# CrystEngComm

# PAPER

Cite this: CrystEngComm, 2013, 15, 3974

Received 27th November 2012, Accepted 8th March 2013

DOI: 10.1039/c3ce26928k

www.rsc.org/crystengcomm

### Introduction

The syntheses and characterization of coordination polymers have been the subject of intense focus during recent years. These new complexes thus prepared have attracted great attention not only due to their intriguing topological features but also their potential applications in areas such as gas storage, separation, catalysis, ion exchange and magnetism.<sup>1</sup> The range and variety of the self-assembling structures that can be constructed relies on the presence of suitable metalligand interactions and supramolecular contacts, *i.e.*, hydrogen bonding and other weak interactions,<sup>2</sup> which are also affected by factors such as counterion,<sup>3</sup> metal-to-ligand ratio<sup>4</sup> and solvent.<sup>5</sup> The dicarboxylate ligands have been widely adopted for the generation of new coordination networks in a

† Electronic supplementary information (ESI) available: TGA curves for 1–4 (Fig. S1).  $\chi$ T–T curves of complexes 1–4 (Fig. S2). Selected bond distances (Å) and angles (°) for complexes 1–4 (Tables S1–S4). C–X–C angles of MBA<sup>2–</sup>, OBA<sup>2–</sup> and SDA<sup>2–</sup> ligands in known metal complexes (Table S5). CCDC 912093–912096. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce26928k

# Structural diversity of Ni(II) coordination polymers containing dipyridyl amide and angular dicarboxylate ligands: synthesis, structures and magnetism<sup>†</sup>

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Four new Ni(II) coordination polymers containing dipyridyl amide and angular dicarboxylate ligands,  $\{[Ni(L^1)(MBA)]\cdot 2H_2O\}_{\infty} [L^1 = N,N'-di(4-pyridyl)-adipoamide; H_2MBA = diphenylmethane-4,4'-dicarboxylic acid],$ **1** $, <math>\{[Ni(L^1)(OBA)]\cdot H_2O\}_{\infty} [H_2OBA = 4,4'-oxybis(benzoic acid)],$ **2** $, <math>\{[Ni(L^1)(SDA)]\cdot 2H_2O\}_{\infty} (H_2SDA = 4,4'-sulfonyldibenzoic acid),$ **3** $, and <math>\{[Ni_2(L^2)(SDA)_2]\cdot 6H_2O\}_{\infty} [L^2 = N,N'-di(4-pyridyl)suberoamide],$ **4**, have been synthesized by hydrothermal reactions and were structurally characterized by single crystal X-ray diffraction analyses. Complex**1** $is a 1D <math>\rightarrow$  2D polycatenane derived from the helical channels, and the 2D layers are further mutually interdigitated, whereas complex **2** forms 2D rhombic grids with the (6,4) topology, which are interwoven with each other to give a two fold 2D  $\rightarrow$  2D interpenetrating net. Complex **3** shows the 1D looped chain structure, and complex **4** shows 2D layers which catenate to each other to form a 2D  $\rightarrow$  3D inclined polycatenation framework with the new  $(4^2 \cdot 6^8 \cdot 8 \cdot 10^4)(4)_2$  topology. The C-X-C (X = CH<sub>2</sub>, **1**; O, **2**; and SO<sub>2</sub>, **3** and **4**) angles are important in determining the structural diversity. Complex **1** exhibits a different magnetic reaction in the ZFC and FC processes, revealing the existence of a meta-state of ferromagnetic ordering, whereas the activation energies of spin–orbit coupling and antiferromagnetic interaction of complexs **2–4** are directed by the N…N and Ni…Ni distances, respectively.

mixed ligand system.<sup>6,7</sup> However, due to the difficult prediction of the resulting structure, the influential principles for such a system are less ascertained and not conclusive. Moreover, the formation of the bridge by the carboxylate groups can inspire spin communication between adjacent paramagnetic metal ions.

By using the linear and angular dicarboxylic acids and the dipyridyl amide ligands N,N'-di(3-pyridyl)adipoamide and N,N'-di(4-pyridyl)adipoamide (L<sup>1</sup>), we have recently shown that the structural types and degree of interpenetration of these Cd(II) coordination networks can be tuned by changing the shapes of the dicarboxylate ligands. For complexes with the L<sup>1</sup> ligands, those with the linear dicarboxylate ligands form the 3D interpenetrated coordination networks, whereas those with the angular dicarboxylate ligands form coordination networks with less dimensionality, involving 1D  $\rightarrow$  2D polycatenane and 2-fold  $2D \rightarrow 2D$  parallel interpenetration network containing a rotaxane-like motif.<sup>7b</sup> To investigate the influence of the bridging atom/group of the angular dicarboxylate ligands on the structural diversity and to explore the relationship between the magnetism and the structures of the obtained coordination networks, we have reacted Ni(II) salts and the flexible dipyridyl amide ligands, N,N'-di(4-pyridyl)adipoamide ( $L^1$ ) and N,N'-di(4-pyridyl)suberoamide ( $L^2$ ), with a

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series of dicarboxylic acids, diphenylmethane-4,4'-dicarboxylic acid (H<sub>2</sub>MBA), 4,4'-oxybis(benzoic acid) (H<sub>2</sub>OBA) and 4,4'-sulfonyldibenzoic acid (H<sub>2</sub>SDA), which afforded  $\{[Ni(L^1)(MBA)] \cdot 2H_2O\}_{\infty}$ , **1**,  $\{[Ni(L^1)(OBA)] \cdot H_2O\}_{\infty}$ , **2**,  $\{[Ni(L^1)(SDA)] \cdot 2H_2O\}_{\infty}$ , **3**, and  $\{[Ni_2(L^2)(SDA)_2] \cdot 6H_2O\}_{\infty}$ , **4**. The syntheses, structures and thermal and magnetic properties of these four complexes form the subject of this report.



