



Coordination polymers with the chiral ligand *N-p*-tolylsulfonyl-*L*-glutamic acid: Influence of metal ions and different bipyridine ligands on structural chirality

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ABSTRACT

Four new polymers, namely $[\text{Ni}(-\text{tsgluO})(2,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ (**1**), $[\text{Co}(-\text{tsgluO})(2,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ (**2**), $[\text{Ni}(-\text{tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$ (**3**), and $[\text{Co}(-\text{tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$ (**4**), where $\text{tsgluO}^{2-} = (+)\text{-}N\text{-}p\text{-tolylsulfonyl-}L\text{-glutamate}$ dianion, $2,4'\text{-bipy} = 2,4'\text{-bipyridine}$, and $4,4'\text{-bipy} = 4,4'\text{-bipyridine}$, have been prepared and structurally characterized. Compounds **1** and **2** are isostructural and mononuclear, and crystallize in the acentric monoclinic space group *Cc*, forming 1D chain structures. Compound **3** is also mononuclear, but crystallizes in the chiral space group *P2*₁, forming a homochiral 2D architecture. In contrast to the other complexes, compound **4** crystallizes in the space group *P*–1 and is composed of binuclear $[\text{Co}_2\text{O}_6\text{N}_2]_n^{4-}$ units, which give rise to a 2D bilayer framework. Moreover, compounds **1**, **2**, and **4** self-assemble to form 3D supramolecular structures through π – π stacking and hydrogen-bonding interactions, while compound **3** is further hydrogen-bonded to form 3D frameworks. We have demonstrated the influence of the central metal and bipyridine ligands on the framework chirality of the coordination complexes.

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1. Introduction

Chiral coordination architectures are currently attracting considerable attention because of their potential utility in enantiomerically selective catalysis and separations [1–4], second-order nonlinear optical (NLO) applications [5], and magnetism [6]. To date, numerous fascinating archetypal chiral networks have been reported [7–10], which have been synthesized using chiral organic ligands [11–20] or chiral metal complexes [21,22], or by spontaneous resolution from achiral materials without any chiral auxiliaries [23–28]. Despite the fact that experimental results and theoretical calculations suggest that chiral hybrid frameworks may readily be prepared from commercially available chiral ligands, this is still a phenomenon worth investigating more thoroughly. In previous studies, it has proved impossible to prepare a number of chiral solids hydrothermally [29,30]. In this regard, it is extremely important for us to gather some information on the construction of MOFs and to find out why the chirality is lost under hydrothermal conditions. Among various chiral organic ligands, amino acid derivatives have attracted considerable attention due to their various coordination modes to metal atoms [31–34]. However, systematic studies of the effects of amino acid derivatives on structure formation in transition metal complexes and systematic elucidations of the

dependence of such factors on the chirality of MOFs have been relatively rare. To the best of our knowledge, the work presented herein represents the first series of investigations on the chiral ligand *N-p*-tolylsulfonyl-*L*-glutamic acid, which may act as a polydentate ligand and present a variety of coordination modes because of the presence of two carboxyl functions and a sulfonamide group. As far as we are aware, only the crystal and molecular structures of Zn^{II} , Cd^{II} , and Mn^{II} complexes with *N-p*-tolylsulfonyl-*L*-glutamic acid and other ligands have been reported [35–37]. Herein, we present a detailed account of the hydrothermal syntheses and crystal structures of four new nickel(II)/cobalt(II) coordination polymers $[\text{Ni}(-\text{tsgluO})(2,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ (**1**), $[\text{Co}(-\text{tsgluO})(2,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ (**2**), $[\text{Ni}(-\text{tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$ (**3**), and $[\text{Co}(-\text{tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$ (**4**), where $\text{tsgluO}^{2-} = (+)\text{-}N\text{-}p\text{-tolylsulfonyl-}L\text{-glutamate}$ dianion, $2,4'\text{-bipy} = 2,4'\text{-bipyridine}$, and $4,4'\text{-bipy} = 4,4'\text{-bipyridine}$. The effects of the central metals and bipyridine ligands on the framework chirality of the coordination complexes have been elucidated.

2. Experimental

2.1. Materials and methods

All reagents were commercially available and were used as received without further purification. Elemental analyses (C, H, N) were performed with an Elemental Vario EL elemental analyzer.

