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Synthesis, structure and interconversion of two Co(II) coordination polymers showing topological isomerism from 1D chain to 3D chiral network

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Abstract

Two Co(II) coordination polymers: $[Co(oda)(H_2O)_2 \cdot H_2O]_n$ (**1**) and $[Co(oda)(H_2O) \cdot H_2O]_n$ (**2**) (H_2oda = oxydiacetic acid) have been synthesized under mild and hydro(solvo)thermal reaction conditions, respectively, which were characterized by single crystal X-ray determination, IR and thermogravimetric analysis. $[Co(oda)(H_2O)_2 \cdot H_2O]_n$ has a covalently linked 1D chain structure, while $[Co(oda)(H_2O) \cdot H_2O]_n$ has a covalently linked 3D chiral network with channels. They show an unusual example of topological isomerism. The structural interconversion between $[Co(oda)(H_2O)_2 \cdot H_2O]_n$ and $[Co(oda)(H_2O) \cdot H_2O]_n$ revealed that self-assembly in the synthesis and interconversion of crystalline solids is a thermodynamically controlled process.

Keywords: Coordination polymer; Hydro(solvo)thermal synthesis; Cobalt oxydiacetate; Topological isomerism; Interconversion; Self-assembly

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1. Introduction

The design and synthesis of coordination polymers [1], often called metal–organic networks, through crystal engineering [2] is currently attracting a great deal of interest not only because of their potential applications as new functional materials with useful electronic, magnetic, optical, or catalytic properties, but also for their intriguing architectures and new topologies [3–6]. Oxydiacetic acid is a versatile complexing agent with three oxygen donor atoms and can strongly complex metal ions by forming up to two five-membered chelate rings. This ligand has been extensively used in lanthanide and actinide chemistry to form polymeric species via bridging modes, and several structures containing this anion in different environments have been determined. $[La_2(C_4H_4O_5)_3(H_2O)_3 \cdot 5H_2O]_n$ is a 3D polymeric structure containing two non-equivalent nine-coordinate La^{3+} ions [7]. $[Er_2(C_4H_4O_5)_3(H_2O)_4 \cdot 2H_2O]_n$ is composed of 2D sheets with the oxydiacetate ligands linking eight- and nine-coordinate Er^{3+} ions [8]. This ligand is also extensively used in the heterometallic complexes [9,10] and mixed-ligand complexes [11–13]. We have synthesized two new isomorphous coordination polymers: $[M_2(\mu\text{-}H_2O)(oda)_2(H_2O)_2]_n$ (where M = Mn(II) and Cd(II)) with a covalently linked 1D chain structure [14]. For the molecular-based, chelated coordination compounds of cobalt(II) and oxydiacetate, Hatfield et al. has studied the structure and the

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magnetic-properties of [Co(oda)$(H_2O)_2 \cdot H_2O]_n$ [15,16]. Herein we report the synthesis, structure and interconversion of [Co(oda)$(H_2O) \cdot H_2O]_n$ and [Co(oda)$(H_2O)_2 \cdot H_2O]_n$, which are prepared by the same starting materials under different reaction conditions. **1** and **2** are different in the topology and connectivity of the coordination network, and show an unusual example of topological isomerism [17].

2. Experimental

2.1. Materials and physical measures

All of the reagents were used as purchased without further purification. Cobalt perchlorate hexahydrate was prepared by the reaction of cobalt carbonate with perchloric acid [18]. *Caution: Co* $(ClO_4)_2 \cdot 6H_2O$ *is potentially explosive and should be used with care!* The IR spectra as KBr discs were recorded on a Bruker VECTOR-22 FT-IR spectrophotometer. CHN analysis was determined on an Elementar Vario ELIII elemental analyzer. Thermal gravimetric analysis was performed on a Shimadzu TGA-50H Thermal Gravimetric Analyzer at a heating rate of 5 °C min^{-1}.