#### **Experimental section**

#### General procedures

Elemental analyses were performed on a PE 2400 series II CHNS/O analyzer or a Vario EL-III analyzer. IR spectra (KBr disk) were recorded on a JASCO FT/IR-460 plus spectro-photometer. Thermal gravimetric analyses (TGA) measurements were carried out on a TG/DTA 6200 analyzer over the temperature range of 30 to 900 °C at a heating rate of 10 °C min<sup>-1</sup>.

#### Materials

The reagents Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O and 4,4'-oxybis(benzoic acid) were purchased from Alfa Aesar Co., Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O from Acros Organics Co., NiBr<sub>2</sub> from Merck Schuchardt, diphenyl-methane-4,4'-dicarboxylic acid from Matrix Scientific Co. and 4,4'-sulfonyldibenzoic from Aldrich Chemistry Co. The ligands N,N'-di(4-pyridyl)adipoamide (L<sup>1</sup>) and N,N'-di(4-pyridyl)suberoamide (L<sup>2</sup>) were prepared according to published procedures.<sup>8</sup>

#### Preparation

 ${[Ni(L^1)(MBA)]} \cdot 2H_2O_{\infty}$ , 1. A mixture of NiBr<sub>2</sub> (0.022 g, 0.10 mmol), L<sup>1</sup> (0.030 g, 0.10 mmol), H<sub>2</sub>MBA (0.026 g, 0.10 mmol) and 5 mL NaOH (0.04 M) solution was sealed in a 23 mL Teflon-lined stainless steel autoclave, which was heated under autogenous pressure to 120 °C for two days. Slow cooling of the reaction system afforded green crystals suitable for single

crystal X-ray diffraction. Yield: 0.037 g (58%). Anal. calcd for  $C_{31}H_{32}N_4NiO_8$  (MW = 647.32): C, 57.52; H, 4.98; N, 8.66. Found: C, 57.65; H, 4.68; N, 8.36%. IR (cm<sup>-1</sup>): 3466 (w), 2991 (br), 1697 (m), 1602 (s), 1523 (s), 1427 (s), 1378 (m), 1327 (m), 1297 (m), 1214 (m), 1178 (m), 868 (m), 841 (m), 765 (m), 527 (m).

{[Ni(L<sup>1</sup>)(OBA)]·H<sub>2</sub>O}<sub>∞</sub>, 2. Prepared as described for 1 except that Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.025 g, 0.10 mmol) and H<sub>2</sub>OBA (0.026 g, 0.10 mmol) in 5 mL CH<sub>3</sub>OH solution were used. Yield: 0.049 g (76%). Anal. calcd for  $C_{30}H_{28}N_4NiO_8$  (MW = 631.27): C, 57.08; H, 4.47; N, 8.87. Found: C, 56.90; H, 4.67; N, 8.81%. IR (cm<sup>-1</sup>): 3535 (m), 3245 (br), 2490 (w), 1711 (w), 1598 (s), 1520 (s), 1418 (w), 1243 (br), 1169 (br), 876 (w), 839 (w), 784 (w), 670 (br).

{[Ni(L<sup>1</sup>)(SDA)]·2H<sub>2</sub>O}<sub>∞</sub>, 3. Prepared as described for 1, except that Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.029 g, 0.10 mmol) and H<sub>2</sub>SDA (0.031 g, 0.10 mmol) in 5 mL CH<sub>3</sub>OH solution were used. Yield: 0.045 g (64%). Anal. calcd for  $C_{30}H_{30}N_4NiO_{10}S$  (MW = 697.33): C, 51.67; H, 4.34; N, 8.03. Found: C, 52.17; H, 4.31; N, 8.14%. IR (cm<sup>-1</sup>): 3408 (m), 3279 (w), 3168 (w), 2332 (w), 1705 (m), 1596 (s), 1513 (s), 1424 (s), 1296 (m), 1162 (m), 1020 (w), 842 (w), 745 (s), 648 (w), 615 (w).

