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Sulfate encapsulation in three-fold interpenetrated metal–organic frameworks with bis(pyridylurea) ligands†

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Self-assembly of two flexible bis-pyridylurea ligands, pentane-1,5-diylbis(3-pyridin-3-ylurea) (L^5) and hexane-1,6-diylbis(3-pyridin-3-ylurea) (L^6) with $ZnSO_4$ or $CdSO_4$ (metal-to-ligand molar ratio 1 : 2) results in three metal–organic frameworks with (4,4) net structures, $\{[ML_2(H_2O)_2]SO_4 \cdot 2H_2O\}_n$ (**1**: Zn, L^5 ; **2**: Cd, L^5 ; and **3**: Zn, L^6). Single-crystal X-ray diffraction analyses reveal that all the compounds are characteristic of a 3-fold parallel interpenetrated framework with cavities suitable for encapsulating the sulfate anion despite the different spacer lengths ($(CH_2)_5$ and $(CH_2)_6$) of the two ligands and variation of the metal ions. The ligand adopts an *anti-anti* conformation and functions as a bridging bidentate linker, while the sulfate ion is selectively bound by four urea functionalities *via* multiple hydrogen bonds.

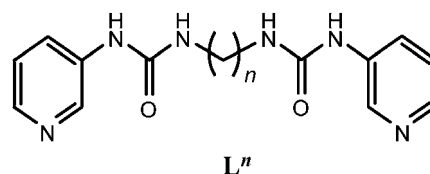
Introduction

There has been considerable interest in the engineering of metal–organic frameworks (or coordination polymers) towards fascinating supramolecular architectures and potential applications in separation, catalysis, non-linear optics, and gas storage, *etc.* by self-assembly of metal ions with bridging organic linkers.¹ The porosity of MOFs is the key to some specific applications as it enables these materials to include guest molecules (*e.g.* anions) of matched dimension, while the size and shape of the pores can be tuned by the judicious choice of metal centers and organic ligands. However, the final outcome is largely unpredictable because the cavities are often filled up by interpenetration or interweaving when long bridging ligands are used which should lead to larger pores.² As a result, the porosity can be significantly reduced or even removed. On the other hand, such interpenetrating species may possess enhanced mechanical strength as separation of the independent rings needs to break chemical bonds. Nevertheless, while porous frameworks of non-interpenetrating systems are numerous, examples of interpenetrating MOFs with remained pores, especially those with well-defined size and shape for special guests, have been relatively rare.³

Anion complexation has become an important aspect in supramolecular chemistry due to the various roles anions play in biological processes, catalysis and environmental events.⁴ In recent years the binding of anions by coordinative compounds

and coordination polymers has attracted much attention.⁵ In particular, the separation of the tetrahedral sulfate is a highlight because of its high hydration energy.⁶ The urea-based pyridyl ligands have proven to be useful agents that combine the abilities of coordination with metal ions and hydrogen-bonding to anions.⁷ Recently we have synthesized a series of mono-, bis- and tris-(pyridylurea) ligands, which showed rich metal coordination and anion binding properties.⁸ Using a bis(pyridylurea), butane-1,4-diylbis(3-pyridin-3-ylurea) (L^4 , Scheme 1) to assemble with $ZnCl_2$, we obtained metallomacrocyclic or helical structures in the presence of different guest molecules.⁹ Such bis(pyridylurea) ligands of the type L^n (Scheme 1, where n is the number of the CH_2 moieties) can function as excellent building blocks for novel anion-binding supramolecular structures as they provide facilities of: (a) the bridging bi-(pyridyl) moieties for coordination with metal ions; (b) multiple hydrogen bonding sites (the urea groups); and (c) the flexible alkyl linker of variable length for interesting structural topologies. For example, the ligand L^2 ($n = 2$) formed a Borromean structure¹⁰ with $AgNO_3$ and coordination polymers with MSO_4 ,^{11,12} while L^5 ($n = 5$) assembled with $AgNO_3$ to yield a quintuple helical polymer.¹³

