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Silver(I) coordination polymers of the 'hinged' pyrazine containing ligand di-2-pyrazinylmethane

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Silver(I) coordination polymers of the 'hinged' pyrazine containing ligand di-2-pyrazinylmethane

Herein, we report a series of 1, 2, and 3D coordination polymers formed from di-2-pyrazinylmethane (**dpzm**) and silver(I) salts in which we examine the role the non-coordinating methylene hinge plays in distorting these structures away from those observed for related pyrazine containing coordination polymers. $\{[Ag_2(\mathbf{dpzm})(NO_3)_2]\}_n$ (**1**) is a 1D ladder-like structure, $\{[Ag(\mathbf{dpzm})]SO_3CF_3\}_n$ (**2**) is a 4^4 connected 2D network, and $\{[Ag_2(\mathbf{dpzm})_3](X)_2\}_n$ (X = ClO_4, **4a**; X = PF_6, **4b**), $\{[Ag_4(\mathbf{dpzm})_5](BF_4)_4\}_n$ (**5**) and $\{[Ag_3(\mathbf{dpzm})_4](SbF_6)_3\}_n$ (**6**) have pseudo-cubic lattices with some connections between Ag(I) centres missing; this is a consequence of the pyrazine in some cases only acting as a monodentate group (**4**) or a low ligand:Ag ratio in **5** and **6**. Most of the structures compare well to previously reported 1D, 2D and 3D assemblies formed with pyrazine, although an evident feature of **dpzm** coordination was the geometrical restriction of the methylene hinge, which was apparent in the long Ag-N bond lengths observed for the 3D materials.

Keywords: silver(I); coordination polymers; N-heterocyclic ligands; pyrazine

Introduction

Considerable research into the synthesis of silver(I) coordination polymers (*1-3*) has been driven by interest in such materials for, among other things, rare examples of their permanent porosity,(*4-7*) physical properties such as luminescence and non-linear optical properties,(*8*) and their antimicrobial activity.(*9-11*) Aside from using it to target particular physical or biological properties, silver(I) is often chosen as a building block due to its exceptionally rich coordination chemistry, possessing an unmatched flexibility in its coordination number (commonly ranging from two to six) and geometry (linear to octahedral).(*12*) Ag(I) prefers soft donors and forms relatively labile bonds with neutral donors. As a consequence, the synthesis of silver(I) coordination polymers can be extremely sensitive to the reaction conditions; subtle changes in the starting

stoichiometry, the coordinating ability of the solvent, or temperature of the reaction can lead to the assembly of quite different structures as non-covalent interactions play a significant role in the overall 3D structure.(*13*)

Owing to their coordinating or non-coordinating behaviour, counter-ions play a crucial role in the dimensionality and structure of silver(I) coordination polymers.(*1, 12, 14, 15*) Even when the anion is non-coordinating, size decreases in the order: $SbF_6^- > PF_6^- > ClO_4^- > BF_4^-$ have a considerable affect on the structure.(*16*) Combined, these properties often lead to the formation of entirely different structures with each individual anion.(*17-21*) The choice of organic ligands naturally contributes significantly to the structure of silver(I) coordination polymers, and consideration is given to length, angle and flexibility of the ligand. Rigid N-heterocyclic azine linkers, such as pyrazine (**pyz**, Figure 1) and 4,4′-bipyridine, have been extensively used in the 'node' and 'linker' approach, often yielding predictable silver(I) assemblies.(*1, 15, 22*) In contrast, flexible azine linkers containing alkyl, S, or O spacers only partially restrict the conformation of the ligand during synthesis, leading to unusual structures.(*1-3, 23, 24*)

While silver(I) coordination polymers of pyrazine(*25-27*) and 2,2′-dipyrazine(*20*) are well known, the coordination chemistry of di-pyrazinyl compounds separated by a one-atom spacer has been attracting recent attention. Notably, this family of ligands can chelate to a single metal while the other two donors can coordinate to two further metal centres, much like that observed for pyrazine. For example, Wan and colleagues reported a series of silver(I) coordination polymers with di-2-pyrazinylmethanediol (**dpzmdOH**),(*28*) di-2-pyrazinylsulfoxide (**dpzmSO**),(*29*) and sulfonyldipyrazine (**dpzmSO₂**)(*30*) (Figure 1) and coordination polymers of another

related ligand, di-2-pyrazinylamine (**dpzmNH**), were reported by Ismayilov and co-workers.(*31*)
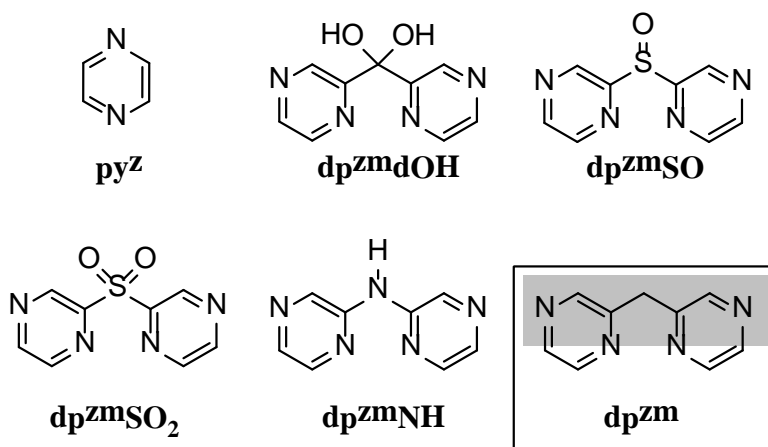
Figure 1. Pyrazine (**pyz**) and examples of hinged di-pyrazinyl compounds that have been used as ligands.

Recently, we have also synthesised porous 3D silver(I) coordination polymers of di-2-pyrazinylmethane (**dpzm**) (Figure 1) which undergo crystal-to-crystal breathing associated with solvent exchange and additional transformations to close-packed 2D and 3D materials upon desolvation.(*32-33*) Interestingly, **dpzm** is the only compound in this family which possesses a spacer that does not engage in coordination. Herein, we report a series of 1, 2, and 3D coordination polymers formed from **dpzm** and silver(I) salts in which we examine the role the non-coordinating methylene hinge plays in distorting these structures away from related pyrazine containing coordination polymers.

Experimental

Materials and methods

Unless otherwise stated, reagents were purchased from commercial sources and used

without further purification. **Dpzm**(*34*) was prepared by reported procedures. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago. Infrared (IR) spectra were recorded on a PerkinElmer Fourier-Transform Infrared (FT-IR) spectrometer using an attenuated total reflectance accessory fitted with a zinc-selenide crystal.

Synthesis

General Procedure:

A methanolic solution of the silver(I) salt (2 mL) was added dropwise to a methanolic solution of **dpzm** (2 mL) resulting in an immediate precipitation. The solid was isolated under reduced pressure and washed with diethyl ether (10 mL). Crystals of the respective coordination polymers were obtained by slow vapour diffusion methods. In all cases the crystals were suitable for X-ray crystallography.

Caution! Whilst no problems were encountered in the course of this work, perchlorate salts are strong oxidising agents and are potentially explosive and should be handled on a small scale with appropriate care.

*{[Ag$_2$(**dpzm**)(NO$_3$)$_2$]}$_n$ (1)*
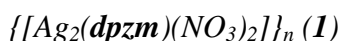
AgNO$_3$ (38.0 mg, 0.22 mmol) and **dpzm** (20.3 mg, 0.12 mmol) were combined according to the general procedure. This afforded a white solid (47.0 mg, 92%) Found C 25.0, H 1.7, 17.5, C$_{18}$H$_{16}$N$_{11}$O$_9$Ag$_3$·¾H$_2$O requires: C 24.9, 2.0, N 17.8. Slow vapour diffusion of dichloromethane into a solution of the white solid (13.2 mg, 0.03 mmol) in DMSO (0.2 mL) yielded thick rod-shaped crystals which were washed with diethyl ether and dried in *vacuo* (10.1 mg, 86%). ν_{max} (neat, cm^{-1}) 1302 (s, N-O), 1380 (s, N-O), 1410 (m, CH$_2$), 1529 (w, C=C), 1589 (w, C=C). Found 21.4, 1.5, 16.3, C$_9$H$_8$N$_6$O$_6$Ag

requires C 21.1, H 1.6, N 16.4%.

*{[Ag(**dpzm**)]SO₃CF₃}ₙ (**2**)*
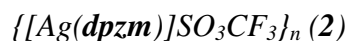
AgSO₃CF₃ (30 mg, 0.12 mmol) and **dpzm** (30 mg, 0.17 mmol) were combined according to the general procedure. The resulting precipitate was isolated as a white solid (36 mg, 72%) Found: C 28.3, H 1.9, 13.0, $C_{10}H_8N_4S_1O_3F_3Ag_1$ requires C 28.0, H 1.9, N 13.1. Slow vapour diffusion dichloromethane into a solution of the precipitate (10.5 mg) in DMSO (0.2 mL) yielded needle-shaped crystals (6.9 mg, 66%). ν_{max} (neat, cm⁻¹): 1026, 1153, 1250 (s, OTf⁻), 1409 (m, CH₂), 1522 (w, C=C). Found: C 28.0, H 1.8, 12.9, $C_{10}H_8N_4S_1O_3F_3Ag_1$ requires C 28.0, H 1.9, N 13.1.

