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## ARTICLE

# Solvent-dependent assemblies, structure diversities and magnetic properties of two homochiral Co(II)/Na(I) coordination polymers

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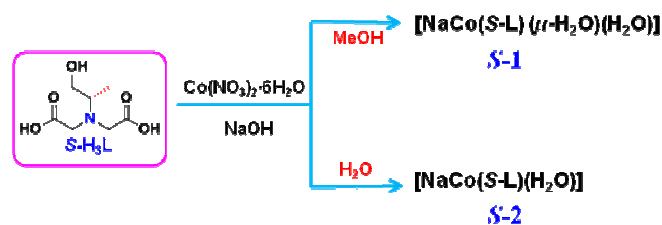
Solvent-induced synthesis of 2D and 3D homochiral Co(II)/Na(I) coordination polymers based on chiral tridentate ligand *S*-N-(1-Hydroxymethylethyl)iminodiacetic acid (*S*-H<sub>3</sub>L), formulated as [NaCo(*S*-L)( $\mu$ -H<sub>2</sub>O)(H<sub>2</sub>O)] (**S-1**) and [NaCo(*S*-L)(H<sub>2</sub>O)] (**S-2**). Compound **S-1** displays a 2D layered structure that is further expanded into a 3D supramolecular architecture by hydrogen bond interactions, while **S-2** features a 3D framework constructed by 1D Co(II) and Na(I) chains. In addition, magnetic study reveals the anti-ferromagnetic interaction in **S-2**.

## Introduction

The construction of chiral coordination polymers (Cps) have attracted great attention not only owing to their aesthetical structures but also because of their potential applications as functional materials in the fields of nonlinear optics and ferroelectrics.<sup>1</sup> Up to now, much effort has been devoted to the design and synthesis of chiral Cps. However, up to now, only a small number of them have been synthesized and structurally characterized.<sup>2</sup> This is because the chance of obtaining chiral Cps is very low and the preparation of them usually require suitable homochiral ligands.<sup>3</sup> Therefore, careful selection of enantiomerically pure ligands with certain features is crucial in the synthesis of chiral Cps.

Tridentate *N,O*-containing ligands are a family of useful ligands in coordination chemistry due to their strong coordination ability and versatile coordination modes. To date, they have been widely used in the assembly of Cps, in particular those with mixed 3d-4f metals.<sup>4</sup> For example, a large number of Cps with Triethanolamine (H<sub>3</sub>tea), Nitrilotriacetic acid (H<sub>3</sub>nta), *N*-(2-Hydroxyethyl)iminodiacetic acid (H<sub>3</sub>heidi) and *N*-(1-Hydroxymethylethyl)iminodiacetic acid (H<sub>3</sub>methedi) have been synthesized.<sup>5</sup> However, none of them are homochiral Cps because all these ligands are not enantiomerically pure. On the other hand, solvents are considered an important factor in controlling the assembly of Cps because they have effects on the control of kinetic or thermodynamic conformers as well as the coordination modes of the ligands.<sup>6</sup> For example, some solvent-dependent synthesis of Cps by changing the size, shape, component, polarity, ratio and coordination ability of the solvents has been documented.<sup>7</sup> In some cases, the dimensionality of the framework from 2D to 3D can occur by varying the reaction solvents.<sup>7</sup>

In order to make homochiral Cps, an enantiomerically pure *S*-N-(1-Hydroxymethylethyl)iminodiacetic acid (*S*-H<sub>3</sub>L) was synthesized. By employing this ligand, two novel homochiral Co(II)/Na(I) Cps, namely [NaCo(*S*-L)( $\mu$ -H<sub>2</sub>O)(H<sub>2</sub>O)] (**S-1**) and [NaCo(*S*-L)(H<sub>2</sub>O)] (**S-2**) were isolated from different solvents at room temperature. Herein, their syntheses, crystal structures and magnetic properties are discussed in detail.

