mode is similar to that observed in **1**. However the conformation of the bridging ligand is quite different. When crystals of **3** are exposed to atmospheric conditions for approximately 15 min, transformation to yet a fourth phase occurs. X-ray intensity data were collected and reveal the presence of two different conformations of the metallocyclic complex in **4**. Crystal structures together with energy level calculations and discussions of color changes will be presented.

[1] Dobrzańska, L.; Lloyd, G.O; Raubenheimer, H. G; Barbour, L.J. *J. Am. Chem. Soc.*, 2005, 127, 13134.

[2] Dobrzańska, L.; Lloyd, G.O; Raubenheimer, H. G; Barbour, L.J. *J. Am. Chem. Soc.*, 2006, 128, 698.

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Recognition of structural helices responsible for optical activity of selected urea adducts

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From among urea adducts, considered for crystal engineering because of the expected chiral and/or polar behaviour, two non-centrosymmetric crystal structures were selected as interesting examples of biaxial crystals with possible optical activity and/or NLO properties: (1) the adduct of malic acid and urea, S-(-)-C₄H₆O₅·(NH₂)₂CO, *P* 2₁, a=6.8074(6), b=6.9408(6), c=9.044(1) Å, β=94.730(4)°, V=425.86(7), D_x=1.514 Mg/m³, Z=2, μ(MoKα)=0.14mm⁻¹, R1=0.0366 (for 1536 observed reflections), wR2=0.0972 (for 1732 unique reflections), S=0.938; (2) hexakis(urea)-zinc sulphate mono hydrate, Zn([(NH₂)₂CO]₆SO₄·H₂O, *P* ca2₁, a=15.1093(1), b=7.2216(2), c=20.0902(2) Å, V=2192.11(7), D_x=1.636 Mg/m³, Z=4, μ(MoKα)=1.29mm⁻¹, R1=0.0405 (for 7557 observed reflections), wR2=0.1070 (for 8170 unique reflections), S=1.043. The crystal structure of (2) had been previously reported [1]. Both structures were examined regarding structural helices virtually responsible for optical rotation along main directions of the appropriate gyration tensor. In the monoclinic structure only one direction is fixed by symmetry, [010], whereas the remaining two directions must be of [u0v] type. The helices have to be formed of atoms with high polarizability (here oxygen and nitrogen atoms) [2]. In (1) two structural helices were detected. One helix along *b* direction is formed of three distinct oxygen atoms of malic acid molecules repeated by 2₁ symmetry axis and connected by intermolecular O–H...O hydrogen bonds. The helix is turning anticlockwise coming towards the viewer (intramolecular distances between non-bonded oxygen atoms are in the range 2.215-3.198 Å). The second helix, non-symmetric, is directed along *c* and built of five distinct atoms: three oxygen atoms of malic acid, one oxygen and one nitrogen atoms of urea molecule. The helix contains two intermolecular hydrogen bonds of O–H...O and N–H...O types, one inter-(O...O) and two intramolecular (O...O, N...O) contacts. The helix is turning clockwise coming towards the viewer. The two helices are responsible for the optical activity of the crystals of (1). Two structural helices are also responsible for the optical activity of (2). The helices run along [110] and [-110] with the repeat distance of 16.746 Å. As related by mirror plane they have opposite handedness. The helices are formed by five intermolecular hydrogen bonds and few contacts of O...O, N...O and N...N (mainly intramolecular, of distances in the range 2.251-2.363 Å, and one intermolecular, O...O = 2.884 Å).

[1] Zhou Zhongyuan, Hu Guozhi, Tang Jinhua, Yu Kaibei, Jiang Guoji (1986). *Huaxue Xuebao* (Chin) (Acta Chim. Sinica). 44, 1045 (acc. CSD, FAXKOE).

[2] A. M. Glazer, K. Stadnicka (1986). *J. Appl. Cryst.* 19, 108.