DALTON
FULL PAPER

Novel three-dimensional networks cross-linked by two sets of hydrogen bonded frameworks based on 1-D $\{[M(H_2O)_4(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})\}_n$ (4,4′-dpdo = 4,4′-bipyridine dioxide; M = Co, Ni, Cu or Zn)

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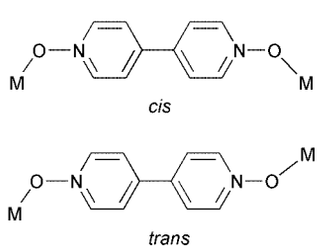
A series of novel coordination polymers $\{[M(H_2O)_4(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})\}_n$ (M = Co **1**, Ni **2**, Cu **3** or Zn **4**; 4,4′-dpdo = 4,4′-bipyridine dioxide) have been synthesized and characterized by X-ray diffraction analysis. They are isomorphous and crystallize in the triclinic system and space group $P\bar{1}$. dpdo bridges the metal centers to form a covalent chain. Two solvate dpdo link these chains through hydrogen bonding to form two sets of three-dimensional networks which are interwoven through a common conjunctive point $[M(H_2O)_4]^{2+}$, leading to three-dimensional open frameworks with triangular channels. ClO_4^- anions are included within these channels through weak C–H · · · O hydrogen bonding.

Introduction

Functional coordination polymers are of great interest due to their potential applications in many areas.[1–3] Considerable effort has been focused on the supramolecular networks assembled by covalent,[4] hydrogen bond[5] or other molecular interactions.[6] Many topologically promising architectures have been constructed from building blocks containing nitrogen donors, such as 4,4′-bipyridine,[7] pyrazine,[8] bis(4-pyridyl)-ethene,[9] 1,4-bis(4-pyridyl)benzene,[10] 2,4,6-tri(4-pyridyl)-1,3,5-triazine[11] and 4,4′-azobis(pyridine).[12] It is surprising that few coordination polymers based on bifunctional neutral ligands containing oxygen donors are documented.[13] We employ 4,4′-bipyridine dioxide (4,4′-dpdo) as building block, considering that it possesses a long bridging spacer and large cavities or channels can be expected. In addition, it is a good acceptor for hydrogen bonding compared with 4,4′-bipy, which may used to align the strands *via* non-covalent forces and assemble novel nanoporous materials from low-dimensional coordination polymers. Moreover, it has flexible *cis* and *trans* coordination modes (Scheme 1), so that novel topological structures can be



Scheme 1

achieved by modifying the relative orientation of 4,4′-dpdo. In the present work a series of novel coordination polymers $\{[M(H_2O)_4(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})\}_n$ (M = Co **1**, Ni **2**, Cu **3** or Zn **4**) are reported.

Experimental

Materials

4,4′-Bipyridine dioxide was prepared according to the literature method.[14] Other chemicals were analytical grade used without further purification.

Synthesis

$\{[Co(H_2O)_4(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})\}_n$ 1. A mixture of an aqueous solution of hydrated cobalt perchlorate (0.5 mmol, 0.183 g) and 4,4′-dpdo (1 mmol, 0.224 g) was heated with stirring to give a clear solution, which was filtered and the filtrate allowed to stand at room temperature. On evaporation, pink block-shaped single crystals were obtained after three days. Yield: 0.5 g, *ca*. 56%. Calc. for $C_{30}H_{32}Cl_2CoN_6O_{18}$: C, 40.27; H, 3.58; N, 9.39. Found: C, 40.28; H, 3.39; N, 8.81%.

$\{[Ni(H_2O)_4(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})\}_n$ 2. This compound was prepared as green block crystals using nickel perchlorate (0.5 mmol, 0.183 g) and 4,4′-dpdo (1 mmol, 0.224 g) in a way similar to that of for **1**. Yield: 0.53 g, *ca*. 60%. Calc. for $C_{30}H_{32}Cl_2N_6NiO_{18}$: C, 40.18; H, 3.68; N, 9.42. Found: C, 40.13; H, 3.73; N, 8.92%.