Scheme 1 The syntheses of *S*-1 and *S*-2

## Experimental

### Materials and methods

All the chemicals were purchased commercially and used as received. The ligand *S*-H<sub>3</sub>L was synthesized following the previous literature procedure.<sup>5c</sup> Thermogravimetric experiments were performed using a TGA/NETZSCH STA-449C instrument heated from 30-800 °C (heating rate of 10 °C /min, nitrogen stream). Elemental analyses (C, H and N) were measured with an Elemental Vairo EL III Analyzer. The powder X-ray diffraction (XRD) patterns were recorded on crushed single crystals in the  $2\theta$  range 5-50° using Cu-K $\alpha$  radiation. The magnetic susceptibility data was collected on Quantum Design MPMS (SQUID)-XL magnetometer.

### Synthesis of [NaCo(*S*-L)( $\mu$ -H<sub>2</sub>O)(H<sub>2</sub>O)] (*S*-1)

A mixture of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (145 mg, 0.5 mmol), NaOH (10 mg, 0.25 mmol) and *S*-H<sub>3</sub>L (48 mg, 0.25 mmol) were dissolved in 20 mL of MeOH. The mixture was stirred at room temperature for another 3 h, then the resulting red solution was filtered and the filtrate was left undisturbed at ambient temperature. After several days, red crystals of *S*-1 were obtained in 50% yield based on Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Anal. calcd for C<sub>7</sub>H<sub>14</sub>CoNNaO<sub>7</sub> (*S*-1): C 27.47, H 4.61, N 4.58. Found: C 27.49, H 4.33, N 4.64.

### Synthesis of [NaCo(*S*-L)(H<sub>2</sub>O)] (*S*-2)

*S*-2 was prepared in a way similar to that described for *S*-1 except that water was used instead of MeOH. Red crystals of *S*-2 were obtained in 58% yield based on Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Anal. calcd for C<sub>7</sub>H<sub>11</sub>CoNNaO<sub>6</sub> (*S*-2): C 29.29, H 3.86, N 4.88. Found: C 29.12, H 4.01, N 4.83.

### Crystal Structure Determination

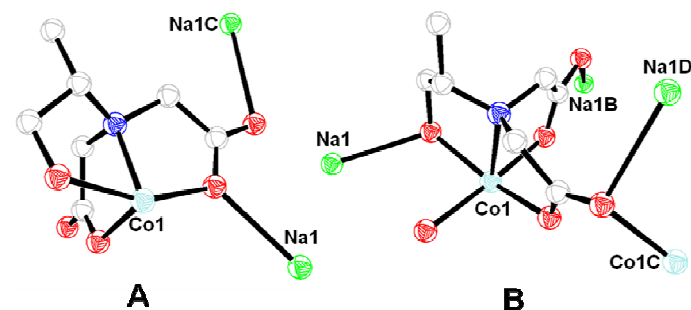
Single-crystal X-ray diffraction data were collected on a Rigaku Diffractometer with a Mercury CCD area detector (Mo K $\alpha$ ;  $\lambda$  = 0.71073 Å) at room temperature. Empirical absorption corrections were applied to the data using the Crystal Clear program.<sup>8</sup> The structure was solved by the direct method and refined by the full-matrix least-squares on  $F^2$  using the SHELXTL-97 program.<sup>9</sup> Metal atoms were located from the  $E$ -maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically.

