Synthesis and characterization of new coordination polymers generated from oxadiazole-containing ligand and inorganic M(II) [M = Cu(II), Co(II)] salts

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The coordination chemistry of the oxadiazole-containing ligand 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L5) with inorganic Cu(II) and Co(II) salts has been investigated. Three new coordination polymers (1–3) and one H-bonded polymer (4) were prepared by solution reactions. [Cu(L5)(H$_2$O)(SO$_4$)]·2(H$_2$O) (1) adopts a novel chiral three-dimensional motif with rhombus channels (ca. 6.04 × 14.09 Å). [Co(L5)(CH$_3$OH)$_2$(SO$_4$)](CH$_3$OH)(H$_2$O)$_{3.5}$ (2) features a novel two-dimensional network. [Cu(L5)$_2$(H$_2$O)$_2$](L5)$_2$(ClO$_4$)$_2$(CH$_3$OH)(H$_2$O) (3) features a two-dimensional rhombus-grid-type layer with inner grid cavity dimensions of 13.22 × 13.22 Å^2. Compound 4, however, is a molecular complex that is bound together by strong N ⋯ H–O and O ⋯ H–O hydrogen bonds into a three-dimensional H-bonded network.

Introduction

The directed supramolecular assembly of organic, inorganic, or organometallic modules into functional solids with, for example, pores of defined size, shape, and chemical environment, or specified three-dimensional structure is currently an active topic in solid state and supramolecular chemistry.[1–3] This is largely due to the range of potential applications in electrical, magnetic, and optical devices and porous materials.[4] In the long run, this line of research can lead to the prediction of the topology and/or the periodicity of crystalline lattices generated from the molecular structures of the participating small building blocks; one can anticipate that the relationship between polymeric structures and physical properties will eventually be elucidated as well. The most efficient approach to access this type of material is *via* the direct chemical combination of functional inorganic and organic components, as has been demonstrated by many previous studies.[1–3]

In general, the polymer topology generated from the self-assembly of inorganic (metal) species and organic ligands can be modified by the chemical structure of the ligands chosen, the coordination geometry preferred by the metal, the inorganic counter ions, the solvent system, and sometimes the metal-to-ligand ratio. Among these factors, the choice of organic ligand is certainly extremely important in determining the ultimate topology of the product. As we know, the organic ligands serve to tether the metal centers and to propagate the structural information expressed in metal coordination preferences throughout the extended structure; therefore properties of organic ligands such as coordination ability, length, geometry and relative orientation of the donor groups play a very important role in dictating polymer framework topology. So far, several types of bidentate rigid *N,N*′-bipyridine-type ligands, such as 4,4′-bipyridine (L1), 1,4-bis(4-pyridyl)ethyne (L2), 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (L3), 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L4) (Fig. 1)[5] and also related spacers have been utilized by us[5] as well as by numerous other research groups[1] to construct coordination polymers. All these rigid bidentate ligands have proven to be among the most important types of organic ligands for the design and construction of coordination polymers exhibiting remarkable
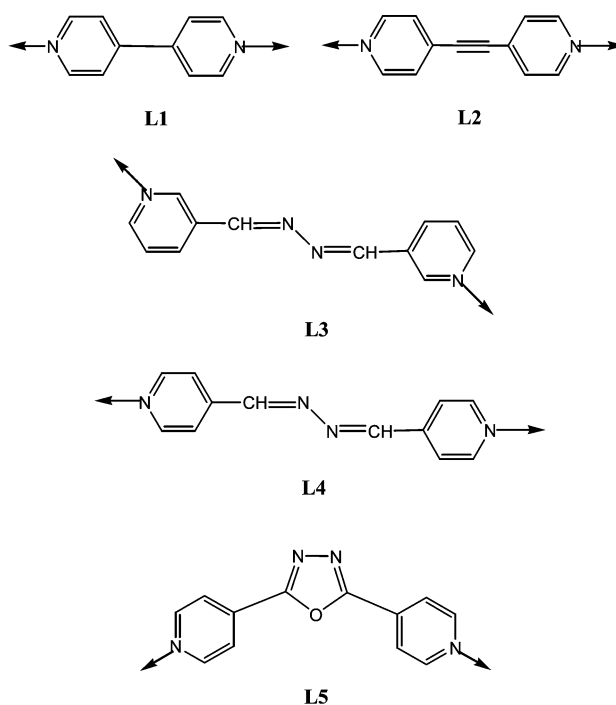

Fig. 1 Rigid organic *N,N*′-bipyridine-type ligands used in the construction of coordination polymer frameworks.

polymeric structural motifs depending on their relative different coordination orientations of nitrogen donors.

We have initiated a synthetic program for the preparation of heterocyclic ring-containing organic/inorganic coordination polymers with variable cavities or channels, in which the rigid (1,3,4)-oxadiazole containing organic ligands[6,7] such as 2,5-bis-(4-pyridyl)-1,3,4-oxadiazole (L5) (Fig. 1) and related species are chosen as the organic building blocks. So far, a series of new types of coordination polymers, some with open channels, have been obtained.[8] The specific geometry of this type of ligand (Fig. 1) may result in coordination polymers with novel network patterns not achievable by other rigid linear bidentate

ligands mentioned in previous papers.[1] Moreover, heteroatoms such as N and O with free electron pairs on the five-membered 1,3,4-oxadiazole ring could be considered as the potential active coordination sites or/and hydrogen bond acceptors to expand polymeric frameworks with coordinative covalent bonds or/and hydrogen bonding interactions.

Herein, we wish to report three new coordination polymers, namely $[Cu(L5)(H_2O)(SO_4)]\cdot2(H_2O)$ (**1**), $[Co(L5)(CH_3OH)_2(SO_4)](CH_3OH)(H_2O)_{3.5}$ (**2**), $[Cu(L5)_2(H_2O)_2](L5)_2(ClO_4)_2(CH_3OH)(H_2O)$ (**3**) and one H-bonded polymer, namely $[Cu(L5)_2(H_2O)_3(ClO_4)](ClO_4)(H_2O)$ (**4**), generated from (1,3,4)-oxadiazole bridged ligand L5 and inorganic Cu(II) and Co(II) salts with novel polymeric motifs.

