CrystEngComm

Cite this: CrystEngComm, 2011, 13, 215

www.rsc.org/crystengcomm

Coordination polymers derived from a flexible bis(pyridylurea) ligand: conformational change of the ligand and structural diversity of the complexes[†]

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Received 12th May 2010, Accepted 8th July 2010 DOI: 10.1039/c0ce00200c

The assembly of a bis(pyridylurea) ligand, N,N'-ethane-1,2-diylbis(3-pyridin-4-ylurea) (L), with $Zn(AcO)_2$, $CdCl_2$, $CdSO_4$ or $CuSO_4$ led to four coordination polymers, $\{[Zn(AcO)_2L] \cdot H_2O \cdot CH_3OH\}_n$ (1), $\{[CdCl_2L_2] \cdot 2DMF\}_n$ (2), $\{[CdSO_4L(H_2O)_3] \cdot 3H_2O\}_n$ (3), and $\{[CuSO_4L(H_2O)_2] \cdot 2H_2O\}_n$ (4). Compound 1 is an infinite 1D zigzag chain with alternate $Zn(AcO)_2$ units and L molecules. The cadmium(II) dichloro complex 2 features a corrugated sheet structure with a (4,4) net topology, while the sulfato complex 3 shows a unique 1O/2U interwoven 3D structure assembled from zigzag chains. The copper(II) complex 4 is an exceptional diamondoid network with an unusual 12-fold [6 + 6] interpenetration mode. Interestingly, the ligand shows the expected flexibility in the formations and is roughly linear, whereas in 2 it assumes a *gauche* form and exists as a V-shaped linker. The structural variation of these coordination polymers as well as the conformational change of the ligand in the presence of different counter anions and metal ions is discussed.

Introduction

Great interest has focused on coordination polymers not only because of their unique advantages in functional solid materials, ion exchange, catalysis and optics, etc., but also for their fascinating structures.1 The variety of self-assembled structures relies largely on the presence of suitable metal-ligand interactions and supramolecular contacts (hydrogen bonding and other weak interactions). By careful selection of metal ion 'nodes' and rigid organic 'linkers' with definite coordination preferences, numerous coordination networks with specific topologies have been successfully constructed.^{1b,2} On the other hand, the structures of metal complexes which contain relatively flexible bridging ligands are less predictable due to the possible supramolecular isomerism, such as the different conformations the ligand may adopt.^{2,3} Nevertheless, the flexible ligands could accommodate different coordination environments by adjusting their conformation, length or inherent angle of the terminal coordinative groups, thus leading to diverse structures of the metal–organic networks.⁴ The pyridyl moiety is probably the most popular building block for the construction of metal–organic networks due to its strong coordination ability to metal ions. Many oligo-pyridyl ligands with both rigid and flexible bridges have been used in the assembly of coordination architectures, and the structural topologies and chemical and physical properties of them were extensively studied.³

The oligo(pyridylurea) ligands, which contain two or more pyridyl ends separated by various linkers, have proven to be both promising anion receptors and excellent building blocks for novel supramolecular architectures.5 Recently, some bis(pyridylurea) ligands with different spacers between the two pyridvlurea fragments have been used for the construction of metal-ligand supramolecular complexes.⁶ By varying the length of the alkyl spacer and the coordination site of the terminal pyridines (3- or 4-position), we have obtained various coordination networks, such as metallomacrocycles and helical chains,^{5d} 3-fold interpenetrated MOFs^{5e} and 1D \rightarrow 1D interpenetrated coordination polymers.^{5f} Herein, we report a bis(4-pyridylurea) receptor bearing a flexible ethylene spacer, N,N'-ethane-1,2-diylbis(3-pyridin-4-ylurea) (L) and four metalorganic coordination complexes constructed with L, including a 1D chain { $[Zn(AcO)_2L] \cdot H_2O \cdot CH_3OH$ }_n (1), a 2D layered structure $\{ [CdCl_2L_2] \cdot 2DMF \}_n$ (2), a 3D intervoven structure assembled from 1D zigzag chains, { $[CdSO_4L(H_2O)_3] \cdot 3H_2O$ } (3), and a diamondoid network with an unusual 12-fold [6 + 6] interpenetration mode, $\{[CuSO_4L(H_2O)_2] \cdot 2H_2O\}_n$ (4) (Scheme 1).

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[†] CCDC reference numbers 761485, 761486, 777155–777157. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00200c



Scheme 1 Illustration of the conformation of L in compounds 1-4.