$\{[Cu(H_2O)_4(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})\}_n$ 3. This compound was prepared as green block crystals using copper perchlorate (0.5 mmol, 0.186 g) and 4,4′-dpdo (1 mmol, 0.224 g) in a way similar to that for **1**. Yield: 0.58 g, *ca*. 64%. Calc. for $C_{30}H_{32}Cl_2CuN_6O_{18}$: C, 39.57; H, 3.56; N, 9.34. Found: C, 39.14; H, 3.48; N, 9.02%.

$\{[Zn(H_2O)_4(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})\}_n$ 4. This compound was prepared as colorless block crystals using zinc perchlorate (0.5 mmol, 0.186 g) and 4,4′-dpdo (1 mmol, 0.224 g) in a way similar to that for **1**. Yield: 0.68 g, *ca*. 75%. Calc. for $C_{30}H_{32}Cl_2N_6O_{18}Zn$: C, 39.55; H, 3.55; N, 9.32. Found: C, 39.11; H, 3.55; N, 8.87%.

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Physical measurements

Elemental analyses of C, H, N were performed by a Carlo Erba 1106 instrument. IR spectra were recorded as KBr pellets on a Nicolet 750 FTIR spectrometer in the 400–4000 cm^{-1} region. The thermogravimetric analysis was made by an LT-1 model thermobalance under a N_2 atmosphere.

Crystallography

Pink (compound **1**), green (**2**, **3**) and colorless crystals of (**4**) were selected for the diffraction analysis. The data collections were performed on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ 0.71073 Å) at 293 K. The structures were solved by the direct method and refined by full matrix least squares based on F^2 using the SHELX 97 program.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were located from a Fourier difference map and refined with a rigid model. Other hydrogen atoms were placed in calculated positions. A few reflections with large differences between F_o^2 and F_c^2 and those of high angle ($2\theta \geq 46°$) for compound **2** were suppressed when making the refinement because of the poor quality crystal. The crystal data for compounds **1**–**4** are listed in Table 1, selected bond lengths and angles in Table 2.

CCDC reference number 186/2272.

See http://www.rsc.org/suppdata/dt/b0/b006142p/ for crystallographic files in .cif format.

Results and discussion

Description of the structure

Compound **1** contains one cobalt ion, four water molecules, three 4,4′-dpdo ligands and two ClO_4^- anions. One 4,4′-dpdo molecule functions as a bridge to connect two Co, leading to a 1-D covalently linked chain running along the [100] direction as shown in Fig. 1. Each Co^{2+} ion is located on a symmetry center and octahedrally coordinated with four aqua ligands [mean $Co–O_{aq}$ 2.083 Å] and two 4,4′-dpdo oxygen atoms [Co–O1 2.120(2) Å] in *trans* position. The N1–O1–Co1 bond angle is 113.12(13)°. Thus, a zigzag Co–4,4′-dpdo–Co chain with Co···Co separation 11.83 Å is formed.

These adjacent zigzag chains are further connected through hydrogen bonding [O5···O1c 2.849 Å, O5–H4···O1c 166.50°; symmetry code: c $-x-1$, $-y$, $-z$] between the bridging 4,4′-dpdo ligands and coordinated water molecules of neighboring chains, leading to a 2-D structural motif in the *a*–*b* plane as illustrated in Fig. 2. These 2-D sheets are linked into a 3-D network through double hydrogen bonding [O4···O3b 2.657 Å, O4–H1···O3b 166.75°; O5···O3 2.639 Å, O5–H3···O3 165.70°; symmetry code: b $x+1$, y, z] produced by a single hydroxyl group of each coordinated water molecule with one non-coordinated 4,4′-dpdo molecule, forming a large channel parallel to the [110] direction with Co···Co separation 16.0 Å (Fig. 3). Alternatively, the three-dimensional network may be regarded as a result of interweaving of two sets of sheets. One is that mentioned above (Fig. 2), and the other is generated by the uncoordinated 4,4′-dpdo and hydrated cobalt(II) ions through hydrogen bonding along the [111] direction as shown in Fig. 4. Meanwhile, these 2-D sheets (Fig. 2) are also connected by another solvated 4,4′-dpdo through single hydrogen bonding [O4···O2 2.617 Å, O4–H2···O2 157.41°] with coordinated water molecules and two terminal oxygen atoms along the [001] direction, leading to a one-dimensional channel with inter-metal connections 11.83 × 16.50 Å (Fig. 5).

