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Synthesis and characterisation of infinite di- and tri-nuclear zinc co-ordination networks with flexible dipyridyl ligands

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Crystallisation of flexible dipyridyl ligands with either $Zn(NO_3)_2\cdot 6H_2O$ or $Zn(ClO_4)_2\cdot 6H_2O$ gave co-ordination networks of composition $[Zn_3(OH)_3\{(NC_5H_4)_2C_3H_6\}_3][NO_3]_3\cdot 8.67H_2O$ **1** [$(NC_5H_4)_2C_3H_6$ = 1,3-bis(4-pyridyl)propane]; $[Zn_2(OH)\{(NC_5H_4)_2C_4H_8\}_3][ClO_4]_3\cdot H_2O\cdot EtOH$ **2** [$(NC_5H_4)C_4H_8$ = 1,4-bis(4-pyridyl)butane] and $[Zn_2(OH)\{(NC_5H_4)_2C_7H_{14}\}_4][ClO_4]_3\cdot 0.5H_2O$ **3** [$(NC_5H_4)_2C_7H_{14}$ = 1,7-bis(4-pyridyl)heptane]. The compounds were characterised by X-ray single crystal diffraction studies. Compound **1** possesses a trinuclear $Zn_3(OH)_3$ 6-membered ring that acts as a template for the co-ordination framework. Both **2** and **3** possess dinuclear zinc sub-units (Zn_2OH) that contain a bridging hydroxyl ion.

Introduction

The discovery of new co-ordination networks using the principles of crystal engineering provides an interesting opportunity to explore assembly and structural diversity in the solid state.[1] An extensive literature on networks crystallised from different dipyridyl ligands[2] and polyaromatic acids[3] with various transition metal ions now exists. As well as the discovery of interesting infinite supramolecular architectures, notable features include porosity and the structural support of void volume,[4] the formation of co-ordination networks that clathrate guest molecules,[5] the inclusion of novel molybdenum anions[6] and the use of dipyridyl ligands with hydrogen bond donor and acceptor functionality.[7] In this paper we report our studies on the crystallisation of zinc ions with dipyridyl ligands that are connected by a flexible $(CH_2)_n$ ($n = 3$, 4 or 7) linking group.

Results and discussion

Crystal structure of $[Zn_3(OH)_3\{(NC_5H_4)_2C_3H_6\}_3][NO_3]_3\cdot 8.67H_2O$ 1

Compound **1** was prepared by mixing a solution of 1,3-bis(4-pyridyl)propane in ethanol with a solution of $Zn(NO_3)_2\cdot 6H_2O$ in water. After 14 days homogeneous colourless crystals were collected. A crystal structure determination revealed an unusual structural motif for a co-ordination network which is shown in Figs. 1 and 2. The zinc cations are assembled into six membered rings connected together by three bridging hydroxyl groups. In addition each zinc atom is co-ordinated by two pyridine nitrogen atoms and possesses a distorted tetrahedral co-ordination environment. Of the four different conformations that 1,3-bis(4-pyridyl)propane can adopt only the *trans-trans* is present in this structure.[8] The dihedral angles are given in Fig. 1. Selected bond lengths and angles are shown in Table 1. Fig. 2 shows a section of the 2-D interwoven network. Each of the three independent ligands bridges two crystallographically equivalent zinc atoms. In result 28 membered rings are formed that are threaded by the ligand bridging from Zn3. The nitrate ions and water molecules occupy the cavities forming a complex hydrogen bonding network. The hydroxyl hydrogen atoms, which were located from the difference map, form hydrogen bonds to adjacent water molecules. Table 2 shows the additional hydrogen bonds that are formed between the water molecules and nitrate anions. The three nitrate ions and all the water molecules were also located without problems except for O21 which is disordered and O20 which has a site occupancy of 0.75. The $Zn_3(OH)_3$ 6-membered ring shown in Fig. 1 adopts a distorted chair conformation. Its shape can be described by the corresponding Cremer–Pople parameters.[9] An analysis of the geometry of the 6-membered $Zn_3(OH)_3$ ring by Cremer–Pople parameters ($Q = 0.539$ Å, $\theta = 48.9°$, $\phi = 243.2°$) indicates a slight departure from an ideal envelope conformation (ideal $\theta = 54.7°$, $\phi = k \times 60°$, $k = 0$–6). The Zn2 atom is puckered out of the average plane formed by the other five ring atoms by 0.75 Å which contrasts with the shape of previously reported $Zn_3(OH)_3$ rings which have a near planar geometry.[10] The Zn–N bond lengths are similar occurring in the range 2.025–2.033 Å except for Zn2–N21 which is shorter (2.000(4) Å). The hydroxyl bridge between each pair of zinc centers is asymmetric with Zn–O bond lengths in the range 1.908–1.934 Å which closely represent covalent interactions (Zn–O) as opposed to dative covalent interactions. The reference value for a pure single covalent Zn–O bond has been adopted as 1.89 Å.[11] The angles Zn1–O2–Zn2 (118.6(2)°) and Zn3–O3–Zn2 (123.5(2)°) are smaller than the Zn3–O1–Zn1 (129.8(2)°) angle which is presumably caused by the puckering of Zn2 out of the mean ring plane. The novel molecular threading of ligands that occurs as a consequence of the $Zn_3(OH)_3$ template probably helps to minimise void volume in the lattice in an analogous manner to interpenetrating lattice networks. A related type of molecular threading has been found in a tubular co-ordination polymer prepared from 1,3–bis(4-pyridyl)propane and $Ag(CF_3SO_3)$.[8] In this structure non-co-ordinated ligands are threaded through the polymer rings and are statistically distributed on two close centrosymmetric locations. To the best of our knowledge structure **1** is the first example in which a self-assembled hydroxometallocycle has formed an integral part of a co-ordination network.

