# Silver(I) polymeric coordination frameworks assembled with the new multimodal ligand 2,2′-azobispyrazine

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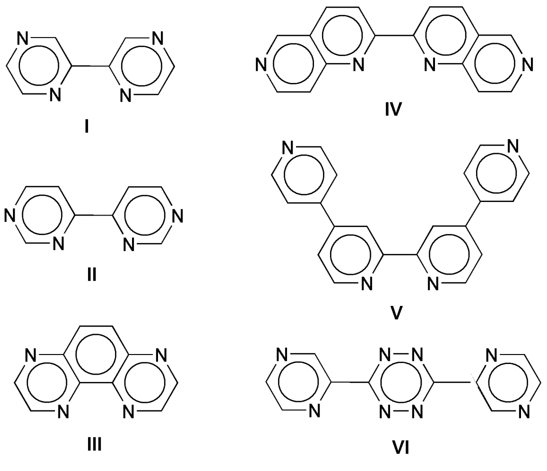
The synthesis of the new polyfunctional ligand 2,2′-azobispyrazine (azpyz), able to bind up to four different metal centres, and the self-assembly of polymeric coordination networks from different Ag(I) salts have been carried out. Four different structural types of polymeric species have been characterized: $[Ag(azpyz)_2]ClO_4$ (**1a**) and $[Ag(azpyz)_2]BF_4$(**1b**) contain 1D helical chains, $[Ag(azpyz)_2]SbF_6 \cdot 0.5CH_2Cl_2$ (**2**) is comprised of undulating 2D layers of (4,4)-topology, $[Ag_2(azpyz)(H_2O)](BF_4)_2$ (**3**) consists of 2D sheets, containing $\mu_4$-$\eta^6$-azpyz ligands, with two distinct types of metal centres, and $[Ag_4(azpyz)_3](ClO_4)_4$ (**4**) is a complex 3D network, exhibiting $\mu_4$-$\eta^6$-azpyz and $\mu_4$-$\eta^5$-azpyz ligands, with four different types of Ag centres. In these compounds the azpyz ligands show varied bonding modes, using from 2 up to all 6 of its N-donor atoms. Most of the silver metal centres exhibit high coordination numbers (up to 5 and 6).

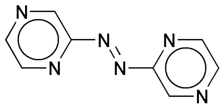
## Introduction

The interest in the assembly of networked coordination polymers,[1] due to their potential properties as novel zeolite-like materials[2] to be applied for molecular sieving, ion exchange, gas storage, molecular sensing and catalysis, has afforded in recent years many noteworthy 2D and 3D frames. However, the crystal engineering of coordination networks with desired topologies and specific properties still remains a difficult challenge, since it depends on a variety of factors that can influence the self-assembly process. Particular attention has been devoted to the use of novel bridging multidentate ligands. Ligand design, together with the coordination properties of the transition metal centres, can be used to achieve control over the structure of the networks and thus to modify the properties of these materials. A relatively new class of bridging ligands, called *multimodal* ligands by Champness and co-workers,[3] contain both chelating sites and monodentate donor sites. Out of the known examples (see ref. 3*c*) a few are reported in Scheme 1. These have been employed for networking (**I**,[3*a*,*b*] **II**,[4*a*] **III**,[3*b*] **IV**,[4*b*] and **VI**[3*c*]) or for the assembly of oligomers (**V**).[5]



**Scheme 1**

We report here on a novel ligand of this class, namely 2,2′-azobispyrazine (azpyz), which, indeed, shows more bonding potentialities in that it contains two chelating sites in addition to two monodentate donor sites. Besides these interesting bonding features, the presence of the –N=N– azo group can lead to metal complexes with unusual electronic properties, as observed for the related 2,2′-azobispyridine,[6] due to the presence in these species of a low-lying azo-centred π* molecular orbital. We are here concerned only with the structural aspects of the interactions of azpyz with Ag(I) ions, selected for the versatility of their coordination geometries,[7] and we describe the formation of four polymeric frames obtained with different silver salts, exhibiting varied bonding modes of this new ligand.



**azpyz**

## Results and discussion

### Synthesis

The ligand azpyz has been obtained using literature methods for the synthesis of azo compounds,[8] by reacting 2-aminopyrazine with NaOCl. The reactions with different silver salts have been carried out by slow diffusion, upon layering an ethanolic solution of the metal salt on a $CH_2Cl_2$ solution of the ligand, with molar ratios Ag(I):azpyz ranging from 1:2 to 2:1. $AgClO_4$, reacted with two equivalents of the ligand, gives dark-red prismatic crystals of $[Ag(azpyz)_2]ClO_4$ (**1a**). $AgSbF_6$ with azpyz in molar ratios from 1:1 to 1:2 affords a unique

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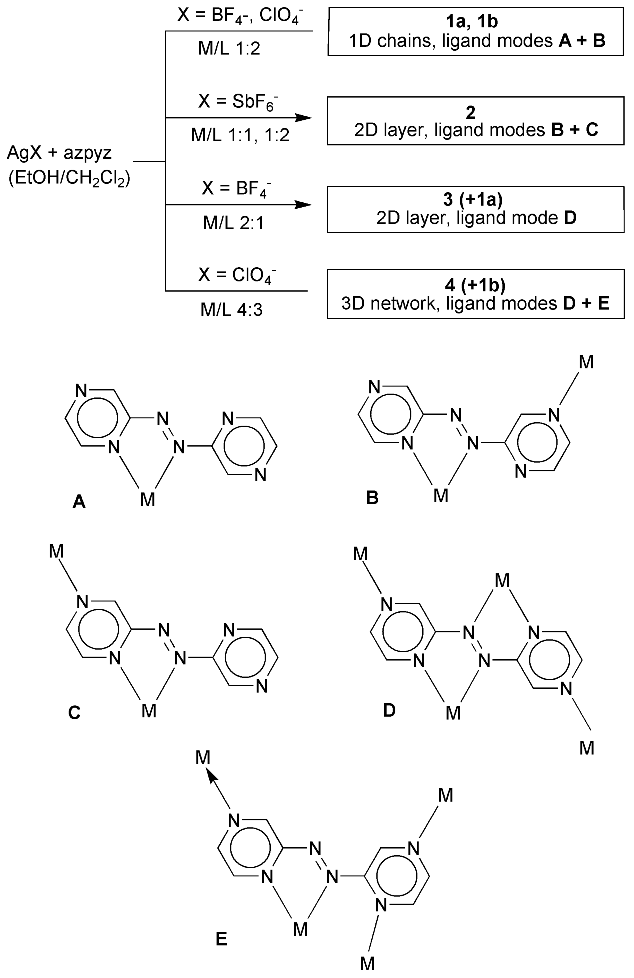

