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Review

Square planar silver(I) complexes: A rare but increasingly observed stereochemistry for silver(I)

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Abstract

The square planar Ag(I) stereochemistry is generally acknowledged as rare, with only ~2% of all reported silver complexes possessing this stereochemistry. Many researchers reporting such complexes often mistakenly believe that their example is one of only a handful of previously reported examples. This is despite the fact that there are currently around 65 well characterised complexes containing square planar Ag(I) ions, about half of which are coordination polymers. In this review, we critically examine each example and draw attention to trends that arise in their formation. The scope is limited to 'traditional' coordination complexes. Inorganic complexes containing extended mineral like structures, and complexes containing silver-π or silver-arene motifs are not considered in this review.

Keywords: Square planar; Ag(I); Silver(I); Axial interactions; Coordination polymers; Imposed symmetry; Blocking groups

1. Introduction

In coordination chemistry, silver in the +1 oxidation state is found to adopt a wide variety of coordination geometries. A Cambridge Structural Database CSD (version 5.27) search yielded 3319 crystal structures containing silver ions coordinated to non-metal atoms [1]. Of these, 24.2% are two-coordinate, 22.7% are three-coordinate, 43.9% are four-coordinate, 4.7% are five-coordinate, 3.9% are six-coordinate, 0.3% are seven-coordinate, and 0.3% are eight-coordinate. This variety is in part due to the lack of stereochemical preference that arises from a d^{10} configuration. Furthermore, the weak nature of the silver-ligand bond [2] means that in the solid state, weak interactions and crystal packing forces have a greater influence on structure than may be expected in more robust metal–ligand systems. With the exception of the higher coordination numbers, the least common geometry is square planar, with around 65 of the 3319 reported crystal structures possessing this stereochemistry. This includes two different studies which report two [3] and three [4] isomorphous crystalline compounds, respectively, that have been characterised by X-ray crystallography. Several other crystal structures have analogues likely to be isomorphous based on spectral measurements. A comprehensive literature survey provided the examples presented herein. This survey included a CSD search where the coordination number of the Ag centre was fixed at four and bonds to donor atoms of any type were allowed. The *trans*-bond angles were specified to be in the range of 175 ± 5° and 165 ± 15°, respectively. These bond angle limits are sufficient to include occurrences where a reasonable degree of distortion towards tetrahedral geometry is present but the Ag(I) coordination geometry still has square planar character.

Structural methods such as X-ray crystallography generally provide an unambiguous assignment of the stereochemistry about a Ag(I) ion. However, the square planar stereochemistry has also been assigned in solution to Ag(I) ions from electronic spectral [5,6] and electron spin-echo modulation studies [7].

With the rarity of the square planar geometry in Ag(I) chemistry, the examples which have been identified have always been of interest. More recently, with the development of supramolecular synthesis and the related rise of coordination polymer chemistry and crystal engineering, the prospect of employing this stereochemistry as a four-connected node or square planar secondary building unit (SBU) in the design of new network topologies has found some success which is likely to continue (Sections 5 and 6).

Early workers who identified square planar Ag(I) complexes were often concerned to show that the Ag ion had not undergone oxidation to Ag(II) d^9 for which a square planar geometry might be more likely. Typically ESR and UV–vis measurements were used in an attempt to probe the likely paramagnetic behaviour of such a Ag(II) square planar complex [8–10]. Improvements in analytical techniques and a better understanding of Ag(I) and Ag(II) coordination chemistry have reduced the ambiguity when determining oxidation numbers of Ag complexes.

The square planar Ag(I) stereochemistry is generally acknowledged as rare and many researchers reporting such complexes often mistakenly claim that their example is one of only a handful of previously reported examples. For example, in 2003, Chowdhury et al. [11] claimed "Our complex 2 provides, most possibly, the third example of a square planar silver complex"; in 2002, Carmona et al. [12] claimed "As far as we know only three previous structures. . .have been described with a Ag(I) atom in a square planar environment."; also in 2002, Suenaga et al. [8] claimed "However, a silver(I) coordination polymer having a square planar geometry has never been reported." This is despite the fact that to our knowledge the first reported and structurally characterised square planar Ag(I) complex was of a flavin complex and was reported in 1972 by Charles J. Fritchie, Jr. [13]. Interestingly, this paper has received only about 23 citations (excluding self-citations) most of which are concerned with flavin chemistry and not the uniqueness of stereochemistry of the Ag(I) ion. To our knowledge, there are currently 65 well characterised square planar Ag(I) complexes of which about half are coordination polymers. Given that half are coordination polymers and most have been reported since 1996, it seems likely that the number of square planar Ag(I) containing complexes will continue to grow, if slowly.

As with the assignment of any stereochemistry, ambiguity results both from whether or not a particular auxiliary species, such as a counterion, is coordinated, and from issues with describing the specific geometry perhaps associated with bond angles being intermediate between well-defined archetypes. In order to distinguish between a formal Ag–ligand bond and a longer weak interaction a number of searches of the CSD [1] were undertaken for this review. General unrestricted searches were conducted for all Ag containing crystal structures with NO_3^-, ClO_4^- and BF_4^- counter anions, respectively. These searches identified all structures that contained Ag· · ·X distances (where X = O–NO_2^-, O–ClO_3^-, or F–BF_3^-) that were less than 4 Å (Fig. 1). These distances represent a combination of formal Ag–ligand bonds, longer weak interactions, and also any other distance found to be shorter than 4 Å. The NO_3^-, ClO_4^- and BF_4^- counter anions were selected for the CSD search because they are generally the most commonly used silver salts. The $CF_3SO_3^-$ anion is frequently found to be disordered within crystal structures, and the PF_6^- anion was found to have too few occurrences to allow a reliable analysis. The resulting searches yielded 519 datasets with 1126 occurrences, 327 datasets with 569 occurrences and 131 datasets with 193 occurrences for NO_3^-, ClO_4^- and BF_4^-, respectively. For each counter anion, the profile of occurrences shows a skewed normal distribution. A tail leading off into the longer distances arises from the distances that are not due to formal Ag–ligand bonds [14]. This profile is well defined for NO_3^- and ClO_4^-, but less so for BF_4^- due to the lower number of occurrences.

Limiting the above CSD searches to distances designated solely as formal Ag–ligand bonds allows the examination of the results according to coordination number. This affects the occurrence profiles by removing the tail at longer distances and leaves an approximate normal distribution of bond lengths. This search gave 370 datasets with 752 occurrences, 142 datasets with 249 occurrences and 16 datasets with 20 occurrences for NO_3^-, ClO_4^- and BF_4^-, respectively. For NO_3^- and ClO_4^- the median Ag–O bond lengths were found to be 2.51 and 2.53 Å, respectively. The anion BF_4^- is traditionally considered to be a more weakly coordinating anion and as such shows a median Ag–F bond length of 2.58 Å. Further limiting of the search parameters to include solely crystal structures containing four coordinate Ag moieties and non-metal donor atoms, both significantly reduced the number of occurrences and slightly compressed the range of formal Ag–ligand bond lengths observed, and the results are shown in Fig. 2. This search gave 123 datasets with 190 occurrences, 40 datasets with 63 occurrences and 5 datasets with 5 occurrences for NO_3^-, ClO_4^- and BF_4^-, respectively. Interestingly for NO_3^- and ClO_4^- the median Ag–O bond lengths were found to be 2.49 and 2.52 Å, respectively. The close similarity between the median bond length for a silver complex of unspecified coordination number and a four-coordinate silver complex is attributed to a combination of the high proportion of four-coordinate complexes compared to other coordination numbers and the fact that four

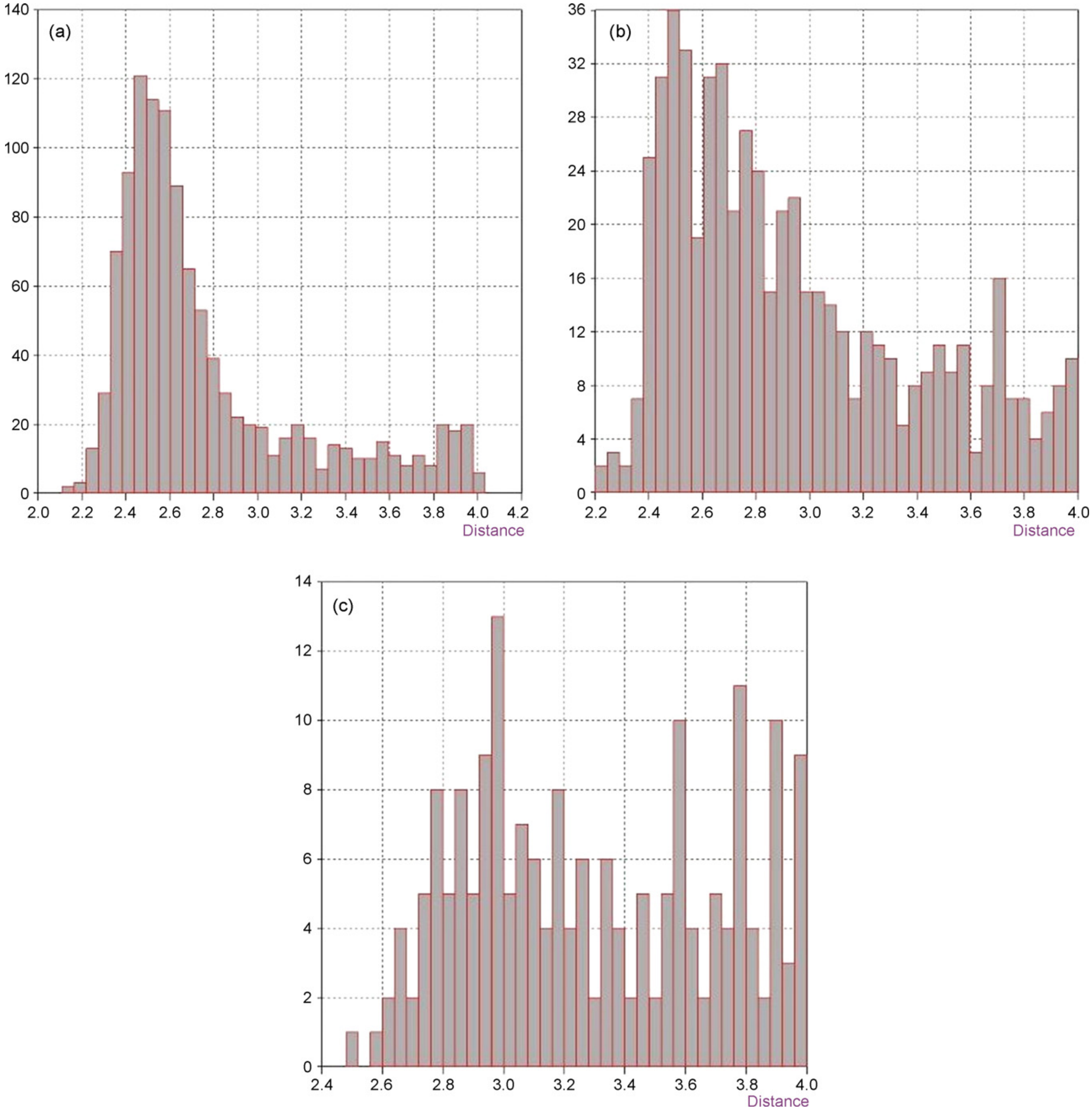


Fig. 1. Occurrences of all Ag containing crystal structures with donor atom distances less than 4 Å, to (a) O–NO_2^-, (b) O–ClO_3^-, and (c) F–BF_3^- counterions.

lies at the midpoint between two and six thereby removing the extreme values from the distribution.

Analysis of the distributions indicates that distances lying 0.2 Å or less above the median bond length can be considered a formal Ag–ligand bond [15]. This range of formal bond lengths includes the vast majority of reported distances at least in the case of NO_3^- and ClO_4^- complexes. Therefore, we generally consider Ag(I)–donor atom distances above this limit of 2.70–2.72 Å to be weak interactions and not formal Ag–ligand bonds.

For many square planar complexes distortion within the square plane due to differing *cis* bond lengths is observed leading to two longer and two shorter bond lengths. In approximately half of the cases this is imposed by the central Ag(I) ion residing on a special position such as a centre of symmetry or two-fold axis. The question arises as to whether this observation is a consequence of the electronic make up of the primary coordination sphere of the silver or an artefact of crystal packing. In order to investigate this issue we undertook molecular orbital calculations using the Gaussian 03W program package. The simple linear model cation $[Ag(NH_3)_2]^+$ has seven occurrences in the CSD with bond lengths in the range 2.11–2.16 Å. A DFT calculation at a B3LYP level of theory using LANL2DZ basis set calculated Ag–N bond lengths of 2.18 Å. A similar calculation was carried out using a more complex pseudo-tetrahedral model

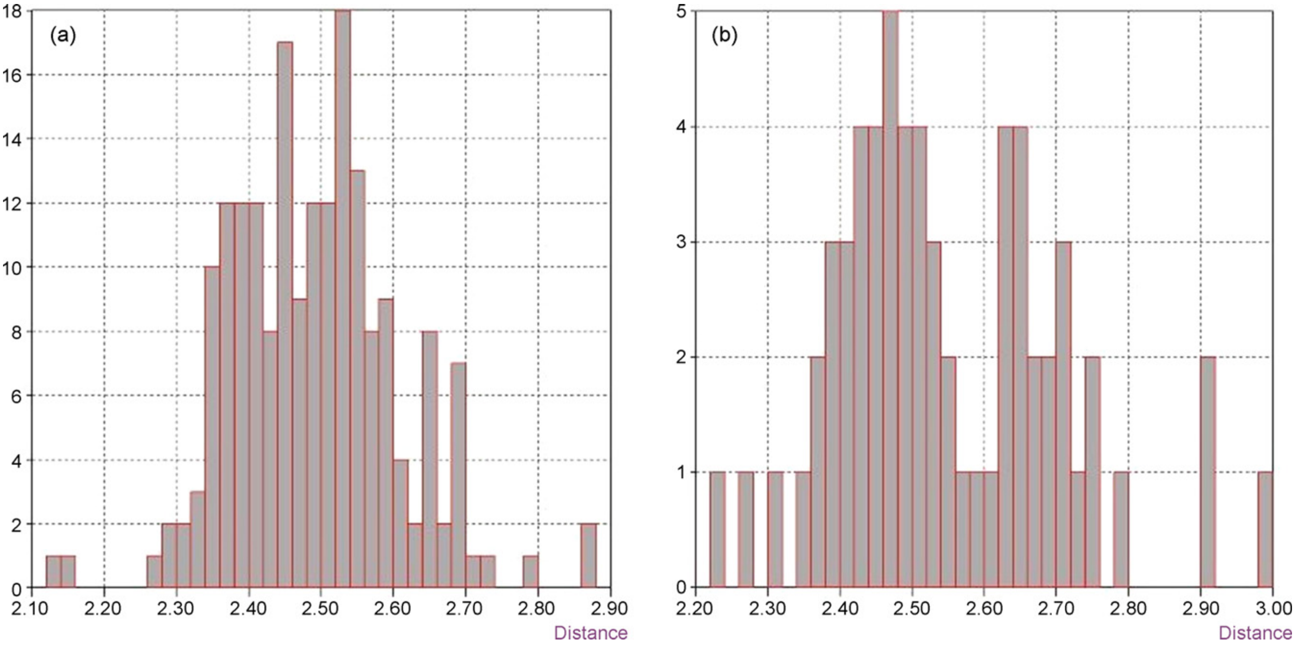


Fig. 2. Occurrences of crystal structures containing four-coordinate Ag centres with only non-metal donor atoms, for (a) O–$NO_2^-$and (b) O–ClO_3^- counterions.

cation $[Ag(pyridine)_4]^+$ which has five occurrences in the CSD with bond lengths in the range 2.27–2.43 Å. The calculated individual Ag–N bond lengths were found to be 2.36, 2.37, 2.39 and 2.44 Å. For both model compounds in the gas phase the calculated bond lengths tended to be at the higher end of the observed ranges for the corresponding cations in the solid state. The LANL2DZ basis set has been criticised because it freezes all core electrons and approximates their effect with an effective core potential. However, for the theoretical square planar $[Ag(pyridine)_4]^+$ cation with pyridine rings orientated perpendicular to the square plane, this calculation yielded the same energies for the cation in both the D_{4h} and D_{2h} point groups. This suggests that electronic effects are not responsible for the variation in bond lengths. Further evidence can be obtained by considering the theoretical model compound $[Ag(NH_3)_4]^+$. DFT calculations were carried out at a B3LYP level of theory using the 6–31G(d) basis set for the ligands and the LANL2DZ basis set for the Ag(I) ion. Beginning from a square planar C_{4h} point group and progressing through less symmetric point groups C_{2h}, C_4, C_2 and ending at C_1, identical molecular energies and Ag–N bond lengths were found for every point group. This result also suggests that there are no favourable molecular energy consequences for having two longer and two shorter *trans*-Ag bonds. The cyclic point groups were selected for these calculations instead of the dihedral point groups because the more symmetric dihedral point groups do not allow for ‘canting’ of the pyridine rings as has been observed in various crystal structures [16,17]. In summary, it seems that the prevalence of two longer and two shorter *trans*-bonds is a consequence of crystal packing effects and crystallographically imposed symmetry.

The bond valence sum (BVS) model has been used to support the assignment of a square planar geometry in contrast to a linear geometry where pairs of bond distances vary significantly [18,19]. This model relates the bond distances around a metal ion to its oxidation state. A BVS of 1.00 ± 0.20 unit represents complete valence satisfaction for a Ag(I) ion. The bond valence sum (BVS) model has been used to show that all four N atoms are required to satisfy the Ag(I) valence, in three reported square planar Ag–N systems. For $\{[Ag(\textbf{pmit})]ClO_4\}_\infty$ (**pmit** is shown in Fig. 66) using two Ag–N(imino) bond lengths of 2.247(5) Å a BVS of 0.70 unit is obtained [11]. This value was outside the stipulated error limit of ±0.20 unit for valence satisfaction. When two Ag–N(pyridyl) bonds are added the BVS increases to 1.02 unit. Similarly for $\{[Ag(\textbf{psdbf})_2]ClO_4\}_\infty$ (**psdbf** is shown in Fig. 61) assuming linear coordination, a BVS of 0.59 unit was calculated with two Ag–N distances of 2.308(2) Å [3]. Conversely, a BVS of 0.88 ± 0.20 unit was calculated when all four Ag–N distances were included. For the corresponding $\{[Ag(\textbf{psdbf})_2]NO_3\}_\infty$ the linear BVS and square planar BVS were calculated at 0.60 ± 0.20 unit and 0.95 ± 0.20 unit, respectively [3].

The square planar geometry often shows some bond angle distortion towards the tetrahedral geometry and in this case an unambiguous stereochemical assignment can be difficult. For example, the complex bis(**miax**)silver(I) nitrite tetrahydrate [20] is shown in Fig. 3. Each flavin ligand binds one Ag(I) ion which lies on a two-fold axis and is chelated through a N and O donor. Benno and Fritchie describe the Ag(I) ion as exhibiting coordination halfway between tetrahedral and square planar. Numerous other complexes containing a similar intermediate Ag(I) stereochemistry have been reported by Bowmaker et al. [21], Blake et al. [22], and Wu et al. [23] An intriguing helical structure containing 16 unique Ag(I) ions with stereochemistries that show a progression from near tetrahedral and becoming increasingly planar has also been reported by Baxter et al. [24].

