Book Chapter

Single-Crystal to Single-Crystal Structural Transformations of Amino-Acid-Based Coordination Polymers: Syntheses and Structural Characterization

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Abstract

A discrete complex \([\text{Zn}(\text{tpro})_2(\text{H}_2\text{O})_2]\) (1, Htpro = L-thioproline), and two structural isomers of coordination polymers, a 1D chain of \([\text{Zn}(\text{tpro})_2]_n\) (2) and a layer structure of \([\text{Zn}(\text{tpro})_2]_n\) (3), have been synthesized and characterized. The discrete complex 1 undergoes a single-crystal to single-crystal temperature-driven structural transformation, leading to a 1D helical coordination polymer 2. Compound 3 has a 2D homochiral layer network with a (4,4) topology. These layers are mutually linked through hydrogen bonding interactions, resulting in the formation of a 3D network. When 1 was heated, it undergoes almost completely conversion to the microcrystalline of compound 2, which was confirmed by powder X-ray diffractions (PXRD). After removing the coordinated water molecules by heating at temperature of up to 150 °C, the carboxylate motifs could be activated and their orientations became distorted, after which, they attacked the activation sites of the Zn(II) centers, leading to a the formation of a 1D helix. Moreover, a portion of the PXRD pattern of 3 was converted into a pattern for 2, and the ratio between 2 and 3 was precisely determined by the simulating study of the synchrotron in situ PXRD patterns. Consequently, such a 0D complex is capable of underdoing single-crystal to single-crystal transformations and can be converted into 1D and/or 2D amino acid-based coordination polymers.
Keywords

Amino-Acid-Based Coordination Polymers; Single-Crystal to Single-Crystal Structural Transformations; Homochiral Helices; Self-Assembly Process; L-Thioproline

Introduction

Various strategies for the rational design of coordination polymers (CPs) or metal–organic frameworks (MOFs) have received considerable attention recently, not only because of their structural diversities and intriguing topologies [1-6], but also due to potential applications in the fields of gas storage, separation, fluorescence, drug delivery, and related fields [7–12]. The creation of desirable CPs or MOFs with variable dimensions relies on the control of a few critical factors, such as functionality on the ligand, concentration, template, pH, temperature, the solvent system, and reaction time, among others [13-17]. One unusual feature of CPs or MOFs is the structural flexibilities, which can lead to remarkable effects, including breathing pore-discriminating adsorption and structural transformations in the solid state, which are completely different from those occurring in solvent systems [18-23]. Of particular interest are single-crystal to single-crystal structural transformations that involve with the replacement or substitution of labile ligands, which provide the crystallographic snapshots that are useful in collecting information in solvent-free chemical reactions [24–27]. The coordination geometries of the metal ions could be changed upon exposure to exogenous stimuli, and some coordinating tectons escaped via metal-ligand bonding breakage, thus facilitating the reforming of new bonding modes in a concerted manner [28–30]. Recent achievements in phase transformations include demonstrations of the mutual sliding of the coordination arrays in the solid state, which may be induced by stimuli, such as solvents, ions, light, temperature, and mechanical force, and their synergistic effect [31–38]. For example, the reversible solvent-responsive phase transformation process driven by water molecules was explored by a multi-metallic coordination polymer [39]. We are interested in
preparing labile compounds as target metal complexes, which contain a chiral amino acid ligand, were shelf-assembled under mild conditions. There are several structural transformations which are primarily influenced by thermal association, condensation, and rearrangement of bonds [40–45], however, employing such amino acid-containing complexes to study their self-reorganizing properties as well as their single-crystal to single-crystal structural transformations has not fully addressed [46–49]. A detailed understanding of these behaviors is thus important in the design of future materials for advanced applications.

