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Observation of Uniaxial Negative Thermal Expansion in an Organic Crystal[**]

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In the past few years, crystal engineering has attracted ever-increasing interest.[1] This subject is concerned with the design of solids with specific, controlled properties. One such coveted property is negative thermal expansion (NTE). Several inorganic systems exhibiting NTE are known[2–4] but organic materials displaying NTE have very rarely been reported.[5] Here we show that the monohydrate of the dipeptide tryptophylglycine[6] (TrpGly · H_2O) crystallizes in a supramolecular helix that extends throughout the entire crystal, thus forming a peptide nanotube,[7] and that the thermal expansion along the helical axis is negative below room temperature.

The crystal structure of TrpGly · H_2O was investigated at 295 and 120 K using bending magnet synchrotron radiation at the Swiss–Norwegian Beam Line (SNBL at ESRF, France).[8] The single-crystal sample had dimensions 20 × 30 × 180 μm^3. In spite of the small size, data of high quality could be collected and refinements proceeded to an R_1(all) below 3.2 % at both temperatures. The molecular structure is shown in Figure 1.

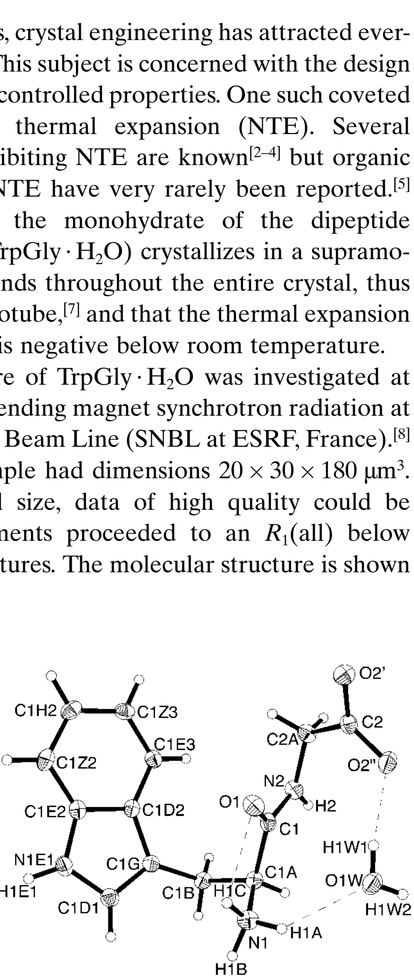

Figure 1. Structure of TrpGly · H_2O as determined at 120 K. Displacement ellipsoids are drawn at the 50 % probability level. Only the majority water site is shown. Hydrogen atoms involved in conventional hydrogen bonds are labeled. Dashed lines indicate hydrogen bonds.

The crystal structure is tetragonal and the peptide forms a helical structure parallel to the *c* axis. This helix, Figure 2, encloses a channel in which the water molecules are located. The peptide channel extends throughout the entire crystal and has approximate internal dimensions of 8.3 × 8.3 Å^2. The van der Waals accessible volume[9] is 80.5 and 76.8 Å^3 per unit cell at 295 and 120 K, respectively. The peptide helix thus forms a peptide nanotube occupied by water molecules. The

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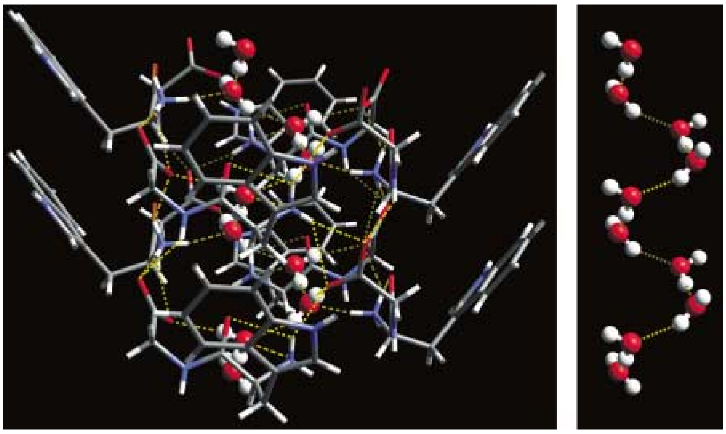

Figure 2. Supramolecular peptide helix parallel to the crystallographic *c* axis. Left: peptide helix enclosing the water helix. Right: water helix. Only the majority water site is shown.

water molecules are disordered at both temperatures. There is one majority site, shown in Figures 1 and 2, and several minor sites distributed in the channel. The minor sites all have slightly less favorable hydrogen-bond geometries than the majority site, which is connected to the peptide framework by a hydrogen bond. The occupation of the majority site, O1W, increases from 0.578(9) at 295 K to 0.693(11) at 120 K. The data were of sufficient quality to allow refining of the positions of all hydrogen atoms bound to hydrogen-bond donors. The strongest hydrogen bond in the structure is the charge assisted, three-center, $-N-H^{+}\cdots{}^{-}OOC-$, intermolecular hydrogen bond involving H1B (Figure 1). In line with the strength of this interaction, the N1−H1B bond is significantly longer than the other NH_3 bonds. Even more interesting, the hydrogen atom on the indole nitrogen atom of tryptophane is displaced out of the indole plane. Thereby a more linear, and hence stronger, hydrogen bond is formed.[10] This observation reflects the importance of refining hydrogen positions when high quality X-ray data are available.