Table 1
Crystallographic data and refinement details for **1** and **2**

Compound	1	2
Formula	$C_4H_{10}CoO_8$	$C_4H_8CoO_7$
Formula weight	245.05	227.03
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a (Å)	7.1256(2)	6.814(1)
b (Å)	10.3731(5)	9.963(2)
c (Å)	11.1124(5)	10.902(2)
α (°)	90	90
β (°)	91.508(2)	90
γ (°)	90	90
V (Å^3)	821.08(6)	740.1(2)
Z	4	4
D_{calc} (g cm^{-3})	1.982	2.038
μ (mm^{-1})	2.106	2.318
$F(0\,0\,0)$	500	460
Crystal size (mm)	0.40 × 0.22 × 0.16	0.18 × 0.08 × 0.08
Scan mode	φ and ω	φ and ω
Scan range 2θ (°)	2.69–25.10	2.77–25.06
λ(Mo Kα) (Å)	0.71073	0.71073
Reflections collected	2673	2360
Unique reflections	1433	1226
Observed reflections ($I > 2\sigma(I)$)	1272	1124
Parameters	118	129
S on F^2	1.055	1.158
R ($I > 2\sigma(I)$)	0.0422	0.0442
R_w ($I > 2\sigma(I)$)	0.1107	0.0825
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	0.779 and −0.432	0.426 and −0.397

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Co–O	2.073(3)	Co–O(1)	2.106(3)
Co–O(3)	2.100(3)	Co–O(2A)	2.027(3)
Co–Ow1	2.087(3)	Co–Ow2	2.124(3)
Bond angles			
O(2A)–Co–O	166.6(1)	Ow1–Co–O(1)	87.7(1)
O(2A)–Co–Ow1	88.8(1)	O(3)–Co–O(1)	149.9(1)
O–Co–Ow1	90.8(1)	O(2A)–Co–Ow2	88.2(1)
O(2A)–Co–O(3)	91.8(1)	O–Co–Ow2	94.4(1)
O–Co–O(3)	75.0(1)	Ow1–Co–Ow2	169.9(1)
Ow1–Co–O(3)	96.7(1)	O(3)–Co–Ow2	93.0(1)
O(2A)–Co–O(1)	118.1(1)	O(1)–Co–Ow2	85.2(1)
O–Co–O(1)	75.2(1)		

Symmetry transformations used to generate equivalent atoms: (A) $x-(1/2)$, $-y-(1/2)$, $z-(1/2)$.

2.2. Synthesis of complexes

2.2.1. [Co(oda)$(H_2O)_2 \cdot H_2O]_n$ (1)

$Co(ClO_4)_2 \cdot 6H_2O$ (0.18 g, 0.50 mmol) and oxydiacetic acid (0.067 g, 0.50 mmol) were thoroughly mixed in water (0.3 ml), ethanol (0.5 ml), and pyridine (0.05 ml) in a beaker. During the evaporation of ethanol in room temperature, dark red–purple block crystals were obtained in a few hours, which were collected, washed with ether, and air-dried to give 0.086 g (70.0%) of product. *Anal.* Calc. (Found) for $C_4H_{10}CoO_8$ (**1**): C, 18.9 (19.6); H, 4.16% (4.11%). IR (KBr, cm^{-1}): 3380(w), 1624(s), 1594(s), 1427(s), 1311(m), 1142(s), 1048(m), 933(m), 739(w), 575(m).

2.2.2. [Co(oda)$(H_2O) \cdot H_2O]_n$ (2)

The synthesis was performed under hydro(solvo)thermal conditions. A heavy-walled Pyrex tube containing a mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (0.18 g, 0.50 mmol) and oxydiacetic acid (0.067 g, 0.50 mmol) in water (0.3 ml), ethanol (0.1 ml), and pyridine (0.05 ml) was frozen in

Table 3
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
Co–O	2.108(4)	Co–O(1)	2.100(4)
Co–O(3)	2.085(4)	Co–O(2A)	2.021(4)
Co–Ow1	2.096(4)	Co–O(4B)	2.128(5)
Bond angles			
O(2A)–Co–O	171.2(2)	Ow1–Co–O(1)	89.7(2)
O(2A)–Co–Ow1	92.1(2)	O(3)–Co–O(1)	152.7(2)
O–Co–Ow1	87.8(2)	O(2A)–Co–O(4B)	94.6(2)
O(2A)–Co–O(3)	112.8(2)	O–Co–O(4B)	85.0(2)
O–Co–O(3)	75.9(1)	Ow1–Co–O(4B)	172.2(2)
Ow1–Co–O(3)	92.3(2)	O(3)–Co–O(4B)	88.7(2)
O(2A)–Co–O(1)	94.3(2)	O(1)–Co–O(4B)	85.9(2)
O–Co–O(1)	76.9(2)		