As part of our ongoing efforts in the design and synthesis of functionally crystalline materials [49–53], we report herein on the preparation and characterization of one discrete complex [Zn(tpro)\(_2\)(H\(_2\)O)\(_2\)] (1, Htpro = L-thioproline), and two structural isomers of coordination polymers, a 1D chain of [Zn(tpro)\(_2\)]\(_n\) (2) and a layer structure of [Zn(tpro)\(_2\)]\(_n\) (3). Their features are as follows: (i) the discrete complex contains two labile water molecules and two strong chelated amino acid ligands, (ii) compounds 2 and 3 have the same formula, but the structures and space groups are completely different, the former is a 1D right-handed helix, while the later is composed of a 2D protuberant-grid-type network, (iii) the use of several different solvents or the addition of structural directing reagents was found to play an important role in promoting the yield of each product, (iv) upon heating at 210 °C, the activated carboxylate oxygens of the complexes were distorted and coordinated to the neighboring Zn(II) centers, i.e., the activation sites, leading to the PXRD pattern of 1 being transformed to that of 2, (v) a small fraction part of 3 (2.4%) could be also obtained, which was verified by in-situ synchrotron powder X-ray diffraction. Furthermore, this methodology provides an opportunity for developing an effective strategy to prepare a diversity of products under mild conditions. This report deals with the issue of labile ligands that can be removed upon heating. Importantly, such a discrete complex exhibited a single-crystal to single-crystal structural transformations via being converted to 1D and/or 2D amino acid-based coordination polymers in the solid state.
Experimental Materials and Physical Techniques

All chemicals were of reagent grade and used as commercially obtained without further purification. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 2400 elemental analyzer. The infrared spectrum was recorded on a Nicolet Fourier Transform IR, MAGNA-IR 500 spectrometer in the range 500–4000 cm⁻¹ using the KBr disc technique. Thermogravimetric analyses (TGA) were performed on a computer-controlled Perkin-Elmer 7 Series/UNIX TGA7 analyzer. Single-phased powder samples of 1 (3.1 mg), 2 (3.2 mg) and 3 (3.4 mg) were loaded into alumina pans and heated with a ramp rate of 5 °C/min from room temperature to 800 °C under nitrogen atmosphere.

Synthesis of [Zn(tpro)₂(H₂O)₂] (1)

An ethanol solution (4 mL) of Zn(CH₃COO)₂•2H₂O (0.100 mmol, 0.0223 g) was carefully layered on the top of an aqueous solution (4 mL) of triethylamine (0.6 mL, 0.3 mmol) and L-thioproline (Htpro, 0.359 mmol, 0.0488 g). The resulting solution was then allowed to stand at ambient conditions for several days, whereupon colorless plate-shaped crystals of 1 were formed in 93% yield (0.034 g, based on Zn(II)). Elemental analysis calcd (%) for C₈H₁₆N₂O₆S₂Zn (1): C 26.13, H 7.68, N 3.86. Found: C 26.13, H 7.68, N 3.86. Notably, complex 1 was obtained as the major product, and the other two kinds of products were minor under mild conditions except by the use of directly mixing instead, suggesting that the laying methodology may play an important role in the synthesis of complex 1.

Synthesis of [Zn(tpro)₂]ₙ (2)

An ethanol solution (4 mL) of Zn(CH₃COO)₂•2H₂O (0.100 mmol, 0.0223 g) was carefully layered on the top of a solution, which consists of an aqueous solution (4 mL) of Htpro (0.359
mmol, 0.0488 g) and triethylamine (0.6 mL, 0.3 mmol), and an ethanol solution (4 mL) of 4,4’-bipyridine (0.0497 g, 0.312 mmol). The resulting solution then allowed to stand at ambient conditions for two weeks, whereupon colorless cubic block crystals were formed in 79% yield (0.026 g, based on Zn(II)). Elemental analysis calcd (%) for C₈H₁₂N₂O₄S₂Zn (2): C 29.12, H 8.50, N 3.64. Found: C 29.18, H 8.49, N 3.65. IR (KBr pellet): \( \nu = 1336 \text{ (m)}, 1370 \text{ (m)}, 1608 \text{ (vs)}, 1645 \text{ (s)}, 3218 \text{ (s)}, 3444 \text{ cm}^{-1} \).