Crystal structure of $[Zn_2(OH)\{(NC_5H_4)_2C_4H_8\}_3][ClO_4]_3\cdot H_2O\cdot EtOH$ 2

Compound **2** was prepared by mixing an ethanolic solution of 1,4-bis(4-pyridyl)butane with $Zn(ClO_4)_2\cdot 6H_2O$ in water. A

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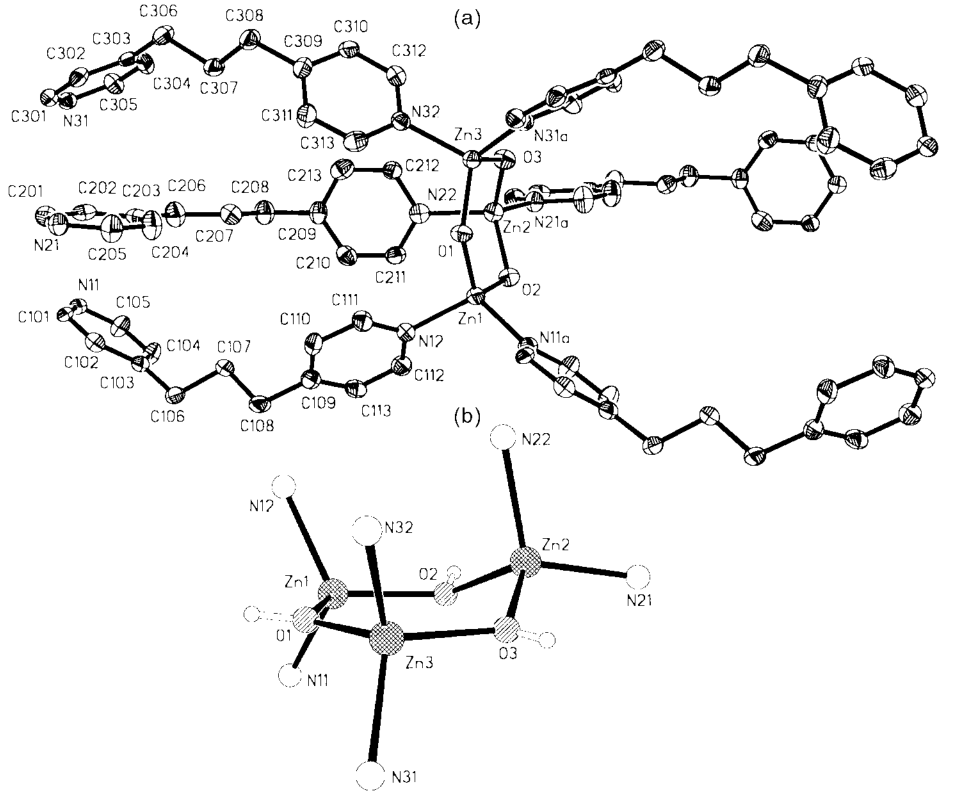

Fig. 1 Top: drawing of a building block for compound **1** showing the atom numbering scheme. Bottom: drawing of the $Zn_3(OH)_3$ building block showing the puckered 6-membered ring. Selected dihedral angles for the ligand [°] : C103–C106–C107–C108 −178.96; C106–C107–C108–C109 −179.28; C203–C206–C207–C208 179.36; C206–C207–C208–C209 −179.86; C303–C306–C307–C308 −178.95; C306–C307–C308–C309 −176.72.

