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Single-Crystal Transformations

Dimerization of a Metal Complex through Thermally Induced Single-Crystal-to-Single-Crystal Transformation or Mechanochemical Reaction**

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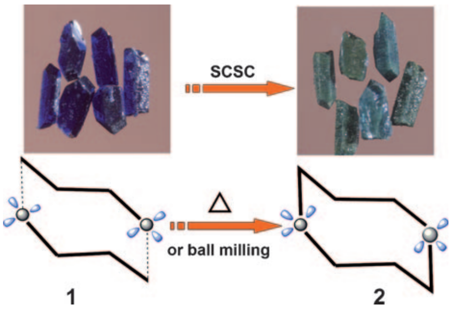
Single-crystal-to-single-crystal (SCSC) transformations, which involve cooperative movement of atoms in the solid state, have received much attention from chemists.[1] Through SCSC transformation, new complexes, which may not be obtained under conventional conditions, can be obtained in high yield. The SCSC transformation was first reported as a photoreaction in organic complexes, which could be considered as a new organic synthetic method.[2] Solid-state photochemical [2+2] cycloadditions of organic molecules have been well studied.[3] Recently, SCSC transformation has been extended to other complexes, such as metal complexes and coordination polymers (or metal–organic frameworks). In the past decades, many metal–organic frameworks (MOFs) that undergo SCSC transformation have been reported.[4] Most of these reports describe the sliding of layers or breathing of 3D porous MOFs through solvent exchange.[5] SCSC transformations involving breaking and forming bonds in the solid state remain quite rare.[6] The MacGillivray and Foxman groups attained considerable success in solid-state photodimerization of organic groups mediated by metals.[7,8] Converting a finite metal complex into an infinite coordination network was also reported by the groups of MacGillivray and Vittal.[9] The reported topochemical dimerizations of metal complexes involve the organization of two double or triple bonds in the solid state: the geometric criteria are very important for such SCSC reactions.[10] However, the coordination geometry of the metal ion remains unchanged in these topochemical dimerizations. More recently, zur Loye and co-workers described a 3D cobalt–organic framework exhibiting reversible shrinkage and expansion involving a change in the cobalt coordination geometry through SCSC transformation induced by the removal and re-absorption of guest molecules.[11] Studies on the change in the metal coordination geometry caused by the removal and addition of ligands from the framework itself through SCSC transformation remain less common.

Herein, we describe a new type of SCSC dimerization of a mononuclear copper complex, specifically, thermally induced head-to-tail dimerization involving the formation of a new Cu$-$O$_{\text{ligand}}$ bond and a change in the metal coordination geometry. The transformation induced a color change from blue to green, which was caused by the change in the copper coordination geometry (Scheme 1). Interestingly, the transformation could also be achieved by mechanochemical reaction, which is a newly developed method in the construction of metal–organic frameworks.[12] Although many examples of metal–organic frameworks synthesized by dry or liquid-assisted grinding have been reported, dimerization of metal complexes by dry grinding has never been documented.



Scheme 1. Thermally induced SCSC dimerization of a copper complex. The dashed line in **1** represents the distance between the uncoordinated carboxy oxygen atom and the central copper ion in two monomers, and the blue ellipsoids in **1** and **2** represent the coordinated small molecules.

Structural transformation in an SCSC manner involving breaking and forming of bonds is an uncommon phenomenon in coordination chemistry and solid-state chemistry. Through

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SCSC transformation, the structure becomes more stable. A 3D zinc coordination polymer, which could be transformed from a 2D polymer through thermal SCSC transformation, has been reported by our group.[13] We now report a mononuclear copper complex $[Cu(NH_3)_3(\mathbf{L}^6)]\cdot(H_2O)_{0.66}$ (**1**) ($H_2\mathbf{L}^6$ = 2,2′-(1,2-phenylenebis(methylene))bis(sulfanediyl)-dibenzoic acid). This complex could be dimerized to form a binuclear complex with an altered copper coordination geometry through thermal SCSC transformation or solid-state reaction under dry grinding conditions.

