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Chromophore containing bipyridyl ligands. Part 1: supramolecular solid-state structure of Ag(I) complexes

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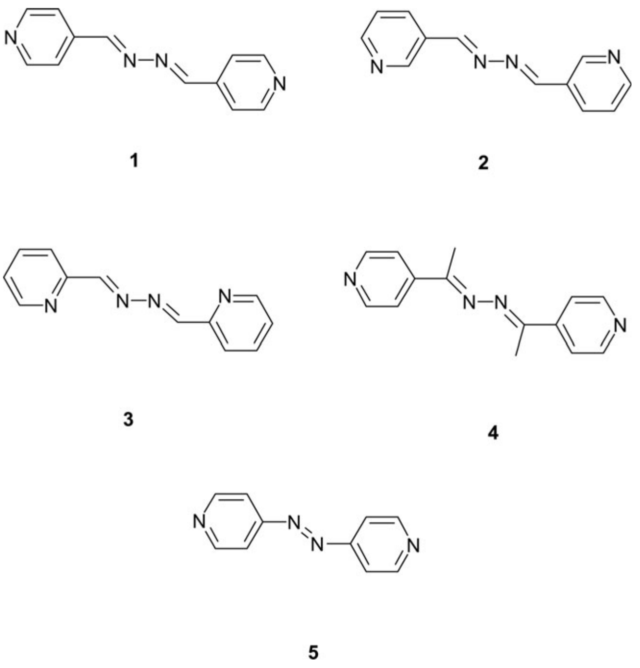
The solid-state structures of a series of azine or azo chromophore containing bipyridyl ligand complexes of Ag(I) salts have been determined by single-crystal X-ray diffraction. The supramolecular structures are dominated by one-dimensional chains formed through pyridyl–Ag–pyridyl bonding, but the packing of these chains through non-covalent intermolecular interactions is unpredictable. Ag···anion interactions are shown to be important, especially for nitrate and perchlorate species, but these may be supported or replaced by Ag···Ag, Ag···solvent, Ag···azine or Ag···π contacts. The molecular structures of the ligands show little alteration on complex formation, except for the $AgNO_3$ complex of *N*,*N′*-bis-pyridin-4-ylmethylene-hydrazine where the normally planar azine ligand adopts a twisted geometry.

Introduction

Surface enhanced Raman scattering (SERS) and surface enhanced resonance Raman scattering (SERRS) have recently been shown to be excellent techniques for the detection and characterisation of a wide range of analytes at high dilutions, including the high explosives Semtex[1] and TNT,[2] drugs of abuse[3] and biopolymers such as DNA and proteins. [4] The detection of hidden high explosives by determining the presence of their vapour in the atmosphere is a major objective of our work, so a significant result was the controlled reduction of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane, a major component of Semtex) to hydrazine and its subsequent trapping with a number of different carbonyl functionalities.[1] This gave a number of azines, including compounds **1** to **4** (Scheme 1), which could be successfully detected at low concentrations using SERS.



Scheme 1

Our methodology for detecting RDX relies upon the analytes **1** to **4** adhering to the surface of aggregated silver nanoparticles. Whilst previous work concentrated on simply detecting these species, it must also be true that the SERS data collected contains information on the nature of the surface species. To get true SERRS, ligand **5**, which absorbs light at higher wavelength and closer to the resonance conditions of the lasers used, was also prepared and utilised. The structures of the Ag(I) complexes of these ligands are of relevance to this work, as knowledge of these will allow solid-state Raman spectra to be correlated with specific ligand coordination modes and geometries. This in turn will be used to interpret SER(R)S spectra from complexed silver nanoparticles, thus giving an insight into ligand binding at silver nanoparticles.

1 to **5** are obviously also of the type of bipyridyl ligands commonly used as linear "spacers" or "rods" in the construction of supramolecular coordination polymers.[5–7] Such networks are of general interest, as the intriguing range of structures which they display often leads to interesting physical (especially electronic and magnetic) properties—and it is hoped that studying their structures will eventually make their self-assembly controllable or at least predictable. The typically 2-coordinate, linear coordination of Ag(I) complexes of these ligands have attracted particular interest. This is both because their labile nature and relative simplicity (as compared to transition metals with higher coordination numbers) makes the growth of single-crystals suitable for X-ray diffraction studies easier and because it is rationalised that complex 2D or 3D networks can be viewed as being formed from aggregations of simpler 1D chains. Therefore, it can be argued that an understanding of what governs the behavior of Ag(I) 1D chains is a prerequisite to understanding the behavior of their higher dimensional equivalents.[5,6] In this paper we report the solid-state structures of a series of complexes formed by the reaction of Ag(I) salts with ligands **1** to **5**. A second paper will deal with SER(R)S spectra obtained from the ligands in aqueous silver colloid solution. In combination with the structures herein and solid-state Raman data, this will provide rare evidence for the nature of the surface of silver nanoparticles and for the surface modification of these nanoparticles by dyes.

