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Various coordination architectures constructed from *N*-[(carboxyphenyl)-sulfonyl]glycine: Structural variation *via* ligand isomerism effects and metal-directed assembly

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ABSTRACT

Using Cu(II), Mn(II) or Co(II) salt and the flexible ligands, *N*-[(4-carboxyphenyl)-sulfonyl]glycine (H₃L₁) and *N*-[(3-carboxyphenyl)-sulfonyl]glycine (H₃L₂), a series of new coordination polymers, [Mn(phen)-(H₂O)₄][HL₁] (**1**), [Co₃(L₁)₂(bipy)₃(H₂O)₆]_{*n*}*8*n*H₂O (**2**), [Cu₄(L₁)₂(OH)₂(bipy)₄]_{*n*}·12*n*H₂O (**3**), [Na(H₂L₁)-(H₂O)]_{*n*} (**4**), [Mn₂(HL₂)₂(dpe)₃(H₂O)₂]_{*n*} ·ndpe (**5**), (phen = 1,10-phenanthroline, bipy = 4,4'-bipyridine, dpe = 1,2-di(4-pyridyl)ethylene), varying from OD to 3D, have been synthesized and structurally characterized. Compound **1** has a [Mn(phen)(H₂O)₄]²⁺ cation and a HL₁²⁻ anion. Compound **2** features a new 1D triple chain, based on octahedral cobalt atoms bridged by bipy molecules and terminally coordinated by two H₃L₁ ligands. Compound **3** has a 2D layered structure, constructed from new alternating chains where H₃L₁, hydroxyl and water molecules simultaneously act as bridging ligands. Compound **4** possesses a bilayer structure in which two adjacent layers are pillared by H₃L₁ ligands into a 2D bilayer network. Compound **5** is a unique 3D coordination polymer in which each Mn center binds two *trans*-located dpe molecules. The thermal stability as well as magnetic properties of **5** was also studied. This work and our previous work indicate that the positional isomer of the anionic *N*-[(carboxyphenyl)-sulfonyl]glycine is important in the construction of these network structures, which are also significantly regulated by the metal centers.

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1. Introduction

The rational design and assembly of inorganic coordination polymers or metal-organic frameworks has received remarkable attention and has developed rapidly in recent years. Being easily and efficiently synthesized from relatively simple subunits, these complexes exhibit fascinating structural topologies and potential applications as functional materials [1-4]. However, the control of dimensionality is still a major challenge in the design and synthesis of organic-inorganic frameworks because the final structure is frequently modulated by various factors such as solvent medium, the geometry of metal ions, coordination character of the organic ligand, temperature, metal-ligand ratio, template and counterion [5]. Among these factors, the selection of appropriate metal ions and organic ligands is often the key in the construction of complexes. Metal ions, and in particular their radii and coordination geometry determine the bridging pattern and coordination modes of the organic ligands, and thus the overall structures of the complexes. In the crystal engineering, the employment of ligand

isomers as the organic component is an effective way to investigate the effect of the ligand geometry. Usually, ligand isomers having similar structures but different coordination modes would lead to different structural motifs, such as seen for benzenedicarboxylates. Benzenedicarboxylate anions have three structural isomers (phthalate, isophthalate and terephthalate) with different angles between the two carboxylato groups, which may exhibit different geometric effects on the construction of coordination polymers [6]. To date, a variety of metal organic frameworks have been reported, however, systematic studies of the isomeric effect on the generation of such coordination frameworks are surprisingly rare [7]. With this in mind, one crucial aim of this work was to explore the effect of two isomers on the structural assembly. This may provide further insights in designing new hybrid crystalline materials.

Furthermore, amino acid is one of the most important biological ligands. Recently, amino acids with flexible coordination modes have been utilized to construct metal–organic supramolecular networks [8]. To date, a number of Ln-amino acid and transition metal–amino acid complexes with mononuclear, binuclear or chain structural motifs have been synthesized [9]. Several reports of polynuclear transition metal clusters or various 3d–4f high-nuclearity clusters with different structural motifs have also





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reported [10]. However, reports of metal complexes of amino acids with high dimensional structures are rare [11]. This may be due to deprotonated amino acids preferring to chelate metal centers through their amine N and carboxylic O atoms to form five-membered rings which prevent extension into high dimensional structures. In order to overcome this problem, our research has focused on designing a new versatile ligand which contains both carboxylate and amino acid groups by introduction of an aromatic carboxylato group at its amino group.