An interesting feature is that the whole structure may be described as a three-dimensional net fused by two three-dimensional open frameworks as shown in Figs. 3 and 5. The two sets of networks cross over through a common conjunctive

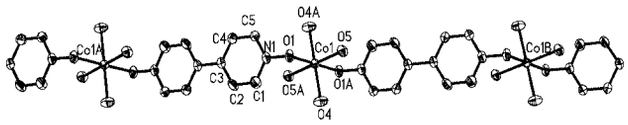

Fig. 1 An ORTEP[16] drawing of the zigzag chain in compound **1**.

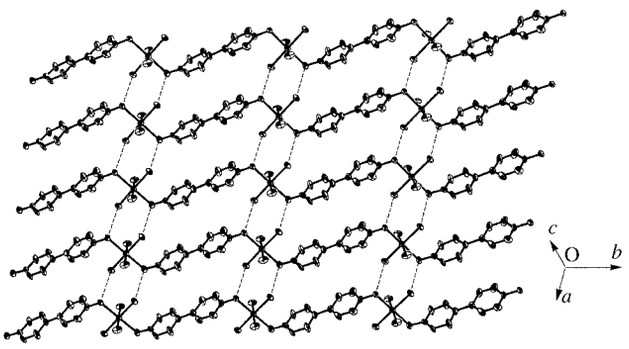

Fig. 2 Two-dimensional sheet of compound **1** formed through hydrogen bonding between bridging 4,4′-dpdo ligands and coordinated water molecules in the [110] plane.

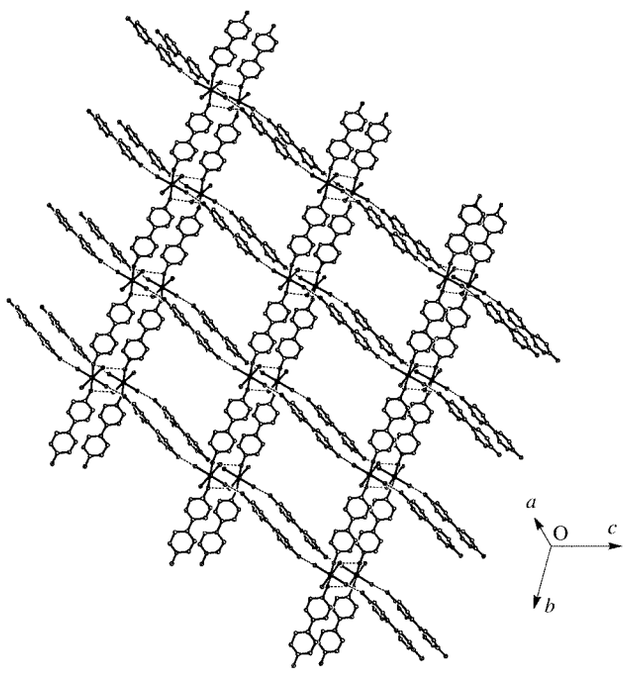

Fig. 3 3-D network in compound **1** generated through the covalent chain and one solvate dpdo ligand (N3) with a large channel parallel to the [110] direction.

