Communication

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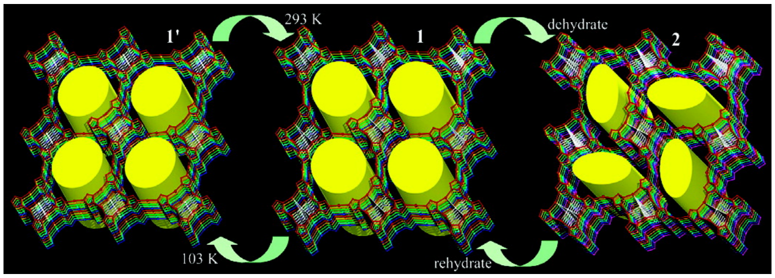

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Temperature- or Guest-Induced Drastic Single-Crystal-to-Single-Crystal Transformations of a Nanoporous Coordination Polymer

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Single-crystal-to-single-crystal transformations have received considerable interest in crystal engineering. However, only limited examples are known since crystals can hardly retain single crystallinity after the solid-state rearrangement of atoms.[1−5] Most of the reported cases involve the dimerization or polymerization of unsaturated molecules[2] or guest exchange of porous materials.[3−5] While retainable host frameworks are important for porous materials,[3] structural transformations of the frameworks triggered by guest exchange or physical stimulus are more interesting as such materials may serve as the next generation of porous materials, and different types of transformations, including sliding of layers and breathing of 3D networks, have been known. However, transformation of the network connectivity or physical stimulus-induced transformation is hitherto unknown for a porous coordination polymer.[4,5]

In our systematic investigation of the chemistry of metal triazolates involving in situ generation of the 3,5-disubstituted-1,2,4-triazolates from organonitriles, ammonia, and Cu(II) salts,[6] we extended our attention to monosubstituted 1,2,4-triazoles, such as 3-amino-1,2,4-triazole (Hatz). Slow evaporation of an ammonia solution of Hatz and AgCl gave colorless needlelike crystals of $[Ag_6Cl(atz)_4]OH\cdot6H_2O$ (**1**) in 80% yield. The formula of **1** was confirmed by the results of microanalysis, TGA, X-ray crystallography, and the control experiment (over 70% yield) by using $Hatz/Ag_2O/AgCl$ in a molar ratio of 8:5:2.

X-ray analysis[7] at 293 K reveals a linear and a bent 2-coordinated Ag^I atom, as well as a μ_3-atz ligand in **1**. Similar to a porous coordination polymer $[ZnF(atz)]\cdot$guest,[2b] the amino group in **1** is also 2-fold disordered by virtue of the crystallographic requirement ($I4_1/amd$). The $Ag_3(atz)_2$ framework represents a 3-connected 4.14^2 (dia-f) net regarding atz as 3-connected nodes and Ag^I as linkers (or 4-connected diamond net, regarding the cyclic $Ag_4(atz)_4$ subunits as flattened tetrahedral nodes and the remaining linearly coordinated Ag^I ions as linkers)[8] (Figure 1). The $Ag_3(atz)_2$ nets are parallel 5-fold interpenetrating along the *c*-axis and closely interlocked to each other, furnishing short inter-net Ag···Ag contacts (3.450 Å) and even shorter inter-net $\pi-\pi$ interactions (3.244 Å). It is very interesting that the chlorides are embedded between the $Ag_4(atz)_4$ subunits of adjacent $Ag_3(atz)_2$ networks, finishing infinite $(\mu\text{-Ag})_4(\mu_8\text{-Cl})$ chains (Ag···Cl 3.060 Å) running along the *c*-axis. In other words, the 5-fold interpenetrating $Ag_3(atz)_2$ nets are cross-linked by the weak Ag···Cl bonds to a single network in **1**. The $(\mu\text{-Ag})_4(\mu_8\text{-Cl})$ chains are constructed by face-sharing $Ag_8(\mu_8\text{-Cl})$ cubes, such an extended $M_8(\mu_8\text{-halide})$ structure has not been reported so far, though few discrete halide-centered M_8 cubic clusters are known to exhibit unusual bonding characteristics.[9] Although **1** represents the highest level of interpenetrated 4.14^2 nets[7] and its openings along the *a*- and *b*-directions are fully occupied, there are still large 1D columned channels in the *c*-direction, accommodating the disordered HO^- or H_2O guests. Taking the van der Waals radii into consideration, we estimate the diameters of these channels to be ca. 8.5 Å and the guest accessible volume to be ca. 32.7%.