**Scheme 2**

red crystalline product, formulated as [Ag(azpyz)$_2$]SbF$_6$·0.5CH$_2$Cl$_2$ (**2**). On the other hand, from the reaction of AgBF$_4$ a mixture of crystals is usually obtained, with two distinct morphologies: the crystals of the dominant species, namely [Ag(azpyz)$_2$]BF$_4$ (**1b**), are dark-red prismatic and isomorphous with those of **1a**, while the second minor product, of formula [Ag$_2$(azpyz)(H$_2$O)](BF$_4$)$_2$ (**3**) gives very flat orange crystals. When the reaction of AgClO$_4$ is carried out using a metal-to-ligand molar ratio of *ca.* 4:3 a mixture of crystalline products is obtained, containing **1a** and another minor species, [Ag$_4$(azpyz)$_3$](ClO$_4$)$_4$ (**4**). The reaction conditions and the products obtained, along with the different modes assumed by the azpyz ligand, are summarized in Scheme 2.

Single crystals of all products have been isolated and compounds **1a**, **2**, **3** and **4** have been characterized by X-ray diffraction. Compound **1b** was found to be isomorphous with **1a** and, therefore, we have not carried out the data collection. The coordination environments of the silver atoms in these species are illustrated in Fig. 1 (with atomic labelling).

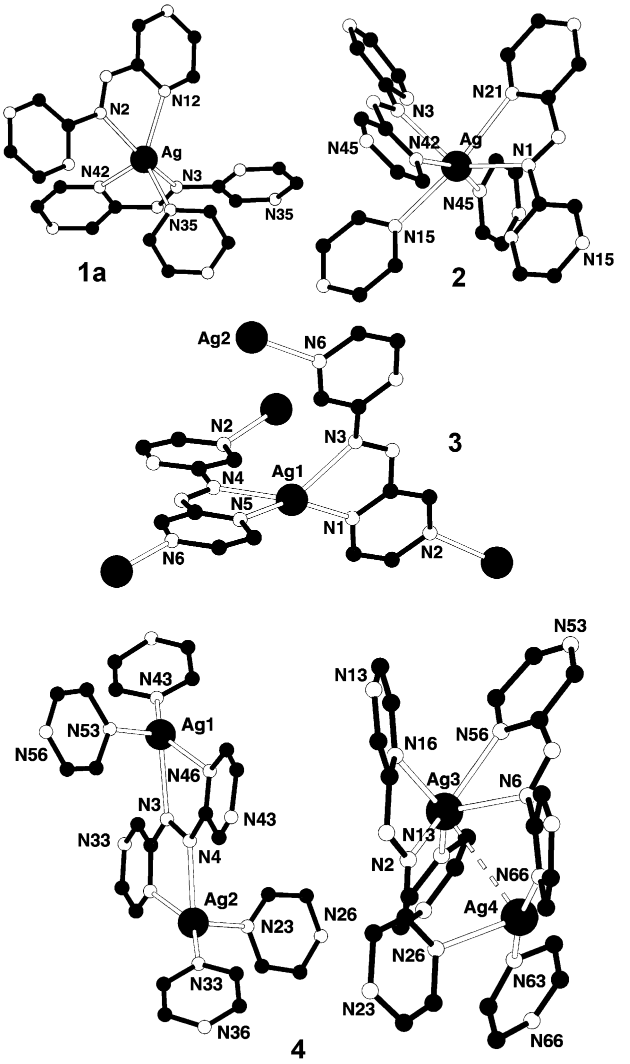

**Fig. 1** The coordination geometries for the silver metals in the reported polymeric species **1a** and **2**–**4**.

## Crystallographic structures

**1a.** The structure of compound **1a** contains 1D chains all extending in the direction of the ***b*** axis. The silver ions are disposed in a zigzag fashion (Fig. 2), with one of the azpyz ligands acting as an asymmetric bridge (mode B in Scheme 2), and the second azpyz ligand being simply chelated to the metal centre (mode A in Scheme 2). One can also envisage the presence of bischelated Ag(azpyz)$_2$ building blocks, joined together *via* the bridging action of one pyrazine unit not involved in the chelation. The polymeric chains run along the $2_1$ crystallographic axis and show a helical disposition of the ligands (with one period of the helix being equal to ***b***, 9.5 Å). The Ag···Ag separation for adjacent metals in the chains is 10.2 Å. The Ag(I) ions are five-coordinated, in a distorted square pyramidal geometry (see Fig. 1), with Ag–N bond distances in the range 2.28–2.53 Å. The chains show a supramolecular organization, forming layers (perpendicular to the ***a*** axis, see Fig. 3) comprised of alternating helices of opposite chirality, *via* π-π interactions[9] involving the rings of the nonbridging azpyz ligands on adjacent chains (interplanar distance 3.67 Å, offset 1.08 Å).