We now show that self-assembly of metal sulfate ($ZnSO_4$ or $CdSO_4$) with L^5 ($n = 5$, pentylene spacer) and L^6 ($n = 6$, hexylene spacer) afforded three 3-fold parallel interpenetrated metal–organic frameworks, $\{[Zn(L^5)_2(H_2O)_2]SO_4 \cdot 2H_2O\}_n$ (**1**), $\{[Cd(L^5)_2(H_2O)_2]SO_4 \cdot 2H_2O\}_n$ (**2**), and $\{[Zn(L^6)_2(H_2O)_2]SO_4 \cdot 2H_2O\}_n$ (**3**), respectively. The interpenetration in these compounds resulted in roughly ellipsoidal cavities which are



Scheme 1 Structure of the bis(pyridylurea) ligand L^n

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† Electronic supplementary information (ESI) available: TGA curves, NMR spectra, and hydrogen bond parameters for compounds **1**, **2** and **3**, anion competition experiments, and crystallographic data. CCDC reference numbers 717079, 750025 and 750026. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b920777e

capable of selectively binding sulfate ions by four pyridylurea fragments.

Results and discussion

Compounds **1–3** were obtained by slow evaporation of a methanol–water solution of the ligand (L^5 or L^6) and $ZnSO_4 \cdot 7H_2O$ or $CdSO_4 \cdot 8/3H_2O$ at room temperature. They were characterized by IR spectroscopy, X-ray crystallography and elemental analysis to have a composition $[ML_2(H_2O)_2]SO_4 \cdot 2H_2O$. Thermal gravimetric analysis (TGA) showed that **1** lost the water molecules in the temperature range 100–160 °C with a total weight loss of 7.4% (calculated 7.8% for four water molecules per formula unit), whereas the compound began to decompose from 228 °C with a sharp weight loss (ESI, Fig. S1).† Compound **2** can easily lose one crystal water molecule even at room temperature, which was reflected in the elemental analysis results, and the dried sample showed a weight loss process of three water molecules at 94–185 °C (measured 6.3%, calculated 5.7%; ESI, Fig. S2).† A similar dehydration process of four water molecules occurred at 90 to 156 °C for **3** (measured weight loss 7.1%, calculated 7.3%; ESI, Fig. S3).† The presence of SO_4^{2-} in **1–3** was confirmed by the characteristic IR absorption band of sulfate at 1108, 1090 and 1097 cm^{-1} , respectively.

The zinc compound **1** and the cadmium analogue **2** are essentially isomorphous, with the same space group $Pbcn$ and very close unit cell dimensions and structural features. Hence, the following structure description focuses only on compound **1**. In the structure of **1** the zinc(II) center is coordinated by four pyridyl N atoms of four ligands and two water molecules with an octahedral geometry (Fig. 1a). There are crystallographic two-fold

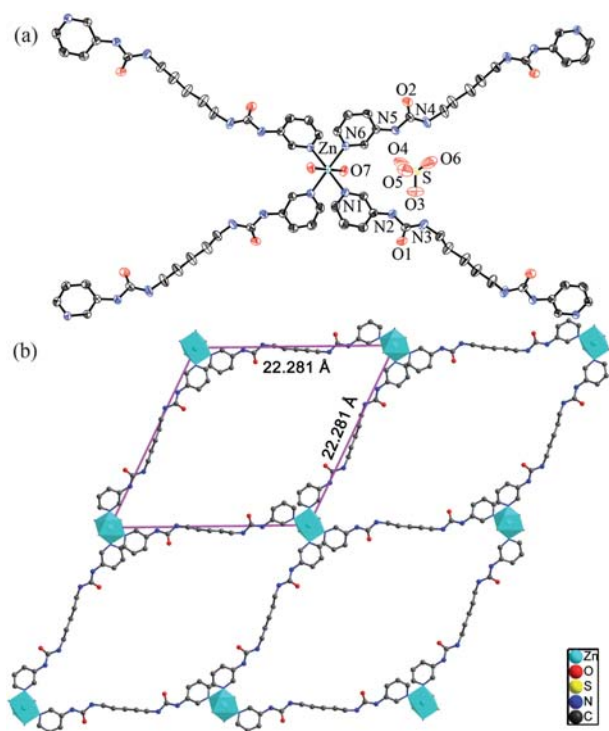


Fig. 1 (a) The coordination environment of the metal center in **1** (Hydrogen atoms are omitted for clarity). (b) Rhombic grids in the sheet-like structure of **1**.