**Synthesis of [Zn(tpro)₂]ₙ (3)**

A methanol solution (4 mL) of Zn(CH₃COO)₂·2H₂O (0.100 mmol, 0.0223 g) was carefully layered on the top of a mixture solution, which consists of an aqueous solution (4 mL) of Htpro (0.359 mmol, 0.0488 g) and triethylamine (0.6 mL, 0.3 mmol) and a methanol solution (4 mL) of 4,4’-bipyridine (0.0469 g, 0.294 mmol). The resulting solution was then allowed to stand at ambient conditions for several days, colorless grainy crystals of 3 were obtained in 88% yield (0.029 g, based on Zn(II)). Elemental analysis calcd (%) for C₈H₁₂N₂O₄S₂Zn (3): C 29.12, H 8.50, N 3.64. Found: C 29.14, H 8.47, N 3.65. IR (KBr pellet): \( \nu = 1326 \text{ (s)}, 1403 \text{ (s)}, 1431 \text{ (s)}, 1476 \text{ (s)}, 1598 \text{ (vs)}, 1692 \text{ (s)}, 2939 \text{ (s)} , 3206 \text{ (s)} \text{ cm}^{-1} \).

**Crystallographic Data Collection and Refinement**

Single crystal X-ray diffraction analyses of compounds 1–3 were performed on a Siemens SMART diffractometer with a CCD detector with Mo Kα radiation (\( \lambda = 0.71073 \text{ Å} \)) at 295(2) K. Cell parameters were retrieved using SMART [54] software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS. Direct phase determination and subsequent difference Fourier map synthesis yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinements. All hydrogen atoms were generated geometrically with the exception of the hydrogen atoms of the coordinated water molecules, which were located in the difference Fourier map with the corresponding positions and
isotropic displacement parameters being refined. The final full-matrix, least-squares refinement on \( F^2 \) was applied for all observed reflections \([I > 2\sigma(I)]\). All calculations were performed using the SHELX software packages software package \([55]\). The Crystal data and structural refinement for compounds 1–3 are listed in Table 1. Selected bond and hydrogen bonding lengths (Å) and angles (°) for 1–3 are summarized in Tables S1–S6 (see the Electronic Supplementary Information (ESI)). The Cambridge Crystallographic Data Centre CCDC-1823036, 1823037 and 1823039 for 1, 2 and 3, respectively, contain the supplementary crystallographic data for the paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; email: deposit@ccdc.cam.ac.uk.

**Powder X-ray Diffraction of Compounds 1–3**

The powder X-ray diffraction patterns of 1 were recorded at the BL01C2 beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The ring energy of NSRRC was operated at 1.5 GeV with a typical current of 300 mA. The wavelength of the incident X-rays was 1.0332 Å (12.0 keV), delivered from the superconducting wavelength-shifting magnet and a Si(111) double-crystal monochromator. The diffraction patterns were recorded with a Mar345 imaging plate detector approximately 300 mm from sample positions and typical exposure duration 5 min. The pixel size of Mar345 was 100 µm. The one-dimensional powder diffraction profile was converted with program

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<th>2</th>
<th>3</th>
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<td>C_8H_{12}N_2O_4S_2Zn</td>
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$R_F = \Sigma||F_o - F_c||/\Sigma|F_o|$; $R_w(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w(F_o^4)]^{1/2}$.

FIT2D and cake-type integration. The diffraction angles were calibrated according to Bragg positions of Ag-Benhenate and Si powder (NBS640b) standards. In-situ synchrotron powder X-ray diffractions of 1–3 were performed at BL01C2 from room temperature to 450 °C with a heating rate approximately 10 °C /min. The powder sample was sealed in a capillary (1.0 mm diameter) and heated in a stream of hot air; each in-situ powder XRD pattern was exposed for about 1.2 min.