Experimental

Materials and methods

$Cu(ClO_4)_2\cdot xH_2O$, $CoSO_4\cdot7H_2O$ and $Cu(SO_4)\cdot5H_2O$ (Acros) were used as obtained without further purification. 2,5-Bis(4-pyridyl)-1,3,4-oxadiazole (L5) was prepared according to the literature method.[9] Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400–4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 2400 analyzer.

CAUTION! One of the crystallization procedures involves $Cu(ClO_4)_2$, which is an oxidizer.

Synthesis

$[Cu(L5)(H_2O)(SO_4)]\cdot2(H_2O)$ (1). A solution of L5 (44.8 mg, 0.20 mmol) in MeOH (8 mL) was layered onto a solution of $Cu(SO_4)\cdot5H_2O$ (25 mg, 0.10 mmol) in H_2O (8 mL). The solutions were left for around three days at room temperature, and blue crystals were obtained. Yield, 84%. Anal. calc. for $CuC_{12}H_{14}O_8N_4S$ (**1**): C, 32.91; H, 3.20; N, 12.79. Found: C, 33.10; H, 3.33; N, 12.90%. IR (KBr, cm^{-1}): 3450(s), 3140(s), 1630(s), 1577(m), 1542(s), 1489(s), 1440(s), 1227(s), 1190(s), 1172(s), 1099(s), 1062(w), 1020(s), 990(w), 965(s), 844(s), 730(s), 700(s).

$[Co(L5)(CH_3OH)_2(SO_4)](CH_3OH)(H_2O)_{3.5}$ (2). A solution of L5 (33.6 mg, 0.15 mmol) in CH_3OH (10 mL) was mixed with a solution of $Co(SO_4)\cdot7H_2O$ (28.1 mg, 0.10 mmol) in H_2O. The solutions were left for about a week at room temperature, and pink crystals were obtained. Yield, 61%. No satisfactory elemental analysis results were obtained for compound **2**, probably due to the badly disordered guest molecules and its unstable nature. Anal. calc. for $CoC_{15}H_{27}N_4O_{11.5}S$ (**2**): C, 33.43; H, 5.01; N, 10.40. Found: C, 34.70; H, 3.55; N, 11.54%. IR (KBr, cm^{-1}): 3250(s), 1615(s), 1567(s), 1538(s), 1484(s), 1423(s), 1334(m), 1179(m), 1222(m), 1164(s), 1140(s), 1098(s), 1055(s), 1013(m), 990(w), 840(m), 726(s), 710(s).

$[Cu(L5)_2(H_2O)_2](L5)_2(ClO_4)_2(CH_3OH)(H_2O)$ (3) and $[Cu(L5)_2(H_2O)_3(ClO_4)](ClO_4)(H_2O)$ (4). A solution of L5 (44.8 mg, 0.2 mmol) in CH_3OH (8 mL) was layered onto a solution of $Cu(ClO_4)_2\cdot xH_2O$ (52.6 mg, 0.20 mmol) in H_2O. The solutions were left for about one month at room temperature, and blue crystals of **3** were obtained. Yield, 78%. Anal. calc. for $CuC_{49}H_{42}N_{16}O_{16}Cl_2$ (**3**): C, 47.21; H, 3.37; N, 17.99. Found: C, 47.19; H, 3.39; N, 17.89%. IR (KBr, cm^{-1}): 3500(s), 3150(m), 1627(s), 1573(s), 1541(s), 1494(s), 1488(s), 1440(s), 1418(s), 1375(w), 1338(w), 1280(m), 1230(m), 1149(s), 1115(s), 1087(s), 1027(w), 1005(w), 968(w), 844(s), 823(m), 742(w), 727(s), 708(s). The above solution was left to stand at room temperature for about three weeks, affording **4** as green crystals, compound **3** disappeared gradually at the same time. Yield, 47%. Anal. calc. for $CuC_{24}H_{24}Cl_2N_8O_{14}$ (**4**): C, 36.78; H, 3.07;

N, 14.30. Found: C, 36.76; H, 3.05; N, 14.28%. IR (KBr, cm^{-1}): 3500(s), 3150(m), 1627(s), 1573(s), 1541(s), 1494(s), 1488(s), 1440(s), 1418(s), 1375(w), 1338(w), 1280(m), 1230(m), 1149(s), 1115(s), 1087(s), 1027(w), 1005(w), 968(w), 844(s), 823(m), 742(w), 727(s), 708(s).

Crystallography

Suitable single crystals of **1**–**4** were selected and mounted onto thin glass fibers. X-Ray intensity data were measured at 293 K for **1**, 190 K for **2** and 150 K for **3** and **4** on a Bruker SMART APEX CCD-based diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The raw frame data for **1**–**4** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[10] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[10] There was no evidence of crystal decay during data collection for any compound. The final unit cell parameters were determined by the least-squares refinement of all reflections from each data set with $I > 5\sigma(I)$ (8102 for **1**, 3454 for **2**, 5612 for **3**, 9426 for **4**). Space groups were determined by a combination of systematic absences in the intensity data, intensity statistics and the successful solution and refinement of the structures. All structures were solved by direct methods followed by difference Fourier synthesis, and refined against F^2 by the full-matrix least squares technique, using SHELX.[10]

Compound **1** crystallized in the chiral space group $P2_12_12_1$. All atoms reside on positions of general crystallographic symmetry. The asymmetric contains the Cu atom, one $C_{12}H_8N_4O$ ligand, one water molecule bound to Cu, and the sulfate counterion. Two additional water molecules of crystallization were identified within the three-dimensional framework. One refined as fully occupied, the other is disordered over three sites with occupancies of 0.25, 0.25, and 0.5. The occupation factors for this water were initially refined but were eventually fixed at the aforementioned values. H atoms for the disordered waters were not located or calculated. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogens bound to carbon were placed in idealized positions and included as riding atoms. The hydrogen atoms attached to the framework water were located and refined with isotropic displacement parameters subject to an O–H distance restraint of 0.84 Å.