To our knowledge, no robust system for classifying square planar geometry has been developed, however some models

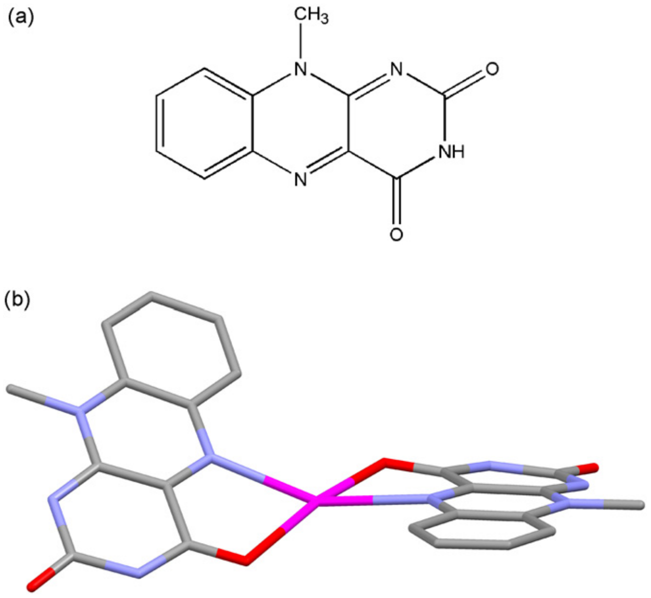


Fig. 3. The ligand **miax** and the cation of the discrete complex bis(**miax**)silver(I) nitrite tetrahydrate, showing geometry half way between tetrahedral and square planar. In all figures, the following colour scheme applies: Ag—purple; C—grey; N—light blue; O—red; F—lime green; P—orange; S—yellow; Cl—green. (For interpretation of the references to colour in all figures, the reader is referred to the web version of the article.)

have been suggested [97]. Constable et al. [25] use a model in which the sum, Σ, of the six inter-bond angles for a four-coordinate complex expresses the degree of planarity ($\Sigma = 720°$ for a perfectly planar complex and $\Sigma = 657°$ for perfectly tetrahedral system). Their CSD search is restricted to Ag–N non-macrocyclic systems and they state two reported examples of complexes with $\Sigma > 700°$ exist. For $[Ag_2(\mathbf{ptp})_2](CF_3SO_3)_2$ where **ptp** is 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, they report $\Sigma = 701.4°$. Unfortunately, this model is not robust enough to apply to all four-coordinate coordination environments that arise. For example, a commonly observed centrosymmetric environment is presented in Fig. 4 below. The calculated $\Sigma = 720°$ but the coordination environment is severely distorted away from square planar. In this case, Σ indicates the planarity but not whether the four donor atoms lie on the corners of a square. Furthermore, if one or both of the two sets of bonds related *trans* about a four-coordinate Ag(I) centre are not parallel (shown in Fig. 4), at least one *trans*-bond angle will be less than 180°. Such systems can be planar [26] with a Σ calculated of 659.8°. In some situations, this degree of planarity model is not applicable.

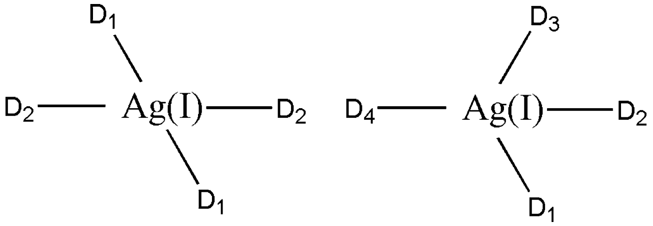


Fig. 4. Schematics of planar unspecified donor atom (D_x) arrangements about a central Ag(I) ion. The left arrangement is centrosymmetric about Ag(I), while the right arrangement contains one set of *trans* bonds that are not parallel.

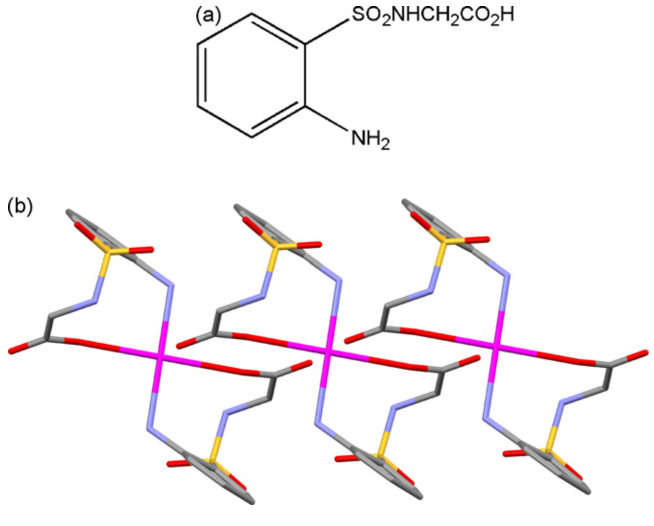


Fig. 5. The ligand *o*-aminobenzenesulfonyl glycine (RH_2) and the complex $H[Ag(RH)_2]$.

More than half of the reported square planar Ag(I) complexes have some degree of diaxial interaction with counterions. This gives rise to a tetragonally distorted environment about the Ag(I) ion. At some point, the diaxial interactions become short enough to be classified as formal bonds, whereby the coordination of the Ag(I) ion becomes distorted octahedral. Our analysis for light donor atoms suggests this point is around 2.70–2.72 Å. For example, in 1979 the complex $H[Ag(RH)_2]$, where $RH_2 = o$–aminobenzenesulfonyl glycine, was reported [27]. This crystal structure has an R-factor of 10.2% given that it was solved from photographic data, and is shown in Fig. 5. The complex contains two RH^- ligands arranged centrosymmetrically about a Ag(I) ion forming nine-membered chelate rings. Ray and Saha claim an approximate square planar arrangement about Ag(I), by two N and two O donor atoms at 2.280(12) and 2.599(12) Å, respectively. Crystallographically, the ligands are identical as the Ag(I) ion resides on a centre of inversion. The authors are uncertain about the position of the H^+ counterion, suggesting that it remains virtually associated with the complex through resonance of the two modes of bonding between Ag and the bound carboxyl O atoms. The non-coordinated carboxyl O atom has an interaction of 2.698 Å with the apical site of a Ag(I) ion of a neighbouring complex. The authors consider the possibility of distorted octahedral coordination about the Ag(I) ion arising from the favourable arrangement of this other carboxyl O atom. Given the quality of the structure and the errors associated with the bond lengths it would seem that all the Ag–O bonds are of similar length. Thus in this structure octahedral coordination is perhaps more appropriate and would in turn give rise to a 1D polymeric chain. This is a good example of the ambiguity of the identity of square planar in the context of additional axial interactions.

Other reported examples have been poorly or incorrectly assigned. The T-shaped coordination polymer $\{[Ag(4\text{-cyanopyridine})_2]BF_4\}_\infty$ is shown in Fig. 6. Carlucci et al. [28]

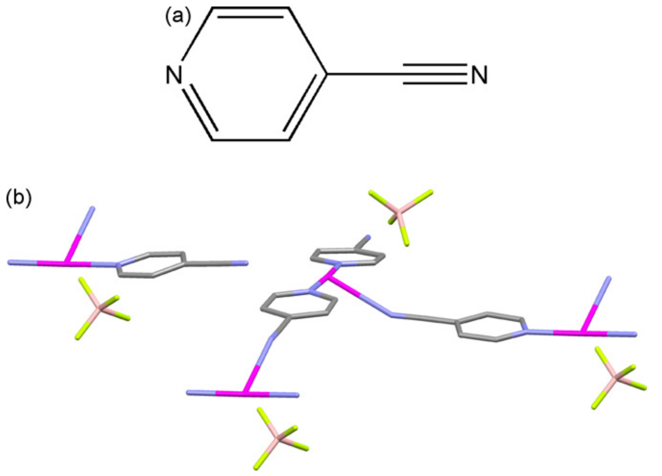


Fig. 6. The ligand 4-cyanopyridine and the polymer $\{[Ag(4\text{-cyanopyridine})_2]BF_4\}_\infty$.

describe the structure of the polymer as consisting of Ag(I) ions linearly coordinated to two pyridine N donors which are further weakly associated with two cyano N donors. One of the *N*(cyano)–Ag bond distances is extremely long at 3.06(1) Å and the Ag(I) ion coordination is described by the authors as distorted square planar. A better description of this structure would be to consider it as T shaped. Interestingly, the authors neglect to mention a similar axial $Ag(I)\cdots F–BF_3^-$ distance of 3.01 Å.

The discrete six coordinate complex Ag(**tap**)$_2$NO$_3$ (**tap** = 1,4,5,8-tetra-azaphenanthrene) is shown in Fig. 7. Nasielski et al. [29] describe the Ag(I) ion as having a strongly folded and twisted square planar stereochemistry. The angle between the normals to the two **tap** planes is 60° and this deviation from coplanarity is assigned to the close proximity of a NO_3^- ion. The authors comment that the complex displays two long and two short bonds to two crystallographically independent **tap** ligands (2.337(5)–2.570(4) Å). However, despite these two long Ag–N bond lengths, the authors claim that the comparable $Ag\cdots O_2NO$ bond lengths of 2.541(10) and 2.656(16) Å are too long for fully covalent but too short for vigorously independent bonding. Also they are reluctant to assign a formal Ag–O bond as the Ag(I) valence shell already contains 18 electrons. Nonetheless, a significant interaction clearly exists between Ag(I) and NO_3^- anion, and the complex should almost certainly be described as six coordinate and not pseudo-square planar as claimed.

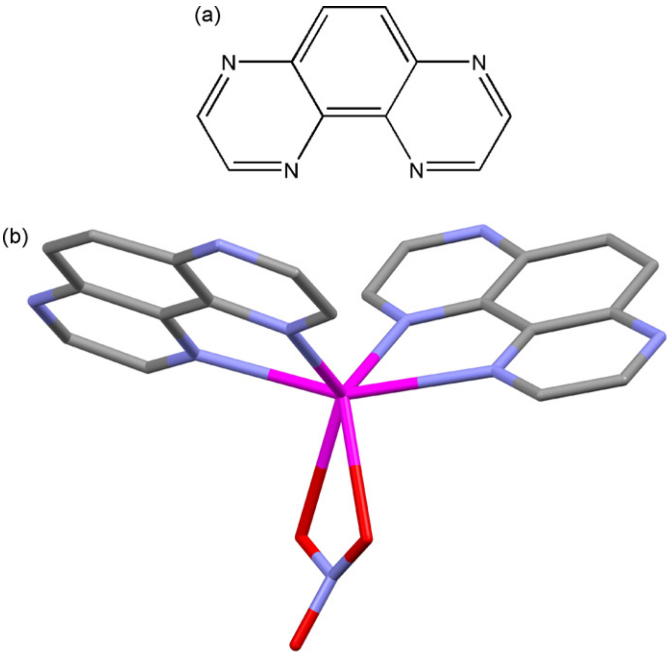


Fig. 7. The ligand **tap** and the complex Ag(**tap**)$_2$NO$_3$.

Within this review, we consider only traditional coordination complexes. We do not consider silver–π complexes where the Ag(I) ion is bound in a π fashion to an arene ring or alkene moiety [30,31]. In these systems, the exact stereochemistry is often ambiguous and their use as directed nodes can be more difficult [32]. A collection of inorganic complexes obtained by solvo-thermal means also display Ag(I) ions in square planar environments. Such complexes are not considered because of their extended mineral-like structures or the absence of any carbon containing ligands [33–39]. Currently, there is considerable debate regarding the existence and nature of d^{10}–d^{10} interactions between neighbouring Ag ions [40–47]. In the main we have disregarded silver complexes where the square plane is completed by Ag–Ag bonds [48], with the exception being where the authors specifically state their Ag(I) complex is square planar as a consequence of a Ag–Ag bond.

In general, a huge variety of donor atoms and ligands are observed in these square planar Ag(I) complexes. These donors range from aromatic, aliphatic and imine N as well as, O, Cl, P and thioether S atoms. Despite this ligand variety some common factors among these complexes can be noted. First, terpyridine-based ligands often enforce pseudo-square planar geometry due to their rigidity and donor atom arrangement. Second, many complexes contain flexible ligands with non-bonding aromatic groups in close proximity to the donor atoms. This means that upon coordination the non-bonding aromatic group shields coordination sites of the central Ag(I) ion.

In this review, the square planar Ag(I) complexes are divided into two categories according to whether they are discrete or polymeric. Within these categories, the complexes are further subdivided in terms of whether or not the square planar Ag(I) ions reside on crystallographic special positions. Finally, in the class of discrete complexes, a special section has been devoted to the complexes containing terpyridine-based ligands, due to their specific geometric requirements.

2. Discrete silver(I) moieties with crystallographically imposed symmetry

2.1. $\{[Rh_2(\mathbf{dfpma})_2(MeCN)_4]_2[Ag(MeCN)_4]\}(PF_6)_5$

The reaction of AgPF$_6$ with [ClRh(cod)]$_2$ in MeCN followed by treatment with bis(difluorophosphine)methylamine (**dfpma**) and subsequent Et$_2$O diffusion, gave red–green iridescent crystals [49]. The product $\{[Rh_2(\mathbf{dfpma})_2(MeCN)_4]_2[Ag(MeCN)_4]\}(PF_6)_5$ is a 1D heterometallic chain which dissociates in solution. The square planar Ag(I) ion resides on a 2/m

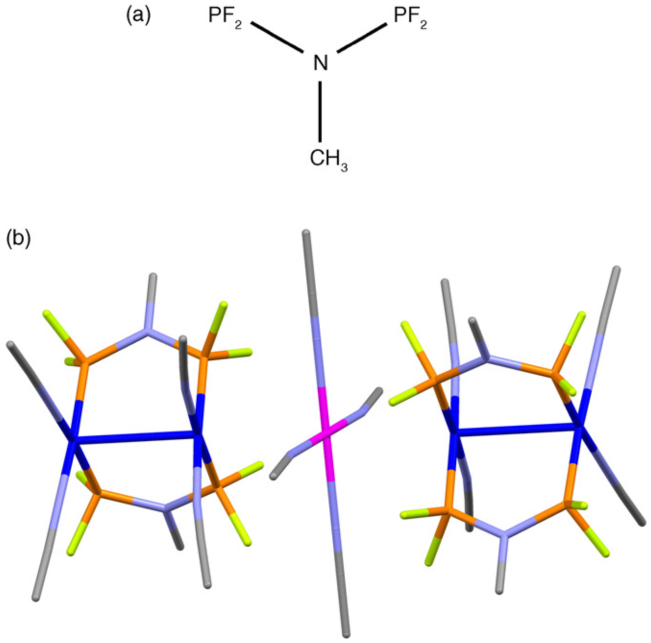


Fig. 8. The ligand **dfpma** and the cations of the complex $\{[Rh_2(\mathbf{dfpma})_2(MeCN)_4]_2[Ag(MeCN)_4]\}(PF_6)_5$.

special position with four coordinated MeCN solvent molecules forming the discrete strictly planar cation. Heyduke et al. comment on the unusual coordination geometry of the bound MeCN molecules to the Ag(I) ion which normally adopt tetrahedral coordination. They suggest a possible reason for the square planar geometry may be that the d_z2 orbital of the Ag(I) ion points towards the empty p_z orbital of the offset Rh dimer. Therefore the cationic Rh(I) dimers reside in axial positions above and below the square plane, and at a Rh···Ag distance of 3.4074(11) Å. The PF_6^- anions have no interaction with the Ag(I) centre. Alignment of the metal-based orbitals along the 1D chain gives rise to novel optical properties, in particular temperature dependent luminescence. The Ag(I) cation perturbs the electronic properties of the 1D chain, when compared with the isolated Rh(I) dimer itself (Fig. 8).

2.2. *[Ag(Pt(NH3)2**omuc**)4](NO3)5·5H2O*

Yellow crystals of $[Ag(Pt(NH_3)_2\mathbf{omuc})_4](NO_3)_5\cdot5H_2O$ were obtained from the reaction of $[Pt_2(NH_3)_4(\mathbf{omuc})_2](NO_3)_2\cdot H_2O$ and $AgNO_3$ in aqueous solution. Lippert and Neugebauer [50] describe the environment about the centrosymmetric Ag(I) centre as square planar from two O donors from each Pt dimer. The Ag···Pt distance is 2.787(1) Å, and adjacent cations are related by another inversion centre. The NO_3^- counterion has no interaction with the Ag(I) centre (Fig. 9).

2.3. *[Ag(**mnso**)2]PF6*

Yellow crystals of $[Ag(\mathbf{mnso})_2]PF_6$ were formed by the 1:1 metal:ligand ratio reaction of the oxa-crowned dithiomaleonitrile ligand (**mnso**) and $AgPF_6$ in MeOH [51]. The Ag(I) ion is located on an inversion centre and is coordinated by a homoleptic donor set of four thioether S atoms from two ligands. Interestingly, Drexler et al. state that 'the overall coordination geometry at Ag(I) cannot be determined in simple terms because the three O atoms of the ligand show long-range interactions (Ag···O distances of 3.077(4), 3.336(4), and 3.339(4) Å)'. Our analysis would describe this stereochemistry as square planar with further weak axial interactions. However, the authors raise a valid and interesting point that illustrates the absolute assignment of stereochemistry in some cases can be somewhat arbitrary. The PF_6^- anion has no interaction with the Ag(I) centre (Fig. 10).

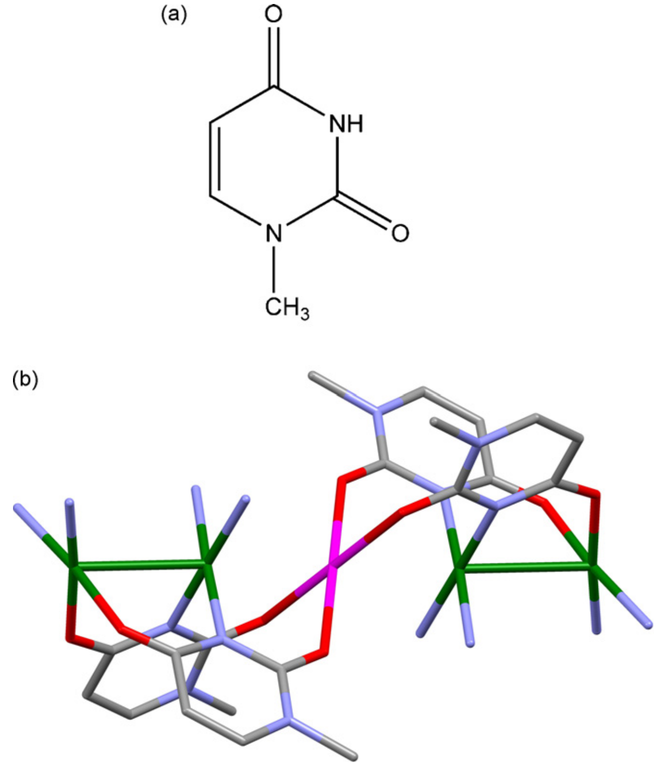


Fig. 9. The ligand 1-methyluracil (H**omuc**) and the cation of the complex $[Ag(Pt(NH_3)_2\mathbf{omuc})_4](NO_3)_5\cdot5H_2O$.