We have recently used such a multifunctional amino acid derivative, namely N-[(3-carboxyphenyl)-sulfonyl]glycine, to create a series of unusual metal-organic frameworks [12,13]. In comparison to benzenedicarboxylic acids, N-[(3-carboxyphenyl)-sulfonyl]glycine not only contains two bridging carboxylato moieties but also possesses another two potential coordination sites, i.e., the nitrogen atom and oxygen atoms of the sulfonate groups. This asymmetric geometry may produce beautiful new structural motifs and useful functional properties. To further probe the influence of systematic variations of ligand structures and metal ions on the overall molecular architectures, we extend the building blocks from the bent N-[(3-carboxyphenyl)-sulfonyl]glycine to its quasilinear isomer N-[(4-carboxyphenyl)-sulfonyl]-glycine to explore the isomeric effect on network assembly. Herein, the synthesis and X-ray crystal structures of eight coordination networks, including our previous reported $[Mn_2(HL_2)_2(phen)_4]_n \cdot 8nH_2O$ (6), $[Co_3(L_2)_2(bipy)_2(H_2O)_6]_n \cdot 2nCH_3OH \cdot 8nH_2O(7)$ and $[Ca(H_2O)_4Cu_2(bi$ $py_{2}(L_{2})_{2}_{n} \cdot 4nH_{2}O(\mathbf{8})$, formed by Cu²⁺, Mn²⁺, Co²⁺ salts with H₃L₁ and H₃L₂ are reported (See Schemes 1 and 2). The influence of ligand isomerism and metal ions on the final structures of the assemblies is discussed.

2. Experimental

2.1. Materials and instruments

All reagents used in the syntheses were of analytical grade. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–600 cm⁻¹) were recorded by using KBr pellet on an Avatar[™] 360 E.S.P.IR spectrometer. The crystal structure determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Thermogravimetric analyses (TG) were carried out on a STA449C integration thermal analyzer. The PXRD patterns were recorded with a Rigaku D/Max 3III diffractometer with a scanning rate of four degrees per minute. Variable-temperature magnetic susceptibilities were measured using a MPMS-7 SQUID magnetometer.

2.2. Synthesis of N-[(4-carboxyphenyl)-sulfonyl]glycine

To a solution of glycine (2.25 g, 0.03 mol) in NaOH 2 M (30 mL), 4-(chlorosulfonyl)benzoic acid (6.78 g, 0.03 mol) was added. The mixture was stirred at room temperature for 2 h, and the aqueous solution was then acidified to pH 4 with 6 M hydrochloric acid, upon which a white solid derivative began to crystallize at once with a yield of about 60%. *Anal.* Calc. for C₉H₉NO₆S: C, 41.70; H, 3.50; N, 5.40. Found: C, 41.79; H, 3.62; N, 5.58%. IR: 3287s, 1718s, 1432s, 1171m, 753m, 1336s, 897m.

2.3. Preparation of 1-5

2.3.1. $[Mn(phen)(H_2O)_4][HL_1]$ (1)

A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.16 g, 0.5 mmol) and H_3L_1 (0.26 g, 1 mmol) was stirred into 15 mL of water. The pH was then adjusted to *ca.* 5 with 1 M NaOH. A solution of phen (0.21 g, 1 mmol) in ethanol (3 mL) was then added. The reaction mixture was heated on a water bath for 10 h at 70 °C, and then filtered. The yellow crystals were separated from the mother liquor by slow evaporation at room temperature after 4 weeks. *Anal.* Calc. for $C_{21}H_{23}MnN_3O_{10}S$: C, 44.69; H, 4.11; N, 7.44. Found: C, 44.51; H, 4.19; N, 7.50%. IR: 3413s, 1676s, 1411s, 1167m, 729m, 1345s, 851m.

2.3.2. $[Co_3(L_1)_2(bipy)_3(H_2O)_6]_n \cdot 8nH_2O(2)$

A mixture of Co(OAc)₂·4H₂O (0.13 g, 0.5 mmol) and H₃L₁ (0.13 g, 0.5 mmol) was stirred into 15 mL of water, and then refluxed for *ca*. 1 h. The pH was then adjusted to *ca*. 6 with 1 M NaOH. A solution of bipy (0.04 g, 0.25 mmol) in methanol (3 mL) was then



Scheme 1. Summary of the products obtained from the reactions of metal ions and H₃L₁.