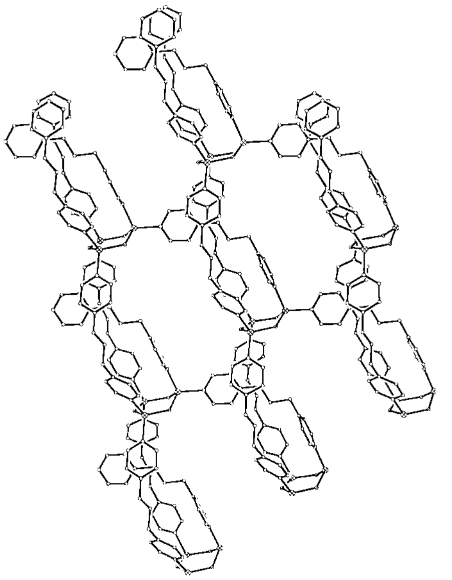

Fig. 2 Drawing of a section of the interwoven 2-D co-ordination network of compound **1**.

single crystal structure determination revealed the presence of a 2-D co-ordination network (Fig. 3). The zinc ions occur in pairs and are bridged by a hydroxyl ion. Each zinc ion is co-ordinated by a further three pyridyl nitrogen atoms adopting a distorted tetrahedral geometry. Selected bond lengths and angles are shown in Table 3. The Zn–N bond lengths fall in the range 2.007–2.085 Å. The Zn–O bond lengths of 1.909(3) and 1.910(3) Å are slightly shorter than the average Zn–O bond length in structure **1** (1.923 Å). The Zn–O–Zn angle of 134.2(2)° is slightly greater than the Zn–O–Zn angles in structure **1**. Four zinc ions and three ligands are connected together to form 41 membered rings. The conformation of the ligand can be described by three dihedral angles which are given in Fig. 3. There are three different ligands in the lattice present in an equal ratio. One of these adopts a *trans-trans-trans* conformation and one a *gauche-trans-gauche* conformation. The third ligand has dihedral angles of 156.6, 129.9 and −67.6° and so resembles a *trans-trans-gauche* conformation. The space left in the lattice is occupied by perchlorate, water and ethanol molecules. The ethanol molecules are disordered and were found in four possible orientations. Hydrogen bonds were detected between the hydroxo group and the water molecule and between the water molecule and perchlorate anion (Table 4).

Table 1 Selected bond lengths [Å] and angles [°] for compound **1**

Zn1–O2	1.922(3)	Zn2–N21	2.000(4)
Zn1–O1	1.931(3)	Zn2–N22	2.031(4)
Zn1–N11	2.027(4)	Zn3–O1	1.919(3)
Zn1–N12	2.033(4)	Zn3–O3	1.922(4)
Zn2–O3	1.908(4)	Zn3–N31	2.025(4)
Zn2–O2	1.934(3)	Zn3–N32	2.026(4)
O2–Zn1–O1	110.0(2)	O3–Zn2–N22	108.0(2)
O2–Zn1–N11	105.7(2)	O2–Zn2–N22	106.5(2)
O1–Zn1–N11	110.5(2)	N21–Zn2–N22	110.7(2)
O2–Zn1–N12	111.9(2)	O1–Zn3–O3	107.2(2)
O1–Zn1–N12	107.3(2)	O1–Zn3–N31	110.1(2)
N11–Zn1–N12	110.6(2)	O3–Zn3–N31	107.8(2)
O3–Zn2–O2	107.2(2)	O1–Zn3–N32	109.8(2)
O3–Zn2–N21	112.9(2)	O3–Zn3–N32	109.7(2)
O2–Zn2–N21	111.2(2)	N31–Zn3–N32	112.1(2)
Zn3–O1–Zn1	129.8(2)	Zn1–O2–Zn2	118.6(2)
Zn2–O3–Zn3	123.5(2)		

Crystal structure of $[Zn_2(OH)\{(NC_5H_4)_2C_7H_{14}\}_4][ClO_4]_3\cdot 0.5H_2O$ 3

Compound **3** was prepared by mixing an ethanolic solution of 1,7-bis(4-pyridyl)heptane with $Zn(ClO_4)_2\cdot 6H_2O$ in water. The crystalline material that formed was always mixed with amorphous material so it was not possible to obtain a pure

Table 2 Hydrogen bonds [Å and °] in compound **1**. O4 ··· O12 are part of NO_3 molecules, O14 ··· O21 are part of H_2O molecules

