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Self-assembly of new Zn(II) supramolecular complexes from 4,4'-dipyridyldisulfide

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Three new supramolecular complexes, $[\text{Zn}(\text{dpds})(\text{C}_6\text{H}_5\text{COO})_2]_n$ (**1**), $[\text{Zn}(\text{dpds})(\text{C}_7\text{H}_7\text{COO})_2]_n$ (**2**), and $[\{\text{Zn}(\text{dpds})[\text{C}_6\text{H}_4(\text{COO})_2]\} \cdot \text{H}_2\text{O}]_n$ (**3**) (dpds = 4,4'-dipyridyldisulfide, $\text{C}_6\text{H}_5\text{COOH}$ = benzoic acid, $\text{C}_7\text{H}_7\text{COOH}$ = *m*-methylbenzoic acid, $\text{C}_6\text{H}_4(\text{COOH})_2$ = phthalic acid), have been synthesized by using the flexible ligand 4,4'-dipyridyldisulfide (dpds) with benzoic acid, *m*-methylbenzoic acid, and phthalic acid. The $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2]$ moieties in **1** are connected by dpds to generate a 1-D helical chain. In **2**, the $[\text{Zn}(\text{C}_7\text{H}_7\text{COO})_2]$ moieties are bridged by two dpds ligands of different chiralities to form a discrete achiral macrocycle chair-like structure. The ZnN_2O_2 tetrahedra in **3** are alternately linked by a pair of dpds and phthalato ligands to form a 1-D double-stranded chain, which are assembled *via* S...S weak interactions into a 2-D layer. The resulting 2-D layers are inclined parallel into 3-D supramolecular architecture.

Keywords: Zn(II); 4,4'-Dipyridyldisulfide; Supramolecular architecture; Crystal structure; Helice

1. Introduction

The supramolecular complexes based on self-assembly provide an efficient tool for the design and construction of supramolecules with unique structural motifs and tunable physical properties. Metal-containing cages, clusters, macrocycles, and helical polymers receive increasing attention, since they can combine the properties of metal centers with the recognition abilities of organic ligands to yield architectures with applications in gas storage, magnetic devices, separation, molecular recognition, etc. [1–8]. Predicting the final supramolecular framework constructed by a set of ligands and metal centers is still difficult as the structure can depend on factors such as the coordination of the metal ion, the structural characteristics of the ligands, the metal:ligand ratio, the possible influences of the counteranion and solvent, and various experimental conditions [9–12].

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Rigid linear and planar ligands, such as 4,4'-bipyridine and its derivatives, have been intensively employed, but systems from twisted ligands are less frequently employed [13–16]. 4,4'-Dipyridyldisulfide (dpds), with the two pyridyl rings bridged by the –S–S– groups, is flexible, adopting a twisted structure with a C–S–S–C torsion angle of *ca* 90°. Additionally, dpds has axial chirality, which generates *M*- and *P*-enantiomers. The sulfurs have additional coordination ability as well as the ability to accept hydrogen bonds or to establish other van der Waals interactions, which may lead to increase in the dimensionality of the resulting network [17–19]. So far, different structural types of complexes with dpds ligand have been reported, including 0-D, 1-D, 2-D, and 3-D networks [20]. The dpds and the shape of counteranions play a crucial role in determining the assembled structures [21–24]. To investigate the coordination characteristics of dpds and the influence of counteranions, we chose 4,4'-dipyridyldisulfide along with benzoic acid, *m*-methylbenzoic acid, and phthalic acid to construct new coordination polymers. In this article, three zinc coordination polymers, $[\text{Zn}(\text{dpds})(\text{C}_6\text{H}_5\text{COO})_2]_n$ (**1**), $[\text{Zn}(\text{dpds})(\text{C}_7\text{H}_7\text{COO})_2]_n$ (**2**), and $[\{\text{Zn}(\text{dpds})[\text{C}_6\text{H}_4(\text{COO})_2]\} \cdot \text{H}_2\text{O}]_n$ (**3**), are presented.

2. Experimental

2.1. Materials and physical methods

Chemicals of reagent grade were commercially available and used without purification. Powder X-ray diffraction (PXRD) measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check the phase purity. C, H, N, and S microanalyses were performed with a Perkin-Elmer 2400II CHNO/S elemental analyzer. FT-IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. Thermogravimetric measurements were carried out from R.T. to 700°C on preweighed samples in a nitrogen stream using a Seiko Exstar 6000 TG/DTA 6300 apparatus with a heating rate of 10°C min^{-1} . Single-crystal XRD data were collected on a Rigaku Raxis-Rapid X-ray diffractometer.

