On the coordination behaviour of NO_3^- in coordination compounds with Ag^+
Part 1. Solubility effect on the formation of coordination polymer networks between $AgNO_3$ and L (L = ethanediyl bis(isonicotinate) as a function of solvent

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The influence of the solubility of $AgNO_3$ in three solvent systems is studied for the reaction between $AgNO_3$ and the ligand L (= ethanediyl bis(isonicotinate)). Three solid state structures are obtained, differing in the relative ratio Ag : L in the first case, and in polymorphism in the second. The Ag–O(NO_3^-) distance correlates strongly with the solubility of $AgNO_3$ in the used solvent. Solution studies prove indeed the existence of close ion contact pairs in the less good solvents, where as ion solvation is observed in good solvents for $AgNO_3$. The three different structures are compared to two solvated structures in which H_2O demonstrates coordination to the nitrate anion *via* H-bonding.

Introduction

During the last fifteen years the number of publications concerning coordination polymer networks has dramatically increased from 100 articles per year to 1000 in 2004 as shown in recent reviews on the subject.[1–3] The numerous literature contributions in the field of coordination polymers are due to several points: (i) incorporating metal ions in supramolecular networks permits the control of the metal atom positions in the materials, giving them some desired properties. The types of metal ions and distances between them can be chosen so that stable functional solid materials can be tuned; (ii) the variety of "nodes and linkers" offers to the chemists infinite possibilities for building new species with intriguing properties, architectures and topologies.[4–7] Moreover, the studies of crystals become much easier thanks to the technological improvements in the field of X-ray measurements and computational resolution techniques.

A large amount of coordination polymer networks involve bipyridyl (*N*-donors) ligands. They include pyrazine[8–10] and its derivatives,[11–14] 4,4′-bipyridine[15–22] and longer bridged bipyridyl ligands[23–41] as linkers with a large diversity of the metal centers as nodes. The coordination polymers derived from Ag^I with N-donor ligands are well-known for making simple 1-D motifs when the metal ion reacts with a bipyridine-type ligand.[42,43] Ag^I prefers mostly a linear geometry with respect to the coordination of N-donor ligands in these cases. Nevertheless, as the coordination sphere of Ag^I is very flexible,[15,21,32,38,45–53] it can adopt coordination numbers between two and six, the geometry changing from linear to octahedral. The coordination geometries of Ag^I are often

distorted owing to the inherent lack of ligand field stabilization effects. This flexibility of the Ag^I ion is used to investigate the role played by the weak interactions during the crystal formation. The lability of the silver-donor atom bonds allows furthermore building complexes, so that the process of coordination polymer formation is reversible.

All building blocks included in one coordination polymer have particular interactions with the solvents, according to their polarity, hydrophilic/hydrophobic groups, *etc*…. The solvent can have a role as coordinating molecules[54] or template molecules.[55] It is assumed that the differences in size and shape of the used solvents affect the self-assembly and result in the formation of different 2-D frameworks.[55]

The work on coordination polymers in our group follows the synthesis of homo- and mixed compounds of group 1 and 2 metals with the aim to synthesise new precursors for CVD and sol-gel techniques used for oxide materials.[56–65] In order to obtain better performing and single source precursors, mixed metal compounds containing transition metal, as well as group 1 and 2 metal ions began to be investigated. The formation of coordination polymers is thus an efficient way to get a good distribution of the metals within the materials.

With regard to the field of coordination polymers formed with group 11 elements, the ligand ethanediyl bis(isonicotinate), L, was chosen[66,67] because it (i) is flexible (structurally adaptive), (ii) contains different functional groups allowing coordination of two different metal ions, and (iii) can be prepared easily, which makes potential applications possible. L can adopt two main conformations, *gauche* or *anti*, due to the free rotation around the ethyl group C–C bond. Obviously, different conformations of the ligand in the coordination polymers can drastically change the resulting framework architecture. Several ligands with the same flexibility have already been used.[50,68,69] In most cases, only one conformation

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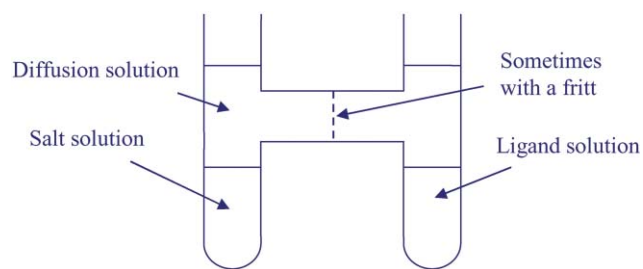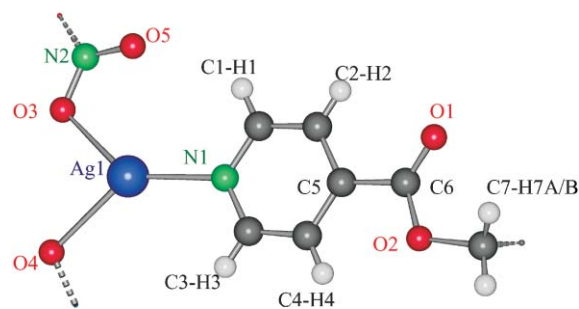
Scheme 1 "H-shaped" tube.

Fig. 1 Asymmetric unit of **1**.

per framework is observed. As we have already reported on pseudo-polymorphism of **L** with CuCl and AgNO$_3$, we here wish to report the effect of solubility on the formation of coordination polymer networks of **L** with AgNO$_3$.

Results and discussion

Crystals of {[Ag$_2$(NO$_3$)$_2$(**L**)]}$_n$, **1**, grow in a "H-shaped" tube (Scheme 1). With the proportion **L** : Ag = 1 : 1, **L** dissolved in THF and silver nitrate in ethanol, are put each in one arm of the tube, the solutions are frozen by immersion of the tube in liquid nitrogen and finally the diffusion solvent (THF) is added. The slow diffusion can take place in order to yield high quality crystals of **1** at the interface EtOH/THF. Unfortunately, the yield is not high and only few crystals grow in each batch. The results of performed reactions in order to get more of **1** in higher quantity are resumed in Table 1. Only the first two reactions gave **1**, but always in very low yield.

Compound **1** crystallizes in the monoclinic space group *C*2/*c* (no.15).[70] There are eight asymmetric units consisting of one silver atom, one nitrate anion and half of a ligand molecule in each unit cell (Fig. 1).

There are thus two silver atoms for one ligand molecule. Each silver atom is coordinated with one ligand molecule, and the distance Ag–N is with 2.226(7) Å in the same range than in comparable silver coordination compounds.[10,36,42,43,67] It is also linked to two oxygen atoms of two different nitrate anions, O3 and O4, the distances Ag–O are 2.354(5) and 2.390(7) Å long. (Table 2) This corresponds to short Ag–O(NO$_3$) distances showing a strong coordination bond between cation and anions (Fig. 2b). These Ag–O distances belong to the shortest ones known in the literature.[54,71,72] The Ag–O(NO$_3$) distances are usually found from 2.3 to 2.6 Å, as the nitrate anion is a moderate good coordinating counter anion.[42,43] The nitrate anions of **1** act as bridging ligands between two silver cations, two oxygen atoms of each anion bridging two adjacent metal ions. This leaves the third oxygen atom, O5, uncoordinated within this chain.

Table 2 Most important bond lengths (Å) and angles (°) in **1**

Ag–N	2.226(7)	O–Ag–N	138.2(3), 135.3(2)
Ag–O(O$_2$N)	2.354(5), 2.390(7) 2.72(1)	O–Ag–O	84.6(2)
C–N	1.334(8), 1.35(1)	C–N–C	118.6(6)

The angle sum around the silver cation arises to *ca.* 358°, showing the quasi-trigonal planar arrangement of closest ligands around the metal ion. Ligand molecules, silver atoms and nitrate anions are organized so that a neutral 2-D motif appears. This motif is called "fishbone"-like layer (Fig. 2a). It is evident from Fig. 2 that the motif is constituted by AgNO$_3$-chains (in the *c* direction), which are linked through the ligand molecules. The ligand molecules are running in symmetric directions on both sides of the silver nitrate chain, explaining the "fishbone" name.

The conformation of the ligand is *anti* as in the free ligand.[66] The pyridine planes within a ligand molecule are parallel as there is an inversion center in the middle of the C7–C7$^{\#1}$ bond, the two planes being separated by 0.46(5) Å. The plane containing the pyridine ring and the plane containing the adjacent ester group form an angle of 10.1(8)° to each other. One hydrogen bond is found between the oxygen atom O1 and the hydrogen atom H7B within a ligand molecule (Table 3).

This intra-ligand hydrogen bond can appear as the ligand is highly distorted with a O2–C7–C7$^{\#1}$ angle of 77(3)° (Fig. 3). The position of O2 is disordered: this atom position is disordered and was split into two positions with 50% occupancy, O2A and O2B in the crystallographic data. In spite of this distortion, the distance Ag–Ag is 17.76 Å long, corresponding to the same Ag–Ag distance observed in other coordination polymers with the *anti*-conformation of **L**.[66,67] The distortion is compensated by *ca.* 0.04 Å longer O–C bonds compared to these literature compounds.

