Crystal Engineering

Thermally Triggered Solid-State Single-Crystal-to-Single-Crystal Structural Transformation Accompanies Property Changes

Quan-Quan Li, Chun-Yan Ren, Yang-Yang Huang, Jian-Li Li, Ping Liu,* Bin Liu, Yang Liu, and Yao-Yu Wang^[a]

Abstract: The 1D complex [$(CuL_{0.5}H_2O)-H_2O]_n$ (1) ($H_4L=2,2'$ bipyridine-3,3',6,6'-tetracarboxylic acid) undergoes an irreversible thermally triggered single-crystal-to-single-crystal (SCSC) transformation to produce the 3D anhydrous complex [$CuL_{0.5}$]_n (2). This SCSC structural transformation was confirmed by single-crystal X-ray diffraction analysis, thermogravimetric (TG) analysis, powder X-ray diffraction (PXRD) patterns, variable-temperature powder X-ray diffraction (VT– PXRD) patterns, and IR spectroscopy. Structural analyses reveal that in complex 2, though the initial 1D chain is still retained as in complex 1, accompanied with the Cu-bound H_2O removed and new O(carboxyl)–Cu bond forming, the coordination geometries around the Cu^{II} ions vary from a distorted trigonal bipyramid to a distorted square pyramid. With the drastic structural transition, significant property changes are observed. Magnetic analyses show prominent changes from antiferromagnetism to weak ferromagnetism due to the new formed Cu1-O-C-O-Cu4 bridge. The catalytic results demonstrate that, even though both solid-state materials present high catalytic activity for the synthesis of 2imidazolines derivatives and can be reused, the activation temperature of complex 1 is higher than that of complex 2. In addition, a possible pathway for the SCSC structural transformations is proposed.

Introduction

Solid-state single-crystal-to-single-crystal (SCSC) transformations of coordination polymers (CPs) have recently turned to be an appealing and promising research field in molecular materials.^[1] Such transformation processes usually involve the coordination and/or covalent bond breakage and formation, which not only lead to drastic structural rearrangement accompanied by changes of the coordination geometry, the coordination number, the dimensionality, etc. but also often result in dramatic property changes such as color, magnetism, luminescence, chirality, gas adsorption/selection, etc.^[2] Especially, sometimes the resulting multifunctional materials cannot be directly obtained by traditional synthetic routes.^[3] More importantly, the procedure of SCSC transformations can provide detailed structural information for better understanding of the mechanism of the transformation, and give insights into the relationship between the structures and properties.^[4] However, such CPs SCSC transformations are relatively scarce because it

[a]	QQ. Li, ⁺ CY. Ren, ⁺ YY. Huang, Prof. Dr. JL. Li, Prof. Dr. P. Liu,				
	Prof. Dr. B. Liu, Y. Liu, Prof. Dr. YY. Wang				
	College of Chemistry & Materials Science				
	Key Laboratory of Synthetic and				
	Natural Functional Molecule Chemistry				
	of the Ministry of Education, Shaanxi Key Laboratory of				
	Physico-Inorganic Chemistry				
	Northwest University, Xi'an 710069 (P.R. China)				
	E-mail: liuping@nwu.edu.cn				
[+]	These authors contributed equally to this work.				

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201405984.

is difficult to harvest intact single crystals for further tests after employing multiple artifices (for example exchange of metal centers, chemical reactions, light, or heat, etc.),^[4] besides, most of the reported examples focus only on the structure research.^[5] So far, further research of the solid-state SCSC transformation, especially for the properties and the relationship between the structures and properties, is imperative and challenging.

Imidazolines and their derivatives, as an important class of bioactive molecules, are widely used in the fields of drugs and pharmaceuticals.^[6] The development of efficient catalyst systems for the synthesis of imidazolines and their derivatives has recently attracted considerable attention. However, the procedures for the construction of imidazoline generally suffer from low product yields, poor functional-group tolerance, or expensive catalysts.^[7] So all the time, the major challenge of this catalytic reaction is to look for new efficient and low-cost catalysts. More recently, studies exhibit that a carboxylate Cu^{II} complex appears to be an efficient Lewis acid catalyst for the synthesis of imidazoline.^[8] In addition, though the application of Cu^{II} CPs in the catalytic synthesis of 2-imidazolines still remains an underexplored area, it is a proven and promising way to use the crystalline CPs as an attractive heterogeneous catalyst due to their tunable structure, single-site active species as well as their easy separation and recycling.^[9] So by considering CPs containing the transition metal Cu^{II} and polycarboxylic aromatic compounds, there is a logical interest in studying their catalytic properties in this sector. Furthermore, when the materials before and after SCSC transformation are simultaneously used as catalysts, analysis and compare of their catalytic activity

Chem. Eur. J. 2015, 21, 1–10

Wiley Online Library

These are not the final page numbers! 77



based on the detailed single-crystal structural characterization have become possible. For the above reasons, it is quite necessary to test the catalytic performances of the obtained Cu^{II} CPs.

Therefore, the main purposes of the present work are to study the solid-state SCSC structural transformation and the properties, particularly for the catalytic and magnetic properties, of the materials before and after SCSC transformation. Based on the ligand 2,2'-bipyridine-3,3',6,6'-tetracarboxylic acid (H₄L) (Figure 1 a), we report herein a typical SCSC "polymeri-



Figure 1. a) Chemical structure of the ligand 2,2'-bipyridine-3,3',6,6'-tetracarboxylic acid. b) Change of the coordination modes of the ligand L⁴⁻ during the SCSC transformation. The ligand L⁴⁻ in complex **1** adopts μ^4 -coordination mode and bridges four Cu atoms, whereas in complex **2** it takes a μ^6 - coordination mode and bridges two more Cu atoms. Hydrogen atoms are omitted for the sake of clarity.