Results and discussion

The ligand N,N'-ethane-1,2-diylbis(3-pyridin-4-ylurea) (L) was synthesized from 4-isocyanatopyridine and 1,2-diaminoethane by a similar procedure to that reported previously for related ligands.⁵ Reaction of L with Zn(AcO)₂·2H₂O, CdCl₂·2.5H₂O, 3CdSO₄·8H₂O or CuSO₄·5H₂O afforded the complexes (1–4) with variable structures, which are dependent on the counter anion and metal ion employed. Very recently, the same ligand was reported, but it was synthesized by a different reaction of 4-aminopyridine and triphosgene in the presence of triethylamine.⁶f

Crystal structures

 $L \cdot 4H_2O$. Colourless crystals (space group $P\overline{1}$) of ligand L were obtained through slow evaporation of its water-methanol (1:1 v/v) solution. The asymmetric unit contains half ligand molecule and two crystal water molecules. The ligand adopts a roughly linear (GAG) conformation with torsion angles of 87.01° , -180.00° and -87.01° for the ethylene diamine spacer. Here the A (anti) or G (gauche) conformation is given when the N-C-C-N or C-C-N-C torsion angle (θ) is in the range 180 \geq $\theta > 90^{\circ}$ and $0 \le \theta \le 90^{\circ}$, respectively (Fig. 1a).⁷ Interestingly, in the packed structure, each L molecule is surrounded by four infinite water chains through Nurea-H...Ow (N...O: 2.935(2)-2.950(2) Å), O_w -H···N_{py} (O···N: 2.766(2) Å) and O_w -H···O_{C=O} (O···O: 2.762(3) Å) hydrogen bonds between the urea NH groups, the terminal pyridyl N atoms, and the urea carbonyl groups, respectively, and the water molecules (Fig. 1b). The ligands are further extended to an infinite chain bridged by two water molecules between two adjacent molecules (Fig. 1c), while the typical urea tape formed by self-association of the urea groups does not occur in this structure.

 $\{[Zn(AcO)_2L] \cdot H_2O \cdot CH_3OH\}_n$ (1). Slow evaporation of a solution of $Zn(AcO)_2 \cdot 2H_2O$ and L(Zn : L = 1 : 1) in CH_3OH -



Fig. 1 (a) Molecular structure of L. Symmetry code: (i) 1 - x, 2 - y, 2 - z. (b) The four water chains around each L molecule. Hydrogen bond parameters (Å, °): O2···O1, 2.732(2); O2–H2A···O1, 172(3); O3···N1, 2.766(2); O3–H3A···N1, 166(3); N2···O2ⁱ, 2.935(2); N2–H2···O2ⁱ, 176.2; N3···O3ⁱⁱ, 2.950(2); N3–H3···O3ⁱⁱⁱ, 156.4. Symmetry codes: (i) 1 + x, y, z; (ii) 1 + x, 1 + y, 1 + z. (c) Part of the infinite chain of the ligand bridged by solvent water molecules. Hydrogen bond parameters (Å, °): N2···O2, 2.935(2); N2–H2···O2, 176.2; O2···O1, 2.732(2); O2–H2C···O1, 172(3).

H₂O (v/v 1 : 1) afforded colourless block crystals of {[Zn(A-cO)₂L]·H₂O·CH₃OH}_n (1). Complex 1 crystallizes in the triclinic space group $P\overline{1}$. The asymmetric unit consists of one Zn atom, two AcO⁻ ions, two halves of the ligand, one solvent CH₃OH molecule and one water molecule. As shown in Fig. 2a, the Zn(II) ion is coordinated by two pyridyl nitrogen atoms from two ligands and four oxygen atoms of two chelating AcO⁻ anions in a distorted octahedral geometry. The ligands act as bridges, linking the zinc atoms to form a one-dimensional zigzag chain (Fig. 2a) with a Zn…Zn separation of 19.62 Å and Zn…Zn…Zn angle of 114.68°. Like the free ligand, the L molecule adopts a roughly linear GAG conformation in 1. Selected bond lengths and bond angles for the complexes 1–4 are given in Table 1.