Symmetry transformations used to generate equivalent atoms: (A) $-x+1$, $y+(1/2)$, $-z+(1/2)$; (B) $x+(1/2)$, $-y+(3/2)$, $-z$.

liquid N_2, sealed under vacuum and placed inside an oven at 125 °C. Dark red–purple block crystals were obtained after 24 h of heating, which were collected, washed with ether, and air-dried to give 0.053 g (46.4%) of product. *Anal.* Calc. (Found) for $C_4H_8CoO_7$ (**2**): C, 21.2 (21.3); H, 3.55% (3.47%). IR (KBr, cm^{-1}): 3440(w), 1587(s), 1437(m), 1324(m), 1125(s), 1045(m), 929(m), 724(w), 590(m).

2.3. X-ray crystallography

X-ray diffraction data of **1** and **2** were collected on a Siemens SMART CCD diffractometer equipped with a graphitemonochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections using the SADABS procedure were applied [19]. The structure was solved by direct methods using SHELXS-97 [20] and refined by the full-matrix least-squares against F^2 [21]. The crystallographic data and other pertinent information are summarized in Table 1. The selected bond distances and angles are listed in Tables 2 and 3.

3. Results and discussion

Both **1** and **2** are stable in air and insoluble in water and common organic solvent. Though they appear as identical dark red–purple block crystals, their infrared spectra indicated a possible difference in structure. The value of $\Delta\nu$ (the difference between ν_{as}(COO) and ν_s(COO)) in complex **1** is 222 and 167 cm^{-1}, while the value of $\Delta\nu$ in complex **2** is 150 cm^{-1}.

3.1. Crystal structures

3.1.1. [Co(oda)$(H_2O)_2 \cdot H_2O]_n$ (1)

The asymmetric unit of **1** contains one Co(II) center, one oxydiacetate group, two aqua ligands and one lattice water molecule. The local coordination environ-