**Table 1** Crystal Data and Structure Refinement of *S*-1 and *S*-2

Compounds	<i>S</i> -1	<i>S</i> -2
CCDC	1020718	1020719
Formula	C <sub>7</sub> H <sub>14</sub> CoNNaO <sub>7</sub>	C <sub>7</sub> H <sub>12</sub> CoNNaO <sub>6</sub>
<i>M<sub>r</sub></i>	306.11	288.10
Crystal System	Tetragonal	Tetragonal
Space group	$P2_12_12_1$	$P2_12_12_1$
<i>a</i> (Å)	7.008(5)	8.342(3)
<i>b</i> (Å)	12.151(7)	9.375(4)
<i>c</i> (Å)	13.928(1)	13.544(5)
$\alpha$ (deg)	90	90
$\beta$ (deg)	90	90
$\gamma$ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	1186.02(1)	1059.11(7)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.714	1.807
<i>M</i> (mm <sup>-1</sup> )	1.505	1.673
<i>F</i> (000)	628.0	588.0
GOF	1.097	1.059
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0310	0.0281
<i>wR</i> <sub>2</sub> <sup>a</sup>	0.0853	0.0792
Flack parameter	0.0219	0.0130

$$^a R = \sum (||F_o| - |F_c||) / \sum |F_o|, wR = \{ \sum w[(F_o^2 - F_c^2)^2] / \sum w[(F_o^2)^2] \}^{1/2}$$

The organic hydrogen atoms were positioned geometrically, while those of the water molecules were located using the difference Fourier method and refined freely. Crystal data and other pertinent information for *S*-1 and *S*-2 are summarized in Table 1. Selected bond distances and angles of *S*-1 and *S*-2 are listed in Table S1†. Bond lengths and angles of hydrogen bonds of *S*-1 are listed in Table S2†. The CCDC number are 1020718 for *S*-1 and 1020719 for *S*-2, respectively.



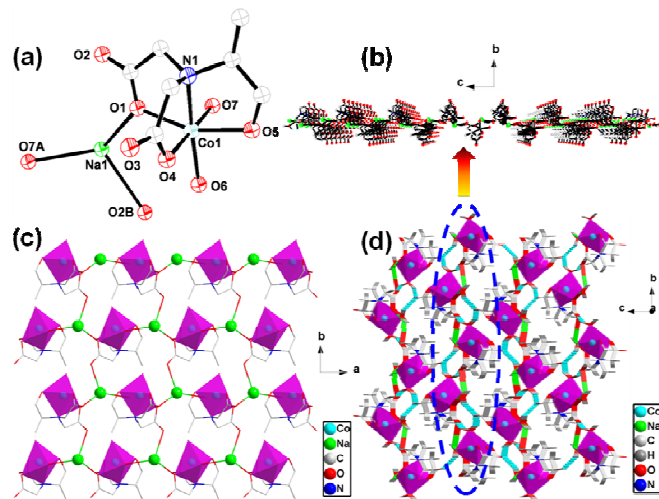
**Scheme 2** The coordination modes of *S*-L<sup>3-</sup> in *S*-1 (A) and *S*-2 (B).

## Results and Discussion

### Synthesis and description of Crystal Structures

Reactions of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with NaOH and *S*-H<sub>3</sub>L in the ratio of 2:1:1 in methanol or water led to two novel homochiral Co(II)/Na(I) Cps, formulated as [NaCo(*S*-L)( $\mu$ -H<sub>2</sub>O)(H<sub>2</sub>O)] (*S*-1) and [NaCo(*S*-L)(H<sub>2</sub>O)] (*S*-2) (Scheme 1). They are obtained in moderate yields under the same conditions except that the solvents used are different. It has been well-documented that solvents play an important role on tuning the structures of Cps. In the case of *S*-1 and *S*-2, the former obtained from methanol is a 2D layer while the latter obtained from water is a 3D framework. It seems likely that water can enhance the ligand-metal interaction of *S*-H<sub>3</sub>L, leading to the increase of framework connectivity.<sup>7f</sup>