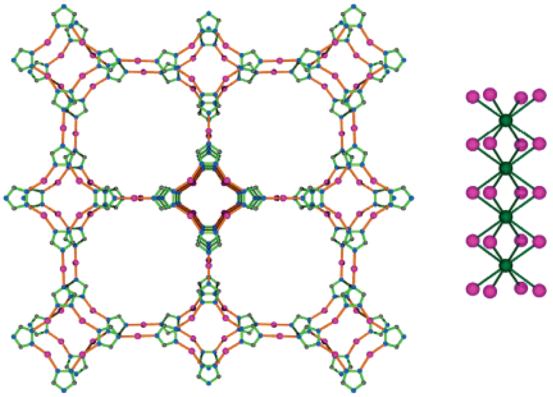

Figure 1. Views of a single $Ag_3(atz)_2$ net (amino groups are omitted for clarity) along the *c*-axis (left) and a $(\mu\text{-Ag})_4(\mu_8\text{-Cl})$ chain in **1** (right).

Tetragonal **1** can be transformed to orthorhombic **1′** (*Fddd*) at 103 K.[7] The amino groups were still 2-fold disordered, and the net connectivity remained unchanged in **1′**, but the channels are slightly elliptical (ca. 7.8 Å × 9.2 Å). The most significant structural change is that the Ag_4 squares (Ag···Ag 3.575 Å) in the $Ag_4(atz)_4$ subunits of **1** are deformed into Ag_4 rhombi (Ag···Ag 3.591 Å, Ag···Ag···Ag 79.7 and 100.3°) in **1′**. Hence, the uniform Ag···Cl interactions in **1** are split into two distinct types in **1′** (Ag···Cl 3.242 and 2.863 Å). Single-crystal diffractions of different single crystals of **1** indicated that the tetragonal cell could be derived down to 240 K. As the temperature was further decreased, no cell parameters could be determined over a temperature range of 240−120 K, although the sharp and strong diffractions were observed. Notably, the orthorhombic phase could only be obtained after decreasing the temperature to 103 K for ca. 8−10 h. When **1′** was heated from 103 to 293 K, it slowly transformed back to **1**. Therefore, the transformation between single crystals of **1** and **1′** were slow and reversible. Although accurate determination of the transition temperature failed using low-temperature PXRD technique because the PXRD patterns of **1** and **1′** are only slightly different, low-temperature DSC analysis did show a reversible transformation in the temperature range of 220−260 K.

TGA revealed that **1** could lose all H_2O guests above 375 K and did not show further weight lost until 580 K. **1** could also readily lose water in dry air. However, the PXRD pattern of the desolvated product was different from that of **1**. Fortunately, we were able to determine the crystal structure of the partially desolvated product $[Ag_6Cl(atz)_4]\cdot OH\cdot xH_2O$ (**2**, $x \leq 2$) at 293 K by placing **1** in a very slow stream of dry air or heating **1** at 375 K for 3 h, and it was found that a better crystal data set could be obtained by the former method. **2** possessed a new tetragonal structure ($P\bar{4}n2$),[7] whose crystal cell was related to the reduced cell of **1** and **1′**. The linear

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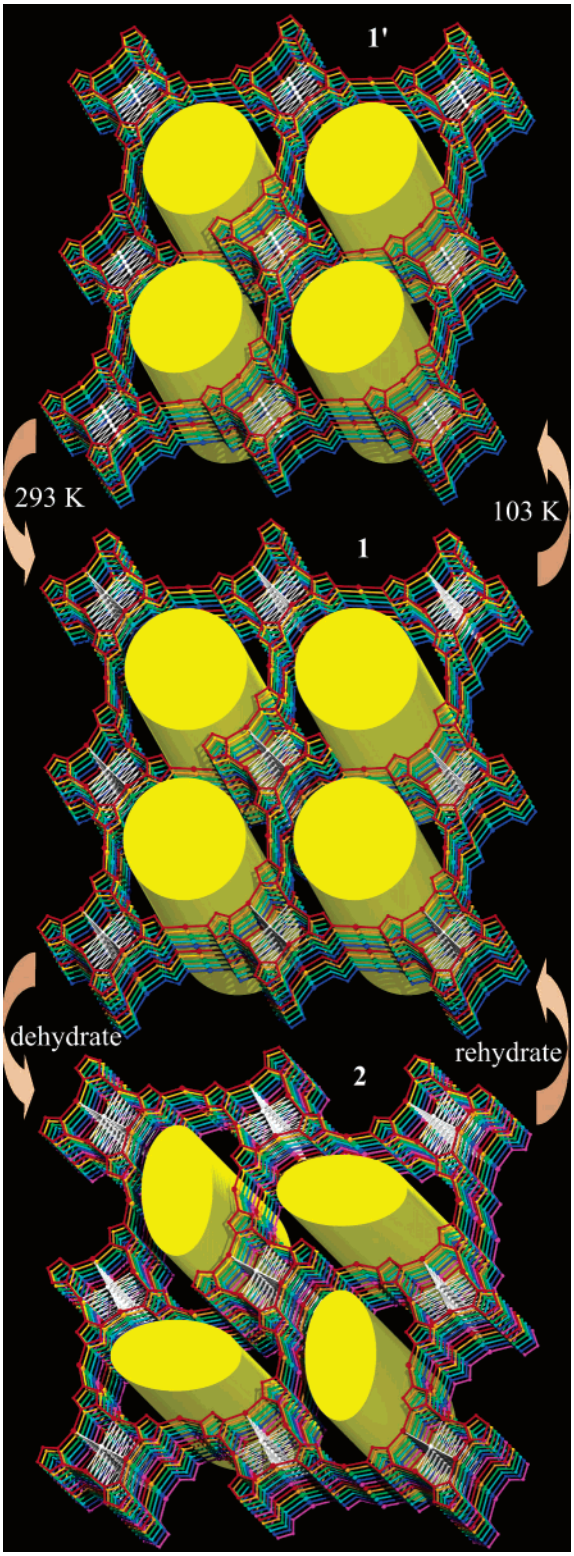