2.2. Synthesis of $[\text{Zn}(\text{dpds})(\text{C}_6\text{H}_5\text{COO})_2]_n$ (**1**)

For the synthesis of compound **1**, 0.0747 g (0.25 mmol) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.0547 g (0.25 mmol) 4,4'-dipyridyldisulfide (dpds), and 0.0305 g (0.25 mmol) benzoic acid were successively dissolved in a stirred aqueous methanolic solution consisting of 5.0 mL MeOH and 20.0 mL H_2O . Then 0.5 mL 1 mol L^{-1} NaOH was added dropwise, forming a white suspension, which was stirred at 80°C for 30 min and filtered off. The colorless filtrate (pH = 5.98) was allowed to stand at room temperature, and colorless platelet crystals formed within 1 week (yield: 71 mg). The phase purity of the product was checked according to PXRD patterns compared with the simulated PXRD based on the single-crystal data (figure S1). Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2\text{Zn}$ (%): C, 54.33; H, 3.25; N, 5.18; S, 12.63. Found (%): C, 54.56; H, 3.41; N, 5.30; S, 12.12. Infrared (IR) (KBr pellet, cm^{-1}): 3055m, 1630vs, 1591vs, 1480w, 1425m, 1360vs, 1223w, 1063w, 1022m, 818m, 719s, 682w, 481w.

2.3. Synthesis of $[\text{Zn}(\text{dpds})(\text{C}_7\text{H}_7\text{COO})_2]_n$ (**2**)

Compound **2** was prepared analogously to **1** with 0.0343 g (0.25 mmol) *m*-methylbenzoic acid instead of benzoic acid. Colorless prism crystals were grown in the filtrate for 1 week (yield: 23 mg). The experimental PXRD patterns (figure S1) match well with the simulated one derived from the single crystal data. Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2\text{Zn}$ (%): C, 56.01; H, 3.77; N, 4.98; S, 10.48. Found (%): C, 56.12; H, 3.96; N, 5.04; S, 11.51. IR (KBr pellet, cm^{-1}): 3045m, 2917w, 1595vs, 1556m, 1483w, 1421s, 1389s, 1222w, 1065m, 1015w, 800w, 754s, 716w, 674w, 498w.

2.4. Synthesis of $[\{\text{Zn}(\text{dpds})[\text{C}_6\text{H}_4(\text{COO})_2]\} \cdot \text{H}_2\text{O}]_n$ (**3**)

The synthetic procedure was similar to **1**, except that 0.0415 g (0.25 mmol) phthalic acid was used instead of benzoic acid. Slow evaporation of the colorless filtrate (pH = 5.03) at room temperature for 1 week gave colorless platelet crystals (yield: 42 mg). The product phase purity was checked according to the experimental PXRD (figure S1) compared with the simulated one based on the single crystal data. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_5\text{S}_2\text{Zn}$ (%): C, 46.24; H, 3.01; N, 5.57; S, 13.03. Found (%): C, 46.17; H, 2.99; N, 5.99; S, 13.68. IR (KBr pellet, cm^{-1}): 3556w, 3444w, 3062w, 1596vs, 1482w, 1370vs, 1229w, 1148w, 1066w, 1024w, 813w, 756w, 716m, 654w, 499w.

2.5. X-ray crystallography

Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on respective fine glass fibers, which are then mounted on a Rigaku R-Axis Rapid IP X-ray diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) for cell determination and subsequent data collection. The data are corrected for *Lp* and absorption effects. SHELXS-97 and SHELXL-97 are used for structure solution and refinement [25]. The respective structures are solved by using direct methods and all non-hydrogen atoms located in the subsequent difference Fourier syntheses. After several cycles of refinement, all hydrogens associated with carbons are geometrically generated, and the rest of the hydrogens are located from successive difference Fourier syntheses. Finally, all non-hydrogen atoms are refined with anisotropic displacement parameters by full-matrix least-squares and hydrogens with isotropic displacement parameters set to 1.2 times the values for the associated heavier atoms. The crystal data and structure determination are summarized in table 1. Selected interatomic distances and bond angles are tabulated in tables S1–S3.

3. Results and discussion

3.1. Syntheses

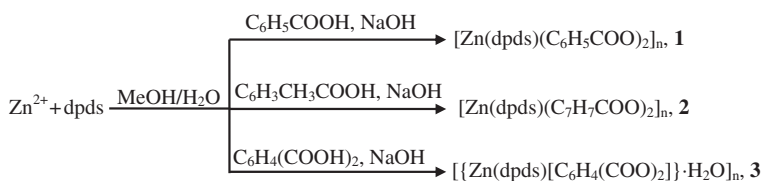
Under ambient conditions, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4,4'-dipyridyldisulfide, and NaOH reacted with benzoic acid, *m*-methylbenzoic acid, and phthalic acid, resulting in the formation of $[\text{Zn}(\text{dpds})(\text{C}_6\text{H}_5\text{COO})_2]_n$ (**1**), $[\text{Zn}(\text{dpds})(\text{C}_7\text{H}_7\text{COO})_2]_n$ (**2**), and $[\{\text{Zn}(\text{dpds})[\text{C}_6\text{H}_4(\text{COO})_2]\} \cdot \text{H}_2\text{O}]_n$ (**3**), respectively. The above reactions can be schematized

Table 1. Summary of crystal data, data collection, structure solution, and refinement details for 1–3.