zation" reaction, transforming a 1D antiferromagnetic complex $[(CuL_{0.5}H_2O) \cdot H_2O]_n$ (1) to a 3D weak ferromagnetic complex $[CuL_{0.5}]_n$ (2), which is driven by heat treatment to remove the lattice H₂O and the Cu-bound H₂O sequentially. A possible pathway for the SCSC structural transformations is proposed. As in both complexes 1 and 2 there exist coordinatively unsaturated Cu^{II} centers, which may have their potential applications in catalysis, the catalytic function of these two obtained Cu products were studied. The results demonstrate that both CPs show excellent catalytic activity for the synthesis of 2-imidazolines, although the activation temperature of complex 1 is higher than that of complex 2, due to the different coordination environment of the active metallic $\operatorname{Cu}^{\scriptscriptstyle I\!I}$ centers. To the best of our knowledge, this is the first representation that the catalytic activities of CPs, especially for the materials before and after SCSC transformation, are simultaneously tested for the synthesis of 2-imidazolines. The catalysts 1 and 2 remain relatively stable, which is proven by the powder X-ray diffraction (PXRD) analyses and by IR spectroscopy of the reused and recovered powders. This fact also accords with the conclusion that this SCSC transformation is a solid-state reaction and has never happened in solution. This work also shows the great potential of developing Cu^{II} CPs as highly efficient, stable, recyclable, and reusable heterogeneous catalysts for the catalytic synthesis of 2-imidazolines.

Discussion

Synthesis and dehydration of complex 1

Complex 1 was synthesized by reacting cheap $Cu(NO_3)_2 \cdot 3(H_2O)$ with the ligand H_4L in 63% yield, which is much higher than the previously reported 10%.^[10] The improved yield and the cheaper reactants have allowed obtaining enough quantity of material for the catalytic tests. When heating at 200°C for 4 h in dry air, single crystals remain single, whereas 1D complex 1 is dehydrated to produce 3D complex 2 with a color changing from blue-green to blackish-green (Figure S1 in the Supporting Information). It is worthy to mention that complex 2 has never been reaped by reactions in solution, which confirms that solid-state reactions can provide access to molecules otherwise difficult or impossible to be obtained from solution reactions.

However, such dehydration process is irreversible. When complex **2** is soaked into water, it cannot revert to the parent complex **1** and could stabilize in water at room temperature at least two weeks. This is not unexpected, as complex **2** exhibits a dense and compact structure. Further water/moisture stability tests of complexes **1** and **2** in air (10 days) and in boiling water (6 h) also reveal that both frameworks are maintained. Their high stabilities toward humidity and even boiling water are confirmed by powder X-Ray diffraction (PXRD) methods (see Figure S2 in the Supporting Information).

Crystal structures of complexes 1 and 2

For the sake of understanding this solid-state SCSC transformation, a detailed crystal structure analysis of complexes 1 and 2 is necessary. X-ray single-crystal structure analysis demonstrates that both of them crystallize in the monoclinic system within the space group C/2c (Table S1 in the Supporting Information). As shown in Figure 2a, complex 1 contains one unique Cu^{II} ion, one half L^{4–} ligand, one coordinated H₂O molecule, and one lattice H₂O molecule in the asymmetric unit. Each Cu^{II} atom is pentacoordinated showing a distorted trigonal-bipyramidal geometry with $\tau = 0.95$ (O5 from a terminal H_2O ligand and N1 from one L^{4-} ligand are arranged at the axial positions).^[11] Each L⁴⁻ ligand connects four contiguous $\mathsf{Cu}^{{\scriptscriptstyle \|}}$ centers with $\mu^{4}\text{-}\mathsf{coordination}$ mode to form a ribbon-like 1D chain (Figures 1b and 2b). The intrachain Cu-Cu distances are 5.571 and 5.410 Å for Cu1...Cu2 and Cu1...Cu3, respectively, whereas the interchain Cu1--Cu4 distance is 7.540 Å and the Cu3-Cu1-Cu4 angle is 111.0° (Figure S3a in the Supporting Information). In the packing motif for complex 1, as shown in Figure 2c, water molecules hold the adjacent chains together through four kinds of hydrogen-bonding interactions (i.e., O5-H5A-O3, O5-H5B-O6, O6-H6A-O1, and O6-H6B-O4) to a 3D supramolecular framework.

The powder X-ray diffraction analysis reveals that the as-synthesized complex **1** is consistent with the simulated patterns from the corresponding single-crystal structure, demonstrating the phase purities (Figure S5 in the Supporting Information). Thermal analysis shows that a weight loss of 13.5% in the

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2









Figure 2. a) Local coordination environment of the Cu^{II} ion in complex 1. Symmetry codes: A: 2-x, 2-y, 2-z; B: *x*, *y*, 1+z. b) 1D chain of complex 1 along the *c* axis. c) 3D supramolecular structure of complex 1, which is constructed by holding the adjacent chains together through four kinds of hydrogen-bonding interactions (i.e., O5–H5A···O3, O5–H5B···O6, O6–H6A···O1, and O6–H6B···O4).

range of 80-140 °C is in good agreement with the release of the coordinated H₂O molecules and lattice H₂O molecules (calcd 13.6%), and then the framework of complex **1** begins to

decompose gradually at 290 $^\circ\text{C}$ (Figure S6 in the Supporting Information).

To determine whether single crystallinity is retained during the dehydration process, the dehydrated crystalline phase **2** is determined by single-crystal X-ray diffraction analysis. Structural analysis reveals that the 1D complex **1** undergoes thermally driven SCSC transformation to produce the 3D anhydrous complex **2** [$CuL_{0.5}I_{n.}$ In complex **2**, the asymmetric unit contains one unique Cu^{II} ion and one half L^{4–} ligand (Figure 3). Different



Figure 3. Local coordination environment of the Cu^{II} ion in complex **2.** Symmetry codes: A: -x, y, 0.5-z; B: x, -y, -0.5+z; C: 0.5+x, 0.5+y, z.

to complex 1, the pentacoordinated Cu^{II} atom in complex 2 shows a distorted square-pyramidal geometry with $\tau = 0.37$.^[11] The basal positions of the square pyramid are occupied by the O1, O3A, O4C, and N1 atoms, whereas the O2B atom locates in the apical position. For complex 2, the initial 1D chain is still retained as in complex 1, although the coordination water molecule in complex 1 is substituted by the uncoordinated carboxylic oxygen atom (O4), which is similar to the previously described work.^[12] To visualize the "dehydrated" chain in the SCSC transformation process, as shown as in Figure 4b, the



Figure 4. Structural transformation from complex 1 to two the different posited products 2' and 2. The hydrated and dehydrated $\{Cu_4L_2\}$ unit in complex 1 (a) and complex 2 (b), respectively, and the eight potentially free coordination sites of each dehydrated $\{Cu_4L_2\}$ unit along four propagation directions (c) and (d) are shown.