**2.** Compound **2** consists of polymeric 2D undulated layers of rhombic meshes, illustrated in Fig. 4. The silver ions are linked by two bridging azpyz ligands that use different bonding modes (B and C modes in Scheme 2). The Ag···Ag contacts

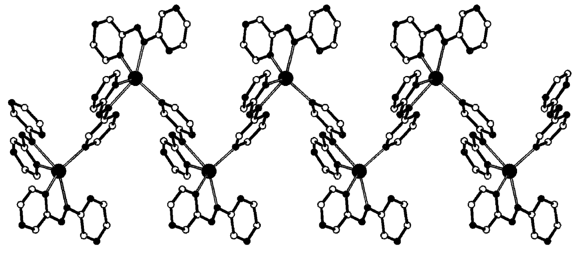

**Fig. 2** Side view of one polymeric helical chain in compound **1a**.

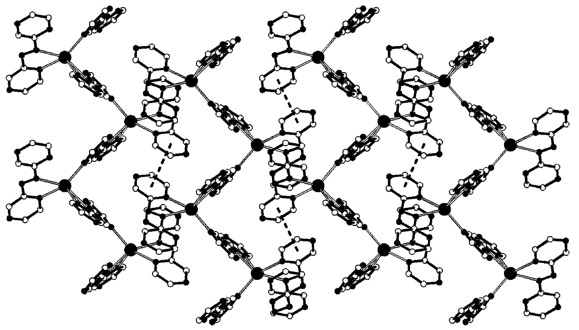

**Fig. 3** A layer formed *via* π-π interactions by the polymeric chains in **1a**.

in the layers exhibit values of 7.75 and 8.14 Å. Also in this case we can observe the presence of bischelated Ag(azpyz)$_2$building blocks, which polymerize using two pyrazine units (one for each azpyz ligand). Each metal ion is surrounded by an asymmetric environment, being chelated by two azpyz ligands and bound to two pyrazine groups of two ligands chelated on adjacent metals, as shown in Fig. 1. The 6-coordination geometry is rather unusual (Ag–N in the range 2.40–2.77 Å), being of a distorted trigonal prismatic type. As can be seen in Fig. 4 (top), each rhombic grid is sorrounded by four azpyz bridging ligands whose molecular planes are disposed in such a way to form the walls of a box. The layers stack, with interdigitation, in the [1 0 −1] direction (stacking distance 12.98 Å), with a sequence AAAA, exhibiting strong π-π interactions (interplanar distance 3.28 Å, offset 1.61 Å) involving the extruding pyrazyl groups of adjacent layers (see Fig. 5). These interactions give raise to an overall 3D architecture, with channels along [1 0 −1], that alternately contain the $SbF_6^-$ anions or the solvated $CH_2Cl_2$ molecules.

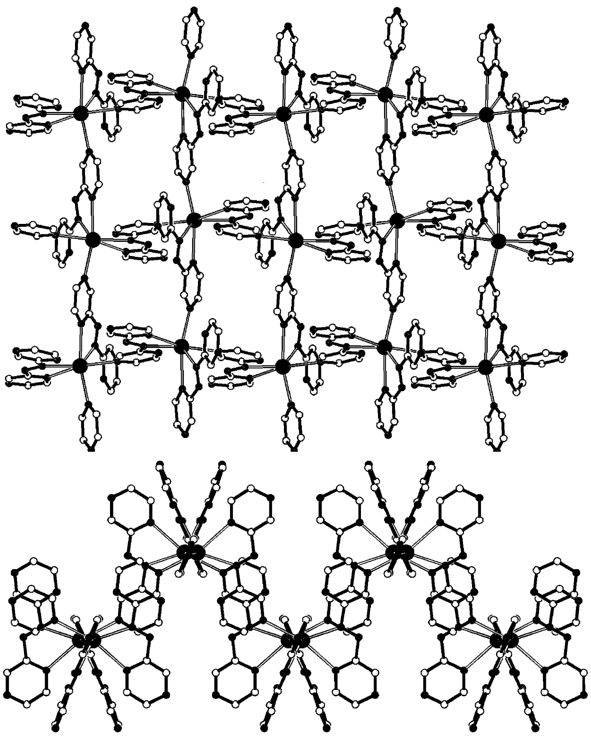

**Fig. 4** Two views of the two-dimensional layers in compound **2**: top, a view down the stacking direction [1 0 −1] showing the channels that contain the anions and the guest solvent (omitted for clarity), and, bottom, a side view down the [1 0 1] direction that evidences the undulated nature of these sheets.