**Results and Discussion**

**Syntheses of Compounds 1–3**

A discrete complex [Zn(tpro)$_2$(H$_2$O)$_2$] (1, Htpro = L-thioproline), and two structural isomers of coordination polymers, a 1D chain of [Zn(tpro)$_2$]$_n$ (2) and a layer structure of [Zn(tpro)$_2$]$_n$ (3), were
synthesized by reacting $\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}$, L-thioproline (Htpro) and triethylamine at ambient temperature for several days through a single-step, self-organization process (Scheme 1). Interestingly, three different single crystal products could be obtained under similar conditions by appropriately tuning the system via the use of different solvents, such as ethanol, methanol, aqueous solution, and inducing a structural directing reagent, such as 4,4’-bipyridine. In order to introduce the chirality into the products, we attempted to use the L-thioproline species as a ligand to achieve self-assembly with Zn(II) ions under mild conditions. Because the five-membered ring of the thiazolidine motif of Htpro is not planar, its conformation is twistable. The tpro$^-$ ligand can adopt two types of bonding modes: a $\eta^1$-O,N-bidentate mode or a $\mu_2$$\eta^2$-syn-anti-chelating mode (Chart 1). It should be noted that the tpro$^-$ ligand could employ the chelating mode thus allowing it to be linked in a helical manner, permitting its chirality to be translated into the target products. The thio and amino functional groups of the tpro$^-$ ligand can participate in hydrogen bonding interactions to increase the dimensions of the target products. However, such tpro-based complexes were still rare as of this writing [56–59]. A chiral L-thioproline species was employed as a ligand to react with the Zn(II) ions under the mild conditions, so that it would permit some labile compounds with coordinated water molecules to be obtained. Thus, such a simple labile complex could be used to investigate the intriguing single-crystal to single-crystal structural transformations.
**Chart 1:** Available Coordination Modes between the tpro⁻ Ligand and the Metal Ion (M⁺)