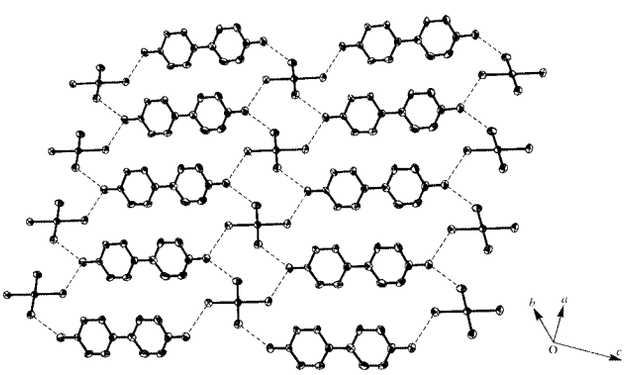

Fig. 4 Two-dimensional sheet in compound **1** formed through hydrogen bonding between one solvated 4,4′-dpdo ligand (N3) and coordinated water molecules in the [111] plane.

Table 1 Crystallographic data for compounds **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{30}H_{32}Cl_2CoN_6O_{18}$	$C_{30}H_{32}Cl_2N_6NiO_{18}$	$C_{30}H_{32}Cl_2CuN_6O_{18}$	$C_{30}H_{32}Cl_2ZnN_6O_{18}$
M	894.45	894.23	899.06	900.89
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	5.5207(3)	5.4646(2)	5.3540(2)	5.4888(2)
b/Å	11.8309(5)	11.8165(7)	11.8921(4)	11.8617(6)
c/Å	14.9809(6)	15.0889(9)	15.2705(6)	15.0146(6)
α/°	107.813(2)	108.759(2)	110.739(2)	108.161(2)
β/°	95.995(2)	95.400(3)	94.0425(19)	95.599(3)
γ/°	100.588(2)	100.163(3)	99.2350(18)	100.334(2)
V/Å^3	902.11(7)	896.12(8)	888.91(6)	901.39(7)
Z	1	1	1	1
μ/mm^{-1}	0.713	0.780	0.855	0.919
No. reflections				
Total	12296	8583	17201	12472
Unique	4299	2225	4157	4300
Observed	3338	1900	3381	3400
R [$I > 2\sigma(I)$]				
$R1$	0.0455	0.0859	0.0421	0.0502
$wR2$	0.1304	0.2063	0.1033	0.1304

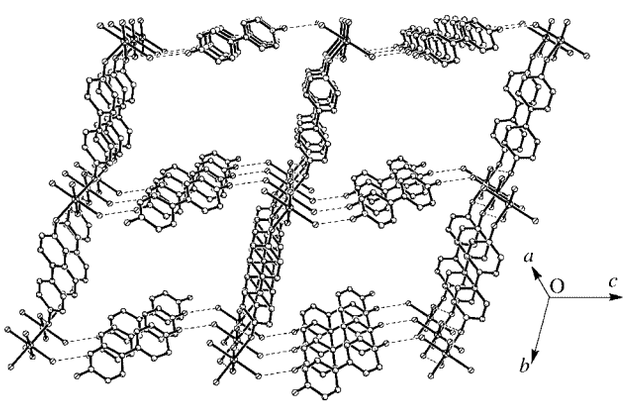

Fig. 5 3-D network in compound **1** generated through the covalent chain and one solvate dpdo ligand (N2) with a large channel parallel to the [100] direction.

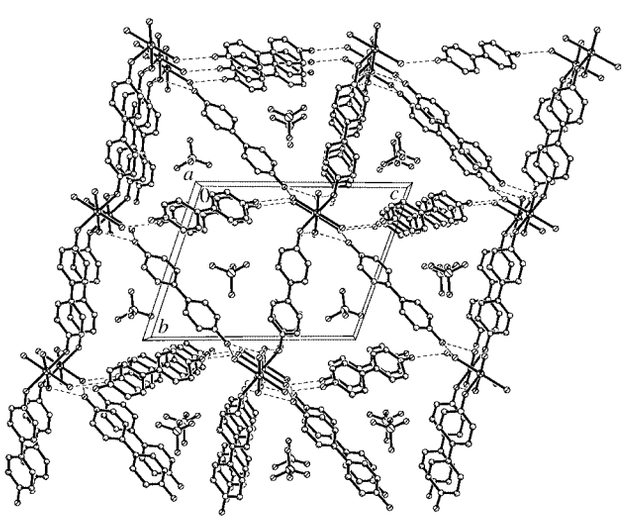

Fig. 6 A three-dimensional framework in compound **1** interweaved by two sets of networks (Figs. 3 and 5). ClO_4^- anions are included within these channels.