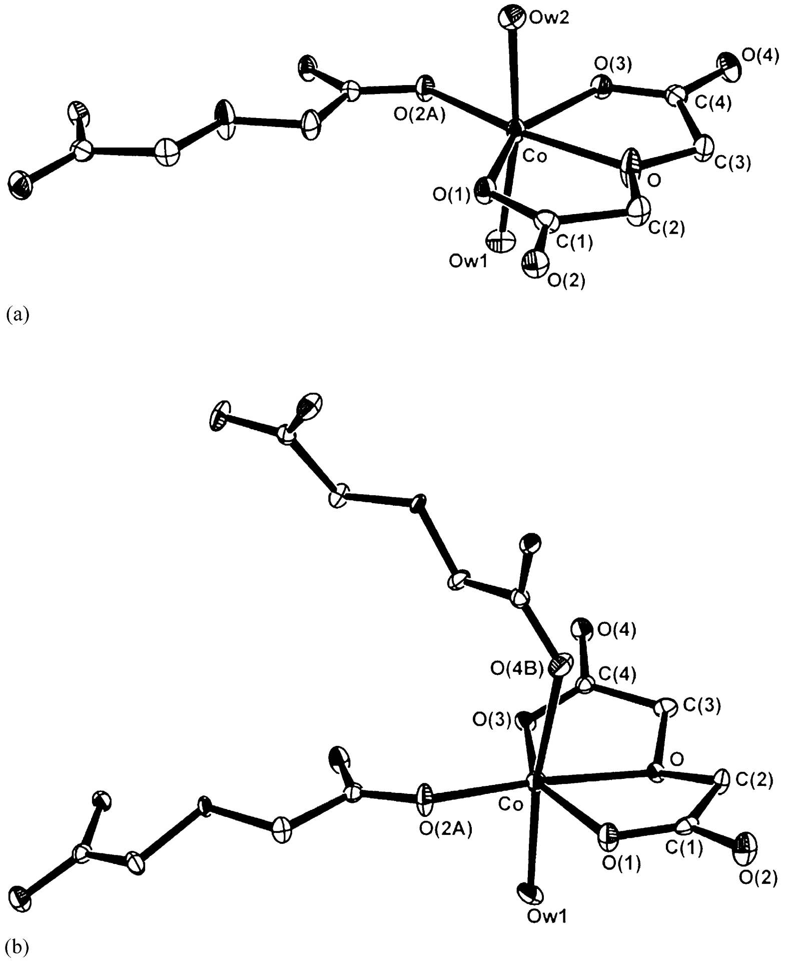


Fig. 1. ORTEP views of the coordination environment including the asymmetric unit (except guest water molecule) present in **1** (a) and **2** (b) with non-hydrogen atoms represented by thermal ellipsoids drawn at the 40% probability level. Atoms labeled with an additional letter ‘A or B’ are symmetrically equivalent to those atoms without such designation.

ment around the Co ion in **1** can best be described as distorted octahedral as shown in Fig. 1(a). Each Co center is coordinated to three oxygen atoms from a chelate oxydiacetate group, one carboxylato oxygen atom from another oxydiacetate group, and two aqua ligands. The bond angles around the central Co atom and the *cis* ligands range from 75.0° to 118.1°, while the bond angles around the central Co atom and the *trans* ligands range from 149.9° to 169.9°. The Co–O distances are 2.027(3)–2.124(3) Å.

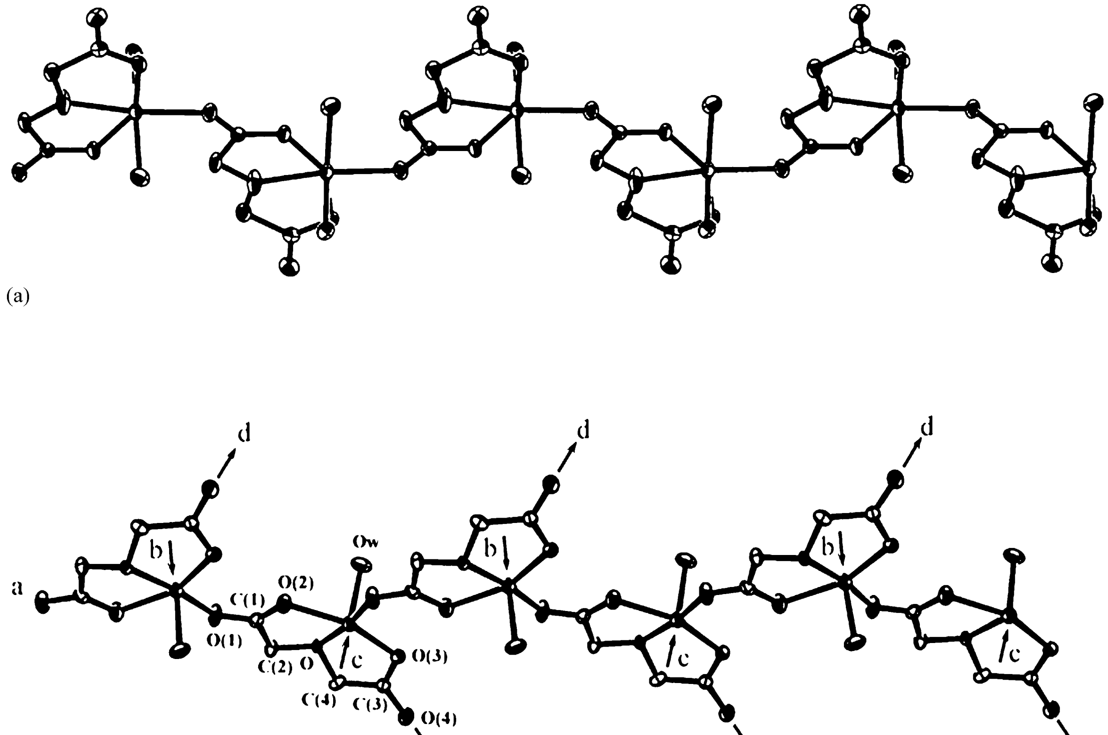
Along the *b* axis, adjacent Co atoms are bridged via the carboxylate groups to form an infinite zigzag chain structure (Fig. 2(a)). All of the carboxylate bridges in the chain adopts an *anti–anti* conformation with a Co–Co separation of 5.91 Å and an angle of 122.9°. These infinite zigzag Co(oxydiacetate) chains are packed together via interchain hydrogen bonds to give a 3D network (Fig. 3(a)). The shortest Co–Co separation between adjacent chains is 7.13 Å.