- $\eta^1$-O,N-bidentate mode
- $\mu_2^2$-syn-anti-chelating mode

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Zn(CH₃COO)₂·2H₂O + Htpro + Et₃N → [Zn(tpro)₂(H₂O)₂] 0-D
One pot reaction
```

**Scheme 1:** The Syntheses of Compounds 1–3

**Structural description of [Zn(tpro)₂(H₂O)₂] (1)**

A single-crystal X-ray diffraction analysis revealed that compound 1 crystallizes in the monoclinic space group $P2_1$. As shown in Figure 1a, the Zn(II) ion is bound to two nitrogen atoms (N1,N2) and two oxygen atoms (O1,O3) from two crystallographically independent tpro⁻ ligands, and two oxygen atoms (O5, O6) from two coordinated water molecules, producing a complex with a distorted octahedral geometry. Two coordinated water and two tpro⁻ ligands were located in a cis conformation, and the latter adopted a chelating coordination mode. Compound 1 belongs to a class of MA₂B₂C₂ type complex, thus, from stereochemical point of view it could be described to have a $trans$-N,N, $cis$-O,O, $cis$-O’,O’ configuration. The Zn–O distances are in the range of 2.051(7)–2.158(6) Å and the Zn–N distances are 2.146(1) and 2.143(1) Å, respectively. It is noteworthy that a variety of hydrogen bonding interactions are operating among these discrete complexes. They were mutually interlinked via the coordinated water molecules (O5, O6) and the carboxylate oxygen atoms (O3, O2, O4) from the tpro⁻ ligands with hydrogen bonding interactions (O–H···O) with distances of 2.64, 2.73 and 2.69 Å, respectively. As a result, these Zn²⁺ ions were linked together through the carboxylate motif of the tpro⁻ ligands, leading to the formation of a 1D chain (Figure 1b), and
these chains were then further staggered in an ABAB manner, resulting in a 2D layer (Figure S1, in the ESI†). Finally,

\[ \eta^1-O,N\text{-bidentate mode} \quad \mu_2-\eta^2\text{-syn-anti-chelating mode} \]

**Figure 1:** Structures of 1: (a) Coordination environment of the Zn(II) ion, (b) a simplified 1D chain connected by hydrogen bonding interactions (orange dash lines).

these hydrogen-bonded layers were further linked by the hydrogen bonding interactions (C–H⋯S) with distances of 3.764 (1) and 3.948 (2) Å, resulting in a 3D supramolecular architecture, as depicted in Figure S2†.

**Structural description of [Zn(tpro)₂]**

A single-crystal X-ray diffraction analysis revealed that compound 2 also crystallizes in the monoclinic space group P2₁, but the unit cell parameters were completely different from that of 1. As shown in Figure 2, the Zn(II) center is surrounded by three tpro⁻ ligands using the N atom and an O atom in a \( \mu_2-\eta^2\text{-syn-anti-chelating mode} \) to form slightly distorted trigonal bipyramidal coordination geometry, in which the O1 and O3 atoms occupy at axial position and the other atoms O2, N1 and N2 are located at equatorial position. The Zn–O distances are 2.004(3), 2.053(3) and 2.128(3) Å and the Zn–N distances are 2.055(3) and 2.080(3) Å. Notably, in compound 2, the O2 atom from the carboxylate motif of the tpro⁻ ligand served as a bridge for the neighboring Zn(II) ions, resulting in the formation of a 1D right-handed helix (Figure 2b). These adjacent helical chains were further connected via the hydrogen bonding interactions (N–H⋯O) with the distances of 2.862(5), 3.170(5) and 3.097(6) Å, forming a 2D homochiral layer structure. Finally, these layers were linked together by hydrogen bonding interactions through
C–H···S, leading to the formation of a 3D supramolecular structure (Figure S3†).

Figure 2: Structures of compound 2: (a) the coordination environment of the Zn(II) ion, (b) a simplified right-handed single-stranded helical chain.

Structural description of [Zn(tpro)$_2$]$_n$ (3)

A single-crystal X-ray diffraction analysis revealed that compound 3 crystallizes in the orthorhombic space group $P2_12_12_1$. As shown in Figure 3a, the Zn(II) ion is six-coordinated via two N and two O atoms of two distinguish chelated tpro$^-$ ligands, and two O atoms from two $\eta^1$-carboxylate from two tpro$^-$ ligands, in a distorted octahedral geometry. It is interesting to note that there are four tpro$^-$ ligands bound to the Zn(II) ions, two ligands are coordinated via N and O atoms adopting a bidentate mode, and thereby forming two five-membered chelated rings. The other two are coordinated through two $\eta^1$-carboxylate motifs in a $\eta^1$-O,N-bidentate mode, each of which is located trans to the bidentate tpro$^-$ ligand. The Zn–O distances are 2.030(2), 2.081(2), 2.099(2) and 2.131(2) Å, respectively. The Zn–N distances are 2.149(2) and 2.289(2) Å. Interestingly, all of the tpro$^-$ ligands are linked to two Zn(II) centers in a $\mu_2$-$\eta^2$-syn-anti-chelating mode, yielding a right-handed helix structure. The two types of helices (along the $a$-, $b$-axis) intersect through the Zn(II) centers, yielding a 2D homochiral layer in the $ab$ plane. The Zn$^{II}$ atom can be regarded as a four-connecting node. The carboxylate motifs of the tpro$^-$ ligands function as an extended linker, bridging two Zn$^{II}$ centers, while the other motifs are omitted for clarity. Interestingly, a protuberant-grid-type network is apparent (Figure 3b). Thus, this layer architecture possesses with a (4,4) topology (Figure 3c). The Zn$^{II}$···Zn$^{II}$
separation distances across the $\mu_2$-$\eta_2^*$-syn-anti-COO$^-$ are 5.883(1) and 5.226(1) Å, respectively. These layers are stacked in an ABAB manner connected by hydrogen bonding interactions (N–H--S) with a distance of 3.418(2) Å, leading to the formation a 3D homochiral supramolecular network (Figure S4†).

![Figure 3](image)