axes along the c direction, and the zinc atoms and one of the $S=O$ bonds of the sulfate ion reside on such symmetry axes. The two C_2 -related water molecules thus occupy the *trans* positions. Unlike the planar, all-*anti* conformation of L^5 in the silver coordination polymers,¹³ the pentamethylene linker of the ligand in **1** assumes the *anti* conformation but the relative orientation of the two pyridylurea moieties is twisted (dihedral angle of 53.3° between the two pyridyl rings).

Each of the four coordinated L molecules acts as a bridge between two neighbouring zinc(II) ions, generating a (4,4) rhombic grid pattern oriented parallel to the ab plane with a zinc(II) center in each of the vertexes (Fig. 1b). The dimension of these grids is *ca.* 22.28 × 22.28 Å with Zn⋯Zn⋯Zn angles of 63.8° and 116.2°, respectively. Extremely large apertures within the grid, defined by through-space Zn⋯Zn distances of 37.83 Å and 23.55 Å, allow the parallel interpenetration of two other identical (4,4) layers to form a three-fold interpenetrating bilayer (Fig. 2; ESI, Fig. S9).† Furthermore, the 2D sheet structure can be considered as comprised of infinite triple-stranded helices running in the direction of interpenetration with a pitch of 37.8 Å (Fig. 3).¹⁴ It is noteworthy that the present framework is significantly different from that constructed by MSO_4 ($M = Ni, Zn$) and the analogous shorter ligand L^2 ($n = 2$, Scheme 1), which showed a rather flat rhomboid grid structure (through-space Zn⋯Zn distances 33.7 × 13.9 Å) without any interpenetration.^{11,12} Another remarkable difference between our compound **1** and those constructed with L^2 is that, besides the two crystal water molecules around the sulfate ion in all cases, there are additional solvent molecules (water, ethanol, acetone,

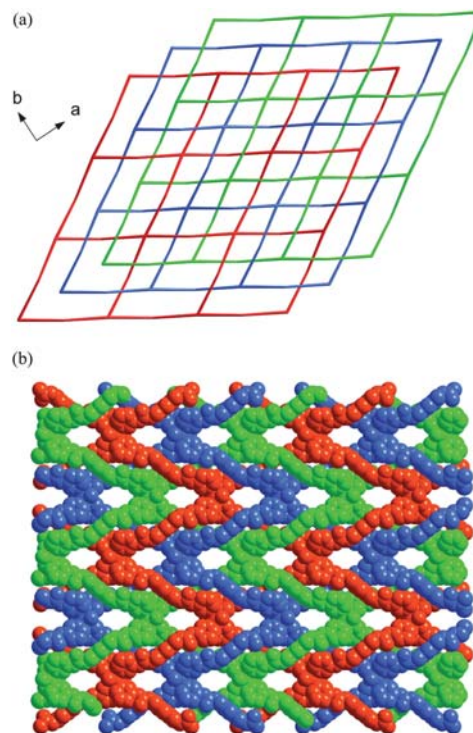


Fig. 2 (a) Schematic description of the 3-fold interpenetrated nets in **1**. (b) Space-filling representation of the 3-fold interpenetrated layers. Hydrogen atoms, solvent water molecules and sulfate anions entrapped in the ellipsoidal cavities have been omitted for clarity.