D–H ··· A	*d*(D–H)	*d*(H ··· A)	*d*(D ··· A)	(DHA)
O1–H1 ··· O13	0.81(2)	1.97(2)	2.776(5)	172(4)
O2–H2 ··· O18	0.83(2)	1.90(2)	2.723(5)	171(5)
O13–H13B ··· O11	0.84	2.01	2.839(5)	171.1
O14–H14B ··· O10	0.84	2.10	2.883(6)	154.9
015–H15A ··· O6	0.86	2.38	3.212(6)	164.3
P15–H15A ··· O5	0.86	2.42	3.132(6)	140.4
O15–H15B ··· O9	0.84	2.06	2.874(7)	164.0
O16–H16A ··· O11	0.86	2.05	2.881(6)	162.9
O16–H16B ··· 09	0.84	2.20	2.842(8)	133.0
O17–H17A ··· O7	0.84	2.21	2.909(7)	141.3
O18–H18B ··· O19	0.84	1.96	2.763(6)	160.2
O19–H19B ··· O21	0.84	1.93	2.762(13)	170.8
O20–H20A ··· O2	0.86	2.10	2.948(7)	171.5
O20–H20B ··· O16b	0.84	2.11	2.830(9)	143.5
O21–H21A ··· O12b	0.86	2.02	2.837(7)	159.2
O19–H19A ··· O17	0.86	2.00	2.856(6)	173.4
O18–H18A ··· O14e	0.86	1.96	2.800(6)	164.7
O3–H3 ··· 017b	0.73(5)	2.03(5)	2.753(6)	173(6)
O14–H14A ··· O15f	0.86	1.95	2.807(6)	173.3
O17–H17A ··· 04c	0.86	1.99	2.850(5)	173.2

Symmetry transformations: b $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; c $x + 1, y, z$; d $-x + 1, -y, z + 1$; e $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; f $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 3 Selected bond lengths [Å] and angles [°] for compound **2**

Zn1–O13	1.909(3)	Zn2–O13	1.910(3)
Zn1–N21	2.019(4)	Zn2–N22	2.007(4)
Zn2–N11	2.030(4)	Zn2–N31	2.027(4)
Zn1–N12	2.085(4)	Zn2–N32	2.041(4)
O13–Zn1–N21	118.5(2)	O31–Zn2–N22	114.8(2)
O13–Zn1–N11	118.2(2)	O13–Zn2–N31	111.4(1)
N21–Zn1–N11	111.6(2)	N22–Zn2–N31	109.9(2)
O13–Zn1–N12	103.7(2)	O13–Zn2–N32	112.8(2)
N21–Zn1–N12	103.1(2)	N22–Zn2–N32	106.6(4)
N11–Zn1–N12	97.6(2)	N31–Zn2–N32	100.7(2)
Zn1–O13–Zn2	134.2(2)	Zn1–O13–H10	102(4)
Zn2–O13–NH10	123(4)		

Symmetry transformations: a $x - 1, y, z$; b $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 4 Hydrogen bonds [Å and °] for compound **2** (O14 is part of a H_2O molecules O7 is part of a ClO_4 molecule)

D–H ··· A	*d*(D–H)	*d*(H ··· A)	*d*(D ··· A)	DHA
O13–H10 ··· O14	0.88(1)	1.88(2)	2.734(6)	165(5)
O14–H3O ··· O7a	0.84	2.16	2.994(8)	171.5

Symmetry transformation: a $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

phase. The formation of an amorphous precipitate, which complicates the synthesis of both compounds **2** and **3**, is thought to be a perchlorate salt of the protonated dipyridyl ligand. This would form as the dipyridyl ligand acts as a base converting $Zn(H_2O)_x$ into Zn(OH) species. An amorphous precipitate does not form in the synthesis of compound **1** probably because the nitrate salt of the protonated ligand (1,3-bis(4-pyridyl)propane) is soluble. However a single crystal structure determination was accomplished and revealed the presence of 1-D chains that are arranged parallel to the crystallographic *a* axis (Fig. 4). The structure consists of infinite chains with symmetric (Zn_2OH) units linked together by two ligands which form a series of 32 membered rings along each chain. In addition there are two ligands in the asymmetric unit which are only co-ordinated to one zinc atom so that N22 and N42 do not co-ordinate to a zinc atom. The Zn–N bond lengths occur in the range 1.975–2.025 Å (Table 5) and are slightly shorter than those in structures **1** and **2**. The Zn–O bond lengths of 1.907 and 1.892 Å are similar