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Experimental

N,*N*′-Bis-pyridin-4-ylmethylene-hydrazine, 1

To a solution of pyridine-4-carbaldehyde (4.494 g, 4 ml, 40 mmol) in ethanol (15 ml) was added dropwise hydrazine hydrate (1.032 g, 1 ml, 21 mmol) with vigorous stirring. After twenty minutes the pale precipitate was collected by filtration, washed with cold methanol and dried to afford **1** as yellow microcrystals (3.150 g, 75%). Mp 178 °C. λ_{max} (MeOH)/nm 286 (ε = 36 702). ^{1}H NMR (CDCl$_3$) δ 7.69 (4H, d, *J* = 4.44 Hz, ArH), 8.56 (2H, s, CH=N), 8.75 (4H, d, *J* = 4.44 Hz, ArH). *m*/*z* (EI) 210.090 76 [$C_{12}H_{10}N_4$ (M)$^+$ < 1.0 ppm]. Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.57; H, 4.76; N, 26.66. Found C, 68.56; H, 4.57; N, 26.53%.

N,*N*′-Bis-pyridin-3-ylmethylene-hydrazine, 2

As per the procedure for azine **1** using pyridine-3-carbaldehyde (4.494 g, 4 ml, 42 mmol) to afford **2** as yellow microcrystals (2.688 g, 64%). λ_{max} (MeOH)/nm 297 (ε = 33 010). ^{1}H NMR (DMSO) δ 7.55 (2H, dd, *J* = 4.80, 4.80 Hz, ArH), 8.27 (2H, d, *J* = 7.88 Hz, ArH), 8.70 (2H, d, *J* = 4.64 Hz, ArH), 8.79 (2H, s, CH=N), 9.02 (2H, s, ArH). *m*/*z* (EI) 210.091 84 [$C_{12}H_{10}N_4$ (M)$^+$ < 6.2 ppm]. Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.57; H, 4.76; N, 26.66. Found C, 68.48; H, 4.71; N, 26.32%.

N,*N*′-Bis-pyridin-2-ylmethylene-hydrazine, 3

As per the procedure for azine **1** using pyridine-2-carbaldehyde (4.494 g, 4 ml, 42 mmol) to afford **3** as yellow microcrystals (3.906 g, 93%). λ_{max} (MeOH)/nm 298 (ε = 308 20). ^{1}H NMR (DMSO) δ 7.52 (2H, t, *J* = 4.96, 6.28 Hz, ArH), 7.95 (2H, t, *J* = 6.40, 7.64 Hz, ArH), 8.11 (2H, d, *J* = 7.84 Hz, ArH), 8.57 (2H, s, CH=N), 8.72 (2H, d, *J* = 4.72 Hz, ArH). *m*/*z* (EI) 210.090 74 [$C_{12}H_{10}N_4$ (M)$^+$ < 0.9 ppm]. Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.57; H, 4.76; N, 26.66. Found C, 68.41; H, 4.71; N, 26.19%.

N,*N*′-Bis-(1-pyridin-4-yl-ethylidene)-hydrazine, 4

To a solution of 4-acetylpyridine (1.089 g, 9.0 mmol) in ethanol (20 ml) was added hrdrazine hydrate (2.30 g, 4.5 mmol) and acetic acid (2 drops). The resulting solution was heated to reflux for two hours, cooled and then neutrilised by dropwise addition of $NaHCO_3$ (1 M, pH 8). Ethanol was removed *in vacuo* to afford **4** as an off white powder. After washing with cold ethanol and drying 0.536 g (50%) were recovered. λ_{max} (MeOH)/nm 269 (ε = 31 105). ^{1}H NMR (CDCl$_3$) δ 2.28 (6H, s, 2 × CH$_3$), 7.75 (4H, d, *J* = 4.56 Hz, ArH), 8.70 (4H, d, *J* = 5.28 Hz, ArH). *m*/*z* (EI) 238.120 74 [$C_{14}H_{14}N_4$ (M)$^+$ < 4.6 ppm]. Anal. Calcd for $C_{14}H_{14}N_4$: C, 70.58; H, 5.88; N, 23.52. Found C, 70.35; H, 5.72; N, 22.99%.

trans-4,4′-Azobis(pyridine), 5

5 was synthesised as the dihydrate in 40% yield using the method of Clarke [8] (treatment of 4-aminopyridine with NaOCl).

Reaction of 1 with Ag(BF$_4$)

0.15 g (0.78 mmol) of AgBF$_4$ was dissolved in 30 ml of acetonitrile and then added to a 30 ml solution of 0.33 g (1.56 mmol) of **1** in CH$_2$Cl$_2$. After stirring for 10 minutes a light yellow precipitate was isolated by filtration, 0.184 g, 58% yield based on [Ag**1**][BF$_4$]·CH$_3$CN. Mp 200–205 °C (decomp.). Major IR peaks (Nujol, cm^{-1}); 1610, 1310, 1290, 1025, 820, 698. Further analysis was limited as the powder degraded over a period of 5 to 7 days.

Reaction of 1 with Ag(SbF$_6$)

0.249 g (0.78 mmol) of AgSbF$_6$ was dissolved in 30 ml of acetonitrile and then added to a 30 ml solution of 0.33 g (1.56 mmol) of **1** in CH$_2$Cl$_2$. After stirring for 10 minutes a light yellow precipitate was isolated by filtration. 0.213 g, 49% yield based on [Ag**1**][SbF$_6$]·CH$_3$CN. Mp 218–225 °C (decomp.). λ_{max} (solid-state) 284 nm. Major IR peaks (Nujol, cm^{-1}); 1625, 1320, 1245, 1070, 950, 815, 650. Anal. of oven dried sample. Calcd for $C_{12}H_{10}AgSbF_6N_4$: C, 26.02; H, 1.82; N, 10.12. Found C, 26.04; H, 1.67; N, 10.02%.

