Hydrogen-Bonded Polyrotaxane-like Structure Containing Cyclic $(H_2O)_4$ in $[Zn(OAc)_2(\mu\text{-bpe})]\cdot 2H_2O$: X-ray and Neutron Diffraction Studies**

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Abstract: The reaction of 4,4′-bipyridylethane (bpe) and 4,4′-dipyridyl disulfide (dpds) with $Zn(OAc)_2\cdot 2H_2O$ has led to the formation of two coordination polymers, $[Zn(OAc)_2(\mu\text{-bpe})]\cdot 2H_2O$ (**1**) and $[Zn(OAc)_2(\mu\text{-dpds})]$ (**2**). Both the compounds have zigzag coordination polymeric structures as revealed by X-ray crystallography. However, the presence of two lattice water molecules in **1** results in an interesting difference between the crystal structures. In **1**, the carboxylate carbonyl oxygen atoms of the $Zn(OAc)_2$ groups from two different adjacent zigzag polymers and four lattice water molecules form 24-membered hydrogen-bonded rings (graph set notation, $\mathbf{R^6_6(24)}$). One of the two bpe ligands associated with each Zn^{II} center passes through the center of this ring to form a two-dimensional hydrogen-bonded coordination polymeric structure. In the solid state, the adjacent 24-membered hydrogen-bonded rings further fuse together through O–H···O hydrogen bonds among four waters to form cyclic $(H_2O)_4$. This results in a one-dimensional hydrogen-bonded ribbon-like polymer comprising fused alternating 24- and eight-membered O–H···O hydrogen-bonded rings. One of the bpe ligands passes through the center of the larger ring to produce an unexpected single self-penetrating three-dimensional hydrogen-bonded network with polyrotaxane-like association. A neutron diffraction study provides a detailed description of the hydrogen bonds involved.

Keywords: crystal engineering · hydrogen bonds · neutron diffraction · noncovalent interactions · rotaxanes · X-ray diffraction · zinc

Introduction

Research in crystal engineering and the construction of coordination polymers with specific topologies has progressed in recent years by virtue of the possible design of materials with specific electronic, optic, magnetic, and catalytic properties.[1] In spite of a few cases wherein the molecules are assembled in a predetermined fashion, prediction of the crystal structure is largely considered to be serendipitous.[2] This could be attributed to the poor understanding of the role played by various factors employed for the growth of the particular crystal, and other subtle attractive or repulsive forces that prevail in the crystal lattice.[3] Coordination polymers of various structural motifs such as one- (1D; e.g. linear chain, zigzag chain, helix, open ladder structures), two- (2D; e.g. square grid, brick wall, honeycomb,) and three-dimensional (3D; e.g. adamantanoid) are known to exist.[4] Of these, 1D coordination polymers are thought to be structurally the least interesting, but nevertheless have been found to have properties such as molecular ferromagnetism, synthetic metallic conductivity, and nonlinear optical response.[5] Moreover, noncovalent interactions between such 1D infinite chains can lead to the formation of interesting architectures.[6–8] For example, subtle differences in the noncovalent interactions such as hydrogen bonds or Ag···Ag interactions in the compounds $[Ag(3\text{-amp})ClO_4]$ and $[Ag(4\text{-amp})ClO_4]$ (amp = aminomethylpyridine) lead to the formation of a triple-helical coordination polymer or helical ladder, respectively.[5] On the other hand, rotaxanes and catenanes are, in all likelihood, considered as molecular machines.[9,10] Many examples of coordination polyrotaxane networks have been reported;[11–14] however, to the best of our knowledge, hydrogen-bonded structures with polyrotaxane-like interactions are rare.[15] The molecular Chinese blinds described by Sharma and Rogers can also be classi-

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[**] bpe = 4,4′-bipyridylethane.

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fied under this category,[16] and a new type of hydrogen-bonded polyrotaxane architecture was reported by Puddephatt and co-workers.[17]

The structures of hydrogen-bonded water clusters and channels continue to attract interest since they play a crucial role in contributing to the stability and function of biological assemblies. Several theoretical calculations and experimental evidence confirm the presence of water oligomers such as trimer, tetramer, pentamer, hexamer, octamer, and decamer.[18] Furthermore, many of these water oligomers and polymers have been stabilized by organic and inorganic hosts.[19]

Herein we report the synthesis and structural characterization of two 1D coordination polymers and their subsequent formation of interesting but contrasting supramolecular architectures of general formula $[Zn(OAc)_2(\mu\text{-bpe})]\cdot 2H_2O$ (**1**) and $[Zn(OAc)_2(\mu\text{-dpds})]$ (**2**) (bpe = 4,4′-dipyridylethane; dpds = 4,4′-dipyridyl disulfide). Of these, one of the bpe ligands in the zigzag coordination polymer is encased by 24-membered hydrogen-bonded rings to furnish an unexpected polyrotaxane-like structure. These 24-membered rings are further fused with eight-membered tetrameric water clusters, $(H_2O)_4$, alternatively to form a 1D hydrogen-bonded ribbon-like polymeric structure of alternating 24- and eight-membered rings. These two structures also illustrate the fact that the structurally similar spacer ligands can lead to interesting differences in the crystal structures of the compounds depending on the presence of solvent molecules and other noncovalent interactions.