Chem. Eur. J. 2015, 21, 1–10 www.chemeurj.org These are not the final page numbers! **77**



Cu-bound water molecules from the 1D chain are omitted. Each dehydrated {Cu₄L₂} unit has eight potentially free coordination sites including four unsaturated Cu^{II} centers and four free O4 atoms and can act as a tetra-bridging ligand (one unsaturated Cu^{II} center and one O4 atom as one conjugate pair being bond to one neighboring "dehydrated" 1D chain). Therefore, each "dehydrated" chain can connect four adjacent chains forming four pairs of new O(carboxyl)-Cu coordination bonds along four propagation directions. It was found that there exist two possible arrangements, as shown in Figures 4c and 4d, to form the different deduced products $\mathbf{2}'$ or $\mathbf{2}$ (Figure 4). In fact, the neighborhood 1D chains move along the a axis to form a denser and more compact production 2. That is to say, this 1D-to-3D SCSC structural transformation is triggered by the entropically favored loss of water molecules, and the main driving force for this transformation is due to the loss of water molecules and the formation of a thermally stable, dense, and compact crystalline 3D network. The topological analysis indicates that the 3D architecture of complex 2 is a dinodal (3,6)-connected net with the point symbol $(4^2.6)_2(4^4.6^2.8^8.10)$ (Figure S7 in the Supporting Information).

Compared with complex 1, it was found that some significant structural changes occur after this SCSC transformation. Firstly, accompanied by the Cu-bound and lattice water losing, a new O(carboxyl)-Cu bond forms with a normal Cu-O bond length 1.964 Å, and the Cu3-Cu1-Cu4 angle is reduced to 104.8° (Figure S3 c in the Supporting Information). Secondly, the coordination geometries around the Cu^{II} ions vary from a distorted trigonal bipyramid to a distorted square pyramid. The O2B atom from the adjacent L⁴⁻ ligand is located in the apical position with a longer Cu1–O2B distance (2.230 Å) due to the Jahn-Teller effect. Thirdly, due to the new O(carboxyl)-Cu bond formed, the L^{4-} ligand adopts a $\mu^6\text{-}coordination$ mode and bridges two more Cu atoms in complex 2 (Figure 1 b). Fourthly, for dragging the neighboring unsaturated Cu^{II} centers and uncoordinated carboxylic O atoms closely to forming new coordination bonds, the dihedral angles are changed, containing the reduced dihedral angles $(\alpha - \delta)$ and the increased dihedral angles $(\alpha - \beta, \alpha - \gamma, \text{ and } \beta - \gamma)$ (Figure S8 in the Supporting Information). Fifthly, the cell parameters



Figure 5. The SCSC structural transformation from complex 1 to complex 2 with the removal of H_2O molecules. The distances between the two interchain Cu atom planes for complex 1 (a) and complex 2 (b) are given. Dashed lines denote hydrogen bonds.

 β (90.068°), *a* (14.387 Å), and *V* (1264.1(2) Å³) of complex **2** are smaller than that of complex **1** (108.978°, 19.884 Å, and 1606(2) Å³, respectively), which implies that the structure is compacted by the interchain distances shortened and the chains slipped during the transformations (Table S1 in the Supporting Information). Actually, as shown in Figures 5 and S9 in the Supporting Information, the adjacent 1D chains will move closer together along *a* axis but farther apart along the *b* and *c* axis in complex **2**. Thus, the distances between the interchain Cu atoms planes, the Cu1…Cu4 distance, and the Cu3-Cu1-Cu4 angle are indeed reduced from 4.209 Å, 7.540 Å, and 111.0° to 1.839 Å, 4.872 Å, and 104.8°, respectively (Figures 5 and S3 in the Supporting Information).

SCSC structural transformation analyzed by various techniques

The SCSC structural transformation is also confirmed by thermogravimetric (TG) analysis, PXRD patterns, variable-temperature PXRD patterns, and IR spectroscopy. Comparison of the IR spectra of complexes 1 and 2 also reveals that complex 2 has been almost completely dehydrated, for the observed strong band in the range $\tilde{\nu} = 3500 - 3320 \text{ cm}^{-1}$ in the spectrum of complex 1, which is attributed to the O-H stretching vibrations of H₂O molecules, is nearly invisible in the spectrum of complex 2 (Figure S10 in the Supporting Information).^[13] The existing extremely weak band for complex 2 is attributable to the moisture in the air. Furthermore, the different frequency numbers and shapes in the range of $\tilde{\nu} = 1343 - 1373$ and 1554-1610 cm⁻¹, which are assigned to the $v_s(COO^-)$ and $v_{as}(COO^-)$ modes, respectively, indicate the different coordination modes of the carboxylic groups.^[13] Actually, the carboxylic group in complex 2 coordinates to the Cu center in a bidentate mode, whereas in complex 1 there is the coexistence of both uniand bidentate coordinating carboxylic groups.