Reaction of 1 with Ag(NO$_3$)

0.132 g (0.78 mmol) of AgNO$_3$ was dissolved in 30 ml of acetonitrile and then added to a 30 ml solution of 0.33 g (1.56 mmol) of **1** in CH$_2$Cl$_2$. After stirring for 10 minutes a light yellow precipitate was isolated by filtration. 0.231 g, 77% yield based on [Ag**1**][NO$_3$]. Mp 232 °C (decomp.). λ_{max} (solid-state) 275 nm. Major IR peaks (Nujol, cm^{-1}); 1615, 1320, 1310, 1220, 820, 680. Anal. Calcd for $C_{12}H_{10}AgO_3N_5$: C, 37.92; H, 2.65; N, 18.43. Found C, 37.32; H, 2.59; N, 18.09%.

Reaction of 2 with Ag(BF$_4$)

A solution of Ag(BF$_4$) (0.156 g, 0.80 mmol) in 30 ml of acetonitrile was added to 30 ml of a CH$_2$Cl$_2$ solution of **2** (0.329 g, 1.57 mmol). After stirring for 10 minutes a pale yellow precipitate of [Ag**2**][BF$_4$] was collected by filtration. 0.084 g, 26% yield based on [Ag**2**][BF$_4$]·CH$_3$CN. Mp 193 °C (decomp.). Major IR peaks (KBr, cm^{-1}); 3095, 2990, 1620, 1420, 1312, 1050, 805, 702.

Reaction of 3 with Ag(NO$_3$)

30 ml of an acetonitrile solution of Ag(NO$_3$) (0.136 g, 0.80 mmol) was added to a solution of **3** (0.331 g, 1.58 mmol) in 30 ml of CH$_2$Cl$_2$. After 10 minutes of stirring a bright yellow precipitate of [{Ag**3**}$_2$][NO$_3$]$_2$ was collected by filtration (0.250 g, 82%). Mp 232 °C (decomp.). Major IR peaks (KBr, cm^{-1}); 3053, 2955, 1634, 1583, 1470, 1400, 1290, 1219, 1030, 738, 702. Anal. Calcd for $C_{24}H_{20}Ag_2O_6N_{10}$: C, 37.92; H, 2.65; N, 18.43. Found C, 37.94; H, 2.46; N, 18.13%.

Reaction of 5 with Ag(NO$_3$)

Orange crystals of [Ag**5**][NO$_3$] were grown at the interface between an acetonitrile solution of AgNO$_3$ (0.20 g, 1.2 mmol) layered onto a CH$_2$Cl$_2$ solution of azo ligand **5** (0.22 g, 1.2 mmol). Mp 286 °C (decomp.). Major IR peaks (KBr, cm^{-1}); 3457, 2427, 1644, 1588, 1480, 1378, 1224, 1050, 840.

Reactions of 1, 2 and 4 with Ag(ClO$_4$)

Due to the safety hazards associated with perchlorate salts no attempt was made to complete these reactions in bulk. In each case a few yellow crystals of the Ag(I) complexes were grown at the interface between 10 ml of an acetonitrile solution of AgClO$_4$ (0.02 g, 0.01 mmol) layered onto a 10 ml CH$_2$Cl$_2$ solution of azine ligand (0.02 mmol).

Crystallography

Measurements on **1A**, **1B**, **2A**, **2B**, **3A**, **4A** and **5A** were made on a Nonius Kappa CCD diffractometer and those on **1C** and **1D** were made with a Rigaku AFC7S diffractometer. Both used graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). Data were corrected for absorption by multi-scan or psi-scan methods respectively, depending on the data collection instrumentation.[9] All structures were refined to convergence on F^2

Table 1 Crystallographic parameters and refinement data for Ag complexes

	1A	1B	1C	1D	2A	2B	3A	4A	5A
	[Ag**1**][BF_4]·MeCN	[Ag**1**][ClO_4]·MeCN	[Ag**1**][SbF_6]·MeCN·$x$$H_2O$	[Ag**1**][NO_3]	[Ag**2**][BF_4]·MeCN	[Ag**2**][ClO_4]·MeCN	[{Ag**3**}$_2$][NO_3]$_2$	[Ag**4**][ClO_4]·0.25[**4**]	[Ag**5**][NO_3]
*F*w	445.97	458.61	626.44[a]	380.12	445.97	458.61	760.24	505.18	354.09
System	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/m$	$P2_1/m$	$P\bar{1}$	$P2_1/a$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	6.0846(2)	6.0509(2)	10.496(2)	6.7441(12)	7.5292(2)	9.3202(4)	8.0933(2)	10.4948(3)	25.0213(5)
b/Å	15.6681(4)	15.8105(4)	11.904(2)	13.452(2)	9.7601(3)	14.2960(6)	8.8628(3)	13.9768(4)	9.3011(2)
c/Å	8.6321(3)	8.6688(2)	8.6632(12)	15.028(2)	11.8669(4)	13.2368(4)	9.3988(4)	14.3519(4)	15.9564(4)
α/°	90	90	97.956(13)	90	75.444(1)	90	89.868(2)	64.474(2)	90
β/°	96.589(1)	97.244(1)	110.611(9)	97.568(13)	74.672(1)	110.178(2)	82.849(2)	88.167(2)	109.683(1)
γ/°	90	90	92.935(13)	90	83.659(2)	90	72.614(4)	77.080(1)	90
V/Å^3	817.50(4)	822.71(4)	997.5(2)	1351.5(4)	813.13(1)	1655.45(11)	637.93(4)	1846.64	3496.49(13)
Z	2	2	2	4	2	4	1	4	12
T/K	150	123	123	123	123	123	123	123	123
No. refl.	8971	3719	4841	3284	15331	32485	17254	15793	13990
Unique	1878	1935	4589	3019	3634	3781	2893	8459	4183
R_{int}	0.0712	0.0289	0.0370	0.0354	0.0429	0.048	0.0520	0.0382	0.0483
R	0.0305	0.0253	0.0307	0.0347	0.0296	0.0300	0.0254	0.0500	0.0311
$wR2$	0.0787	0.0653	0.0804	0.0862	0.0567	0.0686	0.0577	0.1117	0.0645