In the extended structure, the zigzag chains are arranged parallel to each other and are further interlinked into a ladderlike two-dimensional network through N–H···O interactions between urea NH groups and oxygen atoms of the coordinated AcO⁻ anions (Fig. 2b). Such hydrogen bonds play an important role in creating the higher-dimensional structure, as observed in many systems.⁸ A similar Zn(II) chloro complex with L, $[(Zn(\mu-L)Cl_2)\cdot X]_n (X = disordered lattice solvents), was reported$



Fig. 2 (a) Part of the zigzag chain in 1; (b) 2D network formed by N–H··· O hydrogen bonding. Hydrogen bond parameters (Å, °): N2ⁱ···O6ⁱⁱ, 2.8987(52); N2ⁱ–H2A···O6ⁱⁱ, 141.47; N3ⁱ···O3ⁱⁱ, 2.9521(61); N3ⁱ–H3···O3ⁱⁱ, 164.82. Symmetry codes: (i) -1 - x, 4 - y, 1 - z; (ii) -1 - x, 3 - y, 1 - z.

Table 1 Selected bond lengths (Å) and angles (°) for 1-4.^a

Compound 1			
Zn-N(1)	2.049(3)	Zn-O(3)	2.066(3)
Zn-N(4)	2.023(2)	Zn-O(4)	2.342(3)
Zn-O(5)	2.016(2)	O(5)-Zn-N(4)	103.50(10)
O(5)-Zn-N(1)	97.32(10)	N(4)-Zn-N(1)	108.48(11)
O(5)–Zn– $O(3)$	96.94(11)	N(4)– Zn – $O(3)$	141.67(11)
N(1)– Zn – $O(3)$	100.52(11)	O(5)– Zn – $O(4)$	153.13(11)
N(4)-Zn-O(4)	94.36(10)	N(1)-Zn-O(4)	95.81(10)
O(3)– Zn – $O(4)$	57.54(11)	O(5)– Zn – $O(6)$	51.079(78)
Compound 2		., .,	
Cd-N(1)	2.3610(15)	$Cd-N(6)^A$	2.3898(15)
Cd–Cl	2.6294(6)	N(1)-Cd-Cl	89.91(4)
$N(1)-Cd-N(6)^{A}$	87.65(5)	$N(6)^{A}$ –Cd–Cl	89.67(4)
Compound 3			
CdÔ(6)	2.285(3)	Cd-N(4)	2.312(3)
Cd-N(1)	2.312(3)	O(6)-Cd-N(4)	93.81(12)
O(6)–Cd–N(1)	89.54(11)	N(4)-Cd-N(1)	91.56(12)
Compound 4			
Cu-O(1)	2.443(5)	Cu–O(2)	2.627(5)
Cu-O(3)	1.991(3)	Cu-O(5)	1.975(3)
Cu-N(1)	1.999(3)	Cu–N(4)	2.010(3)
O(5)–Cu–O(3)	91.09(11)	O(5)-Cu-N(1)	175.77(13)
O(3)–Cu–N(1) 89.76(12)		O(5)-Cu-N(4)	88.36(12)
O(3)–Cu–N(4)	176.49(13)	N(1)-Cu-N(4)	90.54(13)
^{<i>a</i>} Symmetry code [.] (A)	$x_{1} - v_{2} 0.5 + z_{2}$		

recently which is also a 1D zigzag polymeric chain.^{6f} However, the ligand molecule adopts a G conformation with a disordered ethylene spacer in this complex, which is different from that (A)

in 1. As a result, the zigzag shape of $[(Zn(\mu-L)Cl_2)\cdot X]_n$ is determined by the ligands but not metal nodes, since the Zn atoms within each chain is co-linear rather than bent as in the present work.

 ${[CdCl_2L_2] \cdot 2DMF}_n$ (2). The reaction of L and CdCl₂ in CH₃OH–H₂O–DMF (v/v/v 1:1:1) gave the complex ${[CdCl_2L_2] \cdot 2DMF}_n$ (2) as colourless block crystals crystallizing in the monoclinic space group C2/c. The asymmetric unit contains half a Cd atom, one Cl atom, one ligand and one solvent DMF molecule. In the crystal structure, the Cd(II) center resides on a center of inversion, being coordinated by four pyridyl nitrogen atoms of four ligands and two chloride ions in an octahedral geometry (Fig. 3a). Unlike that in complex 1, the ligand adopts a V-shaped AGA conformation in 2.