Compound **2** crystallized in the space group $I2/a$ (non-standard setting of $C2/c$). Two crystallographically independent Co atoms are present in the asymmetric unit, both of which reside on centers of symmetry; all other atoms are on general positions. All atoms of the infinite two-dimensional framework were readily located and refined. A methanol molecule and a water molecule which are strongly hydrogen bonded to the framework were also located. However, a region of diffuse electron density is located in the intraframework channels which run along [001], and was modeled as water molecules disordered over four positions. The site occupation factors for these guest molecules were initially allowed to refine but were eventually set at reasonable values. Hydrogen atoms for these species were not located or calculated. Eventually all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bound to carbon were placed in geometrically idealized positions and included as riding atoms. The located methanol and aquo hydrogens were refined with isotropic displacement parameters subject to an O–H = 0.84(2) Å distance restraint.

Compound **3** adopts the space group $P2_1/n$. The Cu atom resides on a center of symmetry; all other atoms are on positions of general crystallographic symmetry. The asymmetric unit contains the Cu atom, one coordinated L5 ligand and a coordinated water molecule, one uncoordinated L5 ligand, one ClO_4^- anion, and half a methanol and half a water molecule of crystallization. The MeOH/H_2O guest molecules

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

	1	**2**	**3**	**4**
Empirical formula	$CuC_{12}H_{14}N_4O_8S$	$CoC_{15}H_{27}N_4O_{11.5}S$	$CuC_{49}H_{42}Cl_2N_{16}O_{16}$	$CuC_{24}H_{24}Cl_2N_8O_{14}$
FW	437.87	538.40	1245.43	782.95
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
$a/Å$	5.5067(3)	24.1596(18)	12.4658(7)	7.3841(3)
$b/Å$	10.5119(5)	12.5832(9)	12.1314(7)	11.0490(5)
$c/Å$	28.1794(14)	14.9739(11)	17.8301(10)	20.2981(9)
$a/°$	90	90	90	94.2320(10)
$β/°$	90	91.791(2)	100.1820(10)	91.4680(10)
$γ/°$	90	90	90	109.0700(10)
$V/Å^3$	1631.19(14)	4549.6(6)	2653.9(3)	1558.73(12)
Space group	$P2_12_12_1$	$I2/a$	$P2_1/n$	$P\bar{1}$
Z	4	8	2	2
$\mu(Mo\text{-}K\alpha)/mm^{-1}$	1.520	0.911	0.600	0.954
T/K	293	190	150	150
Data/restraints/parameters	4065/2/262	4657/5/325	5421/3/405	6350/8/511
$R1$; $wR2$ indices $[I > 2\sigma(I)]$	0.0357; 0.0844	0.0504; 0.0894	0.0455; 0.1109	0.0403; 0.0889

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

are disordered over two closely spaced positions in a 50/50 ratio. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms attached to carbons and the guest molecules were placed in geometrically idealized positions and included as riding atoms. Hydrogen atoms on the coordinated water were located in the difference map and refined with isotropic displacement parameters subject to an O–H = 0.84(2) Å distance restraint.

Compound **4** crystallized in the space group $P\bar{1}$. All atoms are on positions of general crystallographic symmetry. One of the two ClO_4^- counterions is disordered over two closely spaced positions in a 62/38 ratio. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms attached to carbon were placed in geometrically idealized positions and included as riding atoms. Aquo hydrogens were located in the difference maps and refined with isotropic displacement parameters subject to an O–H = 0.84(2) Å distance restraint. Crystal data, data collection parameters, and refinement statistics for **1–4** are listed in Table 1. Relevant interatomic bond distances and bond angles for **1–4** are given in Tables 2–4 and 6.

CCDC reference numbers 193468–193471.

See http://www.rsc.org/suppdata/dt/b2/b210811a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Ligand

Ligand L5 was chosen as a simple yet interesting N,N'-bipyridine-type spacer to study due to its presumed conformational flexibility. Compared to L1–L4 (Fig. 1), L5 has the distinct different geometry and orientations of its coordination sites. This ligand has a rigid 144° angle between the central oxadiazole ring and the two 4-pyridyl N-donors. The crooked geometry of this type of ligand might bind metal ions access to polymeric frameworks with novel topology that are not achievable by other types of rigid N,N'-bipyridine ligands. In addition, heteroatoms such as N and O on the (1,3,4)-oxadiazole ring could be considered as potential hydrogen bond acceptors to expand polymeric frameworks with hydrogen bonding interactions. L5 is very soluble in common polar organic solvents such as CH_2Cl_2, $CHCl_3$, THF, CH_3OH and C_2H_5OH, which make crystallization with inorganic metal salts in solution easy.

Structural analysis

Structural analysis of $[Cu(L5)(H_2O)(SO_4)]\cdot2(H_2O)$ (1). Crystallization of L5 with $Cu(SO_4)\cdot5H_2O$ in $CH_3OH–H_2O$ at