Interpenetrating network structures with polyrotaxane-like connectivities are not very common among hydrogen-bonded coordination polymers[20] and are only found abundantly in coordination polymeric network structures.[21] We have therefore decided to investigate the solid-state structure of **1** in more detail by using neutron diffraction.

Results and Discussion

Compounds **1** and **2** were produced by reacting bpe and dpds with zinc acetate in the ratio of 1:1 in suitable solvents, and diffraction-quality single crystals were obtained by slow evaporation. The stoichiometry of these compounds was confirmed by ^{1}H NMR spectroscopy and elemental analysis. Furthermore, thermogravimetry was used to confirm the number of water molecules in **1**, and IR spectra were employed to characterize the bonding mode of the acetate anion. The same 1:1 reaction mixture of $Zn(OAc)_2\cdot 2H_2O$ and bpe in a MeOH/acetonitrile solvent mixture gave a mixture of $[Zn_2(OAc)_4(bpe)]$ and $[Zn_7(\mu_4\text{-}O)_2(OAc)_{10}(bpe)]$.[22]

Structure of $[Zn(OAc)_2(\mu\text{-bpe})]\cdot 2H_2O$ (1): The structure solved by X-ray crystallography is discussed here. A portion of the polymeric segment showing the coordination environment around the Zn^{II} center is shown in Figure 1. Each Zn^{II} atom adopts a four-coordinate tetrahedral geometry, being coordinated to the nitrogen atoms of two crystallographically different pyridyl groups and the oxygen atoms of the two acetate ligands. Two lattice water molecules are found in the asymmetric unit of **1**, which are hydrogen-bonded to the other oxygen atoms of the two acetate anions as shown in Figure 1.

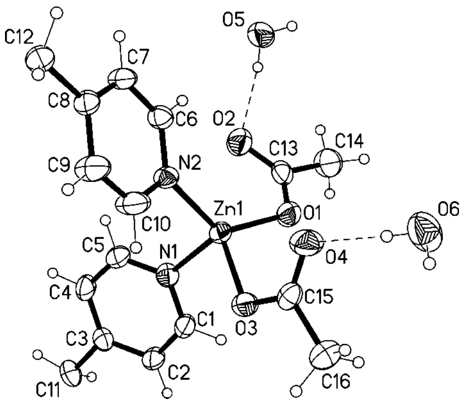


Figure 1. Structure of the asymmetric unit of **1** (an ORTEP diagram; showing 50 % probability ellipsoids for the non-hydrogen atoms).

In **1** the Zn^{II} atom is bonded to two bridging bpe spacer ligands (Figure 2). Selected geometric parameters for **1** are given in Table 1. The two Zn–O bond lengths are unequal at 1.922(3) and 1.949(3) Å. Similarly, the Zn–N distances are also not equal (2.044(3) and 2.010(3) Å), and are slightly shorter than those reported for $[(TPP)Zn]_2(\mu\text{-bpe})(C_6H_5NO_3)]$ (2.179(6) Å)[23] and $[Zn(\mu\text{-bpe})(bpe)_2(H_2O)_2](ClO_4)_2\cdot bpe\cdot H_2O$ (2.151(3)–2.185(4) Å).[24] The tetrahedral Zn^{II} center is highly distorted as inferred from the bond angles, which range between 96.35(1) and 129.72(1)°. A crystallographic inversion center is present in the middle of each bpe spacer ligand. The interplanar angle between the pyridyl rings in bpe is 0° and the two pyridyl rings in bpe have an *anti* conformation with a C-CH$_2$-CH$_2$-C torsion angle of 180°. All the polymeric chains are aligned parallel to each other in the *ab* plane and propagate along the *b* direction.

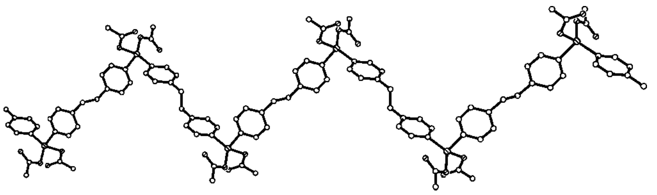


Figure 2. A segment of the zigzag coordination polymer in **1**. Only relevant atoms are shown.

Table 1. Selected bond lengths [Å] and angles [°] from X-ray data for **1**.