*{[Ag₂(**dpzm**)₃](ClO₄)₂}ₙ (**4a**)*
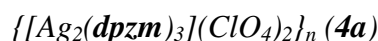
AgClO₄ (23.0 mg, 0.11 mmol) and **dpzm** (29.0 mg, 0.17 mmol) were combined according to the general procedure. The product was isolated as a white solid (33 mg, 64%). Found C 31.0, H 2.3, N 15.9, $C_{27}H_{24}N_{12}Ag_2Cl_2O_8$ requires C 30.9, H 2.3, N 16.0. Slow vapour diffusion dichloromethane into a solution of the precipitate (11.5 mg, 0.02 mmol) in DMSO (0.2 mL) yielded block shaped crystals (7.9 mg, 66%). ν_{max} (nujol, cm⁻¹): 1091 (s, Cl-O), 1413 (m, CH₂), 1523 (w, C=C), 1590 (w, C=C). Found C 34.8, H 2.7, N 17.3, $C_{27}H_{24}N_{12}Ag_2Cl_2O_8 \cdot ¼(CH_2Cl_2)$ requires: C 34.4, H 2.6, N 17.6.
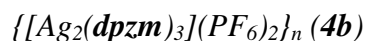
*{[Ag₂(**dpzm**)₃](PF₆)₂}ₙ (**4b**)*

AgPF₆ (41.0 mg, 0.16 mmol) and **dpzm** (42.0 mg, 0.24 mmol) were combined according to the general procedure. This afforded a white solid (62 mg, 75%). Found C 31.6, H 2.4, N 16.3, $C_{27}H_{24}N_{12}Ag_2P_2F_{12}$ requires C 31.7, H 2.4, N 16.5. Slow vapour diffusion of dichloromethane into a solution of the precipitate (11.3 mg 0.03 mmol) in DMSO (0.2 mL) yielded block shaped crystals which washed with ether and dried in

vacuo (7.7 mg, 68%). ν_{max} (neat, cm^{-1}): 827 (s, P-F), 1404 (m, CH$_2$), 1523 (w, C=C).

Found C 31.8, H 2.3, N 16.2, C$_{27}$H$_{24}$N$_{12}$Ag$_2$P$_2$F$_{12}$ requires C 31.7, H 2.4, N 16.5.

{[Ag$_4$(*dpzm*)$_5$](BF$_4$)$_4$}$_n$ (*5*)

AgBF$_4$ (32 mg, 0.15 mmol) and **dpzm** (40 mg, 0.23 mmol) were combined according to

the general procedure. The product was isolated as a white solid (51 mg, 76%). Found:

C 32.9, H 2.5, 16.9, C$_{36}$H$_{32}$N$_{16}$Ag$_3$B$_3$F$_{12}$·2(H$_2$O) requires C 33.0, H 2.8, N 17.1. Slow

vapour diffusion dichloromethane into a solution of the precipitate (11.6 mg) in

acetonitrile (0.2 mL) gave block shaped crystals (10.2 mg, 89%). ν_{max} (neat, cm^{-1}): 1026

(s, B-F), 1407 (m, CH$_2$), 1523 (w, C=C). Found: C 32.5, H 2.7, N 15.8,

C$_{45}$H$_{40}$N$_{20}$Ag$_4$B$_4$F$_{16}$·(CH$_2$Cl$_2$) requires: C 32.0, H 2.5, N 16.2.

{[Ag$_3$(*dpzm*)$_4$](SbF$_6$)$_3$}$_n$ (*6*)

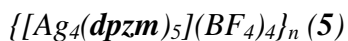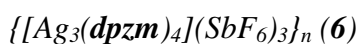AgSbF$_6$ (46 mg, 0.13 mmol) and **dpzm** (35 mg, 0.20 mmol) were combined according

to the general procedure. The product was isolated as a white solid (58 mg, 78%).

Found: C 25.4, H 1.9, N 13.0, C$_{36}$H$_{32}$N$_{16}$F$_{18}$Ag$_3$Sb$_3$ requires: C 25.2, H 1.9, N 13.0.

Slow vapour diffusion dichloromethane into a solution of the precipitate (16.4 mg) in

DMSO yielded block shaped crystals (12.6 mg, 77%) ν_{max} (neat, cm^{-1}): 651 (s, Sb-F),

1402 (m, CH$_2$), 1525 (w, C=C). Found: C 25.4, H 1.8, 12.9, C$_{36}$H$_{32}$N$_{16}$F$_{18}$Ag$_3$Sb$_3$

requires: C 25.2, H 1.9, N 13.0.

Single crystal X-ray crystallography

Single crystals were mounted in paratone-N oil on a plastic loop. X-ray diffraction data

were collected at 150(2) K on an Oxford X-calibur single crystal diffractometer using

Mo Kα radiation. Data sets were corrected for absorption using a multi-scan method,

and structures were solved by direct methods using SHELXS-97(*35*) and refined by

full-matrix least squares on F2 by SHELXL-2013,(*36*) interfaced through the program X-Seed.(*37*) In general, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions, unless specified otherwise in additional details below. Figures were produced using the program CrystalMaker. Table 1 lists the X-ray experimental data and refinement parameters for the crystal structures.

Full details of the structure determinations have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1409035-1409040 (**1**, **2**, **4a**, **4b**, **5**, and **6**, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Street, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Table 1. X-ray experimental data for **1** - **4**.

Compound	1	2	4a	4b
Empirical formula	$C_9H_8N_6Ag_2O_6$	$C_{10}H_8N_4AgF_3O_3S$	$C_{29}H_{28}Ag_2Cl_6N_{12}O_8$	$C_{27}H_{24}N_{12}Ag_2P_2F_{12}$
Formula weight	511.95	429.13	1101.07	1022.26
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*P2₁/n*	*C2/c*	*C2/c*
a (Å)	12.3493(6)	9.1202(5)	22.985(3)	22.771(2)
b (Å)	9.1971(4)	11.1131(5)	20.8148(17)	21.3119(12)
c (Å)	12.8938(7)	14.1599(7)	18.492(2)	19.0100(18)
α (º)	90	90	90	90
β (º)	109.706(5)	104.644(5)	118.116(18)	118.499(13)
γ (º)	90	90	90	90
Volume ($Å^3$)	1378.68(12)	1388.54(12)	7803.1(15)	8107.5(11)
Z	4	4	8	8
Density (calc.) (Mg/m^3)	2.466	2.053	1.875	1.675
Absorption coefficient (mm^{-1})	2.884	1.654	1.480	1.137
F(000)	984	840	4368	4016
Crystal size (mm3)	0.34×0.45×0.71	0.13×0.20×0.50	0.24×0.27×0.35	0.22×0.30×0.38
θ range for data collection (º)	2.82 to 29.34	2.95 to 29.38	2.50 to 29.32	2.63 to 29.41
Reflections collected	7674	15780	18352	46140
Observed reflections [R(int)]	1702 [0.0582]	3408 [0.0437]	9057 [0.0464]	9949 [0.0671]
Goodness-of-fit on F_2	1.087	1.061	1.041	1.088
R_1 [I>2σ(I)]	0.0272	0.0340	0.0604	0.0715
wR_2 (all data)	0.0702	0.0878	0.1748	0.1904
Largest diff. peak and hole (e.$Å^{-3}$)	0.690 and -0.558	1.061 and -0.900	1.673 and -1.635	1.400 and -0.946

Table 1 (cont'd). X-ray experimental data for **5** and **6**.