The structure of this complex can be best described as a corrugated 2D sheet in which four ligands bridge four Cd(II) centers to form a (4,4) network topology (Fig. 3b). It is noteworthy that the (4,4) nets are one of the most frequently occurring motifs in metal coordination polymers; however most of them are constructed with rigid organic linkers, which result in largely planar two-dimensional grids. In contrast, the structures of corrugated grid-like sheet are not very common.^{1d,9} In the current case, the flexible ligand with the bent conformation it adopts is responsible for the corrugated (4.4) grids which show an approximate chair conformation (one unit is shown in yellow in Fig. 3b). Moreover, these corrugated sheets are further linked by N-H···O (N4···O1 = 2.862 Å) hydrogen bonds of the urea groups from adjacent layers, and the solvent DMF molecules are trapped between the layers by N-H···O hydrogen bonds with the urea groups (Fig. 3d).

 $\{[CdSO_4L(H_2O)_3] \cdot 3H_2O\}_n$ (3). When the counter anion was changed from Cl⁻ to SO₄²⁻, the complex $\{[CdSO_4L-(H_2O)_3] \cdot 3H_2O\}_n$ (3) was obtained as colourless block crystals



Fig. 3 Crystal structure of **2**. (a) The coordination environment of the cadmium atom; (b, c) top view and side view of the corrugated sheet with the (4,4) net topology; (d) Hydrogen bonds between the 2D sheets; (e) Topological representation of the (4,4) connected network. Symmetry codes: (i) 0.5 - x, 0.5 - y, 1 - z; (ii) x, -y, 0.5 + z; (iii) 0.5 - x, 0.5 + y, 0.5 - z.

through diffusion of a solution of L in CH₃OH and a solution of CdSO₄ in H₂O. Complex **3** crystallizes in the monoclinic space group *C*2/*c*, with one Cd atom, one SO₄²⁻ ion, two halves of the ligand and six water molecules (three coordinated and three crystallized) in an asymmetric unit. Compared to the cadmium chloro complex **2**, in which the Cd²⁺ ion is coordinated by four ligands and two anions, the octahedral Cd²⁺ center in **3** is coordinated by only two L ligands together with a monodentate SO₄²⁻ anion and three H₂O molecules (Fig. 4a). The ligand molecules show a linear AAA conformation, which is different from that in **1** and **2**. The two ligands that coordinate to the metal center in a *cis* fashion further bridge other Cd atoms to form a one-dimensional zigzag chain structure (Fig. 4b) rather than the 2D (4,4) net in **2**. The Cd···Cd separation is 20.21 Å and Cd···Cd···Cd angle is 70.53° in each chain.

An unusual feature of this compound is that the zigzag chains interweave in a 'one-over/two-under' (10/2U) fashion to create a cloth-like sheet structure as shown in Fig. 4c and 4d. In such a supramolecular entanglement, each chain is chemically independent but physically interwoven with the perpendicular chains.¹⁰ Thus, in contrast to the interpenetrated networks, breaking of chemical bonds is not required to take apart this network structure. It is noteworthy that only a few interwoven "warp-and-woof" sheet networks of zigzag chains have been reported so far.¹¹ For example, Ciani and co-workers^{11a} described a 2D sheet (10/1U) which represents the first interwoven network of 1D rigid zigzag coordination strands. Li et al.^{11b} reported a 2D interwoven network (2O/2U), while Cheng et al.^{11c} illustrated how the 1D zigzag chains in four different directions were hierarchically entangled to generate an unprecedented 3D interwoven framework. Very recently, Peedikakkal et al.^{11d} reported a 10/1U interwoven fabric structure formed by spiral 1D coordination polymeric chains of the Pb^{II} complex. To the best of our knowledge, compound 3 is the first 10/2Uinterwoven fashion in coordination networks. In complex 3,

every interwoven sheet containing chains propagating along two directions (A and B in Fig. 4e) further interweaves with the chains (B' and A') in the neighbouring sheets, also in the 1O/2U mode, and an overall 3D interlocking network is formed (Fig. 4e).

 $\{ [CuSO_4L(H_2O)_2] \cdot 2H_2O \}_n$ (4). Needle-like blue crystals of the copper(II) complex 4 were obtained through slow diffusion of CuSO₄·5H₂O and L in CH₃OH-H₂O. Compound 4 crystallizes in the orthorhombic space group Pnna. The asymmetric unit consists of one Cu atom, two halves of SO42- ion, two halves of the ligand, and four water molecules (two coordinated and two crystallized) with the composition $\{[CuSO_4L(H_2O)_2] \cdot 2H_2O\}_n$. Notably, complex 4 features a 12-fold [6 + 6] interpenetrated diamondoid net. According to the classification of the interpenetration patterns proposed by Blatov et al., the structure belongs to the interpenetration class IIIa. For class III (translational and non-translational), the overall entanglement is generated both by pure translations (TIVs, translating interpenetration vector; or PIVs, partial interpenetration vector) and by space group symmetry elements (NISEs, non-translating interpenetration symmetry element; or PISEs, partial interpenetration symmetry element). If a TIV exists, the array belongs to class IIIa.12

