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Guest-Induced Conformational Switching in a Single Crystal**

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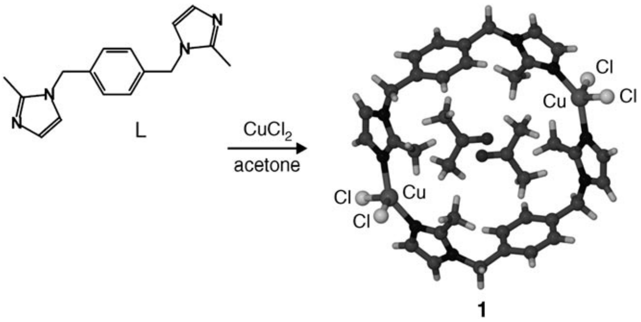
One of the defining characteristics of the crystalline state is that atoms are generally considered to be frozen in place, each with only a modest ability to vibrate about its well-defined equilibrium position. Although solid-to-solid phase transformations as a result of a variety of physical or chemical factors are well known, it is rare for individual crystals to survive such processes by retaining their mosaicity.[1] Considerable mechanical stress is thought to occur at the boundary of two interconverting phases,[1a] particularly if the two phases are incompatible in packing periodicity. Therefore, in order for a crystal to maintain its monocrystallinity during transformation, it seems reasonable either that the structural changes to the principal framework must be insignificant, or that the molecules must cooperate[1d,2] in a concerted fashion as they undergo positional and/or topological reorganization. In this regard, a number of recent reports have advocated the phenomenon of cooperativity in order to account for the apparent fluidity of crystalline building blocks during the uptake or release of solvent molecules, with concomitant rearrangement of the host lattice as a single-crystal transformation.[1d,2,3] These studies have involved relatively small changes of molecular conformation in systems possessing conceptually infinite rigid assemblies.[1b–g,2–4] Furthermore, these reports describe structural switching between only two states.

Crystal engineering[5] encompasses both the "synthesis" and modification of structures. In recent years, the principles of this burgeoning field have been applied vigorously to the design of new porous functional materials[6] with a view to mimicking and even surpassing the important properties of zeolites.[7] Targeted applications include catalysis,[8] as well as the storage,[9] separation,[10] and sensing[1a,11] of molecules. To date, most studies have focused on so-called "soft materials" (that is, organic[1d,10b,12] or metal–organic[1b,c,g,2,3,4b–e] systems), owing to their vast potential for structural diversity.

A common strategy for engineering porous crystals is to first prepare a solvent-templated structure and then to extract the solvent molecules without causing collapse of the resulting metastable apohost framework. Desolvation of molecular (that is, 0D) solids generally results in reorganization of the host molecules into a densely packed nonporous phase,[13] whereas metal–organic frameworks (MOFs) have been shown to maintain structural integrity because of their intrinsic long-range rigidity.[6a] Nevertheless, some MOFs undergo structural modifications in one or more of the following forms: 1) lateral sliding of neighboring layers relative to one another,[3,4d] 2) adjustment of the interlayer spacing,[1b] 3) distortion of 2D or 3D grids,[1b,14] and 4) conformational changes of their components.[4b] In several recently reported cases where such structural changes have been observed, MOF crystals have been shown to retain their macroscopic integrity.[1b,c,g,3,4c,d]

Although useful for characterization of the different phases by means of powerful diffraction techniques, single crystals are generally not required for applications such as catalysis, storage, and separation. On the other hand, if an engineered crystal is to be incorporated into a device such as a substrate-triggered sensor, fully reversible phase transformations with retention of monocrystallinity would be essential for repeated operation. It is therefore of considerable importance to study the processes that govern cooperative fluidity in dynamic crystals with a view to gaining better insight into the fascinating phenomenon of single-crystal transformations.

