

Coordination polymers of d¹⁰ metals and *N,N'*-bis(3-pyridine-carboxamide)-1,2-ethane

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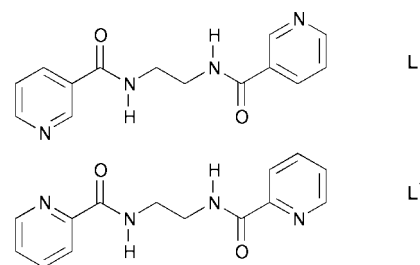
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The ligands *N,N'*-bis(3-pyridinecarboxamide)-1,2-ethane (L) was designed to form coordination polymers capable of assembling into 2-D network *via* complementary amide hydrogen bonds. The reactions of L with AgX (X = ClO₄[−], CF₃SO₃[−] or NO₃[−]), Zn(ClO₄)₂·6H₂O and Cd(ClO₄)₂·6H₂O produced coordination polymers **1–5**, the structures of which were characterized by single crystal X-ray diffraction. The polymer {[AgL][ClO₄]}_∞ crystallized in two polymorphs **1A** and **1B** which consisted of coordination polymers {[AgL]⁺}_∞ in sine-wave and zigzag conformations, respectively. In addition, the X-ray crystal structures of {[AgL][CF₃SO₃]}_∞ (**2**) and {[AgL][NO₃](H₂O)_{1.25}]}_∞ (**3**) showed coordination polymers in zigzag conformation similar to that of **1B**. The polymers in compounds **1**, **2** and **3** aggregate *via* complementary amide hydrogen bonds, forming corrugated sheets in the solid state. Furthermore, the compound *trans*-{[ZnL₂(H₂O)₂][ClO₄]₂·(H₂O)₂·CH₃CN}_∞ (**4**) was shown to be an infinite chain of [Zn₂L₂]metallacycles. The stacking of the Zn polymer leads to the formation of a channel-like structure. The coordination polymer {[CdL(H₂O)₃][ClO₄]₂]}_∞ (**5**) shows zigzag chains which are linked through hydrogen bonds between the anion, amide groups and coordinated water molecules. In contrast to its isomer L, the ligand *N,N'*-bis(2-pyridinecarboxamide)-1,2-ethane (L¹) formed segregated Ag(I) coordination polymer (**6**) in which the Ag ion is four coordinate.

Introduction

Recent studies have shown that coordination-directed aggregation of multidentate organic ligands is highly controllable, mostly due to the high directionality of the metal–ligand bond as well as the regular molecular geometry of transition metal complexes.¹ Based on this synthetic strategy, many discrete supramolecular assemblies with intricate architecture have been created.² Likewise coordination driven self-assembly has produced a myriad of intriguing polymeric structures such as linear chains,³ helicates,⁴ 2-D networks⁵ and 3-D lattices.⁶ Rigid multidentate ligands such as 4,4'-bipyridine⁷ and 2,4'-bipyridine⁸ are popular as the number of possible products arising from the self-assembly reactions of the ligands and metal ions is limited. Nevertheless, it was shown that the conformation and even the assembly pattern of some coordination polymers could be varied by changing their counterions⁹ or the solvent used in the synthesis or recrystallization.¹⁰ For example, Schröder *et al.* showed that the nitrate salt of the silver polymer [Ag(pytz)NO₃]_∞ (pytz = 3,6-di(4-pyridyl)-1,2,4,5-tetrazine) was like a helical staircase in shape while its BF₄[−] and PF₆[−] salts exist as a pair of chains.^{9a} In addition, some coordination polymers of the same molecular composition are found to display entirely different 3-D structures. This phenomenon is called supramolecular isomerism and one of the compounds showing this kind of structural variation is [Co(NO₃)₂(1,2-bis(4-pyridyl)ethane)]_∞.¹¹ Three crystal polymorphs of the compound were obtained and their X-ray crystal structures showed that the cobalt polymer could exist in three different conformations. The variable conformations of the cobalt polymer were due to the flexibility of the bridging ligand (1,2-bis(4-pyridyl)ethane). In our study on the self-assembly of inorganic supramolecules, we were interested in the bidentate ligand *N,N'*-bis(3-pyridinecarboxamide)-1,2-ethane (L) (Scheme 1).



Scheme 1

The ligand, equipped with amide and pyridyl groups, was designed to form coordination polymers capable of self-assembling into 2-D sheets *via* complementary amide hydrogen bonds. In this paper we report the structures of the coordination polymers synthesized from the reactions of L and d¹⁰ metal ions Ag(I), Zn(II) and Cd(II). These d¹⁰ metal ions were chosen because of their different preferences in coordination geometry. The coordination polymers of these ions showed intriguing solid-state structures, and most importantly the silver polymer {[AgL][ClO₄]}_∞ was found to display supramolecular isomerism. Furthermore, the triflate and nitrate salts of the silver polymers were prepared so as to understand the effect of anion on the conformation and solid state arrangement of the polymer. Lastly the isomer of ligand L, ligand *N,N'*-bis(2-pyridinecarboxamide)-1,2-ethane (L¹, Scheme 1) and its silver complex were synthesized. It was found that changing the position of the amide group had a drastic effect on the structure of the coordination polymer.

Results and discussion

Supramolecular isomerism of {[AgL][ClO₄]}_∞

The hydrogen bond has long been harnessed to assemble coordination polymers.¹² Recently, Aakeröy and Beatty showed

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that the mononuclear complex $[\text{Ag}(\text{2-amidocarboxypyridine})_2]^+$ could assemble into various 2-D networks *via* intermolecular $\text{N-H} \cdots \text{O}=\text{C}$ amide hydrogen bonds.^{12d} Based on this finding, we designed the bidentate ligand **L**, which has two amide and two pyridyl groups, in the hope that coordination polymers of the ligand would zip up *via* inter-chain amide hydrogen bonds to form 2-D networks. Reacting **L** with AgX ($\text{X} = \text{ClO}_4^-$, CF_3SO_3^- or NO_3^-) led to white compounds **1**, **2** and **3**. Crystal polymorphism was observed in the compound $\{\text{[AgL][ClO}_4]\}_\infty$ (**1**). Slow diffusion of diethyl ether into an acetonitrile solution of $\{\text{[AgL][ClO}_4]\}_\infty$ gives two colourless crystals **1A** and **1B**. The number of the hexagonal **1A** crystals is about three times that of the rectangular **1B** crystals. Both crystals share the same molecular formula and space group and their unit cell dimensions are very similar (Table 3). The X-ray crystal structures of **1A** and **1B**, depicted in Figs. 1a and b, respectively, show that both crystal forms consist of infinite chains in which the ligands **L** are joined by $\text{Ag}(\text{I})$ ions (see Table 1 for selected bond lengths and angles). Each Ag atom in the polymer chains is coordinated to two N atoms of the pyridyl groups in a linear fashion and the Ag-N bond lengths observed in the two forms are similar. On the other hand, the backbones of ligands **L** in **1A** and **1B** show significant differences; for **1A**, the two pyridyl rings coordinated to the same Ag ion show a dihedral angle of 65.2° whereas the ones in **1B** are nearly coplanar. The amide linkages in **1B** are essentially planar (dihedral angle of $\text{C-N(H)-C(=O)-C} = 5.8^\circ$) but the one in **1A** is slightly twisted, showing a dihedral angle of 23° . Due to the conformation of the ethylene linkage, the two carbonyl groups are in an *anti*-orientation, which facilitates the formation of inter-chain hydrogen bonds (*vide infra*).