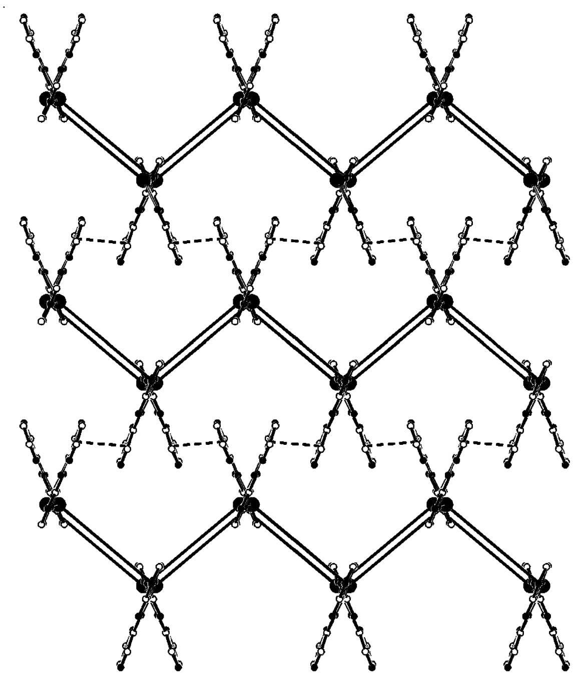

**Fig. 5** A schematic view showing the π-π interactions involving adjacent layers in **2**.

**3.** Compound **3** is a more interesting product because the azpyz ligand shows its highest symmetry coordination (mode D in Scheme 2). The structure consists of complex 2D layers, illustrated in Fig. 6, containing two types of Ag(I) centres. These layers can be described as comprised of linear Ag–azpyz–Ag–azpyz– chains, extending in the direction of the ***a*** axis, which contain four-connected bischelated metal centres, with the azpyz ligands acting as chelating agents on both sides (Ag···Ag separation of 5.52 Å). The chains are interconnected *via* coordination to the second type of Ag(I) ions by means of the remaining N atoms of the pyrazine groups. These metal ions work simply as spacers and display a distorted trigonal coordination geometry, with two N(pyrazine) and one water molecule (Ag–N 2.29–2.34 Å, Ag–O 2.52 Å). The coordination geometry of the four-connected silver ions in the chains is markedly distorted tetrahedral (see Fig. 1, Ag–N in the range 2.26–2.47 Å). The layers stack in the direction of the ***c*** axis (stacking distance 12.10 Å ) with an ABAB sequence, leaving large interlayer regions populated by guest solvent molecules (Fig. 7). While compound **1a** does not contain significant free voids, and the free space available for guest solvents in compound **2** is only 8% of the cell volume (evaluated after removing the $CH_2Cl_2$ solvent molecules), in **3** the free space is much larger, *ca.* 31% of the cell volume. Indeed, it was not possible to refine the disordered molecules in these voids. Using the by-pass method,[10] applied in a number of porous structures, we can assign about three solvated molecules of EtOH per formula unit. This layered material seems, therefore, promising for intercalation of different solvents, but the poor yields have prevented a further investigation of its properties.

**4.** The 3D network of compound **4** is comprised of four different silver centres and three different azpyz ligands. In order to rationalize this complex structure we can observe the view of the network down the ***a*** axis (Fig. 8). There are two different types of two-dimensional layers (A and B), stacking in an ABA′B′ sequence along the ***c*** axis, that are joined in this direction *via* pyrazine groups of azpyz ligands, to give the overall array. The type A layers, of composition $[Ag_2(azpyz)]^{2+}$, are undulating sheets containing one kind of ligand, that is, a $\mu_4$-$\eta^6$-azpyz, that is bischelating on two metals, Ag1 and Ag2

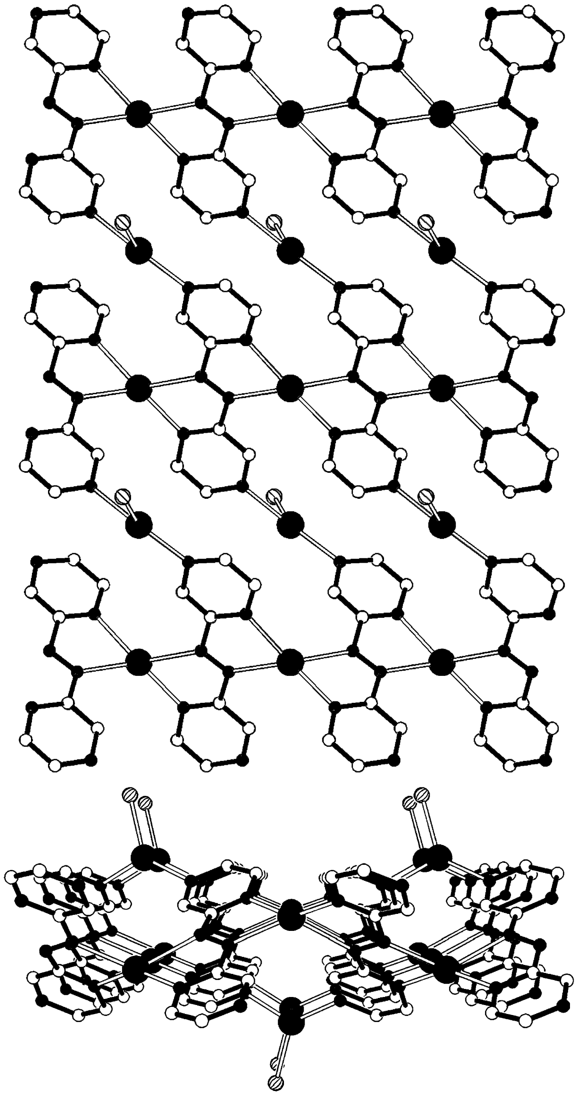

**Fig. 6** Two views (front, down *c*, and side, down *a*) of the complex layers in compound **3**.

(Ag···Ag 5.76 Å), and uses the two remaining N(pyrazine) atoms to bond two other Ag centres in the same layer, as in mode D of Scheme 2 (see Fig. 9). The four-connected coordination geometry of the two Ag metals (see Fig. 1) is similar: they are monochelated by the azpyz ligand (Ag1–N 2.30, 2.47 Å and Ag2–N 2.41, 2.57 Å) and are bonded to two N(pyrazine) atoms, one from the ligand in the same layer and one from a azpyz ligand of an adjacent type B layer (Ag1 by one side and Ag2 by the opposite side), with Ag–N bond distances in the range 2.19–2.37 Å. Note that these layers are completely different from those present in compound **3**, in spite of the similar composition.

The layers of type B (see Fig. 10) have a composition $[Ag_2(azpyz)_2]^{2+}$ and contain two independent ligands that display a similar and novel coordination mode (E in Scheme 2), that is, $\mu_4$-$\eta^5$-azpyz, in which the ligand acts as monochelating and in addition uses three N(pyrazine) atoms to bond to silver centres (two in the same layer and one in an A layer). This coordination mode of azpyz implies a rotation of one pyrazine group with respect to the ideal D mode (of 149.6° and 142.1° in the two ligands), a situation that prevents bischelation but that brings two metal atoms rather close together (Ag···Ag 3.27 Å). At variance from the type A layers the two silver atoms (Ag3 and Ag4) display quite different environments (see Fig. 1). The Ag3 metal is five-connected (ignoring the Ag···Ag interaction): it is bischelated by the two ligands (Ag–N in the range 2.46–2.66 Å) and also bonded to an N(pyrazine) atom (Ag–N 2.28 Å). On the other hand Ag4 is not chelated but is three-connected to three N(pyrazine) atoms, in a T-shaped geometry (Ag–N in the range 2.25–2.47 Å). One can consider this sheet also as an assembly of dinuclear $Ag_2(azpyz)_2$ moieties (see Figs. 1 and 10). Layers A and B are condensed in a way that can be described as a donor (B) → acceptor (A) interaction. The $ClO_4^-$ anions occupy the interstitial cavities of the network and no significant free voids are left for guest solvents.