Our approach to producing porous crystals involves the use of discrete "donut-shaped" dinuclear metal–organic complexes[15] that cannot pack efficiently owing to their lack of self-complementarity in shape.[16] When crystallized from a suitable solvent, these complexes usually enclose appropriate solvent molecules into their apertures. Desolvation necessarily results in the formation of voids or channels if the host complexes retain their shape. As part of our ongoing studies, crystals composed of neutral molecular rectangles were obtained by slow evaporation of an equimolar solution of 1,4-bis[(2-methylimidazol-1-yl)methyl]benzene (L) and $CuCl_2 \cdot 2H_2O$ in acetone (Scheme 1). A single-crystal X-ray diffraction analysis revealed that the coordination geometry about each copper ion is tetrahedrally distorted square-planar. Discrete metallacyclic complexes are eclipsed and stacked parallel to the crystallographic *a* axis to form



Scheme 1. Formation of $[Cu_2Cl_4L_2] \cdot 2(CH_3)_2CO$ (**1**); N black.

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conceptually infinite tubules (see Supporting Information). The resulting channels are occupied by occluded acetone molecules, such that each dinuclear complex enshrouds two molecules (see **1** in Figure 1) to form an efficiently packed binary structure. The acetone templating effect in **1** is inferred from the presence of weak C–H···O hydrogen bonds between the ligand methyl groups and the solvent carbonyl oxygen atoms.

Thermogravimetric analysis shows that desolvation (that is, loss of acetone) occurs at room temperature. Our attempts to obtain a porous material by desolvation involved either heating crystals at 70°C for approximately one hour or exposing them to high vacuum for three hours. During desolvation of **1** by either method, the crystals remained transparent, although their color transformed from light brown to light green. No fracturing was evident and it was therefore possible to determine the structure of the desolvated phase (**2**) by single-crystal X-ray diffraction analysis. In contrast to our previous findings involving analogous dinuclear complexes,[16] the host molecules in **2** undergo significant conformational changes as a result of desolvation and reorganization. The molecular rectangles collapse to assume an "imploded" conformation (Figure 1) with loss of the guest-templated aperture. Implosion of the complex occurs by means of elongation of the intramolecular Cu···Cu distance from 10.2 Å in **1** to 13.3 Å in **2**, with corresponding adjustment of the N-Cu-N angles from 147.2 to 90.1°. Loss of the molecular aperture, in conjunction with spatial rearrangement of the conformationally altered host molecules, results in shrinkage of the crystal volume by approximately 17%.

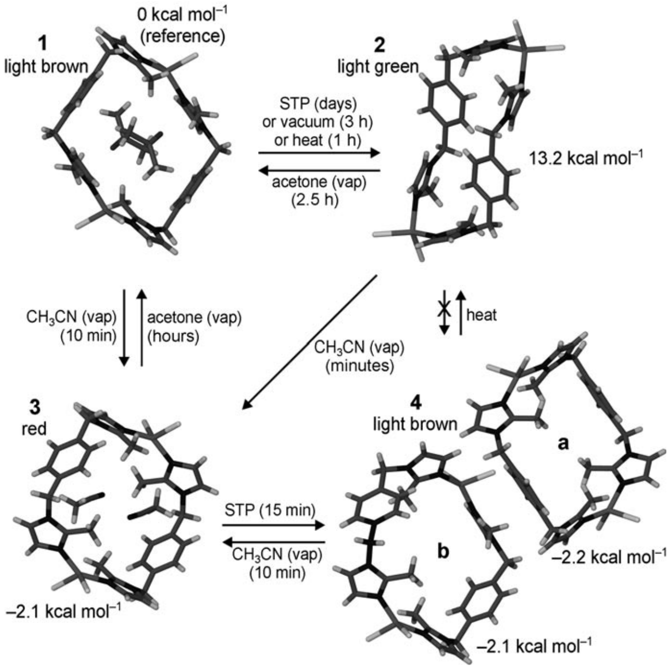

Figure 1. Capped-stick projections of the molecules in phases **1** to **4** viewed along [100]. Conditions for interconversion of the various structures are indicated (vap: vapor, STP: ambient conditions). Calculations were performed at the nonlocal DFT level of theory with the B3LYP/LANL2DZ basis set. Computational details are included in the Supporting Information.