The diamond structure, as one of the most common and important types of topology, has attracted great attention for its potential applications in non-linear optics (NLO) since the pioneering work of Ermer.¹³ For the diamondoid coordination polymers, the *n*-fold interpenetrated networks have been an invariable highlight. As reviewed by Robson,¹⁴ the common interpenetration mode of diamond structure is that the nodes of independent nets are aligned and equally spaced along one of the 2-fold axes. However, exceptional interpenetration modes have also been reported in the literature.^{13b,15} Recently, Hsu *et al.*^{15a} reported a 12-fold interpenetrated diamondoid net with a flexible



Fig. 4 (a) The molecular structure of **3** showing the local coordination geometry around the metal center. (b) Perspective view of the 1D coordination polymeric strand. (c) 10/2U interwoven 2D network. (d) Top view of the schematic representation of the 10/2U cloth-like sheet. (e) Schematic representation of the 3D network in **3**.

ligand N,N'-di(4-pyridyl)adipoamide, $[CuSO_4(L')(H_2O)_2]_{\infty}$, which is the maximum number of interpenetration presently known for coordination polymers, though a hydrogen-bonded structure has been reported very recently to show a 18-fold interpenetration of diamond frame.¹⁶

Compound 4 represents the second example of the highest interpenetrating number (12) for diamondoid coordination polymers. Although compound 4 shows a similar 3D diamondlike topology as the reported first 12-fold interpenetrated diamondoid compound $[CuSO_4(L')(H_2O)_2]_{\infty}$, its composition and the local coordination environment of the Cu2+ ions are significantly different from the latter.^{15a} Compound 4 contains two coordinated and two crystal waters molecules, respectively, while the reported first example has only one coordinated and one crystal water molecule. Consequently, the Cu²⁺ ions in 4 have a six-coordinate, Jahn-Teller distorted octahedral geometry, being coordinated by two nitrogen atoms from two bridging ligands, two oxygen atoms from two bridging sulfate ions, and two water molecules on the axial positions (Fig. 5a). In contrast, the Cu²⁺ centers in $[CuSO_4(L')(H_2O)_2]_{\infty}$ show a five-coordinate distorted square pyramidal geometry with only one coordinated water (in the apical position).^{15a} The Cu–O_w distances (Cu–O1, 2.443(5) Å; Cu-O2, 2.627(5) Å) in 4, however, are longer than that in the latter (2.275(5) Å). Like the case in its analogue $[CuSO_4(L')(H_2O)_2]_{\infty},$ the $SO_4{}^{2-}$ anions in 4 also adopt the μ_2 - η^1 , η^1 -bridging coordination fashion, linking two Cu ions to form an eight-membered cycle with a comparable Cu…Cu separation (4.797 A compared to 4.681 Α in $[CuSO_4(L')(H_2O)_2]_{\infty})$ (Fig. 5a). When the midpoint of the two SO₄-bridged copper atoms is viewed as a connecting node, we

can see that it acts as a tetrahedral node which connects four other neighbours through four bis(pyridylurea) ligands (Fig. 5b). The ligand molecules show two different conformations (AAA and GAG) in 4, and the adjoining nodes are separated by two different distances of 24.03 and 23.46 A, respectively, which are similar to the reported compound (24.46 and 23.62 Å). The structure of 4 consists of a three-dimensional framework with the extended diamondoid topology. The maximum dimensions of the adamantane cage $(37.72 \times 80.92 \times 32.28 \text{ Å}^3)$ are similar to the reported compound $(37.36 \times 82.27 \times 32.61 \text{ Å}^3)$.^{15a} Such a large cavity allows the unusual 12-fold interpenetration of the networks. This interpenetration mode differs from the normal mode and can be described as two sets of normal 6-fold nets. Fig. 5c shows a view from the b axis, in which the two sets of the normal sixfold net are interpenetrated with a relative translation vector of a/2 + b/2.^{2a,15a} Thus, this mode is named a [6 + 6] interpenetrated diamondoid system.