Zn(1)–O(1)	1.922(3)	Zn(1)–N(2)	2.010(3)
Zn(1)–O(3)	1.949(3)	Zn(1)–N(1)	2.044(3)
C(11)–C(11)[a]	1.512(8)	C(12)–C(12)[b]	1.524(8)
O(1)-Zn(1)-O(3)	103.52(1)	O(1)-Zn(1)-N(1)	105.42(1)
O(1)-Zn(1)-N(2)	129.72(1)	O(3)-Zn(1)-N(1)	96.35(1)
O(3)-Zn(1)-N(2)	110.30(1)	N(2)-Zn(1)-N(1)	106.59(1)
C(3)-C(11)-C(11)[a]	112.4(4)	C(8)-C(12)-C(12)[b]	111.8(4)

[a] Symmetry operator: $-x+1$, $-y+2$, $-z+1$. [b] Symmetry operator: $-x$, $-y$, $-z$.

The oxygen atoms of the carboxylate carbonyl groups present in $Zn(OAc)_2$ from two different adjacent polymeric chains are O–H···O hydrogen-bonded to four lattice water molecules to form a 24-membered ring (with graphic set notation, $\mathbf{R^{6}_{6}(24)}$[25]; Figure 3). This ring has the shape of a distorted square in which the O(5)···O(5a) distance is 9.84 Å and the O(6)···O(6a) distance is 7.73 Å. Adjacent polymeric chains below the hydrogen-bonded rings are slip-stacked along the *c* direction such that one of the two bpe ligands goes through the center of the larger hydrogen-bonded ring (Figure 4). The side view of this penetration of the coordination polymeric chain into the hydrogen-bonded ring is shown in Figure 5. It is clear that only the bpe ligand containing the N(2) atom goes through the center of the hydrogen-bonded ring. The center of the two methylene groups of bpe coincides with the crystallographic inversion center present at the center of the hydrogen-bonded ring. However, the bond parameter found in this bpe ligand is very similar to that with the atom N(1). The hydrogen-bonded polyrotaxane-like structure in **1** (Scheme 1) forms a sheetlike structure approximately in the *ab* plane. These hydrogen-bonded rings are further fused with two eight-membered rings formed by four water molecules through O–H···O hydrogen bonds to generate a 1D hydrogen-bonded polymer that propagates approximately along the *c* direction (Figure 6). According to Infantes and co-workers, this hydrogen-bonded tape can be described as T4(2)18(2).[26] In the poly-fused hydrogen-bonded polymer, the acceptors are the carboxylate carbonyl oxygen atoms of the $Zn(OAc)_2$ and the hydrogen-donor group is the water tetramer, $(H_2O)_4$ (graph set notation, $\mathbf{R^{4}_{4}(8)}$).[25] In other words, the 2D hydrogen-bonded structures are further linked through a cyclic quasi-planar water tetramer to provide a single self-penetrating 3D hydrogen-bonded coordination polymeric structure. Although hydrogen-bonded cyclic oligomers and polymers in various hosts have been described in the litera-

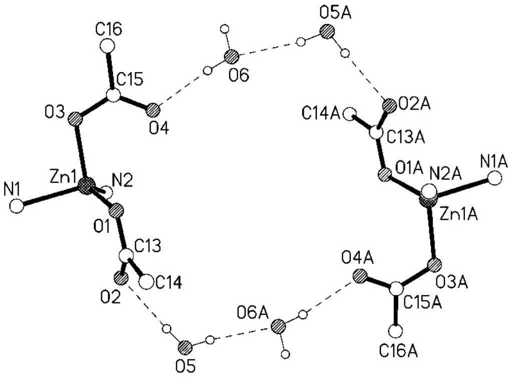


Figure 3. Diagram showing the 24-membered hydrogen-bonded ring in **1**. Only relevant atoms are shown.

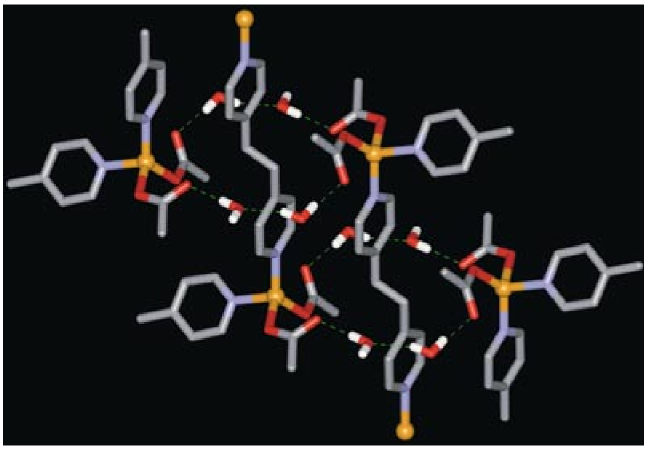


Figure 4. The hydrogen-bonded wheel and bpe axle in the rotaxane-like structure. Only selected atoms are shown for clarity.