Scheme 2. Summary of the products obtained from the reactions of metal ions and H₃L₂.

added. The reaction mixture was heated on a water bath for 10 h at 70 °C, and then filtered. The red crystals were separated from the mother liquor by slow evaporation at room temperature after 2 weeks. *Anal.* Calc. for $C_{48}H_{64}Co_3N_8O_{26}S_2$: C, 40.89; H, 4.58; N, 7.94. Found: C, 40.76; H, 4.67; N, 7.81%. IR: 3412s, 1684s, 1567s 1427s, 1127s, 1160m, 725m, 1396s, 864m.

2.3.3. $[Cu_4(L_1)_2(OH)_2(bipy)_4]_n \cdot 12nH_2O(\mathbf{3})$

Complex **3** was synthesized using a procedure analogous to that of **2** except that $Cu(OAc)_2 \cdot H_2O$ was used instead of $Co(OAc)_2 \cdot 4H_2O$ and 1.2 mmol $Ca(OH)_2$ was added. Blue crystals were produced after 3 weeks. *Anal.* Calc. for $C_{29}H_{35}Cu_2N_5O_{13}S$: C, 42.44; H, 4.30; N, 8.53. Found: C, 42.56; H, 4.26; N, 8.68%. IR: 3415s, 1695s, 1427s, 1159m, 706m, 1332 s, 864m.

2.3.4. $[Na(H_2L_1)(H_2O)]_n$ (**4**)

An aqueous methanol solution of $Mn(OAC)_2 \cdot 4H_2O$ (0.12 g, 0.5 mmol), H_3L (0.13 g, 0.5 mmol) and bipy (0.04 g, 0.25 mmol) was stirred for 6 h at room temperature and then filtered. The pH was then adjusted *ca*. 6 with 1 M NaOH. The filtrate was allowed to stand for 1 week. The colorless crystals obtained were suitable for X-ray analysis. Yield: 26%. *Anal*. Calc. for $C_9H_{10}NNaO_7S$: C, 36.13; H, 3.37; N, 4.68. Found: C, 36.21; H, 3.52; N, 4.61%. IR: 3423s, 1714s, 1417s, 1109s, 1157m, 721m, 1362s, 814m.

2.3.5. $[Mn_2(HL_2)_2(dpe)_3(H_2O)_2]_n \cdot ndpe$ (5)

Complex **5** was synthesized in a procedure analogous to that of **4** except that dpe and H_3L_1 were used instead of bipy and H_3L_2 . Yield: 35%. *Anal.* Calc. for $C_{66}H_{56}Mn_2N_{10}O_{14}S_2$: C, 57.13; H, 4.07; N, 10.10. Found: C, 57.01; H, 3.93; N, 9.98%. IR: 3423s, 1597s, 1420s, 1161m, 731m, 1389s, 857m.

2.4. Crystallographic data collection and structures determination

Single-crystals of **1–5** were put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods with SHELXS-97. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97. The crystallographic data and selected bond lengths and angles for **1–5** are listed in Table 1 and Table S1, Supplementary data. Hydrogen bonds parameters in **1–5** are listed in Table S2.

Table 1

Crystallographic data for complexes 1-5.



Fig. 1. (a) Molecular structure of **1**. (b) View of the 2D supramolecular system of **1** showing the cyclic intramolecular hydrogen bonding interactions.

3. Results and discussion

3.1. Description of the structures

3.1.1. $[Mn(phen)(H_2O)_4][HL_1]$ (1)

As shown in Fig. 1a, the unit of **1** contains a $[Mn(phen)(H_2O)_4]^{2+}$ cation and a HL_1^{2-} anion. The Mn(II) ion is six-coordinated