Noticeably, the framework is supported by extensive hydrogen bonds. Each μ_2 -coordinated sulfate ion is surrounded by two urea fragments and four water molecules (both coordinated and solvent), accepting six hydrogen bonds, including two direct N-H···O contacts (N···O = 2.853, 2.921 Å) with the urea NH groups, two O-H···O bonds (O···O = 2.866, 2.966 Å) with the crystal water molecules, and two O-H···O contacts (O···O = 2.794, 2.916 Å) with the coordinated water molecules, respectively (Fig. 5d). Notably, the two urea groups do not display the eight-membered $R_2^2(8)$ hydrogen bonding mode, but donate only a single N-H···O hydrogen bond using one of the NH donors, while the other NH is bridged to the sulfate ion through an O-H···O interaction with a crystal water molecule. In addition,



Fig. 5 Crystal structure of **4**. (a) The coordination environment around the Cu(II) ions. Symmetry codes: (i) x, 1.5 - y, 1.5 - z; (ii) -x, 1 - y, -z; (iii) 1 - x, 2 - y; -z; (b) Schematic views of the 12-fold interpenetration; (c) The [6 + 6] interpenetration viewed from the *b* axis; (d) Hydrogen bonds around the sulfate ion. Hydrogen bond parameters (Å, °): N²ⁱ···O6, 2.853(4); N²ⁱ–H2Aⁱ···O6, 165.5; O1···O6, 2.966(6); O1–H1Bⁱ···O6, 145(5); N³ⁱ··· O9, 2.864(6); N³ⁱ–H3ⁱ···O9, 148.9; O9···O5ⁱ, 2.795(5); O9–H9C···O5ⁱ, 127(5). Symmetry code: (i) x, 1.5 - y, 1.5 - z.



Fig. 6 Powder X-ray diffraction patterns: as-synthesized (red) and simulated from the single-crystal diffraction data (black): (a) 1; (b) 2; (c) 3; (d) 4.

different O–H···O interactions from the urea carbonyls of the ligand L (O···O = 2.866 Å) or the crystal water (O···O = 2.806 Å) to the coordinated water molecules are also observed. It is noticed that there are only four hydrogen bonds around the sulfate ion in the first 12-fold diamondoid network.^{15a} The enhanced anion binding in our compound **4** should be the result of the existence of two more water molecules (one coordinated and one crystal), which can serve as good hydrogen bond donors and acceptors.

PXRD and TG analyses of the complexes

Compounds 1, 2, 3 and 4 were further confirmed by elemental analyses, IR spectroscopy and powder X-ray diffraction. The PXRD patterns (Fig. 6) revealed the phase purity of the complexes. The thermal stability of the compounds was studied by TGA (Fig. 7). Compound 1 showed a slight weight loss from room temperature to 119 °C corresponding to the release of a CH₃OH and a H₂O molecule (observed weight loss 9.4%, calculated 10.8%), as well as a major weight loss occurring at above 208 °C due to the decomposition of the organic ligand. Compound 2 began to decompose from about 210 °C due to



Fig. 7 TGA curves of the compounds 1-4.

release of the two DMF molecules and loss and/or combustion of the organic components. The TGA curve of **3** showed a weight loss from room temperature to 151 °C corresponding to five water molecules (observed 14.0%, calculated 15.0%). The compound decomposed at 230 °C. Complex **4** has a reasonable stability in the solid state. There is a 13.0% weight loss in the temperature range 49–195 °C, which is attributed to the loss of the two coordinated and two crystal water molecules (calculated 13.5%). The compound began to decompose at above 241 °C with a sharp weight loss. It should be noted that the decomposition temperature of the first 12-fold diamondoid network is relatively low (around 80 °C).^{15a} Thus, complex **4** exhibits an improved stability, which is probably due to the enhanced hydrogen bonding interactions in **4** as mentioned above.

Conclusions

We report four coordination polymers constructed from a flexible bis(pyridylurea) ligand (L). The supramolecular structures of the complexes vary from 1D zigzag chain (1) to 2D corrugated sheet (2) and interwoven 3D network (3), and then to a rare 3D diamondoid network with a 12-fold [6 + 6] interpenetration mode (4). Interestingly, the flexible ligand adopts different conformations in the complexes (roughly linear in 1, 3, and 4, and V-shaped in 2), and geometric needs of the metal atoms and coordination of the anions also play important roles in the construction of the complexes. Moreover, the urea groups participate in various hydrogen bonding interactions in all the complexes, which are essential in the formation of the secondary (or higher-dimensional) supramolecular structures.