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IR spectra were recorded from samples in KBr pellets in the 4000–400 cm^{-1} range with an FTIR-8900 spectrometer. Thermogravimetric analysis (TGA) was performed on a TGA-7 instrument at a heating rate of 15 $^{\circ}\text{C min}^{-1}$.

2.2. Preparation

2.2.1. $[\text{Ni}(-\text{tsgluO})(2,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ (**1**)

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.1 mg, 0.1 mmol), H_2tsglu (22.6 mg, 0.075 mmol), and 2,4'-bipy (0.0078 mg, 0.05 mmol) in H_2O (15.0 mL) were mixed in a 23 mL Teflon reactor, which was then heated to 120 $^{\circ}\text{C}$ for 3 d. The resulting solution was left to cool slowly to room temperature. Green block-shaped crystals of compound **1** suitable for X-ray determination were obtained in 44.9% yield (based on Ni). Anal. calcd. (%) for $\text{C}_{32}\text{H}_{43}\text{N}_5\text{NiO}_{13}\text{S}$: C 49.65, H 4.36, N 7.89; found: C 49.32, H 4.48, N 7.96. IR (KBr pellet, cm^{-1}): 3649 (br), 3391 (w), 1614 (m), 1588 (m), 1558 (m), 1507 (m), 1468 (m), 1436 (m), 1416 (m), 1327 (m), 1221 (m), 1159 (s), 1093 (s), 1067 (m), 1019 (m), 991 (m), 849 (m), 816 (m), 779 (s), 734 (m), 668 (m), 646 (m), 618 (m), 567 (s).

2.2.2. $[\text{Co}(-\text{tsgluO})(2,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ (**2**)

The same synthetic procedure as that for **1** was used except that $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, giving red block-shaped crystals of **2** in 70.3% yield based on Co. Anal. calcd. (%) for $\text{C}_{32}\text{H}_{43}\text{CoN}_5\text{O}_{13}\text{S}$: C 48.24, H 5.44, N 8.79; found: C 48.38, H 5.25, N 8.27. IR (KBr pellet, cm^{-1}): 3429 (br), 3280 (w), 1613 (m), 1588 (m), 1468 (m), 1435 (m), 1416 (m), 1326 (m), 1221 (m), 1159 (s), 1093 (m), 1067 (m), 1017 (m), 992 (m), 849 (m), 816 (m), 778 (s), 734 (m), 665 (m), 644 (m), 618 (m), 566 (m).

2.2.3. $[\text{Ni}(-\text{tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$ (**3**)

The same synthetic procedure as that for **1** was used, except that 2,4'-bipy was replaced by 4,4'-bipy, giving green block-shaped crystals of **3** in 56% yield based on Ni. Anal. calcd. (%) for $\text{C}_{22}\text{H}_{23}\text{NiN}_3\text{O}_7\text{S}$: C 49.12, H 4.68, N 7.81; found: C 49.12, H 4.36, N 7.90. IR (KBr pellet, cm^{-1}): 3412 (br), 3173 (m), 2921 (m), 1605 (s), 1557 (s), 1498 (w), 1425 (s), 1322 (m), 1302 (s), 1219 (m), 1154 (s), 1101 (s), 995 (m), 816 (s), 776 (w), 727 (m), 668 (s), 634 (m), 548 (m).

2.2.4. $[\text{Co}(\text{tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$ (**4**)

The same synthetic procedure as that for **2** was used, except that 2,4'-bipy was replaced by 4,4'-bipy, giving red block-shaped crystals of **4** in 89% yield based on Co. Anal. calcd. (%) for $\text{C}_{22}\text{H}_{23}\text{CoN}_3\text{O}_7\text{S}$: C 49.51, H 4.64, N 7.93; found: C 49.63, H 4.35, N 7.89. IR (KBr pellet, cm^{-1}): 3597 (m), 3354 (br), 3084 (w), 1630 (m), 1604 (m), 1550 (s), 1488 (w), 1433 (m), 1412 (m), 1351 (w), 1326 (m), 1218 (m), 1155 (s), 1115 (m), 1093 (m), 1063 (m), 988 (m), 922 (m), 895 (m), 813 (s), 734 (w), 704 (w), 670 (m), 632 (m), 566 (m).