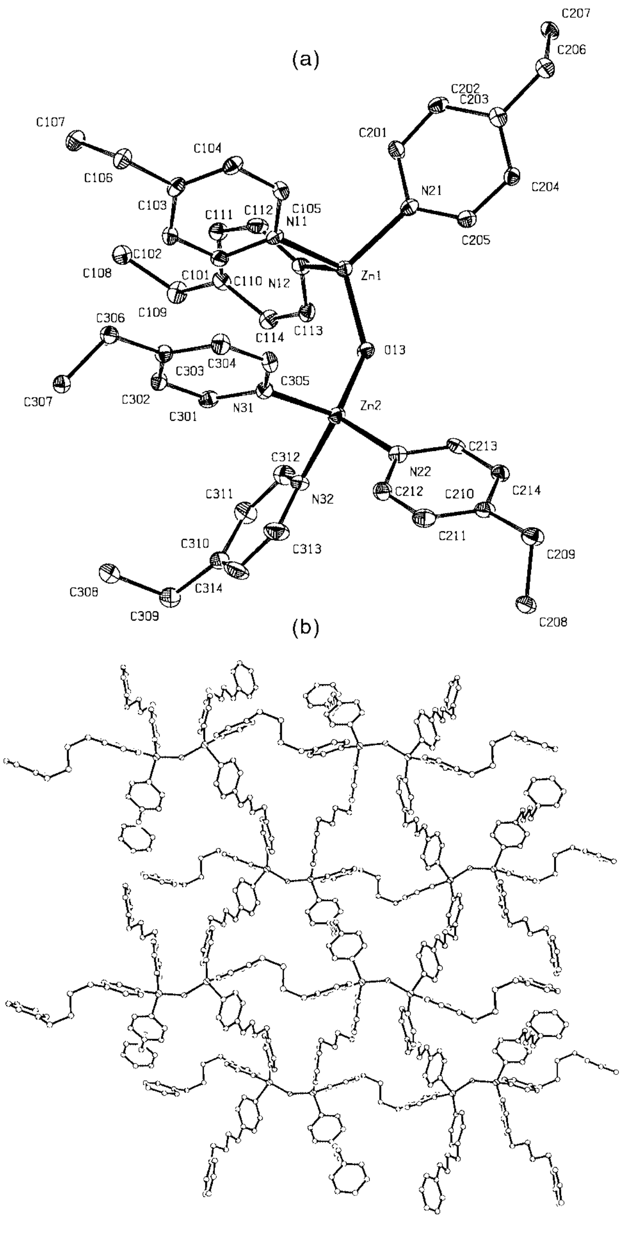

Fig. 3 Top: drawing of the asymmetric unit for compound **2** viewed along [100] showing the atom numbering scheme. Bottom: drawing of a section of the 2-D co-ordination network. Selected dihedral angles for the ligand [°] : C103–C106–C107–C108c −179.9; C106–C107–C108c–C109c −168.5; C107–C108c–C109c–C110c −172.3; C203–C206–C207–C208d −59.1; C206–C207–C208d–C209d −172.1; C207–C208d–C209d–C210d −61.3; C303–C306–C307–C308e 156.6; C306–C307–C308e–C309e 129.9; C307–C308e–C309e–C310e −67.6 Symmetry transformations: c $-x - 1, y - \frac{1}{2}, -z + \frac{1}{2}$; d $x, -y + \frac{3}{2}, z + \frac{1}{2}$ e: $-x - 1, -y + 1, -z$.

to those in **2**. The Zn–O–Zn angles of 135.1(4) and 131.7(6)° are also similar to those of **2**. The long flexible $(CH_2)_7$ chains are disordered and four out of five crystallographically independent anions are disordered *via* a mirror plane. Further problems associated with the crystallographic characterisation are discussed in the Experimental section.

Each of the compounds reported here contains zinc(II) ions which are bridged by hydroxyl ions. Co-ordination networks crystallised from 4,4′-bipyridyl and zinc(II) ions are known[12] although the spontaneous formation of the (Zn_2OH) group in such networks has so far been limited to those based on flexible dipyridyl ligands. This might be a consequence of the (Zn_2OH) co-ordination sphere which could be difficult for rigid ligands such as pyrazine or 4,4′-dipyridyl to bridge between in an infinite network. The tendency for the dinuclear (Zn_2OH) center to form in non-polymeric complexes is evident from the structures

