

Silver(I) coordination chemistry: from 1-D chains to molecular rectangles†

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A series of silver(I) coordination compounds with the ligand 2-(4-pyridyl)imidazole **4-PyIm** has been synthesized and crystallographically characterized in order to explore the role of counterions, solvents and ligand charge in the resulting supramolecular architectures. With perchlorate and hexafluorophosphate, two iso-structural 1-D coordination-polymers were obtained, but when changing the counterion to nitrate and using water as solvent, an unusual molecular rectangle composed of four ligands and four Ag(I) ions was obtained, and the assembly was controlled by hydrogen bonding via the anion and water molecules. Finally, when the ligand was deprotonated, the change in the number of binding sites (from two to three) was reflected in an increase in the coordination number for the silver ion.

Introduction

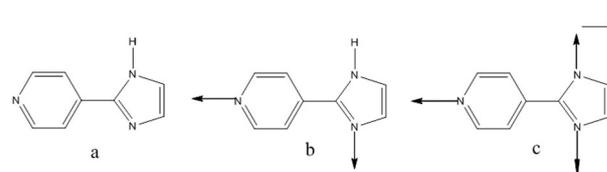
Interest in silver(I) in crystal engineering and supramolecular chemistry remains high due to the diverse structural topologies that this ion can generate,¹ and the potential use of Ag(I)-complexes in a range of optical,² electrical,³ nano-material,⁴ catalytic,⁵ and adsorptive applications.⁶

In coordination chemistry, the silver ion has been widely used due to its soft acceptor characteristic as well as for its relatively flexible coordination sphere. The latter allows the ion to be coordinated by a variety of ligands possessing several geometries and heteroatoms resulting in an extensive array of networks and topologies. Although Ag(I) is frequently thought of as having a strong preference for linear coordination, it has been reported⁷ that out of 3319 solid-state structures of silver(I) complexes, 24% are two-coordinate, 23% are three-coordinate, 44% are four-coordinate, with the remaining 9% displaying coordination numbers greater than four. The flexibility of silver(I) coordination geometries can be traced back to the lack of stereochemical directionality that arises from a d¹⁰ configuration.⁸

As a result, it should be possible to control the coordination number and geometry of silver(I) complexes using non-covalent

interactions due to the relatively weak nature of most silver(I)-ligand bonds.⁹ Factors that influence the supramolecular assembly of silver(I) complexes into extended structures include, in addition to the inherent properties of the metal ion and ligand, non-covalent interactions involving counterions and/or solvent molecules. The balance between these weak interactions determines the structural outcome of any preparation of silver-based coordination complexes, and it is essential to examine these closely, preferably one variable at a time, if we want to gain more control over the way in which silver complexes are assembled in the solid state.

Silver(I) complexes are mostly two, three, or four-coordinate, and for coordination numbers greater than two, the coordination sphere is usually completed by solvent molecules or counterions. In this study we are targeting a relatively simple ligand, 2-(4-pyridyl)imidazole, **4-PyIm**, Scheme 1, with restricted conformational flexibility that can exist in a neutral or anionic form which allows us to explore the supramolecular roles that anions and solvent molecules may play in the assembly of silver(I) containing architectures. **4-PyIm** contains two or three donor atoms (depending on charge) and the donor moieties are positioned at a 90° angle with respect to each other, Scheme 1.



Scheme 1 (a) **4-PyIm** neutral, (b) donor atoms for neutral **4-PyIm**, (c) donor atoms for anionic **4-PyIm**.

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Table 1 Coordination numbers for Ag-py and Ag-Im complexes based on data from the CSD

Ligand	CN				
	2	2 ^a	3	3 ^b	4
Pyridine %	31	40	9	10	10
Imidazole%	62	25.5	7.5	2.5	2.5

^a Two nitrogen atoms coordinated, coordination sphere is completed by solvent or ions. ^b Three nitrogen atoms coordinated, coordination sphere is completed by solvent or ions.