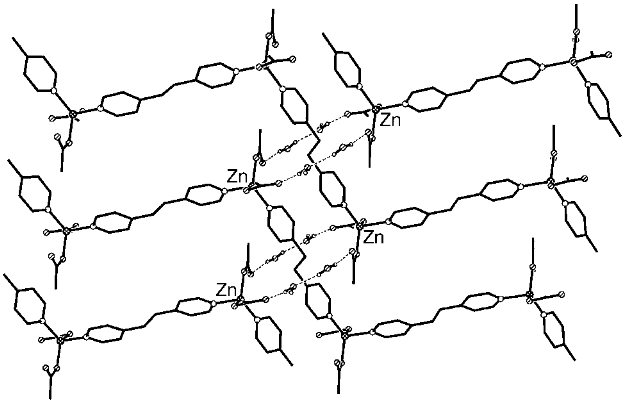
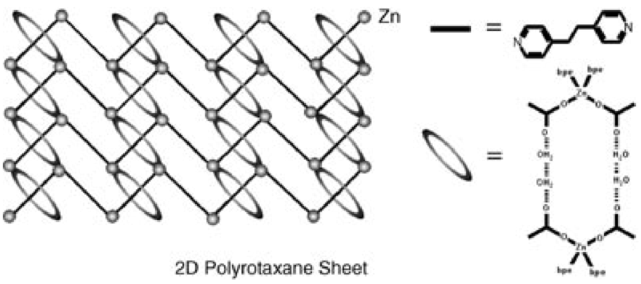


Figure 5. A section of the hydrogen-bonded polyrotaxane-like sheet in **1**.



Scheme 1. The 2D sheet containing the hydrogen-bonded polyrotaxane-like structure in **1**.

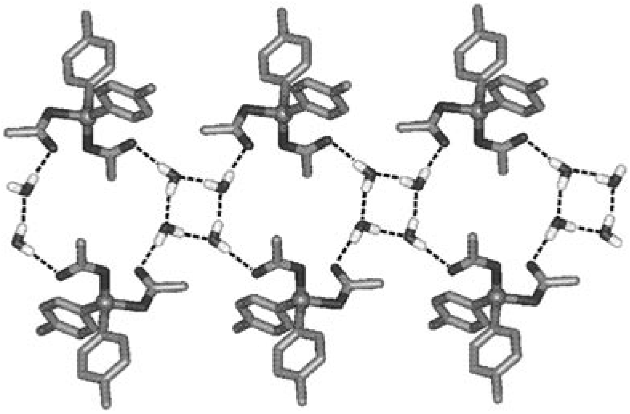


Figure 6. Perspective view of the 1D hydrogen-bonded polymer formed between the $(H_2O)_4$ and $Zn(OAc)_2$ in **1**. Only relevant atoms are shown for clarity.

ture[19a–c,27] they are not similar to that observed in **1**. On the other hand, the metal-containing hydrogen-bonded ring observed for **1** is a feature commonly observed in metal coordination polymeric structures.[20]

The closest interplanar distances between the pyridyl groups of two adjacent bpe spacer ligands are in the range of 4.702(2)–4.844(2) Å, indicating the absence of any π···π interactions between adjacent polymeric chains. The O–H···O hydrogen bonds present in the crystal lattice for **1** are quite strong, to judge from the hydrogen-bond distances (Table 2), together with the results of the neutron study (see below). Recently Infantes and co-workers analyzed various extended motifs of water and chemical functional groups in organic molecular crystals by using the Cambridge Structural Database.[26] In their paper, an interesting tape-like structure (with the notation T4(2)10(2))[28] formed between $(H_2O_2)_4$ and two trifluoroacetate groups generates a 16-membered ring. In **1** this ring size has been increased to 24 owing to $Zn(OAc)_2$ instead of the trifluroacetate groups. The size of the ring is large enough in **1** for a bpe ligand to pass through. On the other hand, in the structure of $[H_{31}O_{14}][CdCu_2(CN)_7]$, reported by Nishikiori and Iwamoto, each $Cu_2(CN)_7$ moiety is encircled by 12 hydrogen-bonded water molecules to form a 22-membered ring.[15]

Table 2. Hydrogen-bond parameters from X-ray and neutron diffraction data for **1**.

D–H···A	D–H	H···A	D···A	∢DHA
X-ray data				
O5–H5A···O2[a]	0.80(2)	1.95(3)	2.744(5)	170(5)
O5–H5B···O6	0.80(2)	1.99(3)	2.769(4)	164(4)
O6–H6A···O4	0.81(2)	1.95(3)	2.752(5)	169(5)
O6–H6B···O5[b]	0.81(2)	1.96(2)	2.763(6)	168(6)
neutron data				
O5–H5A···O2[a]	0.98(2)	1.77(2)	2.75(1)	172(1)
O5–H5B···O6	0.98(1)	1.87(1)	2.80(1)	157(1)
O6–H6A···O4	0.93(2)	1.81(1)	2.73(1)	175(2)
O6–H6B···O5[b]	1.00(2)	1.77(2)	2.76(1)	168(1)

[a] Symmetry operator: $-x+2$, $-y$, $-z$. [b] Symmetry operator: x, y, $z-1$.