room temperature afforded the infinite three-dimensional polymeric compound (**1**) in 84% yield. The metal : ligand ratio is 1 : 2. Crystals of **1** are air stable and can retain their structural integrity at room temperature for a considerable length of time. Single crystal analysis revealed, as shown in Fig. 2, the structure of **1** is constructed from six-coordinate copper sites with a distorted octahedral geometry which are linked into a novel three-dimensional network through crooked L5 ligands. The coordination sphere of Cu(II) is defined by two pyridyl nitrogen donors from each of two L5 ligands, three oxygen donors from three sulfate counter ions, and one aquo oxygen donor. The coordination geometry may be described as a basal plane consisting of three sulfate oxygen [O(3), O(4) and O(5)] and one aquo oxygen O(2) donors with Cu–O bond lengths of 1.9690(18)–2.625(3) Å (Table 2). The long Cu–O(5) bond distance of 2.625(3) Å is indicative of a weak Cu–sulfate interaction. An even longer $Cu–O_{sulfate}$ bond distance [$Cu–O_{sulfate} = 2.673(7)$ Å] has been found in the polymeric compound $[Cu(4,4'\text{-bipyridine})(H_2O)_3(SO_4)]\cdot2H_2O$.[11] It is worth noting that two terminal pyridine rings and a bridged 1,3,4-oxadiazole ring in L5 herein are exactly coplanar.
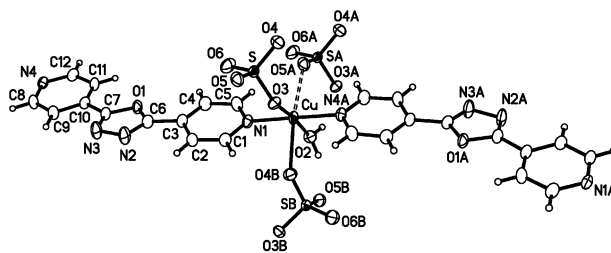

Fig. 2 Displacement ellipsoid plot of the Cu environment in **1** (50% probability).

In the solid state, the one-dimensional sinusoidal $\{Cu(L5)\}_n$ chains extend along the crystallographic c axis. These chains are further crossed-linked to each other through zigzag $Cu_3–SO_4$ linkages into a novel chiral three-dimensional network (Fig. 3). Large and small channels are present resulting from the crooked geometry of the ligand. Guest water molecules are located in the large oval-shaped channels (crystallographic dimensions, 6.04 × 14.09 Å^2) (Fig. 3). TGA shows that water guest molecules were released in the temperature range of 80–120 °C. The framework of **1** is stable up to around 180 °C, which is confirmed by XRPD. It is worth pointing out that compound **1** crystallizes in a chiral space group $P2_12_12_1$. So far, there are several approaches to produce chiral systems, such as starting with achiral components to construct chiral structures,[12] the use of chiral ligands in molecular squares[13] or
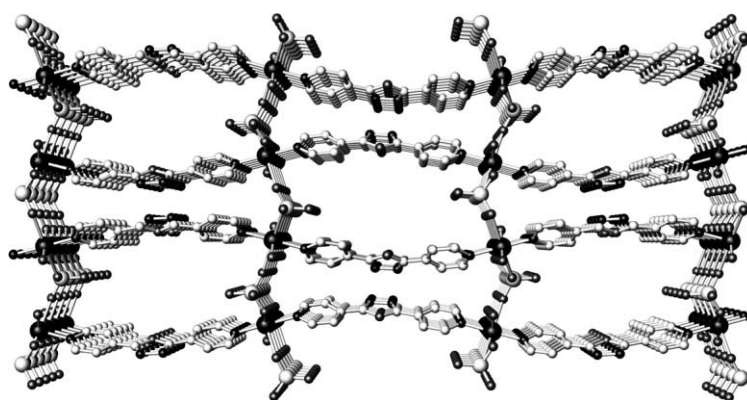
Fig. 3 Open chiral three-dimensional network of **1** (view down the *a* axis). Cu and N atoms are shown as large and small black circles, respectively. S and C atoms are shown as large and small open circles, respectively. O atoms are shown as gray circles. H atoms and guest molecules in the channels are omitted for clarity.

Table 2 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **1**

Cu–N(1)	2.013(2)	Cu–N(4)#1	2.036(2)
Cu–O(3)	1.9690(18)	Cu–O(2)	1.979(2)
Cu–O(4)#2	2.382(2)		
O(3)–Cu–O(2)	173.49(9)	O(3)–Cu–N(1)	89.47(9)
O(2)–Cu–N(1)	89.20(9)	O(3)–Cu–N(4)#1	90.26(9)
O(2)–Cu–N(4)#1	90.99(10)	N(1)–Cu–N(4)#1	179.32(11)
O(3)–Cu–O(4)#2	87.66(8)	O(2)–Cu–O(4)#2	85.97(8)
N(1)–Cu–O(4)#2	90.03(9)	N(4)#1–Cu–O(4)	89.33(9)

Symmetry transformations used to generate equivalent atoms: #1 −*x* + 3/2, −*y* + 1, *z* + 1/2; #2 −*x* + 1, *y* − 1/2, −*z* + 1/2; #3 −*x* + 3/2, −*y* + 1, *z* − 1/2; #4 −*x* + 1, *y* + 1/2, −*z* + 1/2.

Table 4 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **3**

Cu–N(1)	2.0282(18)	Cu–N(4)#2	2.0726(18)
Cu–O(3)	2.5027(18)		
N(1)–Cu–N(1)#1	180.0	N(1)–Cu–N(4)#2	89.12(7)
N(4)#2–Cu–N(4)#3	180.0	N(1)–Cu–O(3)	88.00(7)
N(4)–Cu–O(3)	88.38(7)		

Symmetry transformations used to generate equivalent atoms: #1 −*x*, −*y*, −*z* + 1; #2 −*x* + 1/2, *y* − 1/2, −*z* + 1/2; #3 *x* − 1/2, −*y* + 1/2, *z* + 1/2; #4 −*x* + 1/2, *y* + 1/2, −*z* + 1/2.

extended square-networks[14] and the use of helical chains or helical frameworks.[15–18] The result reported herein extends the concept of chiral polymeric complexes significantly, assembled by using achiral crooked ligands, to non-interpenetrating three-dimensional structures. We believe such completely stereospecific self-assembly of uncoordinated heteroatoms-containing organic spacers and inorganic metal ions without any chiral auxiliary in self-assembly would offer a very useful tool for chiral recognition applications.