Some other weak interactions can be observed within the layer (Fig. 4, Table 3): (i) hydrogen bonds are observed between two parallel ligand molecules (highlighted in yellow in

Table 1 Experiments and products of reaction **L** + AgNO$_3$ (1:1) with ethanol

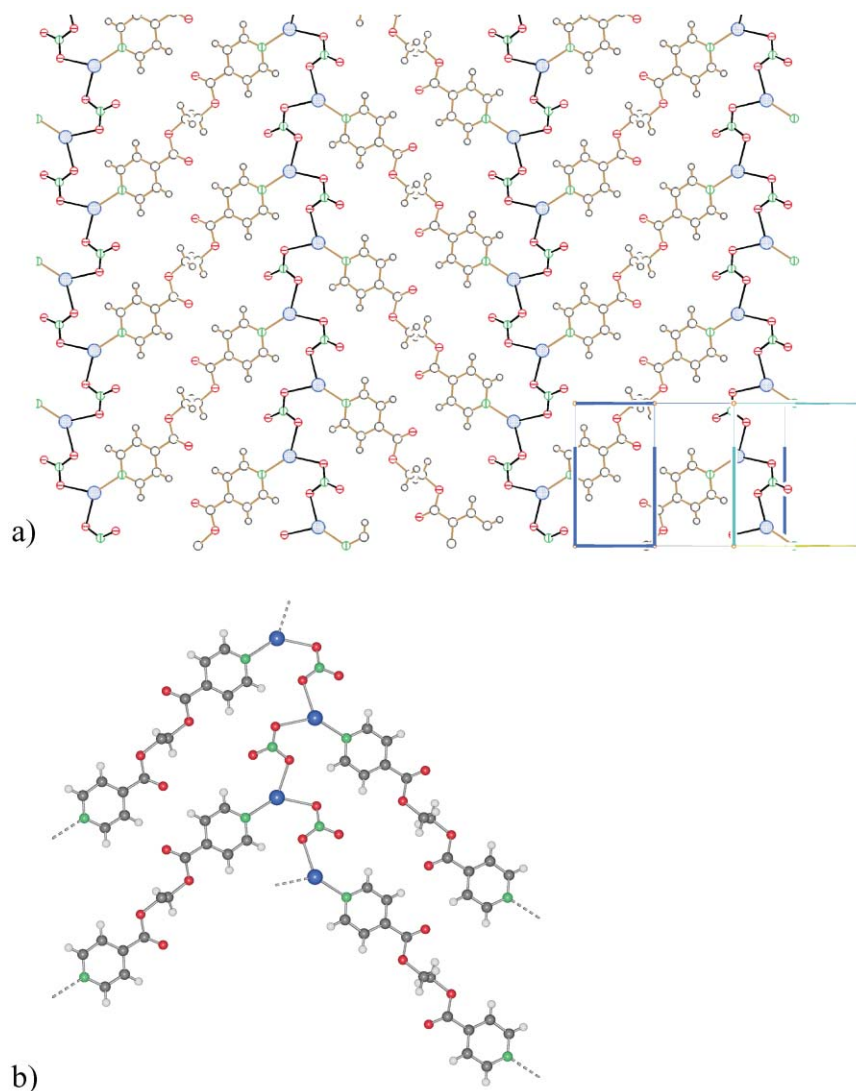| Ligand	AgNO$_3$	Experiment	Diffusion solvent	Product	Concentration/mol L^{-1}
THF	EtOH	"H-shaped" tube	THF	**1**	3.10^{-3}
THF	EtOH	"H-shaped" tube	THF	**1**	1,5.10^{-3}
THF	EtOH	"H-shaped" tube	THF	"{AgLNO$_3$}"	6.10^{-3}
EtOH	EtOH	"H-shaped" tube	EtOH	{[Ag(**L**)](NO$_3$)}$_n$[58]	3.10^{-3}
EtOH	H$_2$O	"H-shaped" tube	EtOH	{[Ag(**L**)](NO$_3$)(H$_2$O)$_2$}$_n$[58]	3.10^{-3}

Fig. 2 (a) The two-dimensional 'fishbone' motif in **1**; (b) detail around the silver atoms.

Fig. 4), and (ii) the nitrate anions are involved in hydrogen bonding to the surrounding pyridyl hydrogen atoms, ranging from 2.46 to 2.89 Å (highlighted in blue in Fig. 4).

The so formed layers are stacked parallel to each other to form the overall 3-D structure (Fig. 5a). The layers are rather flat; however, the silver atoms don't exactly lie in the mean plane of the layers. If one considers the three atoms around one silver atom (N1, O3 and O4), the sum of the three angles

(O3–Ag–N1, N1–Ag–O4, O4–Ag–O3) is smaller than 360° (358°) indicating a weak deformation from the trigonal planar coordination sphere of the silver atom. Indeed the silver atoms are coordinated perpendicular to the layer plane by the O5-atom of a nitrate anion of the next sheet, at a distance of 2.72(1) Å. This distance Ag–O5 is much longer than Ag–O3 and Ag–O4 but is in the range of those of weak coordinating nitrate anions.

Furthermore, there is a weak metal–ring interaction on the other side of the silver atom (Fig. 5b, Table 4). Whereas the literature reports mainly η^2-interactions between aromatic rings and silver ions, we observe a distorted η^3-binding between pyridine and Ag$^+$. The strongest contacts are found between Ag and C5 with 3.39(1) Å, the distances Ag–C4 and

Table 3 Hydrogen bond data for **1** [lengths (Å) and angles (°)]

D–H⋯A	D(D–H)	d(H⋯A)	d(D⋯A)	Angle D–H⋯A
Intra-ligand				
C7–H7B⋯O1[#1]	0.97	2.37	2.98(3)	120.6
Intra-sheet hydrogen bonding interactions				
C2–H2⋯O1[#2]	0.93	2.38	3.27(1)	161.2
C3–H3⋯O3[#3]	0.93	2.49	3.29(1)	143.7
C3–H3⋯O4[#3]	0.93	2.46	3.167(9)	132.9
C4–H4⋯O4[#3]	0.93	2.89	3.37(1)	113.0
C1–H1⋯O5	0.93	2.80	3.55(1)	137.8

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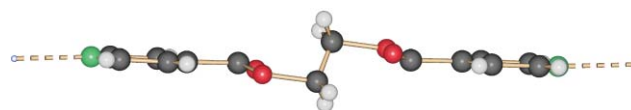

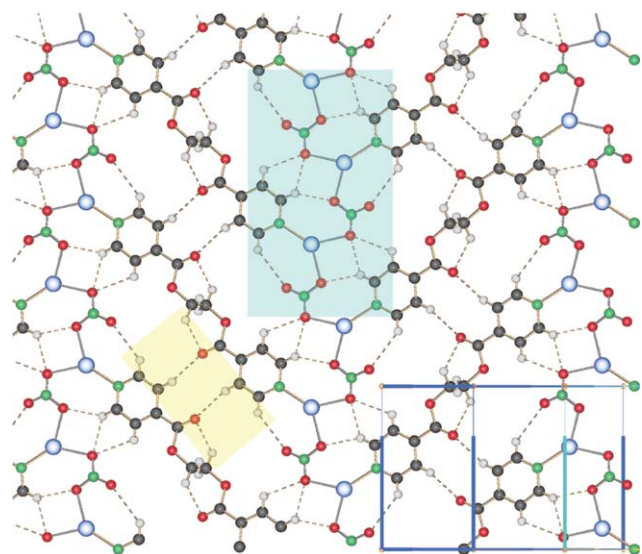**Fig. 3** Top view of the ligand in **1** with the distortion.

Fig. 4 Intra-sheet interactions in **1**: hydrogen bonds between ligand molecules in yellow and hydrogen bonds involving the nitrate counter anions in blue.

Table 4 Ag···pyridine ring interactions lengths (Å) and angles (°) in **1**.

	$d_{M-R}{}^b$	$pd_{M-R}{}^c$	β^d
Ring (N1, C1, C2, C3, C4, C5) ···Ag1[#1 a]	3.472	3.357	14.77

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $-y$, $z + 1/2$. [b] d_{M-R}, distance metal-geometrical center of the ring. [c] pd_{M-R}, perpendicular distance of the metal on the ring. [d] β, shift angle.

[–Ag–(NO$_3$)–]$_n$ are found in the compound {[Ag(1,4-bis(phenylthio)butane)(NO$_3$)]}$_n$,[54] in which the Ag^I center is tetrahedrally coordinated to two S atoms from the ligand and two O atoms from nitrate anions. The structure may be described as [–Ag–(NO$_3$)–]$_n$ linked *via* the ligands as in **1**, but with a different coordination environment for the silver ion and longer silver-nitrate distances (2.452(6) and 2.557(6) Å).

The synthesis of silver coordination polymers using silver nitrate and **L** was also performed in acetonitrile. The solutions of **L** and silver nitrate, each dissolved in acetonitrile, are mixed, stirred and then left at room temperature ($C = 5 \times 10^{-3}$ mol L^{-1}). Self-assembly between silver ions and **L** occurs in darkness giving colourless single crystals of {[Ag(L)]NO$_3$}$_n$, **2**, suitable for X-ray diffraction. The quantity of crystals was not sufficient to perform other analyses on this sample. However the reaction of **L** and AgNO$_3$ in dichloromethane gives a white polycrystalline precipitate. Its powder X-ray spectrum was compared to the calculated one (from single crystal data) showing that the precipitate is isostructural and thus identical with **2**. This precipitate was therefore used for the further characterizations.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ (no.2).[70] The asymmetric unit is composed of one ligand molecule, one silver atom and one nitrate anion (Fig. 6) and there are two of such moieties in the unit cell. The most important bond lengths and angles are listed in Table 5.

In this case, the silver atoms are coordinated by two different ligands through their nitrogen atoms. The ligand molecules thus act as connectors between the silver atoms, the final motif being a charged one-dimensional, also called polyelectrolyte chain (Fig. 7). The distances Ag–N are 2.183(4)

Ag–C2 being 3.56(1) and 3.59(1) Å, respectively (Fig. 5b).[73–77] The remaining distances Ag–ring are longer than 3.85 Å. No other interactions are found between two adjacent layers except these interactions involving the silver atoms.

The arrangement of the main structure made of …–Ag–NO$_3$–Ag–NO$_3$–… chains, is probably due to the poor solubility of AgNO$_3$ in ethanol, which is unable to dissolve the silver nitrate contacts completely. This can be confirmed experimentally by two methods, solution IR and ES-MS, both of which show that NO$_3^-$ exists associated to the silver cations in solution and the gas phase. Indeed, the IR-bands at 1327 and 1412 cm^{-1} can be attributed to coordinating anion.[78] The fragments observed in ES-MS at 431.9 *m/z* confirm the presence of species of the type [Ag$_2$(NO$_3$)$_2$(EtOH)$_2$]$^+$.

To our knowledge, this is the first example of 2-D neutral silver coordination polymer, with a trigonal planar coordination of silver {AgO$_2$N} and this motif. Some
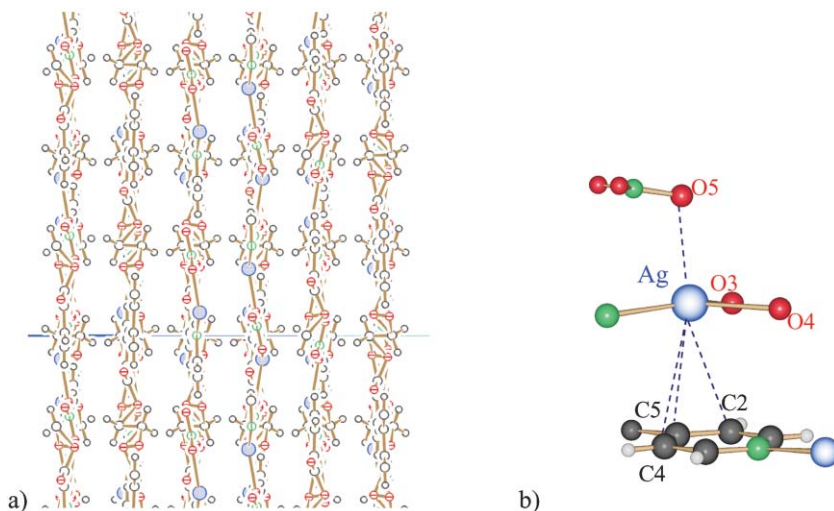

Fig. 5 (a) Three-dimensional structure of **1** in the direction (11 0 10); (b) coordination environment around silver atoms in **1**.
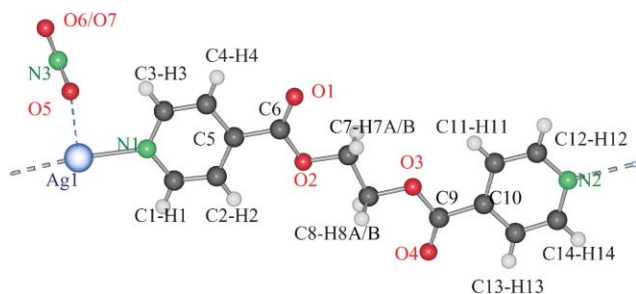
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Fig. 6 Asymmetric unit in **2**.