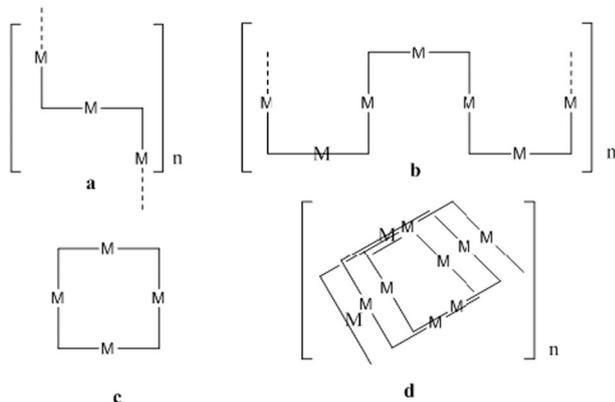
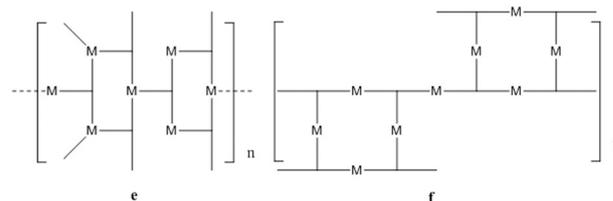
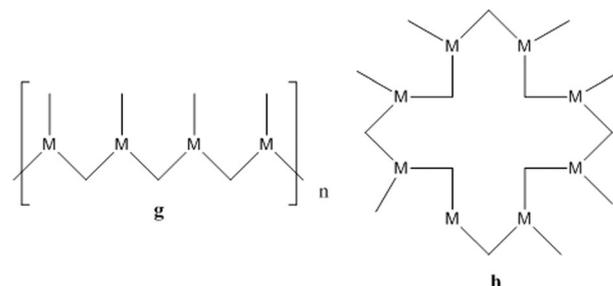
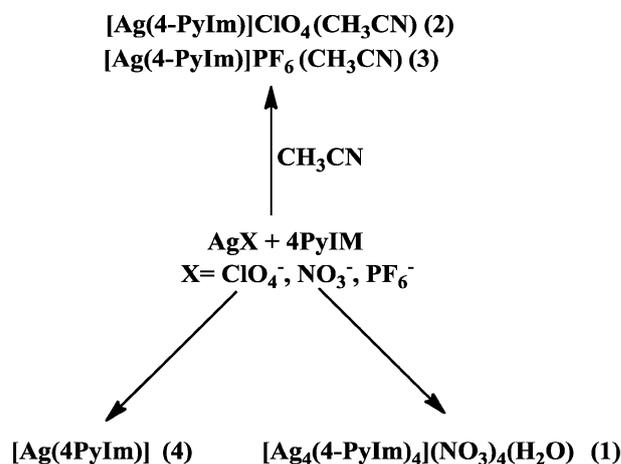
A survey of crystallographically characterized pyridine- and imidazole-based Ag(I) complexes shows a strong bias towards the low coordination number; 90% of all Ag(I)-py complexes (from 1130 hits) and 97% of all Ag(I)-Im complexes (from 250 hits) have a coordination number of either two or three, Table 1.

If **4-PyIm** is deprotonated, the number of donor atoms increases from two to three and they are configured in a T-shaped manner, Scheme 1.

As silver(I) has no preference for a particular site on the ligand, we postulate that any of the following architectures may appear with neutral **4-PyIm** and a coordination number of two: coordination polymers (a and b), cyclic closed structures (c), and helical 1-D coordination polymers (d), Scheme 2 for a neutral ligand and a coordination number of three: cyclic closed structure (h) as well as another coordination polymer (g), Scheme 4. For anionic **4-PyIm** with coordination numbers two and three we can envision coordination polymers with repeating cyclic units (e–f), Scheme 3.

In order to identify and isolate the effects imparted by counterions or solvent molecules on the resulting structures of Ag:**4-PyIm** complexes, a synthetic approach was carried out using acetonitrile, nitromethane and water (acidic to be more soluble and basic to generate anion) as solvents; and nitrate, tetrafluoroborate, perchlorate, and hexafluorophosphate as counterions (summarized in Scheme 5).

We now report the four crystal structures of **4-PyIm** and its corresponding Ag(I) complexes that were obtained as a result of this synthetic effort and our analysis of the effect that each variable has on the eventual crystal structure.

**Scheme 2** Some possible Ag(I) networks, CN=2 (a–d).**Scheme 3** Some possible networks for silver(I) with **4-PyIm** in its anionic form (e–f).**Scheme 4** Some possible structures for Ag(I) networks with **4-PyIm** in its neutral form with CN=3 (g–h).**Scheme 5** Synthetic plan.

Experimental

All chemicals, silver nitrate, silver tetrafluoroborate, silver perchlorate, and silver hexafluorophosphate, were purchased from Aldrich and used with no further purification. The synthesis of 2-(4-pyridyl)imidazole **4PyIm** was carried out according to previously reported procedures. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. ¹H NMR was recorded on a Varian Unity plus 400 MHz spectrometer in d₆-DMSO. Infrared spectroscopy (IR) was done on a Nicolet 380 FT-IR.