{[Ni<sub>2</sub>(L<sup>2</sup>)(SDA)<sub>2</sub>]·6H<sub>2</sub>O}<sub> $\infty$ </sub>, 4. Prepared as described for 1 except that Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.058 g, 0.20 mmol), L<sup>2</sup> (0.033 g, 0.10 mmol) and H<sub>2</sub>SDA (0.062 g, 0.20 mmol) and 7.5 mL CH<sub>3</sub>OH were used. Yield: 0.075 g (66%). Anal. calcd for C<sub>46</sub>H<sub>50</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>20</sub>S<sub>2</sub> (MW = 1160.44): C, 47.69; H, 4.18; N, 4.84. Found: C, 47.72; H, 3.91; N, 4.52%. IR (cm<sup>-1</sup>): 3445 (s), 2922 (w), 2359 (w), 1690 (m), 1602 (s), 1566 (s), 1525 (s), 1430 (s), 1401 (s), 1304 (s), 1216 (s), 1168 (s), 1101 (s), 835 (s), 778 (s), 740 (s), 694 (m), 618 (s).

Thermal gravimetric analysis. The samples were heated up in nitrogen gas at a pressure of 1 atm with a heating rate of 10 °C min<sup>-1</sup> and finished at 700 °C. The thermal gravimetric analysis (TGA) curve of 1 shows the gradual weight loss of water molecules (calculated 5.56%, observed 5.30%) in 56-193 °C. The host framework starts to decompose at *ca.* 251 °C and the weight loss of 84.78% between 251 and 418 °C corresponds to the decomposition of L1 ligand and MBA ligand (calculated 85.31%). For complex 2, the TGA curve shows the gradual weight loss of the water molecule (calculated 2.85%, observed 2.35%) in 84-208 °C. The host framework starts to decompose at ca. 244 °C and the weight loss of 87.84% between 244 and 426 °C corresponds to the decomposition of L<sup>1</sup> ligand and OBA ligand (calculated 87.44%). The TGA curve of complex 3 shows the gradual weight loss of water molecules (calculated 5.17%, observed 3.05%) at 29-108 °C. The weight loss of 87.41% between 233 and 451 °C corresponds to the decomposition of L<sup>1</sup> ligand and SDA ligand (calculated 86.41%). The TGA curve of complex 4 shows the gradual weight loss of water molecules (calculated 9.31%, observed 7.07%) at 31-93 °C, followed by the decomposition of the host framework at ca. 314 °C. The weight loss of 76.22% between 314 and 510 °C is due to the decomposition of L<sup>2</sup> ligand and SDA ligand (calculated 82.56%).

**X-ray crystallography.** The diffraction data for complexes **1–4** were collected on a Bruker AXS SMART APEX II CCD diffractometer at 22 °C, which was equipped with a graphite-monochromated Mo K $\alpha$  ( $\lambda_{\alpha}$  = 0.71073 Å) radiation. Data

reduction was carried by standard methods with use of wellestablished computational procedures.<sup>9</sup> The structure factors were obtained after Lorentz and polarization. An empirical absorption correction based on "multi-scan" was applied to the data for all complexes. The position of some of the heavier atoms, including the nickel atom, was located by the direct method.<sup>10</sup> The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements, while the hydrogen atoms, except those of the water molecules, were added by using the HADD command in SHELXTL 5.10. The hydrogen atoms of the water molecules of 1 were located from alternating difference Fourier maps and refined isotropically, whereas those of 2 and 4 were first located from the alternating difference Fourier maps and then fixed as riding atoms by using the HADD command. The structure of 3 has a disorder problem and the hydrogen atoms of the water molecules were not located. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1. Selected bond distances and angles are listed in Tables S1-S4, ESI.

**Magnetic susceptibility measurement.** Magnetic susceptibility measurements were performed using MPMS-XL (SQUID) from Quantum Design with the standard setup. The samples were cooled to 1.8 K in the absence of an applied magnetic field at the center of signal pickup coils.  $\chi$ -*T* experiments were carried out using both the zero field cooling (ZFC) and the field cooling (FC) methods to determine the ordering temperature of samples. Magnetic hysteresis loops were measured to study the magnetization responses to various applied magnetic fields (*M*-*H* curve), and to determine the thermal average of the *z* component of the saturated magnetic moment  $\langle \mu_z \rangle_s$  per chemical formula unit.

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## **Results and discussions**

#### Structure of 1

Fig. 1a shows the coordination environment about the Ni(II) metal center, which is six-coordinated by two nitrogen atoms from two  $L^1$  ligands [Ni–N = 2.045(3) and 2.050(3) Å] and four oxygen atoms from two  $\mu_2 - \kappa^2 \kappa^2 - MBA^{2-}$  ligands [Ni–O = 2.052(1)-2.191(2) Å], resulting in a distorted octahedral geometry. The Ni(II) ions are interlinked by two L<sup>1</sup> and two MBA<sup>2-</sup> ligands to give 1D infinite helical channels, Fig. 1b, and the Ni(II) ions are separated by distances that are 16.30 (through L<sup>1</sup>) and 14.31 (through MBA<sup>2-</sup>) Å. Each helical channel is polycatenated by two others, giving a  $1D \rightarrow 2D$ polycatenated network, with density of catenation (Doc) = 2and index of separation (Is) = 1,<sup>11</sup> Fig. 1c. In addition, these polycatenated helical channels interdigitate to each other by directing the back-carbon atoms of the L1 ligands into the windows of the adjacent nets, Fig. 1d. The shortest Ni…Ni distance between the adjacent nets is found to be 7.66 Å.