Structural analysis of [Co(L5)(CH₃OH)₂(SO₄)](CH₃OH)-(H₂O)₃.₅ (2).

Structural analysis of [Co(L5)(CH$_3$OH)$_2$(SO$_4$)](CH$_3$OH)-(H$_2$O)$_{3.5}$ (2). When a solution of L5 in methanol was treated with Co(SO$_4$)·7H$_2$O in the same solvent, using a metal-to-ligand ratio of 1 : 1.5, compound **2** was obtained as a pink crystalline polymeric compound displaying two-dimensional architecture. Compound **2** loses guest solvent molecules quickly and is not stable outside of the mother liquor. As shown in Fig. 4, there are two crystallographically independent Co(II) centers present in the asymmetric unit, both of which reside on centers of symmetry. The first kind of Co(II) atom lies in a
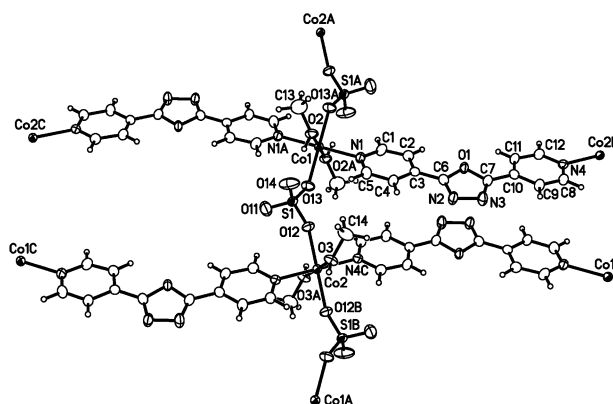

Fig. 4 Displacement ellipsoid plot of the environment of Co(1) and Co(2) in **2** (50% probability).

distorted octahedral coordination environment. The geometry about Co(1) sites is defined by two *trans* nitrogen donors from two L5 ligands and two sulfate oxygen groups in the equatorial plane, with two solvent methanol co-ligands in the axial posi-

Table 3 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **2**

Co(1)–O(13)	2.061(3)	Co(1)–O(2)	2.097(3)
Co(1)–N(1)	2.176(3)	Co(2)–O(12)	2.081(3)
Co(2)–O(3)	2.082(3)	Co(2)–N(4)#3	2.145(3)
O(13)–Co(1)–O(13)#1	180.0	O(13)–Co(1)–O(2)	89.80(10)
O(2)–Co(1)–O(2)#1	180.0	O(13)–Co(1)–N(1)	86.87(11)
O(2)–Co(1)–N(1)	89.02(11)	O(13)–Co(1)–N(1)#1	93.13(11)
N(1)–Co(1)–N(1)	180.0	O(12)#2–Co(2)–O(12)	180.00(14)
O(12)#2–Co(2)–O(3)	90.47(11)	O(12)#2–Co(2)–O(3)#2	90.47(11)
O(3)–Co(2)–O(3)#2	180.0	O(12)#2–Co(2)–N(4)	85.43(11)
O(3)–Co(2)–N(4)#3	91.55(11)	O(12)#2–Co(2)–N(4)	94.57(11)
O(3)–Co(2)–N(4)#4	88.45(11)	N(4)#3–Co(2)–N(4)	180.000(1)

Symmetry transformations used to generate equivalent atoms: #1 −*x* + 1, −*y*, −*z* + 1; #2 −*x* + 1, −*y* + 1, −*z* + 1; #3 *x* + 1/2, *y* + 1/2, *z* + 1/2; #4 −*x* + 1/2, −*y* + 1/2, −*z* + 1/2; #5 *x* − 1/2, *y* − 1/2, *z* − 1/2; #6 −*x* + 3/2, *y*, −*z* + 1.
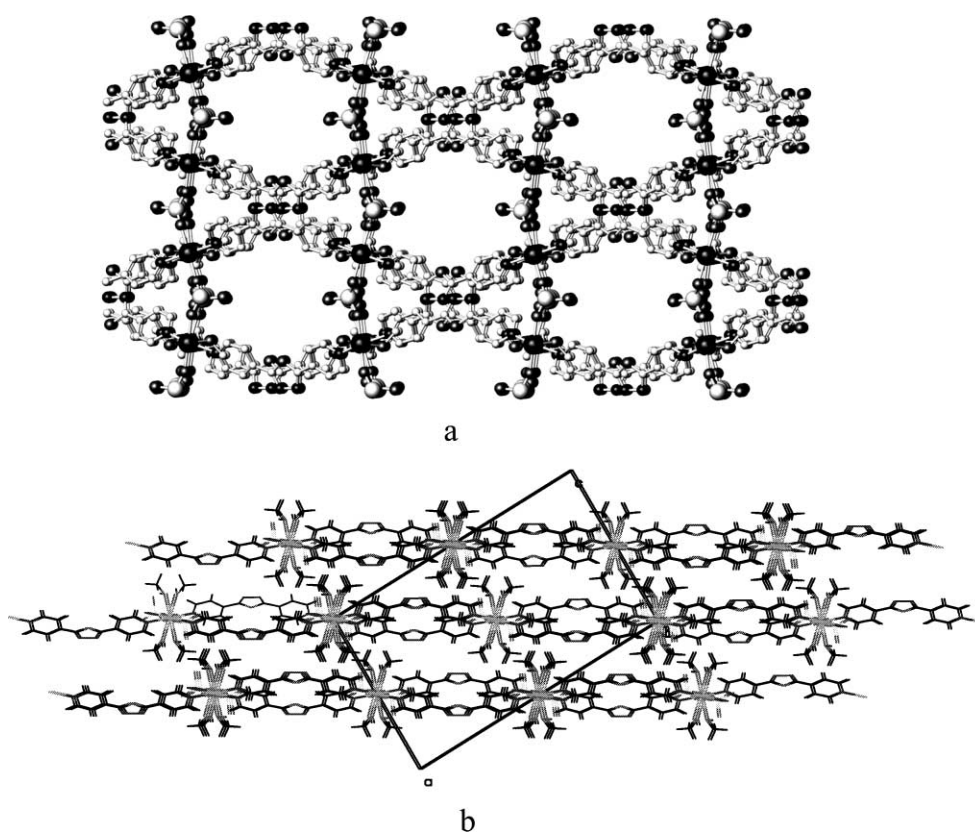
a

b

Fig. 5 (a) Two-dimensional network of **2** (viewed down the *c* axis). (b) Stacking of three layers. Co and N atoms are shown as large and small black circles, respectively. S and C atoms are shown as large and small open circles, respectively. O atoms are shown as gray circles. H atoms and guest molecules in the channels are omitted for clarity.