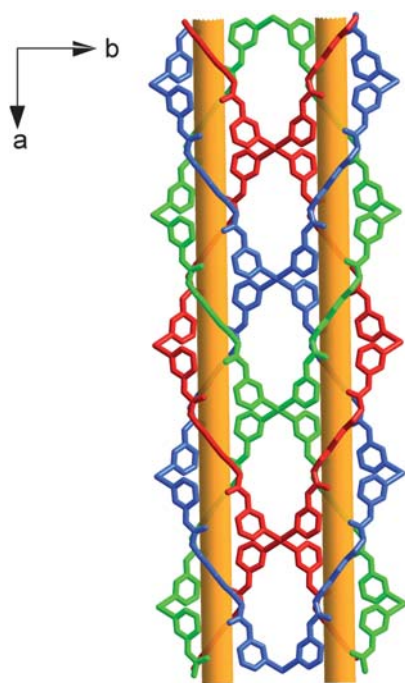


Fig. 3 Triple-stranded helices in the 2D layer of **1**.

1,4-dioxane, THF, *etc.*) in the cavities of the latter compounds, while in **1** this part of space is occupied by interpenetration so that there is no further solvent molecule in the structure.

The interpenetration of the layers led to a tight-knitted self-filling network with ellipsoidal cavities (Fig. 2b). A calculation by PLATON revealed a total void volume of 420.1 Å³ (10.0% of the unit cell volume) corresponding to *ca.* 100 Å³ for each cavity, which conveniently accommodates a sulfate anion and two solvent water molecules. The sulfate anion is surrounded by four urea groups with eight N–H···O hydrogen bonds. Since one of the oxygen atoms (O3) of sulfate resides on a two-fold axis, each of the other three oxygen atoms is disordered into two positions with half occupancy. Interestingly, the fully occupied O3 atom forms four bifurcated hydrogen bonds with two urea moieties in the six-membered motif $R_2^2(6)$ with N···O distances of 2.916 and 2.941 Å, while the other three oxygen atoms (O4, O5 and O6) form four hydrogen bonds with two eight-membered rings of graph set $R_2^2(8)$ with N···O distances ranging 2.869(4)–3.002(7) Å. In addition, the sulfate ion also accepts two hydrogen bonds (O···O distances: 2.926(7) and 2.764(7) Å) from two solvent water molecules, which are also entrapped in the cavity. Thus, each sulfate is surrounded by a total of ten hydrogen bonds (Fig. 4). This is similar to the non-interpenetrating MOFs with the shorter ligand L^2 .¹¹ The crystal water molecules further act either as hydrogen-bond acceptors in the formation of the O–H···O interactions with the coordinated water molecules, or as hydrogen donors to a carbonyl oxygen to link the interpenetrated layers to a 3D stacked structure (ESI, Fig. S10).†

The formation of the interpenetrated MOFs **1** and **2** proved that variation of the alkyl spacer of the L^n -type bis(pyridylurea) ligand may have profound effect on the final architecture of its metal coordination polymers and their anion binding properties, as mentioned in the Introduction. In previous reports, assembly of the sulfate salt MSO_4 ($M = Zn, Ni$) with L^2 generated

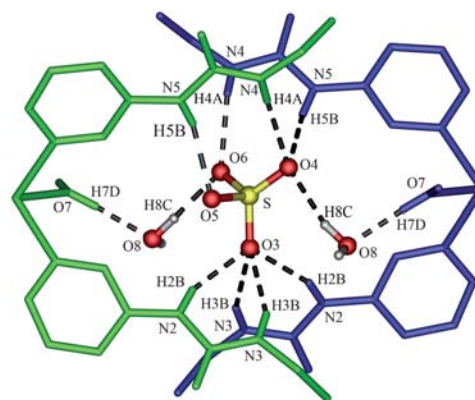


Fig. 4 Ellipsoidal cavities in the 3-fold interpenetrated structure of **1**. The ligands are colour coded to show that each belongs to a different independent network.

non-interpenetrating frameworks,^{11,12} while in the present work the use of the longer L^5 led to the formation of the 3-fold interpenetrating coordination polymers (**1** and **2**). In order to further investigate the effect of the length of the flexible linker on the coordination architectures, we synthesized a longer analogue, hexane-1,6-diylbis(3-pyridin-3-ylurea) (L^6), and obtained the MOF **3** via the reaction of this ligand with $ZnSO_4$.