Synthesis

2-(4-Pyridyl)imidazole, 4-PyIm. The synthesis was carried out according to a method described in the literature.¹⁰ M.p. 208–210 °C (lit. 210–211 °C), IR (neat, ν/cm⁻¹): 3118, 3033, 1608,

1566, 1491, 1438, 1402, 1387, 1218, 1171, 1124, 1094, 992, 963, 830, 782; ^1H NMR (δ_{H} ; DMSO- d_6 , 400 MHz): 8.63 (dd, $J = 0.06$, 0.04), 7.873 (dd, $J = 0.08$, 0.04), 7.274 (s).

Tetrakis(2-(4-pyridyl)imidazole) silver(i) nitrate tetrahydrate [$\text{Ag}_4(\text{4-PyIm})_4(\text{NO}_3)_4(\text{H}_2\text{O})_4$] (1). 145 mg (1 mmol) of 4-PyIm was added to a solution containing 170 mg (1 mmol) of silver nitrate dissolved in 20 cm^3 of water with stirring. The 4-PyIm dissolved in solution with turbidity, three drops of 1 N HNO_3 were added to obtain a clear solution, which was filtered by gravity, protected from light with aluminium foil, and left overnight. The second day, colorless plate-like crystals, suitable for X-ray diffraction, were filtered to give 87 mg (yield 26%). M.p. 225–228 $^\circ\text{C}$ (decomp.). IR (neat, ν/cm^{-1}): 3120, 1615, 1568, 1498, 1459, 1416, 1310(b), 1228, 1119; NMR (δ_{H} ; DMSO- d_6 , 400 MHz): 13.21 (s), 8.65 (dd, $J_1 = 0.12$, $J_2 = 0.03$), 7.937 (dd, $J_1 = 0.08$, $J_2 = 0.04$), 7.532 (s).

[2-(4-Pyridyl)imidazole silver(i)] perchlorate acetonitrile [$\text{Ag}(\text{4-PyIm})\text{ClO}_4(\text{CH}_3\text{CN})$] (2). 145 mg (1 mmol) of 4-PyIm was added to a solution containing 208 mg (1 mmol) of silver perchlorate dissolved in 20 cm^3 of CH_3CN with stirring. The 4-PyIm dissolved in solution and gave rise to a clear solution, which was filtered by gravity and protected from light with aluminium foil. Several days later, colorless needles suitable for X-ray diffraction were filtered to give 112 mg (yield 44%). M.p. 165 $^\circ\text{C}$ (decomp.). IR (neat, ν/cm^{-1}): 3240, 1621, 1569, 1456, 1415, 1300, 1227, 1174, 1099(b), 966, 849; NMR (δ_{H} ; DMSO- d_6 , 400 MHz): 13.17 (s), 8.64 (s), 7.93 (d, $J = 0.01$), 7.37 (s).

[2-(4-Pyridyl)imidazole silver(i)] hexafluorophosphate acetonitrile [$\text{Ag}(\text{4-PyIm})\text{PF}_6(\text{CH}_3\text{CN})$] (3). 145 mg (1 mmol) of 4-PyIm was added to a solution containing 255 mg (1 mmol) of silver hexafluorophosphate dissolved in 20 cm^3 of CH_3CN with stirring on a magnetic stirrer. The 4-PyIm dissolved in solution and gave rise to a clear solution, which was filtered by gravity, and protected from light with aluminium foil. After several days, colorless plate-like crystals suitable for X-ray diffraction were filtered to give 127 mg (yield 38%). M.p. 175 $^\circ\text{C}$ (decomp.). IR (neat, ν/cm^{-1}): 3391, 1619, 1567, 1454, 1380, 1288, 1228, 1174, 1107, 1025, 827(b), 784, 740; NMR (δ_{H} ; DMSO- d_6 , 400 MHz): 13.50 (s), 8.68 (s), 8.04 (d, $J = 0.01$), 7.45 (s).

2-(4-Pyridyl)imidazole silver(i) [$\text{Ag}(\text{4PyIm})$] (4). 145 mg (1 mmol) of 4-PyIm was added to a solution containing 170 mg (1 mmol) of silver nitrate dissolved in 20 cm^3 of water with stirring. The 4-PyIm dissolved in solution and gave rise to a slightly turbid solution, concentrated ammonia was added to the solution until a clear solution was obtained, and the solution was filtered by gravity, protected from light with aluminium foil and left overnight. Colorless needles, suitable for X-ray diffraction, were filtered to give 200 mg (yield 79%). M.p. 250 $^\circ\text{C}$ (decomp.). IR (neat, ν/cm^{-1}): 1601, 1556, 1463, 1432, 1406, 1223, 1202, 1151, 1001.