In addition, the PXRD patterns of complex 2 are consistent with its simulated patterns but significant different to that of complex 1 (Figure S11 in the Supporting Information), clearly indicating that the structural transformation occurs. Compared with complex 1, the main diffraction peaks at approximately 9.4 and 18.8° shift to about 12.2 and 24.7°, respectively, which correspond to the reflection of the (200) and (400) plane for complexes 1 and 2 respectively. These reflection shifts also indicate that the framework transforms from an open one to a closed one, which is consistent with the results of single-crystal X-ray diffraction studies. To track the process of the phase transformation in solid states, VT-XRD was carried out. As shown in Figure S12a in the Supporting Information, the results demonstrate that there are no obvious changes from room temperature to 100 $^\circ\text{C},$ the XRPD patterns at 150 $^\circ\text{C}$ are very similar to the simulated one of complex 2, and the SCSC transformation from complex 1 to complex 2 is almost complete at 200 °C. At 110 °C, the peak at 14 $^{\circ}$ is split and then upon further heating, one of the split peaks at 16° appears more prominently and the peak at 9° disappeared, which is indicative for the formation of an intermediate. Unexpected, though the framework of complex 2 destroys beyond 350°C,

Chem. Eur. J. **2015**, 21, 1–10

www.chemeurj.org

4



the VT-PXRD result shows that some new diffraction peaks appear in the range of $30-50^{\circ}$. Thus, it is imperative to note here that the crystallinity of the compound is still kept. These diffraction peaks are in accord with the mixture of CuO and Cu₂O, indicating that the mixture of CuO and Cu₂O is formed after the decomposition of complex **2** (Figure S13 in the Supporting Information).^[14]

Similar behaviors are observed in the TG analysis results. Complex 1 is heated at different temperatures ranging from 50 to 155 °C for 4 h under air conditions, and then these samples are analyzed by TG (Figure S12b in the Supporting Information). The TG analysis of complex 2 exhibits no weight loss until 290 °C, proving that there is no molecular water in complex 2 (Figures S6 and S12b in the Supporting Information). The curves at 50–80 °C are nearly identical to that of complex 1, and the curve at 155 °C exhibits nearly inexistence of water molecules, which is close to that of complex 2. The curves at 90-125 °C show partial water loss, providing a further evidence for the existence of a potential intermediate during the dehydration process. However, unfortunately our attempt by the single-crystal X-ray diffraction method to characterize the intermediate, which is obtained after "gently" heating the single crystal of compound 1 at 90, 105, 115, and 125 $^\circ C$ for 4 h either in air or under vacuum, was unsuccessful.

The proposed SCSC structural transformation pathway

It is well known that the solid-state reaction occurs depending on the fact that the reactive functional groups are already close and aligned in the correct orientation. Owing to the maintaining of single crystallinity after this structural transformation, a detailed analysis of the substitutable coordination site of coordinated water molecules and the motile 1D chain are possible. So the details of this SCSC transformation pathway may be inferred.

Based on the above-discussed structural analysis, it is known that compound 2 is formed by the Cu-bound water losing and new O4(carboxyl)–Cu bond formation. To get a deeper understanding of the coordination of the O4 atom with Cu, further observation is needed. As shown in Figure 6a, it was found that there are two potential coordination sites, that is, Cu2 or Cu1, around the O4 atom. When selecting the potential coordination sites Cu2 or Cu1 to coordinate with the O4 atom, respectively, different products 2' or 2 will form (Figure 4). Thus, it is meaning that the O4 atom coordinates with Cu1, though Cu2 is closer to the substituent site O4 (Cu1...O4, 5.451 Å; Cu2···O4, 5.107 Å). However, it was found that the O5(Cu1)···O4 distance (3.783 Å) is shorter than the O5(Cu2)--O4 (3.807 Å) distance (Figure 6a). Then the intermolecular hydrogen-bond interactions between the carboxylate carbonyl groups, the free molecular water, and the coordinated water molecules attract our attention. Examples have been reported that lattice water and coordination water can be removed stepwise in the dehydration processes.^[15] If the lattice water is removed firstly, it is reasonable to expect that the hemi-dehydration intermediate, that is, {CuL_{0.5}H₂O}, would be formed, which is also indicated by the results of the TG analysis and the VT-PXRD patterns.



Figure 6. a) The distances of Cu1···O4, Cu2···O4, O5(Cu1)···O4, and O5(Cu2)···O4 as well as the coordination environment of the water molecule between the chains in complex **1**. b) The simulated semi-dehydrated "intermediate" state during the SCSC transformation.

Meanwhile, the new possibly O–H···O hydrogen bonding would be formed between uncoordinated O4 atom as hydrogen-bond acceptor and the Cu1-bound water as hydrogenbond donor, then ultimately the reactive functional group O4 is closer to the Cu1 center and is in the preferred orientation (Figure 6b). The weak hydrogen-bonding interactions may play an important role in bringing the reactive functional groups closer together and in the correct orientations.

On the basis of above-presented analysis and assumption, we could propose a possible pathway involving three steps in the structural transformations (Figure 7). From the microscopic point of view, in the first step, the removal of the lattice water forms the "intermediate" state. The unsaturated carboxylic oxygen atom O4 moves and turns to appropriate location and direction to form hydrogen bonding with the coordinated water molecules of the adjacent chain, accompanied by the chains compaction and slip. In the next step, under higher temperature, the removal of the Cu-bound H₂O leaves the Cu center unsaturated and activated. In the last step, the unsaturated carboxylic O atoms (O4) further move and compensate the vacancy of the activated Cu center to form a stable framework. The initial 1D chain is retained throughout the dehydration process. We have outlined the possible pathways based on both the assumed intermediate and the observation of the initial and final structures of complexes 1 and 2 when taking

Chem. Eur. J. 2015 , 21, 1 – 10	www.chemeurj.org	
These are not the	final page numbers!	77



Figure 7. Three distinct steps in the structural transformations. 1) The first step is the removal of the lattice water molecules to form the "intermediate" state. 2) The second step is the removal of the Cu-bound H_2O leaving the Cu unsaturated and activated. 3) In the last step the unsaturated carboxylic O atoms (O4) further move and compensate the vacancy of the activated Cu for a stable framework.

the dynamics of the H_2O removal into consideration. The mechanistic pathways outlined here provide us a reasonable insight that is necessary to make better control of the desired structures.