Table 5 Most important bond lengths (Å) and angles (°) in **2**

Ag–Ag	4.017(2)		
Ag–N	2.183(4), 2.189(4)	N–Ag–N	169.8(2)
Ag–O(O$_2$NO)	2.599(5), 2.703(7)		
	3.044(4), 3.122(4)		
C–N	1.342(5), 1.343(7)	C–N–C	117.5(4)
	1.352(6), 1.347(5)		116.6(4)

and 2.189(4) Å long, and the N–Ag–N angle is with 169.8(2)° quite deviated from linear.

The linearity in the chain is due to the *anti*-conformation adopted by the ligand molecules. The ligand molecules alternating with the silver atoms have all the same direction and are oriented in the same direction "up-to-down" (Fig. 7). The distance Ag–Ag within the chain is thus 17.66 Å long as in **1** and similar compounds where the same ligand is in *anti* conformation.[66,67] The coordination sphere of the silver atoms is completed by interactions with the nitrate anions. All three nitrate oxygen atoms, O5, O6 and O7, are linked to silver atoms, so that the nitrate anions act as linkers in-between the chains (Fig. 8). The silver–oxygen distances range from 2.599(5) to 3.122(4) Å. These distances in **2** are by 0.25 Å longer on average than in **1** and smaller than in other
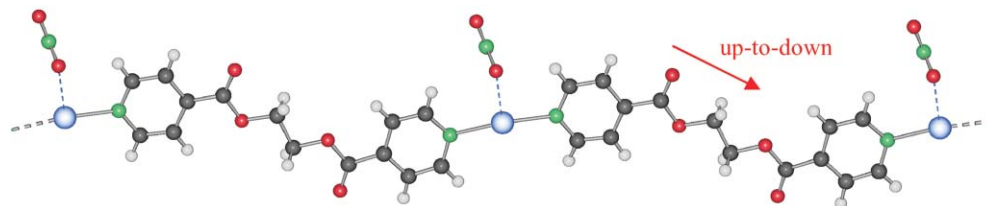
comparable compounds.[10,36,42,43,67] The N–Ag–N deviation from linearity is due to the strong Ag1–O5 interactions (2.599(5) Å). Hydrogen bonds (C8–H8B⋯O1) allow the alignment of the chains and thus the formation of an overall neutral layer. The shortest distance between the silver atoms in the layer is 6.159(1) Å.

As shown on Fig. 9a, the chains are ordered in the direction (−12 10 22) with a slight inclination of the molecular mean plane compared to this direction, the counter anions lying only on one side of the chains. Indeed the coordination of the nitrate molecules is not distributed homogeneously around the silver atoms but they are found only on one side (Fig. 9b). In the 3-D structure of **2**, the layers stack parallel and alternate their orientations: the nitrate anions are pointing in one direction, and in the next layer they are pointing in the opposite one (Fig. 9c).

Two types of inter-sheet areas are thus created: in the first one the anions are embedded, and in the next one the chains are simply parallel to each other, as described in Fig. 10b.

As there are two types of inter-sheets, there are various complementary interactions between the layers (Fig. 10a). In the "empty" inter-sheets, the layers interact *via* π-stacking (Table 6) between the rings N1, C1…C5 and N2, C10…C14 with a center-to-center distance of 3.82 Å and an offset of 1.5 Å. The silver–silver distances are 4.017(2) Å long and are not the shortest contact between two chains. Pairs of chains similar to literature compounds appear (see below),[67] but in contrast to the latter, the counter ion role is different, there are no short Ag–Ag contacts, and only the π-stacking remains. The much shorter Ag–Ag distances of the literature compounds must apparently be supported by the nitrate anions, which is not the case here.

The overall arrangement is strengthened with hydrogen bonds between the ligand molecules of two close layers, and between the nitrate anions and neighboring ligand molecules
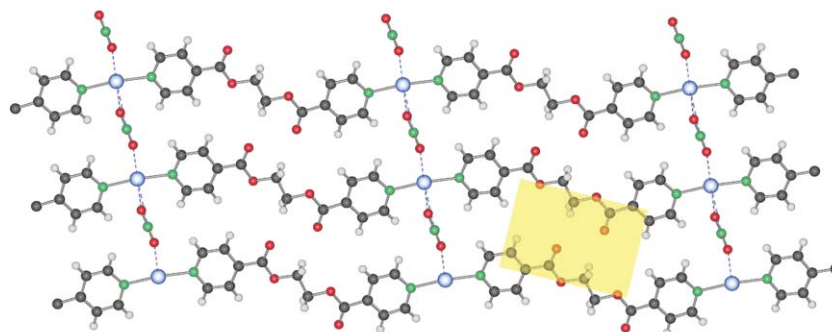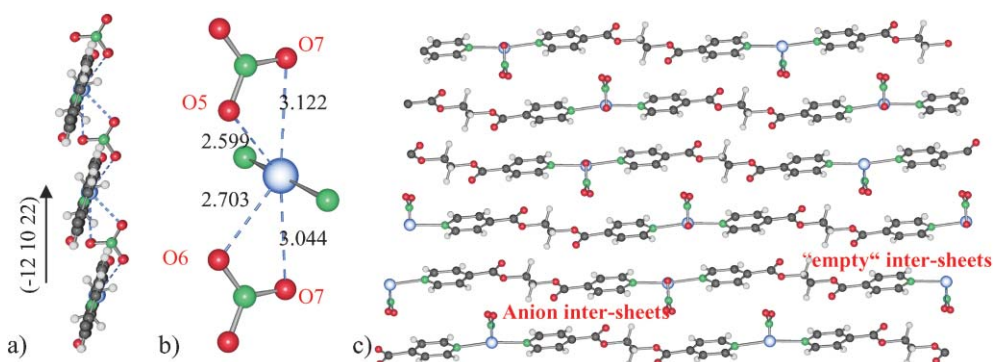

Fig. 7 The linear motif in **2**.

Fig. 8 Alignment of the chains in **2** with the nitrate as linkers and the hydrogen bond region highlighted in yellow.

Fig. 9 (a) Organisation of the chains and the nitrate anions within a layer; (b) coordination of silver; (c) stacking of the layers in the structure of **2**.
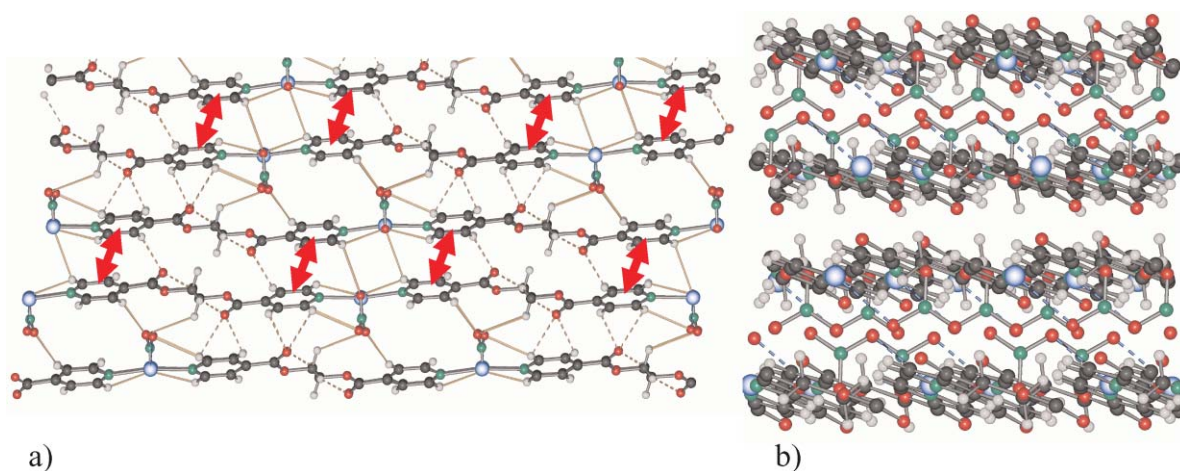

Fig. 10 (a) 3-D structure of **2** with the inter-sheets interactions (red arrows: π-stacking in the empty inter-sheets; dashed lines: hydrogen bonds between ligands; full lines: hydrogen bonding involving the nitrate anions). (b) View of the stacked layers in **2**.

Table 6 Ring interactions lengths (Å) and angles (°) in **2**.

π–π interactions	$d_{R-R}{}^{b}$	$pd_{R-R}{}^{c}$	$β^{d}$	$α^{e}$
Ring (N1, C1, C2, C3, C4, C5) ···Ring (N2, C10, C11, C12, C13, C14)$^{\#1\,a}$	3.82	3.49	24.0	2.1

^{a} Symmetry transformations used to generate equivalent atoms: #1 $-x + 2$, $-y + 1$, $-z + 1$. ^{b} d_{R-R}, distance between the two geometrical centers of the rings. ^{c} pd_{R-R}, perpendicular distance of the geometrical center of one ring on the other. ^{d} $β$, shift angle. ^{e} $α$, inclination angle between the two rings.

(Fig. 10a). These interactions take place in the two kinds of inter-sheet layers (Table 7).