Single crystal X-ray structural analysis reveals that *S*-1 and *S*-2 both crystallize in the chiral space group of  $P2_12_12_1$  with the Flack parameters of 0.0219 and 0.0130, respectively (Table S1). The asymmetric unit of *S*-1 contains one Co(II) ion, one Na(I) ion, one *S*-L<sup>3-</sup> anion and two coordinated water molecules. Each Co(II) center is six-coordinated by one *N* atom from one *S*-L<sup>3-</sup> ligand, three *O* atoms from the *S*-L<sup>3-</sup> ligand and two *O* atoms from two coordinated water molecules. The Na(I) ion is three-coordinated by one  $\mu$ -H<sub>2</sub>O molecule and two carboxylate *O* atoms from two different *S*-L<sup>3-</sup> ligands with the Na–O bond lengths varying from 2.659(3) to 2.828(4) Å (Fig. 1a). The *S*-L<sup>3-</sup> ligand is fully deprotonated and adopts a ( $k^1$ - $\mu_2$ - $k^1$ - $k^1$ - $k^1$ )- $\mu_3$  coordination mode to connect two Co(II) and one Na(I) ion (Scheme 2A). The six-coordinated Co(II) ion adopts a CoNO5 configuration to generate a mononuclear Co(II) unit, which is expanded into 1D chain *via* Na(I) and  $\mu$ -H<sub>2</sub>O bridges (Fig. 1b). These chains are further extended into a 2D layer network through the carboxylate groups of *S*-L<sup>3-</sup> ligands and the Na(I) ions (Fig. 1c).



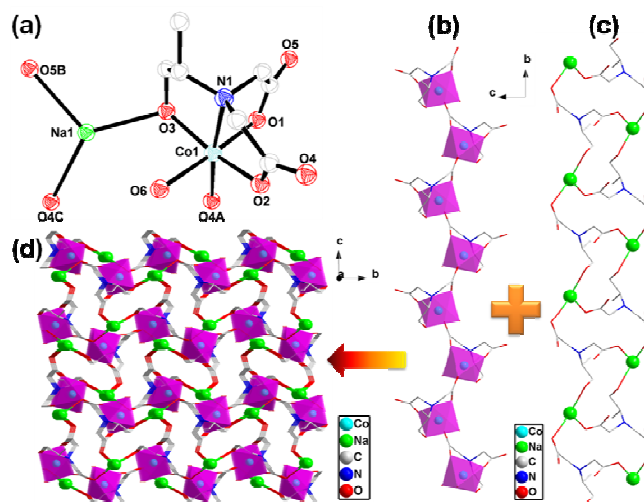
**Fig. 1** (a) View of the coordination environment of Co(II) and Na(I) ions in **S-1**. Symmetry codes: A  $x-1, y, z$ ; B  $-x, y+1/2, -z+3/2$ ; C  $-x, y-1/2, -z+3/2$ ; D  $x+1, y, z$ . (b) The 1D chain constructed by Co(II), Na(I) ions and  $S-L^{3-}$  ligands. (c) The 2D structure of **S-1**. (d) H-bonding interactions in the 3D supramolecular framework of **S-1**.

In addition, the hydrogen bond interactions between the O–H groups in coordinated water molecules and the oxygen atoms from uncoordinated carboxylate groups extend the 2D layers into a 3D supramolecular architecture (Fig. 1d).

The asymmetric unit of **S-2** includes one Co(II) ion, one Na(I) ion, one  $S-L^{3-}$  anion and one coordinated water molecule. Each Co(II) center is six-coordinated by one N atom from one  $S-L^{3-}$  ligand, four O atoms from two different  $S-L^{3-}$  ligands and one O atom from one coordinated water molecule. The Na(I) ion is three-coordinated by three O atoms from three different  $S-L^{3-}$  ligand with the Na–O bond lengths varying from 2.625(4) to 2.901(4) Å (Fig. 2a). The  $S-L^{3-}$  ligand is fully deprotonated and adopts a ( $k^1-k^1-k^1-\mu_2-\mu_2$ )- $\mu_5$  coordination mode to connect two Co(II) and three Na(I) ions through two carboxylate groups, one methoxy group and one N atom (Scheme 2B). Similar to **S-1**, the six-coordinated Co(II) ion in **S-2** also adopts a CoNO5 configuration to generate a mononuclear Co(II) unit, which is expanded into a 1D chain by  $S-L^{3-}$  ligands (Fig. 2b). Each  $S-L^{3-}$  ligand bridges three Na(I) ions to form a 1D Na(I) chain (Fig. 2c). The combination of 1D Co(II)- and Na(I)-carboxylate chains gives rise to a more complicated 3D framework (Fig. 2d).