[a] Based on 1.75 H_2O molecules per asymmetric unit.

using Shelxl-97.[10] Further crystallographic parameters and refinement statistics can be found in Table 1.

CCDC reference numbers 266716–266724.

See http://www.rsc.org/suppdata/nj/b5/b500698h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Solid-state structure of Ag(I) complexes of 1

The dyes **1** to **5** (Scheme 1) are easily prepared in good yield. Of these, the azo **5** has widely been reported to form coordination networks, with a search of the Cambridge Crystallographic database[11] giving 50 structures with coordinated metals,[12] whilst the coordination chemistry of **1** to **4** is less well known.[13] All the dyes would be classified as "off-axis rod type" ligands by the method described in ref. 5 as, in the expected *trans* geometry, each will display two metal–N vectors rotated by 180° but offset from each other by the stepping effect of the azine or azo link. In terms of size and shape, **5** has an obvious analogue in 1,2-bis{4′-pyridyl}ethylene which has itself been widely studied,[14] however we are not aware of any corresponding simple equivalents of the azine ligands. Mixing the ligands with Ag(I) salts led to rapid deposition of fine powders. Scaling down the bulk preparative techniques described in the Experimental section and layering acetonitrile solutions of the Ag salts onto dichloromethane solutions of the ligands gave crystals suitable for single crystal analysis. This showed the crystals to be {[Ag**1**][BF_4]·NCMe}$_\infty$, hereafter **1A**, {[Ag**1**][ClO_4]·NCMe}$_\infty$ **1B**, {[Ag**1**][SbF_6]·xNCMe·$y$$OH_2$}$_\infty$ **1C**, {[Ag**1**][NO_3]}$_\infty$ **1D**, {[Ag**2**][BF_4]·NCMe}$_\infty$ **2A**, {[Ag**2**][ClO_4]·NCMe}$_\infty$ **2B**, [(Ag**3**)$_2$][NO_3]$_2$ **3A**, {[Ag**4**][ClO_4]·0.25(**4**)}$_\infty$ **4A** and {[Ag**5**][NO_3]}$_\infty$ **5A**. These single crystal samples have identical IR and solid-state Raman spectra to their powder counterparts which, taken together with the microanalysis data of the powders where available, allows the assumption that they are chemically similar.

The structures of the silver complexes of **1** and **2** appear on initial examination to consist of simple 1D polymeric chains constructed by the ligands bridging near linear, two-coordinate metal centers (Fig. 1). Closer inspection shows that this apparent simplicity is misleading. The coordinative unsaturation about the Ag atoms encourages the formation of non-covalent intermolecular interactions, which link the individual chains to form higher dimensional networks. In **1A** the octahedral Ag coordination is completed by two mutually *trans* Ag···anion interactions (Ag···F 2.828(2) Å) and two mutually *trans* Ag···π contacts (closest Ag···C3 is 3.280(2) Å). As can be seen in Fig. 2 this causes the 1D chains to form sheets through bridging BF_4 anions. These sheets lie offset to each other and form a 3D network *via* the Ag···π interactions. The importance of the anion in these systems is shown in that replacing BF_4 with the similarly shaped ClO_4 gives an essentially isostructural complex (**1B**) whilst replacing BF_4 with SbF_6 fundamentally alters the inter-chain bonding. As well as being a considerably larger anion, SbF_6 also has a lower charge per F atom than BF_4 or ClO_4, which leads to it being a less effective metal binding species. Thus unlike **1A** and **1B**, the

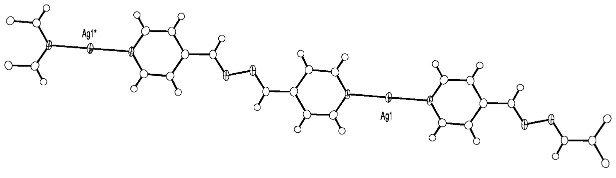

Fig. 1 Part of the linear chain structure of **1A**.

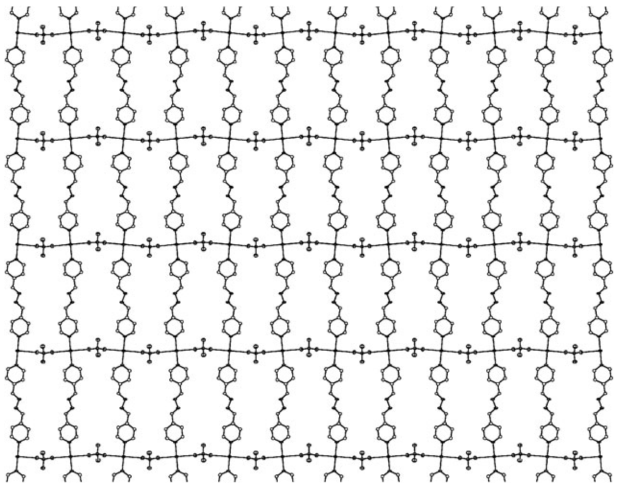

Fig. 2 Part of a 2D sheet in **1A** showing the chains linked by bridging BF_4 anions. The 3D structure is obtained by off-setting the adjoining 2D sheets so that Ag···π bonds are formed with the pyridyl rings.