Coordination polymer synthesis based on **L** and AgNO$_3$ and crystallization were also attempted from a THF/water mixture. Compound **3** is obtained purely by crystallisation from an **L**/AgNO$_3$ mixture in THF/water after slow evaporation of the solution. Elementary analysis for **3** shows a composition: Ag : NO$_3$: **L** of 1 : 1 : 1, as for **2**. {[Ag(**L**)]NO$_3$}$_n$, **3**, crystallizes in the monoclinic space group $P2_1/n$ (no.14).[67] There are four asymmetric units per unit cell, made of one ligand molecule, one silver atom and one nitrate anion (Fig. 11). The pyridine rings coordinate to the silver ions creating a 1-D motif: a chain with alternating silver ions and ligand molecules –Ag–**L**–Ag– **L**–, the silver atoms being coordinated by two nitrogen atoms of two different ligand molecules (Fig. 12). This compound has been described previously in another context together with two pseudo-polymorphs of **3**, {[Ag(**L**)](NO$_3$)(H$_2$O)}$_n$, **4**, and

Table 7 Hydrogen bond data for **2** [lengths (Å) and angles (°)]

D–H···A	d(D–H)	d(H···A)	d(D···A)	Angle D–H···A
Inter-chains interactions				
C8–H8B···O1$^{\#1}$	0.97	2.64	3.580(7)	163.4
Intra-sheets hydrogen interactions				
C11–H11···O1$^{\#2}$	0.93	2.79	3.648(7)	153.2
C13–H13···O3$^{\#3}$	0.93	2.63	3.195(7)	119.3
C14–H14···O4$^{\#3}$	0.93	2.85	3.316(6)	112.3
C7–H7A···O4$^{\#4}$	0.97	2.50	3.436(7)	161.9
Hydrogen bonds involving nitrate anions				
C1–H1···O7$^{\#4}$	0.93	2.65	3.403(7)	138.9
C12–H12···O7$^{\#4}$	0.93	2.58	3.309(8)	135.3
C1–H1···O7$^{\#5}$	0.93	2.80	3.38(1)	121.3
C4–H4···O6$^{\#3}$	0.93	2.53	3.390(8)	154.7
C8–H8A···O6$^{\#3}$	0.97	2.83	3.494(7)	126.5
C14–H14···O5	0.93	2.65	3.308(9)	128.3

^{a} Symmetry transformations used to generate equivalent atoms: #1 $x + 1$, y, z; #2 $-x$, $-y + 2$, $-z + 2$; #3 $-x + 2$, $-y + 1$, $z + 1$; #4 $x - 1$, y, z; #5 $-x + 1$, $-y + 2$, $-z + 2$.
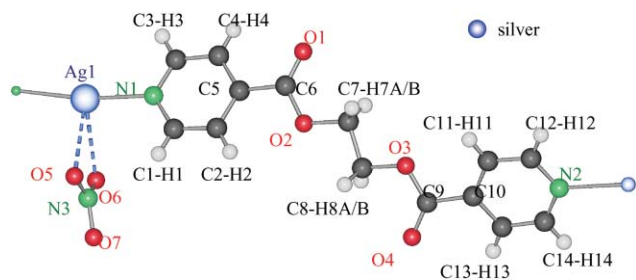
○ silver

Fig. 11 Asymmetric unit in **3** (colour codes given for all following figures).

{[Ag(**L**)](NO₃)(H₂O)₂}$_n$, **5**.[67] Due to the relevance of these structures in the discussion here, their main structural features will briefly be highlighted in the following (Table 8, Fig. 11–16).

The conformation of the ligand within the coordination polymer of **3** is the *anti* one, the same as in the crystalline ligand alone[66] and as in compounds **1** and **2**. In contrast to **2**, the chains of **3** have an undulating form because the direction of the ligand molecules changes after each silver cation, going alternatively "up-to-down" and then "down-to-up" as shown in Fig. 12.

The Ag–N distances of **3** are 2.232(2) and 2.239(2) Å long and the angle N–Ag–N is 170.25(9)°. This non-180° angle at the silver cation is due to the asymmetric coordination of the nitrate anion. Each nitrate anion is connected with two silver atoms and each silver atom with two nitrate anions (Fig. 13b):
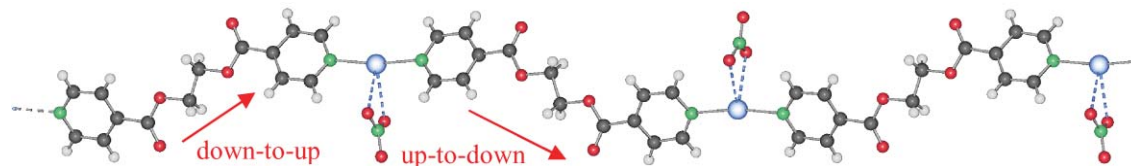
Table 8 Most important bond lengths (Å) and angles (°) in **3**, **4**, and **5**.

3			
Ag–N	2.232(2), 2.239(2)	N–Ag–N	170.25(9)
Ag–O(O₂NO)	2.669(2), 2.724(2)	O–Ag–O	47.05(6)
	2.800 (3)		149.70(7), 103.32(6)
C–N	1.337(3), 1.343(4)	C–N–C	117.7(2)
	1.340(3), 1.335(4)		117.7(2)
4			
Ag–Ag	3.136(1)		
Ag–N	2.171(4), 2.189(4)	N–Ag–N	161.1(2)
Ag–O(O₂NO)	2.671(8), 2.874(5)		
C–N	1.357(6), 1.359(6)	C–N–C	117.1(4)
	1.350(6), 1.332(7)		117.2(4)
O(H2)–O(H2)	2.77(1), 2.81(1)		
O(H2)–O(O₂NO)	3.329(9), 3.243(9)		
5			
Ag–Ag	3.4079(6)		
Ag–N	2.150(2), 2.154(2)	N–Ag–N	173.2(8)
Ag–O(O₂NO)	2.704(2), 2.892(2)		
C–N	1.343(3), 1.347(3)	C–N–C	117.7(2)
	1.345(3), 1.350(3)		118.1(2)
O(H2)–O(H2)	2.761(3), 2.779(4)		
O(H2)–O(O₂NO)	2.827(3), 3.196(3)		
	2.974(3), 3.503(3)		

the nitrate anions act as bidentate linkers between the silvers atoms, perpendicular to the chain propagation direction ···–Ag–**L**–Ag–**L**–··· (Fig. 13a). Each silver ion reaches thus a coordination number of five: the two nitrogen atoms occupy the axial positions of the distorted trigonal bipyramid, whereas three nitrate oxygen atoms occupy the equatorial ones. One of the nitrate anions is coordinated to the silver in an anisobidentate way with Ag–O distances of 2.669(2) and
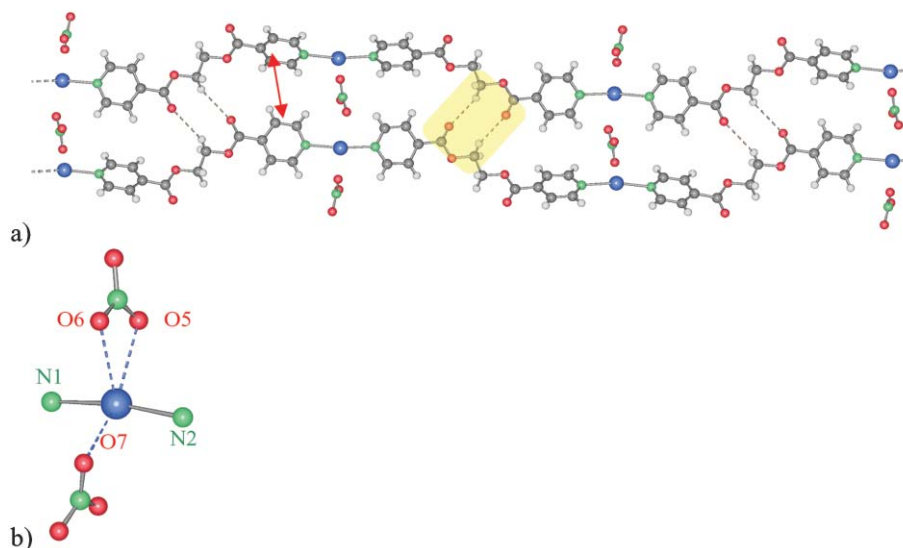

Fig. 12 Chain motif in **3**.

Fig. 13 (a) The nitrate anions act as linkers between the chains in **3**; other interactions between two chains in **3** (C–H···π: red arrow; H-bonds: yellow); (b) coordination sphere of the silver atom in **3**.
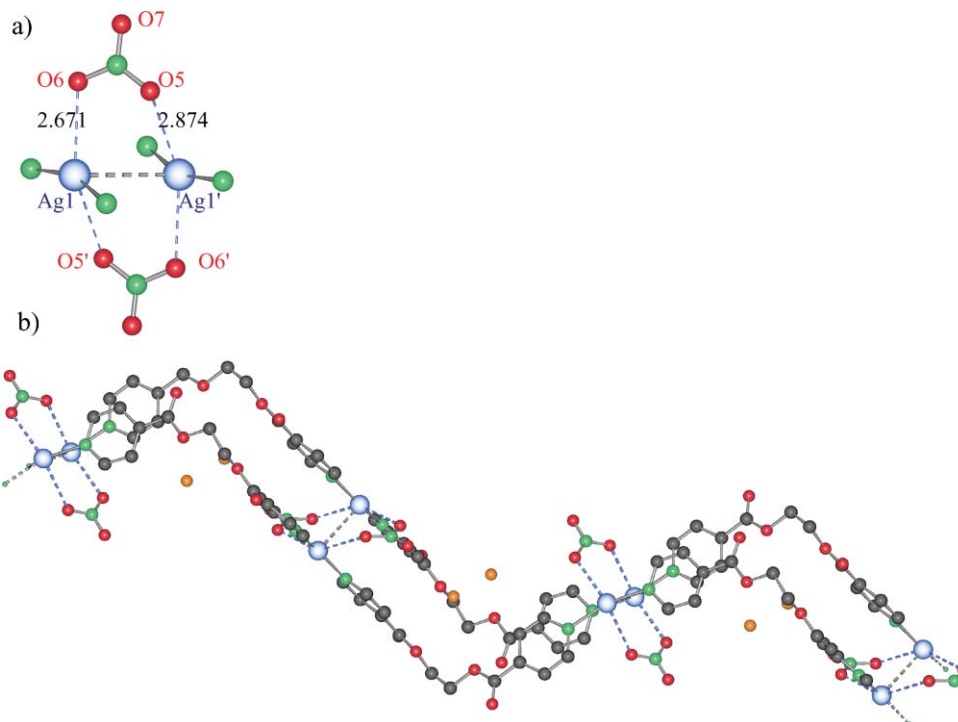
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Fig. 14 (a) The silver environment in **4**; (b) leading to the formation of a pair of chains (hydrogen atoms omitted for clarity).