Neutron diffraction studies on 1: The distances and angles involving non-hydrogen atoms were more accurately obtained by the X-ray data, but none of the neutron values are significantly different, and the trends observed from the X-ray results are also obtained from the neutron data. Where neutron diffraction can make its contribution is when looking at the hydrogen atoms. Looking at the data recorded at 20 K, all hydrogen-bond distances are in the range 1.06(1)–1.11(1) Å for the main structure, and in the range 0.93(2)–1.00(2) Å for the water molecules. These are normal values. The angles involving H(1) through H(10) are in the range 115.8(8)–122.3(8)°, those involving H(11) through H(16) are in the range 107(1)–113(1)°, and those within the water molecules are 102(1)° and 108(1)°, all as to be expected. The latter are comparable to the angles of 105(4)° and 103(4)° obtained from the X-ray data.

Of more interest is the hydrogen bonding. The O···O distances are very similar to those obtained by X-ray diffraction, and those involving the water molecules are in a narrow range: 2.73(1)–2.80(1) Å and the H···O distances are in the range 1.77(1)–1.87(1) Å (Table 2). These are fairly strong hydrogen bonds. The two hydrogen bonds that are almost linear (172(1)° and 175(2)°) are those to the carboxylate oxygen atoms, and the other angles are not far from being linear (157(1)° and 168(1)°), so this configuration is close to optimal.

The standard deviations from the neutron data involving distances of hydrogen atoms are only slightly better than those obtained from the X-ray data. But the positions themselves should be more accurate, since the X-ray locations are biased by the non-spherical electron densities in the X–H bonds, which results in a shortening of the X–H bond of about 0.1 Å, in this structure 0.12–0.19 Å (Table 2), and correspondingly longer H···A distances. The standard deviations obtained from the neutron data for the angles are about a factor of 4 better than those obtained from the X-ray data. The quality of the crystal was not the best, as is not uncommon when growing (relatively) large crystals suitable for neutron diffraction. Also, as noted, the quality degraded further upon cooling, resulting in a refinement that was not optimal. All this resulted in relatively high standard deviations.

There are no other strong hydrogen bonds in the structure. Some of the weaker interactions are: O(2)···H(4) (2.43(2) Å) and O(2)···H(6) (2.45(1) Å), and O(4)···H(7) (2.47(1) Å). The only other potential hydrogen-bond acceptors are O(1) and O(3), each of which has a weak intramolecular interaction with one of the methyl hydrogen atoms (O(1)···H(14B) 2.56(2) and O(3)···H(16C) 2.50(2) Å).

Structure of $[Zn(OAc)_2(\mu\text{-dpds})]_n$ (2): When the bpe ligand is replaced by dpds, the compound does not contain any water molecule and the structure as determined by X-ray crystallography was found to adopt the expected zigzag coordination polymer. A segment of the polymeric structure of **2** is shown in Figure 7. The Zn^{II} center has the same geometry and coordination environment as in **1**.

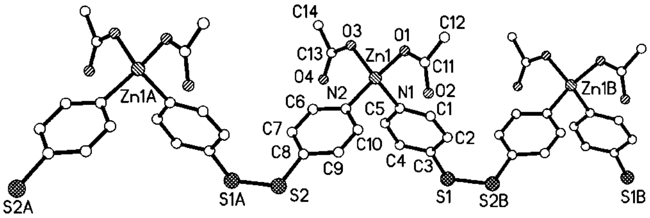
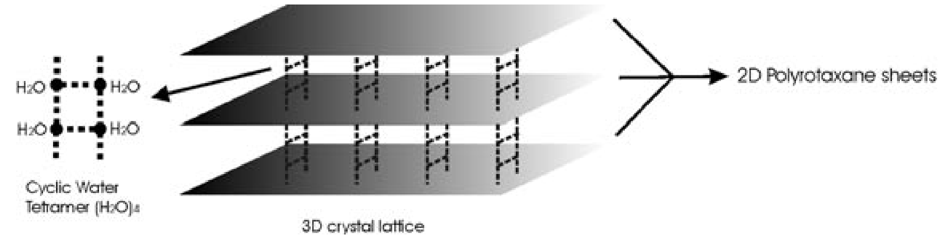


Figure 7. A portion of the one-dimensional polymeric structure of **2** is shown with the numbering scheme. The H atoms are omitted for clarity.

