

Structural transformations from a 1-D chain to two 3-D supramolecular isomers *via* crystal disassembly and reassembly^{†‡§}

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The reaction of L(–)-malic acid (L-H₂mal), manganese salts and triethylamine in methanol–water solution gave a 1-D chiral complex, [Mn^{II}(L-mal)(H₂O)(CH₃OH)]₂ (**1**), which could be rationally controlled to transform into 3-D supramolecular isomers [Mn^{II}(L-mal)(H₂O)₂]·H₂O (**2a** and **2b**, respectively).

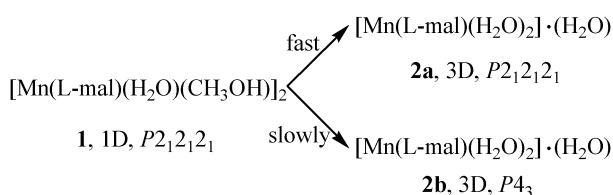
During the past decades in the field of crystal engineering, much effort has been devoted to the design and synthesis of novel coordination frameworks from the combination of metal ions and multi-functional bridging ligands.¹ In this field, the phenomena of structural transformations are often found and play important roles in achieving functional frameworks.² It is well-known that structural transformation, except for single-crystal-to-single-crystal transformation,³ usually occurred in consistence with crystal disassembly and reassembly,⁴ thus resulting in completely different structures, but a rare example has been found to realize the structural transformation to bring out more than one products with an identical formula, *i.e.* supramolecular isomers. Supramolecular isomerism,⁵ the existence of more than one framework superstructure for a given set of components, is currently an interesting subject in crystal engineering. Studies on structural transformation and supramolecular isomerism would open opportunities to gain better understanding of the fundamental factors that influence crystal nucleation and growth and hence help to develop functional materials. We report herein the syntheses and structures of three manganese–malate coordination polymers, namely [Mn(L-mal)(H₂O)(CH₃OH)]₂ (**1**) and [Mn(L-mal)(H₂O)₂]·H₂O (**2a** and **2b**), respectively, and the structural transformation phenomena from a 1-D **1** to 3-D **2a** and **2b**. It is interesting that the transformations from **1** to **2a** and **2b** could be

easily controlled, and **2a** and **2b** are genuine structural supramolecular isomers.⁶ It should be noted that the structure of complex **2a** (CSD refcode MALAMN) has previously been reported,⁷ and a supramolecular isomer of **2a** and **2b**, 2D-[Mn(L-mal)(H₂O)₂]·H₂O,⁸ was also found.

The reaction of MnCl₂·4 H₂O with L-H₂mal in a 1 : 1 ratio in a CH₃OH–H₂O solution in the presence of triethylamine afforded dispersive colorless small block crystals of **1** in one day. The structural transformations from **1** to **2a** and **2b** were depicted in Scheme 1. When **1** was kept undisturbed in solution, they could dissolve in one day and convert to acervate pink plate-like crystals of **2a** after two days. If **1** was sealed in solution, they could dissolve slowly and convert to pink prism-like crystals of **2b** in two months. The crystallization of **1** was obviously kinetically controlled, and the crystallization of **2a** and **2b** was thermodynamically favored.

X-Ray structural analysis revealed that **1**, **2a** and **2b** crystallized in chiral space groups *P*2₁2₁2₁, *P*2₁2₁2₁ and *P*4₃, respectively. The structure of **2a** was the same as that reported.⁷ All malate ligands in these complexes adopted a tetradentate coordination mode, which in **1** was coordinated to two manganese ions with its 1,4-carboxylate oxygen atoms and the hydroxyl group bound to one manganese ion to form five- and six-membered rings (Chart 1), thus resulting in a bended malate backbone, while in both **2a** and **2b** the tetradentate mode was coordinated to three manganese ions by using a 1-carboxylate oxygen atom and a hydroxyl group chelating to one manganese ion and a 4-carboxylate group bridging two other ones.