The most striking difference between the two polymorphs is the chain conformation of the polymers. As shown in Fig. 1a, two successive ligands **L** in **1A** are *syn* to each other and this gives the polymer chain a sine-wave shape. On the other hand,

two successive ligands **L** in **1B** are in an *anti*-orientation, leading to stair-like or zigzag chains (Fig. 1b). Apparently the different conformations arise from Ag-N bond rotation and indeed the polymers in **1A** and **1B** can be regarded as rotamers. The observation of two chain conformations suggests that the backbones of the coordination polymers are highly flexible. Given the long separation between adjacent ligands, it is reasonable to believe that rotation around the Ag-N bonds does not suffer much steric hindrance. As the two isomers share the same molecular composition, the present case can be regarded as an example of supramolecular isomerism of a coordination polymer.

For the coordination polymers in **1A** and **1B**, the amide groups adopt an *anti*-orientation and are ready to form inter-chain hydrogen bonds. Inspection of the crystal structures of **1A** and **1B** shows that the polymer strands are aligned in parallel, *via* complementary amide hydrogen bonds (Figs. 1c and d, respectively). The polymer chains in one sheet are evenly spaced, showing an inter-chain Ag-Ag separation of $5.113(2)$ (**1A**) and $5.124(2)$ Å (**1B**). It is noted that the amide nitrogen atoms of each chain are directed towards the carbonyl oxygen atoms of its adjacent chains. This close association between amide nitrogen and carbonyl oxygen indicates that the chains are held together by complementary amide hydrogen bonds. This is further supported by the $\text{N(H)} \cdots \text{O}=\text{C}$ distances (**1A**: $2.907(2)$; **1B**: $2.897(2)$ Å, see Table 2), which compare favourably with other amide hydrogen bonds.¹³ The collective action of the hydrogen bonds lead to the formation of corrugated sheets in **1A** and **1B** (Figs. 1c and d). Interestingly, the complementary hydrogen bond pattern in the two forms resembles the one observed in the protein β -sheet.¹⁴

The chain conformation is not the only variation in the two crystal forms; the packing of the corrugated sheets in **1A** and **1B** is also different. The sheets in **1A** stack along the *b*-axis and

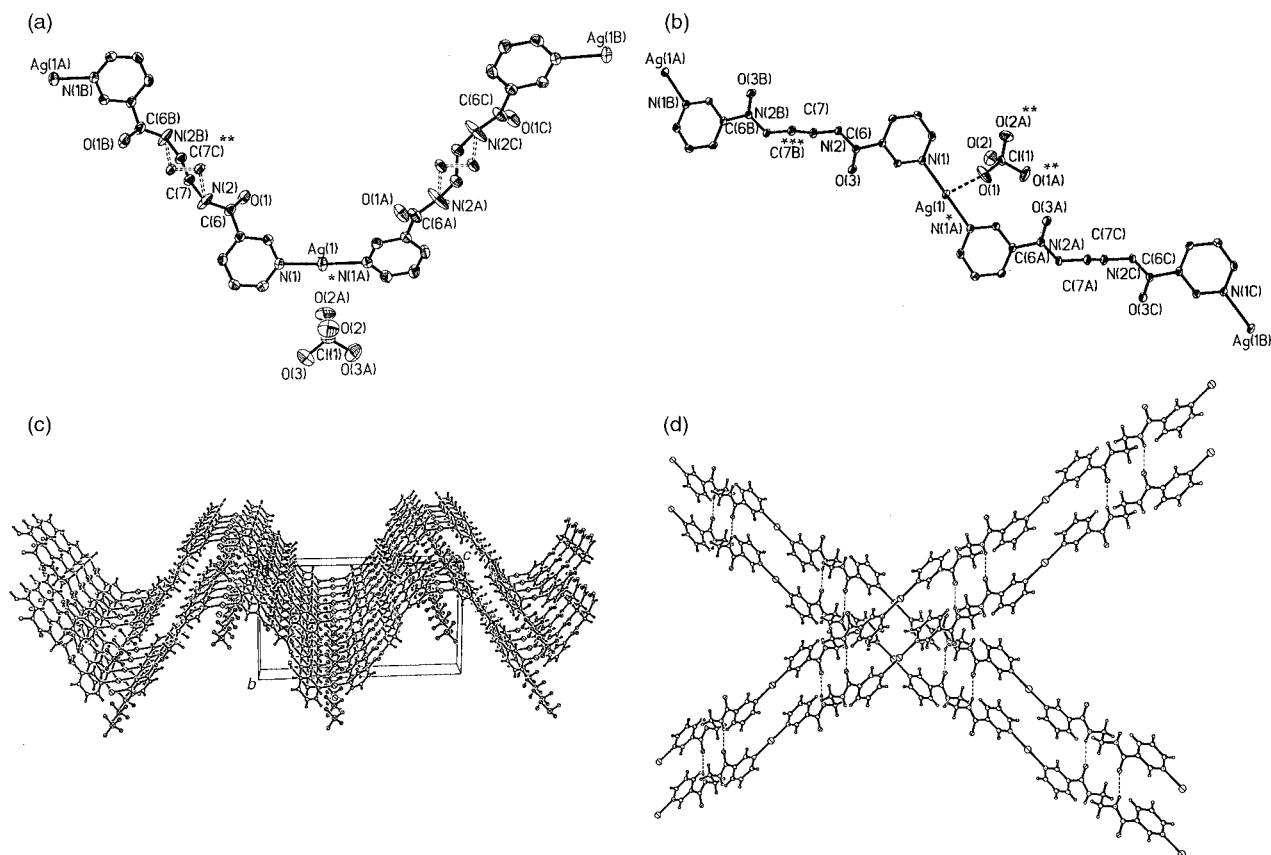


Fig. 1 (a) Molecular structure of the polymer chain in crystal form **1A** (ORTEP²¹ drawing with 50% probability ellipsoids). Symmetry code used for generating equivalent atoms: * $-x, y, -z + 1/2$; ** $-x + 1, -y, -z$. (b) Molecular structure of the polymer chain in crystal form **1B** (ORTEP drawing with 50% probability ellipsoids). Symmetry code used for generating equivalent atoms: * $-x, -y, -z$; ** $-x, y, -z + 1/2$; *** $-x - 1/2, -y - 3/2, -z - 1$. (c) Diagram showing the stacking of corrugated sheets in crystal form **1A**. (d) Diagram showing the hydrogen bonds and stacking of corrugated sheets in crystal form **1B**.