Compounds	1	2	3	4	5
Formula	C21H23MnN3O10S	C48H64C03N8O26S2	C29H35Cu2N5O13S	C ₉ H ₁₀ N Na O ₇ S	C66H56Mn2N10O14S2
Mr	564.42	1409.98	820.76	299.23	1387.21
T (K)	291(2)	291(2)	291(2)	291(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	C2/c	C2/c	P2/n	P1	C2/c
Unit cell dimensions					
a (Å)	23.228(5)	24.906(2)	16.948(3)	5.5061(11)	37.011(3)
b (Å)	13.909(3)	14.9985(12)	11.144(2)	7.6378(16)	8.5952(7)
c (Å)	15.045(3)	17.3262(14)	17.273(3)	14.332(3)	26.729(2)
α (°)				79.301(2)	
β(°)	100.134(2)	117.199(10)	99.373(3)	88.416(2)	129.231(10)
γ (°)				75.341(2)	
V (Å ³)	4784.7(17)	5756.5(8)	3218.9(11)	572.8(2)	6586.5(10)
Ζ	8	4	4	2	4
$ ho (\text{g cm}^{-3})$	1.567	1.627	1.694	1.735	1.399
F(0 0 0)	2328	2916	1688	308	2864
Goodness-of-fit	1.043	1.023	1.028	1.040	1.052
Crystal size (mm ³)	$0.33 \times 0.29 \times 0.22$	$0.27\times0.17\times0.15$	$0.18 \times 0.07 \times 0.07$	$0.26 \times 0.24 \times 0.13$	$0.33 \times 0.26 \times 0.25$
$R_1, wR_2 \left[I > 2\sigma(I) \right]$	0.0292, 0.0725	0.0330, 0.0795	0.0559, 0.1273	0.0326, 0.0856	0.0667, 0.1854
R_1, wR_2 (all data)	0.0361, 0.0773	0.0435, 0.0861	0.1029, 0.1521	0.0394, 0.0903	0.0857, 0.2039
Largest difference in peak and hole (e $Å^{-3}$)	0.246, -0.304	0.523, -0.506	0.774, -0.907	0.289, -0.428	1.734, -0.464

(MnN₂O₄) and the coordination polyhedron is a distorted octahedral geometry. The bond lengths of Mn1-O are in the range of 2.1451(13)–2.2070(13) Å. The phen molecule chelating to the Mn(II) ion with Mn1-N1 and Mn1-N2 bond distances of 2.3010(16) and 2.2738(15) Å, respectively. It is notable that even though HL₁²⁻ does not coordinate to the metal atoms, it plays an important templation role in the crystallization process of compound **1**. Each HL₁^{2–} group is involved in significant intermolecular hydrogen bonding interactions with coordinated water molecules through its two carboxylato groups. Finally, these cation-anion species are organized into a two-dimensional supramolecular architecture (Fig. 1b). The bond lengths and angles of the hydrogen bonding are in the range of 2.658(2)-2.8088(19) Å and 157.8-175.2°, respectively. By comparison, the previously reported [Mn₂(HL₂)₂ $(phen)_4$]_n $8nH_2O$ (6) which displays a binuclear unit and further forms the 2D supramolecular structure through unique $\pi - \pi$ stacking and hydrogen bonding interactions [13]. This structural discrepancy may arise from the different coordination modes displayed by the HL_1^{2-} and HL_2^{2-} ligands. The HL_1^{2-} acts as a bridging ligand in **6** (Scheme 3c) while HL_2^{2-} does not coordinate at all in **1**.

3.1.2. $[Co_3(L_1)_2(bipy)_3(H_2O)_6]_n \cdot 8nH_2O(2)$

Complex **2** crystallizes in the space group C2/c. As illustrated in Fig. 2a, the asymmetric unit contains three Co(II) ions, two L_1^{3-} anions, three bipy, six coordinated water and eight lattice water molecules. The L_1^{3-} ligands use the nitrogen atom and one carboxylato oxygen atom from the glycinato group to chelate one Co atom, while the remaining carboxylato oxygen atom from the glycinato group coordinates to another Co atom. The two carboxylato oxygen atoms of the $C_6H_5COO^-$ group are free, as shown in Scheme 3a. There are two crystallographically independent cobalt atoms, one of which (Co2) lies on a center of symmetry, while the other (Co1) lies on a general position. The geometries around the Co(II) ions are both distorted octahedra, giving rise to a [4+2] type of configuration. Co1 is coordinated by two carboxylato oxygen atoms from two L_1^{3-} ligands and two water molecules in the equatorial plane and two nitrogen atoms of bipy at the axial sites. Co2 is sur-