Magnetic properties

Variable-temperature magnetic susceptibilities of complexes 1 and 2 have been measured in an applied magnetic field (H =1000 Oe) in the temperature range of 1.8-300 K. As shown in Figure 8, at 300 K, the $\chi_{\rm M}T$ values per Cu for complexes 1 and 2 are 0.46 and 0.44 cm³ Kmol⁻¹, respectively, larger than the value expected for one independent Cu^{II} ion (S = 1/2, g = 2.0). For complex 1, upon cooling, the $\chi_{M}T$ value shows a gradual decrease to 0.45 $\text{cm}^3 \text{K}^{-1} \text{mol}^{-1}$ at 20 K, followed by a rapid decline to $0.19 \text{ cm}^3 \text{K}^{-1} \text{mol}^{-1}$ at 1.8 K. The susceptibility data fit the Curie–Weiss law $(\chi_{M} = C/(T-\theta))$ well, giving Curie (C) and Weiss (θ) constants of 0.47 cm³ Kmol⁻¹ and -1.78 K, respectively, with $R = 4.98 \times 10^{-4}$. The behavior of the $\chi_{\rm M}T$ value and the negative θ value indicate a weak antiferromagnetic exchange between the neighboring Cu centers. Different with complex 1, as the temperature is lowered, the $\chi_{M}T$ value of complex 2 increases slowly, reaching a maximum of 0.46 cm³K⁻¹mol⁻¹ at 25.0 K and then quickly decreases to $0.22 \text{ cm}^3 \text{K}^{-1} \text{mol}^{-1}$ at 2.0 K. The susceptibility data fit the Curie-Weiss law well, giving Curie and Weiss constants of $0.42 \text{ cm}^3 \text{K}^{-1} \text{mol}^{-1}$ and 0.69 K, respectively, with $R = 6.17 \times 10^{-4}$. The behavior of the $\chi_{\rm M}T$ value and the positive θ value indicate a weak ferromagnetic exchange between the Cu centers.



Figure 8. $\chi_{\rm M}T$ and $\chi_{\rm M}$ versus T plots for complexes 1 (a) and 2 (b). The solid lines denote the theoretical curves with the best-fit parameters. Inset $\chi_{\rm M}^{-1}$ versus T plots and Curie–Weiss fitting line.

The magnetic data of complexes **1** and **2** were fitted by using the magnetic chain model given in Equation (1).

$$\chi = \frac{Ng^2\beta^2 S(S+1)}{3kT} \frac{1+u}{1-u}$$

$$u = \operatorname{coth}\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$$
(1)

The best-fit parameters obtained are g=2.22, $J=-0.45 \text{ cm}^{-1}$, $zJ=-0.069 \text{ cm}^{-1}$, and $R=1\times10^{-5}$ for complex 1, and g=2.15, $J=0.08 \text{ cm}^{-1}$, $zJ=-0.32 \text{ cm}^{-1}$, and $R=8\times10^{-5}$ for complex 2. The *g* values for complexes 1 and 2 are consistent with the *g* values obtained by the variable-temperature EPR analysis (Figure S14 in the Supporting Information). Here, *R* is calculated from $\Sigma[(\chi_{\rm M}T)_{\rm obs}-(\chi_{\rm M}T)_{\rm calcd}]^2/\Sigma[(\chi_{\rm M}T)_{\rm obs}]^2$ and the other parameters in Equation (1) have their usual meaning.

The resulting different magnetism might be ascribed to the drastic structural variance from the 1D complex **1** to the 3D complex **2**. Structural analysis demonstrates that, for complex **1**, the neighboring Cu^{2+} ions are connected to each other by carboxyl groups in *anti* conformation to forming a ribbon-like 1D chain and the atoms of Cu1-O-C-O-Cu2 are arranged in an approximate horizontal orientation. The Cu1…Cu2 distance is 5.571 Å and the torsion angle Cu1-O-C-O-Cu2 is 172.6°. Whereas for complex **2**, although the Cu1-O-C-O-Cu2 is still kept, the new Cu1-O-C-O-Cu4 is created and the atoms of the Cu1-O-C-O-Cu2 is the cu1-O-C-O-Cu2 is contained to the cu1-O-C-O-Cu2 is still kept.

Chem. Eur. J. 2015, 21, 1 – 10 www.chemeurj.org

6

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

N These are not the final page numbers!



O-Cu4 are located in an obvious non-planar orientation with a short Cu1···Cu4 distance (4.872 Å) and an extra distortional (Cu1-O-C-O-Cu4 torsion angle is 157.9°). In addition, in complex **2** the Cu1···Cu2 distance is 5.610 Å and the torsion angle Cu1-O-C-O-Cu2 is 174.92°. From the magnetic point of view, the new formed Cu1-O-C-O-Cu4 with short Cu1···Cu4 separation and the obvious non-co-planarity of the atoms might be the predominant factor for the ferromagnetic interactions of complex **2**.^[16]

Catalytic property study

Although large amounts of CP structures have been reported, their huge potential in heterogeneous catalysis is still not fully appreciated and far less explored. As observed in the structures **1** and **2**, all Cu^{II} atoms are pentacoordinated and can be used as unsaturated metal centers providing vacant coordination sites/Lewis acid sites, as well as implying their potential applications in catalysis. In addition, the water stability and bulk synthetic technique of complexes **1** and **2** also make them possible to test their catalytic ability as Lewis acid catalysts. To evaluate the catalytic function of both complexes, the catalyzed reaction of 2-cyanopyridine with ethylendiamine (EDA) was performed.

The catalytic reactions were carried out by mixing a heteroaromatic nitrile, ethylenediamine, and the copper catalysts either in solvent or in neat and stirring the mixture for 4 h. The obtained results are summarized in Tables S4 in the Supporting Information and 1. In order to identify the optimal reaction conditions for the reaction, different solvents and reaction temperatures were screened firstly in the presence of 1 mol% catalyst. The data demonstrate that although the reaction at room temperature is negligible (Table S4 in the Supporting Information, entries 1-6), the conversion increases with the temperature. The catalysts 1 and 2 show superior activity under solvent-free reaction conditions at 100°C (under the boiling point of EDA, i.e., 116 °C) (Table S4 in the Supporting Information, entries 21 and 22). Variation of the concentration of the catalyst was investigated under the above-selected reaction conditions in the presence of 0.2, 0.5, and 1.5 mol% catalyst (Table S4 in the Supporting Information, entries 27-32). The optimal conditions are: complex 1 or 2 as the catalyst (0.5 mmol %), solvent free, and 100 $^\circ\text{C}.$ The catalytic activities of complexes 1 and 2 are comparable or higher than that of the reported discrete Cu^{II} complex catalysts, because the reaction temperature and the catalyst concentrations of complexes 1 and 2 are lower.^[17]