Table 1 Selected bond length (Å) and angles (°) for compounds **1–6**

1A			
Ag(1)–N(1)	2.153(2)	N(1)–Ag(1)–N(1A)	177.72(11)
Ag(1)–N(1A)	2.153(2)	N(2)–C(6)–O(1)	123.2(3)
C(6)–N(2)	1.327(4)	N(2)–C(6)–C(4)	115.9(2)
C(6)–O(1)	1.229(3)		
1B			
Ag(1)–N(1)	2.2092(2)	N(1)–Ag(1)–N(1A)	180.00(8)
Ag(1)–N(1A)	2.2092(2)	N(2)–C(6)–O(3)	123.4(2)
C(6)–N(2)	1.340(3)	N(2)–C(6)–C(4)	116.9(2)
C(6)–O(1)	1.231(3)		
2			
Ag(1)–N(1)	2.162(2)	N(1)–Ag(1)–N(2)	173.44(6)
Ag(1)–N(2)	2.163(2)	N(3)–C(6)–O(1)	122.5(2)
Ag(1)–O(5)	2.598(2)	N(3)–C(6)–C(4)	116.8(2)
C(6)–N(3)	1.335(3)		
C(6)–O(1)	1.239(3)		
3			
Ag(1)–N(1)	2.155(2)	N(1)–Ag(1)–N(3)	173.95(8)
Ag(1)–N(3)	2.155(2)	N(2)–C(6)–O(1)	123.3(2)
C(6)–O(1)	1.277(3)	N(2)–C(6)–C(4)	115.82(2)
C(6)–N(2)	1.335(3)		
C(13)–O(2)	1.233(3)		
Ag(1)–O(3)	2.820(3)		
4			
Zn(1)–O(1)	2.150(3)	O(1)–Zn(1)–O(1A)	180.00(2)
Zn(1)–O(1A)	2.150(3)	O(1)–Zn(1)–N(2)	88.91(1)
Zn(1)–N(2)	2.154(3)	O(1A)–Zn(1)–N(2)	91.09(1)
Zn(1)–N(1)	2.239(3)	O(1)–Zn(1)–N(2A)	91.09(11)
O(2)–C(6)	1.236(5)	O(1A)–Zn(1)–N(2A)	88.91(1)
O(3)–C(13)	1.221(5)	N(2)–Zn(1)–N(2A)	180.00(2)
		O(1A)–Zn(1)–N(1A)	92.14(1)
		N(2A)–Zn(1)–N(1A)	88.25(1)
5			
Cd(1)–O(2)	2.257(5)	N(2)–Cd(1)–N(2A)	171.5(2)
Cd(1)–O(3) = Cd(1)–O(3A)	2.269(4)	O(2)–Cd(1)–O(3)	137.86(1)
Cd(1)–N(1) = Cd(1)–N(1A)	2.266(4)	O(3)–Cd(1)–O(3A)	84.3(2)
O(1)–C(6)	1.232(6)	O(2)–Cd(1)–N(1)	85.75(1)
N(2)–C(6)	1.310(7)	O(2)–Cd(1)–O(3A)	137.86(1)
6			
Ag(1)–N(1)	2.203(4)	N(1)–Ag(1)–N(2)	166.47(1)
Ag(1)–N(2)	2.242(4)	O(1)–Ag(1)–O(2)	166.20(1)
Ag(1)–O(1)	2.533(4)	O(1)–Ag(1)–N(2)	96.43(1)
Ag(1)–O(2)	2.480(3)	N(1)–Ag(1)–O(2)	123.73(1)
C(9)–O(2)	1.220(6)	O(1)–Ag(1)–N(1)	70.06(1)
C(6)–O(1)	1.216(6)	N(2)–Ag(1)–O(2)	69.77(12)
C(6)–N(3)	1.327(6)		
C(9)–N(4)	1.332(6)		

completely overlap (Fig. 1c). The *inter-sheet* separation, taken as the distance between two nearest Ag ions in two overlapping sheets, is 7.112(2) Å. The perchlorate ions are sandwiched between the sheets and located slightly away from the inter-sheet Ag–Ag vectors (Ag(sheet 1)–Cl(O₄) = 3.601(2) Å and Ag(sheet 2)–Cl(O₄) = 3.975(2) Å). The shortest Ag–O–ClO₃ distance is 2.820(2) Å and is longer than normal Ag–O bonds (≈2.3–2.6 Å).¹⁵ In contrast to **1A**, the stacking sheets in **1B** are staggered, forming a criss-cross pattern (Fig. 1d) and perchlorate ions are found between the polymer sheets. The inter-sheet separation is 6.964(2) Å. The ion is equidistant from the two Ag ions, showing a Ag–Cl distance of 3.511(2) Å. The oxygen atoms of the perchlorate ion are 2.903(2) and 2.950(2) Å away from the Ag ions, indicating that there is no formal bonding between the ions.

Structures of {[AgL][CF₃SO₃]}_∞ (**2**) and {[AgL][NO₃]}_∞ (**3**)

In order to understand the effect of anion on the 3-D structure of the present polymer, triflate (**2**) and nitrate (**3**) salts of

{[AgL]}_∞⁺ were prepared. Similar to the perchlorate salt, compounds **2** and **3** were readily synthesized by reacting AgCF₃SO₃ and AgNO₃ directly with L in methanol. White solids obtained were shown to be {[AgL][CF₃SO₃]}_∞ and {[AgL][NO₃]}_∞ by elemental analyses. Crystals of the compounds formed from a slow diffusion of a methanolic solution of AgCF₃SO₃ or AgNO₃ into an aqueous solution of L. Fig. 2a shows the X-ray crystal structure of **2**. The Ag ion is coordinated to nitrogen atoms of two pyridyl groups which are nearly coplanar (dihedral angle = 4.4°). Similar to **1B**, adjacent ligands L in **2** are in *syn*-orientation, giving the polymer a zigzag conformation. The bond lengths and angles of **2** and **1B** are also very close. Each Ag(I) ion is bonded to a CF₃SO₃[−] ion, showing a Ag–O distance of 2.598(2) Å. The polymer strands aggregate into corrugated sheets *via* amide hydrogen bonds which show a N(H)⋯O=C distances of 2.953(2) and 2.970(2) Å (Fig. 2b and Table 2). The inter-chain Ag–Ag separation is 5.022(2) Å, close to those in **1A** and **1B**. In spite of their similar conformations, the packing of the undulating sheets in **1B** and **2** is different: instead of forming a criss-cross pattern, the stacking sheets in **2** are completely overlapped. In addition, the