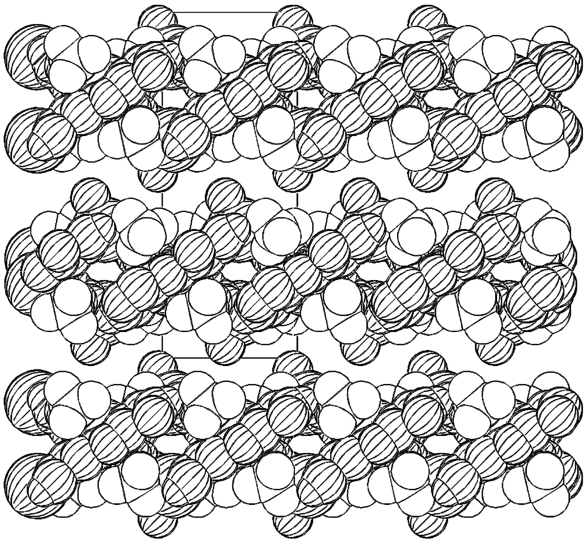

**Fig. 7** Sphere-packing of the stacked layers in **3** showing the large empty interlayer regions. Plain spheres are used for the $BF_4^-$ anions, and hatched spheres for the remainder.

### Comparison of the coordination of azpyz

Finally, we can examine in more detail the structural features of the new azpyz ligand in the different environments encountered within compounds **1a** and **2**–**4**. Indeed, the coordination modes exhibited by the ligand in these polymers (Scheme 2) do not cover all the possibilities for azpyz. The number of N-donor atoms increases from 2 in A, to 3 in B and C, to 5 in E, to 6 in D, but no example with 4 N-donors has been yet observed (different modes are possible, in principle, including bischelation or monochelation, *plus* two bonds *via* pyrazine N atoms). In all cases but one (E) the ligand is essentially planar with maximum out-of-plane displacements of 0.150, 0.172 Å (**1a**), 0.089, 0.099 Å (**2**), 0.103 Å (**3**), 0.175 Å (for the ligand in coordination mode D in **4**). The planarity is favoured by the stability of the extended π system but in mode E a planar situation would bring two coordinated metals too close together. The –N=N– formally double bonds in compounds **1a**, **2** and **3** are all very similar and close to the expected value (range 1.22–1.25 Å). In compound **4** these distances are more scattered (1.19 and 1.27 Å) for the ligands that exhibit the E coordination mode.

## Experimental

### Materials

All reagents and solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied, without further purification. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Milan. $^1$H NMR spectra were collected on a Bruker DRX300. TG analyses were performed under nitrogen on a

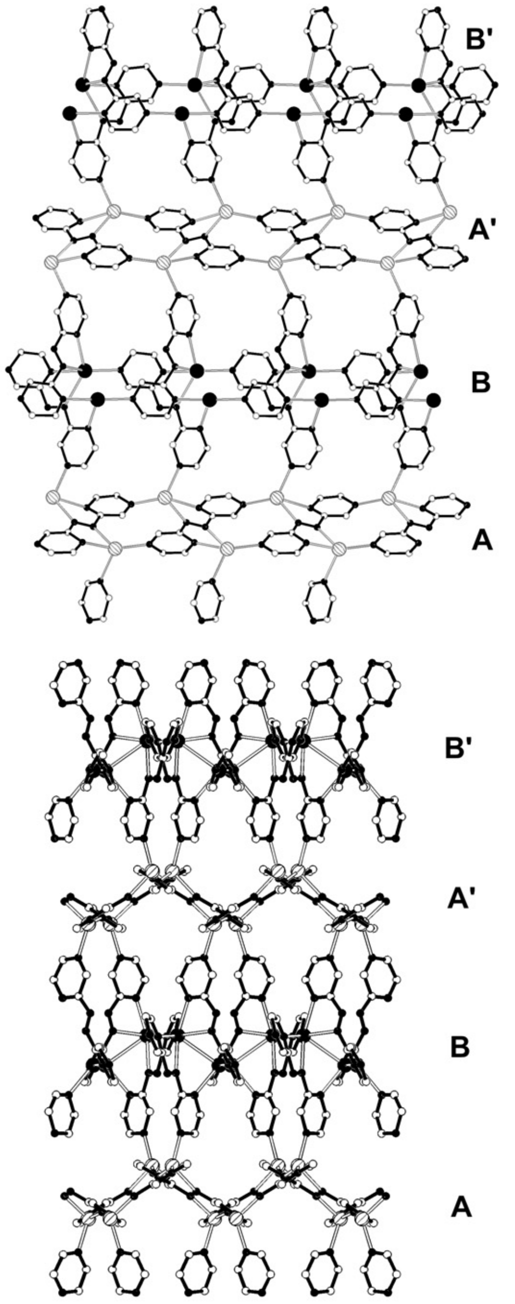

**Fig. 8** Two overall views down the ***a*** (top) and ***b*** (bottom) axes of the 3D network in compound **4**, evidencing the alternance of different two-dimensional submotifs.

Perkin–Elmer TGA 7 instrument with a temperature ramp of 10 °C min$^{-1}$.