point $[Co(H_2O)_4]^{2+}$ to yield a triangular channel enclosed by three hydrated cobalt cations and three 4,4′-dpdo molecules which are located at vertexes and sides of triangular units, respectively. ClO_4^- anions are anchored within these triangular channels through weak C–H···O hydrogen bonding (Fig. 6). The C···O distances are within the range 3.287–3.373 Å.

Two pyridyl groups of three 4,4′-dpdo ligands are completely coplanar. No significant π–π stackings are found between these 4,4′-dpdo molecules. The four coordinated water molecules donate their eight hydrogen atoms to form hydrogen bonding

Table 2 Selected bond lengths [Å] and angles [°] for compounds **1**–**4**

1			
Co(1)–O(4)	2.052(2)	Co(1)–O(5)	2.113(2)
Co(1)–O(1)	2.120(2)	O(1)–N(1)	1.342(3)
O(2)–N(2)	1.315(3)	O(3)–N(3)	1.327(3)
O(4)–Co(1)–O(5)	85.19(9)	O(4)–Co(1)–O(5a)	94.81(9)
O(4)–Co(1)–O(1)	89.45(8)	O(5)–Co(1)–O(1)	86.74(7)
O(4)–Co(1)–O(1a)	90.55(8)	O(5)–Co(1)–O(1a)	93.26(7)
N(1)–O(1)–Co(1)	113.12(13)		
2			
Ni(1)–O(4)	2.019(6)	Ni(1)–O(5)	2.052(6)
Ni(1)–O(1)	2.093(6)	O(1)–N(1)	1.343(9)
O(2)–N(2)	1.305(10)	O(3)–N(3)	1.333(10)
O(4)–Ni(1)–O(5a)	95.5(3)	O(4)–Ni(1)–O(5)	84.5(3)
O(4)–Ni(1)–O(1a)	90.7(2)	O(5)–Ni(1)–O(1a)	93.2(2)
O(4)–Ni(1)–O(1)	89.3(2)	O(5)–Ni(1)–O(1)	86.8(2)
N(1)–O(1)–Ni(1)	112.9(5)		
3			
Cu(1)–O(4)	1.948(2)	Cu(1)–O(5)	1.967(2)
Cu(1)–O(1)	2.407(2)	O(1)–N(1)	1.334(2)
O(2)–N(2)	1.315(3)	O(3)–N(3)	1.327(3)
O(4)–Cu(1)–O(5a)	93.16(9)	O(4)–Cu(1)–O(5)	86.84(9)
O(4)–Cu(1)–O(1a)	92.70(8)	O(5)–Cu(1)–O(1a)	91.56(6)
O(4)–Cu(1)–O(1)	87.30(8)	O(5)–Cu(1)–O(1)	88.44(6)
N(1)–O(1)–Cu(1)	107.87(13)		
4			
Zn(1)–O(4)	2.041(2)	Zn(1)–O(5)	2.088(2)
Zn(1)–O(1)	2.150(2)	O(1)–N(1)	1.342(3)
O(2)–N(2)	1.308(4)	O(3)–N(3)	1.323(4)
O(4)–Zn(1)–O(5)	85.61(10)	O(4)–Zn(1)–O(5a)	94.39(10)
O(4)–Zn(1)–O(1a)	90.20(10)	O(5)–Zn(1)–O(1a)	92.62(8)
O(4)–Zn(1)–O(1)	89.80(10)	O(5)–Zn(1)–O(1)	87.38(8)
N(1)–O(1)–Zn(1)	113.10(15)		

Symmetry code: a $-x, -y, -z$.