2.3. Crystal structure determination

Green blocks of **1** and **3** (of dimensions 0.46 mm \times 0.35 mm \times 0.27 mm for **1** and 0.18 mm \times 0.15 mm \times 0.07 mm for **3**) and red blocks of **2** and **4** (0.49 mm \times 0.28 mm \times 0.25 mm for **2** and 0.21 mm \times 0.12 mm \times 0.11 mm for **4**) were subjected to single-crystal X-ray diffraction analysis on a Bruker SMART-CCD area detector diffractometer using graphite-monochromated Mo- K_{α} radiation ($\lambda=0.71073 \text{ \AA}$) at 298(2) K according to the ω - φ scan technique. The structures were solved by direct methods using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 using the SHELXL-97 program [38]. The hydrogen atoms were added in geometrical positions and were not refined. A semi-empirical absorption correction was applied to the intensity data using SADABS. Compounds **3** and **4** both contain a disordered tsgluO^{2-} ligand, which could be located at several sites between the layers. A summary of the crystallographic data and refinement parameters is given in Table 1. Selected bond lengths are listed in Table S1 (Supplementary data).

3. Results and discussion

3.1. Crystal structure of $[\text{M}(-\text{tsgluO})(2,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ ($\text{M}=\text{Ni}^{\text{II}}$, **1**; $\text{M}=\text{Co}^{\text{II}}$, **2**)

Since compounds **1** and **2** are isostructural, compound **1** is taken as an example to describe the structure in detail. Compound

Table 1
Summary of crystal data and details of intensity collection and refinement.

Compound	1	2	3	4
Empirical formula	$\text{C}_{32}\text{H}_{43}\text{N}_5\text{NiO}_{13}\text{S}$	$\text{C}_{32}\text{H}_{43}\text{CoN}_5\text{O}_{13}\text{S}$	$\text{C}_{22}\text{H}_{23}\text{N}_3\text{NiO}_7\text{S}$	$\text{C}_{22}\text{H}_{22}\text{CoN}_3\text{O}_{6.50}\text{S}$
Formula weight	796.48	796.70	532.20	523.42
T (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	Cc	Cc	$P2(1)$	$P-1$
a (\AA)	22.452(4)	22.546(4)	9.687(2)	8.560(4)
b (\AA)	11.663(2)	11.674(2)	10.619(3)	11.366(5)
c (\AA)	14.688(3)	14.712(3)	11.350(3)	12.148(5)
α (deg.)	90	90	90	79.926(7)
β (deg.)	97.580(2)	97.809(2)	1634.8(6)	84.188(7)
γ (deg.)	90	90	90	79.766(6)
V (\AA^3)	3812.9(12)	3836.5(11)	105.342(4)	1142.1(9)
Z	4	4	2	2
D_c (mg/m^3)	1.387	1.379	1.570	1.522
$F(000)$	1672	1668	552	540
μ (mm^{-1})	0.631	0.569	1.005	0.889
Reflections collected/unique [R_{int}]	9693/6130 [0.0234]	9854/4650 [0.0244]	5965/3695 [0.0378]	5885/4155 [0.0372]
GOF	0.995	1.030	0.966	1.019
$R1, wR2$ [$I > 2\sigma(I)$] ^a	0.0366, 0.0845	0.0304, 0.0748	0.0481, 0.0836	0.0749, 0.1862
$R1, wR2$ (all data) ^a	0.0404, 0.0867	0.0321, 0.0760	0.0593, 0.0878	0.1227, 0.2109

^a $R1 = |F_o - F_c| / \sum F_o$, $wR2 = [\sum (w(F_o^2 - F_c^2))^2] / [\sum (w(F_o^2))]^{1/2}$.