Table 2 Hydrogen bond interactions in compounds **1–5**

Compound	D ... A/Å	H ... A/Å	∠D–H–A/°
1A	N(2)–O(1 ^a)	2.907(2)	2.082
1B	N(2)–O(3 ^b)	2.897(2)	2.138
2	N(3)–O(2 ^c)	2.953(2)	2.279
	N(4)–O(1 ^d)	2.970(2)	2.270
3	N(2)–O(2 ^e)	2.833(2)	2.057
	N(4)–O(1 ^f)	2.881(2)	2.111
4	O(1)–O(8)	2.660(2)	1.826
	O(1)–O(6 ^g)	2.804(2)	1.974
	N(3)–O(7 ^h)	3.236(2)	2.382
	N(4)–O(5 ⁱ)	3.015(2)	2.195
	O(8)–O(2)	2.863(2)	2.055
	O(8)–O(3 ^j)	2.736(2)	1.895
5	O(2)–O(1 ^k)	2.876(3)	1.921
	O(3)–O(1 ^l)	2.833(3)	1.963
	O(3)–O(7 ^m)	2.946(3)	2.110
	N(2)–O(7 ⁿ)	3.049(3)	2.350

Symmetry code: (a) $x + 1, y, z$; (b) $x, y - 1, z$; (c) $-x + 1, -y + 1, -z + 1$; (d) $-x + 1, -y + 1, -z$; (e) $-x + 1, -y + 1, -z + 1$; (f) $-x + 1, -y, -z + 1$; (g) $-x + 1, -y - 1, -z$; (h) $x + 1, y, z$; (i) $-x - 1, -y - 1, -z + 1$; (j) $x - 1, y, z$; (k) $x, -y + 1, z - 1/2$; (l) $-x + 1, -y, -z + 1$; (m) $-x + 3/2, y - 1/2, -z + 1/2$; (n) $x - 1/2, y - 1/2, z$.

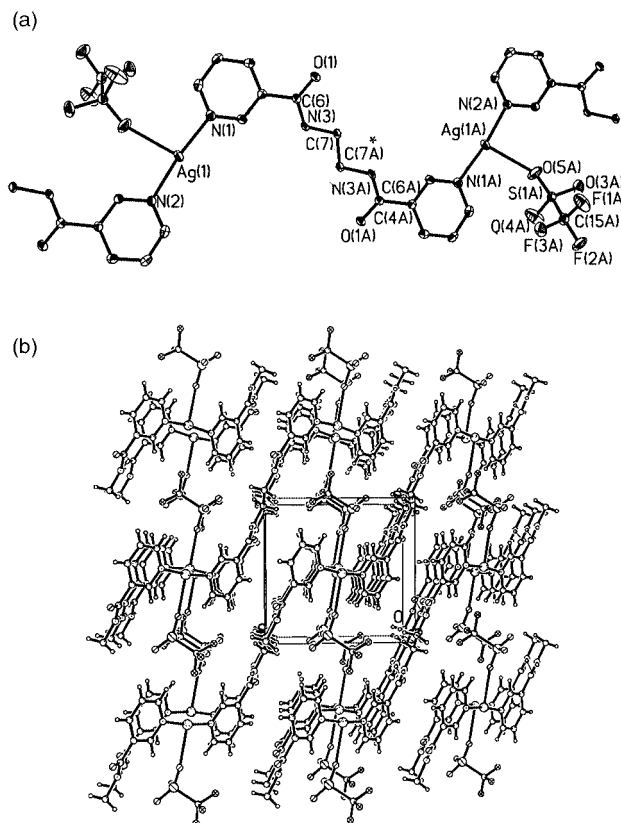


Fig. 2 (a) Molecular structure of compound **2** (ORTEP drawing with 50% probability ellipsoids). Symmetry code used for generating equivalent atoms: * $-x + 2, -y, -z$. (b) Diagram showing the assembly of polymer of **2** into 2-D sheets.

9.130(2) Å inter-sheet distance in **2** is much longer than the ones in **1A** and **1B**.

The X-ray crystal structure of **3** shows infinite coordination polymer in a zigzag conformation (Fig. 3a). Comparing **3** with **1B** and **2** shows no significant difference in bond lengths and angles. Each Ag ion is coordinated to two pyridyl rings that are essentially coplanar (dihedral angle = 0.2°). Stacking of corrugated sheets, composed of the polymer strands linked by intermolecular amide hydrogen bonds, is observed in the crystal structure (Fig. 3b). The compound shows inter-chain N(H) ... O=C distances of 2.833(2) and 2.881(2) Å similar to

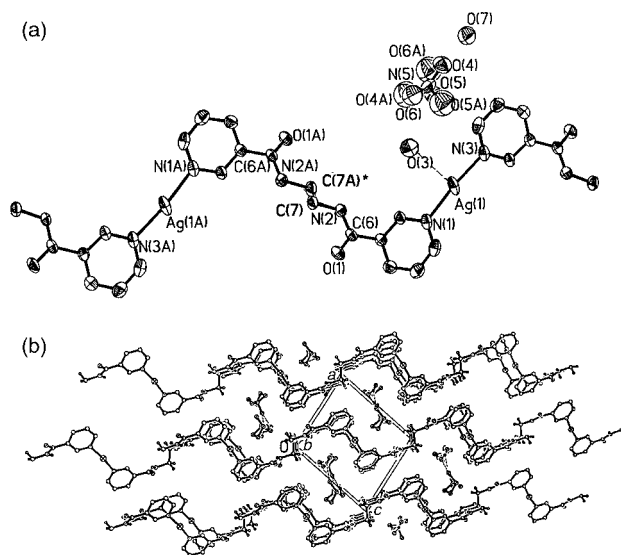


Fig. 3 (a) Molecular structure of compound **3** (ORTEP drawing with 50% probability ellipsoids). Symmetry code used for generating equivalent atoms: * $-x + 2, -y, -z + 2$. (b) Diagram showing the assembly of polymer **3** into 2-D sheets.

those observed in **1** and **2** (Table 2) and the Ag ions in adjacent chains are separated by 5.106(2) Å. The nitrate is disordered and far away from the Ag ion (Ag–ONO₂[−] = 4.601(2) Å). Due to the presence of water of crystallization, compound **3** is non-stoichiometric: on average there are 1.25 water molecules for every Ag ion. In fact there are two types of water molecule in the crystal of **3**: Ag-associated (H₂O(3)) and non-associated (H₂O(7)). The oxygen atom of the Ag-associated water molecule, O(3), is separated from the metal by 2.820(3) Å. The non-associated water molecules are located between sheets of polymer and there is one non-associated water molecule for every four Ag ions. Notably, the inter-sheet distance of 9.086(2) Å is close to that of **2** but longer than the ones in **1A** and **1B**. Despite the different shapes of the anions in **2** and **3**, the polymers share almost the same conformation. It is therefore believed that the anion has no template effect on the conformation of the {[AgL]⁺}_∞ polymer.