Crystallography: data collection and refinement

Datasets were collected on a Bruker SMART APEX II system at 120 K using APEX2 software.¹¹ An Oxford Cryostream 700 low-temperature device was used to control temperature. MoK α radiation was used. Initial cell constants were found by small widely separated “matrix” runs. Data collection strategies were

determined using COSMO.¹² Scan speeds and scan widths were chosen based on scattering power and peak rocking curves. Unit cell constants and orientation matrices were improved by least-squares refinement of reflections “thresholded” from the entire dataset. Integrations were performed with SAINT,¹³ using these improved unit cells as a starting point. Precise unit cell constants were calculated in SAINT from the final merged datasets. Lorenz and polarization corrections were applied. Absorption corrections were applied using SADABS.¹⁴ Datasets were reduced with SHELXTL.¹⁵ The structures were solved by direct methods without incident. Unless noted below, coordinates for all carboxylic acid, amine, ammonium, and phenol hydrogen atoms were allowed to refine. All other hydrogen atoms were assigned to idealized positions and were allowed to ride. Isotropic thermal parameters for the hydrogen atoms were constrained to be $1.5 \times (\text{methyl})/1.2 \times (\text{all other})$ that of the connected atom.

1: Geometry of the solvent water molecules was idealized by using DFIX commands. Coordinates for the imidazole hydrogens H13 and H33 were allowed to refine. 2: The perchlorate anion was disordered and was modeled as two closely spaced molecules. The perchlorate oxygens were assigned to isotropic thermal parameters. Thermal parameters for the chlorines and oxygens for the two anions were pairwise restrained using EADP commands. Geometry was idealized using DFIX commands. Coordinates for the imidazole hydrogen H13 were allowed to refine. 3: Coordinates for the imidazole hydrogen H13 were allowed to refine.

Results

The structure of 2 is dominated by a 1-D zig-zag polymer, where the silver(i) ion coordinates to two ligands in a near-linear fashion (N-Ag-N ; 171°), through one pyridyl nitrogen atom and one imidazole nitrogen atom, Fig. 1. Similar deviations from perfect linearity are commonplace as shown by an examination of relevant structures in the CSD.¹⁶ The 1-D zig-zag polymer corresponds to the motif postulated in Scheme 1a.

Adjacent chains in the structure of 2 are arranged in a parallel and in-phase fashion, Fig. 2, with counterions and solvent molecules filling the space in between. There is a weak hydrogen-bond involving the perchlorate ion and the imidazole moiety ($\text{C(H)} \cdots \text{O}$; 2.84 \AA , but there are no notable $\text{Ag} \cdots \text{Ag}$ or $\text{Ag} \cdots \pi$ contacts, Fig. 3.

The crystal structure of 3 is identical to that of 2, and the main feature is a 1-D polymer with near-linear coordination

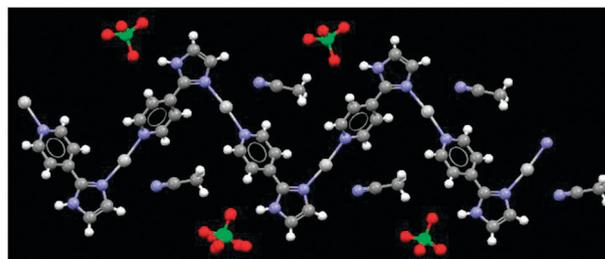


Fig. 1 Part of the crystal structure of 2 showing the infinite 1-D polymer; coordination number for silver(i) is two.

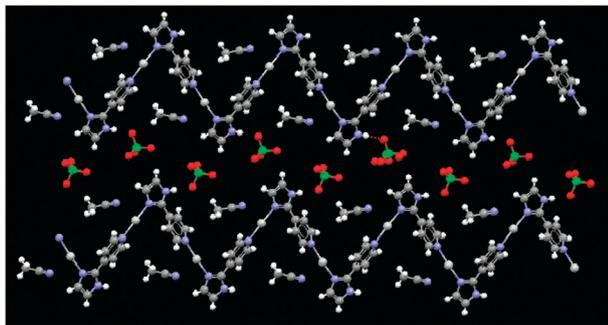


Fig. 2 Adjacent chains in the crystal structure of **2**.