1 crystallizes in the acentric monoclinic space group Cc with an asymmetric unit consisting of one Ni atom, one tsgluO^{2-} ligand, two 2,4'-bipy ligands, two coordinated water molecules, and five lattice water molecules. The crystallographically unique Ni^{2+} ion of **1** is six-coordinated by two O atoms (O1, O3^{#1}) from two distinct tsgluO^{2-} units, two O atoms (O7, O8) from two distinct coordinated water molecules, and two N atoms (N1, N2) from two distinct 2,4'-bipy groups (Ni(1)–O 2.066(2)–2.088(2) Å, Ni(1)–N 2.105(3) Å), giving rise to a distorted octahedral geometry with $L\text{--Ni--}L$ ($L=\text{O, N}$) bond angles ranging from 88.82(8)° to 177.98(9)° (Fig. 1a). The bond distances and angles are very similar to those found in the complexes $[\text{Ni}_2\text{O}(\text{L-Asp})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ and $[\text{Ni}(\text{bipy})_2(\text{tsglyNO})]\cdot 2\text{H}_2\text{O}$ [39,40]. In this structure, 2,4'-bipy acts only as a decorating ligand ligated to one Ni cation, while the carboxyl groups of the tsgluO^{2-} ligands adopt a bridging bidentate mode, $\mu_2\text{-}\eta^1\text{-}\eta^1$, to connect two Ni cations with two carboxylic oxygens (Scheme 1a). This results in an infinite chain of Ni–O–C rods with an Ni···Ni distance of 8.990 Å along the c -axis (Fig. 1b). These neighboring chains interdigitate with each other through $\pi\text{-}\pi$ interactions (the average distance between two pyridyl rings is 3.81 Å) and interchain hydrogen bonds (Table S1), thereby leading to a compact 3D structure.

Single-crystal X-ray diffraction studies revealed that compound **2** adopts a structure very similar to that of **1** (Figs. S1a, S1b), as shown by the detailed structural data listed in the Supplementary material. Moreover, the $\text{Co--}L$ ($L=\text{O, N}$) bond lengths and angles span ranges of 2.0989(18) to 2.162(3) Å and 88.54(8)° to 178.31(9)° for compound **2**, which are comparable to those observed in other cobalt(II) coordination polymers [40,41].

3.2. Crystal structure of $[\text{Ni}(\text{-tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$, **3**

When the chelating ligand 2,4'-bipy in compound **1** was replaced by the linear ligand 4,4'-bipy, compound **3** was obtained.

Single-crystal X-ray diffraction analysis showed that compound **3** crystallizes in the chiral space group $P2_1$ and that each asymmetric unit consists crystallographically of one Ni atom, one bipy ligand, one tsgluO^{2-} ligand, and half of a coordinated water molecule. In contrast to the situation in compounds **1** and **2**, each Ni^{2+} ion in **3** is six-coordinated in a distorted octahedral geometry (Fig. 2a) by two N atoms (N2, N3^{#3}) derived from two different 4,4'-bipy groups, a pair of carboxylate O atoms (O3, O4) originating from the α -carboxyl group of one tsgluO^{2-} ligand, one O atom (O6^{#2}) from the γ -carboxyl group of another disordered tsgluO^{2-} ligand, and one O atom (O5) from the coordinated water molecule. For the Ni^{2+} ions, the Ni– L ($L=\text{O, N}$) distances are in the normal range 2.038(3)–2.147(3) Å and the bond angles in the equatorial plane are in the range 86.88(18)–178.6(3)°, which are comparable with those in the complexes $[\text{Ni}_2(\text{H}_2\text{O})_2(\text{nicotinate})_4(4,4'\text{-bipy})]$ and $[\text{Ni}(\text{HIP})(\text{bipy})(\text{H}_2\text{O})]$ (HIP=5-hydroxyisophthalic acid) [42,43].

It should be noted that each 4,4'-bipy ligand bridges two Ni cations, while the tsgluO^{2-} anions act as $\mu_2\text{-}\eta^1\text{-}\eta^1$ chelating-bridging tridentate ligands through their carboxylate groups towards the two Ni cations (Scheme 1b), involving three carboxylic oxygens (that is, a pair of carboxylic oxygens from the α -carboxyl group and one oxygen from the γ -carboxyl group). This can be regarded as a stabilizing factor for the 2D chiral structure. Based on the above coordination modes, all of the Ni centers are bridged by α - and γ -carboxyl groups of tsgluO^{2-} ligands to form a 1D chain that extends along the a -direction. These 1D chains are further connected by the 4,4'-bipy ligands to form a 2D layer parallel to the ab plane, with shortest Ni···Ni separations between adjacent chains of 11.35 Å (Fig. 2b). These layers are further extended to a 3D supramolecular architecture through hydrogen-bonding interactions between the coordinated water molecule (O5) and the O (O4, O7) or N (N1) atoms of the tsgluO^{2-} ligands $[\text{O}(5)\cdots\text{O}(4) (-x+2, y+1/2, -z+2) 2.764(4) \text{ \AA}; \text{N}(1)\cdots\text{O}(7) (-x+1, y-1/2, -z+2) 2.942(6) \text{ \AA}]$ (Fig. 2c).