Selected bond lengths and angles for **2** are given in Table 3. The Zn–O and Zn–N bond lengths, and angles at the Zn^{II} center are very similar to those found in **1**. The C-S-S-C torsion angle in the dpds spacer ligand is 90.4(2)° and the S–S bond length is 2.0301(7) Å. The C-S-S-C torsion angles in aromatic disulfide groups are known to be within about 20° of 90°.[29,30] Thus, the disulfide moiety in the spacer ligand seems to maintain its characteristic shape even after bonding to the Zn^{II} center. The two carbonyl oxygen atoms are involved in intramolecular C–H···O bonding to



Scheme 2. Schematic representation of the crystal structure of **1**.

Table 3. Selected bond lengths [Å] and angles [°] from X-ray data for **2**.

Zn(1)−O(1)	1.922(3)	O(1)−C(11)	1.307(6)
Zn(1)−O(3)	1.946(4)	O(2)−C(11)	1.244(5)
Zn(1)−N(1)	2.038(3)	C(11)−C(12)	1.457(7)
Zn(1)−N(2)	2.053(4)	O(3)−C(13)	1.252(6)
S(1)−C(3)	1.783(5)	O(4)−C(13)	1.226(5)
S(2)−C(8)	1.771(4)	C(13)−C(14)	1.542(6)
S(2)−S(1)[a]	2.030(1)		
O(1)-Zn(1)-O(3)	101.14(6)	C(6)-N(2)-Zn(1)	117.9(3)
O(1)-Zn(1)-N(1)	111.48(2)	C(11)-O(1)-Zn(1)	123.3(3)
O(3)-Zn(1)-N(1)	113.63(2)	O(2)-C(11)-O(1)	120.6(5)
O(1)-Zn(1)-N(2)	114.50(2)	O(2)-C(11)-C(12)	123.0(4)
O(3)-Zn(1)-N(2)	112.74(2)	O(1)-C(11)-C(12)	116.2(4)
N(1)-Zn(1)-N(2)	103.79(6)	C(13)-O(3)-Zn(1)	122.2(3)
C(1)-N(1)-Zn(1)	122.8(3)	O(4)-C(13)-O(3)	127.2(5)
C(5)-N(1)-Zn(1)	121.0(3)	O(4)-C(13)-C(14)	117.3(5)
C(10)-N(2)-Zn(1)	122.6(3)	O(3)-C(13)-C(14)	115.4(4)

[a] Symmetry operator: x, y, $z+1$.

the pyridyl groups. The H···O distances vary from 2.374 to 2.563 Å, which are considered to indicate very strong hydrogen bonds.[31]

In the crystal lattice, the 1D coordination polymeric strands propagate in the *c* direction and are stacked in such a way that the disulfide and the $Zn(OAc)_2$ groups are below one another along the *b* direction (Figure 8). The bond lengths between the sulfur atom and the hydrogen atoms of methyl group between the adjacent polymer strands (3.545(2)–3.548(2) Å) indicate that there is no C−H···S hydrogen bond interaction between the polymer strands. That the pyridine rings in each of the polymer strands are parallel to each other and the perpendicular distances between the rings are in the range of 4.823(2)–4.877(2) Å appears to suggest that no π···π interaction is present between the adjacent polymer strands. It is interesting to observe that these linear polymers are aligned in parallel as found in **1**.

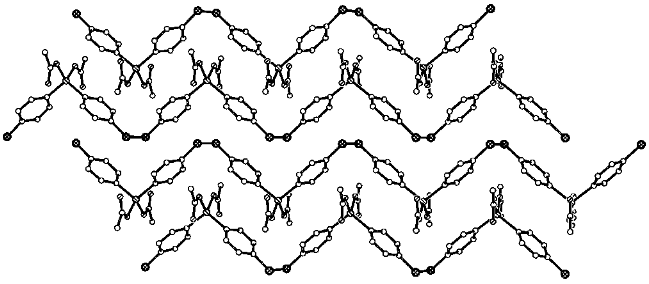


Figure 8. Packing diagram of compound **2** viewed down the *b* axis. Only relevant atoms are shown for clarity.

Conclusion

Both bpe and dpds ligands form 1D polymeric structures with $Zn(OAc)_2$ in the ratio 1:1. Although the two conformationally flexible dinitrogen spacer ligands are expected to give structurally similar polymers, the py-C-C-py fragment in **1** has an *anti* conformation with the torsion angle 180°, whereas the C-S-S-C group in **2** has *syn* geometry with a S-C-C-S torsion angle of 90.4(2)°, and an interplanar angle between the pyridine rings of 89.6(1)°. Owing to the turn at the -S-S- group, all the $Zn(OAc)_2$ groups are on one side of the chain and the disulfide groups are on the opposite side in **2**. It is not clear from this study if the backbone of the spacer group dictates the incorporation of the lattice water molecules that is responsible for the hydrogen-bonded ring pattern in **1** (Scheme 2). In the recently published crystal structure of $[Zn(OAc)_2$-(bpy)], which contains yet another linear spacer ligand, namely 4,4′-bipyridyl (bpy), the 1D coordination polymer was found to adopt ladder (or rail road) geometry[32] with no solvent incorporated in the crystal structure. The unique feature of the hydrogen-bonded polyrotaxane-like structure is the role of a water tetramer, $(H_2O)_4$ to act as a hydrogen-bond donor which bonds to four different oxygen atoms of the $Zn(OAc)_2$ groups to generate a 1D polymer containing alternate 24- and eight-membered fused hydrogen-bonded rings. The size of the $\mathbf{R^6_6(24)}$ hydrogen-bonded ring is large enough to encapsulate one of the bpe ligands in a rotaxane-like fashion. The neutron diffraction study of **1** is the first report of its kind on a 3D hydrogen-bonded network with polyrotaxane-like structures.