The different nets are linked by the water molecules through O–H···O hydrogen bonds to the amide carbonyl oxygen atoms of the L<sup>1</sup> ligands [O···O = 2.827(4) Å,  $\angle$ O–H···O = 165(4)° and O···O = 2.790(4) Å,  $\angle$ O–H···O = 173(4)°] and to the carboxylate oxygen atoms [O···O = 2.769(4),  $\angle$ O–H···O = 173(5)° and 2.753(4) Å,  $\angle$ O–H···O = 172(5)°]. N–H···O [N···O = 2.818(4) Å,  $\angle$ N–H···O = 176.6(2)° and N···O = 2.848(4) Å,  $\angle$ N–H···O = 173.2(2)°] hydrogen bonds from the amine hydrogen atoms of the L<sup>1</sup> ligands to the oxygen atoms of the water molecules are also observed. The solvent-accessible volume calculated by PLATON program<sup>12</sup> is 315.5 Å<sup>3</sup>, which is 10.0% of the unit cell volume.

#### Table 1 Crystal data for complexes 1-4

Complex	1	2	3	4
Formula	C <sub>31</sub> H <sub>32</sub> N <sub>4</sub> NiO <sub>8</sub>	C <sub>30</sub> H <sub>28</sub> N <sub>4</sub> NiO <sub>8</sub>	C30H30N4NiO10S	C46H50N4Ni2O20S2
Formula weight	647.32	631.27	697.35	1160.44
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_{1}/c$	Pnna	Ima2	C2/C
a, Å	11.9158(3)	12.4702(7)	24.5212(18)	21.5324(3)
b, Å	14.3094(4)	22.7872(4)	11.1701(8)	12.8686(2)
c, Å	18.5432(5)	11.0779(2)	12.2369(8)	20.5775(3)
₿,°	94.685(1)	90	90	93.497(1)
<i>V</i> , Å <sup>3</sup>	3151.20(15)	3147.91(9)	3351.7(4)	5691.24 (14)
Ζ	4	4	4	4
$D_{\rm calc}, {\rm mg}{\rm mm}^{-3}$	1.364	1.332	1.382	1.354
F(000)	1352	1312	1448	2408
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	0.671	0.670	0.700	0.808
Range $(2\theta)$ for data collection, °	$3.42 \leqslant 2\theta \leqslant 56.62$	$3.58 \leqslant 2\theta \leqslant 56.58$	$3.32 \leqslant 2\theta \leqslant 66.00$	$3.68 \leqslant 2\theta \leqslant 56.58$
Independent reflections	7822	3921	5574	7030
-	$[R_{int} = 0.0859]$	$[R_{int} = 0.0329]$	$[R_{int} = 0.0297]$	$[R_{int} = 0.0396]$
Data/restraints/parameters	7822/0/413	3921/0/214	5574/37/342	7030/0/323
Quality-of-fit indicator <sup>a</sup>	1.005	1.072	1.091	1.057
Final <i>R</i> indices $[I > 2\sigma(I)]^b$	$R_1 = 0.0555, wR_2 = 0.0900$	$R_1 = 0.0420, wR_2 = 0.1109$	$R_1 = 0.0622, wR_2 = 0.1706$	$R_1 = 0.0567, wR_2 = 0.1515$
R indices (all data)	$R_1 = 0.1526, wR_2 = 0.1125$	$R_1 = 0.0736, wR_2 = 0.1285$	$R_1 = 0.0683, wR_2 = 0.1760$	$R_1 = 0.0990, wR_2 = 0.1736$

<sup>*a*</sup> Quality-of-fit =  $[\sum w(|F_o^2| - |F_c^2|)^2/(N_{observed} - N_{parameters})]^{1/2}$ . <sup>*b*</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$ ,  $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$ . *a* = 0.0493, *b* = 0.0000, **1**; *a* = 0.0606, *b* = 1.1538, **2**; *a* = 0.0681, *b* = 2.7125, **3**; *a* = 0.0877, *b* = 7.5828, **4**.





**Fig. 1** (a) Coordination environment of Ni(II) ion in **1**. Symmetry transformations used to generate equivalent atoms: (A) -x, y + 1/2, -z + 3/2; (B) x, y + 1, z. (b) A drawing showing the 1D helical channel chain. (c) A schematic view of  $1D \rightarrow 2D$  polycatenated framework. (d) The different nets are linked through O–H…O hydrogen bonds, which also interdigitate to each other.

#### Structure of 2

The coordination sphere of the Ni(II) ion is shown in Fig. 2a. The Ni(II) ion has a slightly distorted octahedral coordination

**Fig. 2** (a) Coordination environment of Ni(II) ion in **2**. Symmetry transformations used to generate equivalent atoms: (A) x, -y + 1/2, -z + 1/2. (b) A drawing showing the 2D pleated net. (c) A drawing showing the 2-fold interpenetrated nets. (d) The two-fold interpenetrated sheets are interlinked through N–H···O hydrogen bonds to form a 3D supramolecular structure.