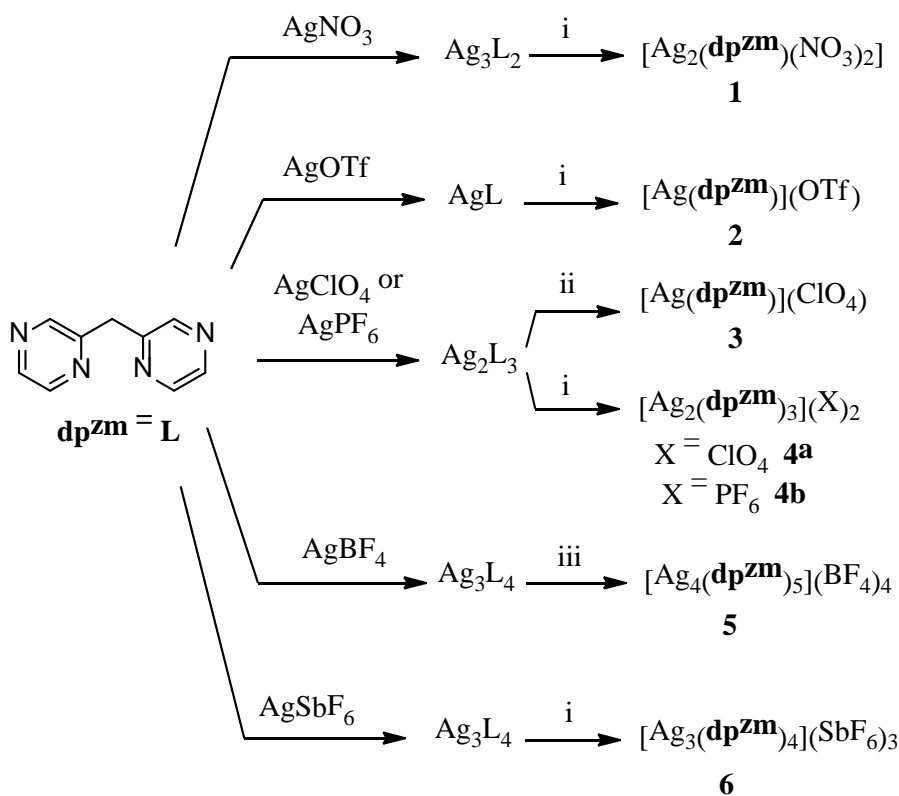| Compound	5	6
Empirical formula	$C_{50}H_{50}N_{20}Ag_4B_4F_{16}Cl_{10}$	$C_{37}H_{34}N_{16}Ag_3Sb_3F_{18}Cl_2$
Formula weight	2064.32	1804.56
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pca2_1$
a (Å)	24.4586(5)	20.2850(10)
b (Å)	12.1823(2)	22.8168(8)
c (Å)	25.8229(6)	11.9863(5)
α (°)	90	90
β (°)	103.108(2)	90
γ (°)	90	90
Volume (Å^3)	7493.8(3)	5547.7(4)
Z	4	4
Density (calc.) (Mg/m^3)	1.830	2.161
Absorption coefficient (mm^{-1})	1.477	2.681
F(000)	4048	3432
Crystal size (mm3)	0.17×0.29×0.54	0.18×0.25×0.32
θ range for data collection (°)	2.57 to 29.24	2.63 to 29.27
Reflections collected	85154	34878
Observed reflections [R(int)]	18419 [0.0426]	12724 [0.0375]
Goodness-of-fit on F2	1.028	1.040
R_1 [I>2σ(I)]	0.0544	0.0374
wR$_2$ (all data)	0.1493	0.0875
Largest diff. peak and hole (e.Å^{-3})	1.501 and -1.848	1.026 and -0.948

Results and Discussion

Synthesis of coordination polymers

Given the prevalence of coordination polymers incorporating pyrazine as a bridging ligand,(*3, 39-40*) we initially undertook reactions of the tetradentate **dpzm** ligand with a selection of 1st row transition metals expecting the ligand to chelate an individual metal centre and bridge to two others. However, due to the reactive methylene hinge decomposition of the **dpzm** was observed with a wide range of metal salts. In one instance, a small selection of crystals suitable for X-ray crystallography were obtained from a reaction of **dpzm** with $Cu(BF_4)_2$ in methanol; single crystal X-ray analysis revealed a discrete ML assembly of an octahedral Cu(II) centre and di(pyrazin-2-yl)methanediol (**dpzmdOH**), identical to a previously reported structure by Mak and colleagues (who utilized di-2-pyrazinylketone in a similar reaction with copper(II)).(*41*) Oxidation of di-2-pyridylmethane (**dpm**) has also been reported to occur under similar conditions with copper(II) nitrate, yielding a M_6L_4 cluster composed of Cu(II) and di(pyridin-2-yl)methanediol.(*42*)

To overcome the issues with the reactivity of **dpzm**, attention was shifted towards silver(I), which, as described earlier, has rich coordination chemistry and does not promote the oxidation of active methylene compounds.(*42*) Reaction of **dpzm** with $AgNO_3$ in methanol resulted in an immediate precipitation of a coordination polymer which analysed as $[Ag_3(\textbf{dpzm})_2(NO_3)_2]\cdot\frac{3}{4}H_2O$. This M_3L_2 species was found to be soluble in DMSO, and recrystallisation by slow vapour diffusion of DCM into a solution of the polymer in DMSO yielded large block crystals $[Ag_2(\textbf{dpzm})(NO_3)_2]$ (**1**) in 86% yield that were suitable for X-ray crystallography (Scheme 1). Formation of **1** was further supported by the characteristic NO_3^- stretches at 1302 and 1380 cm^{-1}. Similarly, a series of coordination polymers could be obtained by reacting different salts

of silver(I) with **dpzm** (Scheme 1). In all cases, combining the metal salt and ligand in methanol produced an immediate precipitate which was isolated and analysed. Reaction of AgOTf with **dpzm** gave a precipitate of a 1:1 metal-to-ligand species. Recrystallisation yielded large crystals with a formula of [Ag(**dpzm**)]OTf (**2**) as determined by X-ray crystallography. The formula obtained by C H N analysis was in agreement with this. A similar 2D structure ([Ag(**dpzm**)(ClO$_4$)] (**3**)) has previously been reported as the product of a transformation of a porous 3D sodalite coordination polymer [Ag(**dpzm**)(DMSO)]ClO$_4$.(*32*) This material could also be prepared directly by slow evaporation of a CH$_3$CN/H$_2$O mixture.

Scheme 1. All initial reactions undertaken in methanol. Crystals of **1** - **6** obtained by: i) slow vapour diffusion of DCM into DMSO; ii) slow evaporation, CH$_3$CN/H$_2$O; and, iii) slow vapour diffusion of DCM into CH$_3$CN. Compound **3** has been previously reported as the product of a 3D to 2D transformation.(*32*)

Unlike coordination polymers **1** and **3**, for the reactions to prepare coordination polymers **4a** and **4b** the Ag_2L_3 metal-to-ligand ratio obtained following initial precipitation of the product was maintained upon recrystallisation. Slow vapour diffusion of DCM into a DMSO solution of the Ag_2L_3 precipitate gave crystals suitable for X-ray crystallography of two related complexes, $[Ag_2(\textbf{dpzm})_3(ClO_4)_2]$ (**4a**) and $[Ag_2(\textbf{dpzm})_3(PF_6)_2]$ (**4b**), in 66% and 68% respectively. Formation of these complexes was supported by C H N analysis and IR spectroscopy. To further explore the effect of a non-coordinating anion, two more coordination polymers were formed by reacting $AgBF_4$ or $AgSbF_6$ with **dpzm**. In the case of $AgBF_4$, the precipitate formed analysed with a Ag_3L_4 composition, and recrystallisation of this material gave the M_4L_5 complex $[Ag_4(\textbf{dpzm})_5(BF_4)_4]$ (**5**) in 89% yield. Reaction of $AgSbF_6$ with **dpzm** in methanol also gave a Ag_3L_4 precipitate, and recrystallisation by slow vapour diffusion gave crystals of the complex $[Ag_3(\textbf{dpzm})_4](SbF_6)_3$ (**6**) in 77% yield. The formation of **5** and **6** was supported by C H N analysis which was in agreement with the formula obtained from the crystal structures, while IR spectroscopy revealed the characteristic stretches corresponding to the respective anions.

Single Crystal X-ray Crystallography

*Crystal structure of **1***

Coordination polymer **1** crystallises in the monoclinic space group *C*2/*c* with one silver(I) metal centre, one nitrate counter ion, and half of a molecule of **dpzm** in the asymmetric unit (Figure 2a). Compound **1** is a 1D polymer with a ladder-like structure and a 2:1 metal-to-ligand ratio. Instead of chelating to the silver(I) centre as expected, two **dpzm** ligands bridge between four symmetry related distorted trigonal planar silver atoms. Each silver(I) centre is coordinated by a pyrazine nitrogen donor from two