### Synthesis of azpyz

Aminopyrazine (5.0135 g; 0.0527 mol) was dissolved in water (40 mL) and cooled to 0 °C in an ice bath. To this solution a 150 mL aliquot of a cooled solution of 13% sodium hypochlorite was added dropwise while stirring. At the end of the addition the reaction mixture was allowed to stir at room temperature for an additional hour and then it was filtered through a glass frit. The tar that was left on the frit was washed with small portions of benzene while the aqueous solution was extracted four times with 40 mL of benzene. The organic phases were combined, dehydrated with $MgSO_4$ and evaporated to dryness under vacuum. The red-brown residue was chromatographed on $SiO_2$ with a 1:2 mixture of acetone–hexane. The azpyz ligand was recovered from the column as a third ruby-coloured band after a small yellow band and a second orange band of uncharacterized species. The removal of the solvent under vacuum from the ruby solution gave azpyz as a red microcrystalline solid (0.490 g; 10% yield). Anal. calcd. for $C_8H_6N_6$: C, 51,61; H, 3,25; N, 45.15%; found C 52.04; H 3.46 N 44.93. $^1$H NMR ($CDCl_3$): $\delta$ 9.291 (1H-3, dd), 8.822 (1H-5, dd), 8.784 (1H-6, dd); $^4J$ H3-H5 = 0.38 Hz; $^5J$ H3-H6 = 1.40 Hz; $^3J$ H6-H5 = 2.43 Hz. $^{13}$C NMR ($CDCl_3$): $\delta$ 139.98 (C3), 147.76 (C5), 144.49 (C6), 157.39 (C2).

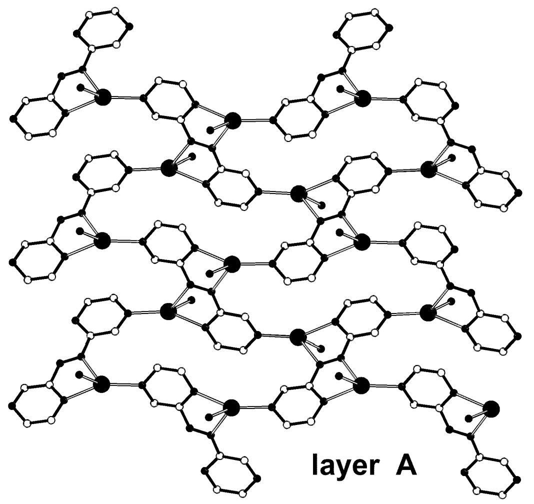

**Fig. 9** A view of the layers of type A in **4**.

### Synthesis of the Ag(I) polymers

**1a, 1b and 2.** [Ag(azpyz)$_2$]$ClO_4$ (**1a**), [Ag(azpyz)$_2$]$BF_4$ (**1b**) and [Ag(azpyz)$_2$]$SbF_6$.0.5$CH_2Cl_2$ (**2**) were prepared by adding a dichloromethane solution of the azpyz ligand to the appropriate silver salt dissolved in ethanol in a ligand-to-metal molar ratio of 2:1.

**1a**. $AgClO_4$ (15.4 mg; 0.074 mmol) dissolved in ethanol (5 mL) was added dropwise to a solution of azpyz (27.,5 mg; 0.148 mmol) dissolved in $CH_2Cl_2$. The mixture was left to react while stirring for about 3 h. A brown precipitate formed, which was collected by filtration and dried in the air. The purity of the solid material was checked by XRPD analysis. Yield (39.4 mg; 92%). Anal. calcd. for $C_{16}H_{12}AgClN_{12}O_4$: C, 33.15; H, 2.09; N, 29.00%; found C 32.75; H 2.12 N 27.83.

**1b**. $AgBF_4$ (18.2 mg; 0.093 mmol) in 5 mL of ethanol was added to azpyz (34.9 mg; 0.187 mmol) in 8 mL of $CH_2Cl_2$. Yield (42.8 mg; 80%). Anal. calcd. for $C_{16}H_{12}AgBF_4N_{12}$: C, 33.89; H, 2.13; N, 29.64%; found C 33.17; H 2.15 N 27.80.

**2**. $AgSbF_6$ (22.6 mg; 0.0658 mmol) in 6 mL of ethanol was added to azpyz (24.5 mg; 0.132 mmol) in 7 mL of $CH_2Cl_2$. Yield (43.8 mg; 88%). Anal. calcd. for $C_{33}H_{26}Ag_2Sb_2F_{12}N_{24}$: C, 26.13; H, 1.73; N, 22.16%; found C 26.48; H 2.17 N 21.34. TG analysis of a sample of **2** showed a weight loss of 5.9 % at *ca.* 150 °C corresponding to the removal of the dichloromethane guest (calcd 5.6%).

**[Ag$_2$(azpyz)(H$_2$O)](BF$_4$) (3).** This species can be obtained only in mixtures. $AgBF_4$ (25.3 mg; 0.130 mmol) was dissolved in EtOH (6 mL) and layered on a dichloromethane solution (6 mL) of azpyz (12.1 mg; 0.0650 mmol). The mixture was left in the dark for some days after which the formation of orange plate-like crystals of **3** in the presence of a dominant amount of crystals of **1b** and of a dark powder was noted. The nature of compounds **3** and **1b** was confirmed by indexing two different single crystals on a diffractometer. On performing the reaction under stirring with the correct stoichiometric ratio of the reagents ($AgBF_4$, 35.8 mg, 0.184 mmol–EtOH, 6 mL–azpyz, 17.1 mg, 0.092 mmol–$CH_2Cl_2$, 6 mL) an amor-