Experimental Section

General remarks: All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out at the Microanalysis Laboratory of the National University of Singapore and the yields are reported with respect to the metal salts. Infrared data were collected on a Bio-Rad FTIR spectrophotometer using the KBr pellet method. Thermogravimetric analysis of **1** was performed (under N_2 atmosphere) using a SDT 2980 TGA Thermal Analyzer instrument with a sample size of about 10 mg.

$[Zn(OAc)_2(\mu\text{-bpe})]_n\cdot 2nH_2O$ (1): Equimolar amounts of $Zn(OAc)_2\cdot 2H_2O$ (0.1 g, 0.5 mmol) and bpe (0.08 g, 0.45 mmol) were mixed together in DMF to give a clear solution. The solvent was evaporated off and colorless platelike single crystals of **1** were formed after a day. The crystals were separated by filtration, washed with Et_2O, and dried under vacuum. Yield: 0.13 g (72%). Elemental analysis calcd (%) for $C_{16}H_{22}N_2O_6Zn$: C 47.60, H 5.49, N 6.94; found: C 48.42, H 5.18, N 6.43; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.62$ (d, $J = 6$ Hz, 4H of py in bpe), 7.20 (d, $J = 6$ Hz, 4H of py in bpe), 3.02 (s, $2CH_2$ of bpe), 2.06 ppm (s, 6H, CH_3 of acetate); IR (KBr): $\tilde{\nu}$vs, C=O), 1560 (s, bpe), 1432 (s, bpe), 1412 (s, C=O), 1343 (vw, bpe), 1212 (w, bpe), 1074 (m, bpe), 1031 (m = 1617, bpe) cm^{-1}. TG weight loss for loss of 2H_2O: expected: 8.9%; found: 8.7%.

Crystals suitable for neutron diffraction studies were obtained by evaporating a concentrated solution of **1** in DMF at room temperature.

[Zn(OAc)$_2$(μ-dpds)]$_n$ (2): A solution of Zn(OAc)$_2$ (0.10 g, 0.45 mmol) in MeOH (0.5 mL) was added to a solution of dpds (0.10 g, 0.45 mmol) in THF (0.5 mL). A clear solution was obtained and the solution was left for slow evaporation at room temperature. Pale yellowish rhombic-shaped single crystals of **2** were formed after a day. The crystals were collected by filtration, washed with Et_2O, and dried under vacuum. Yield: 0.14 g (71%). Elemental analysis calcd (%) for $C_{14}H_{14}N_2S_2O_4Zn$: C 38.23, H 3.20, N 6.30, S 14.58; found: C 37.98, H 3.66, N 6.16, S 14.33. ^{1}H NMR (300 MHz, CD_3OD, 25 °C): $\delta = 8.47$ (d, $J = 6$ Hz, 4H of py in dpds), 7.63 (d, $J = 6$ Hz, 4H of py in dpds), 1.98 ppm (s, 2CH_3 of acetate); IR (KBr): $\tilde{\nu} = 1593$ (vs, C=O), 1484 (m, dpds), 1420 (s, dpds), 1389 (s, C=O), 1336 (w, dpds), 1211 (w, dpds), 1062 (m, dpds), 927 (w, dpds), 818 (m, dpds), 717 (m, dpds), 669 (w, dpds), 498 (m, dpds) cm^{-1}.

Table 4. Crystallographic data and refinement parameters for compounds **1** and **2**.

	1 (X-ray)	**1** (neutron)	**2**
formula	$C_{16}H_{22}N_2O_6Zn$	$C_{16}H_{22}N_2O_6Zn$	$C_{14}H_{14}N_2O_4S_2Zn$
M	403.73	403.73	403.76
T [K]	223(2)	20	223(2)
λ [Å]	0.71073	$0.9 \leq \lambda \leq 2.8$	0.71073
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	Cc
unit cell dimensions			
a [Å]	8.360(1)	8.360[a]	16.462(4)
b [Å]	10.950(2)	10.991	10.054(2)
c [Å]	11.066(2)	10.974	10.936(3)
α [°]	114.292(3)	114.27	90
β [°]	96.613(3)	97.15	109.556(1)
γ [°]	93.051(3)	92.65	90
V [Å^3]	911.3(2)	906.8	1705.46(7)
Z	2	2	4
ρ_{calcd} [g cm^{-3}]	1.471	1.479	1.573
μ [mm^{-1}]	1.381	0.197	0.703
independent reflections (R_{int})	3169 (0.0442)	3100 (0.265)	3309 (0.0276)
data/restraints/parameters	3169/7/244	3095/0/189	3309/2/211
Goof [F^2]	1.048	1.227	1.097
R indices ($I > 2\sigma(I)$)			
$R1$	0.0493	0.1953	0.0303
$wR2$	0.0870	0.2001	0.0801
R indices (all data)			
$R1$	0.0661	0.2711	0.0326
$wR2$	0.0896	0.2157	0.0816