2.4. *[Ag(OH2)2(**pz**Co(NH3)5)2](NO3)7·4H2O*

Orange crystals of $[Ag(OH_2)_2(\mathbf{pz}Co(NH_3)_5)_2](NO_3)_7\cdot4H_2O$ (**pz** = pyrazine) were grown from aqueous solution, and contain Ag(I) ions located on a crystallographic centre of inversion [52]. The Ag(I) ion exhibits crystallographically imposed square planar coordination to two water molecules in *trans* positions and two N donors from the bridging **pz** donor groups. A possible weak axial interaction exists with the NO_3^- counterions (Ag···O–NO_2, 2.899 Å). The complex consists of discrete Co(octahedral)-**pz**-Ag(square planar)-**pz**-Co(octahedral) units (Fig. 11).

2.5. *[Ag(**dptpb**)2]PF6*

Two related square planar structures of $AgPF_6$, $[Ag(\mathbf{dptpb})_2]PF_6$ and $[Ag(\mathbf{pbdb})_2]PF_6$ are reported by

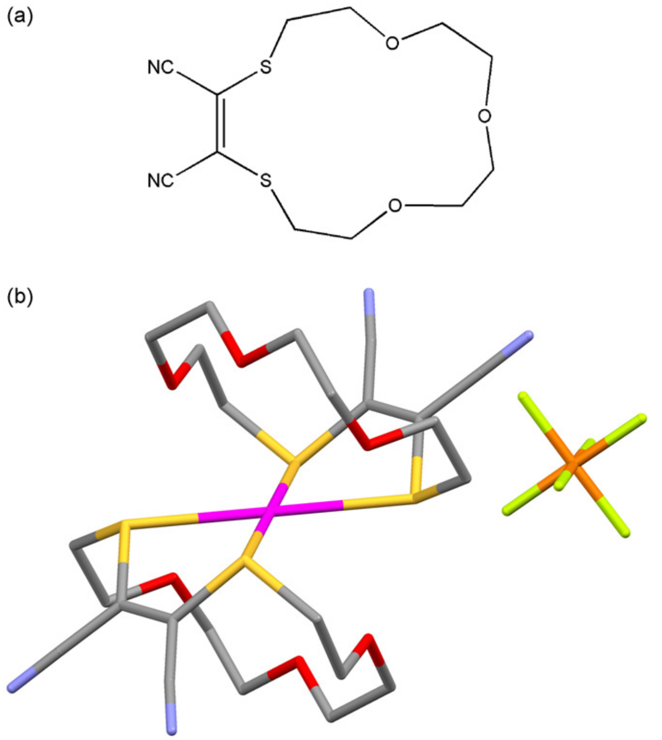


Fig. 10. The ligand **mnso** and the complex $[Ag(\textbf{mnso})_2]PF_6$.

Reger et al. [53] The reaction of $AgPF_6$ with α,α,α′,α′-tetrakis(1-pyrazolyl)-α, α′-bis(2-pyridyl)-1,3-xylene (**dptpb**) gave a colourless, hygroscopic complex $[Ag(\textbf{dptpb})_2]PF_6$ with a 1:2 metal:ligand ratio regardless of reactant ratios used. The complex is labile in solution, and the Ag(I) ion bridges two ligands through the two pyrazolyl groups on each ligand. The Ag(I) ion resides on a centre of symmetry in a distorted square planar environment. The chelate rings, which are formed, adopt a boat like arrangement. The ligand is monotopic rather than ditopic, using only one of its two binding pockets. The authors explicitly comment on the elongation of one axis of the square plane. They attribute the unusual coordination environment to the steric shielding of axial sites by the non-bound pyridine groups above and below the AgN_4 square plane. The pyridine groups appear to be held in place via multiple intramolecular C–H· · ·π weak interactions and the distance from C(ipso) to Ag(I) ion (3.193 Å) is too long to suggest a bonding interaction [92]. These pyridine rings preclude axial interactions with the PF_6^- counterions. The complex forms a 3D net through numerous intermolecular C–H· · ·π and C–H· · ·F interactions (Fig. 12).

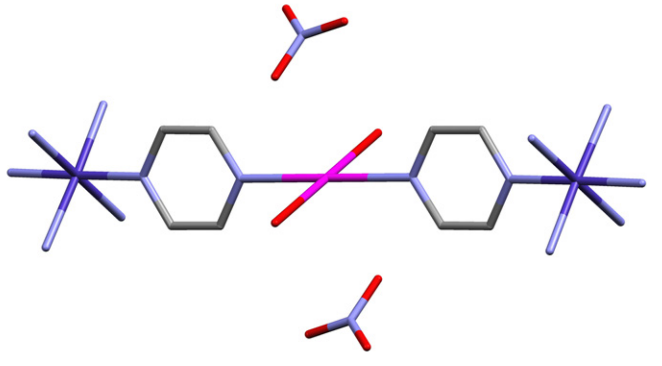


Fig. 11. The cation of the complex of $[Ag(OH_2)_2(\textbf{pz}Co(NH_3)_5)_2](NO_3)_7\cdot 4H_2O$ showing NO_3^- anions associated with the Ag(I) centre.

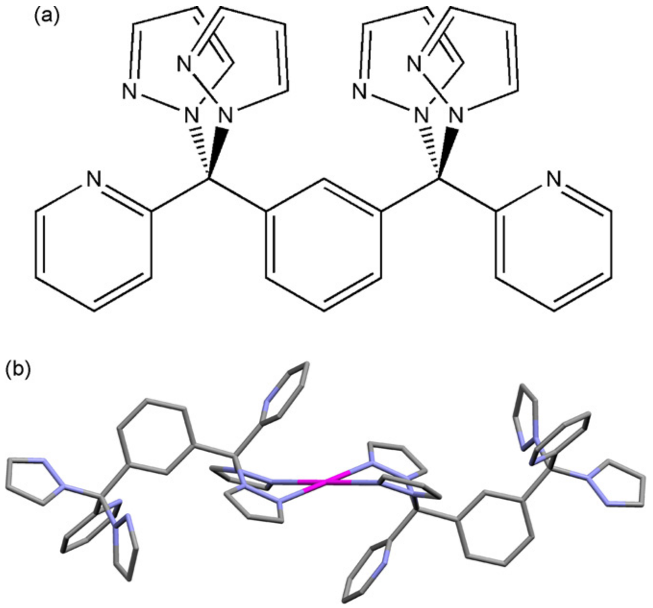


Fig. 12. The ligand **dptpb** and the cation of the complex $[Ag(\textbf{dptpb})_2]PF_6$.

2.6. $[Ag(\textbf{pbdb})_2]PF_6$

Reaction of $AgPF_6$ with α,α-bis(1-pyrazolyl)-α-(2-pyridyl) toluene, **pbdb**, gave a colourless, hygroscopic 1:2 metal:ligand complex $[Ag(\textbf{pbdb})_2]PF_6$ regardless of reactant ratios used [53]. This compound was synthesised to investigate if the meta-linked ligand in $[Ag(\textbf{dptpb})_2]PF_6$ was responsible for the square planar structural motif. Unfortunately, disorder affects almost all components of the system making metrical analysis unreliable. However, the centrosymmetric Ag(I) and square planar geometry found in $[Ag(\textbf{dptpb})_2]PF_6$ persists in $[Ag(\textbf{pbdb})_2]PF_6$, most likely because of the same axial interference by unbound pyridine groups (Fig. 13).

2.7. $[Ag(\textbf{dbdp})_2]PF_6\cdot Me_2CO$

Reger et al. also synthesised $[Ag(\textbf{dbdp})_2]PF_6\cdot Me_2CO$ [54] to continue their investigation of complexes containing short cation· · ·π-interactions [53]. Transparent crystals were grown by diffusion of Et_2O into a solution of $[Ag(\textbf{dbdp})_2]PF_6\cdot Me_2CO$ in Me_2CO. The Ag(I) centre adopts a square planar geometry bound by two equivalent ligands with each binding through two pyrazolyl N donors. This geometry is slightly distorted by the acute bite angle imposed by the chelate ring. The Ag(I) ion sits on an inversion centre and within experimental error the bond lengths to Ag(I) are the same. The proximity of the phenyl groups above and below the AgN_4 plane is again believed to enforce this square planar geometry. The shortest Ag· · ·C (arene) distance of 2.892(2) Å is at the upper limit of the 2.4–2.9 Å range of η^1–Ag(I)· · ·arene π interactions [93], leading to ambiguity

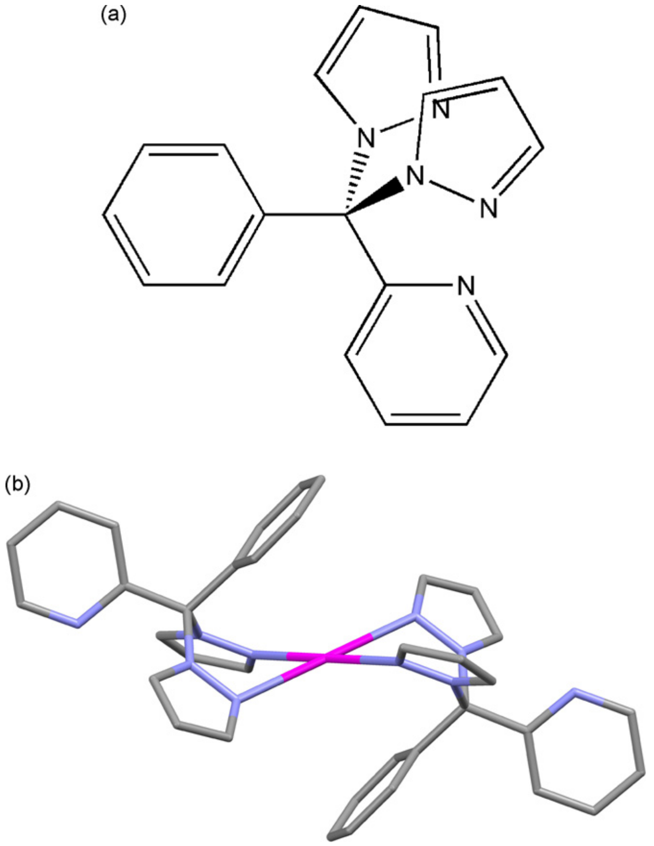


Fig. 13. The ligand **pbdb** and the cation of the complex [Ag(**pbdb**)$_2$]PF$_6$. For simplification, only one form of the disordered ligand is shown.

about its significance. In the solid state, the complex aggregates into chains due to CH$\cdots\pi$ interactions [92]. The structure contains a non-coordinating PF_6^- counterion and a disordered Me_2CO solvent of crystallisation (Fig. 14).

2.8. *[{(**hbtp**)Rh(PPh$_3$)(μ-Cl)$_2$}$_2$Ag]BF$_4$*

The reaction of $AgBF_4$ with the metal complex [(**hbtp**)RhCl$_2$(PPh$_3$)] gave a yellow 1:2 molar Ag to Rh complex [{(**hbtp**)Rh(PPh$_3$)(μ-Cl)$_2$}$_2$Ag]BF$_4$ [12]. The NO_3^- and SbF_6^- analogues of the BF_4^- complex were prepared and display comparable spectroscopic parameters. The structure consists of two octahedral Rh moieties linked to a Ag(I) ion through two double μ-Cl bridges, and the Ag(I) ion sits on a centre of inversion. It has a distorted square planar environment due to different bond lengths and different Cl–Ag–Cl angles. The bond angle differences are due to the restriction caused by the four-membered chloro-bridged rings. Carmona et al. claim that despite the differences the two Ag–Cl distances are in the normal reported range. The Rh$\cdots$Ag distance of 3.6448(4) Å precludes metal-to-metal interactions. They suggest the square planar geometry arises from the high steric requirements of the two bulky Rh centres which favour the formation of the centrosymmetric arrangement. Any axial Ag(I) interactions are sterically prohibited by phenyl groups above and below the $AgCl_4$ plane (Fig. 15).

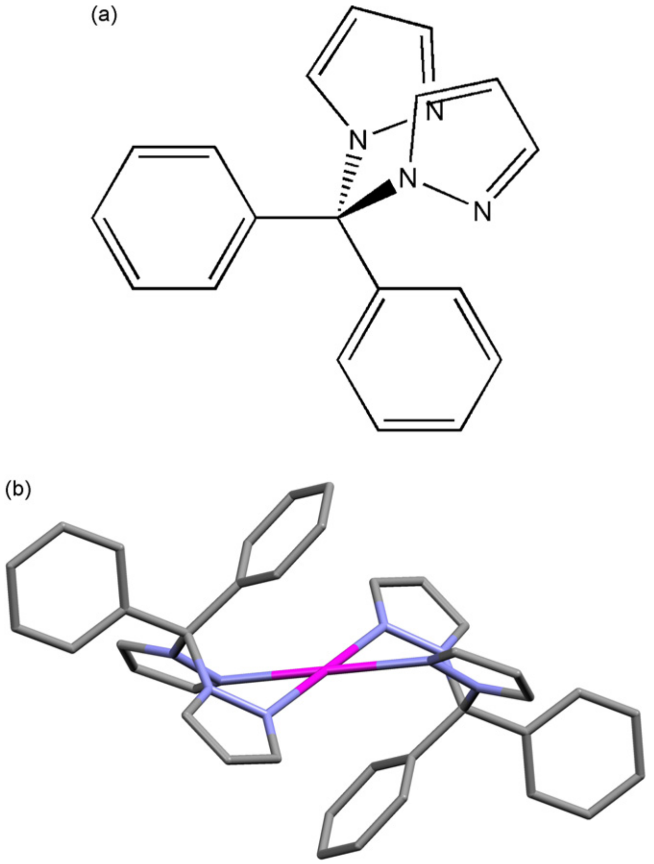


Fig. 14. The ligand **dbdp** and the cation of the complex [Ag(**dbdp**)$_2$]PF$_6$·Me$_2$CO.

2.9. *[Ag(**adpo**)$_4$]SbF$_6$*

The complex [Ag(**adpo**)$_4$]SbF$_6$ is yellow and is formed by the reaction of [Ag(MeCN)$_4$]SbF$_6$ and four equivalents of 5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene (**adpo**) in $CHCl_3$, followed by extraction into CH_2Cl_2 and subsequent addition of hexane [55]. This discrete complex has a Ag(I) ion residing on a four-fold axis perpendicular to the AgP_4 plane. The Ag(I) ion binds four identical ligands through the P donor with the axial sites sterically blocked by crowns of ^{t}Bu ligand substituents (Fig. 16).

2.10. *[Ag$_7$(**bmimen**)$_6$](ClO$_4$)$_7$·MeCN*

The *in situ* preparation of **bmimen** (**bmimen** = 1,2–bis[(1-methyl-2-imidazolyl)methyleneamino]ethane) by reaction of the precursors 1,2-diaminoethane and 1-methylimidazole-2-carbaldehyde, and subsequent addition of $AgClO_4$ followed by the vapour diffusion of Et_2O gave colourless [Ag$_7$(**bmimen**)$_6$](ClO$_4$)$_7$·MeCN crystals [45]. The structure contains a helical heptanuclear cation with its ends capped as double helices. The central Ag(I) ion of the chain of seven approximately linear Ag(I) ions resides on a centre of inversion in a distorted square planar stereochemistry with a *cis* N–Ag–N angle of 70.9(2)°. The donors surrounding the central Ag(I) ion consist of four N atoms (one imidazolyl and one imine N) from

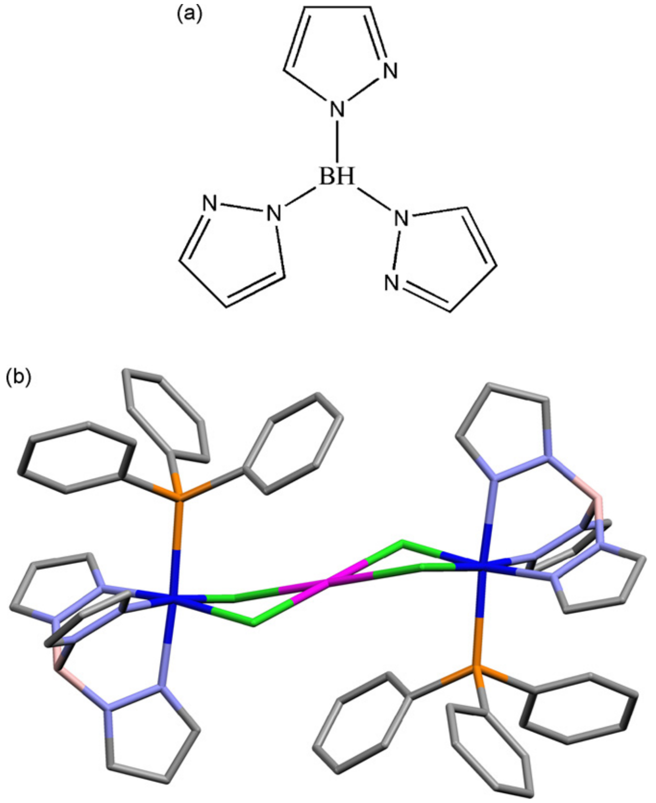


Fig. 15. The ligand **hbtp** and the cation of the complex [{(**hbtp**)Rh(PPh$_3$)(μ-Cl)$_2$}$_2$Ag]BF$_4$.

two different **bmimen** ligands. The axial sites are involved in weak Ag$\cdots$Ag interactions [2.9911(8) Å] between neighbouring three-coordinate Ag(I) ions. The heptanuclear chains are joined end-to-end by further Ag$\cdots$Ag interactions [3.029(1) Å] to give 1D chains (Fig. 17).

2.11. *[Ag$_4$(**oesq**)(**odsq**)(NO$_3$)$_4$]·H$_2$O*

The flexible linear polydentate ligands 1,5-bis(8-quinolylsulfanyl)-3-oxapentane (**oesq**) and 1,8-bis(8-quinolylsulfanyl)-3,6-dioxaoctane (**odsq**), were designed to have a strong influence on the architecture adopted. Su et al. [56] were attempting to construct "novel molecular architectures" that may be unattainable with stereo-rigid metals, because they provide a more limited range of angular motifs (Fig. 18).

The colourless complex [Ag$_4$(**oesq**)(**odsq**)(NO$_3$)$_4$]·H$_2$O was prepared by diffusion of Et$_2$O into a solution of four equivalents of AgNO$_3$ and a 1:1 molar ratio of **oesq** and **odsq**. This structure has been reported on two separate occasions by the same authors [56,57]. The two ligands are arranged face-to-face with crystallographically imposed two-fold symmetry through the **oesq** ether O atom and two crystallographically unique Ag(I) ions. Both of these unique Ag(I) ions have tetrahedrally distorted square planar Ag(I) environments with N$_2$S$_2$ donor sets. Su et al. claim that each of these Ag(I) ions has weak axial interactions to neighbouring ether O atoms (Ag$\cdots$O 2.69 Å). We consider this Ag$\cdots$O distance to be around the lower limit for a weak interaction. The remaining axial site is blocked by the other Ag(I) at 3.73 Å. The remaining Ag(I) ion linking the face-to-face dimers has a square pyramidal geometry.