(d)

geometry by two pyridyl nitrogen atoms from two L<sup>1</sup> ligands and four oxygen atoms from two OBA<sup>2-</sup> ligands, with Ni-O distances of 2.104(3) and 2.126(3) Å and Ni-N distances of 2.022(3) Å. The adjacent Ni(II) atoms are linked to each other by the  $L^1$  ligands and the OBA<sup>2-</sup> ligands through the pyridyl nitrogen atoms and the oxygen atoms, respectively, to form a two-dimensional rhombic grid structure, Fig. 2b, and the Ni(II) ions are separated by distances that are 19.36 (through L<sup>1</sup>) and 14.70 (through  $OBA^{2-}$ ) Å. The grid structure is not planar but undulated, resulting from the inherent bent conformation of the L<sup>1</sup> molecules and OBA ligands. If the O atoms of the OBA<sup>2-</sup> ligands are defined as 2-connected nodes and the Ni(II) ions as 4-connected nodes, the structure of complex 2 can be regarded as a 2,4-connected two-fold  $2D \rightarrow 2D$  parallel interpenetration framework with the  $(6^4 \cdot 8^2)(6)$  topology for the 2D layer,<sup>13</sup> Fig. 2c. The shortest Ni…Ni distance between the adjacent nets is found to be 8.34 Å.

The adjacent two-fold interpenetrated sheets are interlinked through the N–H···O hydrogen bonds [N···O = 2.916(6) Å,  $\angle$  N–H···O = 159.7(3)°] between the carboxylate oxygen atoms and amine hydrogen atoms of the L<sup>1</sup> ligands, resulting in a 3D supramolecular structure, Fig. 2d. The solvent-accessible volume calculated by PLATON program is 400.2 Å<sup>3</sup>, which is 12.7% of the unit cell volume.

#### Structure of 3

The coordination sphere of the Ni(II) ion is shown in Fig. 3a. Each Ni(II) ion is six-coordinated by two pyridyl nitrogen atoms from two L<sup>1</sup> ligands and four oxygen atoms from two tetradentate SDA<sup>2-</sup> ligands, resulting in a slightly distorted octahedral coordination geometry, with Ni-O distances of 2.075(2) and 2.156(2) Å and Ni-N distances of 2.110(1) and 1.957(9) Å. The adjacent Ni(II) ions are linked to each other by the L<sup>1</sup> and SDA<sup>2-</sup> ligands through the pyridyl nitrogen atoms and the oxygen atoms, respectively, to form a one-dimensional looped chain structure, and the adjacent Ni(II) ions are separated by distances that are 12.26 Å. The shortest Ni…Ni distance between the adjacent chains is found to be 8.28 Å. The  $L^1$  and  $SDA^{2-}$  ligands are disordered such that four disordered chains can be resolved. Fig. 3b shows one of the 1D chains and Fig. 3c depicts the overlapped drawing of the four disordered chains. Each chain is symmetry-related by the  $C_2$ axis passing through S atom of SDA<sup>2-</sup> ligand and the middle of C(16)-C(17) bond of the L<sup>1</sup> ligand. Noticeably, the rings of the looped chains are mutually perpendicular but not parallel.

The 1D chains lie parallel to each other, forming 2D sheets in the *ab* plane through N–H···O [N···O = 3.043(5) Å,  $\angle$ N–H···O = 159.1(3)°] hydrogen bonds between the carboxylate oxygen atoms and amine hydrogen atoms of the L<sup>1</sup> ligands, Fig. S2, ESI,† which are further stacked along the *c* direction by the other N–H···O [N···O = 2.923(5) Å;  $\angle$ N–H···O = 158.1(3)°] hydrogen bonds, forming a 3D supramolecular structure, Fig. 3d. The solvent-accessible volume calculated by PLATON program is 243.7 Å<sup>3</sup>, which is 7.3% of the unit cell volume.

#### Structure of 4

Fig. 4a depicts a drawing showing the coordination environment about the Ni(II) ions, in which both of the Ni(1) and Ni(2) ions are five-coordinated by one pyridyl nitrogen atom of the



**Fig. 3** (a) Coordination environment of Ni(II) ion in **3**. Symmetry transformations used to generate equivalent atoms: (A) -x + 1, -y + 1, *z*; (B) x - 1/2, -y + 1, *z*. (b) A drawing showing the 1D looped chain. (c) A drawing showing the disordered structure. (d) The 1D chains are interlinked through N–H···O hydrogen bonds to form a 3D supramolecular structure.

L<sup>2</sup> ligand [Ni–N = 2.063(7) Å] and four oxygen atoms of the  $SDA^{2-}$  ligands [Ni–O = 2.248(7), 2.090(7), 2.066(7) and 2.016(7) Å] to give a distorted square planar coordination geometry [ $\angle$ 



**Fig. 4** (a) Coordination environment of Ni(II) ion in **4**. Symmetry transformations used to generate equivalent atoms: (A) -x + 1, -y + 1, -z + 1; (B) x - 1/2, y - 1/2, z; (C) -x + 3/2, -y + 3/2, -z + 1. (b) A drawing showing the 2D layer. (c) A schematic drawing showing the inclined interpenetration. (d) The different nets are interlinked through N–H···O and O–H···O hydrogen bonds.

  $(4^2 \cdot 6^8 \cdot 8 \cdot 10^4)(4)_2$  topology, determined using TOPOS.<sup>13</sup> Moreover, the 2D layers are interlocked in a inclined fashion, resulting in a 2D  $\rightarrow$  3D inclined polycatenation framework, Fig. 4c.