Blue crystals of **1** were obtained by slow evaporation of a solution of H_2O/MeOH containing $Cu(NO_3)_2\cdot 5\,H_2O$, $H_2\mathbf{L}^6$, and $NH_3\cdot H_2O$ at room temperature. The formula of $[Cu(NH_3)_3(\mathbf{L}^6)]\cdot(H_2O)_{0.66}$ was determined by combination of X-ray single-crystal structure analysis, thermogravimetric analysis, and elemental analysis.

Complex **1** crystallizes in the trigonal space group $R\bar{3}$. The asymmetric unit of **1** consists of one copper cation, one deprotonated $\mathbf{L}^6$ ligand, three coordinated ammonia molecules, and an uncoordinated water molecule with two-thirds occupancy. The copper ion is coordinated by one oxygen atom from the carboxylate group of $\mathbf{L}^6$ and three ammonia molecules in a square-planar geometry (Figure 1, left). The Cu−O bond length and the average Cu−N bond length are 1.968(5) and 2.031(7) Å, respectively. The $\mathbf{L}^6$ ligand adopts an *anti* conformation with the average dihedral angle between the side benzene rings and the central benzene ring being 88.95°, which is quite different from previous results.[14] One of the carboxylate groups adopts a monodentate mode to coordinate one copper ion, and the remaining carboxylate group does not take part in coordination but rather provides the hydrogen-bond acceptor. The hydrogen-bonding interactions between the coordinated ammonia molecules in one monomer and the uncoordinated carboxylate groups in a neighboring monomer (N⋯O distance: 2.835 Å) connect the mononuclear copper complexes to a double-helical chain (Figure S2 in the Supporting Information) with a pitch of 27.24 Å. The existence of weak CH⋯π interactions (3.8 Å) between the two helical chains further stabilizes the double-helical chain. Six double-helical chains are connected to one another through N⋯O hydrogen-bonding interactions to generate a one-dimensional hexagonal tubular subunit with the dimensions of 6.3 × 6.3 Å (from atom to atom). In the 1D tube, the left- and right-handed double-helical chains alternate and are present in equal proportions, resulting in an achiral structure. The tube is occupied by uncoordinated water molecules in a single-file arrangement (Figure S3 in the Supporting Information).

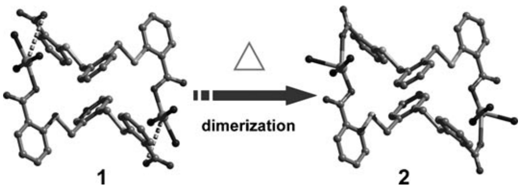

Figure 1. The SCSC dimerization, showing that the monomers of **1** were transformed into the dimer of **2**.

In the 3D packing, every two monomers of **1** are in a head-to-tail arrangement. The distance between the copper ion in one monomer and the oxygen atom of the uncoordinated carboxylate group in the next monomer is 3.796 Å, which is comparable to the distance for a [2+2] photoreaction in a solid[10a] but is shorter than other examples involving SCSC transformations from 2D to 3D.[13] This separation may satisfy the distance criterion for SCSC transformation involving the formation of new coordination bonds.

Differential scanning calorimetry of **1** reveals that the phase transformation occurred at 175.7 °C, thus indicating that a new phase may have been generated. To explore this possibility, as-synthesized crystals of **1** were subjected to a heating–cooling program. The crystals were structurally analyzed by single-crystal X-ray diffraction. Heating **1** to 176 °C for 15 min yielded **2**. The process was accompanied by a color change (blue to green).