Compound	1	2	3
Empirical formula	C ₂₄ H ₁₈ N ₂ O ₄ S ₂ Zn	C ₂₆ H ₂₂ N ₂ O ₄ S ₂ Zn	C ₁₈ H ₁₄ N ₂ O ₅ S ₂ Zn
Formula weight	527.89	555.95	467.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
Description	Colorless platelet	Colorless prism	Colorless platelet
Crystal size (mm)	0.48 × 0.37 × 0.12	0.32 × 0.21 × 0.19	0.44 × 0.33 × 0.14
Temperature (K)	295(2)	295(2)	295(2)
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)
Unit cell dimensions (Å, °)			
<i>a</i>	11.152(2)	13.509(3)	19.517(4)
<i>b</i>	11.432(2)	12.719(3)	14.405(3)
<i>c</i>	18.163(4)	14.886(3)	14.983(3)
β	95.31(3)	101.52(3)	107.48(3)
Volume (Å ³), <i>Z</i>	2305.7(8), 4	2506.1(9), 4	4018.1(1).4
Calculated density (g cm ⁻³)	1.521	1.473	1.547
<i>F</i> (000)	1080	1144	1904
μ (mm ⁻¹)	1.280	1.182	1.462
θ range for data collection (°)	3.03–27.42	3.08–27.46	3.03–27.43
Reflections collected	22,160	22,921	19,386
Unique reflections (<i>R</i> _{int})	5251 (0.0512)	5593 (0.0457)	4568 (0.0440)
Data, restraints, parameters	3667, 0, 298	3945, 0, 316	3138, 0, 254
Goodness-of-fit on <i>F</i> ²	1.093	1.161	1.124
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0356, <i>wR</i> ₂ = 0.0732	<i>R</i> ₁ = 0.0396, <i>wR</i> ₂ = 0.0829	<i>R</i> ₁ = 0.0388, <i>wR</i> ₂ = 0.0750
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0645, <i>wR</i> ₂ = 0.0967	<i>R</i> ₁ = 0.0754, 0.1222	<i>R</i> ₁ = 0.0719, <i>wR</i> ₂ = 0.1144
Extinction coefficients	0	0	0.00026(10)
<i>A</i> , <i>B</i> values in <i>w</i> ^b	0.0333, 1.1051	0.0375, 2.4232	0.0205, 16.9768
$\delta\rho_{\max}$, $\delta\rho_{\min}$ (e Å ⁻³)	0.550, -0.549	0.469, -0.749	0.621, -0.847

^a*R*₁ = $\sum(|F_o| - |F_c|) / \sum|F_o|$, *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; ^b*w* = $[\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where *P* = $(F_o^2 + 2F_c^2)/3$.

as follows:



All the complexes are stable in air and insoluble in water, methanol, ethanol, and acetone at room temperature.

3.2. Description of the crystal structures

3.2.1. [Zn(dpds)(C₆H₅COO)₂]_n (1). The asymmetric unit of 1 consists of one Zn²⁺, one dpds, and two benzoates. The dpds is bis-monodentate bridging with the C–S–S–C torsion angle of 93.9(1)° and dihedral angle of 87.71(1)° between two pyridyl rings. Both crystallographically distinct benzoates are monodentate. Due to the effect of coordination, the two carboxylate groups are no longer coplanar with the benzene ring, and the corresponding dihedral angles are 15.41(2)° and 11.12(2)°, respectively. Zn is

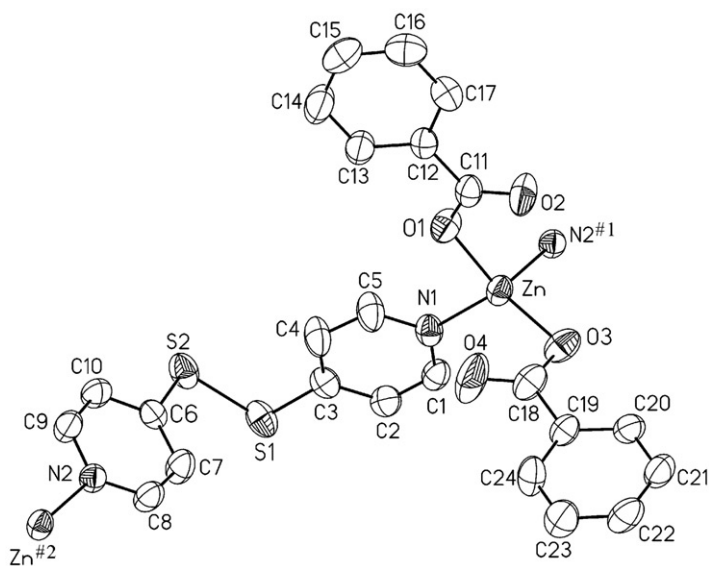


Figure 1. ORTEP view of coordination environments around Zn with atom labeling for **1** (displacement ellipsoids are drawn at 50% probability level; hydrogens are omitted for clarity).