### Solid-state circular dichroism spectra

To further confirm the homochiral nature of the products, solid-state circular dichroism (CD) spectra of **S-1** and **S-2** were measured in KCl pellets to observe the absolute configurations. As shown in Fig. S1†, compound **S-1** exhibits a strong negative Cotton effect at 519 nm. The CD curve of **S-2** is very similar to that of **S-1**, which has the similar wavelength of the negative Cotton effect.



**Fig. 2** (a) View of the coordination environment of Co(II) and Na(I) ions in **S-2**. Symmetry codes: A  $-x+2, y-1/2, -z+1/2$ ; B  $x-1/2, -y+1/2, -z$ ; C  $x, y-1, z$ ; D  $-x+2, y+1/2, -z+1/2$ ; E  $x, y+1, z$ ; F  $x+1/2, -y+1/2, -z$ . (b) View of the 1D Co(II) chain; (c) the 1D Na(I) chain; (d) The 3D layer structure of **S-2**.

### X-ray diffraction and thermal stability analysis

The powder X-ray diffractions (PXRD) are performed to test the purity of **S-1** and **S-2** (Fig. S2†). The experimental results match well with the simulated XRD patterns, indicating the phase purity of the as-synthesized samples. Thermogravimetric analysis (TGA) measurements are conducted in the temperature range of 30–800°C under a flow of nitrogen with the heating rate of 10°C min<sup>-1</sup> (Fig. S3†). The TGA curve of **S-1** indicates that the first step from 40 to 130°C with a weight loss of 11.99% is due to the loss of two coordinated water molecules (calcd 11.76%), and the framework starts to decompose at about 340 °C. The TGA curve of **S-2** is very similar to that of **S-1** with a weight loss of 6.23% from 40 to 150 °C, which is attributed to the loss of one coordinated water molecule (calcd. 6.10%). Then the framework collapses at about 340 °C.

### Magnetic property

Variable-temperature magnetic susceptibility measurement is performed on the crystalline sample of **S-1** and **S-2** in the temperature range of 2–300 K at the field of 1000 Oe. The  $\chi_m T$  vs.  $T$  plots of **S-1** and **S-2** exhibit a similar magnetic behavior (Fig. 3). At 300 K, the  $\chi_m T$  values of **S-1** and **S-2** are 3.45 and 3.12 cm<sup>3</sup> K mol<sup>-1</sup>, respectively, which are greater than that expected for the spin-only value (1.88 cm<sup>3</sup> K mol<sup>-1</sup> with  $S = 3/2$  and  $g = 2.0$ ).<sup>10</sup> The magnetic susceptibility data for the plot of  $\chi_m^{-1}$  vs.  $T$  follow Curie-Weiss behavior ( $C = 3.48$  cm<sup>3</sup> mol<sup>-1</sup> and  $\theta = -8.87$  K for **S-1** and  $C = 3.20$  cm<sup>3</sup> mol<sup>-1</sup> and  $\theta = -10.35$  K for **S-2**). Upon cooling, the value of  $\chi_m T$  continuously decreases, reaching a minimum value of 1.83 cm<sup>3</sup> K mol<sup>-1</sup> for **S-1** and 1.72 cm<sup>3</sup> K mol<sup>-1</sup> for **S-2** at 2 K.

For **S-1**, the nearest neighbor Co(II) atoms are separated by a long distance (–COO–Na–COO–), therefore a weak magnetic interaction between them can be expected. Hence, the gradual decrease of  $\chi_m T$  upon lowering the temperature is mainly due to the zero-field splitting.