rounded by one carboxylato oxygen atom, one nitrogen atom from a L_1^{3-} ligand and two water molecules in the equatorial plane and two nitrogen atoms of bipy in the axial position. The Co-O_{1.1} and Co-N_{bipy} bond lengths are in agreement with those reported for carboxylate and bipy-containing Co(II) complexes. One inner Co1 atom and two outer Co2 atoms are bridged by single carboxylato group in a syn-anti mode to form a linear trinuclear cluster with an adjacent Co...Co distance of 5.736 Å. The similar carboxylato bridged linear trinuclear Co(II) complexes [Co₃(O₂CMe)₆(bpy)₂], [Co₃(O₂CPh)₆- $(base)_2$, $[Co_3(O_2C(C_6H_4NO_2)_6(base)_2)]$ and $[Co_3(O_2CMe)_8]$ have also been reported in the literatures [14–16]. The trinuclear clusters in 2 are connected to each other through bipy bridges to give rise to a new 1D triple infinite chain extending along the *b*-axis (Fig. 2b), which is different from those of the known 1D polymers with linear chain [17], zigzag chain [18], helical chain [19], ladder chain [20], double-stranded chain [21] and 1D double chain motifs [22]. To the best of our knowledge, this is the first example of a 1D triple chain complex containing amino acid-type and linear trinuclear metal arrangements.

In addition, there exist aromatic ring stacking interactions in the trinuclear unit between benzene rings of L_1^{3-} ligands and pyridine rings of bipy, with the centroid to centroid distance being 3.77 Å and a dihedral angle of 4.16°. These π - π stacking interactions encourage the L_1^{3-} ligands to alternately decorate two sides of the 1D triple chain. Extensive hydrogen bonds between coordinated water molecules and lattice water molecules are also formed, which reinforce the intra- and inter-chain linkages, and result in the formation of a 3D extended framework. In 2, the two types of weak interactions, namely hydrogen bonds and aromatic ring stacking interactions, play an important role in the self-assembly and stabilization of the supramolecular structure. Notably, a related compound $[Co_3(L_2)_2(bipy)_2(H_2O)_6]_n \cdot 2nCH_3OH \cdot 8nH_2O$ (7) is obtained by using H₃L₂ under similar conditions, however, this structure shows a 1D alternating chain with [CoL(H₂O)]₂²⁻ binuclear and $[Co(bipy)_2(H_2O)_4]^{2+}$ mononuclear units along the *a*-direction [12]. Furthermore, the coordination mode of L_2^{3-} in **7** (Scheme 3d) is different from that of L_1^{3-} in **2**.



Scheme 3.



Fig. 2. (a) A perspective view of the discrete Co₃ cluster, hydrogen atoms and lattice water molecules are omitted for clarity. (b) The 1D triple polymeric chain architecture in **2**, the L_1^{3-} ligands are omitted for clarity.

3.1.3. $[Cu_4(L_1)_2(OH)_2(bipy)_4]_n \cdot 12nH_2O(\mathbf{3})$

It can be seen from Fig. 3a that 3 contains tetranuclear Cu(II) units. Each tetranuclear unit is composed of four Cu(II) ions, two L₁³⁻ ligands, and two OH⁻ groups. There are also twelve intercalated water molecules per tetramer. Within the tetramer, there are three kinds of crystallographically independent Cu(II) ions with different coordination environments in the unit. Cu1 and Cu2 are bridged by one L_1^{3-} ligand and Cu2 and Cu3 are bridged by a hydroxyl group with distances of 5.374 and 3.369 Å between Cu1/ Cu2 and Cu2/Cu3, respectively. The geometry of Cu1 can be considered as a distorted octahedral geometry with a [N₄O₂] coordination sphere. The four equatorial coordination sites are occupied by N1, N2, N7 and N7A. Two oxygen atoms (O2, O2A) from two different glycinato groups occupy the axial coordination sites. The axial bond lengths (Cu1–O2, 2.354(4)Å) are considerably longer than the equatorial bond lengths (Cu(1)-N(7) = 2.013(4), Cu(1)-N(1) = 2.031(6), Cu(1)-N(2) = 2.079(6) Å) leading to the distortion from regular octahedral geometry. Cu2 is four-coordinated by one bridging carboxylato oxygen atom, two nitrogen atoms from different bipy ligands and one bridging hydroxyl group with a $[N_2O_2]$ coordination sphere. The Cu2–O7_{OH} (1.917(4)Å) distance is shorter than that of Cu2-O1_{L1} (1.969(4) Å), but the Cu2-N distances (Cu2-N3 = 2.045(4), Cu2-N4 = 2.042(4) Å) are the same within error. The Cu3 ion is coordinated by two bridged hydroxyl groups (O7, O7A) and two bipy nitrogen atoms (N5, N6) to form a square planar geometry. The Cu-O and Cu-N bond distances are 1.932(4), 2.039(6) and 2.050(6) Å, respectively.