3.1.2. $[Co(oda)(H_2O)\cdot H_2O]_n$ (**2**)

The asymmetric unit of **2** contains one Co(II) center, one oxydiacetate group, an aqua ligand and a lattice water molecule. The local coordination environment around the Co ion in **2** is similar to that in **1** except that a caboxylato oxygen atom replaces an aqua ligand, shown in Fig. 1(b). The bond angles around the central Co atom and the *cis* ligands range from 76.0° to 112.8°, while the bond angles around the central Co atom and the *trans* ligands range from 152.7° to 172.2°. The Co–O distances are 2.021(4)–2.128(5) Å.

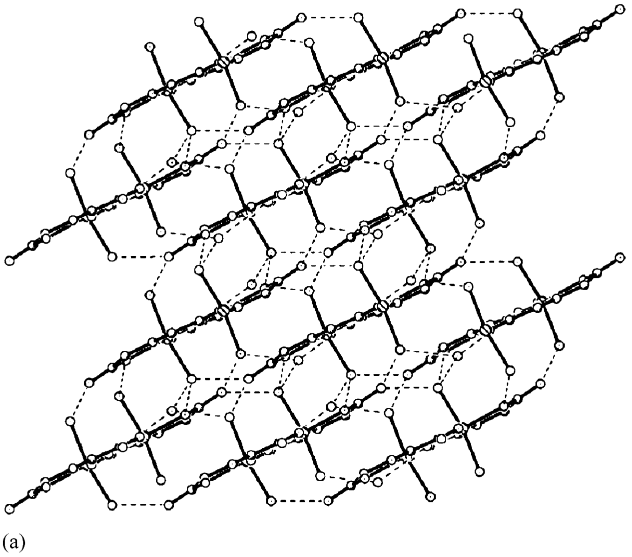
Along the *b* axis, adjacent Co atoms are bridged via the carboxylate groups to form an infinite zigzag chain structure (Fig. 2(b)). All of the carboxylate bridges in the chain adopts a *syn–anti* conformation with a Co–Co separation of 5.41 Å and an angle of 134.0°. Each infinite zigzag Co(oxydiacetate) chain is connected to four adjacent chains via the carboxylate of the oxydiacetate group to form a complex 3D coordination polymer (Fig. 3(b)). The shortest Co–Co separation between adjacent chains is 5.78 Å. Interestingly, a space filling model viewed down the *a* axis reveals that 1D rhomboid channels can be seen with an approximate cross-section of 4.8 × 2.4 Å (Fig. 4). These channels are occupied by the coordinated and lattice water molecules, which are attached by hydrogen bonding to the framework.

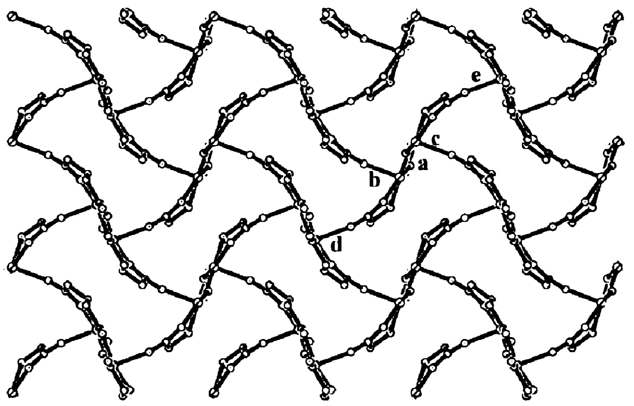
A careful comparison reveals many structural similarities between **1** and **2**. The structure of **2** can be derived from the interconnection of the zigzag chains in **1** through the loss of one coordinated water molecule per structure unit (Fig. 3), though the conformations and coordination modes of the oxydiacetate group undergo a small change. **1** and **2** differ mainly in the


(a)

(b)

Fig. 2. Views of the oxydiacetate-bridged Co–Co polymeric chain in **1** (a) and **2** (b) running along *b* axis.