[a] The value of a was fixed to the 223 K X-ray value at both 295 K and 20 K (see text for details).

X-ray crystallographic study: The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a $Mo_{K\alpha}$ sealed tube at 23 °C. The program SMART[33] was used for collecting frames of data, indexing reflections, and determination of lattice parameters, the program SAINT[33] was used for integration of the intensity of reflections and scaling. SADABS[34] was used for absorption correction, and SHELXTL[35] for determining the space group and the structure and least-squares refinements on F^2. The positional and isotropic thermal parameters of hydrogen atoms associated with lattice water molecules in **1** were varied in the least-squares refinements. Relevant crystallographic data are listed in Table 4.

Neutron diffraction experiments: Neutron diffraction data were collected on VIVALDI, at the Institut Laue-Langevin (ILL), Grenoble, France. VIVALDI uses the Laue diffraction technique on an unmonochromated thermal-neutron beam and with a large solid-angle (8 sterad) cylindrical image-plate detector, to increase the detected diffracted intensity by one-to-two orders of magnitude compared with a conventional monochromatic experiment.[36] A colorless crystal of **1**, with well-developed faces and maximum dimensions $1.7 \times 0.9 \times 0.6$ mm^3, volume ~0.5 mm^3, was selected, wrapped in aluminum foil with some silicon grease, and mounted on a vanadium pin. Seven Laue diffraction patterns were collected at room temperature, at 30° intervals around the vertical axis perpendicular to the incident neutron beam, each exposure lasting 4.5 h. Another seven patterns were collected with a different vertical orientation of the crystal. At a later date the crystal was cooled to 20 K, and 18 patterns were collected at 10° intervals around the vertical axis with an average exposure of 2.2 h.

The diffraction patterns were indexed by using the program LAUEGEN[37,38] and the reflections were integrated by using a 2D version of the $\sigma(I)/I$ algorithm described by Wilkinson et al.[39] and Prince et al.[40] No absorption correction was deemed necessary because of the small size of the crystal. The reflections were normalized to the same incident wavelength, using a curve derived by comparing equivalent reflections and multiple observations, by usingf the program LAUENORM.[41] Only reflections with wavelengths between 0.9 and 2.8 Å were accepted in the normalization procedure, as reflections outside this range were too weak or had too few equivalents to be able to determine the normalization curve with confidence. The total number of observed reflections accepted at 295 K was 7992, which were averaged to give 2192 unique reflections ($R_{int} = 0.0264$), of which 1622 have $F^2 > 1.5\sigma(F^2)$ There were 13062 observed reflections accepted at 20 K, which were averaged to give 3100 unique reflections ($R_{int} = 0.265$), 1906 with $F^2 > 1.5\sigma(F^2)$. The resulting intensities were used in full-matrix least-squares refinement using UPALS.[42] Preliminary refinements indicated negligible extinction, and this correction was thenceforth omitted. In the final refinement at 295 K, the scale factor, the positional and anisotropic parameters for all atoms were refined, 424 variables in all. The diffraction patterns taken at 20 K indicated that the quality had degraded slightly after cooling, with a lot of spots quite elongated. Nevertheless, the refinement at 20 K resulted in an excellent structure using isotropic displacement parameters, 189 variables in all. The R values obtained from the refinements are fairly large, but this reflects the small crystal volume and the large proportion of weak data finally accepted. The values of the goodness-of-fit are however close to 1.0, which indicates that lower R factors cannot be expected. The structural conclusions drawn from the data at 295 K and 20 K are identical, and only the results from the more extensive 20 K data are quoted in Table 2. A summary of the crystal, data collection, and refinement parameters is given in Table 4. The absolute scale of the unit-cell lengths cannot be determined in the white-beam Laue method; a was fixed to the value determined by X-ray diffraction at 223 K at both 295 K and 20 K. In view of the typical thermal expansion of organic materials the neutron hydrogen-bond lengths quoted in Table 2 are overestimated by less than 1.5%, itself similar to the observed estimated standard deviations in the bond lengths.[43]

CCDC 240080–240083 contain the supplementary crystallographic data for **1** and **2** discussed in this paper. The data can be obtained free of charge via www.ccdc.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 to deposit@cccd.ac.uk.

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