2.724(2) Å and the other nitrate anion is coordinated to the same silver atom in a monodentate way with silver–oxygen distances of 2.800(3) Å. The longer Ag–O distances in **3** as compared to **1** and **2** indicate a weaker coordinating effect. The delocalized charge allows generally a bridging or chelating action of the nitrate anion. The interaction Ag–O in **3** is however strong enough to deform the N–Ag–N angle (170.2°) to the side of the bidentate coordination (Fig. 13b).

Another coordination polymer based on silver nitrate and the rigid ligand 1,2-bis(4-pyridyl)ethane (bpe) affords a similar sheet with bridging nitrate between the linear chains. However the coordination geometry of the Ag^{I} nodes is slightly different with a {AgN$_2$O$_2$} unit instead of a {AgN$_2$O$_3$} silver coordination sphere in **3**.[35]

Weak interactions between the close packed chains appear. (i) Hydrogen bonding occurs between the –C=O groups of one
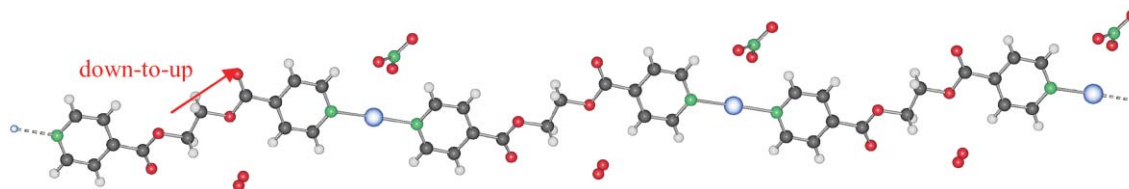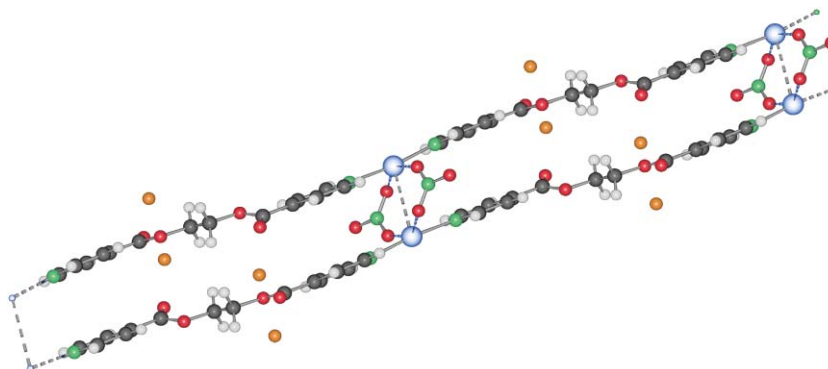

Fig. 15 The chain motif in **5**.

Fig. 16 Organisation of the chains in **5** with the fourth-coordinated silver atoms and the nitrate bridging anions.

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chain and the CH$_2$ moieties of the parallel ones with H$\cdots$O contacts of 2.57 and 2.75 Å. (ii) The two closest pyridine rings seem to be tilted in order to generate C–H$\cdots\pi$ interactions, also called "face-to-edge" interactions.[79] They occur between the tilted pyridine ring and the H1 atom of the next of pyridine group at 3.33 Å, offset by 0.47 Å. This interaction explains the bending within the ligand molecules: the pyridine planes are tilted with an angle of 50.25(7)°, and the planes containing the pyridine group and those of the corresponding ester function form angles of 16.5(3) and 20.9(2)°. The chains have thus a "bow-shaped" form if regarded along the propagation direction and the so-made sheets are not flat but undulating. Additionally to the already described interactions between the chains, other interactions complete the overall structure. (i) Hydrogen bonding occurs between close ligand molecules (C11–H1$\cdots$O4 and C12–H12$\cdots$O4) and between the nitrate anions and pyridine hydrogen atoms or ethyl hydrogen atoms. (ii) weak π-stacking of rings at a distance of 3.62 Å and offset by 1.61 Å is also observed. The closest distances between to silver atoms are 8.02(3) Å, so that no silver–silver contacts can be discussed.

Compound **4**, {[Ag(**L**)](NO$_3$)(H$_2$O)}$_n$, has an asymmetric unit formed of one silver atom, one ligand molecule, one nitrate counter anion and one water molecule. As before, the silver cation is coordinated by two different ligands through their nitrogen atoms leading to a 1-D chain. In contrast to **1**, **2**, and **3**, the ligand adopts the *gauche*-conformation with a torsion angle between its two pyridine planes of 81.8(1)° giving to the strand an undulating zig-zag structure. The distance between two silver atoms within a chain is 13.974(4) Å long, and thus shorter as in **1**, **2** and **3** in accordance with the strong bending of the ligand. It is however longer than in a comparable copper compound (9.167(7) Å), which presents the same ligand conformation, but with a more important bending of **L**.[66] The distances Ag–N in **4** are shorter than in the chains of **3**. Also, the N–Ag–N angle is smaller than in **3**. These differences are due to the different environment around the silver ions in the two structures. Indeed the coordination number of the silver cation in **4** is four with two nitrogen atoms and two oxygen atoms of the nitrate anions. Furthermore Ag–Ag interactions are observed at a distance of 3.136(1) Å (Fig. 14b). These contacts are the shortest distances between the two close chains which stack almost perfectly parallel giving pairs of chains. The arrangement in pairs is possible because the nitrate anions act as bridging linkers between the chains capping the silver–silver contacts (Fig. 14a). The distances Ag–O are longer than in **3** (on average, by 0.04 Å) indicating a weaker coordination to the metal ions. Another difference with **3** is that the third oxygen atom O7 of the nitrate anion is not involved in coordination bonding to another silver atom, but in H-bonding to the water molecule present in the structure.

Compound **5**, {[Ag(**L**)](NO$_3$)(H$_2$O)$_2$}$_n$, has one ligand molecule, one silver ion, one nitrate anion and two water molecules per asymmetric unit. The motif of **5** is a 1-D chain in which silver atoms and ligand molecules alternate, the silver ion being coordinated with two nitrogen atoms of two different ligand molecules, similar to the ones observed in **2** (Fig. 15).

The ligand molecules are in the *anti*-conformation as in **1**, **2** and **3**. The coordination environment of silver in **5** is similar to the one in **4**. However the angle N–Ag–N is larger, the distances Ag–N shorter and the Ag–Ag distance longer than in **4**. This is due to a decrease of coordination by the nitrate anions towards the cations. Indeed, the Ag–O(NO$_3$) distances are longer on average in **5** than in **4** and the other compounds.[67] The chains are also organized in pairs of chains as in **4** with the nitrate anions acting as pincers between the chains (Fig. 16).

Compound **2** is a structural supramolecular isomer of **3** (same Ag–ligand–nitrate system), showing apparently the same arrangement: 1-D chains, and nitrate anions in-between the chains. But paradoxically, the structure of **2** is closer to the structure of **5**. Both 1-D motifs are similar, the apparition of pairs of chains with π-stacking within the pairs, the parallel stacking of the pairs of chains with other π-stacking and the overall parallel stacking in order to build the 3-D network are also very similar (Fig. 17). It seems that the presence of water molecules in **5** increased the separation between the layers, the structural changes in **5** and **2** may be compared to the swelling of clays in case of water infiltration.

It can be thus assumed that the interactions nitrate–water molecules are responsible for the structural differences in **2** and **5**. However, the cell parameters for **5** and **2** do not show any correlation which means that more than simple water elimination is necessary to explain the transformation of one into the other.

In order to get information on the existence of coordination polymers or oligomers in solution, electrospray-ionization mass spectroscopy was performed. For instance, with a solution of compound Ag(**L**)NO$_3$, **2**, in CH$_3$CN at a concentration of 0.5 mg mL^{-1}, no other species were detected other than [Ag(CH$_3$CN)]$^+$ and [Ag(CH$_3$CN)$_2$]$^+$ (149 and 190 m/z respectively). Acetonitrile can easily coordinate to silver ions and the main species in solution are silver–acetonitrile complexes. Nevertheless, if we use a solvent mixture of CH$_3$CN and CH$_2$Cl$_2$ at a ratio 10 : 1, peaks are found at well identifiable m/z with a good isotopic resolution: 273.2, [**L**H]$^+$; 379.1, [**L**Ag]$^+$; 549.9 [**L**Ag$_2$(NO$_3$)]$^+$; 650.9 [**L**$_2$Ag]$^+$; 718.6 [**L**Ag$_3$(NO$_3$)$_2$]$^+$; 821.7 [**L**$_2$Ag$_2$(NO$_3$)]$^+$; 990 [**L**$_2$Ag$_3$(NO$_3$)$_2$]$^+$; 1161.3 [**L**$_2$Ag$_4$(NO$_3$)$_3$]$^+$; 1262.2 [**L**$_3$Ag$_3$(NO$_3$)$_2$]$^+$; 1432.6 [**L**$_3$Ag$_4$(NO$_3$)$_3$]$^+$ m/z.

Other electrospray ionization mass spectroscopy studies were performed in CH$_3$CN/CH$_2$Cl$_2$ in order to follow the evolution of the distribution of the above species in solution as a function of time and ligand to metal proportion. Solutions with M$_2$**L**, M**L**, M**L**$_2$ proportions were prepared and measured just after mixing **L** and AgNO$_3$, and after 24 h. The results are shown in Table 9.