Structure of *trans*-{[ZnL₂(H₂O)₂][ClO₄]₂·(H₂O)₂·CH₃CN}_∞ (**4**)

Reacting Zn(ClO₄)₂·6H₂O and two equivalents of L gave a coordination polymer *trans*-{[ZnL₂(H₂O)₂][ClO₄]₂·(H₂O)₂·CH₃CN}_∞ (**4**). Single crystal X-ray diffraction shows that compound **4** is a coordination polymer consisting of repeating [Zn₂L₂] metallacycles (Fig. 4a). The distorted octahedral coordination sphere of the six-coordinate Zn(II) ion comprises four equatorial pyridyl-groups and two axial H₂O molecules. In contrast to the aforementioned polymers, the ligand L in **5** adopts an *anti*-conformation. Owing to the ligand conformation, the repeating [Zn₂L₂] unit is square in shape. The side of the square is about 8.5 Å long and the diagonal Zn–Zn separation is 13.141(2) Å. Trapped inside the molecular square is a CH₃CN molecule that is disordered by inversion symmetry. The polymer strands stack along the *b*-axis to form channels, a common structural motif in many coordination networks (Fig. 4b).¹⁶ The shortest inter-chain Zn–Zn distance in a channel is 7.854(2) Å. A side view (Fig. 4a) of the polymer reveals an intricate network of hydrogen bonding between two adjacent polymer strands. Aside from the coordinated water, there are two non-coordinated water molecules for every Zn atom. These water molecules are situated between two stacking polymer strands and are hydrogen bonded with two carbonyl oxygen atoms from two adjacent squares (O(8) ... O(2)=C = 2.863(2) and O(8) ... O(3)=C = 2.736(2) Å), and one of the coordinated axial water molecules (O(8) ... O(1) = 2.660(2) Å) (Table 2). In

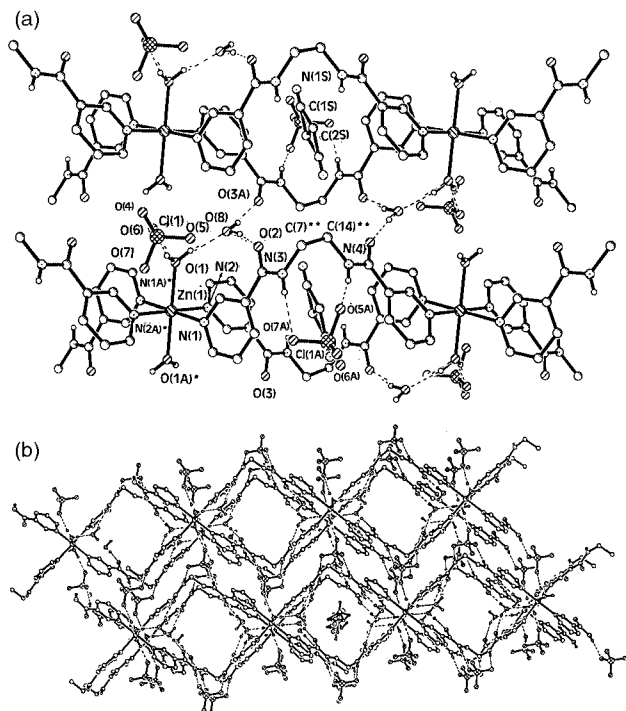


Fig. 4 (a) Molecular structure of compound **4**. All hydrogen atoms except those of water and amide are omitted. The C2S–C1S–N1S unit is the disordered acetonitrile. Symmetry code used for generating equivalent atoms: * $-x, -y, -z$; ** $-x, -y - 1, -z + 1$. (b) Diagram showing the channel-like structure in **4**. For each stack of polymer, only two strands are shown for the sake of clarity. The dotted lines indicate the hydrogen bonds between the perchlorate and axial water molecule and amide groups of **L**.

addition, the perchlorate ions are also involved in hydrogen bonding with the two *syn*-oriented amide N–H groups of **L** ($N(3) \cdots O(7) = 3.236(2)$ and $N(4) \cdots O(5) = 3.015(2)$ Å) and one of the axial water molecules from an adjacent strand ($O(1) \cdots O(6)(ClO_3) = 2.804(2)$ Å).

Structure of $\{[CdL(H_2O)_3][ClO_4]_2\}_\infty$ (**5**)

Reacting $Cd(ClO_4)_2$ with one mol. equiv. of **L** leads to the formation of the colourless compound **5**. The single crystal X-ray structure shows that the compound is a coordination polymer $\{[CdL(H_2O)_3][ClO_4]_2\}_\infty$ (**5**) in a zigzag conformation; the cadmium ion is five coordinate, showing a distorted trigonal bipyramidal geometry in which the axial ligands are two pyridyl groups and the equatorial ligands are three water molecules (Fig. 5a). Both Cd–N bonds ($2.266(4)$ Å) are of the same length but one of the Cd–O bonds ($Cd(1) \cdots O(2)$) is slightly shorter than the other two (Table 1), giving the metal ion a local C_{2v} point group symmetry. The bond lengths and angles of the amide linkage in **5** are similar to the ones observed in the previous compounds and the ligand **L** also shows a *syn*-conformation. Although the overall conformation of the Cd polymer chains is similar to the Ag polymers, the pattern of polymer aggregation observed in **5** is entirely different. It is noted that the silver polymer chains are arranged in the same phase, allowing the formation of complementary amide hydrogen bonds. On the contrary, the polymer chains of **5** are aligned in an out-of-phase fashion (Fig. 5b). This is attributed to the different hydrogen bond pattern in **5**. Instead of forming hydrogen bonds with amide groups in adjacent chains, the carbonyl groups in one polymer chain are hydrogen bonded to the coordinated water molecules in the neighbouring chains. In addition, the perchlorate ions, which are situated between two polymer chains, are hydrogen bonded to the amide groups ($O_3ClO \cdots H-N$) and the water molecules from the chains. The different hydrogen bond pattern observed in **5** could be due