(a)



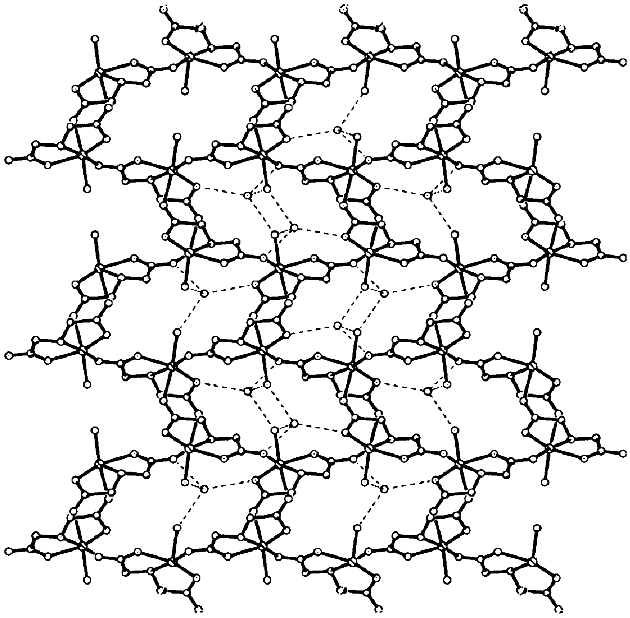
(b)

Fig. 3. (a) Packing view of **1** along *b* axis with all hydrogen atoms omitted for clarity. (b) View of **2** along *b* axis with all hydrogen atoms and water molecules omitted for clarity, showing the connections of chains.

topology and connectivity of their coordination networks, and show an unusual example of topological isomerism [17], which can exhibit superstructural diversities from even the most simple chemical building blocks. Compound **2**, which has a 3D network structure, crystallizes in the chiral space group $P2_12_12_1$. This is also suggestive that rational interconnection or packing of 1D chains can lead to a 3D chiral network structure. That achiral building blocks crystallize in a chiral space group is one strategy for the design of polar crystals that are independent of the need for homochiral molecular components [2a].

3.2. Thermogravimetry

Thermogravimetric analyses showed that **1** loses 21.5% of its total weight in the 53–147 °C temperature range, corresponding to the loss of three water molecules per formula unit (expected 22.1%), while **2** loses 15.4% of its total weight in the 110–215 °C temperature range, corresponding to the loss of two water molecules per formula unit (expected 15.9%) (Fig. 5). Both **1** and **2** lose all the water molecules in a temperature range of approximate 100 °C, but the initial temperature for **2** is much higher than that of **1**, which indicates that the


(a)

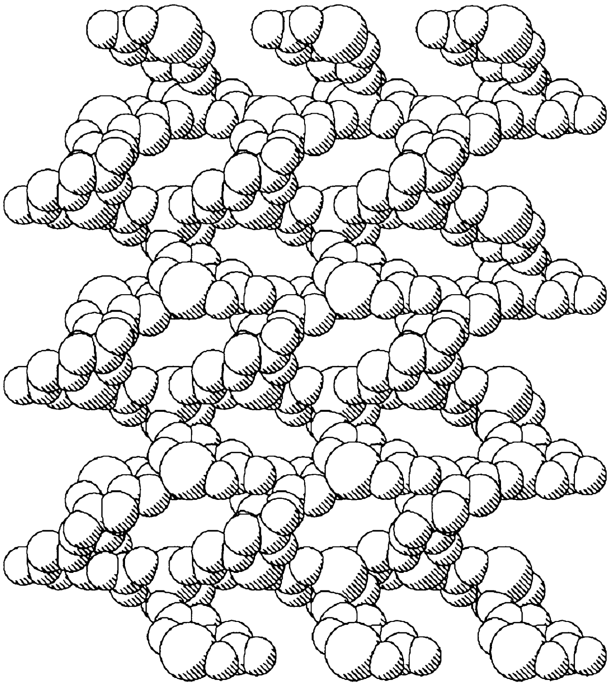

(b)

Fig. 4. (a) View of **2** along *a* axis with all hydrogen atoms omitted for clarity. (b) Space filling view of **2** along *a* axis with all water molecules omitted for clarity.