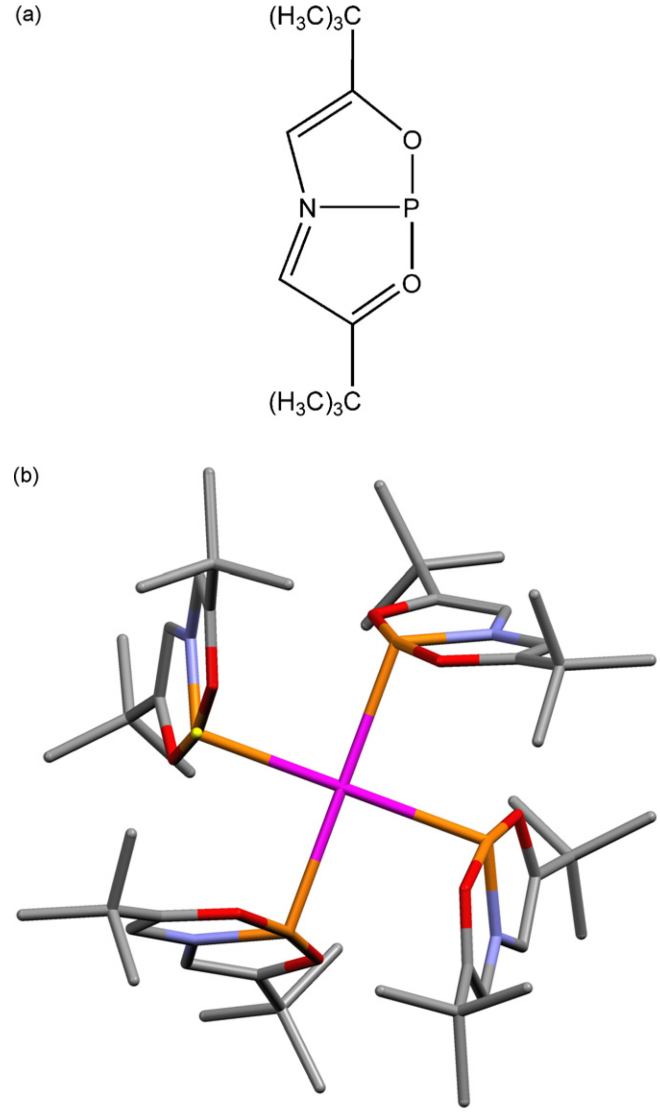


Fig. 16. The ligand **adpo** and the cation of the complex [Ag(**adpo**)$_4$]SbF$_6$.

2.12. *Section summary and comments*

These 11 complexes generally involve aromatic N donors but also include O, Cl, P, S, and imine N donors. Eight of these complexes have homoleptic donor environments. These crystal structures are all examples of a Ag(I) ion in a discrete complex residing on a special position that necessitates that the *trans*-bonds of the square plane are symmetry related. As a result, the Ag ion and donor set are strictly planar, with the exception of [Ag$_4$(**oesq**)(**odsq**)(NO$_3$)$_4$]·H$_2$O and [Ag(**adpo**)$_4$]SbF$_6$ containing Ag(I) ions on two-fold and four-fold rotation axis, respectively. This means that providing the two unique Ag bonds are not of equal length, the complex will exhibit two longer and two shorter bonds. Of these 11 complexes, 5 exhibit steric shielding of Ag(I) diaxial sites by aromatic rings or ^{t}Bu groups. Three of these possess very similar ligands prepared by the same

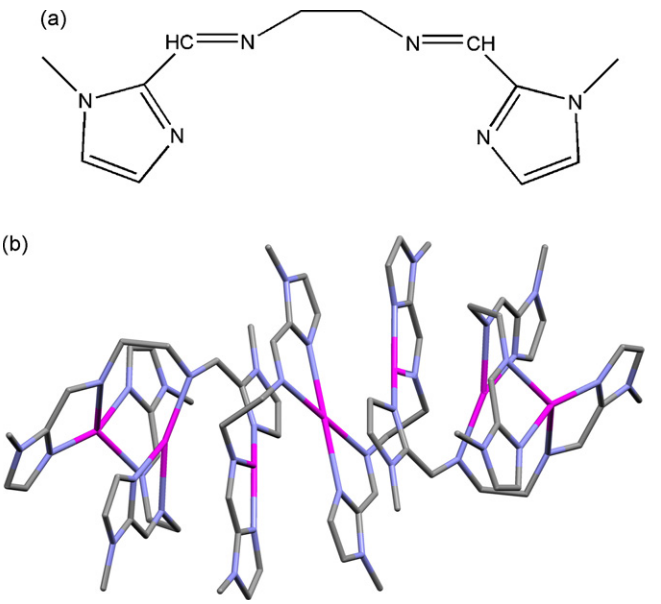


Fig. 17. The ligand **bminen** and the cation of the complex [Ag_7(**bmimen**)$_6$](ClO_4)$_7$·MeCN.

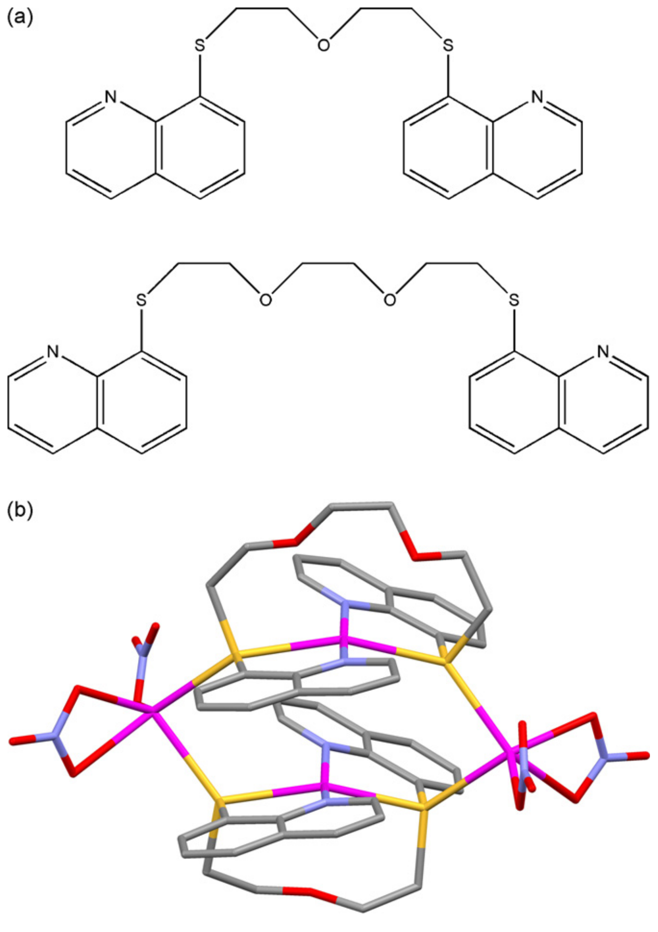


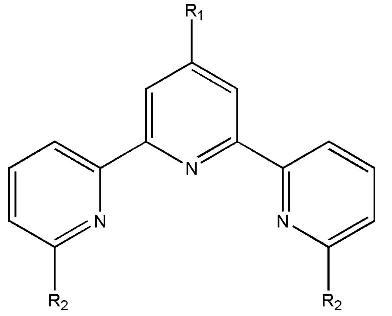
Fig. 18. The ligands **oesq** and **odsq** (top and bottom, respectively), and the complex [Ag_4(**oesq**)(**odsq**)(NO_3)$_4$]·H_2O. Waters of crystallisation have been omitted for clarity.

research group giving similar coordination environments. However, [{(**hbtp**)Rh(PPh_3)(μ-Cl)$_2$}$_2$Ag]BF_4 has a very different ligand but still gives rise to a similar steric environment about Ag(I). Three of the 10 complexes possess possible weak Ag(I) axial interactions with neighbouring cationic metal moieties. The remaining three complexes possess weak axial interactions to neighbouring counterions or ether O atoms.

3. Discrete silver(I) moieties of terpyridine based ligands

*3.1. [{Ag(**tpy**)(MeCN)}$_2$](PF$_6$)$_2$*

As part of an investigation into the formation of dinuclear double helicates using Ag(I) and oligopyridine ligands in a similar manner to their Cu(I) systems, Constable et al. prepared two discrete square plane Ag(I) complexes [58]. The first, [{Ag(**tpy**)(MeCN)}$_2$](PF_6)$_2$, is colourless and prepared by the reaction of AgOAc with 2,2′:6′,2″-terpyridine (**tpy**) and subsequent metathesis by NH_4PF_6. The authors considered the complex to be dinuclear as a result of a weak Ag· · ·Ag interaction (3.1698(12) Å) between two crystallographically distinct square planar [Ag(**tpy**)(MeCN)]$^+$ cations twisted at 137.27° to each other. The authors comment that the sum of the internal angles about each Ag(I) ion is close to 360° in each case. No significant cation–anion interactions were reported. The remaining axial site of each dimer is blocked by the stacking of adjacent dimers giving Ag· · ·pyridine distances in the range 3.34–3.41 Å (Figs. 19 and 20).



tpy: R_1=H, R_2=H
tpyp: R_1=Ph, R_2=H
dptpy: R_1=H, R_2=Ph
tpysm: R_1=SMe, R_2=H

Fig. 19. The terpyridine based ligands utilised in this group of Ag(I) complexes.

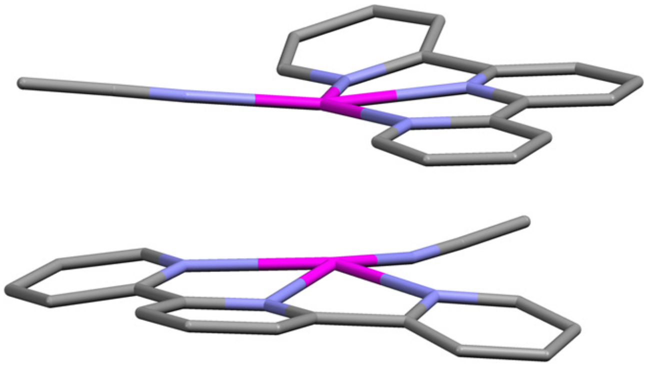


Fig. 20. The cations of the complex [{Ag(**tpy**)(MeCN)}$_2$](PF_6)$_2$.

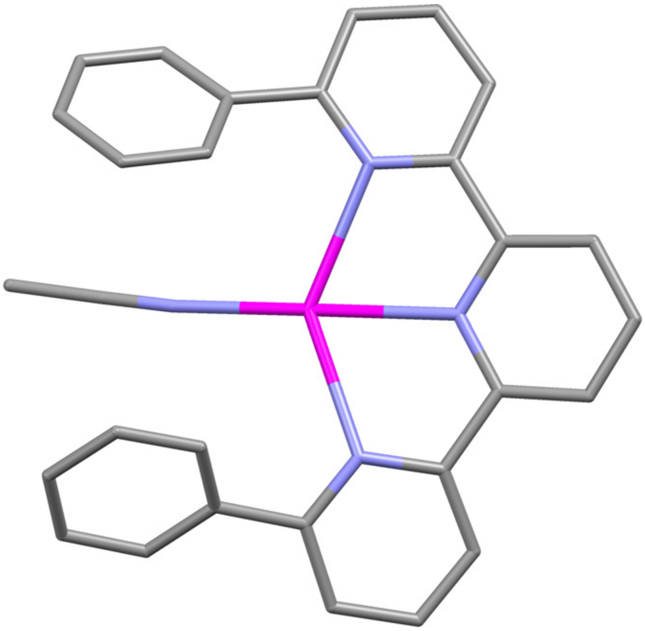


Fig. 21. The cation of the complex [Ag(**dptpy**)(MeCN)]BF_4·MeCN.

3.2. [Ag(**dptpy**)(MeCN)]BF_4·MeCN

The second complex prepared by Constable et al., [Ag(**dptpy**)(MeCN)]BF_4·MeCN is also colourless and was formed from the reaction of the phenyl derivatised terpyridine, 6,6′′-diphenyl-2,2′:6′,2′′-terpyridine (**dptpy**) and [Ag$(MeCN)_4$]BF_4 in MeOH, followed by recrystallisation from MeCN and subsequent addition of Et_2O [58]. The complex is approximately square planar. The ligand **dptpy** is more sterically demanding than **tpy** and seems to prevent formation of a dinuclear unit. The sum of the angles about the Ag(I) ion is 363°. The Ag(I) axial sites are both blocked by Ph rings of adjacent molecules at distances of 3.191 and 4.240 Å (Fig. 21).

3.3. [Ag_3(**tpy**)$_4$][(MeCN)Ag(**tpy**)]$(ClO_4)_4$

The equimolar reaction of $AgClO_4$ and **tpy** in MeCN gave the yellow complex [Ag_3(**tpy**)$_4$][(MeCN)Ag(**tpy**)]$(ClO_4)_4$ [59]. The components of the unit cell are alternating oligonuclear Ag_3 and mononuclear Ag cationic moieties, and ClO_4^- counterions. The counterions have no interactions with the Ag(I) centres. Silong et al. describe the Ag(I) ion at the centre of the mononuclear cation as four-coordinate planar, with a sum of in-plane angles of 359.9°. The Ag(I) ion has three longer bonds to **tpy** and a shorter bond to the MeCN nitrogen atom. The aromatic moieties of the tridentate **tpy** ligand are twisted so the overall structure is somewhat buckled, which the authors attribute to packing forces including inter-ring hydrogen contacts. The more complex trinuclear cation is helical with a collinear Ag_3 array. The coordination environment about the central Ag(I) ion is also described as four-coordinate planar, with a sum of in plane angles of 359.6°. The donors are four crystallographically unique **tpy** nitrogen atoms, with two long and two short Ag–N distances. The shorter two arise from binding to the outer-ring N atoms of a pair of **tpy** ligands; the longer two from binding to the centre-ring N atoms of the same two ligands. These centre-ring N donors also coordinate in a bifurcating nature to the two outer Ag(I) ions which the authors note is unusual. The remaining coordination spheres of two outer Ag(I) ions, which adopt pseudo-square pyramidal arrangements are filled by two further **tpy** ligands that are less twisted than the two central ligands. The central ligands are very twisted resulting in the helical nature of the cation. The central Ag ion of the helix has weak axial interaction with terminal Ag ions of the helix at distances of 3.066 Å. The Ag(I) ion of the mononuclear cation has its axial sites blocked by pyridine rings from adjacent helices at Ag· · ·pyridine distances of 3.15 and 3.66 Å (Fig. 22).

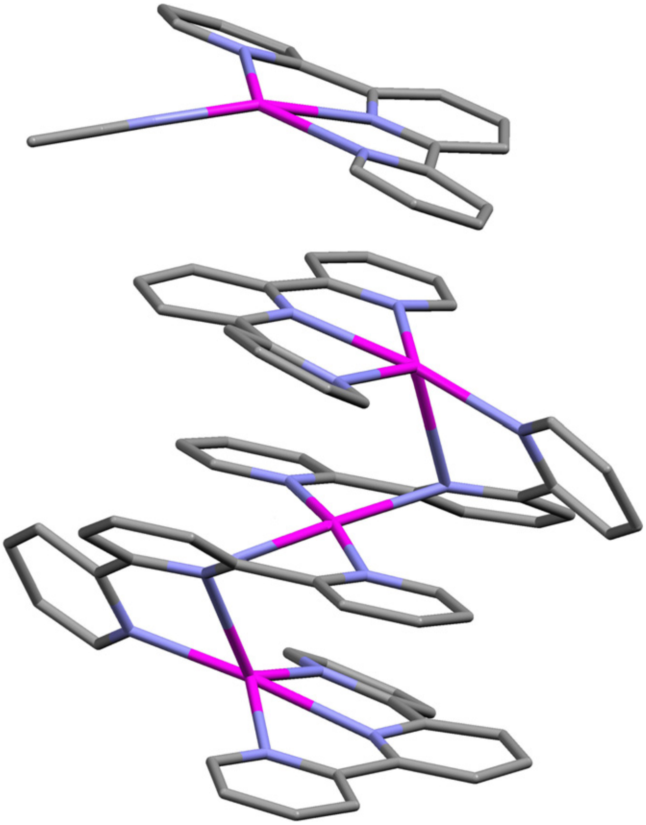


Fig. 22. The cations of the complex [Ag_3(**tpy**)$_4$][(MeCN)Ag(**tpy**)]$(ClO_4)_4$.

3.4. [Ag(**tpyp**)(MeCN)]PF_6·MeCN

The reaction of 4′-phenyl-2,2′:6′,2′′-terpyridine (**tpyp**) with $AgPF_6$ in Me_2CO and subsequent evaporation of the product from MeCN gave yellow crystals [26]. The complex [Ag(**tpyp**)(MeCN)]PF_6·MeCN is a distorted but very planar moiety with no imposed symmetry. The ligand enforces a distorted square planar geometry in which the bond lengths about the Ag(I) ion vary among themselves. Hou et al. comment that there is no aggregation due to Ag· · ·Ag interactions despite this being commonly observed in similar terpyridine systems. The authors do not comment on the stacking which occurs along the b axis and is caused by weak η^2 Ag· · ·pyridine interactions in the range 3.17–3.31 Å. This gives rise to planar neatly stacked

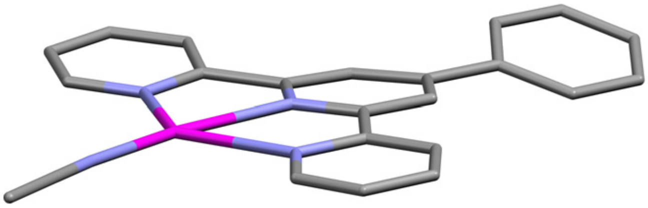


Fig. 23. The cation of the complex [Ag(**tpyp**)(MeCN)]PF_6·MeCN.

adjacent molecules which block the axial sites. The PF_6^- anion has no interaction with the Ag(I) centre (Fig. 23).

3.5. [Ag(**tpysm**)(MeCN)]PF_6·MeCN

After refluxing AgOAc and 4′-thiomethyl-terpyridine (**tpysm**) in MeOH the filtrate was treated with an excess of NH_4PF_6 to give a white precipitate of [Ag(**tpysm**)(MeCN)]PF_6 [60]. The discrete complex [Ag(**tpysm**)(MeCN)]PF_6·MeCN is similar to [{Ag(**tpy**)(MeCN)}$_2$]$(PF_6)_2$ [58]. The Ag(I) environment is described by Hannon et al. as four-coordinate square planar. The planar cations are π stacked in an anti-parallel fashion through the terpyridine aromatic rings. This stacking sterically blocks the axial sites of Ag(I) with the authors commenting on the possibility of a η^2 arene interaction at one site (3.27 Å). The counterions and non bound MeCN have no interactions with the central Ag(I) and interact only with **tpysm** and each other (Fig. 24).

3.6. [Ag(**tpyor**)(MeCN)]PF_6·Et_2O

The reaction of a chirally derivatised tridentate terpyridine ligand (**tpyor**), shown in Fig. 25, with AgOAc followed by precipitation with NH_4PF_6 and subsequent recrystallization from MeCN gave a colourless distorted square planar terpyridine complex [Ag(**tpyor**)(MeCN)]PF_6·Et_2O [61]. There are two chemically identical molecules in the asymmetric unit. These planar cations are stacked anti-parallel to each other. The MeCN bends away from the bulky chiral substituent. The Ag(I) axial sites are blocked by the aromatic π stacking and the authors claim a π-bonding interaction between Ag(I) and the central ring of the terpyridine ligand (3.646 and 3.514 Å).