Almost all species were found in each solution and at all times. For each solution, the main species are found whatever the reaction time: the distribution of the compounds in the solution is similar at $t = 0$ and $t = 24$ h. In the solution M$_2$**L**, the main species is [**L**Ag$_2$(NO$_3$)]$^+$ and species containing more Ag than **L** are favored; in the solution M**L**, a more important variety of species is observed; in the solution M**L**$_2$, only compounds [**L**$_2$Ag]$^+$ and [**L**$_2$Ag$_2$(NO$_3$)]$^+$ are mainly found.
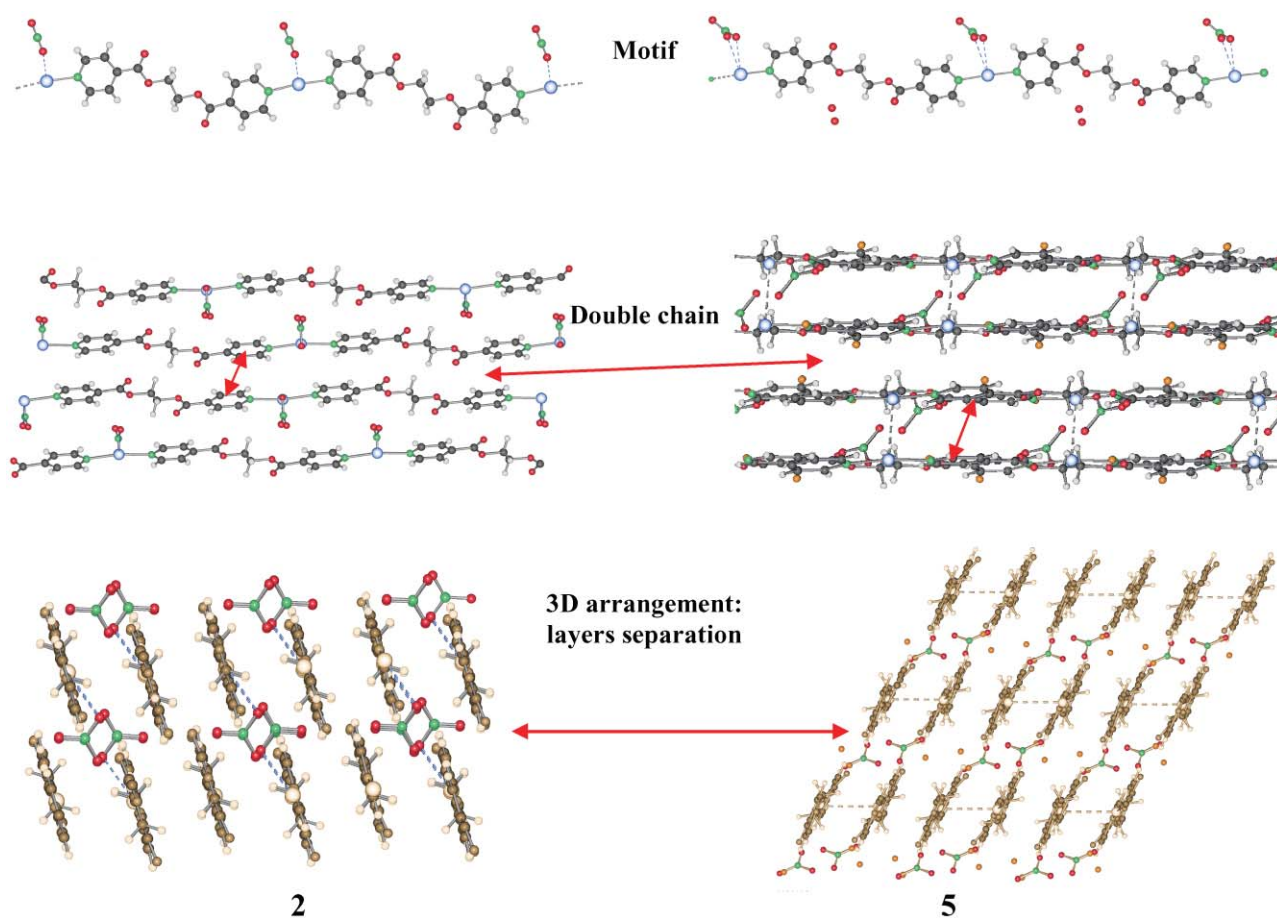
Fig. 17 Structural comparisons between **2** and **5**.

These results indicate that in all cases oligomeric fragments of coordination polymers are formed. This is in agreement with the fact that only the compound $\{[Ag(\mathbf{L})]NO_3\}_n$ is obtained by changing the metal to ligand stoichiometry for the reaction. Indeed the fact that many species are present indicates a fast complexation exchange. Additionally, acetonitrile is in concurrence with the pyridine groups of the ligand for the complexation of silver. The peaks corresponding to $[Ag(CH_3CN)]^+$ and $[Ag(CH_3CN)_2]^+$ (149 and 190 m/z, respectively) are in fact found in the mass spectra.

Table 9 Resume of the detected peaks (the main peaks are presented with the relative abundance ratio (%)) for the three tested solutions at 0 and 24H.

	M$_2$L		ML		ML$_2$	
	0	24 H	0	24 H	0	24 H
$[LH]^+$	ø	ø	√(2%)	ø	√(6%)	√(11%)
$[LAg]^+$	√(11%)	√(7%)	√(3%)	ø	√(1%)	√(4%)
$[LAg_2(NO_3)]^+$	√(**100%**)	√(**100%**)	√(**34%**)	√(**37%**)	√(18%)	√(26%)
$[L_2Ag]^+$	ø	ø	√(9%)	√(19%)	√(18%)	√(**69%**)
$[LAg_3(NO_3)_2]^+$	√(**52%**)	√(**69%**)	√(14%)	√(**37%**)	√(2%)	√(5%)
$[L_2Ag_2(NO_3)]^+$	√(**80%**)	√(**31%**)	√(**100%**)	√(**100%**)	√(**100%**)	√(**100%**)
$[L_2Ag_3(NO_3)_2]^+$	√(**45%**)	√(24%)	√(**30%**)	√(**60%**)	√(12%)	√(19%)
$[L_2Ag_4(NO_3)_3]^+$	√(**62%**)	√(**36%**)	√(18%)	√(**60%**)	√(5%)	√(7%)
$[L_3Ag_3(NO_3)_2]^+$	ø	ø	√(2%)	√(10%)	√(3%)	√(3%)
$[L_3Ag_4(NO_3)_3]^+$	√(18%)	√(8%)	√(7%)	√(**30%**)	√(3%)	√(4%)

Whereas measurements of UV-spectra of the above compounds in solution gave not enough information to calculate formation constants of the various species, a general increase of luminescence at 409 nm is observed in the solid state for all compounds, irradiating at 234 nm (Chart 1).

Solvent influence

It has been stated that the 1-D silver coordination polymer motifs including linear ligands with a poor delocalized π-system and moderately coordinating counter anions (such as nitrate) tend to arrange themselves parallel in the structure and that the coulombic repulsion between the Ag^I centers cannot be compensated by a strong face-to-face ligand stacking or by the coordination of the counter-anions to silver.[43] So, what is the behaviour of **L** in the AgNO$_3$ coordination polymers when diverse solvent conditions are applied?

It is worthy of noting that silver nitrate has a different solubility in the used crystallization solvents, allowing more or less good solvation of the ions. The comparison of the average silver–nitrate distances in the solid as a function of the solubility of the silver salt in the different solvents are shown on Chart 2.

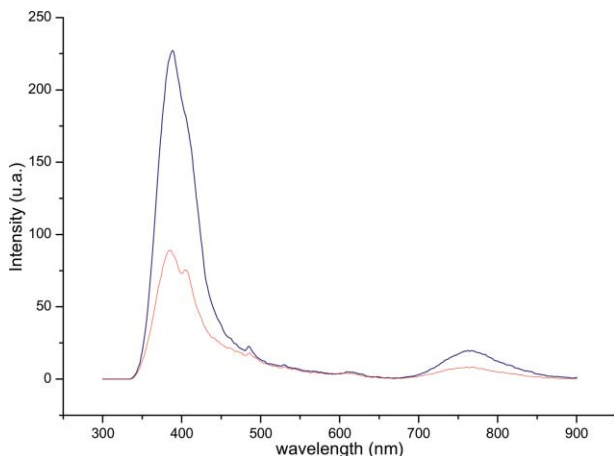IR-measurements in solution as well as ES-MS investigations prove the existence of close AgNO$_3$-aggregates, where

Chart 1 Emission spectra of **5** (blue) and **L** (red) (excitation wavelength: 234 nm).

nitrate is coordinated to the metal ion and even is likely to act as bridging ligand.[78] There is thus a link between these Ag–O(NO$_3$) distances and the solubility of silver nitrate in the mother liquor. The worst solvent for silver nitrate in this series is ethanol and the best is water. This bad solubility of AgNO$_3$ in ethanol can explain the short distances Ag–O(NO$_3$) in the solid state in **1**, and also the existence of the silver nitrate chains. On the other hand, the good solubility of AgNO$_3$ in water prevents Ag and nitrate to be so close. According to these results, it can be said that the solubility seems to be a major parameter for the crystallization. To the best of the authors' knowledge, this dependence has never been outlined in the literature by showing the variance of distances as a function of solubility.

However the importance of the solvent choice is known, without being clearly studied. The solvents are usually classified in two categories: the coordinating and the non coordinating ones. In compounds **4** or **5**, the solvent molecules co-crystallize without being cation coordinating solvents. It is the weak solvation of the anions by the solvent that remains, resulting in longer Ag–anion distances.

In the literature, numerous examples of silver coordination polymers with solvent molecules in the first coordination
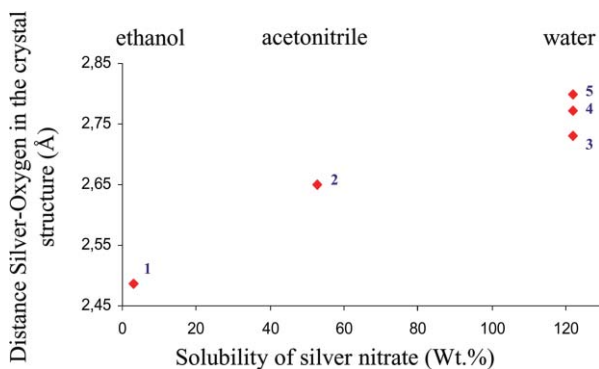

Chart 2 Average distances Ag–O(NO3) in compounds **1 to 5** as a function of the AgNO3 solubility.

sphere can be found. The coordinated solvent molecules are water,[37,39,68,80] acetonitrile[41,81–87] or methanol.[54] Water molecules can be directly coordinated to silver ions even in the presence of nitrate as counter anion. In {[Ag(1,3-bis(2-pyridylethynyl)-2-methyl-benzene)(NO$_3$)(H$_2$O)]}$_n$, there are two crystallographically and chemically different silver ions: both have a distorted tetrahedral coordination sphere containing two ligand nitrogen atoms in addition with either an anisobidentate nitrate anion or a monodentate nitrate anion and a water molecule.[37] This compound grows from a mixture of a solution of ligand in acetone and a solution of silver nitrate in water, illustrating the possible competition in coordination between the water molecules and the nitrate anions.

Acetonitrile has a favorable affinity toward silver ions in solution, and is also more easily involved in the coordination sphere of silver in the resulting coordination polymer structure. Reger *et al.* state that if compounds are crystallized from the coordinating solvent acetonitrile, the anions have less effect on the structure.[84] For instance, the silver ion has a {AgN(pyridyl)$_2$N(acetonitrile)O(nitrate)$_2$} coordination sphere in the compound {[Ag(2,2′,3″-tripyridylamine)(NO$_3$)(CH$_3$CN)]}$_n$.[86] When crystals grow from the mixture **L**/AgNO$_3$ in acetonitrile, we do not observe the formation of such compounds in the solid state. Crystals of **2** do not contain any acetonitrile molecules.