The structural determination of **2** reveals that the crystal system, the space group, and the asymmetric unit remained the same as those of **1** (Table 1). However, SCSC dimerization occurred during the process (Figure 1). The most significant structural change is that the monomer of **1** dimerized to form a 30-membered metallomacrocycle, and the coordination geometry of the copper ion also changed from square-planar in **1** to square-pyramidal in **2**. Two nitrogen atoms from coordinated ammonia molecules and two carboxylate oxygen atoms from two $\mathbf{L}^6$ ligands comprise the equatorial plane, while another ammonia molecule occupies the axial position. The axial Cu−N bond (2.401 Å) is extremely elongated compared with the equatorial Cu−N bonds (2.032 and 1.977 Å). The average Cu−O and Cu−N bond lengths in **2** are 1.947(5) and 2.151(7) Å, respectively, which are slightly different from those in **1**. The average dihedral angle between the side benzene rings and the central benzene ring of the $\mathbf{L}^6$ ligand is 86.35°, which is slightly smaller than that in **1**. The central copper ion and one of the coordinated nitrogen atoms are disordered in **2**, and the discussion and the figures are based on the atoms with higher occupancies.

Table 1: Crystal data for complexes **1** and **2**.

	1	**2**
empirical formula	$C_{66}H_{48}Cu_3N_9O_{13}S_6$	$C_{132}H_{96}Cu_6N_{22.3}O_{29}S_{12}$
formula weight	1558.11	3224.55
crystal system	trigonal	trigonal
space group	$R\bar{3}$	$R\bar{3}$
a [Å]	30.31(4)	29.8177(16)
b [Å]	30.31(4)	29.8177(16)
c [Å]	13.74(2)	13.6808(14)
V [Å^3]	10932(26)	10533.9(14)
Z	6	3
ρ_{calcd} [g cm^{-3}]	1.420	1.525
GOF	1.003	1.075
$F(000)$	4872	4926
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0787, 0.2376	0.0699, 0.1906
$R1$, $wR2$ (all data)	0.1262, 0.2711	0.1031, 0.2141

The dimers of **2** are further connected by hydrogen bonds between the coordinated ammonia molecules and the coordinated or uncoordinated carboxy oxygen atoms (N⋯O distance: 2.777 Å) to generate a 1D double-helical chain, which is slightly different from that in **1** (see Figure S6 in the Supporting Information). The shape of the tubular subunit and the arrangement of the uncoordinated water molecules in the tube remained unchanged relative to those of **1**. Complex **2** could not be reverted back to **1**, even after immersion of crystals of **2** in mother liquor for several days. This finding indicates that the SCSC dimerization is irreversible. Attempts to synthesize complex **2** under conventional conditions failed, thus further indicating that SCSC transformation is a feasible method in the synthesis of new coordination complexes.

As mentioned above, another effective synthetic method in the construction of coordination complexes is mechanochemical synthesis, which has developed rapidly in recent years owing to its low environmental impact and high efficiency. Friščić and co-workers systematically studied mechanochemical synthesis in the construction of metal–organic frameworks or zeolitic imidazolate frameworks.[15] Very recently, supramolecular catalysis in the organic solid state through dry grinding was also studied by MacGillivray and co-workers.[16] The dimerization of metal complexes through solid-state reaction under grinding conditions remains unexplored.

Considering the arrangement of the monomer in **1**, its transformation to **2** through mechanochemical reaction was examined (Figure 2). A weighed amount (138.5 mg) of **1** was used in this study. The ball milling of **1** was done at 20 Hz for 30 min in a QM-3B shaker mill with a 20 mL steel vessel, a 10 mm steel ball, and ten 2 mm steel balls. This procedure resulted in a color change from blue to light gray-blue. Powder X-ray diffraction reveals that the transformation from **1** to **2** occurred, although the diffraction pattern is weak, since the sample partly lost crystallinity during the ball milling (Figure 3).

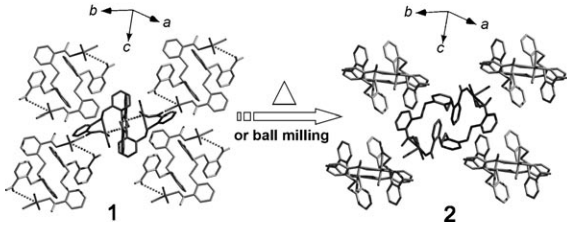

Figure 2. The transformation of **1** to **2** through two different methods: thermal SCSC and solid-state reaction under grinding.