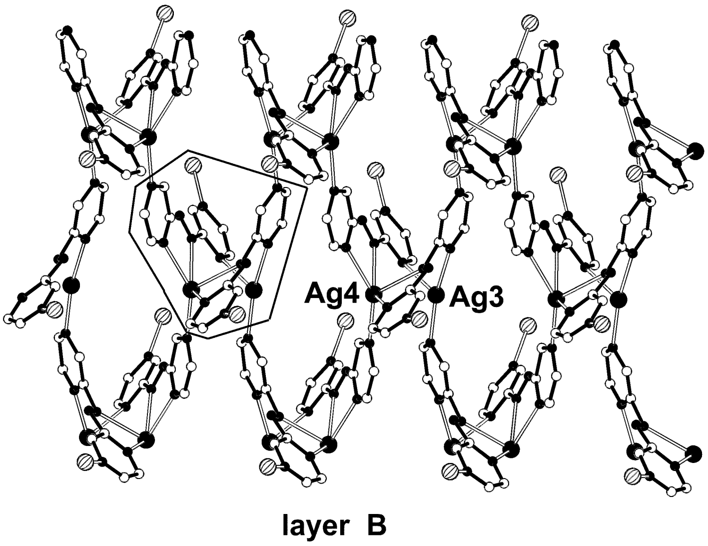

**Fig. 10** The layers of type B in **4**. The dinuclear unit $[Ag_2(azpyz)_2]^{2+}$ generating the layer is outlined.

phous material was obtained, which was recovered after filtration and drying under vacuum (30.8 mg). The elemental analysis performed on this sample agrees with the composition of the almost completely desolvated network of compound **3**, $[Ag_2(azpyz)(H_2O)](BF_4)\cdot0.5(EtOH)$. Anal. calcd. for $C_{18}H_{22}Ag_4B_4F_{16}N_{12}O_3$: C, 17.53; H, 1.80; N, 13.63%; found C 17.96; H 2.07 N 14.62.

**$[Ag_4(azpyz)_3](ClO_4)$ (4).** $AgClO_4$ (20 mg; 0.0965 mmol) dissolved in EtOH (4 mL) was layered on a solution of azpyz (13.5 mg; 0.0723 mmol) in $CH_2Cl_2$. After leaving the mixture in the dark for some days, crystals of complexes **4** and **1a** were grown at the interlayer together with some powdered material. All these materials were recovered by filtration, washed with dichloromethane and dried in air (25 mg). The XRPD analysis showed a poor crystalline pattern, which could be ascribed to the presence of both the 3D complex **4** and the 1D polymer **1a**. The elemental analyses performed on different samples indicated *ca.* 10% of complex **4**. Crystals of **4**, separated under the microscope and showing a peculiar morphology, were also submitted to elemental analysis. Anal. calcd. for $C_{24}H_{18}Ag_4Cl_4N_{18}O_{16}$: C, 20.77; H, 1.31; N, 18.17%; found C, 21.00; H, 1.43; N, 18.57.

## Crystallography

Crystal data are reported in Table 1 and selected bond distances and angles in Table 2. The data collections were performed at 293 K on a SMART-CCD Bruker diffractometer for **1a**, **3** and **4**, by the $\omega$-scan method, within the limits $2° < \theta < 23°$ (**1**), $2° < \theta < 25°$ (**3** and **4**). Data for **2** were collected at 293 K on an Enraf–Nonius CAD4 diffractometer by the $\omega$-scan method, within the limits $3° < \theta < 25°$. Empirical absorption corrections were applied: SADABS[11] for **1a**, **3** and **4**, and $\psi$-scan for **2**. For compound **1b** we have determined only the cell parameters: monoclinic, $a = 11.828(2)$, $b = 9.403(1)$, $c = 19.530(2)$ Å, $\beta = 105.40(2)°$, $U = 2094.1(5)$ Å$^3$. The structures were solved by direct methods (SIR97)[12] and refined by full-matrix least-squares on $F^2$ (SHELX-97)[13] with the WINGX interface.[14] Anisotropic thermal parameters were assigned to all the non-hydrogen atoms. In the case of compound **3**, in order to model the disorderd solvent, we used the Bypass method[10] as implemented in the routine SQUEEZE of PLATON;[15] anisotropic thermal factor were assigned to the silver atoms only. For the acentric species **3** and **4** the absolute structure parameters were refined with TWIN command to 0.40(17) and 0.50(8), respectively, indicating racemic twinnig. Disordered anions were found in **2** and a suitable 55%–45%

**Table 1** Crystallographic data for compounds **1a** and **2**–**4**

| | **1a** | **2** | **3** | **4** |
|---|---|---|---|---|
| Formula | $C_{16}H_{12}AgClN_{12}O_4$ | $C_{16.5}H_{13}AgClF_6N_{12}Sb$ | $C_8H_8Ag_2B_2F_8N_6O$ | $C_{24}H_{18}Ag_4Cl_4N_{18}O_{16}$ |
| $M$ | 579.70 | 758.46 | 593.53 | 1387.84 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $P21/c$ (14) | $P21/n$ (14) | $Pn21a$ (33) | $Pbc21$ (29) |
| $a$/Å | 11.884(1) | 14.944(2) | 10.451(2) | 7.788(1) |
| $b$/Å | 9.501(1) | 12.364(2) | 9.450(2) | 14.259(2) |
| $c$/Å | 19.445(2) | 15.211(3) | 24.193(6) | 36.544(6) |
| $\beta$/° | 105.11(2) | 118.50(2) | 90. | 90. |
| $U$/Å$^3$ | 2119.6(4) | 2469.9(7) | 2389.3(9) | 4058.2(12) |
| $Z$ | 4 | 4 | 4 | 4 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 1.131 | 2.073 | 1.706 | 2.258 |
| Reflections collected | 11 555 | 4523 | 21 240 | 24 189 |
| Indep. reflections | 3045 | 4344 | 4231 | 6825 |
| $R$(int) | 0.0359 | 0.0357 | 0.1045 | 0.0312 |
| Observed [$F > 4\sigma(F)$] | 2535 | 2687 | 2934 | 5894 |
| $R1$ [$F > 4\sigma(F)$] | 0.0226 | 0.0460 | 0.0981 | 0.0876 |
| $wR2$ (all data) | 0.0531 | 0.1125 | 0.2959 | 0.2495 |