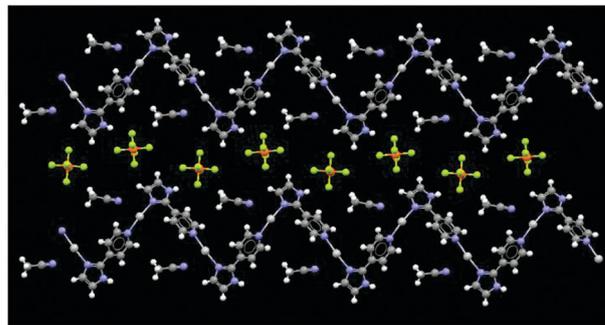


Fig. 5 The 2-D crystal structure of **3** showing the adjacent 1-D polymers.

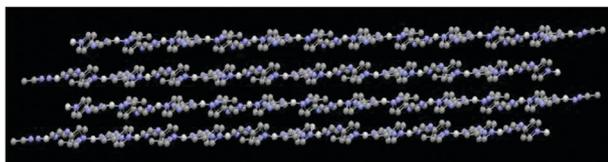


Fig. 3 Close-packing of 2-D layers in the crystal structure of **2**.

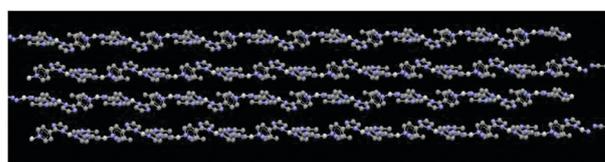


Fig. 6 The antiparallel layers of the crystal structure of **3**.

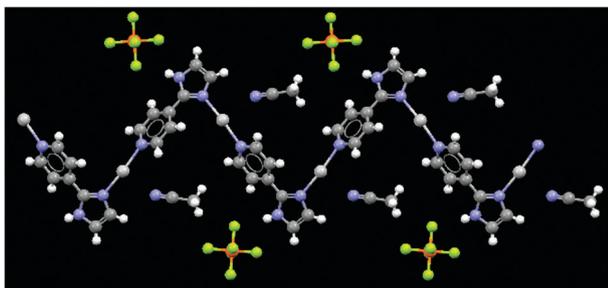


Fig. 4 Part of the crystal structure of **3** showing the infinite 1-D polymer; coordination number for silver(I) is two.

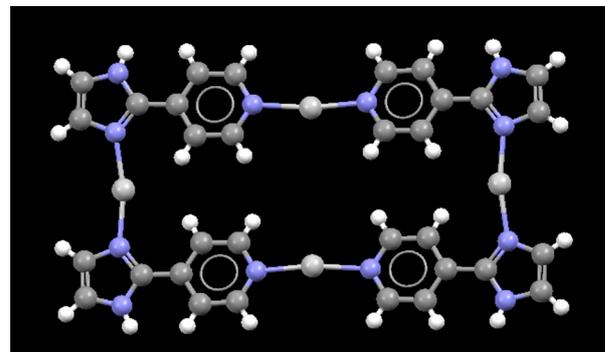


Fig. 7 Molecular rectangle in the crystal structure of **1**.

around each silver(I) ion with solvent molecules and counterions simply occupying the space between chains, Fig. 4. Again, the coordination polymer can schematically be described as postulated in Scheme 1(a).

The adjacent chains in **3** are again parallel and in-phase, Fig. 5, with counterions and solvent molecules filling the space in between them. No notable inter-layer short contacts could be identified, Fig. 6.

Compound **1** comprises a nitrate ion which is well-known for participating in stronger and structurally more relevant interactions than do perchlorate and hexafluorophosphate ions. The structure of **1** is akin to what was postulated in Scheme 1(c), and demonstrates that the 1-D polymers of **2** and **3** have been abandoned in preference for a centrosymmetric molecular rectangle constructed from four silver(I) ions and four ligands, Fig. 7.

The anions and water molecules provide hydrogen-bonded bridges between adjacent rectangles, Fig. 8, and there are no obvious $\pi \cdots \pi$ interactions between these cationic species, Fig. 9.

The crystal structure of **4** contains cyclic repeating units where the silver(I) ions have a coordination number of three, and form a distorted planar geometry, two of the imidazole nitrogen atoms coordinate to silver(I) in a near-linear mode while the third pyridine nitrogen atom is almost perpendicular

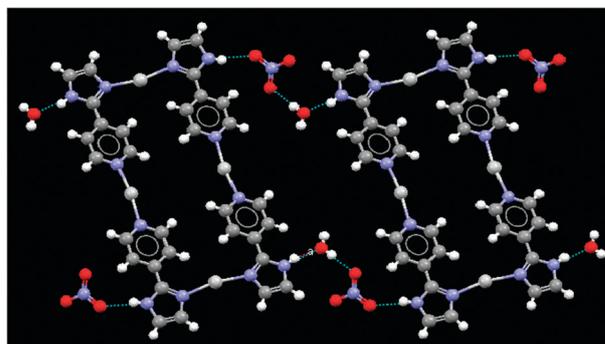


Fig. 8 Non-covalent bridges between molecular squares in the crystal structure of **1**.