The H<sub>2</sub>O molecules of 4 interact with each other to form  $(H_2O)_3$  trimers through O–H···O [O···O = 2.456(21) Å,  $\angle$ O–H···O = 128.6(3)°] hydrogen bonds, which link the 2D nets through N–H···O [N···O = 2.871(3) Å,  $\angle$ N–H···O = 151.6(2)°] and O–H···O hydrogen bonds to the oxygen atoms of the SO<sub>2</sub> groups [O···O = 2.948(11) Å,  $\angle$ O–H···O = 112.6(7)°] and to the oxygen atoms of the carboxylate groups [O···O = 3.299(11) Å,  $\angle$ O–H···O = 150.4(7)°], Fig. 4d. The solvent-accessible volume calculated by PLATON program is 1648.0 Å<sup>3</sup>, which is 29.0% of the unit cell volume.

#### Conformations of the ligands

It has been shown that  $L^1$  can be arranged in *anti-anti-anti* (AAA), anti-anti-gauche (AAG), anti-gauche-anti (AGA), antigauche-gauche (AGG), gauche-anti-gauche (GAG) and gauchegauche-gauche (GGG) conformations, and based on the relative orientation of the C=O (or N-H) groups, each conformation can adopt a cis or trans arrangement.8 The A and G conformations are given when the C–C–C–C torsion angle  $(\theta)$ is  $0 \leq \theta \leq 90^{\circ}$  and  $90 \leq \theta < 180^{\circ}$ , respectively. Accordingly, thirty-eight ligand conformations can be shown for the L<sup>2</sup> ligand. Based on these descriptors, the L<sup>1</sup> and L<sup>2</sup> ligands in 1-4 show four different conformations of AAG trans, AAG cis, GAG cis and AGAGA trans, respectively, which also differ in the dihedral angles between the two pyridyl rings, Table 2. The  $L^1$ and  $L^2$  ligands are thus sufficiently flexible and adopt the conformations that maximize the intra- and intermolecular forces.

#### Structural comparisons

Table 3 lists the C-X-C (X = CH<sub>2</sub>, 1; O, 2; SO<sub>2</sub>, 3 and 4) and dihedral angles of the dicarboxylate ligands in complexes 1-4. The coordination of the dicarboxylate and dipyridyl amide ligands to the Ni(II) ions leads to different dihedral angles between the phenyl rings of the dicarboxylate ligands and different ligand conformations for the dipyridyl amide ligands, respectively, resulting in different structural types. However, the C–X–C angles of 115.3, 121.9, 101.8 and  $102.8^{\circ}$  in these complexes are similar to those of the corresponding MBA<sup>2-</sup>, OBA<sup>2-</sup> and SDA<sup>2-</sup> ligands found for the known metal complexes, which are 114.1°, 117.3-122.5° and 101.4-104.9°, respectively, Table S5, ESI,† indicating that the C-X-C angles are not subjected significantly to the changes of metal ions and co-ligands. The structural diversity in 1-3 can thus be ascribed to the different C-X-C angles due to the different bridging atom/group of the angular dicarboxylate ligands. The structural difference between 3 and 4 is most probably due to the different donor atom positions between  $L^1$  and  $L^2$ . Noticeably, the N···N distances between the two pyridyl nitrogen atoms of the dipyridyl amide ligands are 13.46 Å for 1, 15.70 Å for 2, 9.97 Å for 3 and 16.64 Å for 4. Therefore, flexible spacer ligands that show longer N···N distances in the solid state are better candidates for the formation of entangled coordination networks due to their propensity to form large voids.

Table 2 Ligand conformations and	l corresponding ar	ngles for complexes <b>1–4</b>
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	Diagram	Torsion angle (°)	Conformation	Dihedral angle (°)
1	ainto	-171.5, -178.4, 77.2	AAG trans	75.6
2	airia	174.1, -165.3, -67.7	AAG cis	41.7
3	and	-79.6, 173.4, -70.7	GAG cis	55.9
4	anyo	-173.7, -64.7, -180.0, 64.7, 173.7	AGAGA trans	0

#### Thermal properties

In order to estimate the stability of the frameworks, thermal gravimetric analyses (TGA) of complexes **1–4** were carried out in nitrogen atmosphere from 30 to 700 °C. The TGA results, Fig. S1, ESI,† show that the host frameworks of complexes **1–4** starts to decompose at *ca.* 251, 244, 233 and 314 °C, respectively, indicating that the 2D  $\rightarrow$  3D inclined polycatenation framework of **4** has the better thermal stability.