Experimental

General procedures

All starting chemicals were commercially available and were used as received. Elemental analyses were done on a VarioEL instrument from Elementaranalysensysteme GmbH. IR spectra were recorded on a Bruker IFS 120HR spectrometer as KBr disks (500–4000 cm⁻¹). ¹H NMR spectra were recorded at ambient temperature on a Mercury Plus 400 MHz FT spectrometer in DMSO-*d*₆. Melting points were detected on an X-4 Digital Vision MP Instrument. Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert PRO SUPER diffractometer with Cu-K α radiation ($\lambda = 1.54187$ Å). TG analyses were carried out with a Pyris diamond instrument (Perkin Elmer) under N₂ atmosphere with a heating rate of 10 °C min⁻¹.

Synthesis of L. 4-Pyridyl acyl azide (3.00 g, 20.2 mmol) in freshly dried toluene (100 mL) was refluxed under a nitrogen atmosphere for 1 h to give a pale yellow solution. Then 1,2-diaminoethane (0.61 g, 10.1 mmol) was added and the mixture was refluxed for 30 min and then cooled to r.t. A white powder was collected and washed with toluene, diethyl ether and dried *in vacuo*. Yield: 1.5 g (50%). M.p.: 245–247 °C. Anal. calcd for C₁₄H₁₆N₆O₂·0.7H₂O: C 53.73, H 5.60, N 26.80. Found: C 53.41, H 5.25, N 26.98%. ¹H NMR (DMSO-*d*₆, 400 MHz): 9.05 (s, 2 H, pyridyl-N*H*-), 8.28 (d, 4 H, *J* = 6.4 Hz, Py-H2), 7.37 (dd, 4 H, *J* = 1.4, 6.4 Hz, Py-H3), 6.46 (s, 2 H, CH₂–N*H*-), 3.21 (t, 4 H,

Table 2 Crystallographic data for L, 1, 2, 3, and	14
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Compound	L	1	2	3	4
Empirical formula	C ₁₄ H ₂₄ N ₆ O ₆	C ₁₉ H ₂₈ N ₆ O ₈ Zn	C34H46CdCl2N14O6	C14H28CdN6O12S	C ₁₄ H ₂₄ CuN ₆ O ₁₀ S
$FW/g mol^{-1}$	372.39	533.84	930.15	616.88	531.99
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P\overline{1}$	C2/c	C2/c	Pnna
a /Å	7.2549(13)	10.447(2)	31.510(7)	30.671(12)	18.861(5)
b /Å	7.7629(15)	10.755(3)	8.534(2)	7.551(3)	16.141(4)
c /Å	9.1054(16)	12.473(3)	18.891(4)	24.101(10)	13.487(4)
α /°	98.095(3)	104.330(4)	90.00	90.00	90.00
β /°	99.513(3)	102.140(4)	122.100(2)	122.271(4)	90.00
$\gamma /^{\circ}$	110.281(3)	110.924(3)	90.00	90.00	90.00
$V/Å^3$	463.39(15)	1197.3(5)	4303.4(17)	4720(3)	4106.0(18)
Ζ	1	2	4	8	8
$D_{\rm c}$ /g cm ⁻³	1.334	1.481	1.436	1.736	1.721
Crystal size /mm	0.30 imes 0.25 imes 0.22	0.30 imes 0.28 imes 0.25	0.40 imes 0.35 imes 0.30	0.25 imes 0.20 imes 0.20	$0.40 \times 0.25 \times 0.20$
F(000)	198	556	1912	2512	2200
μ /mm ⁻¹	0.11	1.08	0.69	1.09	1.23
θ range	2.32-25.00	1.79-25.97	1.53-28.20	1.57-25.55	1.86-26.62
Reflections collected	2373	6647	17 308	15 660	22 679
Independent reflections	1620	4614	5184	4383	4299
Observed reflections $[I > 2\sigma(I)]$	1410	3353	4634	3125	2552
R _{int}	0.018	0.027	0.018	0.057	0.084
R_1 ; w $R_2 [I > 2\sigma(I)]$	0.0477, 0.1654	0.0462, 0.0941	0.0269, 0.0693	0.0396, 0.0787	0.0486, 0.1190
R_1 ; w R_2 (all data)	0.0535, 0.1729	0.0722, 0.1042	0.0313, 0.0721	0.0665, 0.0888	0.0986, 0.1450
$\operatorname{GOF}(F^2)$	1.384	1.015	1.062	1.024	1.045

J = 2.8 Hz, urea- CH_2). ¹³C NMR (DMSO- d_6 , 100 MHz): 154.8 (C=O), 149.9 (Py-C4), 147.0 (Py-C2), 111.8 (Py-C3), 39.3 (urea- CH_2 -). IR (KBr pellet, cm⁻¹): 3312 (N–H), 3087, 1681 (C=O), 1601, 1534, 1211, 1004, 826, 530.