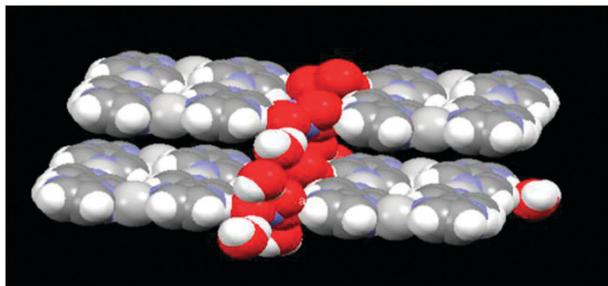


Fig. 9 Packing in the crystal structure of 1.

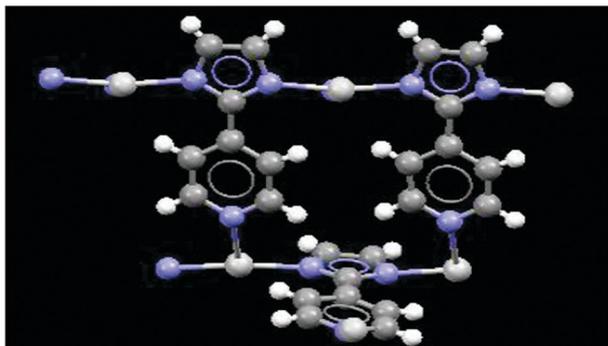


Fig. 10 Cyclic closed unit: the crystal structure of 4.

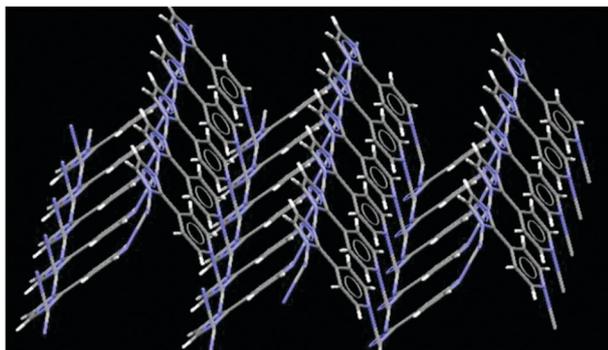


Fig. 11 Extended network in the crystal structure of 4.

to this linear motif, Fig. 10. The overall topology of this assembly is similar to what was postulated in Scheme 3(e). The ligand is anionic and contains three coordination sites, all of which are engaged with Ag(I) ions. These repeating units are further linked by metal–ligand coordinate covalent bond, Fig. 11.

Discussion

Four coordination complexes of silver(I) and 4PyIm have been characterized by single crystal X-ray diffraction, Table 2, in order to examine how counterions and solvent molecules may affect the assembly and coordination geometry of these complexes.

IR spectroscopy was initially employed for characterizing the ligand and the four complexes, Table 3. An important feature in the spectrum of the free ligand is the peak at 1608 cm^{-1} , which

shifts toward higher wavenumbers upon formation of a coordination compound with a neutral ligand, while in the anionic complex the shift is toward lower wavenumbers. The presence of the ligand in the anionic form was confirmed by the absence of the N–H peak.

The ^1H NMR study of the ligand and the soluble complexes indicates the presence of a well-defined N–H peak in all the complexes with the neutral ligand, while in the ^1H NMR spectra of the free ligand the peak is absent (see ESI †). No evidence could be found in the ^1H NMR data to indicate that the molecular square observed in the solid-state structure of 1 is retained in solution.

Structural analysis of 1–4 reveals the effect of the anion and the solvent on the structural outcome of the desired compounds. In the case of the compounds with perchlorate and hexafluorophosphate counterions and in the presence of acetonitrile as solvent we noticed that both structures are iso-structural and give the same 1-D zig-zag polymer, Fig. 12, with anions and the solvent molecules providing charge-balance and space-filling, respectively. An examination of the CSD for silver(I) complexes bearing a pyridine moiety as a coordinating ligand showed that changing the counterion from perchlorate to hexafluorophosphate produced iso-structural architectures in 80% of all occurrences (given similar experimental conditions). These two counterions have similar shape and are also relatively non-coordinating, which consequently means that most of the time, they will produce similar crystalline assemblies.