coordinated by two nitrogens from different dpds ligands and two carboxylate oxygens from two crystallographically different benzoates to furnish distorted ZnN_2O_2 tetrahedra (figure 1). The bond distances range from 1.944(2) to 2.097(2) Å and the bond angles from 95.40(1)° to 131.56(1)°, deviating from an ideal tetrahedron (table S1). The $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2]$ moieties are bridged by the M-form dpds ligands to generate 1-D left-hand helical chains extended infinitely along the [100] direction with Zn...Zn separation of 11.152 Å (figure 2a). The carbons in the pyridyl ring of dpds donate hydrogens to the un-coordinating carboxylate oxygen of benzoate. Owing to such weak hydrogen-bonding interactions, adjacent 1-D helical chains are interconnected into 2-D left-hand helical layers parallel to (001) (figure 2b), and the 2-D layers are stacked in an ...ABABAB... sequence with each layer due to van der Waals forces (figure 2c). Layer A is a left-hand helix and layer B is a right-hand helix; the crystal is achiral. Complex **1** is similar to the reported complex $[\{\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4\}_2(\text{dpds})_2]_n$ [26].

3.2.2. $[\text{Zn}(\text{dpds})(\text{C}_7\text{H}_7\text{COO})_2]_n$ (2**).** The asymmetric unit of **2** contains one Zn^{2+} , one dpds, and two *m*-methylbenzoates. Similar to **1**, dpds function as a bis-monodentate ligand with C–S–S–C torsion angle of 79.59(2)° and dihedral angles of 83.43(1)° between two pyridyl rings. Two crystallographically distinct *m*-methylbenzoates coordinate to zinc, and the dihedral angles between the carboxylate and the benzene ring are 7.71(3)° and 23.61(2)°, respectively. The Zn's at crystallographically general positions are each six coordinate by two nitrogens from two dpds ligands and four carboxylate oxygens of two *m*-methylbenzoates (figure 3). The Zn–N/O bond distances vary from 2.060(2) to 2.290(3) Å, and the *trans*- and *cis*-oid bond angles fall in the ranges 59.59(1)°–101.81(1)° and 152.82(1)°–159.19(1)° (table S2), respectively, indicating significant deviation from regular octahedral geometry. The $[\text{Zn}(\text{C}_7\text{H}_7\text{COO})_2]$ moieties