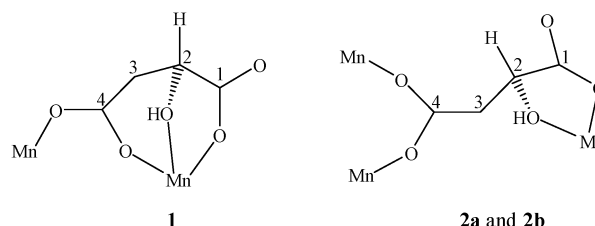
As shown in Fig. 1a, two crystallographically independent manganese ions in **1** locate in slightly distorted octahedral coordination environments. Either Mn1 or Mn2 is coordinated to one hydroxyl oxygen atom and three carboxylate oxygen atoms from two different malate ligands, and two oxygen atoms from water and methanol molecules. The average bond distances of Mn1–O_{carboxylate} (2.172 Å) and Mn1–O_{methanol} (2.144 Å) are slightly longer than those of Mn2–O_{carboxylate} (2.149 Å) and Mn2–O_{methanol} (2.128 Å), respectively, while the distance of Mn1–O1 W (2.158 Å) is almost equal to that of Mn2–O2 W (2.157 Å). The Mn–O_{hydroxyl} distances are 2.234 and 2.269 Å for Mn1 and Mn2, respectively. The 4-carboxylate



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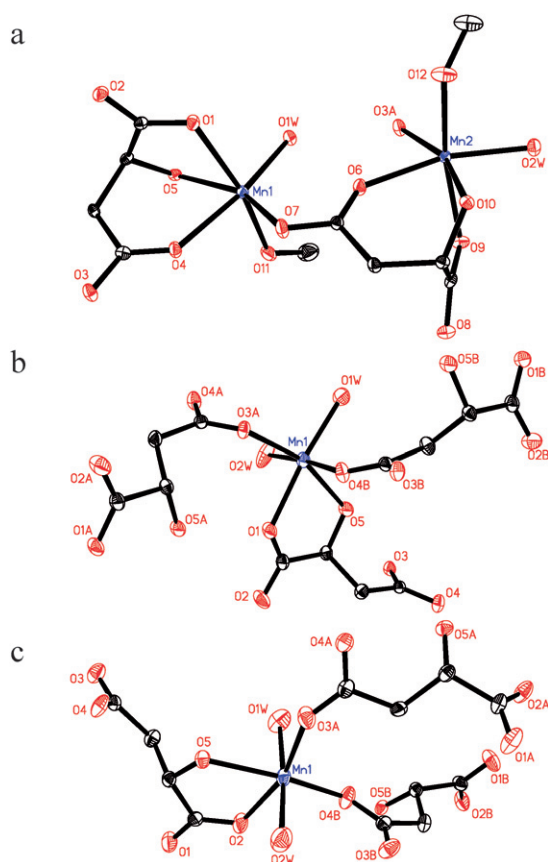


Fig. 1 ORTEP drawings of coordination units of **1** (a), **2a** (b) and **2b** (c) with a 35% probability level, respectively. Lattice water molecules are omitted for clarity. Symmetry codes: (A) $x - 1, y, z$ for **1**; (A) $-x + 3/2, -y + 1, z - 1/2$, (B) $-x + 2, y - 1/2, -z + 3/2$ for **2a**; (A) $-y + 1, x + 1, z - 1/4$, (B) $-x - 1, -y + 2, z - 1/2$ for **2b**.

group exhibits an *anti-syn* coordination mode and links hydroxyl- and 1-carboxylate-chelated manganese moieties to generate an infinite chiral chain (Fig. 2a) with alternative manganese separations of 4.939(1) Å and 5.073(1) Å, respectively. The chain is extended along the *a* axis and sustained by intrachain hydrogen bonds between coordinated water molecules and carboxylate groups (O1 W...O3A, O2 W...O7A) and interchain hydrogen bonds among the coordinated water molecules, hydroxyl groups and carboxylate groups in the *ab* and *ac* planes.

2a and **2b** are structural supramolecular isomers with identical chemical composition. Each manganese ion in **2a** and **2b** is chelated by one carboxylate oxygen atom and the hydroxyl oxygen from one malate ligand (Fig. 1b and 1c) to form a five-membered ring, and coordinated to two carboxylate oxygen atoms from two other malate ligands as well as two water molecules achieving distorted octahedral coordination geometry. The average Mn–O bond lengths are 2.155 and 2.163 Å for **2a** and **2b**, respectively. The two coordination water molecules locate at *cis*- and *trans*-positions, leading to the *trans*- and *cis*-arrangements of carboxylate oxygen atoms (O3A and O4B) around the metals in **2a** and **2b**, respectively. This delicate difference therefore results in completely different architectures.