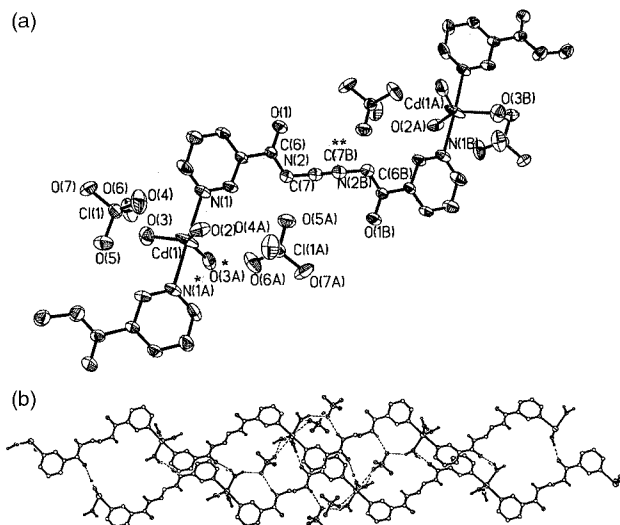


Fig. 5 (a) Molecular structure of compound **5**. Symmetry codes used for generating equivalent atoms: * $-x + 1, y, -z + 1/2$; ** $-x + 1/2, -y + 1/2, -z + 1$. (b) Diagram showing the assembly of polymer chains and intermolecular hydrogen bonds in compound **5**.

to steric reasons. The Cd ions, unlike the Ag ions in the polymers **1–3**, possess three equatorial ligands. “In-phase” arrangement of the polymer chains may lead to steric repulsion between the water molecules on adjacent Cd ions. In addition, the coordinated water molecules are more polarized because of the Lewis acidity of the Cd(II) ion, making them better hydrogen bond donors than the amide N–H groups.

Structure of $\{[AgL^1][ClO_4] \cdot CH_3CN\}_\infty$ (**6**)

The ligand *N,N'*-bis(2-pyridinecarboxamide)-1,2-ethane (**L**¹), an isomer of **L**, was synthesized¹⁷ and reacted with one equivalent of $AgClO_4$ to produce the coordination polymer $\{[AgL^1][ClO_4]\}_\infty$ (**6**). Colourless crystals of **6** were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the compound. The X-ray structure of **6** shows quasi-linear chains of coordination polymer $\{[AgL^1][ClO_4] \cdot CH_3CN\}_\infty$ (Fig. 6). In contrast to the silver polymers in **1–3**, the Ag(I) ions in **6**

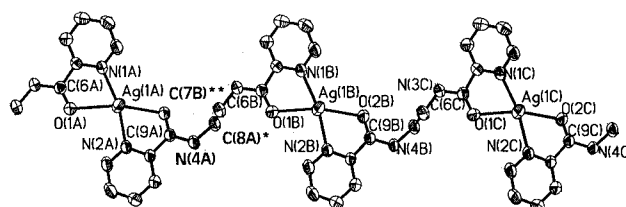


Fig. 6 Molecular structure of compound **6** (ORTEP drawing with 50% probability ellipsoids). Symmetry codes used for generating equivalent atoms: * $x, y + 1, z$; ** $x, y - 1, z$.

are four coordinate, showing a rhombic planar geometry Fig. 6. Whereas **L** is a bidentate ligand, **L**¹ acts as a tetradentate chelating ligand with both pyridyl nitrogen and carbonyl oxygen atoms coordinating to the Ag ion. The small bite angles of the five-membered rings are close to 70° . The nitrogen atoms are *trans* to each other and the N–Ag–N bond angle ($166.47(1)^\circ$) and O–Ag–O angle ($166.20(1)^\circ$) deviates significantly from linearity. The carbonyl O atoms, being coordinated to the metal centres, are not available for inter-chain hydrogen bond formation, and as a result the polymer chains in **6**, unlike those in compounds **1–3**, are segregated.

Concluding remarks

In this study the coordination chemistry of the ligand **L** with d¹⁰ metals was explored. It was demonstrated that all the

$\{[AgL]^+\}_\infty$ polymers could form corrugated sheets *via* complementary amide hydrogen bonds. Interesting crystal polymorphism was observed in the compound $\{[AgL][ClO_4]\}_\infty$. The supramolecular isomerism of the silver polymer arose from two rotamers in which the ligand L was in *syn*- and *anti*-orientations. Furthermore, it was demonstrated that triflate and nitrate salts of the silver polymer have more open structures. However, different anions have no effect on the conformation of the coordination polymer. The Zn polymer of L was an infinite chain of $[Zn_2L_2]$ metallacycles which stacked to form channels. In addition, a different pattern of interchain hydrogen bonds was observed in $\{[CdL(H_2O)_3][ClO_4]_2\}_\infty$ and it is possibly due to steric factors and the fact that the coordinated water is a better hydrogen bond acceptor. Finally it was shown that the ligand L¹ behaved very differently from its isomer L. Given its ability to form 2-D networks with metal ions, the ligand L could be promising in the synthesis of mesoporous materials.

Experimental

General

All commercial chemicals were purchased from Aldrich and used without further purification. ¹H NMR spectra were recorded on a Bruker ACF 300 spectrometer. Elemental analyses were performed in the microanalysis laboratory in the Department of Chemistry, The National University of Singapore.

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities and with care.

Preparations

***N,N'*-Bis(3-pyridinecarboxamide)-1,2-ethane (L).** 1,2-Diaminoethane (1 ml, 0.016 mol) was slowly added to a stirred 50 ml pyridine solution of 3-pyridinecarboxylic acid (4.0 g, 0.032 mol) and the solution was stirred for 15 min before the addition of triphenyl phosphite (9.0 ml, 0.032 mol). The mixture was refluxed for 6 h and then the volume was reduced to 5 ml under vacuum. A white precipitate was obtained from the solution after standing at room temperature for 24 h. The solid was filtered and washed with ethanol. Recrystallization from ethanol afforded colourless crystals. Yield: 63%. ¹H NMR (D₆-DMSO, δ): 9.00 (2H, s, H2 of py), 8.79 (2H, s, NH), 8.71 (2H, d, H6 of py), 8.21 (2H, d, H4 of py), 7.48 (2H, t, H5 of py), 3.48 (4H, s, CH₂), mp: 218 °C. Anal. calc. (%) for C₁₄H₁₄N₄O₂: C, 62.2; H, 5.2; N, 20.7. Found (%): C, 61.8; H, 5.2; N, 20.6. EI-MS (*m/z*): M⁺, 270; [M + H]⁺, 271.