In addition, it was found that at relatively low temperatures such as 40 and 70 °C, the yield of compound **3a** catalyzed by complex **1** is much lower than that received by using complex **2** as catalyst (40 °C: 18% (1) vs. 51% (2); 70 °C: 47% (1) vs. 67% (2)), whereas at 100 °C, complexes **1** and **2** exhibit improved and comparable reaction activities for the synthesis of compound **3a** in excellent yield (97% for complex **1** and 91% for complex **2**) (Table S4 in the Supporting Information, entries 21 and 22). These results indicate that the activation temperature of complex **1** is higher than that of complex **2**, proba-

bly due to the different coordination environment of the metal Cu^{II} ions (a distorted trigonal-bipyramidal geometry in complex **1** and a distorted square-pyramidal geometry in complex **2**). In order to further verify the catalytic performance of complexes **1** and **2** in this system, various aromatic and heteroaromatic nitriles were reacted with EDA to obtain the corresponding 2-substituted imidazolines under the optimized reaction conditions. As shown in Table 1, reactions catalyzed by both com-



plexes 1 and 2 show excellent or good conversions. For comparison, a blank experiment in the absence of catalysts was performed to prove that no reaction occurs even at stirring under optimal conditions for a longer reaction time (10 h). Furthermore, the shutdown of the reaction by either removing the catalysts or adding cupric nitrate/cupric sulfate verifies the heterogeneous catalysis by complexes 1 and 2.

After the reactions were finished, the catalysts (i.e., complexes 1 and 2) can be easily recovered by filtration, washed with ethanol, and dried at room temperature. The recovered powders were collected and characterized by PXRD analyses and IR spectroscopy. The PXRD patterns of the recovered catalysts 1 and 2 were found to well match those of the as-synthesized complexes 1 and 2 (as shown in Figure S15 in the Supporting Information), indicating that complexes 1 and 2 are stable in the catalytic process. Furthermore, direct comparisons of the IR resonances show that no deviations were observed

Chem. Eur. J. 2015 , 21, 1–10	www.c	hemeurj	.org	

These are not the final page numbers! **77**



between the fresh and recovered catalysts (Figure S16 in the Supporting Information), which further proves that the original structure is maintained. Taken together, these data suggest that the catalysts 1 and 2 remain structurally stable after the reaction. Moreover, reuse experiments based on complexes 1 and 2 were carried out three times under the conditions described above. Almost no catalytic activity loss was observed in the repeated tests for both complexes 1 and 2.

Conclusion

At elevated temperature, the Cu^{II} complex 1 undergoes a 1Dto-3D solid-state SCSC structural transformations to form complex 2 by losing both lattice and coordinated H₂O molecules and by forming new O(carboxyl)-Cu coordination bonds. This transformation exhibits structural changes, such as the sliding of the 1D chains, the conformation of the L⁴⁻ ligand, the coordination environment of the metal Cu^{II} ions changed from a distorted trigonal-bipyramidal geometry to a distorted square-pyramidal. Furthermore, a relevant structure-function correlation has been established among the structure of 1/2 and its magnetic and catalytic properties. Magnetic analyses show that the new formed Cu-O-C-O-Cu array might be the predominant factor for the significant magnetic changes from antiferromagnetic to weak ferromagnetic. Both of these two Cu^{II} polymers materials present highly effective, recyclable, reusable, and selective catalytic activity for the synthesis of 2-imidazolines and its derivatives, though the activation temperature of complex 1 is higher than that of complex 2.

Experimental Section

Synthesis

Synthesis of $[(CuL_{0.5}H_2O) \cdot H_2O]_n$ (1): Cu(NO₃)₂·3(H₂O) (0.10 mmol, 0.024 g) and the ligand H_4L (0.05 mmol, 0.017 g) were added in H_2O (10 mL), the pH was adjusted to 7.0 with 1 μ KOH. Then the mixture was transferred to a Teflon-lined stainless steel container and kept at 105 °C for 72 h. After cooling to room temperature, the blue-green block-shaped crystals of compound 1 were isolated by washing with distilled water and they were dried in vacuum. The yield was about 62.6% based on H₄L. IR (KBr): $\tilde{\nu} = 3390.54$ (s), 3120.96 (s), 1607.91 (vs), 1563.37 (m), 1449.70 (w), 1373.00 (s), 1253.61 (w), 1153.39 (w), 1079.99 (w), 843.86 (m), 782.94 cm⁻¹ (w); elemental analysis calcd % for C₇H₆CuNO₆: C 31.89, H 2.29, N 5.31; found: C 31.83, H 2.32, N 5.28.

Synthesis of $[CuL_{0.5}]_n$ (2): When heating a sample of complex 1 at 200 °C for 4 h in dry air, the blackish green block-shaped crystals of complex **2** were obtained. IR (KBr): $\tilde{\nu} = 3390.51$ (w), 3120.98 (w), 1609.93 (s), 1554.39 (m), 1433.75 (w), 1343.01 (m), 1235.65 (w), 1156.57 (w), 1056.79 (w), 843.55 (m), 781.46 cm⁻¹ (w); elemental analysis calcd (%) for C7H2CuNO4: C 36.93, H 0.89, N 6.15; found: C 36.98, H 0.92, N 6.17.

Catalysis studies

A mixture of nitrile (4 mmol), ethylenediamine, and Cu catalyst was stirred 4 h. The progress of the reaction was monitored by TLC (EtOAc/MeOH 3:1). After completion of the reaction, the mixture was cooled to room temperature, then CH_2CI_2 (10 mL) was added, and the catalyst was removed by filtration. The solvent of the filtrate was removed under reduced pressure and the residue was purified by silica gel chromatography to give the pure product (EtOAc/MeOH, 3:1). The characterization data for the products are given in the Supporting Information.

Reuse experiments were carried out for the reaction of 2-cyanopyridine with EDA under the optimal conditions. Once the reaction was completed, the catalyst was recovered by centrifugation, washed with ethanol, and dried at room temperature. The recovered powder was placed in a vial to repeat the reaction under the same conditions twice. Every time the recovered powder was characterized by PXRD and IR spectroscopy.