3.7. Section summary and comments

The six crystal structures in this group are Ag(I) complexes of terpyridine style ligands. In these complexes, the ligands enforce a planar four-coordinate environment about the Ag(I). The constrained nature of the ligand donor set is such that the three bonds to the Ag(I) centre are very prescribed, and are significantly distorted away from square planar geometry towards the ideal bite angles of the terpyridine ligand. Interestingly, in every case the fourth donor is a MeCN nitrogen atom with MeCN–Ag(I) distances in the range 2.155–2.236 Å. This bond is significantly shorter than the three Ag(I)–N(py) bonds. The prescribed nature of the **tpy** ligand and the short MeCN bond means that these complexes do not exhibit two longer and two shorter bonds about the Ag(I) ion as is often observed in square planar Ag(I) complexes. The one exception to the formation of a simple planar four coordinate environment about a Ag(I) centre is the complexation of terpyridine and $AgClO_4$ in [Ag_3(**tpy**)$_4$][(MeCN)Ag(**tpy**)]$(ClO_4)_4$. The bifurcated bonding by terpyridine in the trinuclear moiety removes the usual terpyridine geometric constraints giving two longer and two shorter Ag(I)–N bonds about the central Ag(I) ion. All Ag(I) centres in this group have their axial sites blocked either by aromatic rings, or for the few exceptions weak axial interactions with neighbouring Ag(I) ions. The stacking of aromatic rings in these six crystal structures follows an approximate anti-parallel pattern. These ligands are arguably less useful as nodes in crystal engineering compared to most others presented in this review, because the structurally enforcing nature of the ligand generally produces similar planar discrete moieties by locking up most of the ligands binding sites.

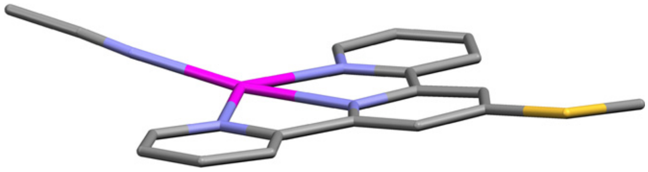


Fig. 24. The cation of the complex [Ag(**tpysm**)(MeCN)]PF_6·MeCN.

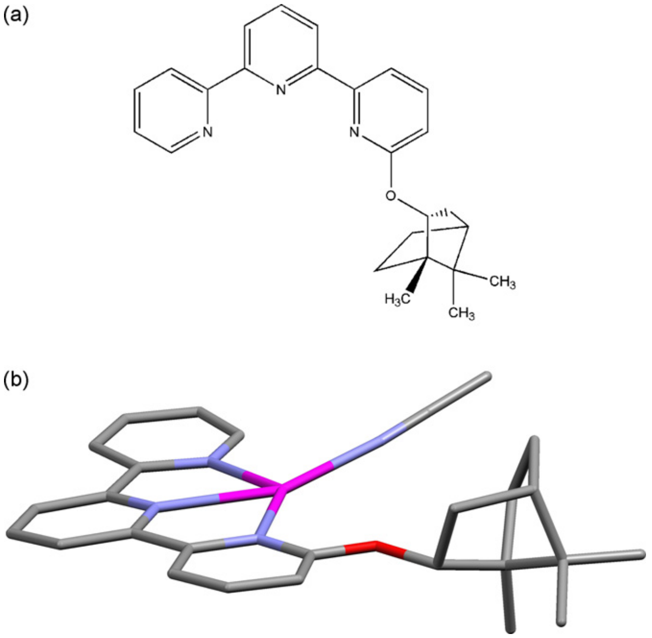


Fig. 25. The ligand **tpyor** and the cation of the complex [Ag(**tpyor**)(MeCN)]PF_6·Et_2O.

4. Other discrete silver(I) moieties

4.1. [Ag_2(**ptp**)$_2$]$(CF_3SO_3)_2$

The complex [Ag_2(**ptp**)$_2$]$(CF_3SO_3)_2$ is a deep red 2:2 planar dimer formed from 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**ptp**) and $AgCF_3SO_3$ in $MeNO_2$ and recrystallized from MeCN

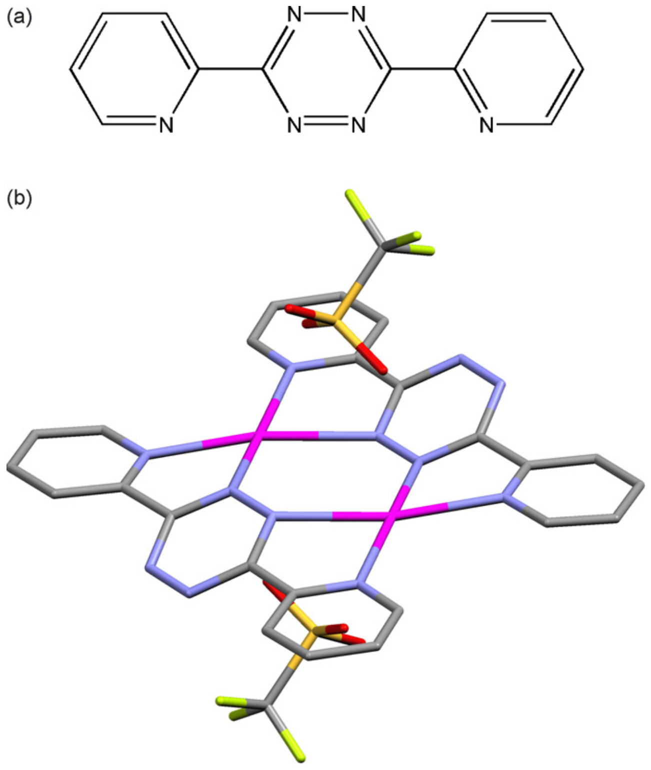


Fig. 26. The ligand **ptp** and the complex $[Ag_2(\textbf{ptp})_2](CF_3SO_3)_2$.

[25,62]. The dimer has a centre of inversion through the centre of the molecule and each Ag ion is surrounded by four crystallographically independent N donors. The complex shows one Ag–N bond distance which is much longer than the three others (Fig. 26). Constable et al. were attempting to form a 4:4 grid complex in which the Ag(I) ions adopt a tetrahedral stereochemistry as found in the complex of **ppp** (ligand shown in Fig. 27) with Cu(I) [94]. Instead they found a distorted square planar Ag(I) complex in which adjacent molecules are intercalated through weak π-stacking interactions (centroid-to-centroid distance 3.56 Å) involving the terminal pyridine rings. There are weak axial Ag···O–SO_2CF_3 interactions of 2.806(9) and 2.969(8) Å. The authors state these interactions preclude intermolecular Ag···Ag interactions by causing adjacent molecules to be offset, with the closest Ag···Ag distance being 5.430 Å. Electrospray mass spectrometry indicates that the BF_4^- analogue probably has a similar 2:2 structure. It is suggested that square planar Ag(I) ions may have a role in fine tuning aspects of the synthesis of topologically novel species. No explanation is provided for why such a small change between the two related ligands **ptp** and **ppp** causes this change in stereochemistry.

4.2. $[Ag(\textbf{ppp})_2]CF_3SO_3$

Constable et al. have prepared the yellow $[Ag(\textbf{ppp})_2]CF_3SO_3$ from the reaction of 3,6-bis(2-pyridyl)pyridazine (**ppp**) with $AgCF_3SO_3$ in $MeNO_2$ and subsequent crystallization from a hot MeCN/Et_2O solution [10]. Dimers of cations with a Ag···Ag distance of 3.223(1) Å are present in the complex, with this Ag···Ag distance blocking one axial site. No short cation–anion interactions exist and the remaining axial sites are blocked by pyridine N atoms from adjacent dimers at a distance of 3.234 Å. The ligands are approximately planar and there is extensive π-stacking between the coplanar ligands both within dimers and between adjacent dimmers (Fig. 27).

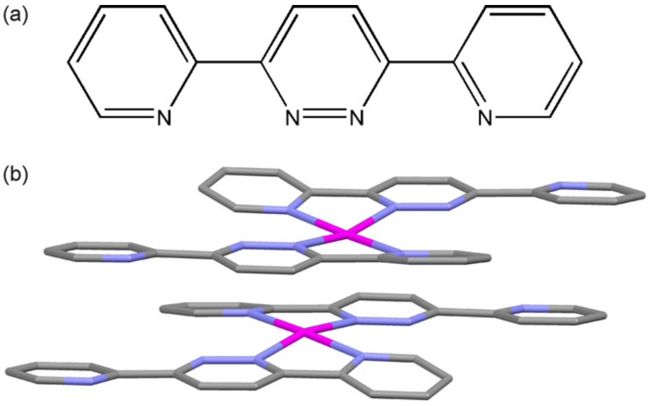


Fig. 27. The ligand **ppp** and the cations of the complex $[Ag(\textbf{ppp})_2]CF_3SO_3$.

4.3. $[Ag_2(\textbf{tipm})_2](BF_4)_2$

Orange needles of a 2:2 dimer similar to $[Ag_2(\textbf{ptp})_2](CF_3SO_3)_2$ in Fig. 26 were formed from the reaction of **tipm** with $AgBF_4$, and subsequent diffusion of Et_2O vapour into a $MeNO_2$ solution [63]. Price et al. describe the coordination environment as tetrahedrally distorted square planar with further weak interactions to a BF_4^- counterion at 2.920(3) Å. The remaining axial site would appear to be blocked by both a BF_4^- anion at 3.556 Å and a methyl hydrogen atom from a neighbouring molecule at 3.654 Å. The shortest Ag···Ag distance is 3.8001 Å, and is significantly shorter than that observed in $[Ag_2(\textbf{ptp})_2](CF_3SO_3)_2$ above. The authors attribute the square planar geometry to the bulky trimethyl phenyl groups causing a twist out of planarity of the ligand, and comment on the plasticity of Ag(I) offering the opportunity to explore the effects of secondary bonding interactions on supramolecular architectures (Fig. 28).

4.4. $[Ag(\textbf{mpp})]_4(CF_3SO_3)_4$

The complex $[Ag(\textbf{mpp})]_4(CF_3SO_3)_4$ was prepared by reaction of 4-(2-pyridyl)-pyrimidine (**mpp**) and $AgCF_3SO_3$ in $MeNO_2$ [64]. It is a centrosymmetric tetranuclear molecular rectangle containing two unique Ag(I) ions, neither of which occupy any special positions. Beauchamp and Loeb describe these two Ag(I) ions as having a distorted square planar geometry coordinated to the chelating sites of two different **mpp** ligands, and a linear geometry bridging N donor atoms of two different **mpp** ligands, respectively. These bridging Ag(I) ions are spanned by $CF_3SO_3^-$ counterions, which help contribute to the formation of the rectangle, given that the BF_4^- analogue forms a molecular square and the NO_3^- analogue forms a 1D chain. The authors draw attention to the distortion of the rectangle from planarity, and attribute it to tetrahedral distortion about the chelated Ag(I) ion. They note the chelated Ag(I) ion has a

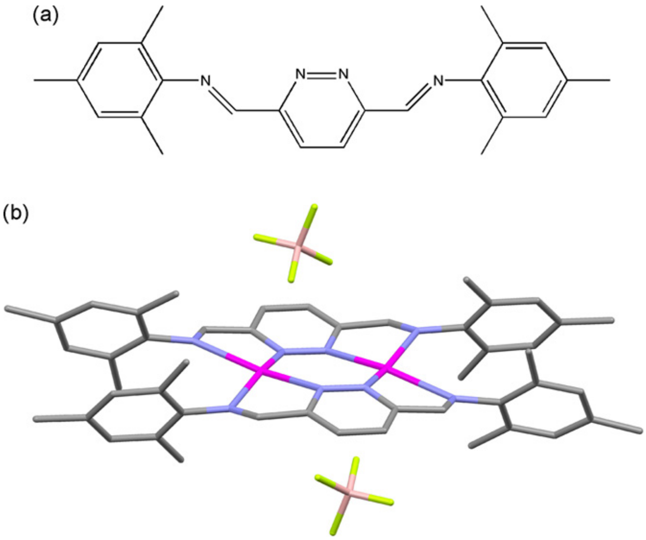


Fig. 28. The ligand **tipm** and the complex $[Ag_2(\textbf{tipm})_2](BF_2)_2$.

Ag$\cdots$O–SO_2CF_3 distance of 2.83 Å, however our analysis of their crystal structure clearly shows that Ag$\cdots$O–SO_2CF_3 distance to be 2.566 Å. We consider 2.566 Å is well inside the range for a formal Ag–O bond and as such this geometry would be more accurately described as five coordinate. In a similar manner, the authors note Ag$\cdots$O–SO_2CF_3 distances of 2.592 and 2.829 Å from a counterion to the two bridging Ag(I) ions. Again we consider a distance of 2.592 Å to constitute a Ag–O bond and think this environment should more correctly be described as three coordinate and not linear (Fig. 29).

4.5. $[Ag(\textbf{dpbipy})_2]BF_4\cdot(11/3)DMF\cdot(1/3)Me_2O$

The complex $[Ag(\textbf{dpbipy})_2]BF_4\cdot(11/3)DMF\cdot(1/3)Me_2O$ was prepared as yellow crystals from the 2:1 reaction of the bisphenol ligand **dpbiby** and $AgBF_4$ in MeCN/DMF followed by the reduction of solvent and addition of EtOH [65]. Constable et al. have solved the X-ray diffraction data by including a ‘chemically meaningless but crystallographically acceptable’ Me_2O molecule. The two independent $Ag(\textbf{dpbipy})_2{}^+$ cations are described as close to planar. The two unique Ag(I) ions are both four coordinate and have their axial sites blocked by aromatic C atoms from adjacent cations at Ag$\cdots$C distances of 3.233–3.280 Å. One Ag(I) ion occupies an inversion centre while the other has no special symmetry and has a more distorted coordination stereochemistry. The authors comment that the dominant factor in the formation of the planar Ag(I) centres appears to be a combination of π–π and Ag$\cdots$π interactions (Fig. 30).

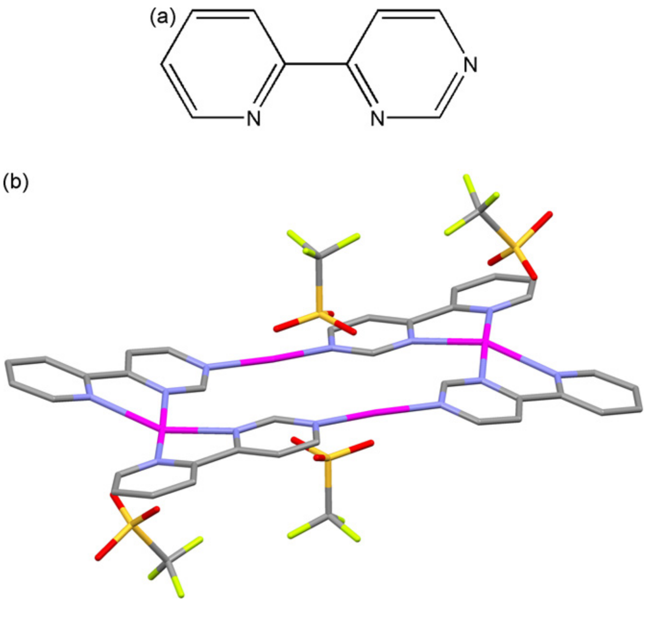


Fig. 29. The ligand **mpp** and the complex $[Ag(\textbf{mpp})]_4(CF_3SO_3)_4$.

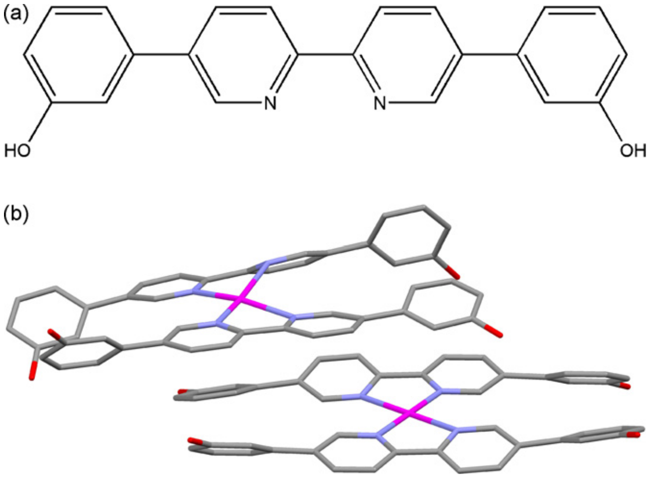


Fig. 30. The ligand **dpbipy** and the complex $[Ag(\textbf{dpbipy})_2]BF_4\cdot(11/3)DMF\cdot(1/3)Me_2O$. Counter anions and solvent of crystallisation molecules have been removed for clarity.

4.6. $[Ag_2(\textbf{dmpp})_4(CO_2CF_3)_2]$

Colourless crystals of $[Ag_2(\textbf{dmpp})_4(CO_2CF_3)_2]$ were obtained from cooling a MeCN solution of $AgCO_2CF_3$ and 2,6-bis(3′,5′-dimethylphenyl)pyrazine (**dmpp**) [66]. The geometry about the Ag(I) ion is somewhat buckled and Schultheiss et al. do not attempt to define the stereochemistry. The 1:2 metal:ligand complex has a centre of symmetry through the middle of the dimer. The authors draw attention to the Ag$\cdots$Ag distance of 3.1014(3) Å at one axial site and refer to the controversy surrounding potential interactions. The remaining axial site is sterically blocked by a pyridine ring of an adjacent π-stacked dimer at a distance of 3.912 Å (Fig. 31).

4.7. $[Ag(\textbf{fmip})]BF_4\cdot CHCl_3$

The reaction of $AgBF_4$ and the bisbidentate Schiff-base ferrocene ligand **fmip** and subsequent slow evaporation from $CHCl_3$ gave the red complex $[Ag(\textbf{fmip})]BF_4\cdot CHCl_3$ [67]. The ligand coordinates four donors (two pyridine and two imine nitrogen atoms) to a single Ag(I) ion with a resulting square planar stereochemistry. One axial site may have

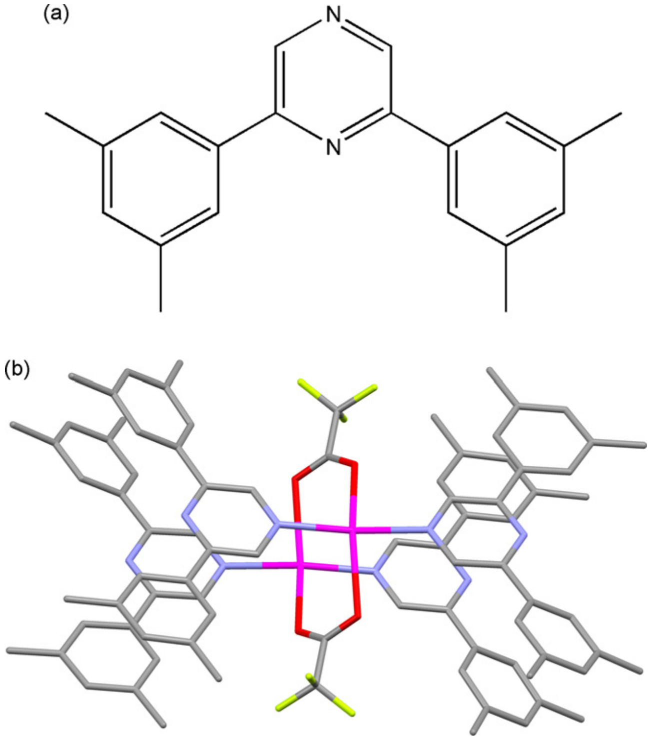


Fig. 31. The ligand **dmpp** and the discrete complex [Ag_2(**dmpp**)$_4$(CO_2CF_3)$_2$].

a weak η^2 Ag···pyridine interaction (3.27 Å) with an adjacent molecule while the other axial site is blocked by an adjacent cyclopentadiene ring (3.61 Å). Interestingly, slow evaporation from MeCN/MeOH gave a similar red complex, [Ag(**fmip**)(MeCN)]BF_4 with the only difference being a bound MeCN and no solvent of crystallisation. The stereochemistry of [Ag(**fmip**)(MeCN)]BF_4 is pseudo square pyramidal ($\tau = 0.02$) [95] showing the structurally enforcing nature of this ligand with its propensity to bind in a planar four-coordinate arrangement (Fig. 32).