***N,N'*-Bis(2-pyridinecarboxamide)-1,2-ethane (L¹).** This compound was synthesized according to the reported method.¹⁷ To a solution of 2-pyridinecarboxylic acid (73.8 g, 0.6 mol) in pyridine (250 ml) was added 1/2 equivalent of 1,2-diaminoethane (18.3 g, 0.3 mol) in pyridine (60 ml). The mixture was stirred for 10 min during which time a white precipitate formed. The mixture was then refluxed and triphenyl phosphite (167 g, 0.6 mol) was added slowly to the mixture. The mixture was refluxed for 4 h. Upon cooling, a pale yellow solid appeared. Recrystallization from chloroform produced colourless needles. Yield: 90%. ¹H NMR (CD₃CN, δ): 8.55 (2H, m, H6 of py), 8.40 (2H, b, NH), 8.20 (2H, d, H5 of py), 7.81 (2H, t, H4 of py), 7.41 (2H, t, H3 of py), 3.76 (4H, d, CH₂). Anal. calc. (%) for C₁₄H₁₄N₄O₂: C, 62.2; H, 5.2; N, 20.7. Found (%): C, 62.0; H, 5.2; N, 20.5.

$\{[AgL][ClO_4]\}_\infty$ (forms 1A and 1B). Addition of AgClO₄ (0.2 g, 0.96 mmol) to a methanol solution of L (0.26 g, 0.96 mmol) gave white precipitate instantaneously. The solution was stirred for an hour and then filtered. The white solid collected

was washed with excess methanol and hexagonal (1B) and rectangular (1A) crystals of $\{[AgL][ClO_4]\}_\infty$ were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the compound. Form 1A: Yield 15%. ¹H NMR (CD₃CN, δ): 8.93 (2H, s, H2 of py), 8.65 (2H, m, H6 of py), 8.12 (2H, d, H4 of py), 7.62 (2H, s, NH), 7.46 (2H, m, H5 of py), 3.58 (4H, s, CH₂). Anal. calc. (%) for C₁₄H₁₄N₄O₆ClAg: C, 35.2; H, 2.9; N, 11.7. Found (%): C, 35.6; H, 2.7; N, 12.0. Form 1B: Yield 45%. ¹H NMR (CD₃CN, δ): 8.93 (2H, s, H2 of py), 8.65 (2H, m, H6 of py), 8.12 (2H, d, H4 of py), 7.62 (2H, s, NH), 7.46 (2H, m, H5 of py), 3.58 (4H, s, CH₂). Anal. calc. (%) for C₁₄H₁₄N₄O₆ClAg: C, 35.2; H, 2.9; N, 11.7. Found (%): C, 35.4; H, 2.8; N, 12.0.

Syntheses of $\{[AgL][CF_3SO_3]\}_\infty$ (2) and $\{[AgL][NO_3] \cdot 1.25H_2O\}_\infty$ (3). The compounds were synthesized by layering an ethanol solution of L (0.2 g, 0.74 mmol) on an aqueous solution of AgCF₃SO₃ (0.19 g, 0.74 mmol) or AgNO₃ (0.13 g, 0.74 mmol). The slow diffusion of the solutions led to the formation of crystals of the products in the interface between the layers. Compound 2: Yield 58%. ¹H NMR (D₆-DMSO, δ): 9.00 (2H, s, H2 of py), 8.78 (2H, s, NH), 8.69 (2H, m, H6 of py), 8.17 (2H, m, H4 of py), 7.52 (2H, m, H5 of py), 3.49 (4H, s, CH₂). Anal. calc. (%) for C₁₅H₁₄AgF₃N₄O₅S: C, 34.2; H, 2.7; N, 10.6. Found (%): C, 34.2; H, 2.6; N, 10.6. Compound 3: Yield: 63%. ¹H NMR (D₆-DMSO, δ): 9.00 (2H, s, H2 of py), 8.79 (2H, s, NH), 8.69 (2H, m, H6 of py), 8.20 (2H, m, H4 of py), 7.51 (2H, m, H5 of py), 3.48 (4H, s, CH₂). Anal. calc. (%) for C₁₄H_{16.5}N₅AgO_{6.25}: C, 36.3; H, 3.6; N, 15.1. Found (%): C, 36.3; H, 3.0; N, 14.7.

Synthesis of *trans*- $\{[ZnL_2(H_2O)_2][ClO_4]_2 \cdot (H_2O)_2 \cdot CH_3CN\}_\infty$ (4). Zn(ClO₄)₂·6H₂O (0.34 g, 0.92 mmol) was added to a methanol solution of L (0.5 g, 1.8 mmol) and stirred for 1 h at room temperature. Slow evaporation of the mixture gave colourless crystals. X-Ray quality crystals were obtained by slow diffusion of diethyl ether into a mixture of acetonitrile and methanol mixture of the compound. Yield: 74%. ¹H NMR (D₆-DMSO, δ): 8.99 (2H, s, H2 of py), 8.78 (2H, b, NH), 8.69 (2H, d, H6 of py), 8.17 (2H, m, H4 of py), 7.51 (2H, m, H5 of py), 3.49 (4H, d, CH₂), 2.07 (3H, CH₃CN). Anal. calc. (%) for C₃₀H₃₉N₉O₁₆Cl₂Zn: C, 38.4; H, 4.2; N, 12.8. Found (%): C, 37.6; H, 4.3; N, 12.5.

Synthesis of $\{[CdL(H_2O)_3][ClO_4]_2\}_\infty$ (5). Cd(ClO₄)₂·6H₂O (0.58 g, 1.85 mmol) was added to a warm methanol solution of L (0.5 g, 1.85 mmol) and stirred for 1 h at room temperature. Slow evaporation of solvent left white solid. X-Ray quality crystals were obtained by slow diffusion of diethyl ether into a methanol solution of the compound. Yield: 74%. ¹H NMR (D₆-DMSO, δ): 8.99 (2H, s, H2 of py), 8.78 (2H, b, NH), 8.69 (2H, d, H6 of py), 8.17 (2H, m, H4 of py), 7.51 (2H, m, H5 of py), 3.49 (4H, d, CH₂), 2.07 (3H, CH₃CN). Anal. calc. (%) for C₁₄H₁₉CdCl₂N₄O₁₃: C, 26.5; H, 3.2; N, 8.8. Found(%): C, 27.1; H, 3.5; N, 8.7.

Synthesis of $[AgL^1][ClO_4] \cdot CH_3CN$ (6). To a methanolic solution of AgClO₄ was added 1 mol equivalent of L¹. The solution was filtered and the white solid was washed with methanol. Colourless crystals were obtained from diethyl ether–acetonitrile diffusion. Yield: 55%. ¹H NMR (CD₃CN, δ): 8.57 (2H, m, H6 of py), 8.44 (2H, b, NH), 8.06 (2H, d, H5 of py), 7.92 (2H, t, H4 of py), 7.50 (2H, t, H3 of py), 3.62 (4H, d, CH₂). Anal. calc. (%) for C₁₄H₁₄N₄O₆ClAg: C, 35.2; H, 2.9; N, 11.7. Found (%): C, 35.8; H, 3.2; N, 11.1.