#### Magnetism

Magnetic hysteresis loop (*M*–*H* curve) and susceptibility ( $\chi$ –*T* curve) were measured to identify the magnetic properties of complexes **1–4**. The hysteresis behaviors of all samples were measured at both 1.8 K and 300 K to verify the formation of the loop, Fig. 5. All the magnetizations of these complexes increased linearly with the applied magnetic field below 1 T at both 1.8 K and 300 K and gradually approached saturation at 1.8 K in a field of 7 T. Since no hysteresis loop can be found, the Langevin function

$$<\mu_z(H)>=<\mu_z>_{s}\left[\operatorname{coth}(x)-\frac{1}{x}\right], \quad x\equiv\frac{\mu H}{k_{\rm B}T}$$

was applied to these four curves to yield  $\langle \mu_z \rangle_s$  (saturation  $\langle \mu_z \rangle$ ), which are listed in Table 4. The obtained  $\langle \mu_z \rangle_s$  of complexes **1–3** are 2.63, 2.55, and 2.17  $\mu_B$  per f.u., respectively, which are close to

2  $\mu_{\rm B}$  (spin 1, g = 2,  $\langle \mu_z \rangle_s = gJ\mu_{\rm B} = 2 \mu_{\rm B}$ ) of the [Ar]3d<sup>8</sup> electronic configuration. The fractional magnetic moments may originate from the asymmetric distribution of charges in the bonding environments, due to the different bonding strengths and crystal fields from the two surrounding N and four O atoms. This environmental factor may have weakened the effect of quenching the orbital angular momentum orbital, further increasing  $\langle \mu_z \rangle_s$ .<sup>14</sup> For complex **4**, a relatively smaller  $\langle \mu_z \rangle_s$  of 0.32  $\mu_{\rm B}$ per f.u. was obtained, and an extra  $\chi_0 H$  term must be taken into account in the Langevin equation. This result implies that the Pauli exclusion principle plays an important role at 1.8 K, and tends to arrange the spins of the bonding valence electrons of nearest-neighbor Ni(II) ions in an anti-parallel manner and leads to a reduction of the net magnetic moment.

Fig. 6 shows the experimentally determined curves of magnetic susceptibility against temperature. Both ZFC and FC processes were performed for the four complexes. The modified Curie–Weiss law in the form

$$\chi(T) = \chi_0 + \frac{C}{T + T_\theta}$$

was first employed to fit the curves in the weakest applied fields.<sup>14</sup> Here, *C* is the Curie constant, *T* is the temperature at which the measurements were made, and  $T_{\theta}$  is the fitted Weiss temperature.

Table 3 C–X–C angle (°) and dihedral angle (°) of the dicarboxylate ligands in complexes 1–4

Complex	Dicarboxylate/X <sup>a</sup>	C-X-C angle	Dihedral angle	Structure
1	$MBA^{2-}/CH_2$	115.3	89.9	$1D \rightarrow 2D$ polycatenane
2	$OBA^{2-}/O$	121.9	61.3	2-fold 2D $\rightarrow$ 2D interpenetrating net
3	$SDA^{2-}/SO_{2}$	101.8	80.9, 86.0	1D looped chain
4	$SDA^{2-}/SO_{2}$	102.8	84.3	$2D \rightarrow 3D$ inclined polycatenation

<sup>a</sup> X is the bridging atom/group of the dicarboxylate ligand.



Fig. 5 Magnetic hysteresis loop of complexes (a) 1 (b) 2 (c) 3 and (d) 4. Solid curves at 1.8 K are consistent with Langevin function.

Positive and negative signs of  $T_{\theta}$  represent antiferromagnetic (AFM) and ferromagnetic (FM) interaction of magnetic ions, respectively. The proper temperature range of Curie-Weiss fitting is determined by the linear part of the  $1/\gamma' - T$  curve. The insets in Fig. 6b and 6c reveal that complexes 2 and 3 yield almost linear 1/  $\chi'$ -T curves over the entire temperature range of interest, and no difference between the FC and ZFC processes can be found. The  $T_{\theta}$ values obtained from these two curves were both positive and close to zero, implying very weak AFM interactions between Ni(II) ions. The FC and ZFC curves of complex 1 separated at 25 K, indicating the formation of magnetic ordering. The negative  $T_{\theta}$ reflects FM interactions at high temperatures, which become AFM interactions when an antiferromagnetic cusp appears in the  $\chi$ -T profile of the 50 Oe ZFC process at 25 K. Notably, only the application of a 50 Oe magnetic field in the FC process alters the shape of the  $\gamma$ -T curve to make it ferromagnetic-like, indicating the existence of a meta-state of FM ordering below 25 K. This may arise from the helical structure with the octahedrally coordinated Ni(II) ions, as shown in Fig. 1b, such that the frustrated AFM interactions occur between ions in the absence of an external magnetic field. Alternatively, in an applied external magnetic field, the Ni(II) moments tend to arrange parallel to each other, forming

ferromagnetic-like shape. For complex **4**, the  $\chi$ -*T* curve exhibited Curie–Weiss behavior only above 50 K and the relatively large  $T_{\theta}$  (14 K) indicates the strong antiferromagnetic coupling between Ni(II) ions. To study further the magnetic behavior of these complexes, the Rueff's equation,<sup>15</sup>