Table 2 Coordination geometry about the Ag atom (Å and °)

	1A	1B	1C	1D	2A	2B	4A′	4A″	5A′	5A″
Dative bonds										
Ag–N (py)	2.143(2)	2.153(2)	2.168(3)	2.181(3)	2.147(2)	2.155(2)	2.134(4)	2.143(3)	2.170(2)	2.187(2)
Ag–N (py)	2.143(2)	2.153(2)	2.177(2)	2.182(3)	2.153(2)	2.157(2)	2.134(4)	2.154(4)	2.177(2)	2.187(2)
Ag–N (NCMe)			2.586(4)		2.600(2)	2.702(2)				
py–Ag–py	180.0	180.0	167.9(1)	173.4(1)	167.03(7)	175.56(8)	174.47(13)	174.28(13)	168.27(9)	180.0
Ag···anion										
Ag···F	2.828(2)		3.247(4)		3.387(2)					
Ag···F	2.828(2)									
Ag···O[a]		2.837(2)		2.682(3)		2.911(2)	2.813(7)	2.653(7)	2.764(2) 2.811(2)	2.838(2) 2.906(2)
Ag···O[a]		2.837(2)		2.730(3)		3.009(2)	2.830(11)	2.865(7)	2.791(2) 3.119(2)	2.838(2) 2.906(2)
Ag···O				2.747(3)						
Ag···π										
Ag···C or N (shortest)	3.280(2) *para*-C	3.271(2) *para*-C	3.116(4) azine-*N*		3.328(2) *ortho*-C		3.371(4) *meta*-C	3.329(4) *meta*-C		3.308(2) *ortho*-C
Ag···C or N (shortest)	3.280(2) *para*-C	3.271(2) *para*-C	3.366(4) ring centroid							3.308(2) *ortho*-C
Ag···Ag										
Ag···Ag					3.1131(4)		3.2719(5)	3.2719(5)		

[a] For both geometries of **5A** the nitrate anions bind in an η^2 mode. Both **4A** and **5A** have two crystallographically independent molecules present, these are denoted above as **4A′**, **4A″**, **5A′** and **5A″**.

structure of **1C** is not cross-linked through anion interactions. Although in **1C** the Ag atom can be described as having six pseudo-octahedral contacts, two of these are very long (Ag···F is 3.247(4) and the shortest Ag···C is 3.586(4) Å, which are approximately 0.42 and 0.30 Å longer than their respective equivalents in **1A**) leaving four shorter/stronger Ag–N bonds (see Table 2 for details). Of these stronger bonds, that to the NCMe solvent is terminal, and so as far as network formation is concerned each Ag site acts as a T-shaped 3-fold junction and a ladder structure is formed (Fig. 3). Although the ladder is drawn so as to emphasise its inter-chain Ag···N(azine) "rungs" it should be noted that the ladder is also positioned so as to allow face-to-face aromatic interactions of the pyridyl rings (C···C min. 3.337 Å). These are in the more common and energetically favourable head-to-tail orientation[15] and it may largely be this rather than the Ag···N(azine) interaction that holds the ladders together. The looser interconnectivity of **1C** leaves space for extra, disordered solvent (a mixture of NCMe and water) and also for the anion to be disordered.

Overall the Ag···anion and Ag···π interactions of **1A** and **1B** are replaced in **1C** by Ag···solvent and Ag···N(azine) contacts. All the contacts observed in **1C** are potentially available to **1A** and **1B** (both have non-bonded NCMe in their lattices) and so it can be concluded that for this system the relatively highly coordinating BF_4 and ClO_4 anions dominate inter-chain packing, as only in their absence do Ag···solvent and Ag···N(azine) contacts occur. It would thus be expected that introduction of the more highly coordinating NO_3 anion would increase the domination of the inter-chain interactions by Ag···anion contacts. Examination of the structure of **1D** shows that this is so.[16] There are no contacts with Ag apart from the Ag–N(py) and Ag···O_3N interactions. In **1D** the Ag coordination is five-coordinate and square-pyramidal with both NO_3 groups and azine ligands acting as bridges between metals. This gives a structure based around 2D sheets lying perpendicular to the *b* axis. Pairs of sheets are joined by ligating NO_3 anions to give a "double-layer" sheet. This architecture is tightly enough packed to exclude solvent molecules, and it also seems that it is energetically favoured enough to overcome the azine's preferred[13a,17] flat geometry (the torsion angle around the central N–N bond, C6N2N3C7, is 138.1(4)°). This is the only complex reported herein where there is a significant change in the geometry of the ligand upon metal complexation (Fig. 4). It is possible that this is because the structural motif imposed by the strongly coordinating nitrate groups features head-to-head ordering of the pyridyl groups. As mentioned above this is relatively unfavourable for pyridyl groups (due to the large electrostatic effect caused by metal complexation),[15] and so the azines twist to give edge-to-face

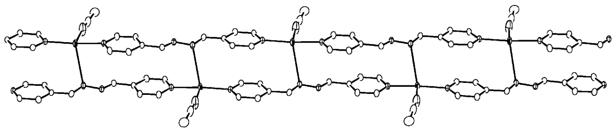

Fig. 3 The ladder structure of **1C** with H-atoms omitted for clarity.