different **dpzm** molecules, and a weakly coordinating nitrate. The Ag-N bond distances are 2.274(3) Å (Ag1-N1) and 2.306(3) Å (Ag1-N4) respectively. The obtuse angle between N4-Ag1-N1 is 168.84(10)°, owing to the weakly coordinating nitrate anion, which is situated 2.509(3) Å from the silver atom. This coordination motif gives rise a 14-membered [2+2] dimetallocycle (Figure 2b) which extends to a 1D coordination polymer.
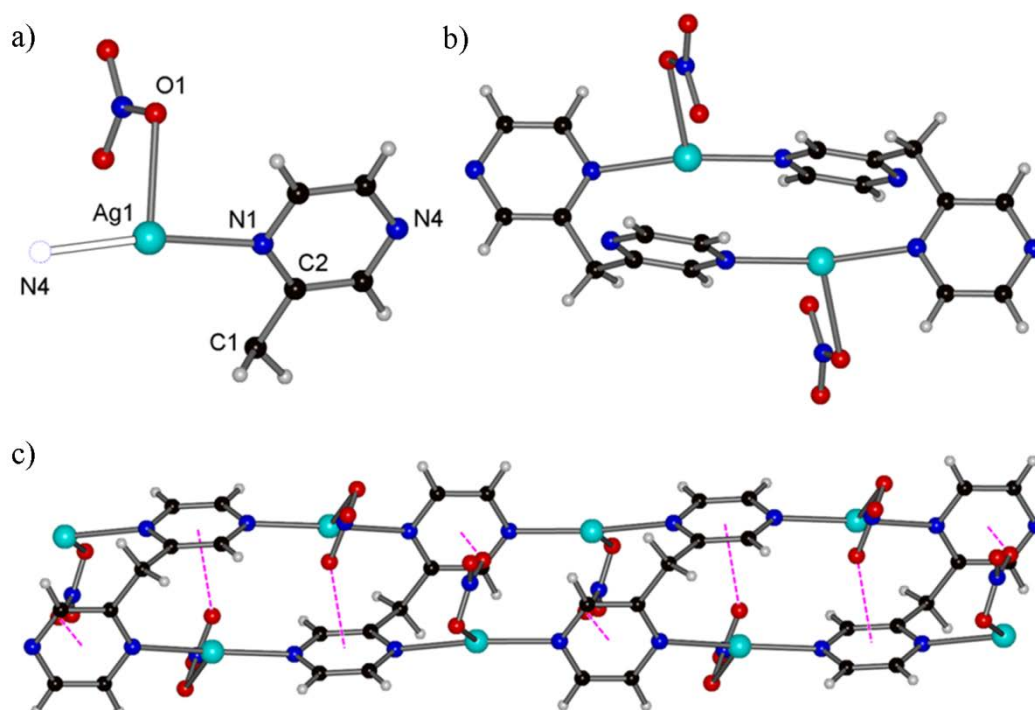
Figure 2. The structure of **1**. A perspective views of (a) the asymmetric unit showing the symmetry generated atom N4 as a blank sphere (selected bond lengths [Å] and angles [°]: Ag1-N1 2.274(3), Ag1-N4 2.306(3), Ag1-O1 2.509(3), N4-Ag1-N1 168.84(10)°); ; b) the [2+2] metallomacrocycle; and c) the 1D ladder coordination polymer (the dashed lines represent the anion-π interactions between a nitrate oxygen atom and a pyrazine ring of **dpzm**).

The 1D chain is stabilised by weak anion–π interactions between the oxygen atom of nitrate anion and the π system of a pyrazine ring of **dpzm**, with a distance of 3.34 Å (O-centroid) (Figure 2c).(*43-45*) In addition, weak silver-arene π-interactions

shield the silver atom, with the shortest Ag-C distance of 3.061 Å; the mean distance for such interactions has been reported to be 2.82 Å.(*1*) Within the [2+2] metallomacrocycle, the Ag – Ag separation is 4.74Å which is well outside the range of a typical Ag-Ag bond.(46) Within the adjacent polymer chains, there are longer bonds between the oxygen of a coordinated nitrate from one chain, and the silver(I) atom from another chain, with a distance of 2.65 Å. Besides this, there are no other notable interactions in the packing of the structure.

Crystal structures of 2 (and 3)

Compounds **2** and **3** are both 2D polymers with a 4^4 net structure; while **3** has previously been reported(*32*) it will be discussed here as there are a number of interesting comparisons to be made with **2**. Even though **2** and **3** have the same overall structure, subtle differences exist in the coordination of the ligand and the supramolecular interactions of the respective anions. Both structures crystallise in primitive monoclinic space groups and contain one molecule of **dpzm**, a silver(I) atom, and one counter anion in the asymmetric unit (Figure 3).

Compound **2** crystallises in the space group *P*2$_1$/*n* and contains a weakly coordinating triflate anion which is located 2.637(3) Å from the silver atom. The silver centre is essentially four-coordinate and has a distorted tetrahedral geometry (Figure 3a, however, with consideration of a long Ag1-O1 bond from the triflate anion, the silver(I) centre approaches a square pyramidal geometry ($\tau = 0.2$; τ is an index of trigonality for 5-coordinate metal centres where $\tau = (\alpha-\beta)/60$, α is the largest angle around the metal centre and β is the second largest).(*47*) The coordination sphere is composed of one chelating **dpzm** molecule and two symmetry related N-donors (N4 and N14). As previously noted, **3** crystallises in the space group *P*2$_1$/*c* and contains a non-

coordinating perchlorate anion, which is located 4.385(5) Å from the nearest silver atom. In absence of coordinative interactions from the anion, the silver(I) centre possess a distorted tetrahedral, with a wide range of angles (85.79(12) - 148.04(12)°). The atoms in the asymmetric unit are similar to that of **2**, aside from the presence of a water solvate molecule, located 2.88 Å from the Ag(I) atom. In accommodating this quite distorted tetrahedral geometry, the donors N1 and N11 bond with distances of 2.262(3) and 2.454(3) Å to the silver(I) centre respectively. This is in contrast to **2**, which contains more consistent bond lengths from these two donors, at 2.436(3) and 2.402(3) Å respectively.
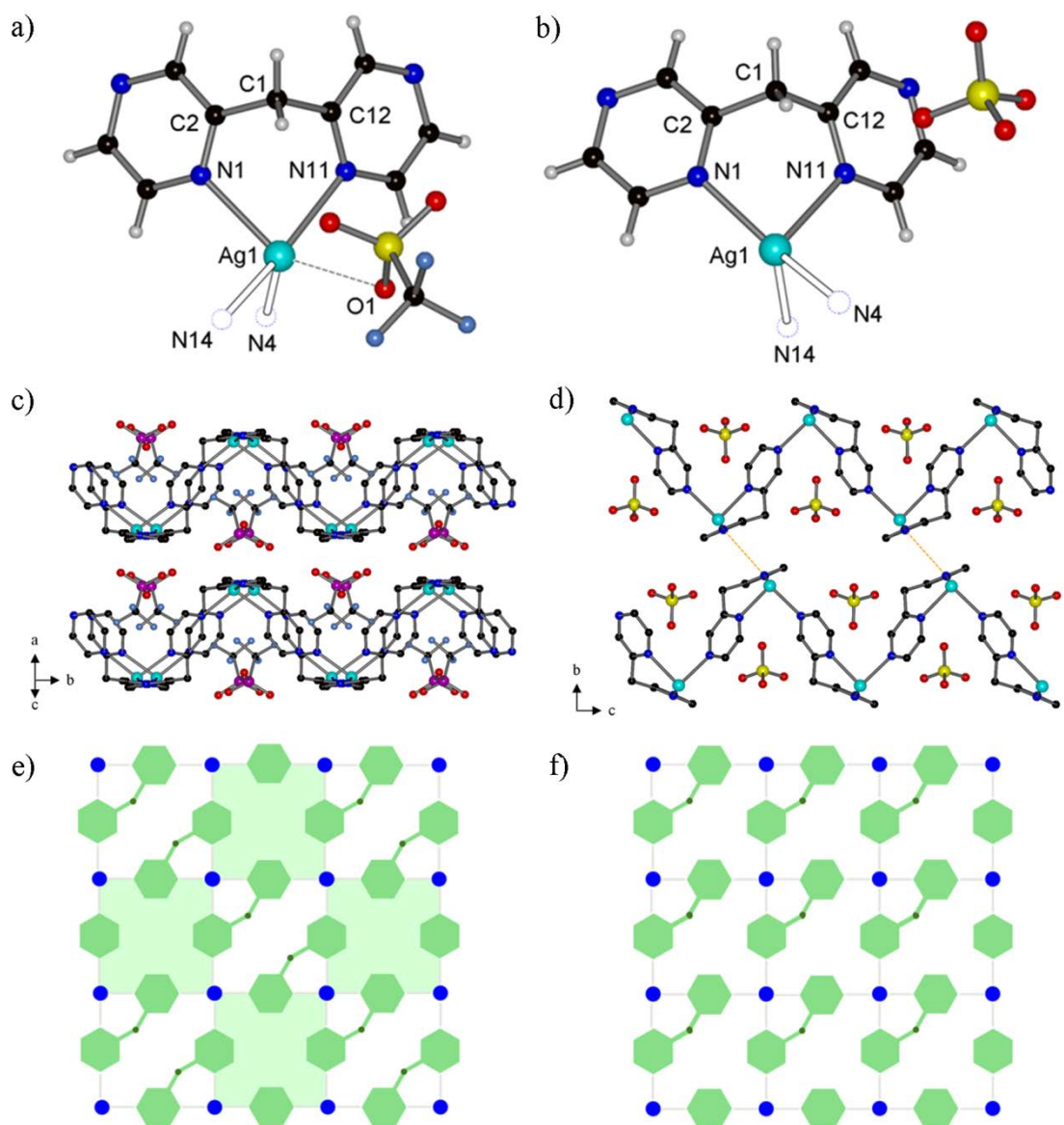
Figure 3. Perspective views of a) the asymmetric unit of **2**, showing the weakly coordinating triflate anion, denoted by the dashed bond (selected bond lengths [Å] and angles [°]: Ag1-N4 2.345(3), Ag1-N14 2.387(3), Ag-O1 2.637(3), N1-Ag1-N11 81.66(10), C2-C1-C21 112.3(2)); and b) the asymmetric unit of **3** (selected bond lengths [Å] and angles [°]: Ag1-N4 2.263(3), Ag1-N14 2.432(4), N1-Ag1-N11 85.79(12), C2-C1-C21 113.4(3)). For each structure the symmetry generated atoms N4 and N14 are shown as hollow spheres. Perspective view of the packing of c) **2** along the 101 plane, showing the eclipse of the puckered layers and d) a perspective view of **3** along the *a* axis, showing the π-stacking between the staggered layers (dotted lines, hydrogen atoms removed for clarity). Illustrations of the configuration of the 2D layers in e) **2** and f) **3**.