Compound **3** (space group $Pbcn$) features a 3-fold interpenetrated (4,4)-net structure very similar to **1** and **2**. Notably, each of the central four carbons of the hexylene moiety in **3** is disordered over two positions and the ligand adopts a staggered conformation (Fig. 5a). The ligand L^6 bridges the metal atoms to form equilateral rhombic grids as in the MOFs **1** and **2** (Fig. 5b). Interestingly, although the alkyl spacer in L^6 is one carbon longer than L^5 , the dimension of the cavities of *ca.* 22.92 × 22.92 Å and the vertex angles of *ca.* 61.7° and 118.3° in **3** are only slightly elongated (by 0.64 Å) and flattened (by 2.1°) compared with **1**. The spacer lengths (measured by the distance of the two terminal carbon atoms of the $(CH_2)_n$ fragment) for the “bent” L^6 and “linear” L^5 are 5.270 and 4.882 Å, respectively, in **3** and **1**.

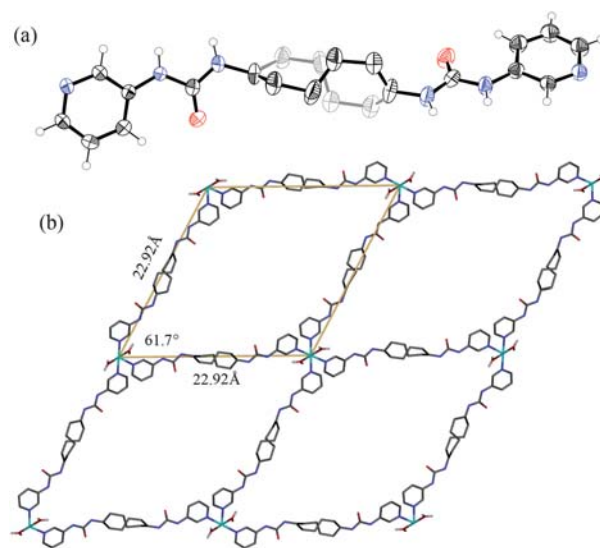


Fig. 5 (a) The disordered backbone of the ligand L^6 in **3**. (b) Rhombic grids in **3**.

Furthermore, same guest molecules, *i.e.* one disordered SO_4^{2-} ion and two water molecules are included in each cavity in **3**. These features suggest that the flexible backbone of L^6 is capable of adjusting its spatial torsion so that the urea groups are properly oriented to encapsulate the guests. Different from the case of **1** and **2**, a total of eleven hydrogen bonds chelate the disordered sulfate anion (ESI, Fig. S11)[†] in the ellipsoidal cavity of compound **3** (ESI, Table S3 lists the geometric parameters for the observed hydrogen bonds of **3**).[†] As in **1**, when the 3-fold parallel interpenetrating grids are regarded as a helical layer, the pitch of the racemic helices is slightly elongated by 1.6 Å (39.4 Å in **3**).

To evaluate the anion selectivity of the system, we have carried out the assembly process in the presence of competitive anions. The ligand L^5 was adopted to react with other Zn(II) salts (*e.g.*, ZnCl_2 , ZnBr_2 , $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{ClO}_4)_2$ or $\text{Zn}(\text{AcO})_2$) in a mixed water–MeOH solution at *r.t.*, as in the synthesis of **1**. However, no crystals were gained after several weeks. When the reaction of L^5 and ZnSO_4 was performed in the presence of NaCl, NaNO_3 , and NaClO_4 , colorless crystals were isolated after a week, which were identical to **1** as confirmed by powder X-ray diffraction (Fig. 6) and FT-IR spectroscopy (ESI, Fig. S12).[†]

Conclusions

In conclusion, three 3-fold parallel interpenetrated metal–organic frameworks have been synthesized by self-assembly of two flexible bis(pyridylurea) ligands with transition metal sulfates. The interpenetration results in ellipsoidal cavities suitable for encapsulation of sulfate ion selectively. These complexes represent a rational approach to incorporate anion binding motifs within an interpenetrated structure using a building block with long, flexible spacers. In addition, the formation of the sulfate capsules further demonstrates that the alkyl-linked bis(pyridylureas) L^n are excellent building blocks for anion-binding MOFs.