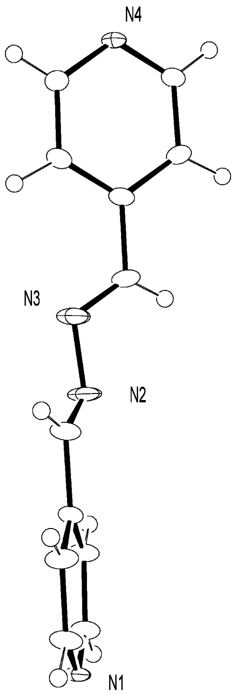

Fig. 4 Detail of the molecular structure of **1D** showing the twisted nature of the dye ligand.

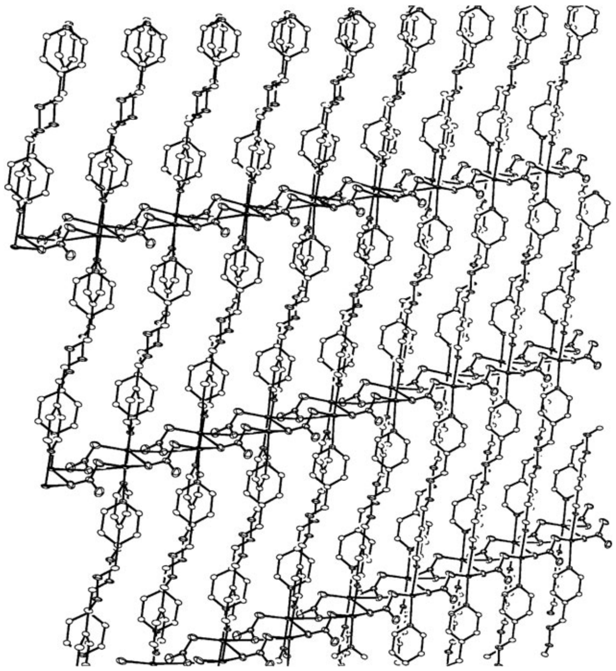

Fig. 5 Part of the double sheet structure of **1D** highlighting the edge-to-face nature of the ring-to-ring contacts.

aromatic interactions instead of the more common face-to-face interactions (Fig. 5). Calculations in ref. 17 show that in azines the N–N bond is rotationally soft and so the energy needed to twist **1** can be easily regained by maximising inter-chain interactions.

Solid-state structure of Ag(I) complexes of 2, 3, 4 and 5

The difficulties of deciphering the rules that predict 3D packing are illustrated by extending the study to the structures of Ag(I) complexes of **2**, **3**, **4** and **5**. Whereas the complexes of **1** form a series of structures that can be rationalised by understanding the simple differences between their anions' bonding characteristics, attempting to extrapolate this behaviour to the other ligands fails. Reaction of **2** with AgBF$_4$ or AgClO$_4$ gives **2A** and **2B**, the chain structures of which contrast with those of the linear complexes of **1** as they adopt pronounced zig-zag shapes (compare Fig. 1 with Fig. 6). Similar effects are seen, amongst others, on going from $\{[\mathrm{Ag}(4,4'\text{-pytz})][\mathrm{BF}_4]\}_\infty$[18] to $\{[\mathrm{Ag}(3,3'\text{-pytz})][\mathrm{BF}_4]\}_\infty$[19] (pytz = 3,6-bis(pyridinyl)-1,2,4,5-tetrazine) and have been discussed in terms of the change from linear to off-axis rod ligands.[5] That this is not quite accurate is shown here as both **1** and **2** are of the off-axis type. It would be better to describe the change from linear chain to zig-zag chain in terms of the angle between the rod axis and the N–Ag axis. Only if these are approximately parallel can a straight chain form.

2A has the expected py–Ag–py polymer chain, but the BF$_4$ anion does not then dominate the inter-chain packing as in **1A**. This may be because the zig-zag nature of the chains leads to the dye molecules impinging on the space needed for a putative BF$_4$ bridge. The coordination network is instead completed by a short Ag$\cdots$Ag contact (3.1131(4) Å). This leads to a corrugated 2D sheet of the brick wall type (Fig. 7) that is internally supported by short Ag$\cdots\pi$ interactions (with the pyridyl rings *trans* to the Ag$\cdots$Ag contacts). The coordination shell of Ag is completed (Table 2) by a terminally bonded NCMe (*trans* to a BF$_4$ anion that is itself too far from Ag to be considered as a ligand). Whilst the structural difference between **1A** and **2A** can be rationalised once it is realised that the zig-zag nature of the **2A** chains profoundly effect the chain packing, it is harder to explain why for **1** the BF$_4$ and ClO$_4$ salts are isostructural but for **2** they are not. **2B** differs from **2A** as here the polymeric chains pair through η^2-ClO$_4$, $[\mathrm{Ag}\cdots\mathrm{O{-}Cl{-}O}\cdots]_2$ bridges (see Fig. 8) and do not aggregate further. The Ag$\cdots\pi$ and Ag$\cdots$Ag contacts seen in **2A** are absent and the Ag to solvent distance is lengthened.