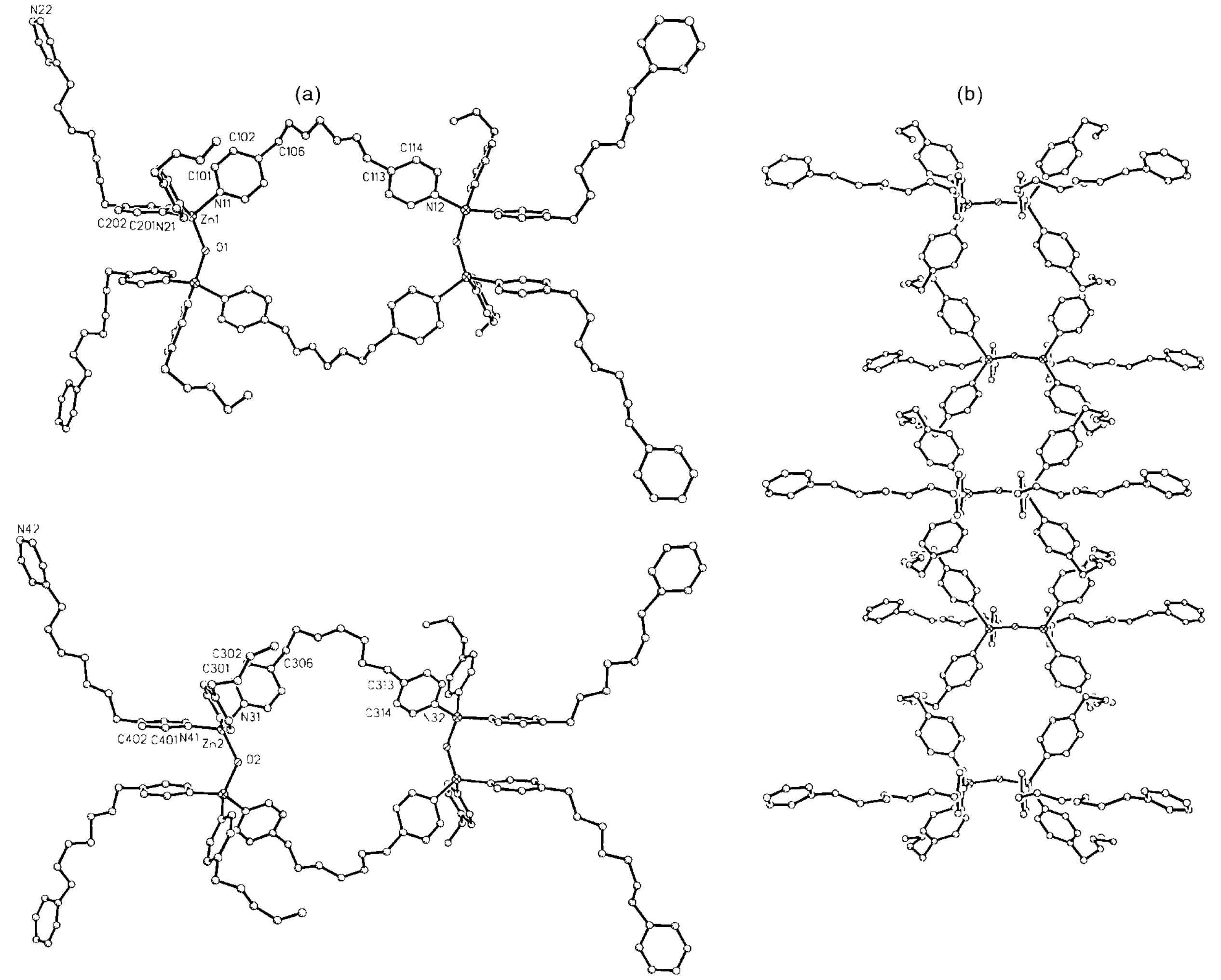

Fig. 4 Top: drawing of a section of compound **3** showing the atom numbering scheme. Bottom: sideways view of the 1-D chains in compound **3**.

Table 5 Selected bond lengths [Å] and angles [°] for compound **3**

Zn1–O1	1.892(3)	Zn2–N41	1.975(9)
Zn1–N12a	2.006(8)	Zn2–N32c	1.984(8)
Zn1–N21	2.011(8)	Zn2–N31	2.025(9)
Zn1–N11	2.025(8)	Zn2–O2	1.907(5)
Zn1–O1	1.892(3)	Zn2–N32c	1.984(8)
Zn2–O2	1.907(5)	Zn1–N12a	2.006(8)
Zn1–O1–Zn1b	135.1(4)	Zn2–O2–Zn2b	131.7(6)
O1–Zn1–N12a	111.7(4)	O2–Zn2–N41	113.5(4)
O1–Zn1–N21	114.1(3)	O2–Zn2–N32c	115.4(4)
N12a–Zn1–N21	110.2(4)	N41–Zn2–N32c	109.8(4)
O1–Zn1–N11	109.6(4)	O2–Zn2–N31	107.7(4)
N12a–Zn1–N11	106.0(3)	N41–Zn2–N31	103.3(4)
N21–Zn1–N11	104.8(4)	N32c–Zn2–N31	106.2(3)

Symmetry transformations used to generate equivalent atoms: a $x + \frac{1}{2}$, y, $-z + \frac{1}{2}$; b x, $-y + \frac{1}{2}$, z; c $x + \frac{1}{2}$, y, $-z + \frac{1}{2}$.

of some chelate complexes[10] and its occurrence at the active site in certain enzymes.[13] Our studies show that flexible dipyridyl ligands can be exploited for the assembly of co-ordination networks, and have led to a new structural motif, although long aliphatic spacers show a tendency to disorder. Further studies on co-ordination networks using flexible dipyridyl ligands are in progress.