Experimental

General

^1H NMR spectra were recorded on a Mercury plus-400 spectrometer with calibration against the solvent signal ($\text{DMSO}-d_6$ 2.50 ppm for ^1H). IR spectra were carried out using a Nicolet AVATAR 360 FT-IR spectrometer as KBr disks. Elemental

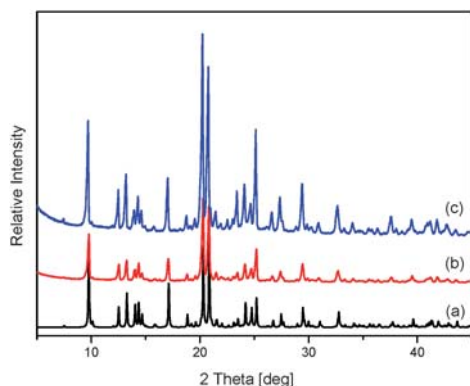
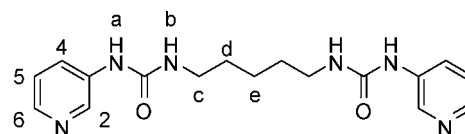


Fig. 6 PXRD patterns. (a) Simulated for **1**; (b) experimental result of **1**; (c) experimental result of the solid crystallized in the presence of the anionic mixture.

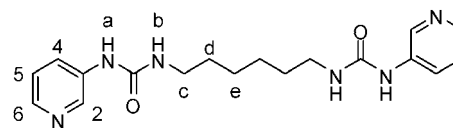
analyses were done on a VarioEL from Elementaranalysensysteme GmbH. ESI-MS measurements were carried out using a Waters ZQ4000 spectrometer with methanol being the solvent. Melting points were detected on an X-4 Digital Vision MP Instrument. X-Ray powder diffraction data were recorded with an X'Pert Pro instrument. TGA analyses were carried out under N_2 flow with a STA 449C DSC/DTA-TG instrument.

Synthesis of the ligands (L^5 and L^6) and compounds (**1**–**3**)

Ligand L^5 . To a solution of 3-isocyanatopyridine (1.50 g, 12.5 mmol) in toluene (25 mL) was added pentane-1,5-diamine (0.51 g, 5.0 mmol). A mass of precipitate appeared immediately. The reaction mixture was stirred at 60 °C for 1 h and cooled to room temperature before filtration. The crude solid was purified by recrystallization from CH_3OH – H_2O (1 : 2) as colourless crystals. Yield: 1.36 g (80%). M.p.: 174–176 °C. Anal. calcd for $\text{C}_{17}\text{H}_{22}\text{N}_6\text{O}_2$: C 59.63, H 6.48, N 24.54. Found: C 59.82, H 6.35, N 24.38. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz, ppm): δ = 1.32 (2 H, t, J = 7.6 Hz, H_c), 1.45 (4 H, m, H_d), 3.09 (4 H, dd, J = 12.8, 6.8 Hz, H_e), 6.28 (2 H, t, J = 4.8 Hz, H_b), 7.23 (2 H, dd, J = 8.4, 4.4 Hz, H_5), 7.87 (2 H, d, J = 8.0 Hz, H_6), 8.09 (2 H, d, J = 4.0 Hz, H_4), 8.51 (2 H, d, J = 2.0 Hz, H_2), 8.59 (2 H, s, H_a). ^{13}C NMR ($\text{DMSO}-d_6$): δ = 155.07 (C=O), 141.95, 139.46, 137.19, 124.33, 123.39, 38.86, 29.42, 23.73. IR (KBr, ν/cm^{-1}): 3326 (N–H), 2937, 2863, 1637 (C=O), 1559, 1479, 1282, 809, 703. ESI-MS: m/z 343.2 (100%), $[\text{M} + \text{H}]^+$.