As early reported,⁷ **2a** is a 3-D polymeric structure involving 1-D channels running along the *c* axis (Fig. 2b) that are occupied by lattice water molecules, where each malate ligand is coordinated to

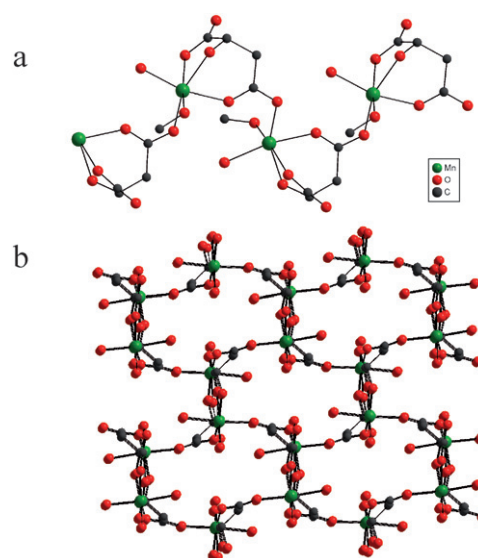


Fig. 2 The chiral chain structure of **1** (a) and a 3-D framework of **2a** (b). Hydrogen atoms and guest water molecules are omitted for clarity. Color codes for C, O and Mn atoms are grey, red and green, respectively.

three different manganese atoms as well as each manganese ion is attached to three different malate ligands. It is worthy of mentioning that, in addition to those hydrogen bonds in ref. 7, the hydroxyl group is also involved in hydrogen bonding, *i.e.* inter-malate O5...O1 (2.718(2) Å) hydrogen bond.

2b features a 3-D framework in which the malate ligands and manganese ions form rectangular channels with S_4 symmetry (Fig. 3a). The manganese ions in **2b** locate on two sites, A and B, respectively, which on the A sites are linked to each other by malate ligands through the carboxylate oxygen atoms (O3) and the chelate groups (O2 and O5) to form a helical chain (as shown with a solid line). And the manganese ion on the B site is, on one hand, bridged to that one on A site through the carboxylate group (O3, O4) and on the other hand, is chelated by a hydroxyl oxygen and carboxylate oxygen atom from one malate ligand (as shown in a fine line), whose carboxylate oxygen atom (O4) is coordinated to an adjacent manganese ion on the A site ($-x, -y + 1, z + 1/2$) as well as its another carboxylate oxygen atom (O3) is bound to an A-site manganese ion in adjacent helical architecture. The manganese ion on the B site is further coordinated to one carboxylate oxygen atom (O3) from another malate ligand which, along with the manganese ions forms the adjacent helical structure.

As shown in Fig. 3b, each larger rectangular channel is occupied by lattice water molecules (O3 W) ranked in a helical chain with S_4 symmetry. Each lattice water molecule involves in hydrogen bonds with coordination water molecules and a carboxylate oxygen atom, those are O2 W...O3 W (2.957(10) Å) in which O3 W acts as hydrogen-bond acceptor, and O3 W...O2 (3.060(8) Å) as well as O3 W...O1 W (2.852(9) Å) in which O3 W acts as a hydrogen-bond donor.

In summary, we have successfully realized structural transformations from a kinetically-controlled 1-D complex (**1**) to two 3-D supramolecular isomers (**2a** and **2b**), the transformations are believed to be related to the disintegration and reorganization of crystals. The presence of methanol is essential for the transformation process, because any attempts to use other solvents instead of methanol have not succeeded.