The asymmetric unit in **3** forms uniform tetranuclear cycles $(Cu_1Cu_2Cu_3Cu_2)$. The tetranuclear units are then connected together by the coordination bonds between oxygen atoms from the glycinato groups and Cu(II) ions to form a new \cdots Cu₁Cu₂Cu₃Cu₂Cu₁Cu₂Cu₃Cu₂ \cdots 1D chain. These 1D chains are further interconnected by bipy ligands to generate a 2D wave-like rectangular grid layer along the *a*-axis, as shown in Fig. 3b and c.

It is interesting that the aromatic ring containing C(4) atom is almost parallel to the related pyridine ring containing N(1) atom in a tetranuclear unit. (the dihedral angle between two planes was *ca.* 12.13°) with a close intramolecular separation of *ca.* 3.83 Å. The stacking interactions encourage the L_1^{3-} ligands to lie alternatively above and below the 2D planes, and further extensive hydrogen bonds exist between coordinated water and lattice water molecules between the adjacent 2D layers, generating an overall 3D network. The structure of **3** is different from that of $[Ca(H_2O)_{4-}Cu_2(bipy)_2(L_2)_2]_n \cdot 4nH_2O$ (**8**), which has a 2-fold 3D interpenetrating network where Cu atoms are joined by bipy to generate a 1D zigzag chain [12]. Every L_2^{3-} ligand adopts a tetradentate bridging mode to link one Ca and two Cu atoms in **8** (Scheme 3e) while L_1^{3-} acts as a tridentate bridging mode to link two Cu atoms forming a uniform chain in **3**.

3.1.4. $[Na(H_2L_1)(H_2O)]_n$ (4)

Single-crystal X-ray structural analysis shows that 4 is a bilayer structure in which two single layers are linked by H₂L₁ ligands to generate a 2D bilayer framework. Each sodium is primarily coordinated by two oxygen atoms [Na(1)-O(5), 2.4514(18); Na(1)-O(6)]2.4290(17) Å] from two different glycinato groups, two oxygen atoms [Na(1)–O(3), 2.4996(17); Na(1)–O(4), 2.4818(17) Å] from sulfonate groups, one oxygen atom from a carboxylato group of H_2L_1 [Na(1)–O(2), 2.4137(17)Å] and one oxygen atom from a water molecule [Na(1)–O(7), 2.491(2)Å] to furnish a distorted octahedral geometry (Fig. 4a). Unlike compounds 1-3, oxygen atoms from both sulfonate groups and C₆H₅COO⁻ groups coordinate to metal ions. The $H_2L_1^-$ ligand in **4** acts as a pentadentate ligand, as shown in Scheme 3b, where two carboxylato oxygen atoms from the glycinato group adopt a *syn-anti* bridging mode, while the other two oxygen atoms from the sulfonate group exhibit a syn-syn bridging mode, and the carboxylate from the C₆H₅COO⁻ group adopts a monodentate coordination mode. Thus, each H₂L₁⁻ ligand links five sodium atoms and each sodium center interacts with five $H_2L_1^-$ ligands.

On the basis of these connection modes, pairs of Na(1) centers are doubly bridged by oxygen atoms from glycinato and sulfonate groups to form an eight-membered ring with a Na \cdots Na separation of 5.506 Å. These dinuclear units are arranged uniformly to form a



Fig. 3. (a) The coordination environment of a tetranuclear Cu(II) unit in **3**, hydrogen atoms, lattice water molecules and coordinated bipy are omitted for clarity. (b) 2D layer of **3** constructed from the 1D chain. (c) Schematic representation of a 2D layer structure.

1D chain. These chains are linked by $-SO_2NHCH_2COO-$ groups to build a 2D layer (Fig. 4b). Interestingly, the 2D layers are linked by $H_2L_1^-$ to generate a new 2D bilayer framework with a distance of 10.899 Å (based on Na...Na) between the two single layers (Fig 4c). The adjacent 2D bilayers are further linked to each other by O-H···O hydrogen bonds [O(7)-H(2W)···O(7A), 2.845(6) Å; O(7)-H(1W)···O(6), 2.992(3); O(1)-H(1)···O(5), 2.569(2) Å] to complete



Fig. 4. (a) The local coordination environment of Na ion with atomic numbering scheme in **4**. (b) Perspective view of the single Na-H₃L sheet; (c) Side view along the *a*-axis showing bilayer motif in **4**.

the final 3D supramolecular architecture. This is, to our knowledge, the first example of bilayer architecture assembled by alkali metal with amino acid derivatives.