In addition, a blank experiment was performed by the reaction of 2-cyanopyridine with EDA under otherwise identical reaction conditions described above to probe the role of the catalysts. No formation of compound 3a was observed even for stirring under reflux conditions for a longer reaction time (10 h).

X-ray crystallographic measurements

Diffraction data were collected with a $Mo_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å) at 296(2) K on a Bruker-AXS SMART CCD area detector diffractometer. The single-crystal crystallographic data for complexes 1 and 2 were received by using a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated Mo_{Ka} radiation ($\lambda = 0.71073$ Å) by using ϕ/ω scan technique at room temperature. The structure was determined by direct methods and refined by the full-matrix least-squares techniques on F^2 with the SHELXS-97 crystallographic program package.^[18] Anisotropic thermal parameters were applied to all non-hydrogen atoms. All the hydrogen atoms were generated geometrically ideal positions and refined isotropically. CCDC 958426 (1) and 958427 (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.

Crystal data for $[(CuL_{0.5}H_2O)\cdot H_2O]_n$: C₇H₆CuNO₆; M = 263.67; bluegreen block; 0.3×0.25×0.22 mm³; monoclinic; space group C2/c (no. 15); a = 19.884(2), b = 8.133(6), c = 10.500(8) Å; $\beta =$ 108.978(1)°; $V = 1606(2) \text{ Å}^3$; Z = 8, $\rho_{calcd} = 2.181 \text{ g cm}^{-3}$; $F_{000} = 1056$; Bruker SMART APEX II CCD diffractometer; synchrotron radiation, $\lambda = 0.71073$ Å; T = 296(2) K; 2 $\theta_{max} = 51.98^{\circ}$; 4177 reflections collected; 1568 unique ($R_{int} = 0.0250$); final GooF = 1.172; $R_1 = 0.0395$; $wR_2 = 0.1284$; R indices based on 1361 reflections with $l > 2\sigma(l)$ (refinement on F²); 136 parameters; 0 restraints; lp and absorption corrections applied; $\mu = 2.730 \text{ mm}^{-1}$.

Crystal data for [CuL_{0.5}]_n: C₇H₂CuNO₄; M=227.64; blackish green block; $0.3 \times 0.25 \times 0.22$ mm³; monoclinic; space group C2/c (no. 15); $a = 14.387(7), b = 8.358(7), c = 10.512(7) \text{ Å}; \beta = 90.068(2)^{\circ}; V =$ 1264.1(2) Å³; Z=8, ρ_{calcd} =2.392 g cm⁻³; F_{000} =896; Bruker SMART APEX II CCD diffractometer; synchrotron radiation, $\lambda = 0.71073$ Å; T = 296(2) K; $2\theta_{max} = 50.20^{\circ}$; 2588 reflections collected; 1100 unique ($R_{int} = 0.0871$); final GooF = 1.092; $R_1 = 0.0622$; $wR_2 = 0.1483$; *R* indices based on 741 reflections with $l > 2\sigma(l)$ (refinement on F^2); 118 parameters; 0 restraints; lp and absorption corrections applied; $\mu = 3.425 \text{ mm}^{-1}$.

Acknowledgements

8

This work was supported by the National Natural Science Foundation of China (No. 21143010, 21371142, 20931005, and 91022004), the Natural Science Foundation of Shaanxi Province

Chem. Eur. J. 2015, 21, 1-10 www.chemeurj.org

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



of China (No. 2012JQ2007), the Natural Scientific Research Foundation of Shaanxi Provincial Education Office of China (No. 2010JS116 and 2010JK875) and Xi'an Committee of Science and Technology of China (No. CXY1429(6) and CXY1434(7)). We thank Prof. W. W. Zuo for their dedication to this work.

Keywords: catalysis • coordination polymers • magnetic properties • single-crystal-to-single-crystal

- a) J. J. Vittal, Coord. Chem. Rev. 2007, 251, 1781–1795; b) G. J. Halder,
 C. J. Kepert, Aust. J. Chem. 2006, 59, 597–604; c) H. L. Wang, W. Cao, T.
 Liu, C. Y. Duan, J. Z. Jiang, Chem. Eur. J. 2013, 19, 2266–2270; d) Y. C.
 Ou, D. S. Zhi, W. T. Liu, Z. P. Ni, M. L. Tong, Chem. Eur. J. 2012, 18, 7357– 7361; e) M. Du, C. P. Li, J. M. Wu, J. H. Guo, G. C. Wang, Chem. Commun.
 2011, 47, 8088–8090.
- [2] a) D. Armentano, G. D. Munno, T. F. Mastropietro, M. Julve, F. Lloret, J. Am. Chem. Soc. 2005, 127, 10778–10779; b) X. N. Cheng, W. X. Zhang, Y. Y. Lin, Y. Z. Zheng, X. M. Chen, Adv. Mater. 2007, 19, 1494–1498; c) G. C. Lv, P. Wang, Q. Liu, J. Fan, K. Chen, W. Y. Sun, Chem. Commun. 2012, 48, 10249–10251; d) Y. Q. Lan, H. L. Jiang, S. L. Li, Q. Xu, Inorg. Chem. 2012, 51, 7484–7491; e) M. H. Xie, X. L. Yang, C. D. Wu, Chem. Eur. J. 2011, 17, 11424–11427; f) L. X. Shi, W. F. Zhao, X. Xu, J. Tang, C. D. Wu, Inorg. Chem. 2011, 50, 12387–12389; g) A. Aslani, A. Morsali, Chem. Commun. 2008, 3402–3404.
- [3] a) Y. J. Zhang, T. Liu, S. Kanegawa, O. Sato, J. Am. Chem. Soc. 2009, 131, 7942–7943; b) M. Wriedt, A. A. Yakovenko, G. J. Halder, A. V. Prosvirin, K. R. Dunbar, H. C. Zhou, J. Am. Chem. Soc. 2013, 135, 4040–4050.
- [4] a) S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, P. D. Southon, J. D. Cashion, J. F. Letard, B. Moubaraki, K. S. Murray, C. J. Kepert, J. Am. Chem. Soc. 2008, 130, 2869–2876; b) J. Campo, L. R. Falvello, I. Mayoral, F. Palacio, T. Soler, M. Tomas, J. Am. Chem. Soc. 2008, 130, 2932–2933; c) D. Sarma, S. Natarajan, Cryst. Growth Des. 2011, 11, 5415–5423; d) K. D. Demadis, M. Papadaki, M. A. G. Aranda, A. Cabeza, P. Olivera-Pastor, Y. Sanakis, Cryst. Growth Des. 2010, 10, 357–364.
- [5] a) Q. X. Yao, J. L. Sun, K. Li, J. Su, M. V. Peskov, X. D. Zou, *Dalton Trans.* 2012, 41, 3953–3955; b) G. Mahmoudi, A. Morsali, *Cryst. Growth Des.* 2008, 8, 391–394; c) A. S. R. Chesman, D. R. Turner, G. B. Deacon, S. R. Batten, *Chem. Commun.* 2010, 46, 4899–4901.
- [6] A. O. Dolinkin, M. S. Chernov'yants, Pharm. Chem. J. 2010, 44, 99-106.