The hexagonal units represent the pyrazine rings of **dpzm** and the blue circles represent Ag(I) centres.

In the packing of the structures, both coordination polymers accommodate their respective anions in cavities formed between the puckered 2D layers. However, **2** possesses eclipsed layers, while in the structure of **3** the 2D sheets are staggered (Figures 3c and 3d). In the structure of **2**, the triflate anion shows weak C-H···O hydrogen bonding interactions with the **dpzm** ligand. These occur between an oxygen atom of the triflate anion and H6 of a pyrazine ring of **dpzm** (2.34 Å, 130.7°). The triflate anion also participates in weak anion-π interactions, with distances of 3.15 and 3.33 Å to the centroids of two separate pyrazine rings. These weak interactions stabilise the eclipsed layers of **2**. In contrast, the ClO_4^- anion of **3** does not possess any notable hydrogen bonding or anion-π interactions. Instead, the most prominent secondary interaction is π-stacking which occurs between two offset pyrazine rings of two separate 2D layers. The centroid-centroid distance is 3.52 Å, which is relatively short and thus a strong interaction.(*48*)

Although **2** and **3** both possess a 4^4 net structure, the connectivity of the ligand is quite different between the respective structures. Figures 3e and 3f illustrate the connectivity of the two coordination polymers. In the structure of **2**, two types of four-connecting windows make up the net; one containing two chelating **dpzm** molecules, while the other only bridging pyrazine moieties. In contrast, the windows of **3** are all alike; each four-connecting unit contains one chelating **dpzm** molecules, and two bridging pyrazine moieties.

*Crystal structures of **4a** and **4b***

The 3D coordination polymers **4a** and **4b** contain pseudo-octahedral silver(I) metal

centres and thus can be best thought of as pseudo-cubic lattice (Figure 4). Compound **4a**

crystallises in the monoclinic space group *C*2/*c* and the asymmetric units contains three

molecules of **dpzm**, one square pyramidal silver(I) centre ($\tau = 0.11$), two octahedral

silver(I) atoms (on special positions), two perchlorate anions, and two dichloromethane

solvate molecules. The three silver(I) atoms in the asymmetric unit are

crystallographically and chemically unique. The square pyramidal silver(I) centre (Ag1)

is coordinated by one chelating **dpzm** ligand, and three nitrogen atoms from two

separate molecules of **dpzm**. The nitrogen atom of another pyrazine donor (N34) is well

outside the range for a Ag-N bond (3.98 Å, Figure 4b), but adopts the position of a

potential sixth donor that could give an octahedral geometry to Ag(1). The other two

silver(I) centres (Ag2 and Ag3) are chelated by two symmetry related **dpzm** molecules,

and further coordinated by two symmetry related pyrazine N-donors. In the case of Ag2

(Figure 4c), two N-donors coordinate with a distance of Ag2-N31 2.339(5) Å, which is

in the range of a normal Ag-N bond, while the other four N-donors coordinate with

bond lengths outside this range; Ag2-N21 is 2.635(5) Å and Ag2-N4 2.694(5) Å. Ag3

also possesses quite long coordination bonds; Ag3-N14 2.578(6) Å and Ag3-N41

2.789(5) Å. If these are considered as weak bonds then Ag2 and Ag3 possess an
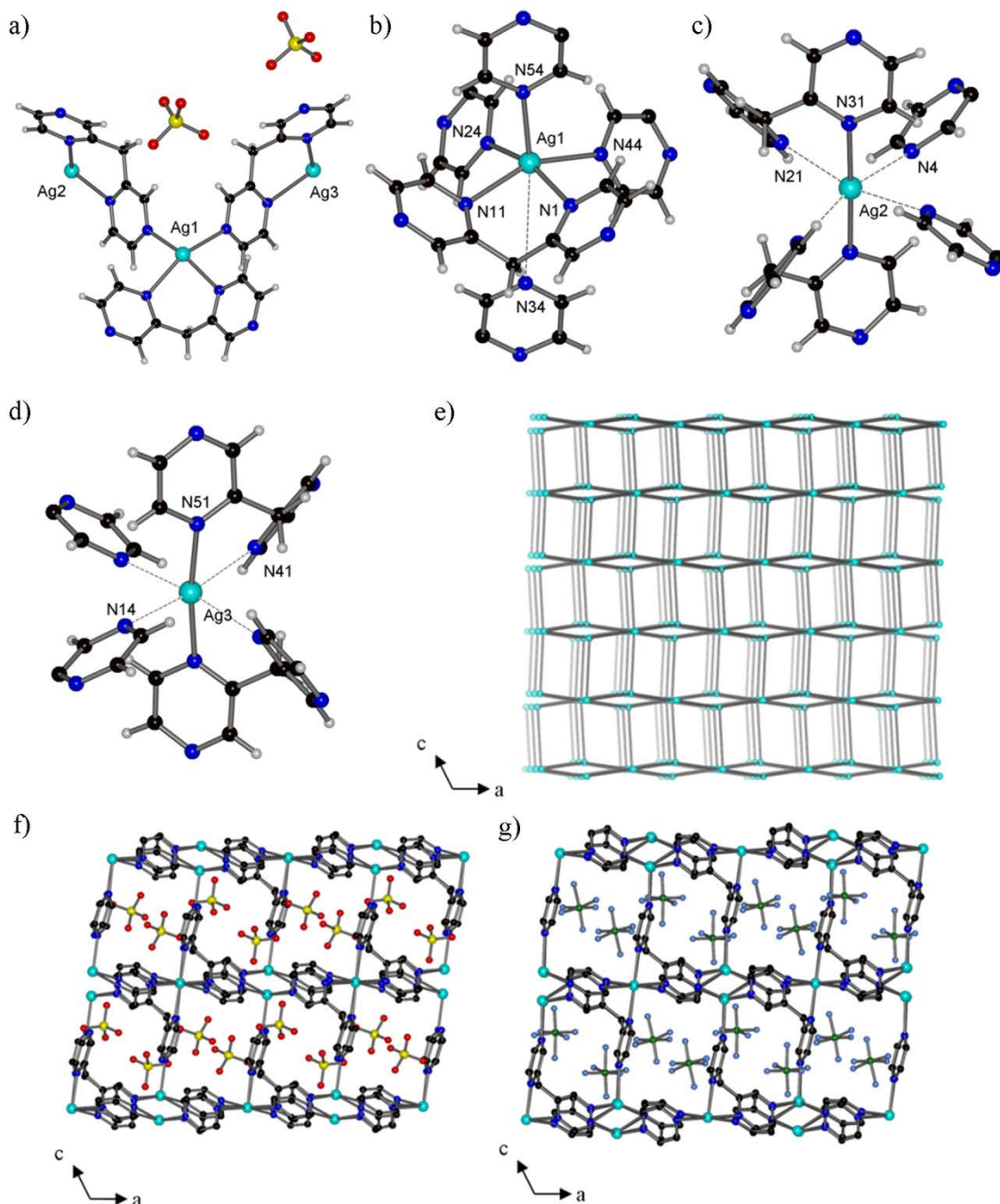
octahedral geometry.

Figure 4. The structure of **4**. Perspective views of a) the asymmetric unit of **4a**, showing the three distinct silver(I) atoms (disordered dichloromethane solvate molecules removed for clarity); b) the coordination sphere of Ag1 (selected bond lengths [Å] and angles [°]: Ag1-N1 2.413(5), Ag1-N11 2.432(5), Ag1-N24 2.400(5), Ag1-N44 2.448(5), N1-Ag1-N11 83.82(17)); c) the coordination sphere of Ag2 (selected bond lengths [Å] and angles [°]: Ag2-N21 2.635(5), Ag2-N31 2.339(5), Ag2-N4 2.694(5), N21-Ag2-N31 80.35(16)); and d) the coordination sphere of Ag3 (selected bond lengths [Å] and angles [°]: Ag3-N14 2.578(6), Ag3-N41 2.789(5), Ag3-N51

2.312(5), N41-Ag3-N51 82.09(16)). e) **A** perspective view of the net in **4a** and **4b** and .
views of f) **4a** and g) **4b** along the *b* axis (disordered dichloromethane solvate molecules
and hydrogen atoms omitted for clarity).