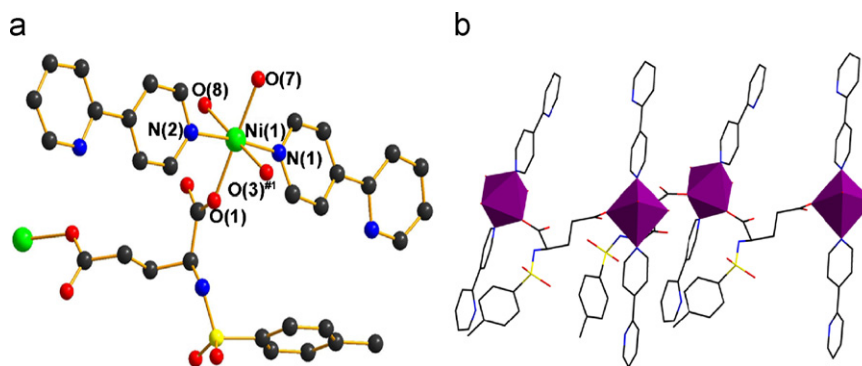
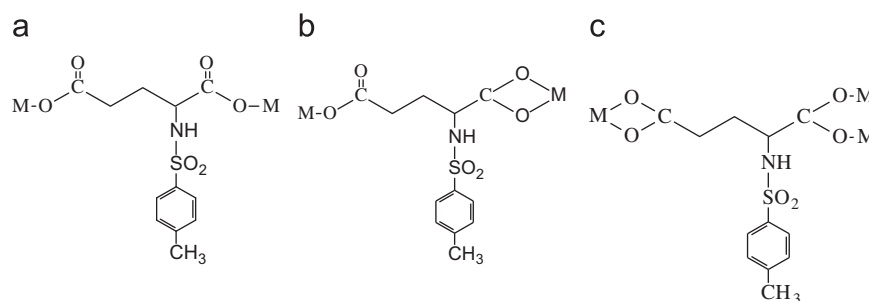


Fig. 1. (a) The coordination environments of Ni(II) ions in compound **1**; all hydrogen atoms are omitted for clarity. Symmetry codes: #1 $x, -y+1, z+1/2$; #2 $x, -y+1, z-1/2$. (b) The 1D chain structure of compound **1**; all hydrogen atoms are omitted for clarity.



Scheme 1. The coordination modes of the tsgluO^{2-} ligand in (1a) compounds **1** and **2**; (1b) compound **3**; (1c) compound **4**.