3.1.5. $[Mn_2(HL_2)_2(dpe)_3(H_2O)_2]_n \cdot ndpe$ (5)

The fundamental building unit of **5** is composed of two Mn(II) cations, two monodentate coordinated dpe, one μ_2 -dpe, two HL₂²⁻ anions, two coordinated water molecules and one guest dpe molecule. The coordinated and uncoordinated dpe molecules are disordered over two sites. For clarity, only one of these sites is shown in Fig. 5. The dpe molecules exist in three types of coordination modes (monodentate, bis-monodentate and uncoordinate) in **5**, which is unusual in the construction of polycarboxylate and dpe polymers. Each Mn center exhibits a distorted octahedral geometry with two pyridyl nitrogen atoms from two dpe ligands in the axial positions, and four oxygen atoms in the equatorial plane composed of three oxygen atoms from three HL₂²⁻ ligands and one from coordinated water molecule. The Mn–O bond distances fall in the range of 2.120(3)–2.189(2) Å, and the Mn–N bond distances are 2.296(3) and 2.304(3) Å, respec-



Fig. 5. (a) 2D sheets bridged by HL_2^{2-} molecules. (b) View of the channels formed by the 3D network. (c) Space-filling model of **5** as viewed down the *b*-axis (disordered guest dpe molecules are omitted for clarity). (d) A view of the 1D supramolecular dpe chain constructed by the intermolecular π - π aromatic stacking interactions.

tively. The HL_2^{2-} ligand displays both monodentate and bis-monodentate bridging coordination modes in the assemblies, as shown in Scheme 3f. In addition, two HL_2^{2-} ligands bridge two Mn(II) ions to form a 22-membered ring and another four Mn(II) ions and four HL_2^{2-} ligands form a 30-membered ring. Therefore, a [Mn(HL₂) (H₂O)]_∞ layer is formed through an alternating arrangement of the 22- and 30-membered rings (Fig. 5a). The resulting 2D sheets are pillared by dpe to generate an overall 3D framework in which free disordered dpe are encapsulated as guest molecules (Fig. 5b and c). The adjacent dpe molecules in the channels stack along the *b*-axis through π - π stacking interactions through the pyridine rings to form a 1D supramolecular chain (Fig. 5d). Each Mn center binds two *trans*-located dpe molecules. One is a terminal dpe which lies in the interlayer region and the other is a bridging dpe which lies alternatively between the 2D planes to link the 2D layers into a 3D framework.

3.2. Structural diversity of 1-8

It is noteworthy that a variety of framework structures can be achieved on the basis of the choice of the *N*-[(carboxyphenyl)-sulfonyl]glycine isomers. The slight positional differences of the carboxylato groups between these two isomers may lead to significant geometric diversification of the resulting coordination polymers. We have successfully isolated and characterized eight coordination polymers containing Mn, Co, Cu, Na and Ca centers varying from 0D to 3D. These results illustrate the isomeric effect of the bridging ligands on coordination polymers. In 1-8, these isomers exhibit several coordination patterns as illustrated in Scheme 3, in which the glycinato and carboxylato groups can adopt the unidentate, chelating and bridging modes. Thus, the variation of the N-[(carboxyphenyl)-sulfonyl]glycine isomers used in the assembled process has a significant role in the structural diversity shown by 1-8. Secondly, the N-donor auxiliary ligands are good connectors in mediating and constructing MOFs with specific structure. In this study, phen, bipy and dpe with different conformations and flexibility were used to investigate their influence on the structure of the complexes. The steric hindrance of the phen molecule may contribute to the formation of the discrete units of complexes **1** and **6**, while the introduction of the bipy and dpe leads to the polymeric structures of complexes 2, 3, 5, 7 and 8.