Figure 2. Interconversion of the $[Ag_6Cl(atz)_4]$ host of **1**, **1′**, and **2** (amino groups and guests are omitted for clarity, 1D channels are highlighted as yellow columns).

Ag^I coordinations in both **1** and **1′** are now bent in **2**, forming weak interactions (Ag···O 2.719 and 2.823 Å) to the disordered HO^- or H_2O guests. The guest accessible volume of **2** is reduced to 25.2%, and the 1D channel is now very elliptical (4.3 Å × 10.4 Å). Although the host framework of **2** is dramatically distorted from that of **1**, the 4.14^2 topology of the $Ag_3(atz)_2$ net is retained with similar structural parameters (Ag···Ag 3.552 Å, Ag···Cl 3.053, 3.070 Å) of the infinite $Ag_4(\mu_8\text{-}Cl)$ chain. However, the $Ag_3(atz)_2$ nets in **2** now exhibit 6-fold interpenetration! Obviously, the transformation of **1** to **2** requires not only distortion of the nets but also Ag^I−ligand bond cleavages and formations. On the basis of the structural relationship between **1** and **2**, we reasoned that this rearrangement should occur at the linear Ag^I ions of **1**, and the OH^- or H_2O guests may coordinate to these Ag^I ions to form intermediate structures (see Supporting Information for details). Upon exposure to saturated water vapor for 1 day, powder **2** could give the PXRD pattern of **1**. Single crystals of **2** could also be reversely converted back to single crystals of **1**, though only the crystal cell of **1** could be determined. Meanwhile, no temperature-induced phase transition was observed for **2** at low temperature.

In conclusion, the nanoporous material exhibits unprecedented temperature-induced structural transformation and guest desorption/absorption-triggered 3D net rearrangements between 5- and 6-fold interpenetrations.

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Supporting Information Available: Additional figures and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data for **1** $[Ag_6Cl(atz)_4]\cdot OH\cdot 6H_2O$: 293(2) K, tetragonal $I4_1/amd$, $a = 29.601(4)$ Å, $c = 3.4496(3)$ Å, $V = 3022.5(5)$ Å^3, $Z = 4$, $D_c = 2.505$ g cm^{-3}, final $R_1 = 0.0507$ ($I > 2\sigma$), $wR_2 = 0.1318$ (all data), $S = 1.006$; **1′** $[Ag_6Cl(atz)_4]\cdot OH\cdot 6H_2O$: 103(2) K, orthorhombic $Fddd$, $a = 3.4099(2)$ Å, $b = 39.805(3)$ Å, $c = 43.607(3)$ Å, $V = 5918.9(7)$ Å^3, $Z = 8$, $D_c = 2.559$ g cm^{-3}, final $R_1 = 0.0668$ ($I > 2\sigma$), $wR_2 = 0.1677$ (all data), $S = 1.034$; **2** $[Ag_6Cl(atz)_4]\cdot OH\cdot 2H_2O$: 293(2) K, tetragonal $P\bar{4}n2$, $a = 19.598(2)$ Å, $c = 3.5015(4)$ Å, $V = 1344.8(2)$ Å^3, $Z = 2$, $D_c = 2.638$ g cm^{-3}, final $R_1 = 0.0879$ ($I > 2\sigma$), $wR_2 = 0.2493$ (all data), $S = 1.022$ using TWIN instruction of SHELXTL. Cell parameters for the fully dehydrated sample of **2**: $a = 19.358(2)$ Å, $c = 3.513(2)$ Å.

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