tions. The Co(1)–N(1) distance of 2.176(3) Å (Table 3), is comparable to the corresponding Co–N bond lengths found in related compounds such as $[Co(NO_3)_2(1,2$-bis(4-pyridyl)-ethane)$_{1.5}]_n$,[19] $Co(NO_3)_2(4,4'$-bpy)$_{1.5}]_n$,[19] and $Co(NO_3)_2(C_{12}$-$N_2H_8)_{1.5}\cdot MeOH)$.[5] The axial Co(1)–O(2) distance of 2.097(3) Å is slightly longer than the equatorial Co(1)–O distance, whereas the Co(1)–O(13) distance is 2.061(3) Å. The second kind of Co(II) centers adopt a similar distorted octahedral coordination sphere. The Co(2)–N(4) bond length of 2.145(3) Å is slightly shorter than that in the Co(1) coordination sphere. Almost the same axial and equatorial Co(2)–O bond distances [Co(2)–O(12) = 2.081(3) and Co(2)–O(3) = 2.082(3) Å] have been found in the Co(2) coordination environment.

In the solid state, the Co(1) and Co(2) centers are connected to each other by L5 ligands through both terminal N-donors into zigzag chains along the crystallographic [101] direction. The intra- and inter-chain Co(1) ··· Co(2) distances are 14.012(3) and 6.292(3) Å, respectively. These one-dimensional chains are further linked together by bridged sulfate counter ions through zigzag Co(2)–O(12)–S(1)–O(13)–Co(1) linkages along the crystallographic [010] direction into a novel two-dimensional net parallel to the crystallographic [10–1] plane (Fig. 5). These two-dimensional nets further stack together along the crystallographic *c* axis to produce large rhombic channels (crystallographic dimensions, 6.29 × 14.01 Å²), in which methanol and water guest molecules are located. The shortest interlayer Co(1) ··· Co(2) contact is 7.487(3) Å. Two terminal pyridine rings and bridged 1,3,4-oxadiazole ring are also exactly coplanar, which is similar to compound **1**.

Structural analysis of [Cu(L5)₂(H₂O)₂](L5)₂(ClO₄)₂(CH₃OH)-(H₂O) (3) and [Cu(L5)₂(H₂O)₃(ClO₄)](ClO₄)(H₂O) (4). When a solution of L5 in methanol was treated with $Cu(ClO_4)_2\cdot xH_2O$ in water, compounds **3** and **4** were obtained successively as deep-blue and green crystalline solids, respectively. Compounds **3** and **4** are not air stable. As shown in Fig. 6, the Cu(II) centers in
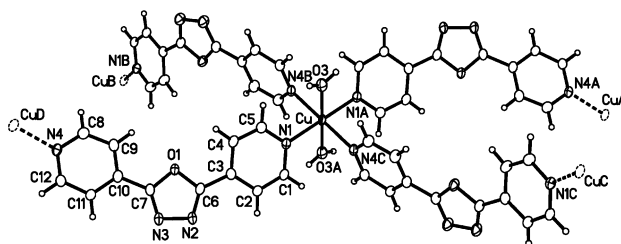

Fig. 6 Displacement ellipsoid plot of the Cu environment in **3** (50% probability).

3 lie in the usual 4 + 2 distorted octahedral $\{CuN_4O_2\}$ environment with the axial positions occupied by two aquo oxygen donors [Cu–O(3) = 2.5027(18) Å, Table 4] and the equatorial positions occupied by four *trans* nitrogen donors from four L5 ligands [Cu–N(1) = 2.0282(18) and Cu–N(4) = 2.0726(18) Å].

Compared to **1** and **2**, two terminal pyridine rings and the bridged 1,3,4-oxadiazole ring in L5 are no longer in the same plane. The pyridine rings of L5 in **3** are found to be rotated around 20° from coplanarity relative to each other. In the solid state, the polymeric structure of **3** generated from such coordination consists of two-dimensional rhombus-grid-type layers, in this case, with inner grid cavity dimensions of 13.22 × 13.22 Å², which is larger than that generated from 4,4′-bipyridine with similar transition metals,[20] but smaller than that generated from longer rigid bidentate ligands 1,4-bis(4-pyridyl)butadiyne, 9,9-diethyl-2,7-bis(4-pyridylethynyl)fluorine and 9,9-bis[(*S*)-2-methylbutyl]-2,7-bis(4-pyridylethynyl)fluorine.[21] The rhombus grid layers are parallel to the crystallographic [011] plane and stack together to generate channels along the crystallographic [100] direction (Fig. 7). Interestingly, the channels contain π–π stacked pairs of uncoordinated L5 ligands which interact with coordinated L5 ligands in a face-to-face fashion in the framework ($d_{\pi-\pi}$ = 3.48 Å).[22]

Table 5 Hydrogen bonds for **3** (Å and °)

D–H $\cdots$ A	d(D–H)/Å	d(H $\cdots$ A)/Å	d(D $\cdots$ A)/Å	$\angle$(DHA)/°
O(3)–H(3A) $\cdots$ N(5)#5	0.824(18)	2.002(19)	2.804(3)	164(3)
O(3)–H(3B) $\cdots$ O(2S)#6	0.827(19)	2.53(4)	3.035(7)	120(3)
O(3)–H(3B) $\cdots$ N(6)	0.827(19)	2.42(3)	3.155(3)	148(4)
O(1S)–H(1S) $\cdots$ O(13)	0.84	2.06	2.854(7)	158.2
O(2S)–H(2SA) $\cdots$ O(13)	0.85	2.32	3.167(8)	179.7