Upon exposure of **2** to acetone vapor for 2.5 h, the crystals reversibly transformed back to phase **1** with stoichiometric uptake of the solvent. Once again the bulk integrity of each individual crystal was maintained (as confirmed by successful single-crystal X-ray diffraction analysis) and the color reverted back to light brown. In a subsequent experiment, exposure of **2** to acetonitrile vapor for several minutes resulted in a change in color to red, again with no apparent fracturing of the individual crystals. Single-crystal X-ray diffraction analysis revealed that a third phase (**3**, Figure 1) is formed upon stoichiometric uptake of acetonitrile. The host complex reconforms to once again yield a rectangular complex that enshrouds two molecules of acetonitrile. The packing mode is similar to that observed for **1**. However, examination of the complex in **3** reveals that, although metrically similar to that in **1**, the conformation of the bridging ligands is quite different, especially with regard to the relative positions of the methyl substituents of the imidazole groups (Figure 2).

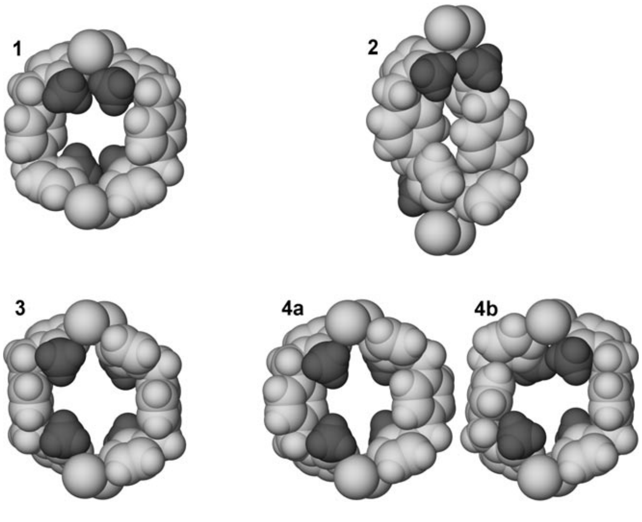

Figure 2. Space-filling projections of the metal complexes in phases **1** to **4**. The methyl groups on the imidazole moieties are darkened to highlight the most significant conformational differences.

In phases **1**–**3**, the metal complexes are all situated on crystallographic inversion centers with half of the complex unique in each case. In all three cases, two methyl substituents on the imidazole moieties are situated on one side of the mean plane of the dinuclear complex, while the remaining two methyl groups are situated on the opposite side of this plane. With reference to the projections in Figure 2, we can refer to the methyl groups as "U" or "D" if they are directed up or down, respectively. Starting with the upper-left methyl group and proceeding in a clockwise direction, the conformation of **1** with respect to the orientations of the methyl groups can be expressed as UUDD. Although the ligand conformation changes significantly during the transformation from **1** to **2**, the positions of the methyl groups relative to the metallacyclic complex are retained as UUDD. However, the conformation in **3** is UDDU, and comparison of the relative positions of the methyl substituents of the complexes in **1** and **3** shows the most notable difference to be rotation of two of the imidazole groups by approximately 120° about their Cu–N vectors.

Phase **3** can be also be obtained directly from phase **1** by exposure of the latter to acetonitrile vapor for approximately 10 min. The single-crystal integrity is maintained and X-ray diffraction analysis showed that acetone is exchanged for acetonitrile. This process can be reversed, although not as readily as the transformation from **1** to **3**; that is, exposure of **3** to acetone vapor requires several hours for reversion to phase **1** as a single-crystal transformation. When crystals of **3** are exposed to atmospheric conditions for approximately 15 min, transformation to yet a fourth phase (**4**, Figure 1) occurs, again with maintenance of the macroscopic integrity of the crystals.