- [7] a) S. L. You, J. W. Kelly, Org. Lett. 2004, 6, 1681–1683; b) H. Salgado-Zamora, E. Campos, R. Jimenez, H. Ceevantes, Heterocycles 1998, 47, 1043–1049.
- [8] J. Zhang, X. Wang, M. P. Yang, K. R. Wan, B. Yin, Y. X. Wang, J. L. Li, Z. Shi, *Tetrahedron Lett.* **2011**, *52*, 1578–1582.
- [9] a) A. Dikhtiarenko, S. A. Khainakov, I. de Pedro, J. A. Blanco, J. R. García, J. Gimeno, *Inorg. Chem.* 2013, *52*, 3933–3941; b) N. Mizuno, M. Misono, *Chem. Rev.* 1998, *98*, 199–217; c) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* 2012, *112*, 1196–1231; d) G. Kumar, R. Gupta, *Inorg. Chem.* 2013, *52*, 10773–10787.
- [10] A. Kochel, M. Hołyńska, Inorg. Chim. Acta 2013, 408, 193-198.
- [11] A. W. Addison, T. N. Rao, J. Reedijk, J. Vanrijn, G. C. Verschoor, J. Chem. Soc. Dalton Trans. 1984, 1349–1356.
- [12] D. L. Reger, A. Leitner, M. D. Smith, Inorg. Chem. 2013, 52, 10041– 10051.
- [13] a) D. Deya, S. Roya, R. N. D. Purkayastha, R. Pallepogu, P. McArdle, J. Mol. Struct. 2013, 1053, 127–133; b) T. Premkumar, S. Govindarajan, J. Therm. Anal. Calorim. 2005, 79, 685–689; c) E. G. Bakalbassis, J. Mrozinski, C. A. Tsipis, Inorg. Chem. 1986, 25, 3684–3690; d) Y. B. Huang, T. F. Liu, J. X. Lin, J. Lü, Z. J. Lin, R. Cao, Inorg. Chem. 2011, 50, 2191–2198.
- [14] a) Z. G. Guo, M. V. Reddy, B. M. Goh, A. K. P. San, Q. L. Bao, K. P. Loh, *RSC Adv.* 2013, *3*, 19051–19056; b) H. Thakuria, G. Das, *Polyhedron* 2007, *26*, 149–153; c) N. N. Sheno, A. Morsali, S. W. Joo, *Mater. Lett.* 2014, *117*, 31–33; d) R. B. Wu, X. K. Qian, F. Yu, H. Liu, K. Zhou, J. Wei, Y. Z. Huang, *J. Mater. Chem. A* 2013, *1*, 11126–11129; e) F. Millange, R. E. Osta, M. E. Medina, R. I. Walton, *CrystEngComm* 2011, *13*, 103–108.
- [15] a) X. Y. Wang, M. Scancella, S. C. Sevov, Chem. Mater. 2007, 19, 4506– 4513; b) D. Sarma, V. Srivastava, S. Natarajan, Dalton Trans. 2012, 41, 4135–4145.
- [16] a) R. Baldomá, M. Monfort, J. Ribas, X. Solans, M. A. Maestro, *Inorg. Chem.* 2006, *45*, 8144–8155; b) R. Carballo, B. Covelo, M. S. E. Fallah, J. Ribas, E. M. Vázquez-López, *Cryst. Growth Des.* 2007, *7*, 1069–1077; c) S. K. Dey, B. Bag, K. M. A. Malik, M. S. E. Fallah, J. Ribas, S. Mitra, *Inorg. Chem.* 2003, *42*, 4029–4035.
- [17] a) H. X. Li, Z. G. Ren, D. Liu, Y. Chen, J. P. Lang, Z. P. Cheng, X. L. Zhu, B. F. Abrahams, *Chem. Commun.* 2010, 46, 8430–8432; b) J. H. Fu, H. J. Li, Y. J. Mu, H. W. Hou, Y. T. Fan, *Chem. Commun.* 2011, 47, 5271–5273; c) M. Panera, J. Díez, I. Merino, E. Rubio, M. P. Gamasa, *Inorg. Chem.* 2009, 48, 11147–11160.
- [18] G. M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Göttingen (Germany), 1997.

Received: November 6, 2014 Published online on ■■ ■, 0000

www.chemeurj.org

Chem. Eur. J. 2015, 21, 1-10





FULL PAPER

Crystal Engineering

Q.-Q. Li, C.-Y. Ren, Y.-Y. Huang, J.-L. Li, P. Liu,* B. Liu, Y. Liu, Y.-Y. Wang

Thermally Triggered Solid-State Single-Crystal-to-Single-Crystal Structural Transformation Accompanies Property Changes



SCSC: A 1D Cu complex undergoes an irreversible thermally triggered single-crystal-to-single-crystal (SCSC) transformation to produce the 3D anhydrous complex (see figure). With the drastic structural transition, significant magnetic changes from antiferromagnetism to weak ferromagnetism occur. Both materials present high catalytic activity for the synthesis of 2-imidazolines.

10