The used solvents are not the unique important factor but also the crystallization techniques have to be carefully studied. The "H-shaped" tubes allow slow diffusion of the reagents, and mostly the crystals are of better quality than if obtained by direct mixing. The drawbacks of this technique are the weak concentration and the non-homogeneous conditions depending on the localization in the tube. Indeed the crystallization can occur in one or the other arm, on the fritt if present, at the solvent/air interface, in the curved part, *etc…*, where the concentration and the ratio metal to ligand can be locally different. However, we always get pure phases during the direct mixing: **3** crystallizes in a THF/water solution of **L** and AgNO$_3$; **2** is obtained in a solution of both reagents in acetonitrile. The comparison between the diffusion techniques and the direct self-assembly methods is made by Champness and Schröder.[88] Contrary to our studies, their recommended method is the diffusion technique because they obtained mixtures of products with direct methods.

Another solvent influence in the formation of coordination polymers based on flexible organic ligand is the correlation between the presence of inclusion solvent molecules in the structures and the conformation of the ligand. In **4**, the presence of water molecules coincides with the *gauche*-conformation. The *gauche* conformation of **L** is also observed in a related copper coordination polymer in the presence of THF as co-crystallizing solvent.[66] However, in **5**, water molecules co-crystallize and the ligand adopts the *anti*-conformation. In all other products, the ligand adopts the *anti*-conformation as in free **L**. It can be concluded that the presence of non-coordinating co-crystallized solvent molecules may induce the change of conformation of the ligands in the crystallographic structures from *anti* to *gauche*. This confirms previous findings.[69]

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Conclusions

The nitrate anion is very flexible in its bridging mode and strength. It is therefore able to act as bridging ligand between two silver atoms as in **3** or **2** in which it links several chains together. It also shows its ability to support a metal–metal contact in **4** and **5**. Its coordination strength can be tuned by the number of hydrogen bonds in which it can be involved, with for instance water molecules. Thus, the Ag–O(nitrate) distances increase with the number of co-crystallizing solvent. Solvation of the cations and anions of $AgNO_3$ also plays a role in final Ag–NO_3 distances in the products' crystal structure. The influence of the solvent has been outlined with different compounds. A solvent contribution can here be distinguished: the different solvation of the reagents by the solvent in the crystallization process. In some cases, the interactions between solvent molecules and reagents remain in the solid state, like in **1** and **2**, and in other cases, solvent molecules co-crystallize, as in **4**, and **5**.

Experimental

The synthesis of **L** has been reported previously.[66] Synthesis of **3**, **4** and **5** have been described elsewhere.[67]

$\{[Ag_2(NO_3)_2(L)]\}_n$ (1)

A solution of **L** (20 mg, 0.07 mmol) in THF (5 mL) is introduced in one arm of an "H-shaped" tube, a solution of $AgNO_3$ (12 mg, 0.07 mmol) in ethanol (5 mL) in the other one (molar ratio 1 : 1). The solutions are frozen in liquid nitrogen and THF is then layered into the tube in order to bridge the two reagent solutions. There is a fritt in the linking part of the tube. The slow diffusion occurs through the THF layer and the fritt. Crystals of **1** appear after several months at the interface EtOH/THF. After using some single crystals for X-ray diffraction, the product is collected. Yield: 4 mg (11%). This quantity was not sufficient to perform a satisfying elementary analysis.

$\{(Ag(L)](NO_3)\}_n$ **2**

Reaction A: Crystals of **2** are obtained at room temperature from a solution of **L** (13.6 mg, 0.05 mmol) and silver nitrate (8.5 mg, 0.05 mmol) in acetonitrile (10 mL) (molar ratio 1 : 1). The crystals grow on the glass walls of the beaker at the solution surface after slow evaporation of the solution. The colorless crystals are suitable for single crystal X-rays diffraction and allow the resolution of the crystallographic structure. Not enough crystals were collected in order to make further investigations on this sample.

Reaction B: A polycrystalline white powder is obtained from a mixture of **L** (60 mg, 0.22 mmol) and $AgNO_3$ (37.5 mg, 0.22 mmol) in CH_2Cl_2 (a large volume as $AgNO_3$ is less well soluble in CH_2Cl_2) (molar ratio 1 : 1). The powder X-ray spectrum of the compound shows that this polycrystalline precipitate has the same structure than **2**. It is worth noting that if the molar ratio is changed, the same product is obtained. Yield: 79 mg (81 %). Analysis calculated for [Ag(**L**)NO_3]: C 38.03, H 2.74, N 9.50; found C 37.26, H 2.64, N 9.4%. A certain amount of dichloromethane is adsorbed on the sample. IR (GB, cm^{-1}): ν(C=O) 1726 s, ν(C=C) 1612 w, ν(ArC–C, C=N) 1412 w, ν(NO_3) 1380–1330 s, ν(C–O) 1272 s, δ(ArC–H) 985, 992 (split) m, ν(ArC–H) 825 m. UV-Vis (CH_3CN): absorption at 212 and 273 nm. ESI/MS (CH_3CN/CH_2Cl_2 10/1, m/z): 273.2, [**L**H]$^+$; 379.1, [**L**Ag]$^+$; 549.9, [**L**Ag$_2$(NO_3)]$^+$; 650.9, [**L**$_2$Ag]$^+$; 718.6, [**L**Ag$_3$(NO_3)$_2$]$^+$; 821.7, [**L**$_2$Ag$_2$(NO_3)]$^+$; 990, [**L**$_2$Ag$_3$(NO_3)$_2$]$^+$; 1161.3, [**L**$_2$Ag$_4$(NO_3)$_3$]$^+$; 1262.2, [**L**$_3$Ag$_3$(NO_3)$_2$]$^+$; 1432.6, [**L**$_3$Ag$_4$(NO_3)$_3$]$^+$. FAB (fast atom bombardment) mass spectroscopy (m/z): [**L**H]$^+$, [**L**Ag]$^+$, [**L**Ag$_2$$NO_3$]$^+$ and [**L**$_2$Ag]$^+$ at, respectively, 273, 379, 550 and 651.

References

1 C. Janiak, *Dalton Trans.*, 2003, 2781.
2 S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.
3 A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006 in the press.
4 Examples for porous coordination polymer compounds: S. Kitagawa, R. Kitaura and S. I. Noro, *Angew. Chem., Int. Ed.*, 2004, **116**, 2388; M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Poc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4900.
5 Examples for luminescent coordination polymer compounds: S.-L. Zheng and X.-M. Chen, *Aust. J. Chem.*, 2004, **57**, 703.
6 Examples for magnetic coordination polymer compounds: D. Maspoch, D. Rioz-Molina and J. Veciana, *J. Mater. Chem.*, 2004, **14**, 2713; S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*, 2003, **246**, 103.
7 Examples for polycatenated, polythreaded coordination polymer compounds: L. Carlucci, G. Ciani and D. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
8 K. T. Holman, H. H. Hammud, S. Isber and M. Tabbal, *Polyhedron*, 2005, **24**, 2, 221–228.
9 S. Kawata, S. Kitagawa, H. Kumagai, S. Iwabuchi and M. Katada, *Inorg. Chim. Acta*, 1998, **267**, 1, 143–145.
10 R. G. Vranka and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 6, 1020–1025.
11 J. L. Manson, T. Lancaster, L. C. Chapon, S. J. Blundell, J. A. Schlueter, M. L. Brooks, F. L. Pratt, C. L. Nygren and J. S. Qualls, *Inorg. Chem.*, 2005, **44**, 4, 989–995.
12 B. M. Wells, C. P. Landee, M. M. Turnbull, F. F. Awwadi and B. Twamley, *J. Mol. Catal. A*, 2005, **228**, 1–2, 117–123.
13 L. C. Tabares, J. A. R. Navarro and J. M. Salas, *J. Am. Chem. Soc.*, 2001, **123**, 3, 383–387.
14 C. Naether and I. Jess, *Eur. J. Inorg. Chem.*, 2004, 14, 2868–2876.
15 O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 1, 295–296.
16 S. R. Batten, J. C. Jeffery and M. D. Ward, *Inorg. Chim. Acta*, 1999, **292**, 2, 231–237.
17 S. D. Huang, R.-G. Xiong, J. Han and B. R. Weiner, *Inorg. Chim. Acta*, 1999, **294**, 1, 95–98.
18 H. Hou, Y. Wei, Y. Fan, C. Du, Y. Zhu, Y. Song, Y. Niu and X. Xin, *Inorg. Chim. Acta*, 2001, **319**, 1,2, 212–218.
19 S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 12, 2082–2084.
20 M. Du and X.-J. Zhao, *Inorg. Chem. Commun.*, 2004, **7**, 9, 1056–1060.
21 F. Robinson and M. J. Zaworotko, *Chem. Commun.*, 1995, 23, 2413–2414.
22 H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, **236**, 1–2, 91–119.
23 Y.-B. Dong, R. C. Layland, M. D. Smith, N. G. Pschirer, U. H. F. Bunz and H.-C. Zur Loye, *Inorg. Chem.*, 1999, **38**, 13, 3056–3060.

24 H. Zhu, C. Huang, W. Huang and S. Gou, *Inorg. Chem. Commun.*, 2004, **7**, 10, 1095–1099.

25 R. Wang, L. Han, L. Xu, Y. Gong, Y. Zhou, M. Hong and A. S. C. Chan, *Eur. J. Inorg. Chem.*, 2004, 18, 3751–3763.

26 R. Horikoshi and M. Mikuriya, *Cryst. Growth Des.*, 2005, **5**, 1, 223–230.

27 L. Carlucci, G. Ciani, D. W. v. Gundenberg and D. M. Proserpio, *Inorg. Chem.*, 1997, **36**, 18, 3812–3813.

28 X.-M. Ouyang, B.-L. Fei, T.-a. Okamura, H.-W. Bu, W.-Y. Sun, W.-X. Tang and N. Ueyama, *Eur. J. Inorg. Chem.*, 2003, 4, 618–627.

29 M. Du, X.-H. Bu, Y.-M. Guo, H. Liu, S. R. Batten, J. Ribas and T. C. W. Mak, *Inorg. Chem.*, 2002, **41**, 19, 4904–4908.