$$\chi T = A \mathrm{e}^{-\frac{L_1}{kT}} + B \mathrm{e}^{-\frac{L_2}{kT}}$$

is used. Here, the sum of A and B equals the Curie constant C, and  $E_1$  and  $E_2$  are the "activation energies" of spin-orbit coupling and the antiferromagnetic exchange interaction. This equation describes the  $\chi T$  curve of complexes 2-4, but not complex 1, owing to the antiferromagnetic phase transition. Table 4 and Fig. S2, ESI,<sup>†</sup> present the obtained fitting parameters and curves, respectively. Clearly, the sums of A and B for complexes 2-4 are equal or close to Curie constant C, obtained from the Curie-Weiss law, indicating consistency between both models. The activation energies of spin-orbit coupling,  $E_1$ , which are 5.92, 61, and 0.32 K for complexes 2, 3, and 4, respectively, are correlated with the N···N distances between the two pyridyl nitrogen atoms of the dipyridyl amide ligands (15.70 Å for 2, 9.97 Å for 3 and 16.64 Å for 4). The higher spin-orbit coupling energy of 3 is associated with complicated bonding status of the four disordered chains of L<sup>1</sup> and SDA<sup>2-</sup> ligands. The order of magnitude of this energy is similar to that reported for complexes that contain magnetic ions.15-17 The fact that the activation energies of the antiferromagnetic exchange interaction,  $E_2$ , of 2 and 3 are smaller than that of 4 reflects the larger separation between Ni(II) ions in 2 and 3. The shortest distances between the Ni(II) ions are 8.34 and 8.28 Å in 2 and 3, respectively, whereas the shortest separation is 2.71 Å in 4. The obtained energies  $E_2$  of 2, 3, and 4 are highly consistent with the fitted  $T_{\theta}$  values from the Curie–Weiss Law, indicating that Rueff's equation is also applies to these complexes and provides deeper insight into the magnetic properties and surrounding environments of Ni(II) ions.

### Conclusions

By using the flexible dipyridyl amide ligands,  $L^1$  and  $L^2$ , and the angular dicarboxylic acids,  $H_2MBA$ ,  $H_2OBA$  and  $H_2SDA$ , four new Ni(II) coordination polymers were successfully

Table 4 Fitted magnetic parameters of complexes 1–4						
Complex	$1^{a}$	1	2	3	4	
$M_{\rm s} (\rm emu \ g^{-1})$ $\leq \mu \geq (\mu_{\rm p} \ {\rm per \ f \ u} \ {\rm at \ 1.8 \ K})$		11.67(1)	14.23(1) 2 55(1)	12.11(1) 2 17(1)	14.68(1) 0.32(1)	
$\chi_0 (10^{-7} \text{ emu g}^{-1} \text{ Oe}^{-1})$ $C (10^{-3} \text{ emu K} \text{ g}^{-1} \text{ Oe}^{-1})$	-0.05(10)	-2.41(53)	-49(5)	-1.92(93)	1.18(27)	
$\mu_{\rm eff}$ ( $\mu_{\rm B}$ per Ni)	3.24(1)	2.84(5) 2.35(1)	3.41(1)	3.01(4)	2.42(2) 2.37(1)	
$T_{\theta}$ (K) A (10 <sup>-4</sup> emu K g <sup>-1</sup> Oe <sup>-1</sup> )	-0.67(3)	-2.33(21)	1.55(5) -6(2)	0.72(2) 1.8(2)	14.0(2) 3.5(1)	
$B (10^{-3} \text{ emu K g}^{-1} \text{ Oe}^{-1})$ $E_1 (\text{K})$			2.68(15) 5.92(81)	1.44(2) 61(7)	2.07(1) 0.32(1)	
$E_2$ (K)			1.47(9)	0.53(19)	16.03(10)	

<sup>*a*</sup> The fitting parameters were obtained from the  $\chi$ -*T* curve of 50 Oe FC process.



Fig. 6 ZFC and FC magnetic susceptibility curves of complex (a) 1 (b) 2 (c) 3 and (d) 4. Inset shows Curie–Weiss fitting result and  $1/\chi - T$  plots.

accomplished. Complex **1** is a  $1D \rightarrow 2D$  polycatenane derived from the helical channels and the 2D layers are further mutually interdigitated, whereas complex 2 forms a two fold  $2D \rightarrow 2D$  interpenetrating net and complex 3 shows a 1D looped chain. Complex 4 displays 2D layers which catenate to each other to form a 2D  $\rightarrow$  3D inclined polycatenation framework. A comparison of the structures reveals that the C-X-C angles are important in determining the structural diversity. Complex 1 exhibits a different magnetic reaction in the ZFC and FC processes, revealing the existence of a metastate of ferromagnetic ordering. The activation energies of spin-orbit coupling and antiferromagnetic interaction of complexes 2 to 4 are directed by the N…N distances between the two coordinated pyridyl nitrogen atoms in a dipyridyl amide ligand and the shortest Ni…Ni distances, respectively. Moreover, the breaking of the spatial symmetry around Ni(II) ions weakened the quenching of the orbital angular momentum and increased the effective magnetic moments of all complexes. The various magnetic behaviors revealed the strong correlation between the structural and bonding environments of these four complexes.

# Acknowledgements

We are grateful to the National Science Council of the Republic of China for support, under Grants NSC 101-2112-M-033-004 and NSC 99-2113-M-033-004-MY3. We also thank Miss C.-W. Lu of the Instrumentation Center, National Taiwan University, for CHNS (EA) analysis experiments.

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