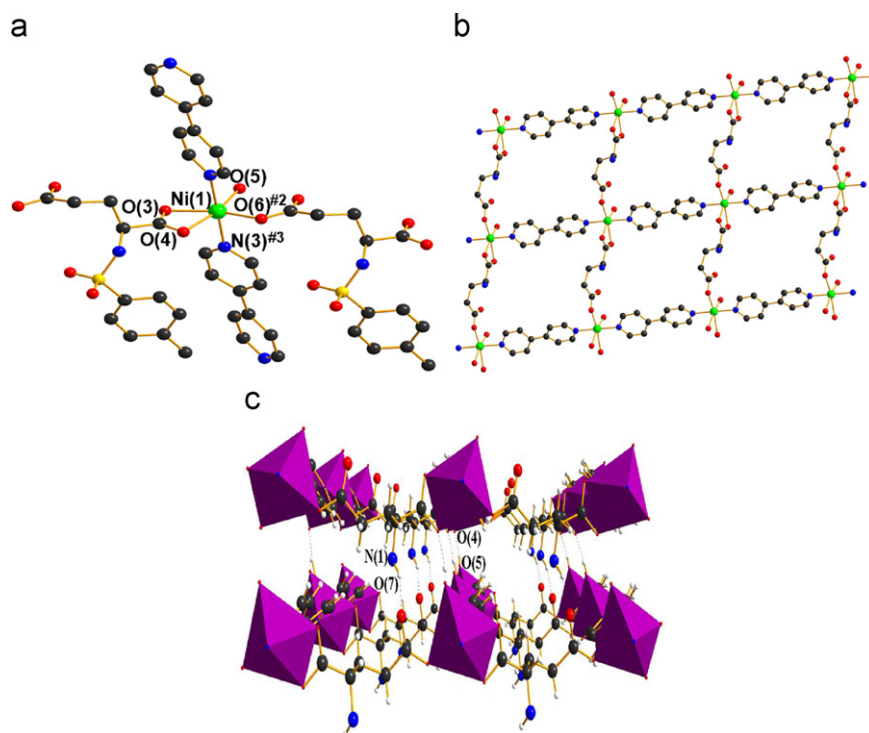


Fig. 2. (a) The coordination environments of Ni(II) ions in compound **3**; all hydrogen atoms are omitted for clarity. Symmetry codes: #1 $x, y, z+1$; #2 $x+1, y, z$; #3 $x, y, z-1$; #4 $x-1, y, z$. (b) The 2D layered structure parallel to the ab plane of compound **3**. (c) The hydrogen-bonding interactions linking layers into a 3D supramolecular network of compound **3**; the p -tolylsulfonyl groups of the tsgluO^{2-} ligands and all hydrogen atoms are omitted for clarity in (b) and (c).

3.3. Crystal structure of $[\text{Co}(-\text{tsgluO})(4,4'\text{-bipy})]_n \cdot 0.5n\text{H}_2\text{O}$, **4**

Single-crystal X-ray diffraction analysis showed that compound **4** crystallizes in the triclinic space group $P\bar{1}$ and that each asymmetric unit consists of one Co atom, one bipy ligand, one tsgluO^{2-} anion, and half of a lattice water molecule. Each Co^{2+} ion of **4** is six-coordinated in a distorted octahedron with an N_2O_4 donor set comprising two N atoms (N2, N3^{#3}) from two 4,4'-bipy groups, a pair of O atoms (O3^{#1}, O4^{#1}) from the γ -carboxyl group of one tsgluO^{2-} ligand, and two O atoms (O1, O2^{#2}) from two α -carboxyl groups of two different tsgluO^{2-} ligands (Fig. 3a). The Co–L ($L=\text{O}, \text{N}$) bond lengths lie in the normal range 1.991(4)–2.204(5) Å and the L–Co–L ($L=\text{O}, \text{N}$) bond angles range from 59.91(17)° to 177.47(19)°, which is comparable to the range found in the compounds $[\text{Co}_2(\text{hupa})_2(4,4'\text{-bipy})]$ and $\{[\text{Co}(\text{bpe})(\mu\text{co})(\text{H}_2\text{O})_2] \cdot 4(\text{H}_2\text{O})\}_n$ ($\text{H}_2\text{hupa}=\text{hydroxyphenylacetic acid}$, $\text{bpe}=4,4'\text{-bipyridyl ethylene}$, $\text{H}_2\text{-muco}=\text{trans,trans-muconic acid}$) [44,45]. Notably, as in the structure of compound **3**, each 4,4'-bipy ligand bridges two Co cations, while the tsgluO^{2-} anions act as $\mu_3\text{-}\eta^1\text{-}\eta^2$ chelating-bridging tetradentate ligands through their carboxylate groups towards three Co cations (Scheme 1c), involving four carboxylic oxygens (that is, two carboxylic oxygens from the γ -carboxyl group completing a 16-membered ring ($\text{C}_{10}\text{O}_4\text{Co}_2$) and two oxygens from the α -carboxyl group completing an 8-membered ring ($\text{C}_2\text{O}_4\text{Co}_2$)). This can be regarded as a stabilizing factor for compound **4**.