Compound **4b** also crystallises in the monoclinic space group *C*2/*c* and contains
a similar composition of atoms in the asymmetric unit, including three
crystallographically and chemically unique silver (I) centres. In comparison to **4a**, the
structure **4b** differs only subtly in bond lengths due to the larger PF_6^- anion. In this
structure, the square pyramidal silver(I) centre is disordered over two positions in a ratio
of 95:5. Two pseudo octahedral silver(I) centres are present which also contain varying
bond lengths from surrounding pyrazine donors, ranging from 2.297(6) to 2.776(6) Å.

In the structures of both **4a** and **4b**, the square pyramidal silver(I) ion links to
five octahedral silver(I) centres extending to a 3D pseudo-cubic lattice (Figure 4e).(*49*)
Both structures contain relatively small 1D channels along the *b* axis, which are
occupied by counter-ions and disordered dichloromethane solvate molecules (Figure 4f
and 4g). There are no unusually short distances between the ClO_4^- anion and
surrounding atoms in **4a**, as the anion is situated approximately at the centre of the
cubic pore. In **4b** however, there is a notable hydrogen bonding interaction between an
aromatic hydrogen of **dpzm** and a fluorine atom of the PF_6^- anion, with a H⋯F
distance of 2.29Å. Otherwise, there are no unusually short anion-π interactions in these
two coordination polymers.

Crystal structure of 5

3D coordination polymer **5** crystallises in the monoclinic space group *P*2$_1$/*n* and
contains four crystallographically unique silver(I) centres in the asymmetric unit. Five
molecules of **dpzm**, four BF_4^- counter-ions, and five disordered dichloromethane

solvate molecules are also included in the asymmetric unit. Like the previous examples, the **dpzm** ligand both chelates and bridges silver(I) metal centres. The 3D network in this instance is composed of two distorted square pyramidal silver atoms (Ag1 τ = 0.12, Ag2 τ = 0.11), one octahedral silver(I) atom (Ag3) and one distorted tetrahedral silver(I) (Ag4). Ag1 is chelated by two molecules of **dpzm**, and coordinated by one symmetry related pyrazine donor (Figure 5a). Ag2, on the other hand, is chelated by only one **dpzm** ligand, and further coordinated by three N-donors of two separate **dpzm** molecules (Figure 5b). The octahedral silver atom (Ag3) is chelated by two **dpzm** ligands and further two pyrazine N-donors, one which is symmetry related. Notably, Ag3 (Figure 5c) contains one long Ag-N bond from each chelating **dzpm** ligand, at 2.628(4) Å and 2.758(4) Å. In contrast, the distorted tetrahedral silver atom Ag4 is composed of four monodentate pyrazine N-donors with varied N-Ag-N angles (98.26(15) – 152.41(16)°) (Figure 5d). Interestingly, a dichloromethane molecule appears to bridge Ag1 and Ag4 with the chloride atoms located 3.04 Å and 3.08 Å from the two atoms respectively. While this is somewhat unusual dichloromethane has been previously observed to act as a bridging ligand and a number of examples have been reported.(*50, 51*)

The four-, five- (two), and six-connecting metal nodes give rise to a 3D network (Figure 5e).(*52*) In the packing of the structure, BF_4^- anions and DCM solvate molecules occupy the space of the rectangular shaped channels along the *b* axis. (Figure 5f) Channels are also present along the *a* axis, and are occupied only by DCM molecules. When considering van der Waals radii, these pores span 4.3×3.9 Å. The BF_4^- anions exhibit relatively weak hydrogen bonding interactions with molecules of **dpzm**, but none of these are unusually short distances. In addition, no specific

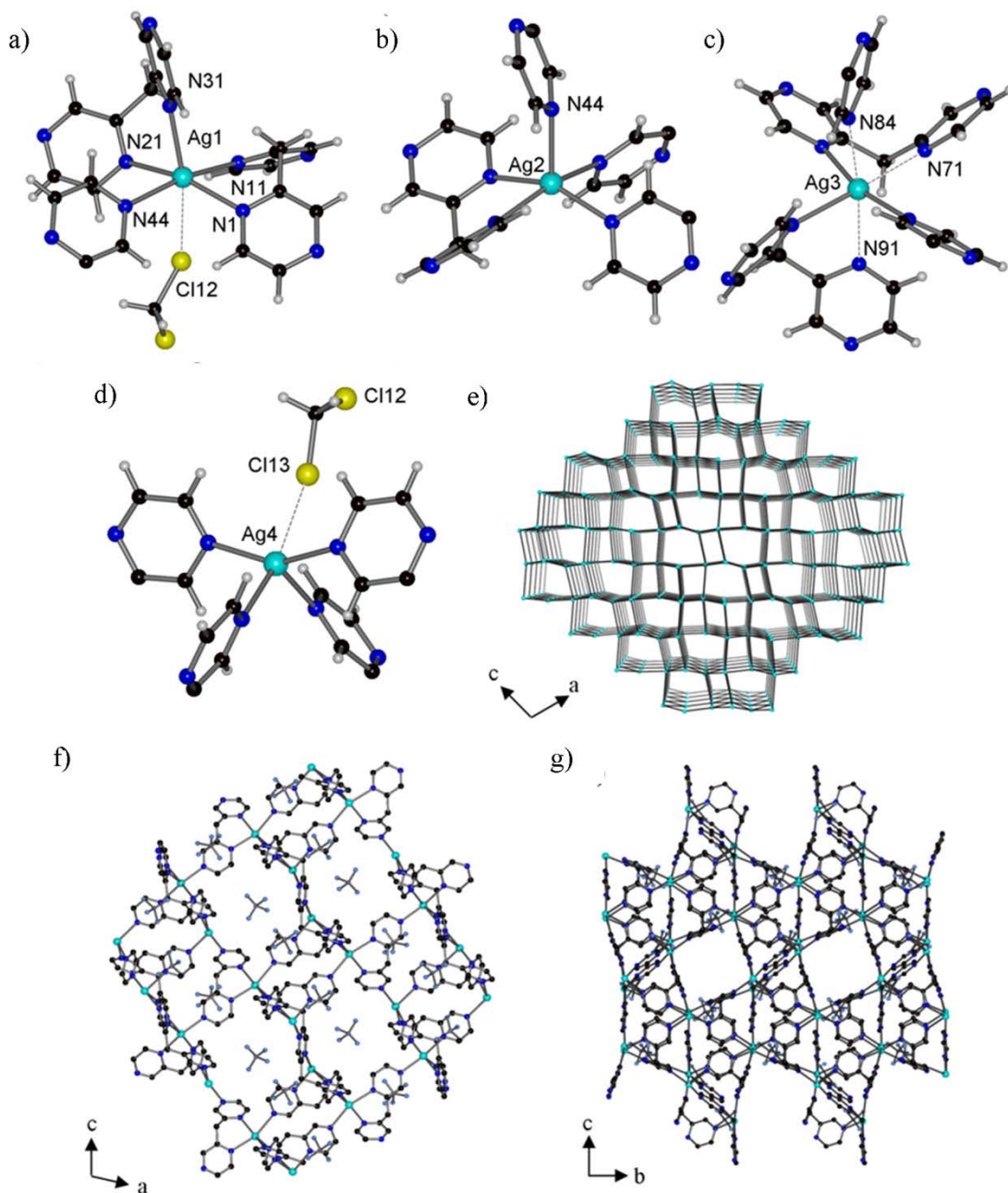interaction exist between the anion and the silver(I) atoms, with the shortest Ag-F distance being 4.29 Å.

Figure 5. Structural detail for **5**. (a) The coordination sphere of Ag1, showing the weak interaction with a dichloromethane solvate molecule (selected bond lengths [Å] and angles [°]: Ag1-N1 2.512(5), Ag1-N11 2.367(5), Ag1-N21 2.520(6), Ag1-N31 2.411(5), Ag1-N44 2.392(4), Ag1-Cl12 3.04, N1-Ag1-N11 78.32(19), N21-Ag1-N31 83.33(18)). b) The coordination sphere of the octahedral atom, Ag2 (selected bond length [Å]: Ag2-N54 2.544(5)). c) The coordination sphere of Ag3 (selected bond

lengths [Å]: Ag3-N71 2.626(5), Ag3-N94 2.628(4), Ag3-N101 2.759(4)). d) The coordination sphere of Ag4, showing the weak interaction with a dichloromethane solvate molecule (selected bond lengths [Å]: Ag4-Cl13 3.08). e) A view of the 3D net of **5** along the *b* axis. Views of **5** along the f) *b* axis and g) *a* axis, showing the channels with the dichloromethane molecules removed (hydrogen atoms omitted for clarity).