**Figure 3:** Structures of compound 3: (a) the coordination environment of Zn(II) ion, (b) a simplified 2D homochiral layer with the Zn(II) ions and the carboxylate motifs from the tpro$^-$ ligands in the ab plane, while the other motifs are omitted for clarity, (c) a 2D layer structure with a (4, 4) topology.

**The Study of Thermogravimetric Analysis and Powder X-Ray Diffraction**

Thermogravimetric analyses (TGA) of 1 indicated that the coordinated water molecules are removed in the temperature range of 66–106 °C (Figure S5a†). The resulting 9.8% weight loss is consistent with the calculated value (9.0%). After the water molecules are removed, the complex was stable up to the temperature of about 213 °C. TGA patterns of 2 showed no significant change and it was thermally stable at temperature of up to 209.6 °C, after which it was gradually decomposed (Figure S5b†). The TGA pattern of 3 revealed that it was thermally stable up to 215 °C, after which, decomposition took place (Figure S5c†).
Figure 4: The PXRD patterns at different temperatures for compounds: 1 (a), 2 (b).

Powder X-ray diffraction (PXRD) patterns showed that the crystallinity of 1 does not change appreciably upon the removal of the coordinated water molecules at temperature of up to 120 °C (Figure 4a). A new crystalline pattern, however, was observed at 150 °C, and this pattern remained unchanged at temperature of up to 240 °C. However, at temperature higher than 240 °C, a second new crystalline pattern appeared, indicating that some interesting structural changes had likely occurred. In addition, powder X-ray diffraction (PXRD) patterns showed that the crystallinity of 2 does not change appreciably until the temperature reaches to 240 °C, suggesting that this 1D polymeric chain is thermally stable at this temperature (Figure 4b). The PXRD patterns of 3 showed that the crystallinity of 3 does not change until the temperature reaches to 240 °C, indicating that it is relatively thermally stable (Figure S6†).
Solid-State Thermal-Driven Structural Transformations

Figure 5: A plausible mechanism for compound 1 underwent a single-crystal to single-crystal structural transformation. Upon the removal of labile water (O6), creating the activation sites on the Zn(II) centers and the neighbouring carboxylate oxygen atoms (O2, O4) form the tpro⁻ ligands were also activated and distorted to a suitable orientation, so that they were facilely attacked to the Zn(II) centers in the solid state.

We were astonished at what occurred during this thermally driven structural transformations in the solid state. We are inspired by the bottom-up approach that employs the assembly of secondary building units (SBUs), which play an important role in controlling the growth of higher dimensional metal–organic frameworks or coordination polymeric networks. It is noteworthy that upon heating at 240 °C, the PXRD pattern of the dehydrated 1 underwent a complete change, suggesting that it was truly activated and a single-crystal to single-crystal structural transformation had occurred (Figure S7†). As a result, upon the removal of two coordinated water molecules, the Zn(II) centers of the complexes were transformed into two uncoordinated sites. These adjacent carboxylate oxygen atoms (O2,O4) from the neighboring complexes were probably slightly distorted and, as a result, were capable of being coordinated alternately to the active sites of Zn(II) ions, resulting in the formation of a 1D helical chain of 2 (Figures 5 and S8†).
Finally, in order to further study the details involved in these phase transformations, we carried out a precise examination of 1 using in-situ synchrotron powder X-ray diffraction. As shown in Figure 6, the simulated results of synchrotron powder X-ray diffraction reveals that the ratio of 2 : 3 is 97.6 to 2.4 %. Indicating that small amounts of compound 3 were also produced during this crystal to crystal structural transformation. It was probably attributed that the orientation of carboxylate motifs of 2 was arranged in the helical form, thus, their related orientations were probably difficult to be changed in the solid state (Figure S10†). Therefore, these in-situ synchrotron powder X-ray diffraction analyses demonstrate that two phase transformations are induced from discrete complex in crystalline state. It is likely that because of the close molecular packing, the restricted migration and reorientation of functional groups are relatively sluggish to form the higher dimensional structures [60].
Conclusions

In conclusion, three compounds have been successfully synthesized, including a discrete complex, a 1D right-handed helical chain and a 2D amino-acid-based coordination polymer having a protuberant-grid-type network with a (4,4) topology. The labile water molecules of discrete complex are removed upon heating, and the carboxylate oxygens become activated with their orientations being distorted. Consequently, these carboxylate motifs from the neighbouring complexes could be induced to attack the Zn(II) ions with the activation sites. Therefore, the ligand, tpro\(^{-}\), which possesses chirality, and a carboxylate motif with a \(\mu_2-\eta^2\)-syn-anti-chelating mode appear to play an important role in the distortion effect that facilitates the structural transformation of the discrete complex into a 1D polymeric chain. Such a single-crystal to single-crystal phase conversion was confirmed by a synchrotron powder X-ray diffraction study. Thus, these complexes can also be further converted into 2D structures, albeit the amount that is converted is small. It provides the deep insights into the single-crystal to single-crystal transformations of a discrete complex, which can be converted to 1D and/or 2D amino-acid-based coordination polymers.

*Electronic Supplementary Information (ESI) available: additional structures, PXRD, FT–IR and TGA.*

References

3. Sen S, Neogi S, Rissanen K, Bharadwaj PK. Solvent induced single-crystal to single-crystal structural