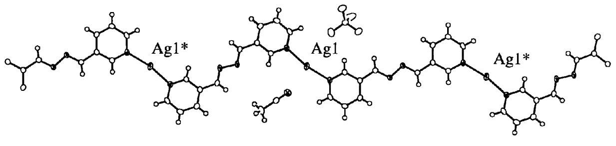

Fig. 6 The primary structural feature of **2A** is a zig-zag chain.

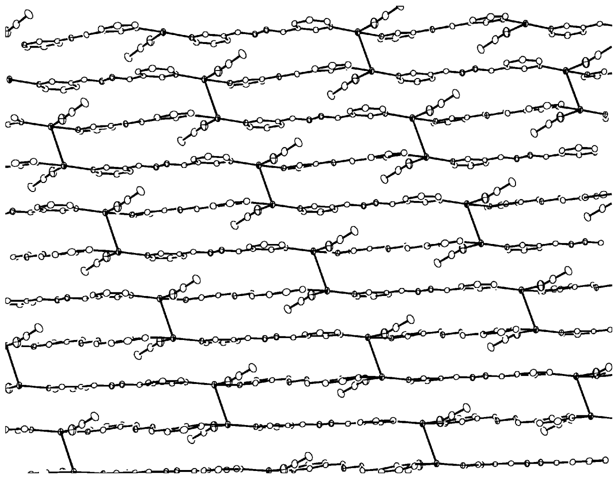

Fig. 7 Brick-wall structure of **2A**.

The AgClO$_4$ complex of **4**, a methyl substituted derivative of **1**, reverts to the straight chain structural type found for all the complexes of **1**. However, the extended structure of **4A** is similar to **2B** in that the pairs of crystallographically independent polymeric chains link together by ClO$_4$ bridges between Ag atoms. Here, however, the bridge involves only one O atom (at least in the major configuration of the disordered anions), leading to a much shorter Ag$\cdots$Ag contact distance (3.2719(5) and 3.814(1) Å in **4A** and **2B**, respectively). Despite the short Ag$\cdots$Ag contact the structure is very different from that of **2A**, as in **4A** there is no solvent to Ag interaction. Indeed, the NCMe seems to have been replaced by a discrete molecule of **4** lying orthogonal to the polymeric Ag**4** chains, see Fig. 9.

The structure of **5A** is also hard to predict. Not only is a psuedo-polymorphic structure, **5B**, formed under slightly dif-

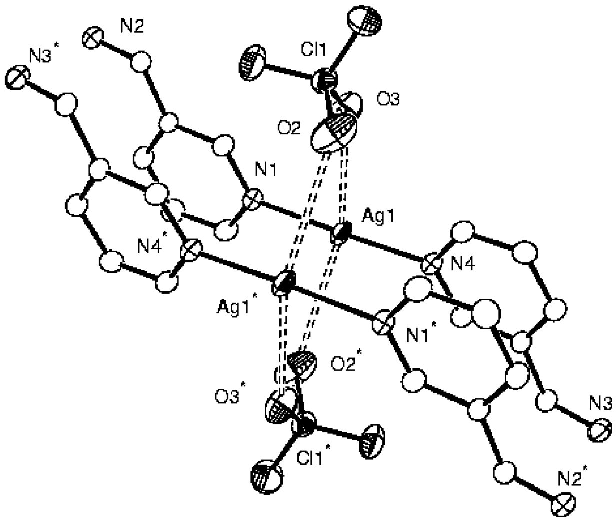

Fig. 8 Detail of the structure of **2B** illustrating the perchlorate bridging mode.

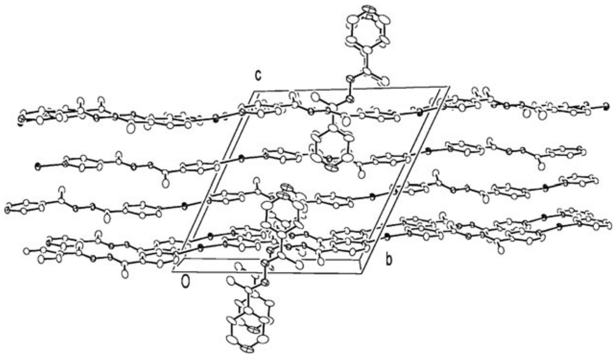

Fig. 9 View of **4A** down the *a* axis, showing the relative orientations of the polymer chains and the free molecules of ligand **4**.

ferent reaction conditions,[20] but **5A** itself contains two different linear-chain geometries, which interconnect through anion bridges and π interactions. Both chains exhibit the expected governing linear N–Ag–N motif (N3–Ag1–N4 168.27(9) and N6–Ag2–N6* 180.0°) but whilst both Ag centres also contact two bidentate nitrate anions only Ag2 makes further connections through two Ag···pyridyl interactions (Ag2···C1* 3.308(2) Å). This is very different from the reported structure of **5B** [20] in which the nitrate unexpectedly plays no role in inter-chain contacts with only Ag···Ag and longish π···π contacts reported. **5A** is also unusual (and again differs from **5B**) as the 1D chains do not all run parallel to each other,[5] eschewing this simple and effective packing mode to instead cross at a pronounced angle (Fig. 10). A crystallographic curiosity is that the structure contains approximately 3% of the monochlorinated azo dye as an impurity (as often happens when forming azos through amine reduction by sodium hypochlorite),[8] but that this impurity is only included in the chain bonding through Ag2.