In this structure, each adjacent Co^{2+} ion is connected by two tsgluO^{2-} ligands through the α - and γ -carboxyl groups to form a centrosymmetric dinuclear $[\text{Co}_2\text{O}_6\text{N}_2]_n^{4-}$ unit, with Co \cdots Co distances of 6.410 Å for the 16-membered rings and 4.136 Å for the 8-membered rings. The most interesting feature of **4** is that it presents two double-chains connected by tsgluO^{2-} ligands that extend along the crystallographic b -axis to form a 1D ladder-like structure. Each dinuclear building block interacts with another four dinuclear blocks through the coordination of 4,4'-bipy

ligands, forming a 2D bilayer framework that extends parallel to the ab plane (Fig. 3b). These bilayers are further extended into 3D supramolecular architectures, with 1D parallelogram channels, through π - π stacking interactions of the aromatic rings of tsgluO^{2-} ligands from two adjacent structures (with face-to-face distances of ca. 3.942 Å) and hydrogen-bonding interactions between the free water molecule (O7) and the O or N atoms of the tsgluO^{2-} ligands [$\text{N}(1) \cdots \text{O}(7)$ ($x+1, y, z$) 2.865(11) Å; $\text{O}(7) \cdots \text{O}(4)$ 2.752(8) Å] (Fig. 3c). The approximate dimensions of the channels are 5.7×7.6 Å, and free water molecules are located within these channels.

Comparative analysis of the structures of this series of compounds and the chiral H_2tsglu ligand indicates that the natures of the central metal and the bipyridine ligand play important roles in determining the chirality of the final crystalline products obtained under hydrothermal conditions. The chiral H_2tsglu ligand used in the synthetic procedure was chirally pure, and this chirality was preserved in the tsgluO^{2-} ligands in **3**. However, this was no longer the case in compounds **1**, **2**, and **4**, in which half of the tsgluO^{2-} ligands had undergone inversion and were present as the D enantiomer, i.e. the acid had been racemized during the synthetic procedure involving hydrothermal treatment. The racemization of amino acids in this way has been reported previously [46].

In addition, we note that 2,4'-bipy acts only as a decorating ligand, coordinating to just one metal ion, which prevents the formation of the desired homo-chiral compounds for **1** and **2**. For **3** and **4**, it was interesting to find that upon reaction with H_2tsglu , subtle differences in the preferred coordination geometries of the metal ions (Ni^{II} for **3**; Co^{II} for **4**) generate different structural forms that dramatically change the chiral units. Ni^{II} and Co^{II} cations in asymmetrical coordination modes without mirror or inversion symmetry can be considered as initial chiral centers. At the same time, chiral compounds can be installed based on noncentrosymmetric molecular arrangements. In compound **4**,