Synthesis of {[Zn(AcO)₂L]·H₂O·CH₃OH}_{*n*} (1). The ligand L (20 mg, 0.07 mmol) and Zn(OAc)₂·2H₂O (12.2 mg, 0.07 mmol) were dissolved in a mixed solvent of CH₃OH–H₂O (1 : 1 v/v, 5 mL). Slow evaporation at r.t. for several days yielded colourless crystals of **1** (27 mg, 71%). M.p.: 206–207 °C. Anal. calcd for Zn(AcO)₂L·H₂O·CH₃OH: C 42.75, H 5.29, N 15.74%. Found: C 42.42, H 4.94, N 15.93%. IR (KBr pellet, cm⁻¹): 3357 (N–H), 3157, 3010, 2946, 1714 (C=O), 1600, 1507, 1437, 1270, 1201, 1026, 835, 682, 632, 532.

Synthesis of {[CdCl₂L₂] 2DMF} (2). The ligand L (20 mg, 0.07 mmol) and CdCl₂·2.5H₂O (15.2 mg, 0.07 mmol) were dissolved in methanol–water–DMF (1 : 1 : 1 v/v/v, 5 mL). Slow evaporation at r.t. for a month yielded colourless crystals of 2 (14 mg, 42%). M.p.: > 300 °C. Anal. calcd for CdCl₂L₂·2DMF: C 43.90, H 4.98, N 21.08%. C 43.85, H 4.89, N 20.78%. IR (KBr pellet, cm⁻¹): 3367 (N–H), 3068, 1699 (C=O), 1595, 1517, 1427, 1263, 1208, 1096, 1011, 835, 715, 537.

Synthesis of {[CdSO₄L(H₂O)₃]·3H₂O}_{*n*} (3). A methanol solution (5 mL) of L (10 mg, 0.03 mmol) was layered on top of an aqueous solution of $3CdSO_4 \cdot 8H_2O$ (8.5 mg, 0.01 mmol), and the mixture was allowed to diffuse at room temperature. After two weeks, colourless needle-like crystals were obtained at the interface. Yield: 8.5 mg (46%). M.p.: > 300 °C. Anal. calcd for CdSO₄L·5H₂O: C 28.08, H 4.38, N 14.03%. Found: C 28.47, H 4.53, N 14.00%. IR (KBr pellet, cm⁻¹): 3328 (N–H), 3086, 1696 (C=O), 1599, 1527, 1435, 1338, 1264, 1213, 1092, 1016, 829, 602, 529.

Synthesis of $\{[CuSO_4L(H_2O)_2] \cdot 2H_2O\}_n$ (4). A methanol solution (5 mL) of L (30 mg, 0.1 mmol) was layered on the top of

an aqueous solution (5 mL) of CuSO₄·5H₂O (25 mg, 0.1 mmol), and the mixture was allowed to diffuse at room temperature. Blue block crystals were formed at the interface in several days. Yield: 26 mg, (50%). Mp: 230–231 °C. Anal. calcd for CuSO₄L·3H₂O: C 32.72, H 4.31, N 16.35. Found: C 32.56, H 4.42, N 16.17%. FT-IR (KBr pellet, cm⁻¹): 3399 (N–H), 3253, 1688 (C=O), 1601, 1519, 1209, 1092, 1027, 842, 533.

X-Ray crystallography

Data collection was performed on a Bruker-AXS SMART CCD area detector diffractometer at 293 K using ω rotation scans with a scan width of 0.3° and Mo-K α radiation ($\lambda = 0.71073$ Å). Multi-scan corrections were applied using SADABS.¹⁷ Structure solutions and refinements were performed with the SHELX-97 package.¹⁸ All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 . The hydrogen atoms were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of carbon and nitrogen atoms. Hydrogen atoms of water molecules in L and 1 were located from the difference Fourier map and then refined by restraints (O–H = 0.85(1) Å), with U(H) fixed at 0.08 Å². Crystallographic data for the compounds are summarized in Table 2.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant no. 20872149).

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