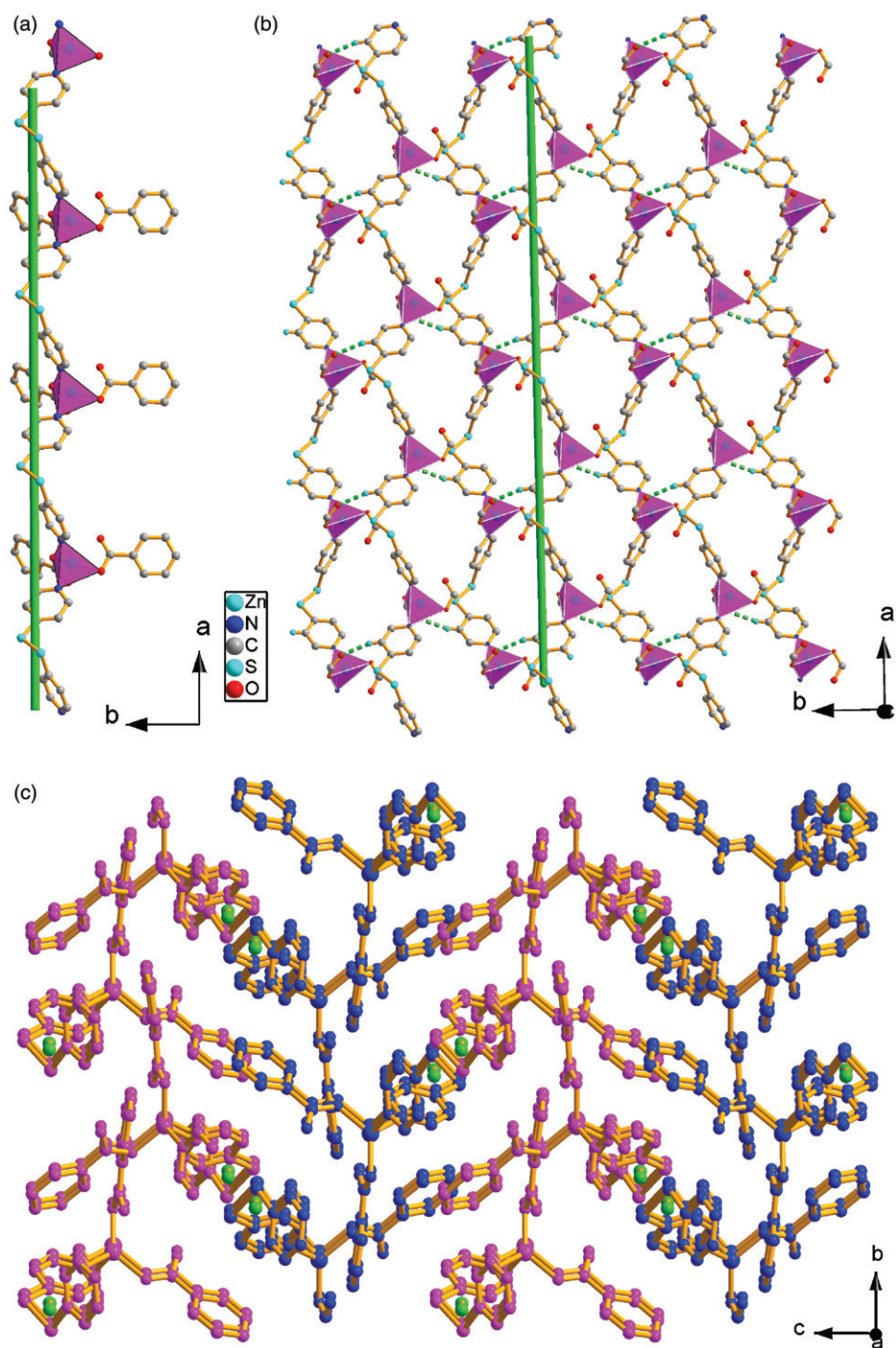


Figure 2. (a) Helical chain structure of **1** viewed along the *a*-axis. (b) 2-D left-handed helical layers of **1** (green dotted lines represent the C–H...O hydrogen bonds). (c) Crystal structure of **1** (red is left-hand helix and blue is right-hand helix).

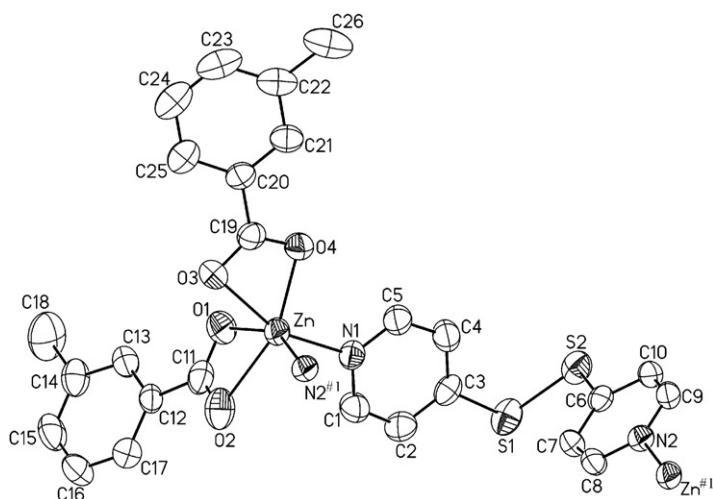


Figure 3. ORTEP view of coordination environment of Zn ions, *m*-methylbenzoic acid, and dpds with displacement ellipsoids (45% probability) and atomic labeling in **2** (hydrogens are omitted for clarity).

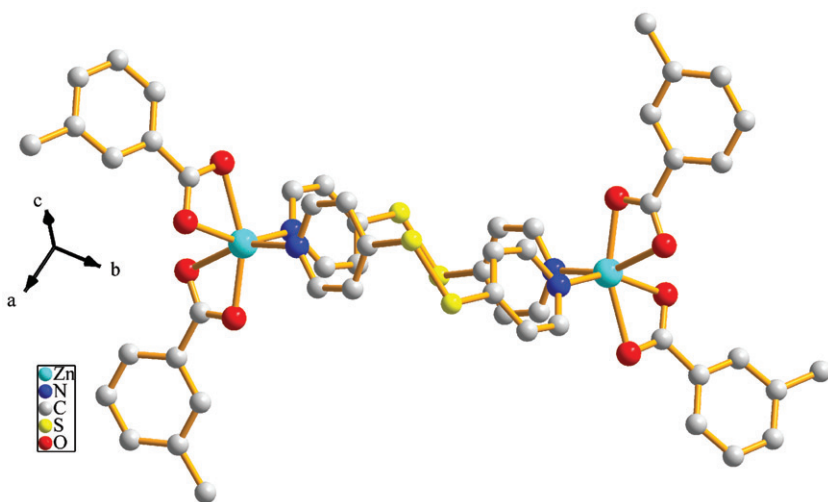


Figure 4. Macrocycle structure in **2**.

are bridged by two dpds ligands of different chirality to form an achiral macrocycle chair-like structure with Zn...Zn separation of 12.506 Å through dpds (figure 4). Along the [010] direction, these macrocycles are interlinked by weak hydrogen bonds between carbons in pyridyl rings and carboxylate oxygens to generate 1-D chains. The adjacent chains are related by a rotation of 180° in the *c*-axis and shifted by $\frac{1}{2}b$ along the [010] direction with respect to the neighbor. The resulting chains are further driven by interchain $\pi \cdots \pi$ stacking interaction (mean interplanar distance between adjacent pyridyl ring and benzene ring: 3.662(2) Å) to construct a 2-D layer parallel to (100) (figure 5). Due to van der Waals forces, the resulting layers are stacked in a