4.8. $(NBu_4)_4[Ag_2(Mo_5O_{13}(OMe)_4NO)_2]$

Purple crystals of $(NBu_4)_4[Ag_2(Mo_5O_{13}(OMe)_4NO)_2]$ were obtained by the equimolar reaction and of $(NBu_4)_2[Mo_5O_{13}(OMe)_4NO\{Na(MeOH)\}]\cdot 3H_2O$ and $AgNO_3$ in MeOH [68]. Villanneau et al. describe a complex containing two crystallographically identical square planar Ag(I) ions related by a centre of inversion through the centre of the anionic molecule. The square planar Ag(I) coordination environment is slightly distorted, and the authors comment on the unusually small Ag···Ag distance of 2.873 Å between the Ag(I) ions. The remaining axial sites are blocked by the bulky butyl side arms of the counter cations (Fig. 33).

4.9. $[Ag_4$(**odsq**)$_2(NO_3)_4]$

The colourless complex [Ag_4(**odsq**)$_2$(NO_3)$_4$] was prepared by diffusion of Et_2O into an MeOH/MeCN solution of $AgNO_3$ and **odsq**. The tetranuclear complex is a face-to-face dimer of [Ag_2(**odsq**)(NO_3)$_2$] units with a crystallographic inversion centre between them. Each of the two units contains two Ag(I) ions in different coordination geometries. The first is square planar and binds to a single ligand through two quinoline N donors and two thioether S donors. The authors claim one axial site has weak interactions with two ether O atoms of the ligand backbone (Ag···O(ether) 2.678(6) and 2.764(6) Å). Our analysis indicates this smaller distance is around the lower limit for such interactions. The other axial site is blocked by the remaining half of the dimer with a Ag···Ag distance of 4.41 Å. The second Ag(I) ion bridges the ligand bound moiety to form the tetranuclear dimer and is square pyramidal through the binding of the thioether S atoms of each odsq ligand and three further nitrate O donors (Fig. 34).

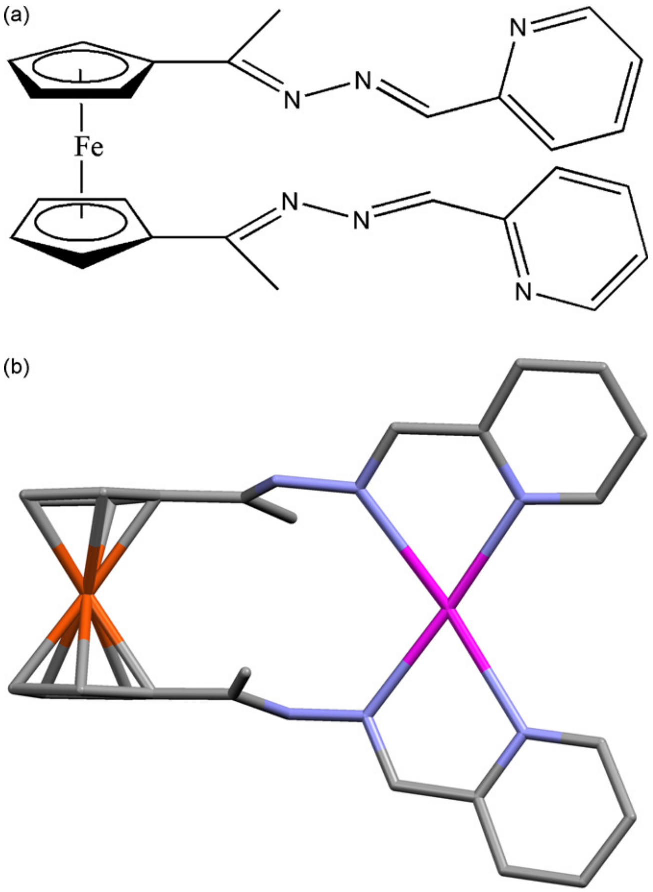


Fig. 32. The ligand **fmip** and the cation of the complex [Ag(**fmip**)]$BF_4\cdot CHCl_3$.

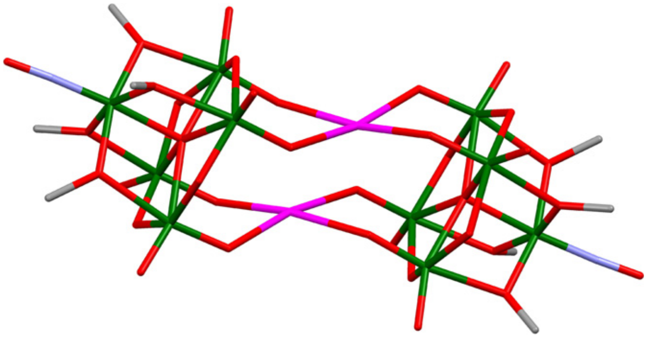


Fig. 33. The anion of the complex $(NBu_4)_4[Ag_2(Mo_5O_{13}(OMe)_4NO)_2]$.

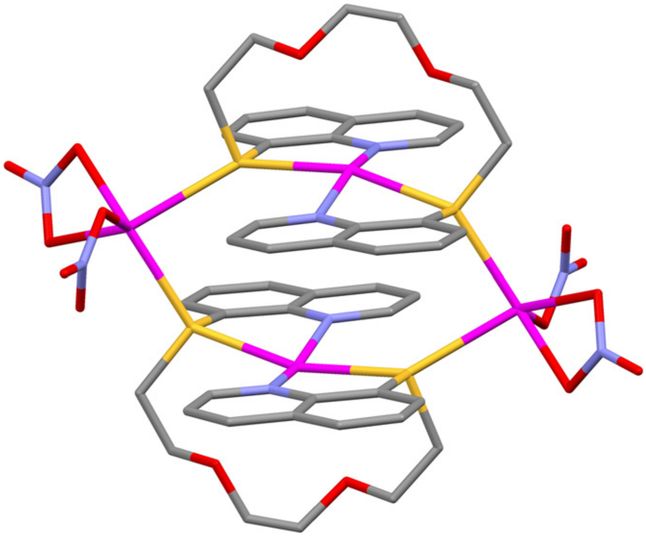


Fig. 34. The complex [Ag_4(**odsq**)$_2$(NO_3)$_4$]. The ligand **odsq** is shown in Fig. 18.

4.10. [Ag(*acp*)NO_3]

Colourless crystals of [Ag(**acp**)NO_3] were obtained from reaction of *N*,*O*-2-acetylpyridine (**acp**) and $AgNO_3$ in MeCN [69]. Bowmaker et al. note that in this mononuclear unit devoid of any symmetry, the NO_3^- counterion is ‘seriously chelating’ (Ag–O–NO_2 distances of 2.293(8) and 2.553(9) Å, respectively) and that the Ag(I) ion has a planar four coordinate environment. These mononuclear units stack in an anti-parallel manner to generate a dimer containing a central inversion centre. One Ag(I) axial site has a weak interaction with a nitrate O atom from the other half of the dimer (Ag· · ·O–NO_2 distance of 2.824 Å), and the other axial site is blocked by a pyridine N atom of an adjacent dimer at a distance of 3.151 Å (Fig. 35).

4.11. [Pd(*nhc*)$_2$]$_2$(Ag_2X_6)·2Me_2CO

1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium bromide (**nhc**Br) in CH_2Cl_2 was reacted with Ag_2O, followed by precipitation with Et_2O producing the complex [Ag(**nhc**)$_2$][$AgBr_2$] that contains a $AgBr_2^-$ counter anion. Red crystals of [Pd(**nhc**)$_2$]$_2$(Ag_2X_6)·2Me_2CO (X = Cl and Br) were prepared by transmetalation of [Ag(**nhc**)$_2$][$AgBr_2$] with [$PdCl_2$(MeCN)$_2$] in CH_2Cl_2, followed by purification and then crystallisation from Me_2CO/Et_2O. Mayr et al. [70] make no comment on the Ag(I) stereochemistry, but note disorder of the halide ions in the $Ag_2X_6^{4-}$ anion in a 0.527:0.473 Cl:Br ratio. Neither of the two unique Ag(I) ions occupies a crystallographic special position and all Ag(I) axial sites are blocked by various Pd(**nhc**)$_2^{2+}$ molecules (Fig. 36).

4.12. Section summary and comments

The first five in this group of 11 discrete square planar Ag(I) complexes all have ligands with similar azine neighbouring chelate sites composed of N atoms. The remaining six ligands have little in common with each other or the first three. In all cases the axial sites are sterically blocked or have additional weak interactions to surrounding moieties. Five of the complexes exhibit two long and two short *trans*-Ag(I) bonds while the remaining six display no obvious trend in bond lengths. While the authors of the complex [Ag(**mpp**)]$_4$(CF_3SO_3)$_4$ describe their complex as containing a four coordinate Ag(I) ion, we consider that the very close proximity of a neighbouring counterion means this complex should be considered five coordinate. In the com-

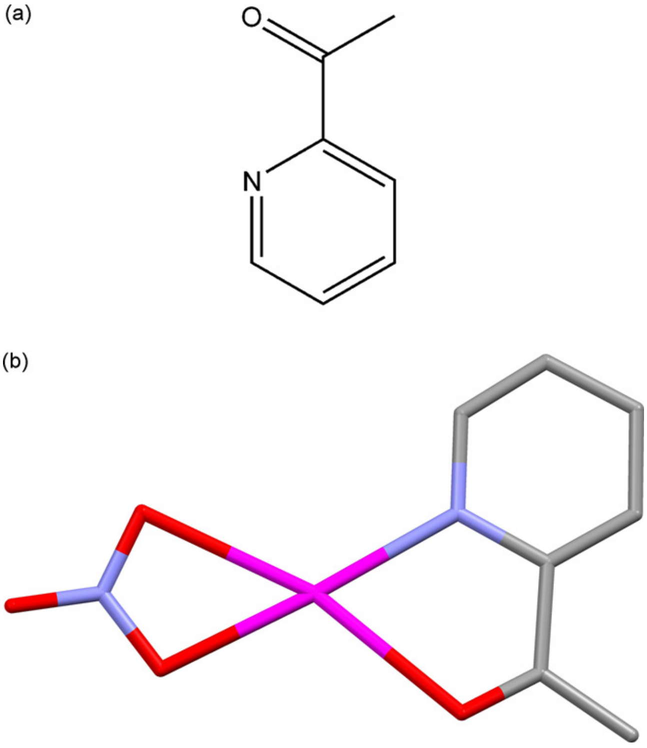


Fig. 35. The ligand **acp** and the complex [Ag(**acp**)NO_3].

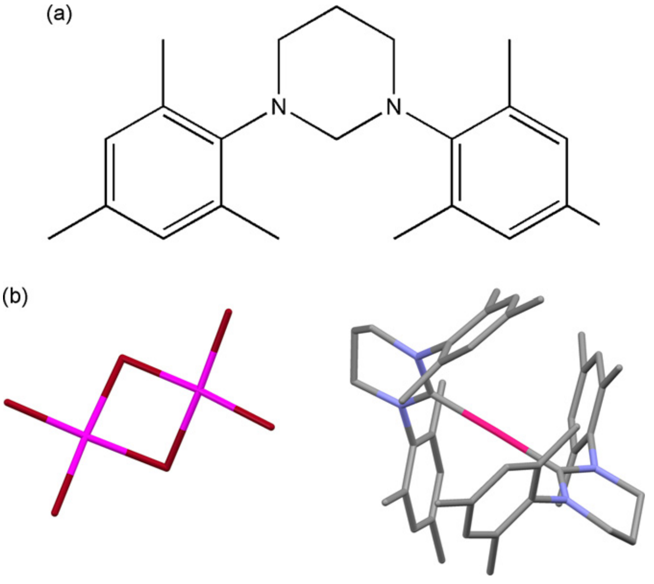


Fig. 36. The ligand **nhc** and the complex [Pd(**nhc**)$_2$]$_2$(Ag_2X_6)·2Me_2CO (X = Cl and Br). One Pd(**nhc**)$_2^{2+}$ and the disordered Me_2CO molecule have been removed for clarity.

plex [Ag(**dpbipy**)$_2$]BF$_4$·3 (2/3)DMF·(1/3)Me$_2$CO, in addition to the square planar Ag(I) ion that does not occupy a special position there is also a square planar Ag(I) ion residing on an inversion centre. The complex is included here, rather than in Section B, due to the similarity of the ligand with others in this section.

5. Polymeric silver(I) moieties with no imposed symmetry

5.1. *{[Ag(**htsb**)]PF$_6$}$_\infty$*

The yellow-coloured {[Ag(**htsb**)]PF$_6$}$_\infty$ is a polymer with a 1D zigzag chain formed from hexakis(4-tolylsulfanyl)benzene (**htsb**) and AgPF$_6$ in Me$_2$CO with subsequent diffusion of pentane into the reaction mixture [8]. The compound is ESR silent consistent with Ag(I). The environment about the Ag(I) ion is square planar with four sulfur donors which only show a very small deviation from the plane. The ligand does not seem to enforce square planar geometry about the Ag(I) ion since it gives a polymer with square pyramidal geometry containing solvent molecules when crystallized from 2-butanone. Suenaga et al. [8] suggest that the steric bulk of the tolyl side arms is responsible for the square planar geometry. The axial Ag(I) sites are shielded by crowns of vertically arranged tolyl groups and the PF$_6$$^-$ counterion has no interaction with the metal ion (Fig. 37).

5.2. *{[Ag(**dpk**)]ClO$_4$}$_\infty$*

Colourless crystals of {[Ag(**dpk**)]ClO$_4$}$_\infty$ were obtained from reaction of 2,2′-dipyridylketone (**dpk**) and AgClO$_4$ in MeCN [21]. The structure consists of two chemically similar 1D polymer strands. Bowmaker et al. make no comment on the stereochemistry of the three unique Ag(I) ions which do not occupy any special positions, however they are all exceedingly similar and have distorted square planar coordination environments. All three have Ag–N and Ag–O distances in the range 2.14(1)–2.21(1) and 2.56(1)–2.60(1) Å, respectively, and have weak axial counterion interactions at Ag···O–ClO$_3$ distances of 3.004 Å upwards. The authors undertake a structural comparison with the isostructural complex {[Ag(**dpk**)]BF$_4$}$_\infty$ discussed later in this review, pointing out that the ClO$_4$$^-$ structure is a perturbation/superlattice on the BF$_4$$^-$ structure (Fig. 38).

5.3. *{[Ag(urea)$_2$]ClO$_4$}$_\infty$*

The colourless 2D polymer {[Ag(urea)$_2$]ClO$_4$}$_\infty$ was formed from the evaporation of an EtOH solution of AgClO$_4$ and urea [71]. The square planar Ag(I) ion has two bonds to *trans* related N atoms from two independent urea molecules and two bonds to different symmetry generated urea O atoms. The donor atoms only show a small deviation from planarity. Smith et al. [71] state that the ClO$_4$$^-$ anions are weakly axially associated with the Ag(I) ion at 2.900(3) and 2.964(3) Å. The overall 3D structure is strongly hydrogen bonded and also includes two inter-urea N···O interactions. The authors suggest no reason for the formation of a square planar system but they draw a comparison to their analogous AgNO$_3$–urea 2:2 adduct. In this adduct, both NO$_3$$^-$ and urea bind to Ag(I) ion to give two different Ag coordination environments with tetrahedral and trigonal planar stereochemistries. The stereochemistry

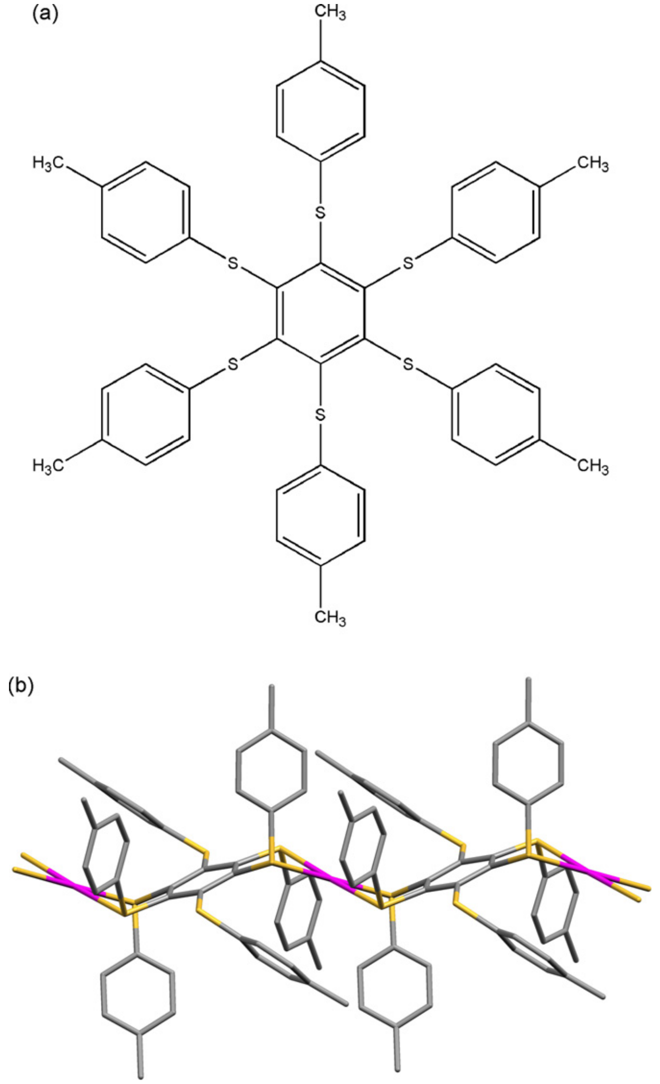


Fig. 37. The ligand **htsb** and the cationic chain of the 1D coordination polymer {[Ag(**htsb**)]PF$_6$}$_\infty$.

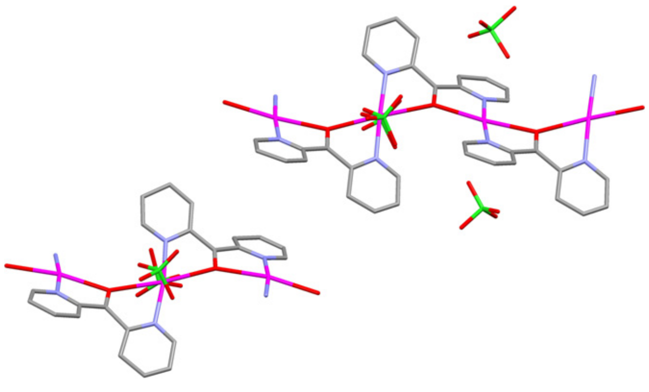


Fig. 38. The complex {[Ag(**dpk**)]ClO$_4$}$_\infty$. The ligand **dpk** is shown in Fig. 52.