Although some 2-pyridyl species are known to form coordination polymers with Ag(I),[21] the presence of hetero-atoms between the pyridyl rings in **3** favours chelation. Indeed reaction with $AgNO_3$ gives the planar, centrosymmetric, dimer $[(Ag\mathbf{3})_2][NO_3]_2$, **3A**, as shown in Fig. 11. The structurally similar O_3SCF_3 and PF_6 salts of $[(Ag\mathbf{3})_2]$ have been reported [22,23] but the BF_4 salt is reported to form a polymeric network [24] similar to that known for a Cu(I) complex of **3**.[23] Anion control of these structures is not obvious, however it may be worth noting the site disorder present in the structure of the PF_6 salt. This can be interpreted as evidence of a polymeric nature[23] and if this was the case then the greater bonding capabilities of the O containing anions may be what favours dimer formation over polymer formation. In **3A** the N coordination about Ag is distorted from T-shaped trigonal due to the small bite angle of the chelate (N3–Ag1–N4 71.45 (7)°) and, interestingly, whilst the distance to the azine N is comparable to that to the *trans* pyridyl (2.264(2) and 2.228(2) Å, respectively) it is considerably shorter than the Ag to chelated pyridyl bond (2.435(2) Å). As reported above, only the twisted ligand geometry of **1D** shows any sign that complex formation alters the dye ligands' internal geometry. Even for **3A** with its direct azine to Ag bond there is no apparent change in the azines' bond lengths or angles (for example N2–N3 is 1.411(3) compared to 1.407(5) to 1.416(6) Å found herein for complexes of **1** and **2**, the $C{=}N$ distances and the angles subtended by N in **3A** also lie within the ranges found for the other complexes).

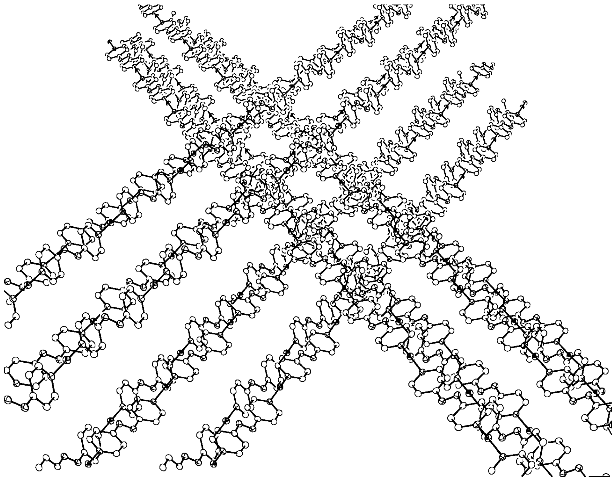

Fig. 10 Part of the crystal structure of **5A** viewed along the *a* axis, illustrating the non-parallel packing of the polymer chains.

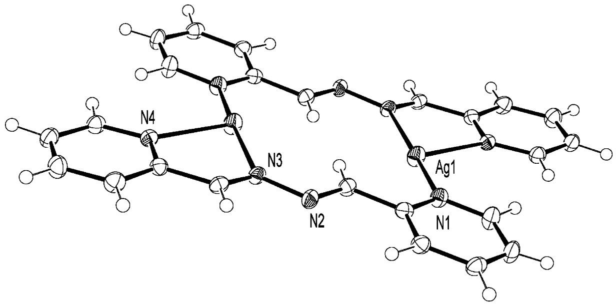

Fig. 11 The dimeric molecular structure of **3A** with nitrate ions omitted.

Conclusions

From the structural descriptions above it is obvious that predicting the packing arrangement of py–Ag–py chains is not trivial. Changing the anion changes the structure and to some extent this change is predictable when the anion's metal bonding characteristics are considered. Thus, for ligand **1** the relatively highly coordinating NO_3 anion dominates the inter-chain packing in **1D** and excludes all other contact types, in **1B** and **1A** the similarly sized and shaped ClO_4 and BF_4 anions contribute to inter-chain packing whilst, in **1C**, the SbF_6 anion makes little contribution and other intermolecular interactions dominate. In agreement with this trend, NO_3 also dominates the inter-chain bonding in **5A**. Indeed it may be the strength of these interactions that leads to the absence of NCMe from all three of the NO_3 salts examined herein. The other six complexes all contain NCMe—except for **4A** where its place is unexpectedly taken by a "solvent" molecule of **4**. The behaviour of the ClO_4 anions is also consistent, in that all bridge two metal centers. However, there is much more that does not fit any obvious pattern. For example, the NO_3 and ClO_4 anions all bridge metals but they do not do so in any consistent way and adopt a variety of bonding modes. Furthermore, the previously published polymorph of **5A**, **5B** has non-bonding NO_3 anions and, for ligand **1**, the BF_4 anion acts in the same fashion as ClO_4, but for ligand **2** the two anions give different structures. A final unpredictable feature is the non-parallel packing of py–Ag–py chains found for **5A**.

In conclusion, we have synthesised and examined a series of silver compounds which further our understanding of the fundamental forces that govern the packing of 1D polymeric coordination compounds into 2D and 3D networks. Of particular note is the crucial role played by the anions and the differences in packing arrangements available to linear as opposed to zig-zag chains but other, currently unidentified, factors also contribute and thus make general structure prediction unreliable.

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