The crystal structure of TrpGly$\cdot H_2O$ was recently determined independently of our investigation by using room temperature laboratory X-ray data on a crystal measuring $440 \times 120 \times 20\ \mu m^3$.[11] The microcrystal data presented here are of far better quality and provide much more detailed information on the structure.

The single-crystal data showed that the *c* lattice parameter expands when lowering the temperature. To investigate this unusual behavior, we undertook a study of the thermal expansion by powder diffraction using the MAR345 imaging plate at SNBL as the detector.[12] This approach allows for very rapid data collection[13] as a function of temperature. In the present case, 25 powder diagrams were measured between 270 and 120 K in only 75 min. The resulting temperature dependence of the lattice parameters is plotted in Figure 3. The thermal expansion along the *c* axis is negative in the entire range, but of much smaller absolute magnitude than that along the *a* axis. Therefore, the volume thermal expansion is positive. The data were fitted by Equation (1). The coefficients of thermal expansion thus obtained are $a_0 = 15.932(2)$ Å, $\alpha_a = 2.92(12) \times 10^{-5}\ K^{-1}$, $\alpha'_a = 1.2(2) \times 10^{-3}\ K^{-1}$, $c_0 = 5.2104(5)$, $\alpha_c = -0.106(10) \times 10^{-5}\ K^{-1}$, and $\alpha'_c = -1.92(7) \times 10^{-3}\ K^{-1}$. We propose that the water ordering is linked with the NTE. When the temperature is lowered, the enthalpy gain of water ordering starts to dominate the free energy and the occupancy of the favored major site increases. The increased localization of water molecules in the major site leads to an enhanced correlation along the *c* axis which in turn requires more space and results in NTE. This model is akin to the explanation of the expansion of ice relative to water. In this picture, it can be expected that when and if the water orders completely, the thermal expansion along the *c* axis will change sign. We are presently undertaking very low temperature diffraction studies to confirm this theory.

$$p(T) = p_0(1 + \alpha_p T(1 + \alpha'_p T)) \quad (1)$$

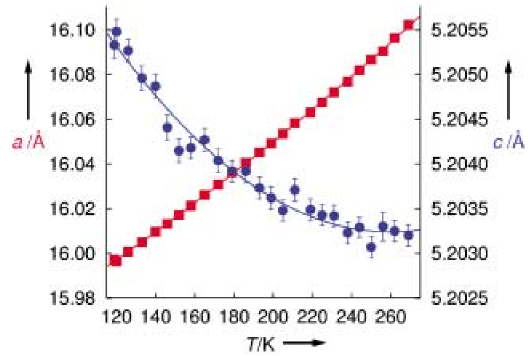

Figure 3. Temperature dependence of the independent tetragonal lattice parameters, *a* (red) and *c* (blue). Note the negative thermal expansion of the *c* axis.

In summary, we have shown that the crystal structure of TrpGly$\cdot H_2O$ consists of peptide nanotubes. These tubes contain water molecules, which gradually order upon lowering the temperature. This ordering is accompanied by negative thermal expansion along the tube axis. This study demonstrates how the combination of high quality single-crystal and powder diffraction data can provide valuable insight into the physical properties of materials. The use of synchrotron radiation greatly facilitates these studies and increases the attainable precision.

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Supramolecular Templating of the Double-Cubane $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]Cl_6$ (Hpz^{tBu} = 5-*tert*-Butylpyrazole)[**]

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While the $[M_4(\mu_3\text{-}X)_4]^{4+}$ (M = transition ion, X = anion or dianion) cubane structure is a common motif in transition metal chemistry and biochemistry, only a few examples of vertex-sharing double-cubane compounds are known.[1–8] We note in particular **1** (bipym = 2,2′-bipyrimidine), which is the only compound with this topology whose magnetochemical properties have been fully elucidated to date.[5] We report here a new example of a heptacopper double-cubane complex, **2**, whose molecular structure and magnetochemistry differ substantially from those of **1**. Moreover, the unusual structure of **2** is supported by a unique pattern of supramolecular cation:anion interactions.

$[\{Cu_3(bipym)_3(OH_2)(\mu_3\text{-}OH)_4\}_2Cu](NO_3)_6$ **1**

$[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]Cl_6$ **2**

Turquoise crystals of $\mathbf{2} \cdot 2\,CH_2Cl_2$ were grown from CH_2Cl_2/pentane mixtures.[9] The asymmetric unit of these crystals contains half a complex molecule with Cu(1) lying on a crystallographic inversion center, forming a $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]^{6+}$ double-cubane (Figure 1). The shared-vertex Cu(1) is ligated by six OH^- ligands, with an axis of Jahn – Teller elongation along the O(7)-Cu(1)-O(7′) vector. The other Cu ions exhibit tetragonal geometries, with two OH^- and two Hpz^{tBu} ligands in the basal plane and axial contacts to two Cl^- ions. Cu(3) and Cu(4) adopt almost identical geometries, with contacts of 2.7949(5) – 2.9129(6) Å to Cl(62) and one other Cl^- ligand. However, Cu(2) has a shorter distance of 2.5502(5) Å to Cl(62), and a much longer distance of 3.7433(6) Å to Cl(63) (not shown in Figure 1).

In addition to Cl(62) and its symmetry-generated equivalent, there are six Cl^- ions disposed in a ring around the heptacopper core of the molecule (Figure 2). Each of these Cl^- ions accepts three hydrogen bonds, from one OH^- and two Hpz^{tBu} N–H donors. Cl(64) and Cl(65) are in near-

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