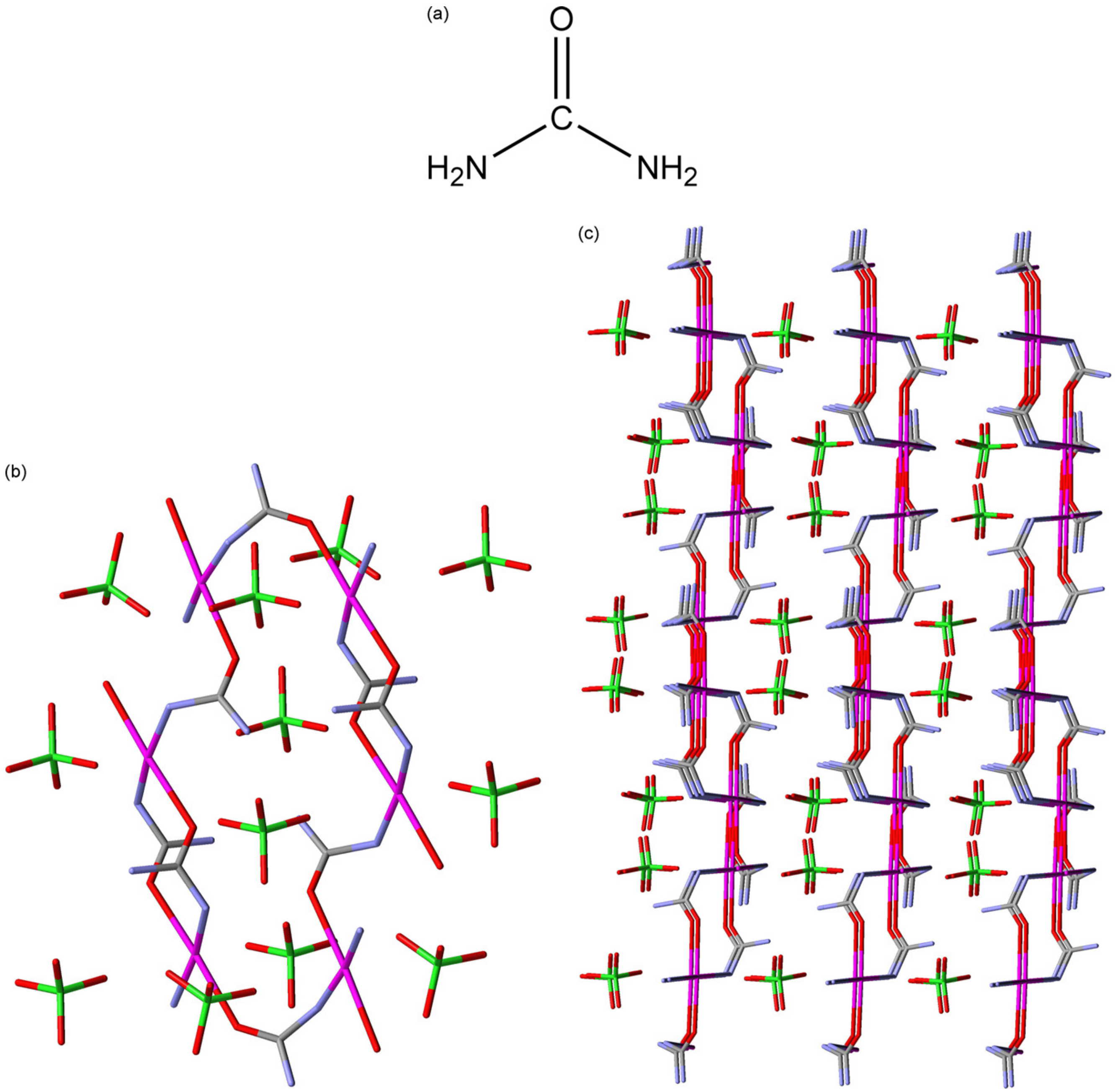


Fig. 39. The ligand urea and the 2D coordination polymer $\{[Ag(urea)_2]ClO_4\}_\infty$. The left view of the complex shows the Ag(I) coordination sphere and the right view shows the polymer packing.

of the other Ag–urea adducts also appear to be very sensitive to the nature of the counterion (Fig. 39).

5.4. $\{[Ag_5(\mathbf{nopca})_4]NO_3\}_\infty$

Colourless crystals of $\{[Ag_5(\mathbf{nopca})_4]NO_3\}_\infty$ were prepared from the reaction of $AgNO_3$ and 2-pyridinecarboxylic acid N-oxide (H**nopca**) and subsequent evaporation from aqueous solution [72]. Jaber et al. describe the polymer as a 3D polymeric network, but it is far better described as a 2D polymer separated by NO_3^- counterions with the shortest contact being $\pi C(5)\cdots O(7a)–NO_2$ at 3.19 Å. Three different Ag(I) coordination environments exist. The authors claim that two Ag(I) ions are linked by a Ag···Ag interaction of 2.9094(3) Å. Both of these Ag(I) ions are bridged by two carboxylate groups. One Ag(I) ion resides in a pseudo-square planar environment with its coordination sphere completed by the second Ag(I) ion and the two bridging carboxylate oxygen atoms, and a further N-oxide oxygen atom of another ligand molecule. The square planar nature of this complex could be debated on the basis of whether this Ag···Ag interaction actually constitutes a bond. This Ag(I) ion has no weak axial interactions because the sites are blocked by other Ag(I) ions at 3.44 and 3.49 Å. The authors assign the two non-square planar Ag(I)

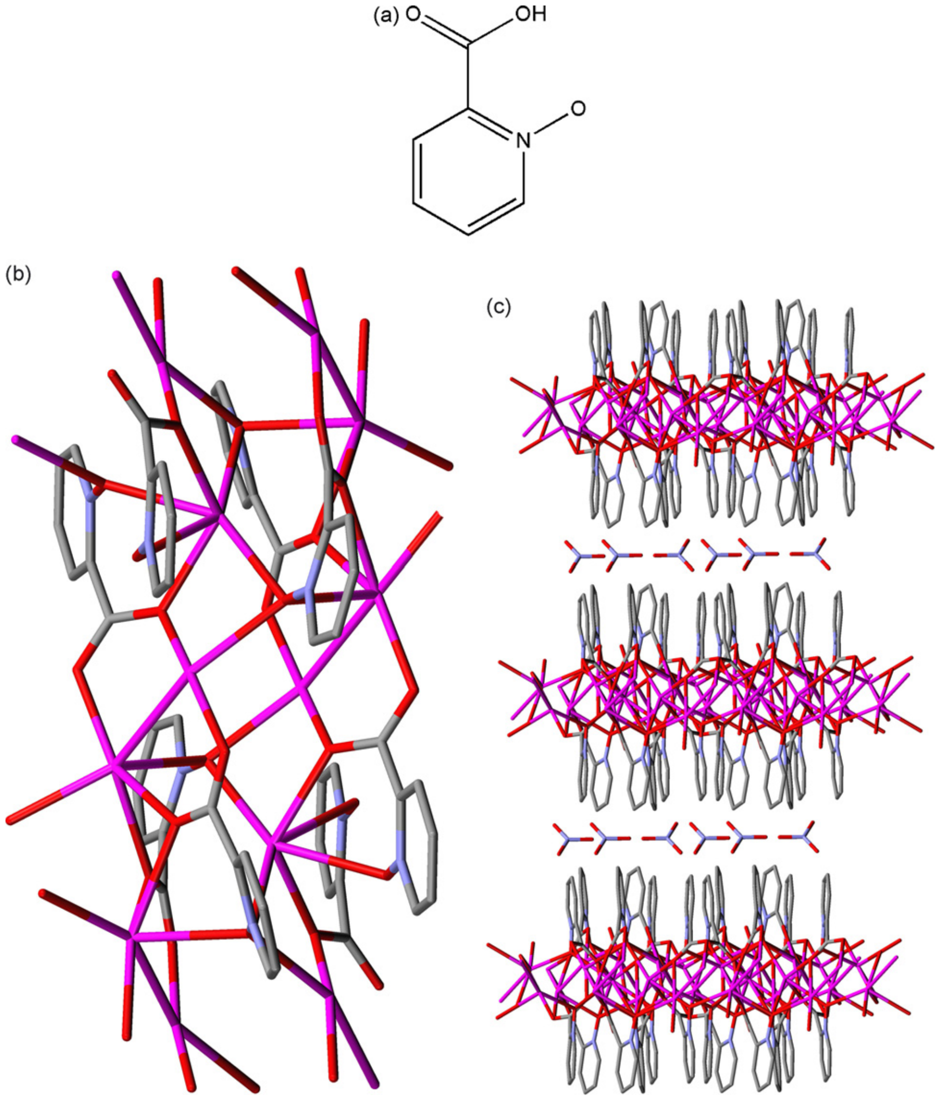


Fig. 40. The ligand **nopca** and the 2D coordination polymer $\{[Ag_5(\textbf{nopca})_4]NO_3\}_\infty$. The left view shows the square planar Ag(I) environment and the right view shows the polymeric sheets separated by NO_3^- counterions.

ions to severely distorted octahedral coordination environments (Fig. 40).

5.5. $\{[Ag_8(\textbf{ttba})_2(MeOH)_{(1/2)}(H_2O)_{(3/2)}]\cdot 4MeOH\cdot 4H_2O\}_\infty$

Colourless crystals of $\{[Ag_8(\textbf{ttba})_2(MeOH)_{(1/2)}(H_2O)_{(3/2)}]\cdot 4MeOH\cdot 4H_2O\}_\infty$ were prepared by the slow diffusion of a solution of the tetrathiacalix[4]arene ligand Na_4**ttba** in MeOH with a solution of $AgNO_3$ in water [73]. Akdas et al. describe this 2D coordination polymer as discrete binuclear $Ag_2(\textbf{ttba})^{2-}$ complexes interconnected by Ag(I) cations. The ligand **ttba** adopts a 1,3-alternate conformation and consequently presents two chelate carboxylate binding sites on each face. Eight unique Ag(I) ions are present, none of which occupy any type of crystallographic special position. Half of these are described by the authors as having strongly distorted square planar geometries and they mention the possibility of tetragonal distortion due to the nearby aromatic C atoms at the Ag(I) axial sites for all Ag(I) ions (Ag···C distances of 3.181–3.313 Å). One of these square planar Ag(I) ions has two rather long *cis* bond lengths of 2.730 and 2.880 Å, both of which fall just outside the upper limit that we consider reasonable for a bonding interaction. The remaining four unique Ag(I) ions interconnect the $Ag_2(\textbf{ttba})^{2-}$ complexes. Half are three-coordinate with two carboxylate O donors and one-coordinated water molecule. The last two unique Ag(I) ions are four coordinate with two O donor atoms from a chelating carboxylate group, one further carboxylate O donor, and a coordinated water or MeOH molecule occupies the fourth site (Fig. 41).

5.6. $\{[Ag(\textbf{sac})\textbf{py}]\}_\infty$

The polymer $\{[Ag(\textbf{sac})\textbf{py}]\}_\infty$ was prepared by reaction of $AgNO_3$ and $Na(\textbf{sac})\cdot 2H_2O$ in MeOH and subsequent addition of pyridine (**py**), which yielded colourless crystals after 2 days [74]. Each Ag(I) ion is coordinated by one N atom each from **py** and saccharinate. Hamamci et al. claim the complex consists of asymmetric units of Ag(**sac**)**py** linked together

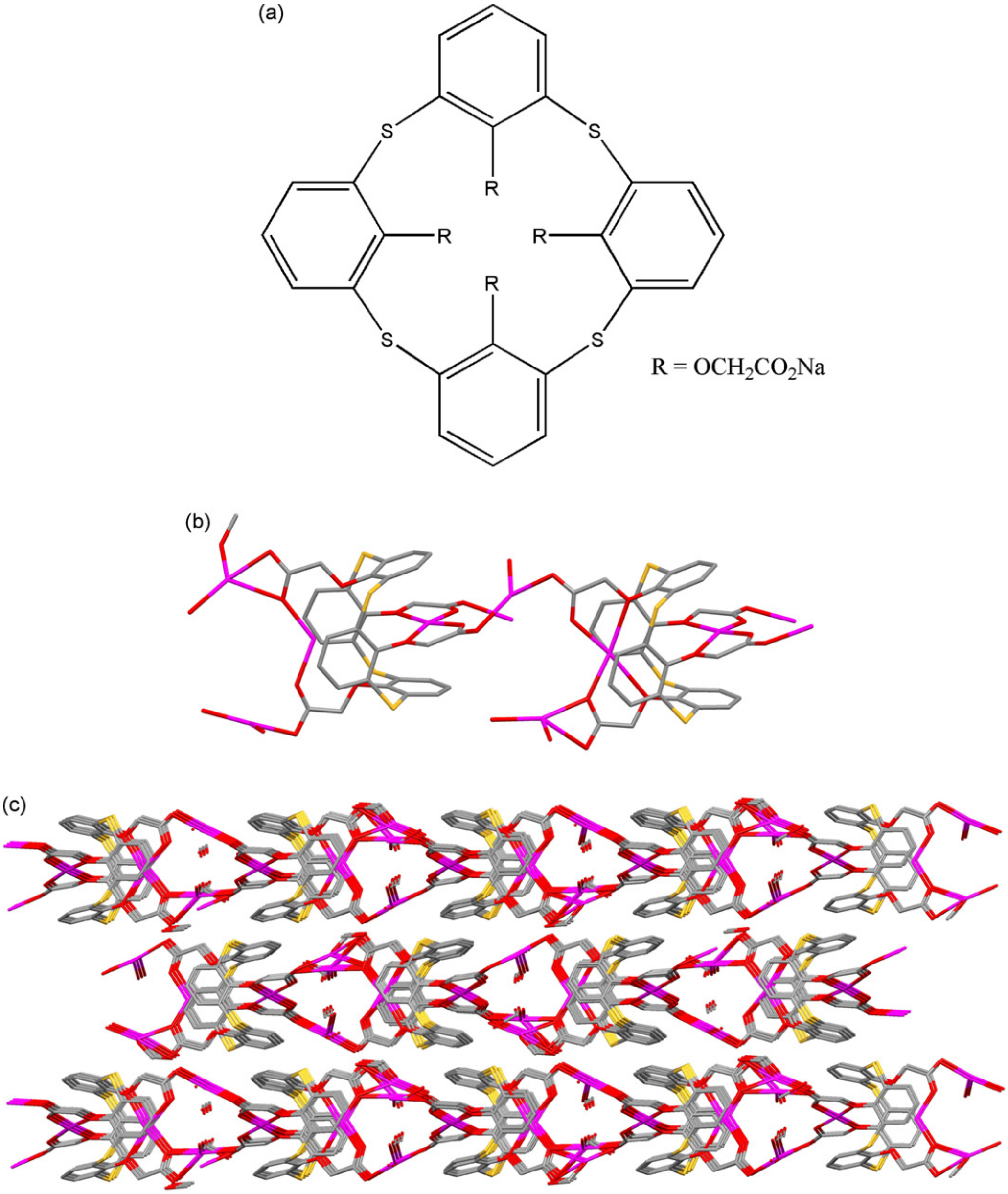


Fig. 41. The ligand Na$_4$**ttba** and the complex $\{[Ag_8(\textbf{ttba})_2(MeOH)_{1/2}(H_2O)_{(3/2)}]\cdot 4MeOH\cdot 4H_2O\}_\infty$. Solvents of crystallisation have been omitted for clarity. The polymer packing and solvents of crystallisation are shown below.

by Ag···Ag interactions, and that because these Ag···Ag distances of 2.909(2) and 2.985(1) Å are much smaller than the van der Waals radii (3.40 Å) a significant interaction exists. These Ag···Ag interactions form a 1D infinite helical chain of Ag atoms. The authors describe the Ag(I) environment as distorted square planar. One axial site is blocked by a sulfonyl oxygen atom while the other would appear to be blocked by the steric bulk of a **py** and **sac** ligand coordinated to neighbouring Ag(I) ions (Fig. 42).

5.7. $\{[Ag(\textbf{dpms})]CF_3SO_3\}_\infty$

Colourless X-ray crystals were obtained from the diffusion of **dpms** in MeNO$_2$ into AgCF$_3$SO$_3$ in EtOAc, layered with Me$_2$CO [75]. The 1D coordination polymer prepared by Amoore et al. contains Ag(I) ions in a distorted square planar environment and ligands in a stretched out endo-*anti*-arrangement. Each Ag(I) coordination sphere is completed by two pyrazine N donor atoms and two thioether S donor atoms from two ligand molecules. Additional weak interactions to neighbouring CF$_3$SO$_3$$^-$ counterions at 2.690 and 2.833 Å occur at the axial sites. The counterions are disordered which suggests they are not strongly bound (Fig. 43).

5.8. $\{[Ag(\textbf{bipy})H_2O][Ag(\textbf{bipy})(\textbf{ndc})H_2O]\cdot H_2O\}_\infty$

The 1D coordination polymer was formed by the reaction of AgNO$_3$ and H$_2$**ndc** in aqueous solution followed by addition of 4,4-bipyridine (**bipy**) and subsequent solvent evaporation. The complex consists of cationic complex chains, anionic com-

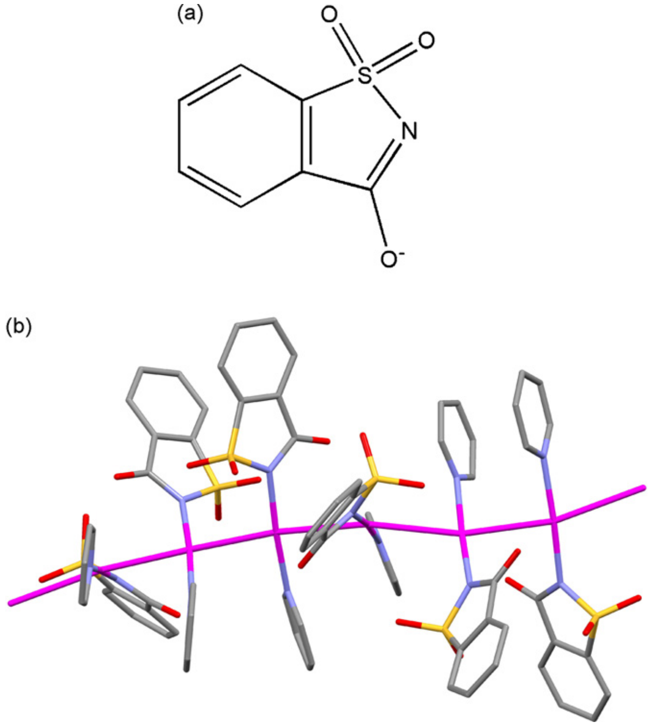


Fig. 42. The ligand **sac** and the 1D coordination polymer $\{[Ag(\mathbf{sac})\mathbf{py}]\}_\infty$.

plex chains, and solvent water molecules. Ye and Wu [76] describe the Ag(I) coordination environments as distorted trigonal and distorted square planar, respectively. This second environment has two N donor atoms from two different **bipy** molecules at 2.163(2) and 2.166(2) Å, one water O atom at 2.831(3) Å, and one **ndc** O atom at 2.826(3) Å. The authors have assigned this geometry as square planar based on the Ag···O distances being shorter than the van der Waals radii. Based on our analysis we consider 2.8 Å to be above the upper limit of bonding interactions, and it would better to describe this geometry as linear with two weakly interacting O donors (Fig. 44).