In summary, the monomeric copper complex (**1**) was synthesized using a flexible dicarboxylate ligand. Complex **1** possesses a 3D supramolecular architecture containing 1D tubular subunits composed of double-helical chains. Complex **1** can be transformed into complex **2** through SCSC dimerization, with a change in copper coordination geometry but not in symmetry. The color also changed from blue to green; this change indicates that the transformation may have potential application in sensing devices. The current results represent the first example of thermally induced dimerization of a metal complex by SCSC transformation involving change in the coordination geometry of the metal ion. The transformation from **1** to **2** could also be achieved by solid-state reaction under dry grinding, which represents the first dimerization of a metal complex through mechanochemical reaction. In **1** and **2**, all of the uncoordinated water molecules are in a single-file arrangement in the 1D tubular subunit. This structure may be used to build a new model for mimicking biological structures involved in transmembrane transport of small molecules and ions.[17]

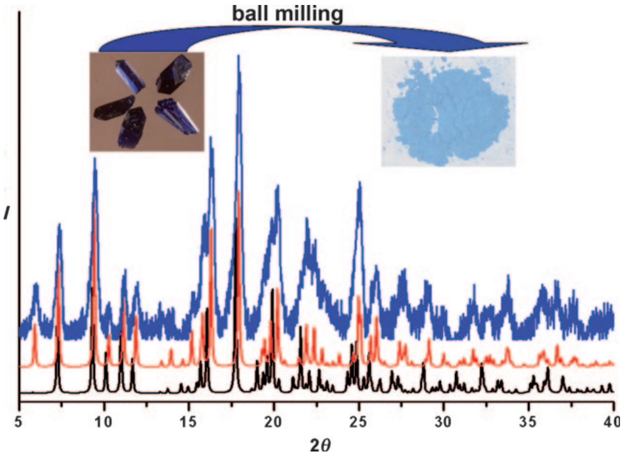

Figure 3. XRPD patterns for complexes **1** and **2**. Black **1** (simulated); red **2** (simulated); blue ball milling of **1** for 30 min. Pictures show the sample before (left) and after (right) ball milling.

Experimental Section

1: NaOH (0.1 mL, 1.1 M) was added to a suspension of H_2L^6 (0.015 g, 0.037 mmol) in H_2O (1 mL) to give a clear solution. $Cu(NO_3)_2{\cdot}2.5\,H_2O$ (0.045 g, 0.019 mmol) in MeOH (9 mL) was added to the clear solution, upon which lots of blue precipitate formed immediately. $NH_3{\cdot}H_2O$ (0.1 mL, 25–28%) was added to generate a blue solution, which was filtered and transferred to a test tube. After slow evaporation at room temperature for two weeks, large blue crystals of **1** were formed (yield: 47%). Elemental analysis calcd (%) for **1**: C 49.39, H 4.96, N 7.85; found: C 49.21, H 4.54, N 7.69%.

Transformation of **1** to **2**: Method 1 (SCSC transformation): Blue crystals of **1** were heated at 176 °C for 15 min in an oven, which led to green crystals of **2**. The structure of **2** was determined by single-crystal X-ray diffraction. Method 2 (mechanochemical reaction): Complex **1** (138.5 mg) was ground with a QM-3B shaker mill in a 20 mL steel vessel with a 10 mm steel ball and ten 2 mm steel balls at 20 Hz for 30 min. The color of the product changed from blue to light gray-blue. The structural transformation was confirmed by comparison of its XRPD pattern with a pattern simulated from single-crystal X-ray data.

X-ray crystallography: Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source ($Mo_{K\alpha}$ radiation, graphite monochromated). Structures were solved by direct methods using SHELXTL and were refined by full matrix least squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. CCDC 792534 (**1**) and 792535 (**2**) 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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