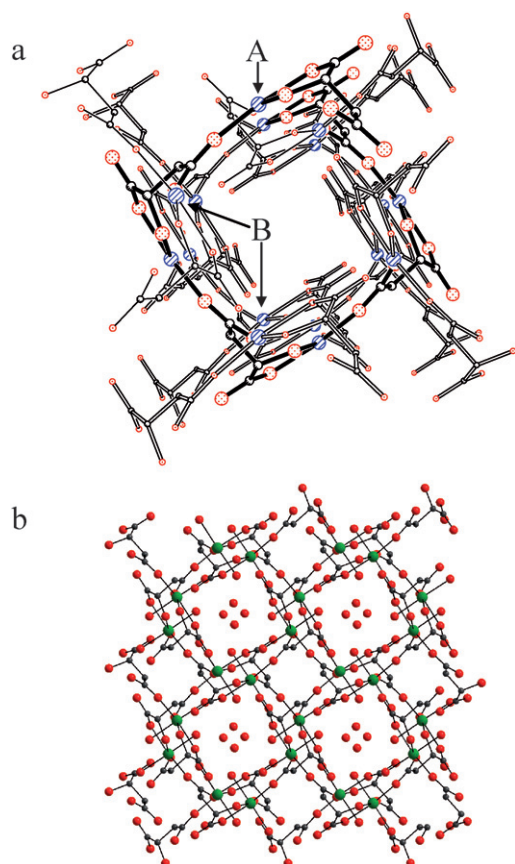


Fig. 3 (a) The rectangular subunit of **2b** showing the manganese ions located on two types of sites, coordination water molecules were omitted for clarity, and (b) 3-D framework of **2b** with 1-D channels occupied by water chains with S_4 symmetry.

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Notes and references

§ Synthesis of **1**: A methanol–water (6 mL, v/v 5 : 1) solution containing $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ (0.2 mmol, 40 mg), L-H₂mal (0.2 mmol, 27 mg) and triethylamine (100 μL) was stirred for 20 min at room temperature and filtered immediately. The crystals of **1** were collected in one day, washed with methanol and dried in air. Yield, 44% (based on malate). Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_{14}\text{Mn}_2$: C, 25.31; H, 4.22. Found: C, 25.43; H, 4.13. Synthesis of **2a**: The crystals of **1** in mother liquor were left undisturbed, they dissolved in two days and **2a** began to crystallize with quick evaporation of the solvents. Synthesis of **2b**: Crystals of **1** in mother liquor were sealed with parafilm (with several pinholes) and left undisturbed, they slowly dissolved and **2b** crystallized when the solution was almost dry (about two months). The crystals of **2a** and **2b** were collected, washed with water and dried in air, respectively. Yields, 78% (**2a**) and 75% (**2b**). Anal. Calcd for $\text{C}_4\text{H}_{10}\text{O}_8\text{Mn}$: C, 19.93; H, 4.15. Found: C, 20.14; H, 4.04 for **2a** and C, 20.26; H, 4.03 for **2b**, respectively. Crystal data for **1**: $\text{C}_{10}\text{H}_{20}\text{O}_{14}\text{Mn}_2$, $M = 474.14$, orthorhombic, $P2_12_12_1$, $a = 8.6831(18)$ Å, $b = 12.128(3)$ Å, $c = 15.999(3)$ Å, $V = 1684.7(6)$ Å³, $Z = 4$, $T = 173(2)$ K, $D_c = 1.869$ Mg m⁻³, $R_1 = 0.0389$, $wR_2 = 0.0906$, $\mu = 1.572$ mm⁻¹, $S = 1.097$. Crystal data for **2a**: $\text{C}_4\text{H}_{10}\text{O}_8\text{Mn}$, $M = 241.06$, orthorhombic, $P2_12_12_1$, $a = 9.1210(19)$ Å, $b = 9.3174(19)$ Å,

$c = 10.414(2)$ Å, $V = 885.0(3)$ Å³, $Z = 4$, $T = 293(2)$ K, $D_c = 1.809$ Mg m⁻³, $R_1 = 0.038823$, $wR_2 = 0.0569$, $\mu = 1.506$ mm⁻¹, $S = 1.116$. Crystal data for **2b**: $\text{C}_4\text{H}_{10}\text{O}_8\text{Mn}$, $M = 241.06$, tetragonal, $P4_3$, $a = b = 7.9539(9)$ Å, $c = 13.189(3)$ Å, $V = 834.4(2)$ Å³, $Z = 4$, $T = 273(2)$ K, $D_c = 1.919$ Mg m⁻³, $R_1 = 0.0375$, $wR_2 = 0.0970$, $\mu = 1.597$ mm⁻¹, $S = 1.138$. X-Ray crystallographic data were collected at 293 K with a Mo K α radiation source ($\lambda = 0.71073$ Å) by using a Bruker SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection, for indexing the reflections and for determining the unit cell parameters; the collected data were integrated by using the SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations (F^2) by using the SHELXTL-97 software. All non-H atoms were refined in the anisotropic approximation against F^2 for all reflections. All H atoms were placed at their calculated positions and refined in the isotropic approximation.

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