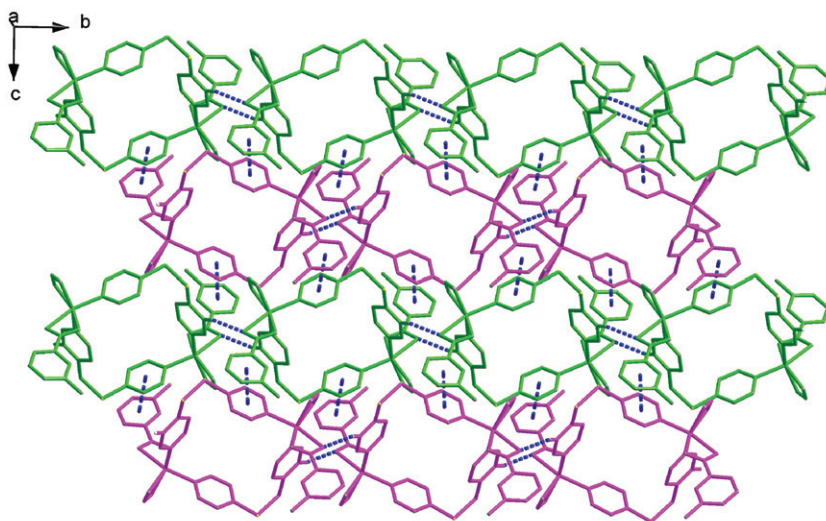


Figure 5. 2-D layer in **2** (blue dotted lines represent weak interactions).

$\cdots\text{AAA}\cdots$ sequence along the [001] direction. Complex **2** is similar to $[\text{Pt}(\text{PEt}_3)_2(4\text{DPDS})]_2(\text{NO}_3)_4$, in which platinum is bridged by two dpds ligands of different chirality to form an achiral macrocycle structure [27].

3.2.3. $\{[\text{Zn}(\text{dpds})[\text{C}_6\text{H}_4(\text{COO})_2]\} \cdot \text{H}_2\text{O}\}_n$ (3**).** The asymmetric unit of **3** consists of one Zn^{2+} , one dpds, one phthalate, and one uncoordinated water. Similar to **1** and **2**, dpds is a bis-monodentate bridging ligand with C–S–S–C torsion angle of $80.1(2)^\circ$ and dihedral angles of $80.6(1)^\circ$ between two pyridyl rings. The phthalate is bis-monodentate bridging, and the dihedral angles between carboxylate and the benzene ring are $70.6(3)^\circ$ and $19.6(3)^\circ$. Zn is a distorted tetrahedral ZnN_2O_2 environment defined by two nitrogens from different dpds ligands and two carboxylate oxygens from different phthalato ligands with Zn–N(O) distances of $1.935(3)$ – $2.064(3)\text{Å}$ and the corresponding angles of $97.98(1)^\circ$ – $116.90(1)^\circ$ (figure 6, table S3). Zincs are alternately bridged by a pair of different chirality dpds and phthalato ligands to generate 1-D achiral repeated rhomboids propagating in the [001] direction (figure 7); the Zn \cdots Zn separations through dpds and phthalate are 9.755 and 5.237 Å, respectively. Along the [110] directions, adjacent repeated rhomboids are interlinked via S \cdots S weak interactions (S \cdots S distance: 3.584 Å) into 2-D layers (figure 8a). Topologically, the dpds molecules are linked via interlayer S \cdots S weak interactions to form di-dpds units, defined as four-connected nodes to four zincs with a vertex symbol of $(4.4.6.6.8_2.8_2)$, and each Zn links two di-dpds units and one Zn as three-connected with $(4.6.6)$ vertex symbol. Hence, the 2-D layer is described as a 2-D (3, 4)-connected sheet with the Schläfli symbol of $(4.6^2)_2(4^2.6^2.8^2)$. The 2-D sheets are inclined parallel into a 3-D network with an inclined angle of $75.7(1)^\circ$, as shown in figure 8b. Such a binodal topological structure is rarely observed in the abundantly growing area of coordination polymers. The uncoordinated waters, which reside in the cavities of repeated rhomboids, form hydrogen bonds to one

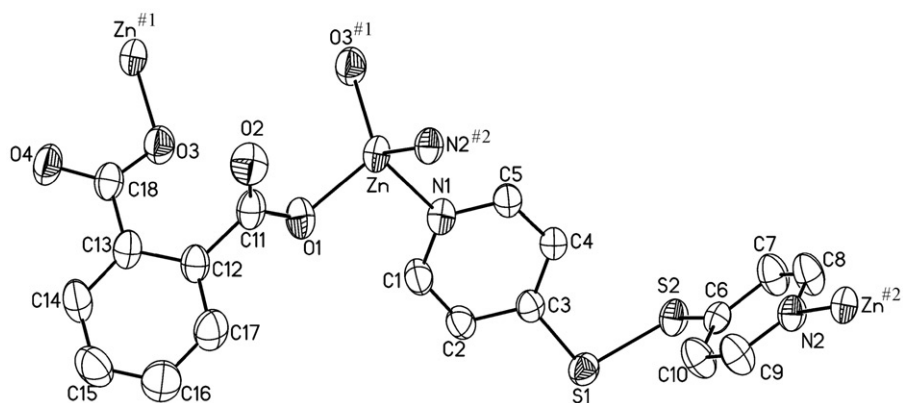


Figure 6. ORTEP view of coordination environment around Zn with atom labeling for **3** with ellipsoids at 45% probability (hydrogens are omitted for clarity).