Experimental

1,3-Bis(4-pyridyl)propane was purchased from Aldrich. 4-Methylpyridine was distilled from calcium hydride and stored over molecular sieves before use. 1,4-Bis(4-pyridyl)butane was made by the reductive dimerisation of 4-vinylpyridine at a mercury cathode in wet DMF.[14,15] 1,7-Bis(4-pyridyl)heptane was obtained by the treatment of 4-methylpyridine with potassium amide and a carbon electrophile in liquid ammonia.[16] All infrared spectra were recorded on KBr discs using a ATI Mattson Genesis series FTIR spectrometer. The CHN microanalyses were performed by Butterworth Laboratories Ltd.

Preparations

$[Zn_3(OH)_3(\{(NC_5H_4)_2C_3H_6\}_3][NO_3]_3\cdot 8.67H_2O$ 1. A solution of 1,3-bis(4-pyridyl)propane (3.0 g, 15.15 mmol) in ethanol (20 ml) was layered on top of a solution of zinc nitrate hexahydrate (2.0 g, 6.72 mmol) in water (10 ml). These liquids were rapidly combined by shaking the tube. The tube was allowed to stand undisturbed for a weekend, giving a colourless solid which was washed with 1 : 1 water–ethanol (8 ml) then with water before being placed in a desiccator for 6 h. The solid obtained (0.31 g, 21%) was in the form of needles which lost solvent readily at room temperature. At 40 °C in a nitrogen atmosphere the solid lost 17% of its mass. The crystals were homogeneous in appearance but lost solvent readily at room temperature (Found: C, 43.5; H, 4.1; N, 11.3% $[Zn_3(OH)_3\{(NC_5H_4)_2C_3H_6\}_3][NO_3]_3\cdot 3H_2O$ requires C, 43.3; H, 4.4; N, 11.6%); IR (KBr, cm^{-1}): 3430s br, 3069w, 3038w, 2950m, 2861m, 1620m, 1606sh, 1560w, 1508w, 1458w, 1433m, 1384vs, 1224m, 1070m, 1031m, 855w, 824m, 811w, 619w, 567w, and 518w. TGA: the material loses mass at room temperature; above 200 °C an exothermic mass loss occurred.

$[Zn_2(OH)\{(NC_5H_4)_2C_4H_8\}_3][ClO_4]_3\cdot H_2O\cdot EtOH$ 2. A saturated solution of 1,4-bis(4-pyridyl)butane in ethanol (10 ml) was

Table 6 Summary of crystal data for compounds **1**–**3**

	1	**2**	**3**
Formula	$C_{39}H_{62,33}N_9O_{20,67}Zn_3$	$C_{44}H_{57}Cl_3N_6O_{15}Zn_2$	$C_{136}H_{180}Cl_6N_{16}O_{27}Zn_4$
M	1184.10	1147.05	2945.14
T/K	150	150	293
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$Pnma$
Z	4	4	4
a/Å	13.1599(4)	10.5216(6)	17.2550(4)
b/Å	21.636(1)	16.7671(9)	34.4538(6)
c/Å	19.4741(9)	28.704(2)	24.519(1)
β/°	103.855(2)	89.988(1)	
V/Å^3	5383.5(4)	5063.9(5)	14576.6(7)
μ/mm^{-1}	1.405	1.177	0.834
Reflections collected	68514	20263	72134
Independent reflections/R_{int}	9523/0.071	8742/0.062	10274/0.151
Data/restraints/parameters	9523/2/735	8742/10/695	10274/930/722
$R1/wR2$ [$F^2 > 2\sigma(F^2)$]	0.059/0.132	0.048/0.100	0.111/0.200
(all data)	0.122/0.150	0.073/0.108	0.239/0.221
Largest difference peak and hole/e Å^{-3}	0.63/−0.62	0.49/−0.43	0.93/−0.63