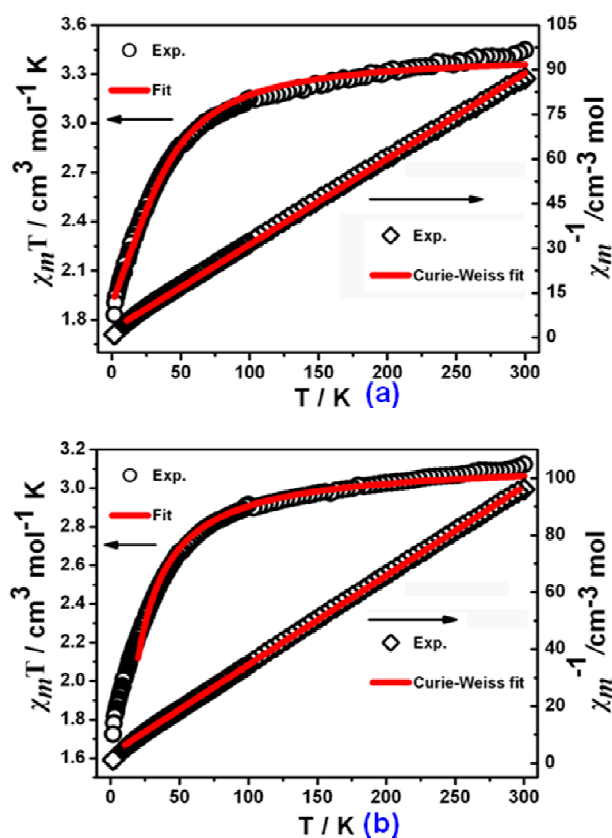


Fig. 3 Temperature dependence of  $\chi_m T$  and  $\chi_m^{-1}$  (inset) values for **S-1** (a) and **S-2** (b).

The magnetic data can be fitted according to an  $S = 3/2$  spin state for Co(II) with a dominant zero-field splitting effect (ZFS) and a Zeeman interaction based on the spin Hamiltonian.<sup>11</sup> The best fits were obtained with  $g_{\parallel} = 3.00$ ,  $g_{\perp} = 2.54$  and  $|D| = 36.20$   $\text{cm}^{-1}$ . The value of  $|D|$  is comparable to that observed for similar mononuclear Co(II) complexes.<sup>11</sup>

For **S-2**, the magnetic Co(II)-carboxylate chains ( $-\text{COO}-\text{Co}-\text{COO}-$ ) are separated by Na(I) ions, so the averaged curve of magnetic data can be fitted by the polynomial given in  $\chi_m = Ng^2\beta^2/4\kappa_B T ((5 + 2.59277x + 4.00094x^2 - 0.23392x^3)/(1 + 3.03193x + 5.58780x^2 + 7.92507x^3))$ ,  $0.5 < \kappa_B T/|J| < 5.0$ , where  $\chi_m = |J|/\kappa_B T$ .<sup>12</sup> The best fitting gives:  $g = 2.60$ ,  $J = -2.14$   $\text{cm}^{-1}$  and  $J/k_B = -3.08$ . Here, we do not attempt to fit the low temperature data as they are significantly perturbed by ZFS.<sup>12</sup>

## Conclusions

In summary, two novel 2D and 3D homochiral Co(II)/Na(I) coordination polymers have been successfully synthesized and structurally characterized. **S-1** displays a 2D layer structure which is further extended into a 3D supramolecular architecture by hydrogen bonding interactions, while **S-2** exhibits a 3D framework of *hcb* net. Magnetic susceptibility measurement reveals that **S-2** exhibit antiferromagnetic interaction between the adjacent Co(II) ions. The successful preparation of **S-1** and **S-2** may provide a useful and promising approach to synthesize new homochiral coordination polymers.

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## Notes and references

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†Electronic Supplementary Information (ESI) available: Selected bond lengths and angles, hydrogen bonds for **S-1**, figure of topology network of **S-2**, TGA curves, CD spectra and XRD patterns. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

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