30 B.-L. Fei, W.-Y. Sun, T.-a. Okamura, W.-X. Tang and N. Ueyama, *New J. Chem.*, 2001, **25**, 2, 210–212.

31 R. Horikoshi, T. Mochida, N. Maki, S. Yamada and H. Moriyama, *Dalton Trans.*, 2002, 1, 28–33.

32 G. K. Patra and I. Goldberg, *Dalton Trans.*, 2002, 6, 1051–1057.

33 L.-C. Song, W.-X. Zhang, J.-Y. Wang and Q.-M. Hu, *Transition Met. Chem.*, 2002, **27**, 5, 526–531.

34 A. J. Blake, N. R. Brooks, N. R. Champness, L. R. Hanton, P. Hubberstey and M. Schroder, *Pure Appl. Chem.*, 1998, **70**, 12, 2351–2357.

35 R. L. LaDuca, Jr., R. S. Rarig, Jr., P. J. Zapf and J. Zubieta, *Solid State Sci.*, 2000, **2**, 1, 39–45.

36 M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 20, 5278–5281.

37 T. Kawano, C.-X. Du, T. Araki and I. Ueda, *Inorg. Chem. Commun.*, 2003, **6**, 2, 165–167.

38 A. J. Blake, G. Baum, N. R. Champness, S. S. M. Chung, P. A. Cooke, D. Fenske, A. N. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schroder, *Dalton Trans.*, 2000, 23, 4285–4291.

39 S. Muthu, J. H. K. Yip and J. J. Vittal, *Dalton Trans.*, 2001, 24, 3577–3584.

40 M.-L. Tong, Y.-M. Wu, J. Ru, X.-M. Chen, H.-C. Chang and S. Kitagawa, *Inorg. Chem.*, 2002, **41**, 19, 4846–4848.

41 A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *Chem. Commun.*, 2000, 8, 665–666.

42 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schroder, *Coord. Chem. Rev.*, 1999, **183**, 117–138.

43 A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schroder, *Coord. Chem. Rev.*, 2001, **222**, 155–192.

44 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1994, 24, 2755–2756.

45 J. H. Liao, P. L. Chen and C. C. Hsu, *J. Phys. Chem. Solids*, 2001, **62**, 9–10, 1629–1642.

46 W. Bi, D. Sun, R. Cao and M. Hong, *Acta Crystallogr., Sect. E*, 2002, **E58**, 7, m324–m325.

47 M. Hong, W. Su, R. Cao, M. Fujita and J. Lu, *Chem.-Eur. J.*, 2000, **6**, 3, 427–431.

48 L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2002, **4**, 121–129.

49 L. Carlucci, G. Ciani and D. M. Proserpio, *Chem. Commun.*, 1999, 5, 449–450.

50 Y.-B. Dong, H.-Y. Wang, J.-P. Ma, R.-Q. Huang and M. D. Smith, *Cryst. Growth Des.*, 2005, **5**, 2, 789–800.

51 Y.-B. Dong, X. Zhao, R.-Q. Huang, M. D. Smith and H.-C. Zur Loye, *Inorg. Chem.*, 2004, **43**, 18, 5603–5612.

52 H.-P. Wu, C. Janiak, G. Rheinwald and H. Lang, *J. Chem. Soc., Dalton Trans.*, 1999, 183.

53 C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski and T. G. Scharmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3121.

54 X.-H. Bu, W. Chen, W.-F. Hou, M. Du, R.-H. Zhang and F. Brisse, *Inorg. Chem.*, 2002, **41**, 13, 3477–3482.

55 X.-H. Bu, Y.-B. Xie, J.-R. Li and R.-H. Zhang, *Inorg. Chem.*, 2003, **42**, 23, 7422–7430.

56 K. M. Fromm, E. D. Gueneau, G. Bernardinelli, H. Goesmann, J. Weber, M. J. Mayor-Lopez, P. Boulet and H. Chermette, *J. Am. Chem. Soc.*, 2003, **125**, 12, 3593–3604.

57 K. M. Fromm, *CrystEngComm*, 2002, **4**, 318–322.

58 M. Mayor, M. Buschel, K. M. Fromm, J.-M. Lehn and J. Daub, *Chem.-Eur. J.*, 2001, **7**, 6, 1266–1272.

59 K. M. Fromm, E. D. Gueneau and H. Goesmann, *Chem. Commun.*, 2000, 22, 2187–2188.

60 K. M. Fromm and H. Goesmann, *Acta Crystallogr., Sect. C*, 2000, **C56**, 10, 1179–1180.

61 K. M. Fromm, H. Goesmann and G. Bernardinelli, *Polyhedron*, 2000, **19**, 15, 1783–1789.

62 K. M. Fromm, G. Bernardinelli, M. J. Mayor-Lopez and H. Goesmann, *Z. Anorg. Allg. Chem.*, 2000, **626**, 7, 1685–1691.

63 K. M. Fromm, *Chem. Commun.*, 1999, 17, 1659–1660.

64 K. M. Fromm, *Angew. Chem., Int. Ed. Engl.*, 1998, **36**, 24, 2799–2801.

65 K. Fromm and G. Bernardinelli, *Z. Anorg. Allg. Chem.*, 2001, **627**, 7, 1626–1630.

66 A. Y. Robin, K. M. Fromm, H. Goesmann and G. Bernardinelli, *CrystEngComm*, 2003, **5**, 405–410.

67 A. Y. Robin, M. Meuwly, K. M. Fromm, H. Goesmann and G. Bernardinelli, *CrystEngComm*, 2004, **6**, 336–343.

68 M. Sarkar and K. Biradha, *CrystEngComm*, 2004, **6**, 310–314.

69 B. Li, X. Zhu, J. Zhou, Y. Peng and Y. Zhang, *Polyhedron*, 2004, **23**, 18, 3133–3141.

70 Single crystal data for **1**: $C_7H_6N_2O_5Ag$, M = 306.1 g mol^{-1}, monoclinic, space group $C2/c$ (No. 15), α = 20.976(7), b = 9.346(2), c = 9.903(3) Å, β = 106.98(2)°, V = 1856.7(9) Å^3, Z = 8, T = 240(2) K, μ(Mo Ka) = 2.174 mm^{-1}, 1972 reflections of which 1452 unique and 1452 observed, 147 parameters refined, R(int) = $\sigma|F_o^2 - F_o^2(\text{mean})|/S[F_o^2]$ = 0.0777, $R1$ = $\sigma||F_o| - |F_c|| / \sigma|F_o|$ = 0.0733, $wR2$ = $\{\sigma[w(F_o^2 - F_c^2)^2] / \sigma[w(F_o^2)^2]^{1/2}$ = 0.1742 for $I > 2\sigma$ and $R1$ = 0.0854, $wR2$ = 0.1885 for all data. Single crystal data for **2**: $C_{14}H_{12}N_3O_7Ag$, M = 442.14 g mol^{-1}, triclinic, space group $P\bar{1}$ (No. 2), a = 6.159(1), b = 8.895(3), c = 14.439(3) Å, α = 93.15(2), β = 99.90(2), γ = 91.43(2)°, V = 777.6(4) Å^3, Z = 2, T = 293(2) K, μ(Mo Ka) = 1.341 mm^{-1}, 1565 reflections of which 1494 unique and 1494 observed, 226 parameters refined, R(int) = 0.0213, $R1$ = 0.0312, $wR2$ = 0.0686 for $I > 2\sigma$ and $R1$ = 0.0408, $wR2$ = 0.0732 for all data. Crystals **1**, and **2** were measured on a STOE IPDS diffractometer with monochromated graphite Mo Ka radiation, λ = 0.71073 Å, an Oxford Cryosystems open flow cryostat,[89] with an absorption correction by analytical integration.[90] The structures were solved with direct methods and refined by full-matrix least-squares on F^2 with the SHELX-99 package.[91] All heavy atoms could be refined anisotropically. Crystallographic data for the structures reported here **1**, and **2** have been deposited with the Cambridge Crystallographic Data Cente. CCDC reference numbers 285368 and 285369. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517191a. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

71 L. Yang, X. Shan, Q. Chen, Z. Wang and J. S. Ma, *Eur. J. Inorg. Chem.*, 2004, 7, 1474–1477.

72 G. Zhang, G. Yang, Q. Chen and J. S. Ma, *Cryst. Growth Des.*, 2005, **5**, 2, 661–666.

73 D. Kim, S. Hu, P. Tarakeshwar, K. S. Kim and J. M. Lisy, *J. Phys. Chem. A*, 2003, **107**, 8, 1228–1238.

74 E. L. Elliott, G. A. Hernandez, A. Linden and J. S. Siegel, *Org. Biomol. Chem.*, 2005, **3**, 3, 407–413.

75 D. L. Reger, J. R. Gardinier and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 13, 3825–3832.

76 E. Bosch and C. L. Barnes, *Inorg. Chem.*, 2002, **41**, 9, 2543–2547.

77 M. Mascal, J.-L. Kerdelhue, A. J. Blake, P. A. Cooke, R. J. Mortimer and S. J. Teat, *Eur. J. Inorg. Chem.*, 2000, 3, 485–490.

78 C. Mabillard, *Thesis n°505* EPFL (Ecole Polytechnique fédérale de Lausanne) 1983.

79 C. Janiak, *Dalton Trans.*, 2000, 21, 3885–3896.

80 S. Q. Liu, T. Kuroda-Sowa, H. Konaka, Y. Suenaga, M. Maekawa, T. Mizutani, G. L. Ning and M. Munakata, *Inorg. Chem.*, 2005, **44**, 4, 1031–1036.

81 N. S. Oxtoby, A. J. Blake, N. R. Champness and C. Wilson, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 8, 4905–4910.

82 J. J. M. Amoore, C. A. Black, L. R. Hanton and M. D. Spicer, *Cryst. Growth Des.*, 2005, **5**, 3, 1255–1261.

83 S. Muthu, Z. Ni and J. J. Vittal, *Inorg. Chim. Acta*, 2005, **358**, 3, 595–605.

84 D. L. Reger, R. F. Semeniuc, V. Rassolov and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 2, 537–554.

85 S.-L. Zheng, M.-L. Tong, S.-D. Tan, Y. Wang, J.-X. Shi, Y.-X. Tong, H. K. Lee and X.-M. Chen, *Organometallics*, 2001, **20**, 25, 5319–5325.

86 C. Seward, J. Chan, D. Song and S. Wang, *Inorg. Chem.*, 2003, **42**, 4, 1112–1120.

87 M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, W.-S. Li and M. Schroder, *Cryst. Eng.*, 1999, **2**, 2/3, 123–136.

88 D.-L. Long, A. J. Blake, N. R. Champness, C. Wilson and M. Schroder, *Chem.-Eur. J.*, 2002, **8**, 9, 2026–2033.

89 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

90 E. Blanc, D. Schwarzenbach and H. D. Flack, *J. Appl Crystallogr.*, 1991, **24**, 1035.

91 G. M. Sheldrick, SHELX-99, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, 1999.