Ligand L^6 . According to previous reports¹⁵ and in a similar manner for the synthesis of L^5 , the analogue L^6 was synthesized from 3-isocyanatopyridine (1.50 g, 12.5 mmol) and hexane-1,6-diamine (0.58 g, 5.0 mmol). Yield: 1.38 g (77%). M.p.: 205–207 °C. Anal. calcd for $\text{C}_{18}\text{H}_{24}\text{N}_6\text{O}_2$: C 60.66, H 6.79, N 23.58. Found: C 60.41, H 6.82, N 23.72. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz, ppm): δ = 1.33 (4 H, t, J = 7.6 Hz, H_e), 1.45 (4 H, m, H_d), 3.10 (4 H, dd, J = 12.8, 6.8 Hz, H_c), 6.27 (2 H, t, J = 4.8 Hz, H_b), 7.23 (2 H, dd, J = 8.4, 4.4 Hz, H_5), 7.87 (2 H, d, J = 8.0 Hz, H_6), 8.11 (2 H, d, J = 4.0 Hz, H_4), 8.51 (2 H, d, J = 2.0 Hz, H_2), 8.60 (2 H, s, H_a). ^{13}C NMR ($\text{DMSO}-d_6$): δ = 155.31 (C=O), 142.75, 138.96, 137.31, 124.63, 123.59, 38.68, 29.39, 24.23. IR (KBr, ν/cm^{-1}): 3319 (N–H), 2928, 2858, 1633 (C=O), 1559, 1476, 1279, 811, 703. ESI-MS: m/z 357.7 (100%), $[\text{M} + \text{H}]^+$.



$\{[\text{Zn}(\text{L}^5)_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}\}_n$ (1**).** A methanolic solution (10 mL) of L^5 (68.4 mg, 0.2 mmol) and an aqueous solution (5 mL) of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (28.8 mg, 0.1 mmol) were mixed and

Table 1 Crystallographic data and refinement details for compounds 1–3

Compound	1	2	3
Empirical formula	C ₃₄ H ₅₂ N ₁₂ O ₁₂ SZn	C ₃₄ H ₅₂ N ₁₂ O ₁₂ SCd	C ₃₆ H ₅₆ N ₁₂ O ₁₂ SZn
FW	918.31	965.34	946.36
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>
<i>a</i> /Å	12.610(3)	12.7357(12)	13.1181(14)
<i>b</i> /Å	23.552(6)	23.931(2)	23.502(2)
<i>c</i> /Å	14.121(4)	14.2117(13)	14.1772(15)
<i>V</i> /Å ³	4193.6(18)	4331.4(7)	4370.9(8)
<i>Z</i>	4	4	4
<i>D_c</i> /g cm ^{−3}	1.455	1.480	1.438
Crystal size/mm	0.34 × 0.28 × 0.20	0.34 × 0.30 × 0.28	0.32 × 0.27 × 0.25
<i>F</i> (000)	1928	2000	1992
μ /mm ^{−1}	0.710	0.624	0.683
θ range	1.73–31.24	1.70–27.50	1.73–25.39
Reflections collected	27 239	24 274	21 885
Independent reflections	6116	4974	4024
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4155	3228	2845
<i>R</i> _{int}	0.0364	0.0477	0.0542
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0395, 0.0998	0.0344, 0.0777	0.0559, 0.1672
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.0679, 0.1127	0.0657, 0.0915	0.0803, 0.1860
GOF (<i>F</i> ²)	1.028	1.016	1.079