Single-crystal X-ray diffraction analysis revealed the presence of two different conformations of the metallacyclic complex in **4**. Although one of these conformations (**4a**) is similar to that of **3** with regard to the relative positions of its methyl substituents (UDDU), the angle of the phenylene ring of the ligand with respect to the mean plane of the coordinated nitrogen atoms is significantly different (70.3° in **3** and 114.9° in **4a**). The second conformation (**4b**) of the complex present in **4** is unlike any of the conformations observed in **1** to **3**. This new conformation is DUDU and does not possess inversion symmetry. In an attempt to rationalize the transformation from **3** to **4**, it is interesting to consider the two distinct complexes in **4** in relation to two corresponding molecules in **3**. A projection of two neighboring molecules in **3**, related to one another by a crystallographic 2_1 screw axis, is shown in Figure 3, and it seems reasonable to suggest that these molecules correspond to the two crystallographically distinct molecules in **4**, which are also shown in Figure 3. Apart from rotation of the phenylene group of the ligand, as described above, there is little change in the conformation or the relative position of the molecule at the upper left. However, the second molecule undergoes a transition from its original conformation, but only by rotation of its imidazole groups at one end (its upper left-hand side, as shown in Figure 3). Energetically, the DUDU conformation of **4b** and the UDDU conformation of **3** differ by less than 0.01 kcal mol^{-1}.

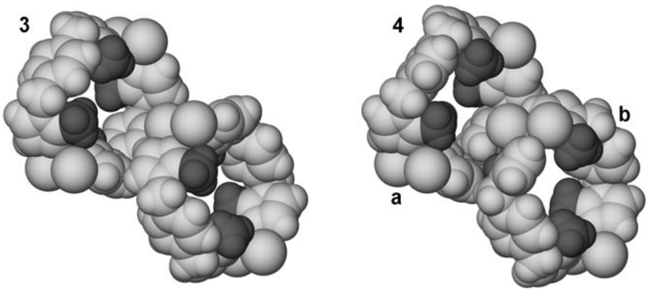

Figure 3. Space-filling projections of the metal complexes in phases **3** and **4**, showing the positional relationships of **4a** and **4b** with respect to their counterparts in **3**. The methyl groups on the imidazole moieties are darkened to highlight the most significant conformational differences.

The orientations of the methyl groups on the two imidazole moieties represent the most dramatic conformational attributes of the ligand, while the angle of the phenylene spacer group is a comparatively minor structural characteristic. The series of interconvertible structures described herein encompasses all the possible permutations of major conformational features that the dinuclear complexes can possess, with the exception of UUUU. The near completeness of a set of mutable structures is an important consideration for further study of monocrystalline conformational switching aimed at understanding why only a small number of crystals appear to have this remarkable ability.

Chromatic changes in single crystals are potentially important phenomena that can be implemented in gas- or vapor-sensing devices.[1a] A single-crystal transformation accompanied by a vapochromic response can easily be rationalized when changes in the composition of the coordination sphere occur.[1a,f] However, Lee and Suh have recently demonstrated that alteration of only the geometry of the coordination sphere can also result in vapochromism, although a simple explanation for this has not yet been postulated.[1c] To date, conformational switching of a structure between only two states has been reported for several systems possessing long-range rigidity (extensively hydrogen-bonded networks, 2D layers, or infinite 1D, 2D, and 3D frameworks that allow rows or sheets of molecules to move in unison).[1b–f,2–4] However, monocrystalline switching between four (and possibly even more) states, as described herein, is unprecedented, as is the magnitude of the conformational changes that we have described. It seems self-evident that a significant level of cooperation must occur between the contorting molecules within the crystal in order for such large conformational changes to be accommodated without catastrophic disruption of the packing continuity.

In summary, we have described the single-crystal to single-crystal interconversion of four distinct molecular crystal forms consisting of neutral, dinuclear metal complexes. During uptake and release of solvent vapors, the host molecules undergo significant conformational, positional, and topological changes, each of which is accompanied by a vapochromic response. Moreover, these monocrystalline transformations are reversible and meet the requirements for the development of functional devices based upon structural modification of "soft" crystalline materials as an extension of the field of crystal engineering.

Experimental Section

1,4-Bis[(2-methylimidazol-1-yl)methyl]benzene was synthesized by the S_N2 reaction of 2-methylimidazole with α,α′-dichloro-*p*-xylene. Crystal data can be found in the Supporting Information. CCDC-602877, CCDC-602878, CCDC-602879, and CCDC-602880 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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