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z + 1$; #2 $-x + 1/2, y - 1/2, -z + 1/2$; #3 $x - 1/2, -y + 1/2, z + 1/2$; #4 $-x + 1/2, y + 1/2, -z + 1/2$; #5 $-x + 1/2, y - 1/2, -z + 3/2$; #6 $x - 1, y, z$.
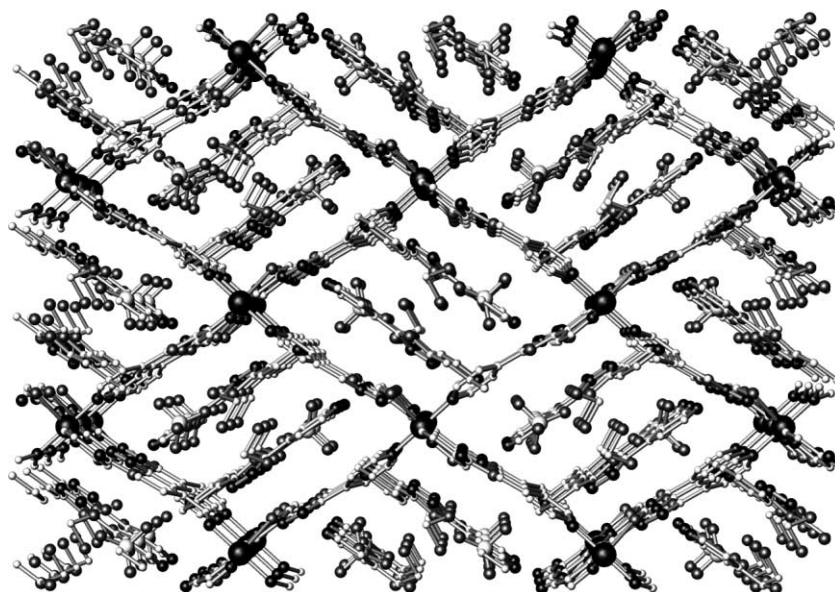

Fig. 7 Two-dimensional network of **3** with uncoordinated L5 ligands, ClO_4^- counter ions and MeOH and H_2O guest in the channels (viewed down the a axis). Cu and N atoms are shown as large and small black circles, respectively. Cl and C atoms are shown as large and small open circles, respectively. O atoms are shown as gray circles. H atoms are omitted for clarity.

Table 6 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **4**

Cu–O(4)	1.9487(19)	Cu–O(5)	1.954(2)
Cu–N(8)	2.020(2)	Cu–N(1)	2.032(2)
Cu–O(3)	2.362(2)	Cu–O(11)	2.4651(18)
O(4)–Cu–O(5)	176.94(9)	O(4)–Cu–N(8)	88.75(8)
O(5)–Cu–N(8)	92.52(8)	O(5)–Cu–N(1)	90.41(8)
N(8)–Cu–N(1)	176.91(8)	O(4)–Cu–O(3)	93.57(8)
O(5)–Cu–O(3)	89.17(8)	N(8)–Cu–O(3)	91.88(8)
N(1)–Cu–O(3)	89.15(8)	O(4)–Cu–O(11)	93.39(7)
O(5)–Cu–O(11)	83.87(8)	N(8)–Cu–O(11)	88.61(7)
N(1)–Cu–O(11)	90.72(7)	O(3)–Cu–O(11)	173.04(7)

A few examples have shown that the organic ligands involved in the nucleation process use both coordination and π–π interactions to construct the framework, but in most of cases, free (uncoordinated) organic ligands have not been involved.[23] We have reported a coordination polymer, namely [Cd(NO$_3$)$_2$-(L3)$_{1.5}$·0.5(L1)]$_n$,[24] in which the free L3 organic spacers play a critical role in the formation of a π–π stacking system and, moreover, serve as the agent which allows π–π interactions to expand the dimensionality of the compound from two to three. Herein, however, the free L5 ligands serve as the templating agent instead of extending the dimensionality of the framework. In addition, these free ligands are also held to the framework by C–H $\cdots$ N and O–H $\cdots$ N hydrogen bonding interactions.[25] The corresponding data for those hydrogen bonds are shown in Table 5. Besides free L5 ligands, uncoordinated ClO_4^- counter ions and also disordered methanol and water guest molecules are encapsulated in the grid channels, which is quite common for coordination polymers containing void spaces.[1]

Compared to **3**, the Cu(II) centers in **4** also lie in a pseudo-octahedral coordination environment, but with different coordination atoms. As shown in Fig. 8, the coordination sphere is defined by two pyridyl nitrogen donors from each of the two L5 ligands, three aquo oxygen donors, and the oxygen of a ClO_4^- counter ion. The basal plane consisting of the *trans* nitrogen donors N(1) and N(8), with Cu–N distances of 2.032(2) and 2.020(2) Å (Table 6), respectively, and the aquo ligands associated with O(4) and O(5), with Cu–O bond lengths of 1.9487(19) and 1.954(2) Å, respectively. The axial positions are occupied by the aquo ligand O(3) and the oxygen-donor O(6) of the ClO_4^- anion. The Cu–O(3) distance of 2.362(2) Å is significantly longer than the equatorial Cu–O distance, wheres the Cu–O(11) bond length of 2.4651(18) Å is indicative of a weak Cu–ClO$_4^-$ interaction.
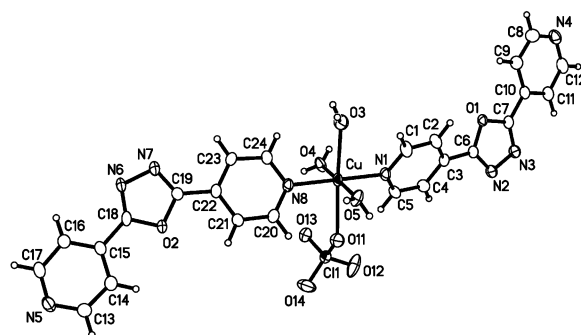