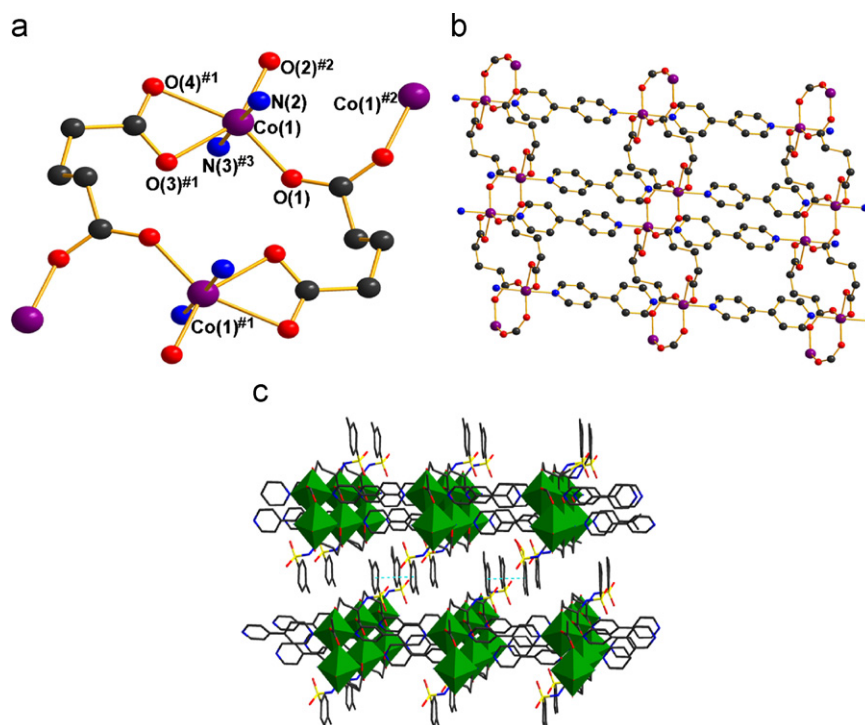


Fig. 3. (a) The coordination environments of Co(II) ions in compound **4**; symmetry codes: #1 $-x+1, -y, -z+2$; #2 $-x+2, -y, -z+2$; #3 $x, y+1, z$. (b) The 2D bilayered structure of compound **4** parallel to the ab plane. (c) The 3D supramolecular structure of compound **4**; the p -tolylsulfonyl and amido groups of the tsgluO^{2-} ligands and hydrogen atoms are omitted for clarity in (a) and (b).

however, the Co^{II} cations form centrosymmetric dinuclear blocks and the tsgluO^{2-} anions act as chelating–bridging tetradentate ligands, and this causes the chirality to vanish. Moreover, compounds **1**, **2**, and **4** self-assemble to form supramolecular structures through π – π stacking and hydrogen-bonding interactions, while compound **3** is further hydrogen-bonded to form a 3D framework.

3.4. Thermal analysis

To investigate their thermal stabilities, thermogravimetric analyses (TGA) of compounds **1–4** were carried out at a heating rate of $15\text{ }^{\circ}\text{C min}^{-1}$. TGA showed the thermal decomposition behaviors of compounds **1** and **2** to be similar. For **1**, the first weight loss of 13.78% in the range $25\text{--}122\text{ }^{\circ}\text{C}$ corresponded to the release of the coordinated and lattice water (calcd 11.30%). Further weight losses in the range $122\text{--}550\text{ }^{\circ}\text{C}$ could be attributed to decomposition of the framework to form NiO as the final product (observed 10.02%; calcd 9.38%). According to the TGA curves, compounds **3** and **4** display similar thermal decomposition behavior. Continuous weight losses in the range $69\text{--}641\text{ }^{\circ}\text{C}$ were seen for both **3** and **4**, with the remaining weight corresponding to MO ($M=\text{Ni}$, **3**; Co , **4**; observed 14.31%, 13.88%; calcd 14.03%, 14.32%, respectively). Comparing the studied compounds, the different decomposition temperatures of the frameworks may be ascribed to their diverse structures. TGA traces for **1–4** are depicted in Figs. S2 (1a, 2a, 3a, and 4a) (Supplementary data).

4. Conclusions

In summary, four new polymers have been constructed under hydrothermal conditions. Compounds **1** and **2** are isostructural and have 1D chain structures, compound **3** forms a homochiral 2D architecture, and compound **4** presents a 2D bilayer framework.

Moreover, compounds **1**, **2**, and **4** self-assemble to form supramolecular structures through π – π stacking and hydrogen-bonding interactions, while compound **3** is further hydrogen-bonded to form a 3D framework. The obtained results suggest that half of the tsgluO^{2-} ligands underwent inversion, leading to racemization under the hydrothermal synthetic conditions. In compounds **1–3**, the 2,4'-bipy ligand, which prevents the formation of the desired homochiral compound, acts merely as a decorating ligand, coordinating to just one metal ion, thereby making the tsgluO^{2-} ligand adopt a bridging bidentate mode, while 4,4'-bipy bridges two metal centers to afford chains, thereby allowing the tsgluO^{2-} anion to act as a chelating–bridging tridentate ligand, producing structures with homochirality. In **3** and **4**, the Co^{II} cations form centrosymmetric dinuclear blocks, which leads to loss of the chirality. In addition, it has been demonstrated that the nature of the central metal and bipyridine ligand results in chiral ligands with different coordination modes, which would provide a great deal of scope for maintaining the chirality of the coordination complexes.

Supplementary material

CCDC-721310 (**1**), CCDC-725882 (**2**), CCDC-708870 (**3**), and CCDC-710038 (**4**) contain the supplementary crystallographic data. Copies of the data can be obtained free of charge via the Internet at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or by post from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033, Email: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.07.005.

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