On the other hand, the choice of metal centers may also have a significant effect on the binding fashions of the *N*-[(carboxy-phenyl)-sulfonyl]glycine isomers as well as the resultant extended networks of **1–8**. For *N*-[(4-carboxyphenyl)-sulfonyl]glycine/bipy systems containing **2** and **3**, two coordination modes of H_3L_1 are observed, and interestingly, two different types of 1D triple chain or 2D layer frameworks are generated depending on the metal centers Co or Cu. The structures of **7** and **8** are also metal-controlled, and notably, Co^{2+} -based complex **7** shows an alternating chain while a unique 3D interpenetrating architecture is formed in the case of mixed Ca²⁺ and Cu²⁺ in **8**. This is consistent with the fact that the radius of Cu²⁺ and Ca²⁺ ions are larger than that of Co²⁺ ion. This result indicates that the choice of metal ion has a significant effect on these polymeric structures as well as the binding modes of the ligands.

3.3. Thermal stability

Thermogravimetric experiments were conducted to study the thermal stability of **5**, which is an important parameter for porous metal–organic framework materials (Fig. S1, Supplementary data). The TGA curve for **5** suggests that the first weight loss of 16.37% in the region of 30–275 °C corresponds to the loss of two coordinated water and one guest dpe per formula unit (calculated 15.59%), which is also in agreement with the results of elemental analysis. The residual framework starts to decompose beyond 300 °C with a series of complicated weight losses and does not stop until heating ends at 550 °C. In principle, TGA measurements alone cannot

be used to determine the stability of an open structure since it may collapse without a notable change in the weight. As shown in Fig. 6, the peak positions of the simulated and experimental XRPD patterns for **5** are in agreement with each other, demonstrating the good phase purity of **5**. XPRD measurements at different temperatures (Fig. 6) show that after heating at 275 °C, the spectra are similar to the original one, suggesting its crystalline nature is still maintained after removing the guest dpe molecules.

3.4. Magnetic properties

The magnetic susceptibilities, χ_M , of **5** were measured in the 2– 300 K temperature range, and shown as $\chi_M T$ and χ_M versus *T* plots in Fig. 7. The experimental $\chi_M T$ value of **5** at room temperature is 4.18 cm³ K mol⁻¹ per Mn(II) ion, close to the spin value expected for an uncoupled high-spin Mn(II) ion (4.38 cm³ K mol⁻¹). The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) of **5** obeys the Curie–Weiss law above 5 K with $\theta = -2.1$ K, C = 4.59cm³·K/mol, $R = 4.9 \times 10^{-5}$, which indicates that antiferromagnetic interactions are operative in **5**. According to the structure of **5**, it could be presumed that the main magnetic interactions between the metal centers might happen between two carboxylate bridged Mn(II) ions, whereas the superexchange interactions between



Fig. 6. Comparison of XRPD patterns of the simulated pattern from the singlecrystal structure determination, the as-synthesized and the product after heating at 275 $^{\circ}$ C for **5**.



Fig. 7. Temperature dependence of $\chi_M T$ and χ_M for **5**. The solid line represents the theoretical values based on Eq. (1) described in the text.

Mn(II) ions through the HL_2^{2-} and dpe bridges can be ignored because of the long length of the HL_2^{2-} and dpe ligands. The magnetic susceptibility data were fitted assuming that the carboxylate bridges Mn(II) ions to form a uniform chain with an exchange constant *J*, and then dpe and HL_2^{2-} connect the chains to form a 3D structure with an exchange constant *zJ'*. The susceptibility data were thus approximately analyzed by a chain mode of spin S = 5/2[23,24]. The least-squares analysis of magnetic susceptibilities data led to $J = -0.18 \text{ cm}^{-1}$, g = 2.04, $zJ' = -0.04 \text{ cm}^{-1}$ and $R = 1.65 \times 10^{-4}$, The *J* value indicates a weakly antiferromagnetic interaction between the nearest Mn(II) ions bridged by H₃L₁.

4. Conclusions

In summary, we have successfully synthesized eight new complexes by using two versatile ligands, *N*-[(4-carboxyphenyl)-sulfonyl]glycine and its isomer *N*-[(3-carboxyphenyl)-sulfonyl] glycine. Their structures range from a OD cation–anion species to a 3D network with different structural motifs and this result demonstrates that ligand isomers and metal centers have a tuning effect upon the motifs of the resultant structures. Subsequent work will be focused on the construction of new polymers by using these two isomers or other related amino acid derivatives as basic building units.

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Appendix A. Supplementary data

CCDC 659934–659937, 675251 contain the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.04.044.

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