*Crystal structure of **6***

Coordination polymer **6** crystallises in the orthorhombic space group *Pca*2$_1$ and is composed of the **dpzm** ligand and AgSbF$_6$ in a 4:3 ratio. In the asymmetric unit, four molecules of **dpzm** bridge between and chelate three crystallographically unique silver(I) metal centres, two with square pyramidal geometries (Ag1 τ = 0.13, Ag2 τ = 0.02) and one as pseudo-octahedral centre (Ag3). Two chelating **dpzm** ligands and one monodentate pyrazine donor make up the coordination sphere of Ag1 (Figure 6a), while Ag2 is also coordinated by five pyrazine N-donors, though only two from a chelating **dpzm** ligand (Figure 6b). Ag3 has a similar composition to that of Ag2 and can also be considered square pyramidal, although a longer interaction with an additional pyrazine N-donor located 3.006(6) Å from the silver centre completes an octahedral geometry (Figure 6c).
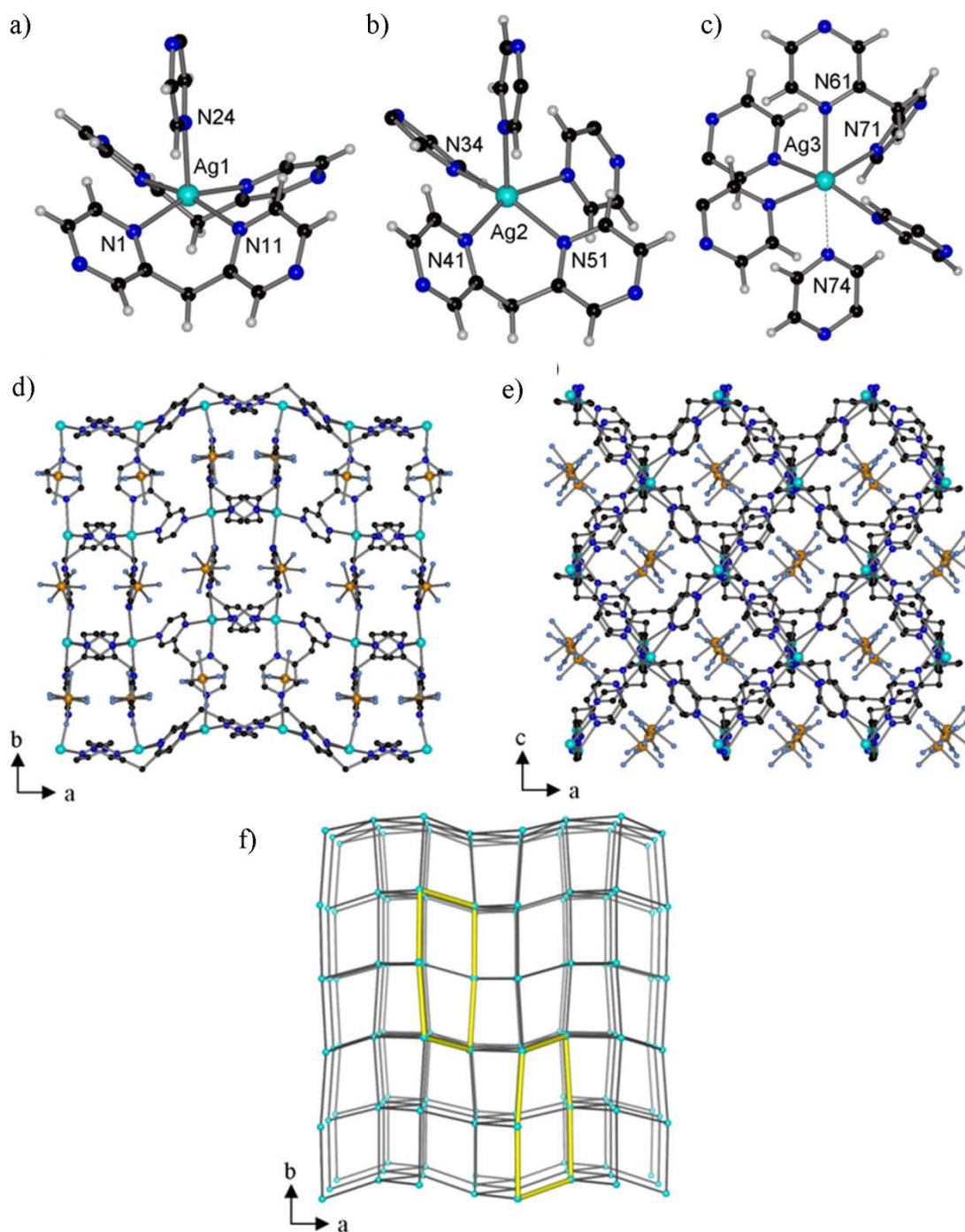
Figure 6. Details of the structure of **6**. a) Coordination sphere the square pyramidal Ag1 atom (selected bond lengths [Å] and angles [°]: Ag1-N1 2.549(5), Ag1-N11 2.362(6), Ag1-N24 2.386(6), N1-Ag1-N11 79.09(17)). b) The coordination sphere of the square pyramidal Ag2 atom (selected bond lengths [Å] and angles [°]: Ag2-N34 2.562(5), Ag2-N41 2.349(5), Ag2-N51 2.416(5), N41-Ag2-N51 79.09(17)). c) Coordination sphere of the octahedral Ag3 atom (selected bond lengths [Å] and angles [°]: Ag3-N61 2.548(6), Ag3-N71 2.433(5), Ag3-N74 3.006(6), N61-Ag3-N71 77.52(19)). Views of **6**

along the d) *c* axis and e) the *b* axis (dichloromethane solvate molecules and hydrogen atoms omitted for clarity). f) A view of the net in **6**, with two distorted rectangles highlighted.

The 5- (two) and 6-connecting Ag(I) nodes comprise a complicated 3D net, composed of square and distorted six-membered rectangular windows (Figure 6f).(*53*) The undulating pattern of the Ag(I) centres can be seen along the *c* axis, while along the *b* axis square-shaped channels are occupied by SbF_6^- anions (Figure 6 d, e). No obvious anion-π interactions are present, and no unusually short distances exist between the anions and the framework of **6**. The most notable is a weak hydrogen bonding interaction occurs between a fluorine atom of a SbF_6^- anion and an aromatic hydrogen of **dpzm** with a C-H···F distance of 2.47 Å.

Discussion of the structures

The dimensionality of the coordination polymers investigated can be related to the coordination strength of the counter-ions employed. A 1D coordination polymer was formed with NO_3^-, while with the weaker coordinating anion, OTf^-, a 2D polymer was yielded. On the other hand, non-coordinating anions such as ClO_4^-, PF_6^-, BF_4^-, and SbF_6^- all favoured 3D close-packed coordination polymers (excepting perchlorate which also allows a 2D material to form). Interestingly, three and four coordinate silver(I) centres were observed in the 1D and 2D structures, while the 3D assemblies possessed a combination of five and six-coordinate silver(I), showcasing the flexible coordination number of silver(I).

We have previously shown that the inert nature of the methylene hinge facilitates crystal-to-crystal breathing in 3D sodalite materials.(*32, 33*) Of interest for this series of close-packed systems was the effect of the hinge on structures of these

materials in comparison to topologically related pyrazine based coordination polymers. Aside from acting as the 'rungs' of the ladder in **1**, the methylene hinge of **dpzm** does not dramatically modify the coordinating mode expected for pyrazine.

The structures of **2** and **3** compare well with other 2D polymers formed with silver(I) and related di-2-pyrazinyl ligands.(*28-30*) In particular, these structures more closely resemble the coordination polymer formed with AgOTf and di-2-pyrazinylmethanediol (**dpzmdOH**, Figure 1) which forms a 4^4 net,(*28*) containing triflate counter-ions situated in between the eclipsed and undulating sheets, similar to that observed for **2**. In this example, the hydroxyl groups of di-2-pyrazinylmethanediol were not engaged in coordination, though other structures were also reported where coordination of these donors was observed.(*28*) As the methylene spacer of **dpzm** does not engage in coordination, structures **2** and **3** also compare favourably with coordination polymers of the classical bridging ligand, pyrazine. Carlucci and colleagues reported the polymeric structure [Ag(**pyz**)$_2$]PF$_6$ (**pyz** = pyrazine), which consist of 2-D undulating sheets, separated by non-coordinating PF$_6^-$ anions.(*27*) The staggered 2-D sheets of [Ag(**pyz**)$_2$]PF$_6$ are very similar to **3**, and the only difference lies in the covalent connection via the methylene hinge of two pyrazine rings.