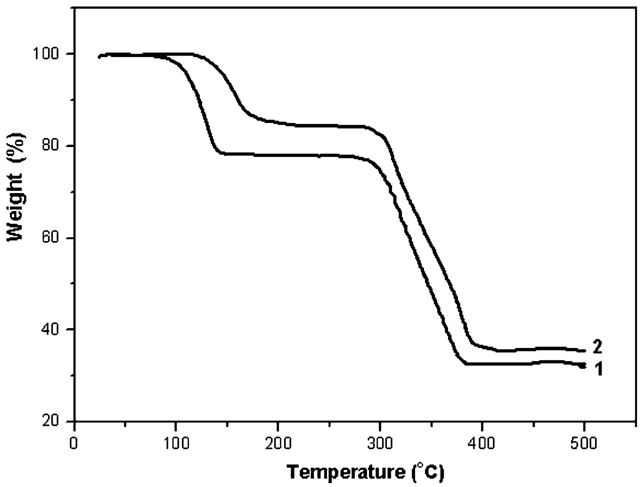


Fig. 5. Thermogravimetric data for **1** and **2** from room temperature to 500 °C.

water molecules in **2** are held more tightly than those in **1**. This result may be attributed to the compact 3D structure of **2**.

3.3. Structure reversibility

After a ground sample of **1** in mixed water/ethanol was subjected to hydro(solvo)thermal condition for 1 day, the measured infrared spectra and powder X-ray diffraction data indicated that **1** was converted to **2** quantitatively (Fig. 6). When a freshly ground sample of **2** was immersed into a mixed solvent of water and ethanol at room temperature for 12 h, the structure changed to **1** according to its powder X-ray diffraction pattern (Fig. 7). We can therefore conclude that **1** and **2** are thermodynamically stable at high temperature (125 °C) and low temperature (room temperature), respectively, and self-assembly, which is important in the synthesis and interconversion of crystalline solids, is a thermodynamically controlled process.

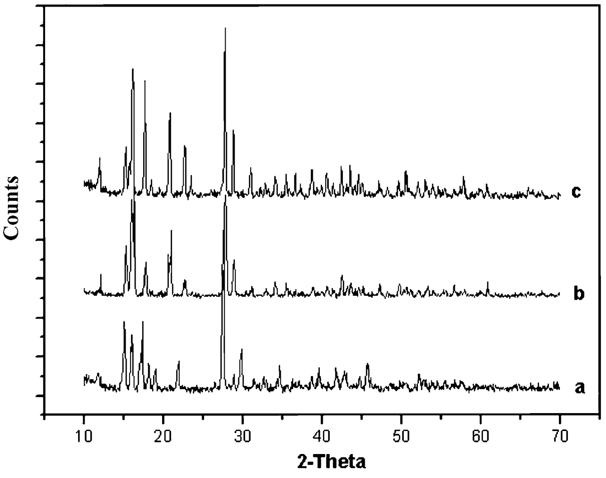


Fig. 6. Powder X-ray diffraction pattern of **1** (a), ground sample of **1** treated in the mixed solvents of water and ethanol under hydro(solvo)thermal conditions for 1 day (b), **2** (c).