The case when using a nitrate ion as a counterion is markedly different. First of all the ion has smaller volume, Table 4, and secondly this counterion is frequently involved in strong and structure-directing hydrogen-bond interactions with most suitable hydrogen-bond donor molecules such as water, methanol, and ethanol. In this particular case, it seems that the nitrate ion is interacting with the initial polymer in such a way that the rotation around the C–C single bond between the two aromatic rings is slowed down which, in turn, facilitates the assembly of a closed molecular rectangle in preference to an infinite 1-D motif. The effect of the ion size on the formation of coordination polymers was examined by Kim *et al.*¹⁷ and they found that with a bent bipyridine ligand with C–C based conformational flexibility small-volume counterions gave rise to helical and cyclic structures whereas larger ions produced a 1-D zig-zag polymer. Similarly, Ag(I) complexes of bis(aminopyridine)¹⁸ change from cyclic to polymeric structures as the volume of the counterion increases.

Formation of closed cyclic structures with rectangular geometry composed of two ligands and two silver(I) ions is relatively common in the literature,¹⁹ and there are a few examples of square metallocyclic composed of four ligands and four silver(I) ions.²⁰ As far as we are aware, however, the structure of 1 contains the first metallocycle comprising four ligands and four silver(I) ions having a rectangular geometry.

The range of sizes of the counterions in our study is shown in Table 4, and it is important to note that there is a larger difference between ClO_4^- and PF_6^- than between ClO_4^- and NO_3^- , yet the former are iso-structural, whereas the nitrate containing complex is very different. Although a simple close-packing argument may occasionally help to explain structural

Table 2 Crystallographic data for 1, 2, 3, and 4

	1	2	3	4
Systematic name	Tetrakis(2-(4-pyridyl)imidazole) silver(I) nitrate tetrahydrate	[2-(4-Pyridyl)imidazole silver(I)] perchlorate acetonitrile	[2-(4-Pyridyl)imidazole silver(I)] hexafluorophosphate acetonitrile	2-(4-Pyridyl)imidazole silver(I)
Formula moiety	(C ₈ H ₇ N ₃) ₄ (AgNO ₃) ₄ (H ₂ O) ₃	(C ₈ H ₇ N ₃) Ag(ClO ₄) (C ₂ H ₃ N)	(C ₈ H ₇ N ₃) (AgPF ₆) (C ₂ H ₃ N)	(C ₈ H ₆ N ₃) Ag
Empirical formula	C ₃₂ H ₃₄ Ag ₄ N ₁₆ O ₁₅	C ₁₀ H ₁₀ AgClN ₄ O ₄	C ₁₀ H ₁₀ AgClN ₄ O ₄	C ₈ H ₆ AgN ₃
Molecular weight	1314.23	393.54	439.06	252.03
Color, Habit	Colorless plate	Colorless needle	Colorless plate	Colorless needle
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group, Z	<i>P</i> $\bar{1}$, 1	<i>P</i> 2 ₁ / <i>c</i> , 4	<i>P</i> 2 ₁ / <i>c</i> , 4	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	6.9704(4)	6.9519(6)	6.7927(3)	6.4496(5)
<i>b</i> /Å	7.8319(5)	14.9904(13)	15.7016(7)	13.5953(11)
<i>c</i> /Å	19.4544(11)	12.8623(13)	13.1938(6)	8.6168(6)
α (°)	79.749(2)	90.00	90.00	90.00
β (°)	85.086(2)	103.276(6)	102.723(2)	94.244(3)
γ (°)	81.023(2)	90.00	90.00	90.00
<i>V</i> /Å ³	1030.46(11)	1304.6(2)	1372.65(11)	753.49(10)
X-ray wavelength	0.71073	0.71073	0.71073	0.71073
μ mm ⁻¹	1.963	1.768	1.655	2.609
Absorption corr	Multi scan	Multi scan	Multi scan	Multi scan
Trans min/max	0.8913/0.5723	0.9326/0.6762	0.9072/0.6195	0.9028/0.5976
Reflections collected	24 393	13 548	16 389	7600
Independent	7216	3745	4609	2502
Observed	6483	2271	3931	2115
Threshold expression	> 2sigma(<i>i</i>)	> 2sigma(<i>i</i>)	> 2sigma(<i>i</i>)	> 2sigma(<i>i</i>)
<i>R</i> ₁ (observed)	0.0261	0.0667	0.0278	0.0321
<i>wR</i> ₂ (all)	0.0596	0.1769	0.0648	0.0712
Goof	1.091	0.970	1.020	1.151
Completeness	0.919	0.944	0.857	0.902
θ_{\max}	33.140	30.500	33.460	32.720