**Table 2** Selected bond distances (Å) and angles (°) for compounds **1a** and **2–4**

| Compound **1a** | | | |
|---|---|---|---|
| Ag–N(35) | 2.278(2) | Ag–N(3) | 2.526(2) |
| Ag–N(2) | 2.385(2) | N(1)–N(2) | 1.248(3) |
| Ag–N(42) | 2.402(2) | N(3)–N(4) | 1.249(3) |
| Ag–N(12) | 2.405(2) | | |
| N(35)–Ag–N(2) | 119.09(7) | N(42)–Ag–N(12) | 118.37(8) |
| N(35)–Ag–N(42) | 108.73(8) | N(35)–Ag–N(3) | 89.78(7) |
| N(2)–Ag–N(42) | 99.93(7) | N(2)–Ag–N(3) | 150.91(7) |
| N(35)–Ag–N(12) | 130.92(7) | N(42)–Ag–N(3) | 64.42(7) |
| N(2)–Ag–N(12) | 66.69(7) | N(12)–Ag–N(3) | 98.09(7) |
| Compound **2** | | | |
| Ag–N(45) | 2.402(6) | Ag–N(15) | 2.596(6) |
| Ag–N(1) | 2.435(7) | Ag–N(21) | 2.769(7) |
| Ag–N(3) | 2.448(6) | N(1)–N(2) | 1.233(8) |
| Ag–N(42) | 2.593(6) | N(3)–N(4) | 1.225(8) |
| N(45)–Ag–N(1) | 99.7(2) | N(3)–Ag–N(15) | 88.3(2) |
| N(45)–Ag–N(3) | 118.6(2) | N(42)–Ag–N(15) | 80.0(2) |
| N(1)–Ag–N(3) | 127.2(2) | N(45)–Ag–N(21) | 87.4(2) |
| N(45)–Ag–N(42) | 163.1(2) | N(1)–Ag–N(21) | 60.9(2) |
| N(1)–Ag–N(42) | 90.3(2) | N(3)–Ag–N(21) | 84.6(2) |
| N(3)–Ag–N(42) | 63.3(2) | N(42)–Ag–N(21) | 109.4(2) |
| N(45)–Ag–N(15) | 83.2(2) | N(15)–Ag–N(21) | 163.8(2) |
| N(1)–Ag–N(15) | 133.8(2) | | |
| Compound **3** | | | |
| Ag(1)–N(1) | 2.255(14) | Ag(2)–N(6) | 2.285(13) |
| Ag(1)–N(4) | 2.336(11) | Ag(2)–N(2) | 2.340(17) |
| Ag(1)–N(5) | 2.348(12) | Ag(2)–O(1S) | 2.52(3) |
| Ag(1)–N(3) | 2.469(10) | N(3)–N(4) | 1.243(14) |
| N(1)–Ag(1)–N(4) | 128.1(4) | N(5)–Ag(1)–N(3) | 125.2(4) |
| N(1)–Ag(1)–N(5) | 150.1(4) | N(6)–Ag(2)–N(2) | 134.0(4) |
| N(4)–Ag(1)–N(5) | 67.4(4) | N(6)–Ag(2)-O(1S) | 134.4(7) |
| N(1)–Ag(1)–N(3) | 68.6(4) | N(2)–Ag(2)-O(1S) | 90.4(7) |
| N(4)–Ag(1)–N(3) | 128.7(4) | | |
| Compound **4** | | | |
| Ag(1)–N(3) | 2.473(13) | Ag(3)–N(56) | 2.475(15) |
| Ag(1)–N(46) | 2.296(17) | Ag(3)–N(6) | 2.549(18) |
| Ag(1)–N(43) | 2.198(12) | Ag(3)–N(2) | 2.657(17) |
| Ag(1)–N(53) | 2.367(17) | Ag(4)–N(63) | 2.253(15) |
| Ag(2)–N(33) | 2.193(15) | Ag(4)–N(66) | 2.291(16) |
| Ag(2)–N(23) | 2.297(16) | Ag(4)–N(26) | 2.469(15) |
| Ag(2)–N(36) | 2.412(12) | N(1)–N(2) | 1.19(2) |
| Ag(2)–N(4) | 2.565(11) | N(3)–N(4) | 1.284(17) |
| Ag(3)–N(13) | 2.280(15) | N(5)–N(6) | 1.28(3) |
| Ag(3)–N(16) | 2.461(17) | | |
| N(43)–Ag(1)–N(46) | 149.5(5) | N(16)–Ag(3)–N(56) | 88.6(6) |
| N(43)–Ag(1)–N(53) | 121.6(6) | N(13)–Ag(3)–N(6) | 127.3(6) |
| N(46)–Ag(1)–N(53) | 83.6(6) | N(16)–Ag(3)–N(6) | 86.1(6) |
| N(43)–Ag(1)–N(3) | 121.2(5) | N(56)–Ag(3)–N(6) | 63.6(5) |
| N(46)–Ag(1)–N(3) | 66.4(5) | N(13)–Ag(3)–N(2) | 120.3(5) |
| N(53)–Ag(1)–N(3) | 96.6(5) | N(16)–Ag(3)–N(2) | 62.2(6) |
| N(33)–Ag(2)–N(23) | 125.1(5) | N(56)–Ag(3)–N(2) | 136.7(5) |
| N(33)–Ag(2)–N(36) | 144.6(5) | N(6)–Ag(3)–N(2) | 82.0(5) |
| N(23)–Ag(2)–N(36) | 87.7(5) | N(63)–Ag(4)–N(66) | 170.7(6) |
| N(33)–Ag(2)–N(4) | 114.3(4) | N(63)–Ag(4)–N(26) | 101.4(6) |
| N(23)–Ag(2)–N(4) | 101.7(5) | N(66)–Ag(4)–N(26) | 85.9(6) |
| N(36)–Ag(2)–N(4) | 64.5(4) | N(63)–Ag(4)–Ag(3) | 99.1(4) |
| N(13)–Ag(3)–N(16) | 146.3(5) | N(66)–Ag(4)–Ag(3) | 87.4(4) |
| N(13)–Ag(3)–N(56) | 101.9(6) | N(26)–Ag(4)–Ag(3) | 82.8(3) |

disorder model was refined. All the diagrams were drawn using the SCHAKAL99 program.[16]

CCDC reference numbers 199929–32. See http://www.rsc.org/suppdata/nj/b2/b209580g/ for crystallographic files in CIF or other electronic format.

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