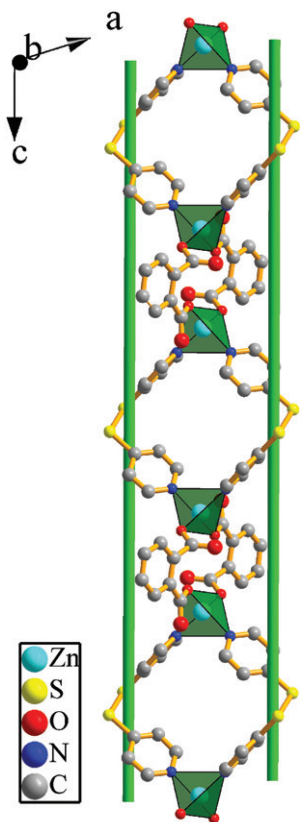


Figure 7. 1-D achiral repeated rhomboids in **3**.

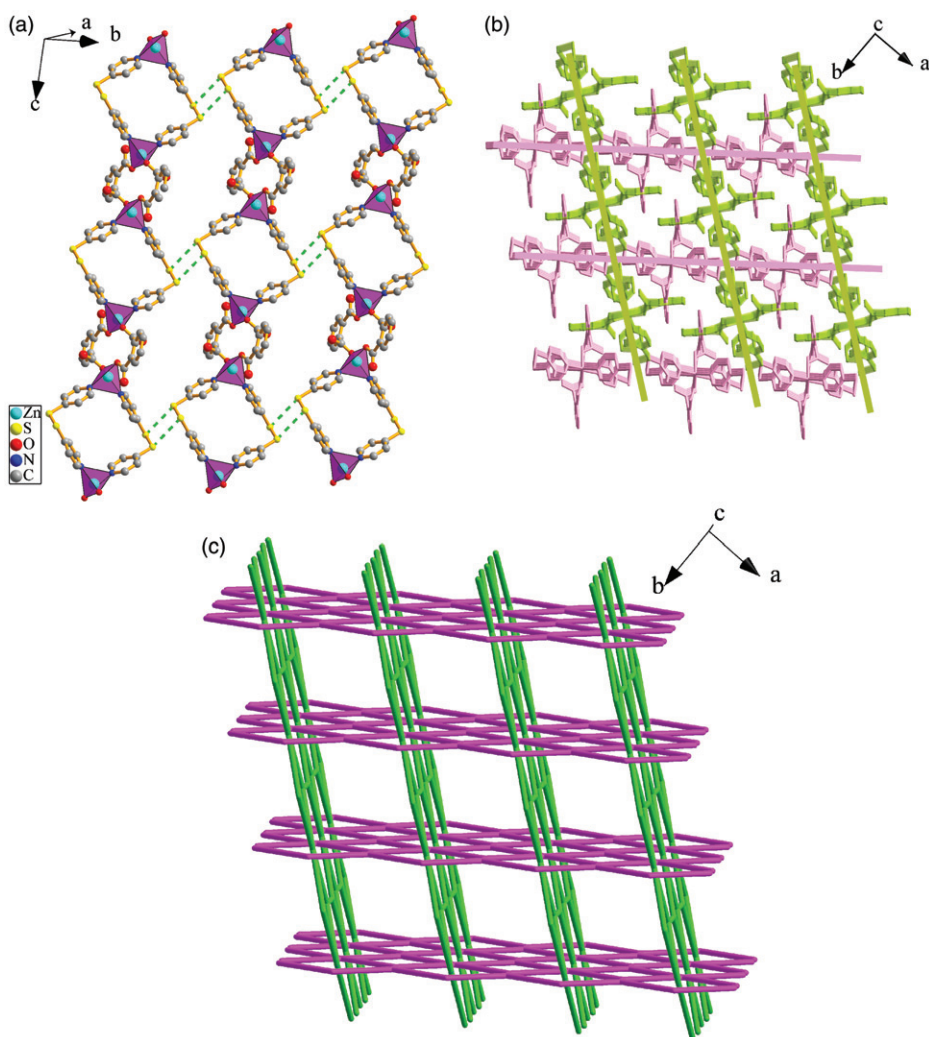


Figure 8. (a) 2-D layer in **3** (green dotted lines represent $S \cdots S$ interactions). (b) Two interpenetrated 2-D networks in the structure of **3**. (c) The interpenetrating topological representation of **3**.

coordinated and one un-coordinated carboxylate of two different phthalates from the same rhomboid.

3.3. Comparison of Zn dpds complexes

According to the literature, the most extensively studied coordination polymers for Zn are 0-D and 1-D. A survey of CCDC [CSD V5.32] reveals only 16 zinc 4,4'-dipyridyldisulfide complexes in the absence of any counteranions [28–35]. The dpds, due to the flexible $-S-S-$ group interconnect metal cations to afford a series of motifs ranging from 0-D discrete molecules through 1-D zigzag/helices/repeated rhomboids.