In contrast to the 1D and 2D assemblies formed with weakly coordinating anions (NO$_3^-$ and OTf$^-$), non-coordinating anions (ClO$_4^-$, PF$_6^-$, BF$_4^-$, and SbF$_6^-$) favour 3D assemblies of Ag(I) and **dpzm**. The conditions in forming all but one of these assemblies (**3**) involved slow vapour diffusion of DCM into either a DMSO or CH$_3$CN solution of the M$_x$L$_y$ precipitate. Thus, the types the metal-to-ligand ratios and types of assemblies formed were primarily influenced by the size and shape of the non-coordinating anion; the ClO$_4^-$ (55 Å^3) and PF$_6^-$ (75 Å^3) anions gave isomorphous structures, while the slightly smaller BF$_4^-$ anion (53 Å^3) and the larger SbF$_6^-$ (85 Å^3)

anions induced different 3D structures under these conditions. The distorted cubic lattices of **4a** and **4b** are comparable to the perfect cubic lattice of the complex $[Ag(\mathbf{pyz})_3]SbF_6$ reported by Carlucci and colleagues.(*25*) In this structure, the SbF_6^- anions were located at the centre of the cubic pores framed from the six-connecting octahedral silver(I) atoms. In contrast, all the 3D coordination polymers investigated in this study contained at least one long coordination bond, which is likely to be caused by the geometrical restrictions induced by the methylene hinge of **dpzm**.

Conclusion

Di-2-pyrazinyl methane (**dpzm**) distinguishes itself from other dipyrazinyl hinged ligands by the coordinatively inert methylene spacer. This appears to allow it to form coordination polymers with similar structures to those encountered with pyrazine, yet with distortions due to the hinge moiety restricting the angles between adjacent pyrazine rings. Unlike the slow crystallisation conditions used to form the previously reported porous sodalite materials, the silver(I) coordination polymers described here were crystallised by relatively rapid vapour diffusion conditions. These scenarios yielded crystals of coordination polymers which possessed either 1D, 2D, or 3D structures. These coordination polymers were close-packed, and their relatively small channels were occupied by anion guests. Although some of the close-packed coordination polymers compared well to previously reported assemblies with pyrazine, an evident feature of **dpzm** was the geometrical restriction of the methylene hinge, which was apparent in the long Ag-N bond lengths, particularly in the pseudo-cubic lattices of **4a** and **4b**.

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(49)   For simplicity, the structures of **4a** and **4b** have been described as a 3D pseudo-cubic lattice due to the precence a pyrazine ring ~4.0 Å from Ag2 (obviously this is well outside the range of a Ag-N bond). Formally, the square pyramidal silver(I) ion gives a 5-connecting node and the two octahedral silver(I) centres are 4-connecting (with a square planar arrangement) and 6 connecting nodes. Each 5-connecting node coordinates to two 4-connecting silver(I) centres and three 6-connecting silver(I) centres to give an 3D α-Po topology that lacks two formal connections between the 4-connecting node and two five connecting nodes (although the pyrazine ring occupies this space).

(50)   Newbond, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762–3764.

(51)   Bown, M.; Waters, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2442–2443.

(52)   The four crystallographically unique silver(I) centres in **5** can be considered as a four connecting node (a seesaw arrangement of the connections), two five connecting nodes and a 6-connecting node that combine to give the 3D net. The 4-connecting node has connections with three 6-connecting nodes and a 5-connecting node but connections to two other 5-connecting nodes are 'absent' (a weakly bonded dichloromethane molecule actually sits in one of these

vacancies, connecting the 4-connecting centre to a 5-connecting centre). If the dichloromethane is considered as a connection then the the structure can be considered to be composed of two 5-connecting nodes and two six connecting nodes. Based on this analysis the structure is very similar to the above structure but lacks a pyrazine ring that spans but does not connect two of the nodes and this gives rise to the rectangular channels in the structure seen down the *b*-axis.

(53)   Again there are similarities to the structures of **4** and **5** with three different silver centres that are 5-connecting (two) and 6-connecting nodes. This combination of nodes gives rise to a structure very similar to **4** but lacks a pyrazine ring that spans but does not connect two of the nodes; this gives rise to the rectangular windows in the structure.

Silver(I) coordination polymers of the 'hinged' pyrazine containing ligand di-2-pyrazinylmethane

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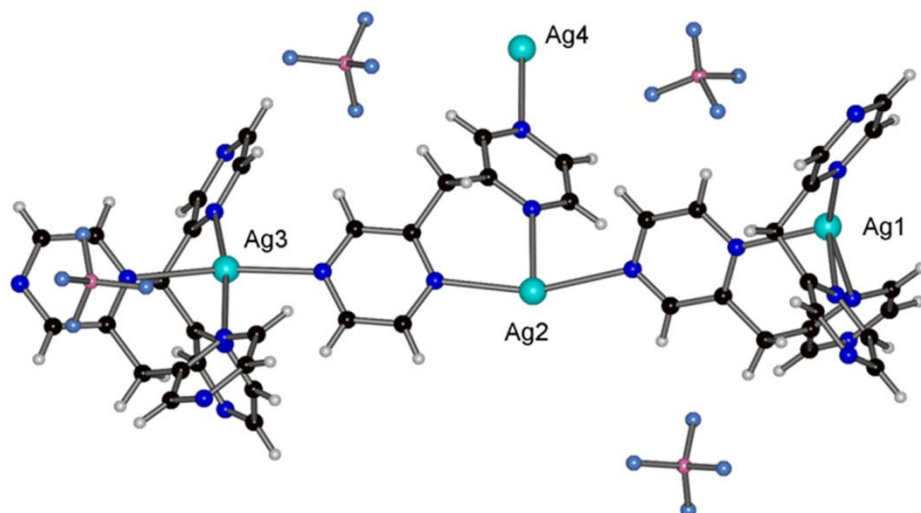
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Figure SI 1. A perspective view of the asymmetric unit of **5** showing the crystallographically unique silver(I) centres (labelled), **dpzm** ligands, and anions.
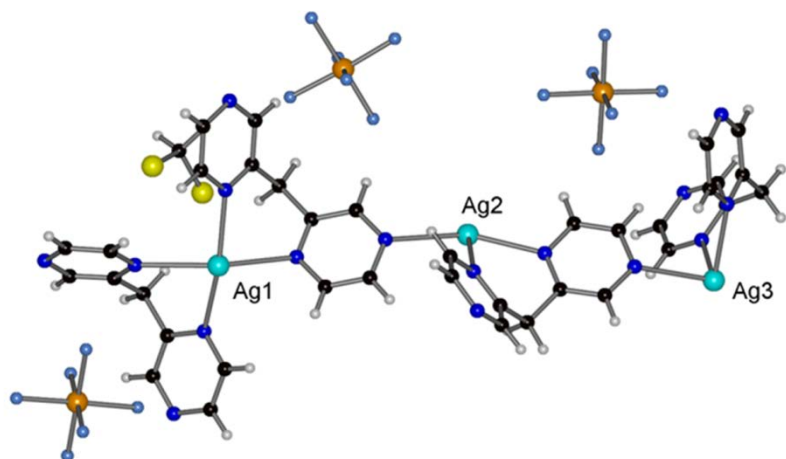
Figure SI 2. A perspective view of the asymmetric unit of **6** showing the crystallographically unique silver(I) centres (labelled), **dpzm** ligands, solvate molecules and anions.

Additional Refinement Details

Structure of 1: The refinement software suggested an extinction correction due to secondary diffraction (crystal dimensions). Adding the command 'EXTI' resulted in an improvement in GOF, R_1, and wR_2.

Structure of 2: The hydrogen atoms of the water solvate molecule were successfully located in the difference map and DFIX restrains were used to maintain chemically sensible O-H bond lengths.

Structure of 4a: The structure contains a disordered DCM molecule which was modelled over two positions. DFIX restrains were used to maintain chemically sensible C-Cl bond lengths and the carbon atoms of this disordered molecule were refined with isotropic displacement parameters.

Structure of 4b: The structure contains a disordered silver(I) atom which was modelled over two positions. The structure has solvent accessible voids. These contained two highly disordered DCM molecules which could not be adequately modelled. The SQUEEZE routine of PLATON(*38*) was applied to the collected data, which resulted in significant reductions in R_1 and wR_2 and an improvement in the GOF. R_1, wR_2, and GOF before SQUEEZE routine: 24.48%, 61.07%, and 2.664; after SQUEEZE routine: 7.15%, 19.04%, 1.087. The contents of the solvent region calculated from the result of SQUEEZE routine equates to two DCM molecules per asymmetric unit.

Structure of 5: The structure contains a disordered BF_4^- anion which was modelled over two positions. The two boron atoms were refined with isotropic displacement parameters and DFIX restraints were used to maintain sensible B-F bond lengths. The structure also contains a disordered DCM molecule which was modelled over two positions. DFIX restraints were used to maintain chemically sensible C-Cl

bond lengths and one of the two carbon atoms was refined with isotropic displacement parameters. Finally, one of the silver(I) atoms (Ag4) contained disorder which was modelled over two positions.