X-Ray crystallography

The diffraction experiments were carried out on a Bruker AXS SMART CCD 3-circle diffractometer with a Mo-K α sealed tube. SMART¹⁸ for collecting frames of data, indexing

Table 3 Crystal data for 1-6

Compound	1 (A form)	1 (B form)	2	3	4	5	6
Formula	C ₁₄ H ₁₄ AgClN ₄ O ₆	C ₁₄ H ₁₄ AgClN ₄ O ₆	C ₁₅ H ₁₄ AgF ₃ N ₄ O ₅ S	C ₁₄ H _{16.5} AgN ₅ O _{6.25}	C ₃₀ H ₃₉ ZnCl ₂ N ₉ O ₁₆	C ₁₄ H ₁₉ CdCl ₂ N ₄ O ₁₃	C ₁₂ H ₁₇ AgClN ₃ O ₆
Formula weight	477.61	477.61	527.23	462.69	917.97	634.63	518.69
Crystal size/mm	0.42 × 0.10 × 0.04	0.26 × 0.14 × 0.06	0.44 × 0.36 × 0.06	0.38 × 0.22 × 0.20	0.34 × 0.24 × 0.14	0.24 × 0.10 × 0.03	0.42 × 0.10 × 0.04
Temperature/K	223(2)	223(2)	203(2)	293(2)	243(2)	223(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	C2/c	P $\bar{1}$
<i>a</i> /Å	5.1132(2)	5.1239(1)	9.1297(1)	9.0861(1)	7.8536(2)	17.8353(2)	7.1569(2)
<i>b</i> /Å	13.2742(3)	13.9276(2)	9.6318(1)	9.5617(1)	12.2091(3)	7.5368(8)	10.6650(2)
<i>c</i> /Å	24.2679(7)	24.0654(6)	9.8647(1)	10.1841(1)	12.3860(2)	17.1661(2)	13.2643(2)
<i>a</i> °	90	90	86.833(1)	92.612(1)	64.587(1)	90	88.496(1)
β °	95.284(1)	110.757(1)	87.100(1)	98.041(1)	77.101(1)	112.487(2)	88.816(1)
γ °	90	90	89.493(1)	97.386(1)	80.065(1)	90	76.881(1)
<i>V</i> /Å ³	1640.2(1)	1605.92(6)	865.01(2)	866.997(16)	1041.67(4)	2132.0(4)	985.57(4)
<i>Z</i>	4	4	2	2	1	4	2
<i>D_c</i> /g cm ⁻³	1.934	1.975	2.024	1.772	1.463	1.977	1.748
Absorption coefficient/mm ⁻¹	1.434	1.465	1.357	1.207	0.795	1.353	1.202
No. of parameters varied	137	121	319	258	293	168	283
Final <i>R</i> indices ^a	<i>R</i> 1 = 0.0253, <i>wR</i> 2 = 0.0625	<i>R</i> 1 = 0.0231, <i>wR</i> 2 = 0.0625	<i>R</i> 1 = 0.0253, <i>wR</i> 2 = 0.0666	<i>R</i> 1 = 0.0262, <i>wR</i> 2 = 0.0705	<i>R</i> 1 = 0.0646, <i>wR</i> 2 = 0.1798	<i>R</i> 1 = 0.0489, <i>wR</i> 2 = 0.1088	<i>R</i> 1 = 0.0505, <i>wR</i> 2 = 0.1280
Final diff. ρ_{max} /e Å ⁻³	0.525 and -0.541	0.418 and -0.274	0.786 and -0.842	0.397 and -0.576	0.778 and -0.582		0.784 and -0.683
GOF ^b	1.097	1.059	1.010	1.037	1.057	1.047	1.054

^a $R1 = (|F_o| - |F_c|)/(|F_o|)$; $wR2 = [w(F_o^2 - F_c^2)/(w(F_o^4))]^{1/2}$. ^b Goodness of fit = $[w(F_o^2 - F_c^2)/(n - p)]^{1/2}$. For all structures determined, the scan type is ω and the Mo-K α wavelength is 0.71073 Å.

reflection and determination of lattice parameters; SAINT¹⁸ for integration of intensity of reflections and scaling; SADABS¹⁹ for empirical absorption correction; and SHELXTL²⁰ for space group determination, structure solution and least-squares refinements on $|F|^2$. The crystals were mounted at the end of glass fibres and used for the diffraction experiments. A brief summary of crystal data and experimental details are given in Table 3. For all the structures, anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms and hydrogen atoms were placed in their ideal positions.

{[AgL][ClO₄]}_∞, Form 1A. A total of 4189 reflections were collected of which 1441 ($R_{\text{int}} = 0.0163$) were independent. The two carbon atoms of the ethylene were found to be disordered. Two orientations of carbon atoms were included in the model with occupancies of 0.6 and 0.4. Common isotropic thermal parameters were refined for each groups. An extinction coefficient was refined to 0.0008(2).

Form 1B. A total of 3923 reflections were collected of which 1408 ($R_{\text{int}} = 0.0224$) were independent. An extinction coefficient was refined to 0.0009(2).

{[AgL][CF₃SO₃]}_∞ (2). A total of 6364 reflections were collected of which 3021 ($R_{\text{int}} = 0.0247$) were independent. An extinction coefficient was refined to 0.0016(6).

{[AgL][NO₃](H₂O)_{1.25}]}_∞ (3). A total of 6347 reflections were collected of which 3000 ($R_{\text{int}} = 0.0148$) were independent. The oxygen atoms of the NO₃[−] are disordered and are modeled with occupancies of 0.65 and 0.35. Anisotropic thermal parameters were refined for the major component whereas a common isotropic thermal parameter was refined for the minor model. An extinction coefficient was refined to 0.0048(15).

trans-{[ZnL₂(H₂O)₂][ClO₄]₂·(H₂O)₂·CH₃CN]}_∞ (4). A total of 6800 reflections were collected of which 4030 ($R_{\text{int}} = 0.0451$) were independent. Anisotropic thermal parameters were refined for rest of the non-hydrogen atoms. The acetonitrile is disordered by inversion.

{[CdL(H₂O)₃][ClO₄]₃]}_∞ (5). A total of 5994 reflections were collected of which 1884 ($R_{\text{int}} = 0.0605$) were independent.

{[AgL₂][ClO₄]₂·CH₃CN]}_∞ (6). A total of 7712 reflections were collected of which 3903 ($R_{\text{int}} = 0.0281$) were independent. The oxygen atoms of the perchlorate were found to be disordered and two orientations of oxygen atoms were included in the model with occupancies of 0.6 and 0.4. An extinction coefficient was refined to 0.0003(11).

CCDC reference numbers 171770–171776.

See <http://www.rsc.org/suppdata/dt/b1/b105696b/> for crystallographic data in CIF or other electronic format.

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