added to a solution of zinc perchlorate (1.0 g, 2.69 mmol) in water (3 ml). Initially the solution turned cloudy then a light brown solid formed at the bottom of the tube. Later colourless crystals formed in the higher parts of the tube. Crystals suitable for crystallography were harvested. An alternative synthesis has been devoloped which yields a pure homogeneous product. A hot solution of 1,4-bis(4-pyridyl)butane (1.12 g, 5.28 mmol) in ethanol (30 ml) was mixed with a solution of zinc perchlorate hexahydrate (1.02 g, 2.74 mmol) in water (4 ml). The mixture became cloudy and was heated for 30 min. The clear solution was then decanted off from a heavy tar and allowed to stand for 2 days. During this time large colourless crystals formed (774 mg, 59%) (Found: C, 48.7; H, 4.6; N, 7.8%. $[Zn_2(OH)\{(NC_5H_4)_2C_4H_8\}_3][ClO_4]_3$-$OH_2O$ requires C, 48.7; H, 5.0; N, 8.1%) (the compound readily loses ethanol). IR (KBr, cm^{-1}): 3448br, 3076w, 2947s, 2925s, 2867m, 1622s, 1559m, 1508m, 1454w, 1438m, 1281w, 1236m, 1212m, 1164sh, 1090vs, 1067s, 1033s, 989w, 966w, 898w, 823m, 801sh, 759w, 741w, 622m, 589m, 527m and 418w, TGA: the material loses mass at room temperature; above 250 °C an exothermic mass loss occurred.

$[Zn_2(OH)\{NC_5H_4)C_7H_{14}\}_4][ClO_4]_3\cdot0.5H_2O$ 3. Zinc perchlorate (1.0 g, 2.69 mmol) was dissolved in water (3 ml) and treated with 1,7-bis(4-pyridyl)heptane (1.36 g, 5.35 mmol) in ethanol (3 ml). The resulting mixture became cloudy. On standing crystals formed which were admixed with amorphous material. The product was not homogenous and could not be isolated as a pure phase (Found: C, 56.5; H, 6.1; N, 7.4% $[Zn_2(OH)\{NC_5H_4)_2C_7H_{14}\}_4][ClO_4]_3\cdot0.5H_2O$ requires C, 55.4, H, 6.0, N, 7.6%). IR (KBr cm^{-1}): 1635sh, 1604sh, 1559m, 1509w, 1501sh, 1460w, 1419m, 1384w, 1371w, 1233sh, 1223w, 1110sh, 1091s, 995w, 943w, 873w, 844w, 817sh, 803m and 723w, TGA: the material loses mass at room temperature; above 175 °C an exothermic mass loss occurred.

Structure determination

Crystallographic data for structures **1**, **2** and **3** are shown in Table 6. Data were collected on a Nonius Kappa CCD area-detector diffractometer at the window of a rotating anode FR591 generator (Mo-Kα radiation, $\lambda = 0.71073$ Å) and controlled by the Collect software package.[17] Collected images were processed using Denzo[18] Data were corrected for absorption by using the empirical method employed in Sortav.[19] Structures **1** and **2** were solved using direct methods (SHELXS 97), **3** was solved *via* heavy atom Patterson interpretation (DIRDIF 96).[20,21] All structures were refined by full-matrix least-squares refinements on F^2 (SHELXL 97).[22]

Compound 1. The network has an additional non-crystallographic translation symmetry (approximate B-centering) which is not matched by the anion and water molecules.

Compound 2. Although the lattice matrix is apparently orthorhombic the structure could not be solved in either of the possible space groups. From comparison of R_{int} values (0.067 monoclinic, 0.125 orthorhombic) and from systematic absences a (pseudo-orthorhombic) monoclinic structure with space group $P2_1/c$ was suggested. The early stages of the refinement showed rather poor results leading to the assumption of pseudomerohedral twinning. The introduction of the twin law (1 0 0 0 −1 0 0 0 −1) reduced $R1$ from 31 to 8% (isotropic, all non-hydrogen atoms). The ratio between both twin components was calculated in the final refinement as 2 : 3. Ten restraints for chemically equivalent bonding and non-bonding distances were applied to refine the four possible orientations of the disordered Et_2O molecule.

Compound 3. Four data sets were collected at different temperatures although a solution in space group *Pnma* could only be found from the set collected at room temperature. As a result of a low quality diffraction pattern, the refinement of the structure is relatively poor. Refinement of the $(CH_2)_7$ chains and the pyridyl rings was possible by application of 930 distance restraints for chemically equivalent bonding and non-bonding C–C, C···C and C–N interactions in the four crystallographically independent ligands. However, high displacement parameters were obtained for the carbon atoms of the $(CH_2)_7$ units and the atoms in the centre of each chain must be kept isotropic. From this we conclude that the refined atomic positions for the alkyl chains represent the most likely out of a number of disordered conformations. Four out of five crystallographically independent perchlorate anions are disordered *via* a mirror plane making refinement possible with a rigid body model. The highest difference peaks remained around the central parts of the $(CH_2)_7$ chains and around the four disordered anions. No attempts were made to refine the hydrogen atoms of the water molecule or to investigate possible hydrogen bonds owing to the data quality.

CCDC reference number 186/1993.

See http://www.rsc.org/suppdata/dt/b0/b000566p/ for crystallographic files in .cif format.

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