Table 3 Hydrogen bonding interactions (bond angles [°]/bond lengths [Å]) in **1**–**4**

	1	**2**	**3**	**4**
O4–H2 · · · O2	157.41/2.617	159.77/2.626	151.11/2.584	154.12/2.618
O4–H1 · · · O3b	166.75/2.657	165.53/2.664	173.16/2.630	175.51/2.650
O5–H4 · · · O1c	166.50/2.849	165.55/2.856	163.43/2.736	165.68/2.828
O5–H3 · · · O3	165.70/2.639	165.48/2.601	163.68/2.613	160.95/2.629

Symmetry code: b $x + 1, y, z$; c $-x - 1, -y, -z$.

with 4,4′-dpdo molecules and each serves as a double hydrogen bonding acceptor.

Compounds **2**–**4** have similar structural motifs to those of **1**. It was noted that the Cu in **3** has a significantly elongated octahedral coordination environment. Four water molecules lie in the equatorial positions [Cu1–O4 1.948(2), Cu1–O5 1.967(2) Å] and two dpdo oxygen atoms occupy the axial positions [Cu1–O1 2.407(2) Å]. Their hydrogen bonding connections are listed in Table 3. As expected, these interactions are considerably strong, and consolidate the framework backbone. In addition, the metal–metal distances are significantly larger than those organized by 4,4′-bipy,[7b,17] such as in $[Zn(H_2O)_4(4,4'\text{-bipy})][NO_3]_2\cdot 4,4'\text{-bipy}$, $[Cu(4,4'\text{-bipy})(H_2O)_2(ClO_4)_2]\cdot 4,4'\text{-bipy}$ and $[Cu(4,4'\text{-bipy})(H_2O)_2(BF_4)_2]\cdot 4,4'\text{-bipy}$.

IR spectra

Compound **1** has two absorption peaks at 1195 and 1232 cm^{-1}. Compared with the IR spectrum of free 4,4′-dpdo, the ν(NO) band is shifted by 47 and 10 cm^{-1} to lower wavenumbers from 1242 cm^{-1}, which can be attributed to the coordinated and hydrogen bonded NO, respectively. It also indicates that the hydrogen bonding interactions are remarkably strong and efficient. A broad absorption band for ν(OH) appears at 3400 cm^{-1}, showing the presence of water molecules in the complex.

Thermogravimetric analysis

The TGA diagrams of the crystalline samples showed a weight loss in the temperature range 98–125 °C, corresponding to four water molecules (8.34, 7.64, 7.43 and 7.85% for **1**–**4**, respectively; calculated 8.05%). The anhydrous compounds began to decompose at 340, 330, 315 and 350 °C, respectively, indicating their higher thermal stability.

Crystal engineering assembled through 4,4′-bipy has intensively been investigated and many promising structures documented.[18] However, compounds based on the oxide derivative 4,4′-dpdo have rarely been investigated. Two studies were reported very recently, when we completed this work.[13] $\{[Sm(dpdo)_2(NO_3)_3]\cdot 0.5H_2O\}_n$ and $\{[Er_2(dpdo)_3(NO_3)_6]\cdot 2CH_3OH\}_n$ exist in a $CdSO_4$-like framework and a 2-D 4.8^2 topology, respectively; $[M(hfac)_2(dpdo)]_n$ (M = Cu or Co; hfac = hexafluoroacetylacetonate anion) has a chain structure. All the dpdo molecules participate in the coordination and no solvate ones are included in these compounds. In fact, the striking advantages of this ligand lie not only in its rigid longer spacer, but also in its strong ability to form hydrogen bonding. It is a good candidate to assemble organic–inorganic hybrid open frameworks involving hydrogen bonding. As presented herein, our compounds represent a new family of supramolecular species containing O,O′-donors, namely a three-dimensional net fused by two three-dimensional hydrogen-bonded open frameworks. We are currently in the process of constructing other novel frameworks based on this kind of ligand.

Acknowledgements

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