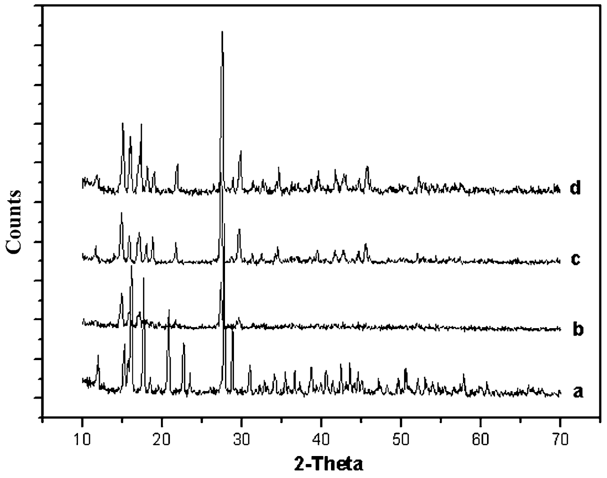


Fig. 7. Powder X-ray diffraction pattern of **2** (a), ground sample of **2** heated at 200 °C for 12 h (b), ground sample of **2** heated at 200 °C for 12 h and then immersed into the mixed solvents of water and ethanol at room temperature for 12 h (c), **1** (d).

4. Conclusion

The synthesis and characterization of two Co(II) coordination polymers under different reaction conditions, provide another example of topological isomerism in the chemistry of coordination polymers. The interconversion of **1** and **2** at different temperatures show that their self-assembly is a thermodynamically controlled process.

5. Supplementary material

Crystallographic data have been deposited with The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) and are available on request quoting the deposition number CCDC-195026 and CCDC-195027 for compounds **1** and **2**.

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References

[1] (a) B.F. Hoskins, R. Robson, J. Am. Chem. Soc. 112 (1990) 1546;
(b) P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem., Int. Ed. Engl. 38 (1999) 2638;
(c) M. Eddaoudi, D.B. Moler, H.L. Li, B.L. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.

[2] (a) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
(b) A.J. Blake, N.R. Champness, P. Hubberstey, W. Li, M.A. Withersby, M. Schröder, Coord. Chem. Rev. 183 (1999) 117.

[3] O.R. Evans, R. Xiong, Z. Wang, G.K. Wong, W. Lin, Angew. Chem., Int. Ed. 38 (1999) 536.

[4] W. Lin, O.R. Evans, R. Xiong, Z. Wang, J. Am. Chem. Soc. 120 (1998) 13272.

[5] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982.

[6] O.M. Yaghi, G.M. Li, H.L. Li, Nature 378 (1995) 703.

[7] I. Elding, Acta Chem. Scand. Ser. A 31 (1977) 75.

[8] R. Baggio, M.T. Garland, M. Perec, D. Vega, Inorg. Chem. 35 (1996) 2396.

[9] Q.D. Liu, J.R. Li, S. Gao, B.Q. Ma, F.H. Liao, Q.Z. Zhou, K.B. Yu, Inorg. Chem. Commun. 4 (2001) 301.

[10] R. Baggio, M.T. Garland, Y. Moreno, O. Pena, M. Perec, E. Spodine, J. Chem. Soc., Dalton Trans. (2000) 2061.

[11] R. Baggio, M.T. Garland, M. Perec, Inorg. Chim. Acta 310 (2000) 103.

[12] J.C. Trombe, S. Roméro, Solid State Sci. 2 (2000) 279.

[13] S. Roméro, J.C. Trombe, Polyhedron 18 (1999) 1653.

[14] C. Jiang, X. Zhu, Z.P. Yu, Z.Y. Wang, Inorg. Chem. Commun. 6 (2003) 706.

[15] W.E. Hatfield, J.H. Helms, B.R. Rohrs, P. Singh, J.R. Wasson, R.R. Weller, Proc.-Indian Acad. Sci., Chem. Sci. 98 (1987) 23.

[16] B.R. Rohrs, W.E. Hatfield, Inorg. Chem. 28 (1989) 2772.

[17] J. Blake, N.R. Brooks, N.R. Champness, M. Crew, A. Deveson, D. Fenske, D.H. Gregory, L.R. Hanton, P. Hubberstey, M. Schröder, Chem. Commun. (2001) 1432.

[18] The Chemical Society of Japan, Handbook of Inorganic Compounds Synthesis, vol. 2, Chemical Industry Press, Beijing, 1986, p. 480.

[19] G.M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.

[20] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[21] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.