Fig. 8 Displacement ellipsoid plot of the Cu environment in **4** (50% probability).
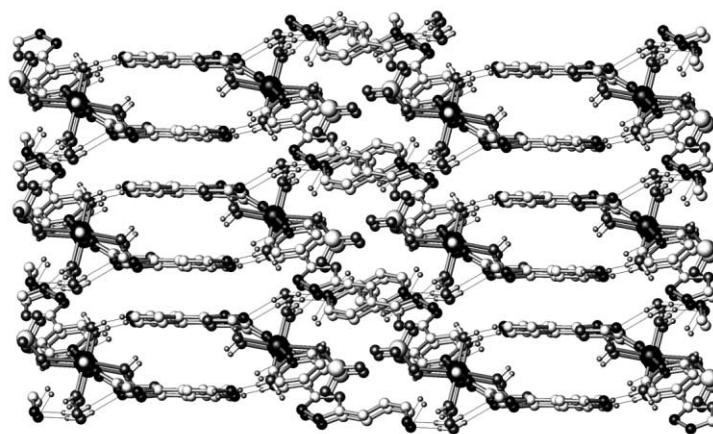
Fig. 9 View of the H-bonded 3-D network of **4** (viewed down the *b* axis).

Table 7 Hydrogen bonds for **4**

D–H · · · A	*d*(D–H)/Å	*d*(H · · · A)/Å	*d*(D · · · A)/Å	∠(DHA)/°
O(4)–H(4B) · · · O(13)	0.822(14)	2.65(3)	3.058(3)	113(3)
O(3)–H(3A) · · · N(3)#1	0.836(14)	2.016(19)	2.821(3)	161(4)
O(3)–H(3B) · · · O(24B)#1	0.829(14)	1.90(3)	2.68(2)	156(4)
O(3)–H(3B) · · · O(24A)#1	0.829(14)	2.25(2)	3.024(14)	156(3)
O(4)–H(4B) · · · O(6)#1	0.822(14)	1.982(17)	2.782(3)	164(3)
O(4)–H(4A) · · · N(4)#2	0.840(14)	1.815(15)	2.651(3)	173(3)
O(5)–H(5A) · · · N(6)#3	0.822(14)	1.984(17)	2.791(3)	167(3)
O(5)–H(5B) · · · O(6)#4	0.815(14)	1.899(17)	2.690(3)	163(3)
O(6)–H(6A) · · · N(2)#5	0.807(14)	2.105(15)	2.907(3)	173(3)
O(6)–H(6B) · · · N(5)#6	0.823(14)	1.984(15)	2.801(3)	172(3)

Symmetry transformations used to generate equivalent atoms: #1 *x*, *y* + 1, *z*; #2 −*x* + 1, −*y*, −*z* + 1; #3 *x* − 1, *y* − 1, *z*; #4 *x* − 1, *y* + 1, *z*; #5 *x* + 1, *y*, *z*; #6 −*x* + 2, −*y* + 1, −*z*.

Compound **4** is a molecular complex instead of a polymeric compound. Only one terminal N-donor in each L5 ligand coordinates to the Cu(II) center, the other is free. A very complicated hydrogen bonding system has been found in **4**. This H-bonding system is comprised of three coordinated water molecules, one uncoordinated water molecule, two N-donors on a (1,3,4)-oxadiazole bridging linkage and the free pyridyl N-donor. The corresponding H-bonding data are given in Table 7. Such a hydrogen bonding system act as the connectors to link molecular Cu(L5)$_2$(H$_2$O)$_3$ building blocks into a three-dimensional H-bonded network (Fig. 9), in which the intermolecular Co · · · Co contacts are 10.54(2) and 10.09(2) Å, respectively. It is well known that the supramolecular network can be assembled from mono- or poly-nuclear metal complexes *via* hydrogen bonding interactions.[1,5] For example, the materials bis(3-aldoximepyridine)silver(I) hexafluorophosphate, bis(3-aldoximepyridine)silver(I) perchlorate, bis(3-acetyloximepyridine)silver(I) hexafluorophosphate and bis(3-acetyloximepyridine)silver(I) perchlorate represent an attractive group of two-dimensional architectures formed by the combination of pyridine-oxime ligands with silver(I) salts.[26] By this approach, the geometry encoded in the coordination complexes is propagated into the architectures of the metal-containing hydrogen-bonded networks through intermolecular hydrogen bonds.

The one-pot reaction of the ligand L5 with Cu(ClO$_4$)·xH$_2$O in a methanol–water mixed solvent system leads to the successive formation of two distinctly different compounds with both different structural motifs and chemical formulae, which strongly suggests a dissolution/recrystallization mechanism for this phase transformation.[27]

Conclusions

This study demonstrates that the oxadiazole-containing rigid organic ligands 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L5) are capable of coordinating transition metal ions to generate novel coordination polymers. Three new coordination polymers **1**–**3** and one extensively H-bonded complex **4** were synthesized from reactions of L5 with Cu(II) and Co(II) salts by solution reactions. The relative orientation of the nitrogen donors on the pyridyl rings and the five-membered oxadiazole spacing in L5 resulted in unusual building blocks, leading to the construction of polymeric motifs which have not been grown using normal linear rigid bidentate organic ligands, such as 4,4′-bipy and related organic spacers. We are currently extending this result by preparing new oxadiazole-containing ligands of this type with different coordination functional groups and with different orientations of the nitrogen donors on the pyridyl rings. We anticipate this approach to be useful for the construction of a variety of new coordination polymers with novel polymeric patterns.

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