A typical 0-D is exemplified in $\text{Zn}(\text{Ac})_2(\text{dpds})_2$ [29], where the Zn cations are connected by monodentate dpds. Different from the monodentate dpds in $\text{Zn}(\text{Ac})_2(\text{dpds})_2$, dpds is bis-monodentate forming macrocycles, zigzag, helical, and repeated rhomboids. The macrocyclic units are chiral in most cases, but form racemic crystals no chiral crystals have been discovered. $[\text{Zn}(\text{dpds})(\text{C}_7\text{H}_7\text{COO})_2]$ (**2**) is the first Zn dpds discrete macrocyclic compound. The zigzag chain is achiral in most cases, only one complex, $[\text{Zn}(\text{dpds})(\text{NCS})_2]$, with a chiral zigzag chain structure is known [30]. The helical chain is chiral, containing ligands with the same chirality. However, no chiral crystals have been isolated; all known crystals crystallize in an achiral space group, for example $[\text{Zn}(\text{dpds})(\text{C}_6\text{H}_5\text{COO})_2]$ (**1**). Repeated rhomboid structures can be regarded as similar to that of the macrocycles propagating in one direction, which can be seen in $[\text{Zn}(\text{dpds})(\text{NO}_3)_2]$ [31].

3.4. IR spectra

As demonstrated in figure S2, strong sharp absorptions at 1630 and 1591 cm^{-1} for **1**, 1595 and 1556 cm^{-1} for **2**, and 1596 cm^{-1} for **3** result from antisymmetric stretching (ν_{as}) of carboxylate; symmetric stretching (ν_{s}) of the carboxylates cause strong sharp absorptions at 1425 and 1360 cm^{-1} for **1**, 1421 and 1389 cm^{-1} for **2**, and 1370 cm^{-1} for **3**, respectively. The separations fall in the region 231 – 205 cm^{-1} for **1**, 174 – 167 cm^{-1} for **2**, and 226 cm^{-1} for **3**, corresponding to monodentate coordination carboxylate for **1**, **3**, and chelate coordination carboxylate for **2** [36], agreeing with the X-ray structural analysis. The dpds, due to its pyridyl C–H stretching vibrations, causes weak absorptions at 3055 cm^{-1} for **1**, 3045 cm^{-1} for **2**, and 3062 cm^{-1} for **3**, and the out-of-plane bending vibrations of the pyridyl C–H bonds yield sharp peaks of medium intensities at 719 cm^{-1} for **1**, 754 cm^{-1} for **2**, and 716 cm^{-1} for **3**.

3.5. Thermal analysis

The TG/DTA curves are depicted in figure S3. The DTA curve of **1** shows two endothermic peaks at 233°C and 424°C . The TG curve indicates that **1** is thermally stable up to 200°C and experiences a rapid weight loss of 75.3% from 200°C to 500°C , corresponding to decomposition of dpds and benzoic acid. The residual weight of 24.7% corresponds to 23.68% calculated for one mole “ ZnCO_3 .” In general, “ ZnCO_3 ” with heat decomposes to zinc oxide and carbon dioxide. From this evidence, it follows that the residue is not “ ZnCO_3 .” We could not distinguish components of the residue. The DTA curve of **2** displays one strong endothermic peak at 182°C . The TG curve suggests that **2** is thermally stable to 140°C and undergoes rapid weight loss of 84.87% from 140°C to 600°C , corresponding to decomposition of *m*-methylbenzoic acid and the loss of dpds. The final residual weight of 14.73% is consistent with that (14.63%) calculated for one mole “ ZnO .” The DTA curve of **3** shows two endothermic peaks at 65°C and 232°C . The TG curve shows dehydration of **3** from 30°C to 90°C with weight loss of 3.9% corresponding to the removal of one water molecule per formula unit (calculated 3.85%). Upon heating, the observed weight loss of 77.51% over 180°C – 610°C corresponds to decomposition of phthalic acid and release of dpds. The remaining weight of 17.61% corresponds to 17.40% calculated for one mole “ ZnO .”

4. Conclusion

Three new zinc coordination polymers, $[\text{Zn}(\text{dpds})(\text{C}_6\text{H}_5\text{COO})_2]_n$ (**1**), $[\text{Zn}(\text{dpds})(\text{C}_7\text{H}_7\text{COO})_2]_n$ (**2**), and $[\{\text{Zn}(\text{dpds})[\text{C}_6\text{H}_4(\text{COO})_2]\} \cdot \text{H}_2\text{O}]_n$ (**3**), have been obtained. Compounds **1** and **3** feature 1-D chains based on bridging dpds, while the 3-D supramolecular architecture **3** from 2-D networks is through inclined interpenetration. In **2**, the dpds unit bridges the metal ions into an achiral macrocycle chair-like structure. Structural analysis indicates that the anion with different coordination ability is a key factor to construct the supramolecular architecture.

Supplementary material

Crystallographic data for **1–3** deposited with the Cambridge Crystallographic Data Center, CCDC-803532 (**1**), CCDC-803533 (**2**), and CCDC-803534 (**3**) [CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom; Fax: (44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; Website: <http://www.ccdc.cam.ac.uk>].

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