Table 3 FTIR data for 4-PyIm and 1–4

	4-PyIm	(1)	(2)	(3)	(4)
ν (cm ⁻¹)	1608	1615	1621	1619	1601

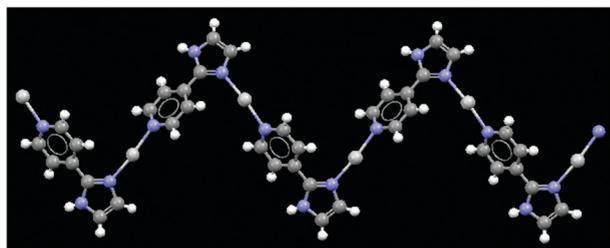


Fig. 12 1-D polymer in compound (2) and (3).

Table 4 Size of anions

Ion	NO ₃ ⁻	ClO ₄ ⁻	PF ₆ ⁻
Volume (Å ³)	40	54	75

differences in closely related systems, such behavior cannot be generalized to all systems²¹ and we need therefore to also examine other possible non-covalent interactions that may be induced or activated by the chemical nature of the counterion.²²

An important distinction of the nitrate ion in the structure of 1 is related to its ability to form strong hydrogen bonds and this also means that it is likely to bring suitable hydrogen-bond

Table 5 Metal-coordinating ability based upon CSD data

Percentage of the ion as coordinating ligand	NO ₃ ⁻	ClO ₄ ⁻	PF ₆ ⁻
	54	23	1

donors along into the crystalline lattice thereby producing a hydrated complex. It seems that the molecular rectangles present in the crystal structure of 1 are quite stable, and the Ag(I) does not need to increase the coordination number beyond two. Instead, the nitrate ion (which is frequently coordinated to metal ions), simply acts as a bridge between adjacent rectangles using water molecules as appropriate hydrogen-bond donors. Again, an examination of the CSD demonstrates that for silver(I) complexes with pyridine-based ligands, similar structures were observed 80% of the time. However, when the solvent was altered from non-polar organic solvents to polar solvents (H₂O and EtOH), capable of supporting strong hydrogen bonds, dramatic structural changes were obtained which also agrees with what we observed when changing from acetonitrile to water as a solvent.

The Cambridge Structural Database (CSD) supports the idea that ClO₄⁻ and PF₆⁻ are weaker coordinating anions, while NO₃⁻ is a stronger coordinating ion,²³ Table 5, and in several cases it competes with the ligand in coordination. The nitrate ion can form bonds with solvent molecules with great ease, and when combining an aqueous medium with nitrate ions there are considerable possibilities for incorporating water molecules within the lattice, especially if the nitrate ion is not 'needed' for metal-ion coordination. For example, more than 24% of all structures in the CSD containing nitrate ions also include one

or more water molecules. The counterion may obviously play an important role in directing the final crystalline motif in the supramolecular array itself, but frequently it also changes the structure by virtue of bringing in solvent molecules capable of forming structure-directing hydrogen bonds.

Moving from a charged complex with counterions (1–3) to an uncharged complex in the absence of counterions produces a dramatic change in coordination behavior; the anionic ligand has three available coordination sites, which are all consumed and, interestingly, this also increases the coordination number for silver(I) from two to three in this family of compounds.

Conclusions

Any systematic structural examination of the coordination geometry and supramolecular chemistry of metal-complexes requires a detailed analysis of the coordinating ability of counterions and solvent molecules as well as of their capacity for forming strong non-covalent interactions.²⁴ In this study, we have focused on a system that allows us to change one variable at a time (solvent, counterion, and ligand charge), in order to try to elucidate cause and effect in the solid-state behavior in this family of compounds. Size is certainly less important than the chemical nature of the counterions in this series, and the introduction of the nitrate ion effectively ‘activated’ a new set of intermolecular interactions by virtue of bringing polar solvent molecules into the lattice. Although the unique molecular rectangle obtained in the crystal structure of **1** does not hold opportunities for host–guest chemistry or ion recognition behavior, we now have access to a set of guidelines that can inform the next step in this investigation, which will focus on the synthesis of larger metallocycles with rectangular geometry with potential applications as functional materials. The results and observations regarding the effect of counterions and solvents are important for controlling the synthesis of the desired target compound and also contribute to more refined and versatile guidelines for inorganic crystal engineering.

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