allowed to evaporate slowly at room temperature. Colourless crystals were obtained after a week. Yield: 52 mg (54%). Anal. calcd for Zn(L⁵)₂SO₄·4H₂O (C₃₄H₅₂N₁₂O₁₂SZn, 918.32): C 44.47, H 5.71, N 18.30. Found: C 44.50, H 5.25, N 18.58. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): δ = 1.33 (2 H, d, *J* = 6.4 Hz, H_e), 1.43 (4 H, m, H_d), 3.08 (4 H, dd, *J* = 12.0, 6.4 Hz, H_c), 6.55 (2 H, s, H_b), 7.24 (2 H, dd, *J* = 8.0, 4.4 Hz, H₅), 7.93 (2 H, d, *J* = 7.2 Hz, H₆), 8.09 (2 H, d, *J* = 4.4 Hz, H₄), 8.55 (2 H, s, H₂), 8.85 (2 H, s, H_a). IR (KBr, ν /cm^{−1}): 3297 (N–H), 3059, 2931, 2858, 1676 (C=O), 1559, 1487, 1314, 1268, 1108 (S–O), 807, 708, 616.

{[Cd(L⁵)₂(H₂O)₂]SO₄·2H₂O}_{*n*} (2). In a similar manner, compound 2 was synthesized from L⁵ (68.4 mg, 0.2 mmol) and CdSO₄·8/3H₂O (26.4 mg, 0.1 mmol) as colourless needle crystals. Yield: 30 mg (30%). M.p.: 183–185 °C. Anal. calcd for Cd(L⁵)₂SO₄·3H₂O (C₃₄H₅₀N₁₂O₁₁SCd, 947.31): C 43.11, H 5.32, N 17.74. Found: C 43.00, H 5.00, N 17.65. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): δ = 1.40 (m, 6 H, H_e + H_d), 3.07 (m, 4 H, H_c), 6.91 (s, 2 H, H_b), 7.20 (dd, *J* = 8.0, 4.8 Hz, 2 H, H₅), 7.93 (d, *J* = 7.6 Hz, 2 H, H₆), 8.06 (d, *J* = 4.4 Hz, 2 H, H₄), 8.60 (s, 2 H, H₂), 9.20 (s, 2 H, H_a). FT-IR (KBr, ν /cm^{−1}): 3299 (N–H), 3070, 2930, 2863, 1680 (C=O), 1608, 1558, 1486, 1413, 1314, 1270, 1236, 1090 (S–O), 807, 705, 618.

{[Zn(L⁶)₂(H₂O)₂]SO₄·2H₂O}_{*n*} (3). In a similar manner, compound 3 was synthesized from L⁶ (71.3 mg, 0.2 mmol) and ZnSO₄·7H₂O (28.8 mg, 0.1 mmol). Colourless block crystals were obtained after three days. Yield: 31 mg (33%). M.p.: 167–169 °C. Anal. calcd for Zn(L⁶)₂SO₄·3H₂O (C₃₆H₅₄N₁₂O₁₁SZn, 928.36): C 46.58, H 5.86, N 18.11. Found: C 46.13, H 5.39, N 18.09. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): δ = 1.31 (s, 4 H, H_e), 1.44 (t, *J* = 5.6 Hz, 4 H, H_d), 3.09 (dd, *J* = 12.4, 6.4 Hz, 4 H, H_c), 6.37 (t, *J* = 5.6 Hz; 2 H, H_b), 7.25 (dd, *J* = 8.4, 4.8 Hz, 2 H, H₅), 7.90 (d, *J* = 8.4 Hz, 2 H, H₆), 8.10 (d, *J* = 4.4 Hz, 2 H, H₄), 8.53 (d, *J* = 2.4 Hz, 2 H, H₂), 8.68 ppm (s, 2 H, H_a). FT-IR (KBr, ν /cm^{−1}): 3332 (N–H), 3079, 2932, 2880, 1674 (C=O), 1649, 1560, 1485, 1265, 1097 (S–O), 811, 701, 650.

X-Ray crystal structure determination

Diffraction data were collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS¹⁶ was applied for the data. The structure was solved by direct methods using the SHELXS program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on *F*² by the use of the SHELXL program.¹⁷ The hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Oxygen atoms of the sulfate anion are disordered in two positions with 50% occupancy. Crystallographic data for compounds 1–3 are summarized in Table 1.

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