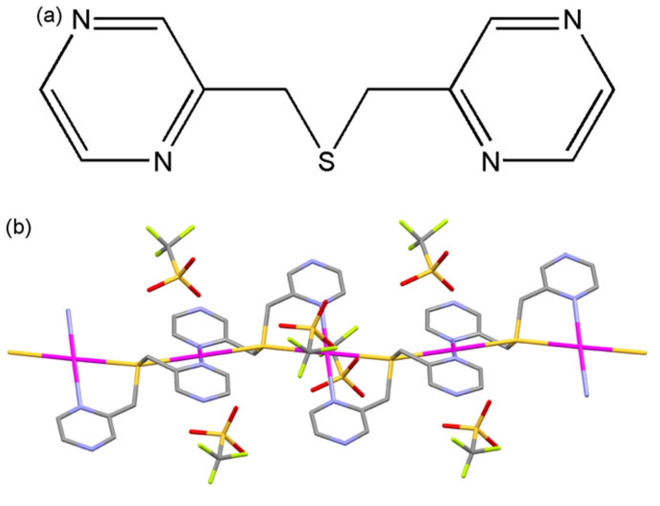


Fig. 43. The ligand **dpms** and the 1D coordination polymer $\{[Ag(\mathbf{dpms})]CF_3SO_3\}_\infty$.

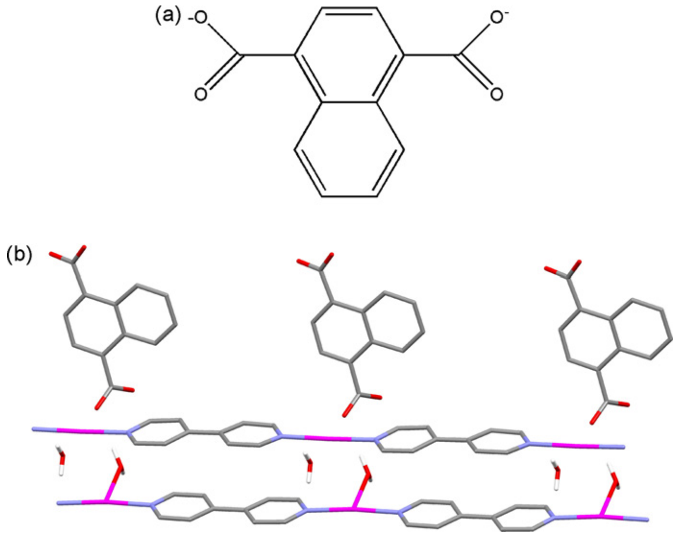


Fig. 44. The ligand **ndc** and the 1D coordination polymer $\{[Ag(\mathbf{bipy})H_2O][Ag(\mathbf{bipy})(\mathbf{ndc})H_2O]\cdot H_2O\}_\infty$. A water of crystallisation has been omitted for clarity.

5.9. $\{[Ag(\mathbf{tsa})\mathbf{pz}]\}_\infty$

Colourless crystals of $\{[Ag(\mathbf{tsa})\mathbf{pz}]\}_\infty$ were produced by the reaction of *p*-toluenesulfonic acid (H**tsa**) and Ag_2CO_3 in aqueous solution, followed by addition firstly of pyrazine (**pz**) in MeOH and then of aqueous NH_3 [77]. Only one unique Ag(I) ion is present and Li et al. describe its stereochemistry as flattened tetrahedral, and this complex is on the verge of what we consider square planar. Two N donors from two opposing **pz** ligands and two O donors from two different **tsa** ligands complete the Ag(I) coordination sphere. The closest Ag···Ag distance is 3.413 Å, and an inversion centre exists between these two atoms. The remaining Ag(I) axial site is sterically blocked by a toluene ring of a neighbouring chain at a distance of 3.040 Å. The overall structure of the 1D polymer is that of a double chain (Fig. 45).

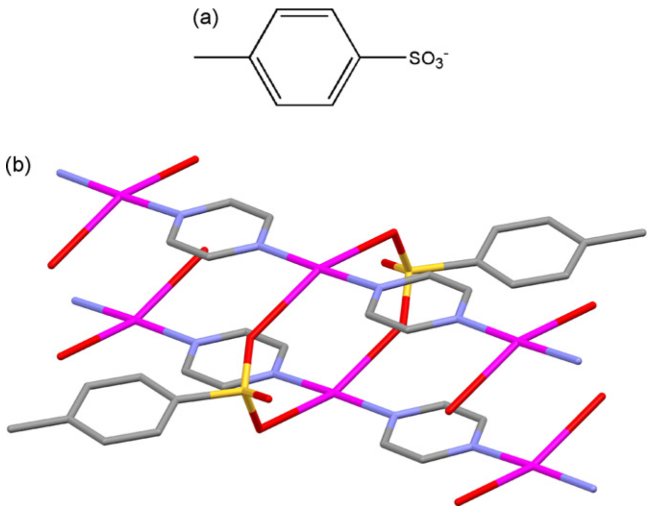


Fig. 45. The ligand **tsa** and the 1D coordination polymer $\{[Ag(\mathbf{tsa})\mathbf{pz}]\}_\infty$.

5.10. $\{[Ag(\mathbf{nsa})\mathbf{pz}]\cdot H_2O\}_\infty$

Colourless crystals of $\{[Ag(\mathbf{nsa})\mathbf{pz}]\cdot H_2O\}_\infty$ were produced by the reaction of sodium 1-napthalenesulfonate (Na**nsa**) and $AgNO_3$ in aqueous solution, followed by addition of pyrazine (**pz**) in EtOH [77]. This 1D polymer is very similar to $\{[Ag(\mathbf{tsa})\mathbf{pz}]\}_\infty$ reported in the same study by Li et al. above, with the same flattened tetrahedral stereochemistry of the Ag(I) ion and same overall structure of a double chain. They report that Ag· · ·Ag distance is 3.546 Å, and again an inversion centre exists between these two atoms. The remaining Ag(I) axial site is sterically blocked by a naphthalene ring of a neighbouring chain at a distance of 2.968 Å. The water of crystallisation has no interaction with the Ag(I) ion. Again, this complex resides in the grey area between what is tetrahedral and square planar (Fig. 46).

5.11. Section summary and comments

These 10 structures include seven 1D and three 2D polymers. In two cases the Ag(I) stereochemistry may be altered by the choice of solvent or counterion employed in crystallisation. With the obvious exception of the last two sulfonate ligands, the ligands have little in common providing S, N and a variety of O donor atoms. This section includes complexes that contain square planar Ag(I) ions with Ag bond lengths that are not controlled by symmetry. It is interesting that in all but one polymer, the square planar Ag(I) ions in these six polymers have two long and two short bonds which are *trans* to each other. In the 1D polymer $\{[Ag(\mathbf{htsb})]PF_6\}_\infty$ the difference in *trans*-bond lengths is less extreme than in the other complexes. Unusually, the donor set in the square planes of $\{[Ag_5(\mathbf{nopca})_4]NO_3\}_\infty$ and $\{[Ag(\mathbf{sac})\mathbf{py}]\}_\infty$ incorporate a Ag(I) ion leading to ambiguity over the assignment of the stereochemistry of the other central Ag(I) ion. The authors of the polymer $\{[Ag(\mathbf{bipy})H_2O][Ag(\mathbf{bipy})(\mathbf{ndc})H_2O]\cdot H_2O\}_\infty$ above have also been generous with their Ag(I) stereochemistry assignment by including donor atoms with Ag bond distances well outside what we consider to be reasonable for a formal Ag–ligand bond. Three of the polymers show weak axial Ag(I) interactions with counterions while the remaining seven have their axial sites of the Ag(I) square plane blocked by the intrinsic arrangements of the polymers.

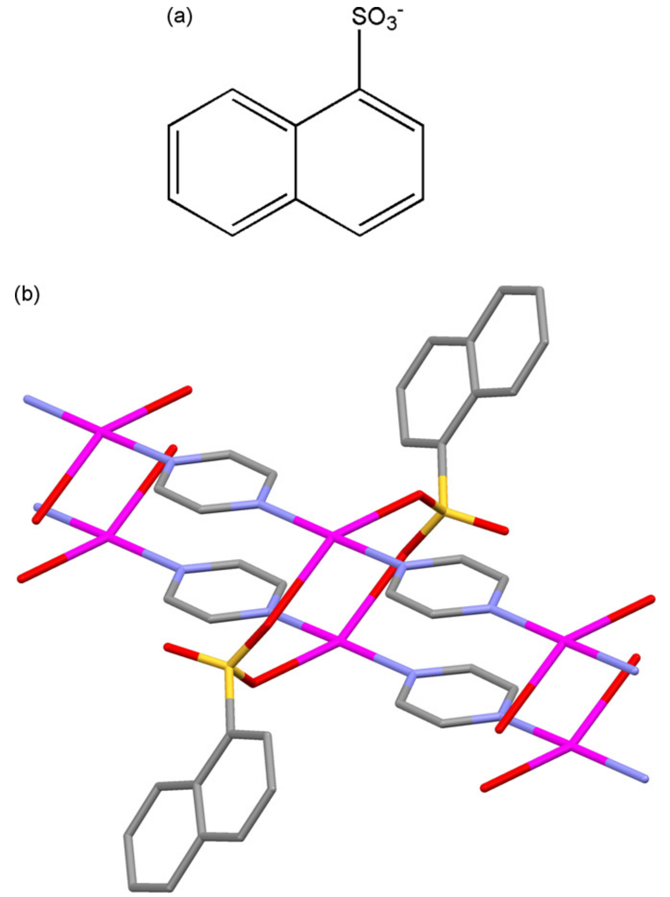


Fig. 46. The ligand **nsa** and the 1D coordination polymer $\{[Ag(\mathbf{nsa})\mathbf{pz}]\cdot H_2O\}_\infty$.

6. Polymeric silver(I) moieties with crystallographically imposed symmetry

6.1. $\{[Ag(\mathbf{pz})_2][Ag_2(\mathbf{pz})_5](PF_6)_3\}_\infty$

Diffusion of $AgPF_6$ solutions in EtOH into pyrazine (**pz**) solutions in various chlorinated solvents (G) produced the polymers $\{[Ag(\mathbf{pz})_2][Ag_2(\mathbf{pz})_5](PF_6)_3\cdot G\}_\infty$ ($G=CH_2Cl_2$, $CHCl_3$ and CCl_4) [4]. Only the crystal structure of $G=CH_2Cl_2$ is reported as all three structures are isomorphous. The complex consists of layers of two different 2D Ag(I) networks separated by PF_6^- anions. The first layer consists of cubes with Ag(I) ions at the vertices and **pz** ligands as edges. The Ag(I) ion is in a square pyramidal geometry and the cubes encase PF_6^- counterions. The second layer consists of a flat sheet of Ag(I) ions and **pz** ligands. The Ag(I) ions sits on an *mmm* special position and is square planar. Carlucci et al. comment on the weak Ag(I) axial interactions of 2.685(11) Å with the PF_6^- ions. They describe the overall coordination environment about Ag(I) as a tetragonally distorted octahedron which is consistent with our analysis (Fig. 47).

6.2. $\{[Ag(\mathbf{miax})NO_3]\}_\infty$

In 1972, Fritchie reported a red $AgNO_3$ complex of 10-methylisoalloxazine (**miax**), a flavin [13]. To our knowledge, this was the first ever reported crystal structure containing Ag(I) ions in a square planar stereochemistry. The complex $\{[Ag(\mathbf{miax})NO_3]\}_\infty$ is a polymer with a 2:2 Ag to flavin ratio, and is formed by cooling the reaction mixture of $AgNO_3$ and **miax** in MeOH/formic acid. Each flavin binds two different Ag(I) ions in different binding sites. The first Ag(I) ion adopts a centrosymmetric square planar arrangement chelated through N and O donors giving a five-membered ring and bridging two flavin molecules. There are weak axial interactions at 2.824(6) Å with NO_3^- anions of adjacent polymer chains. The second Ag(I) is six coordinate through two chelating NO_3^-

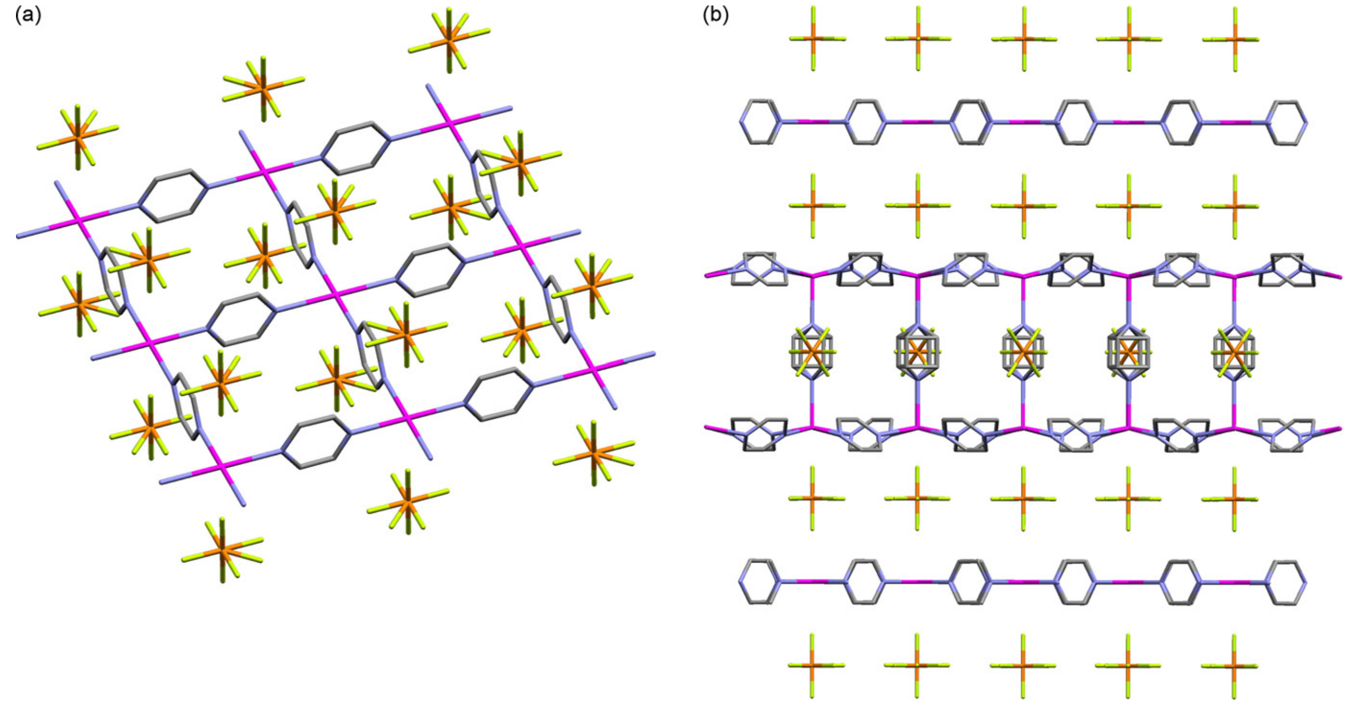


Fig. 47. The 2D coordination polymer $\{[Ag(\mathbf{pz})_2][Ag_2(\mathbf{pz})_5](PF_6)_3\}_\infty$ containing disordered PF_6^- counterions. The layer containing flat sheets of square planar Ag(I) ions and pyrazine ligands is shown to the left, and the polymer packing structure is shown to the right.

anions and two flavin O donors on different flavin ligands (Fig. 48).

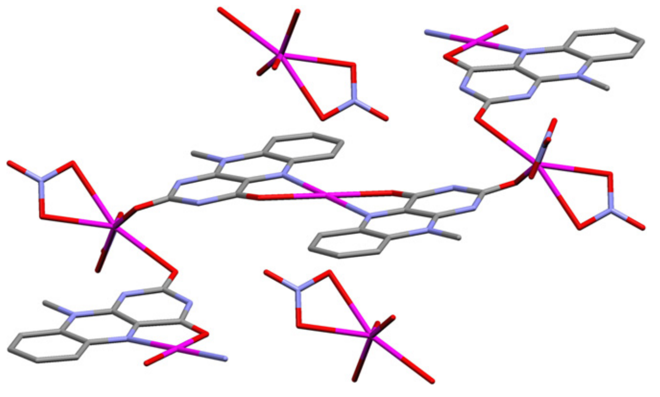


Fig. 48. The 1D coordination polymer $\{[Ag(\mathbf{miax})NO_3]\}_\infty$. The ligand **miax** is shown in Fig. 3.

6.3. $\{[Ag_2(\mathbf{cmi})_2]\}_\infty$

The slow diffusion of $AgClO_4$ and 1,3-bis(dicyanomethylidene)indan (**cmi**) in MeOH gave a gold coloured polymer $\{[Ag_2(\mathbf{cmi})_2]\}_\infty$ [78]. The structure, reported by Ino et al., is an intricate combination of five-fold interpenetrating 3D nets. The structure contains four crystallographically unique Ag(I) ions, all coordinated through nitrile groups. Three are linearly coordinated while the remaining centrosymmetric Ag(I) ion adopts a square planar environment through coordination to four separate **cmi** ligands. The Ag(I) axial sites are sterically blocked by aromatic rings of different nets at a Ag(I)$\cdots$centroid distance of 3.36 Å. The network is constructed through two different ligand-bridging modes. In the first mode the ligand bridges three Ag(I) ions to give a 2D sheet of 52-membered rings. In the second mode, the ligand links two Ag(I) ions from adjacent sheets to form 3D nets which interpenetrate and are held in place by the π stacking of aromatic moieties of adjacent nets (Fig. 49).

6.4. $\{[Ag_3(\mathbf{tcbb})_3(Me_2CO)](BF_4)_3\cdot 4Me_2CO\}_\infty$

Colourless crystals of $\{[Ag_3(\mathbf{tcbb})_3(Me_2CO)](BF_4)_3\cdot 4Me_2CO\}_\infty$ were prepared from reaction of 1,3,5-tris(4-cyanobenzoyl)benzene (**tcbb**) and $AgBF_4$ in Me_2CO and subsequent cooling of the filtered reaction mixture [79]. Four unique Ag(I) ions and three different **tcbb** ligand conformations are present in this 2D coordination polymer. Pigge et al. discuss how each **tcbb** ligand has a conformation where the three carbonyl O donor atoms all point towards one face of the central benzene ring, while the three cyano groups point towards the opposite face. One ligand is also disordered over two sites. The first Ag(I) ion has a centrosymmetric square planar stereochemistry coordinating four cyano groups from four different ligands. The axial site is blocked by an arene ring at Ag$\cdots$C distances of 3.316 and 3.330 Å. The second Ag(I) ion also has a centrosymmetric square planar stereochemistry coordinating two cyano groups and two acetone solvent molecules. There is a weak axial interaction with a nearby **tcbb** carbonyl O atom at a distance of 2.903 Å. The third Ag(I) ion does not occupy a crystallographic special position, and has a four coordinate environment that is distorted between

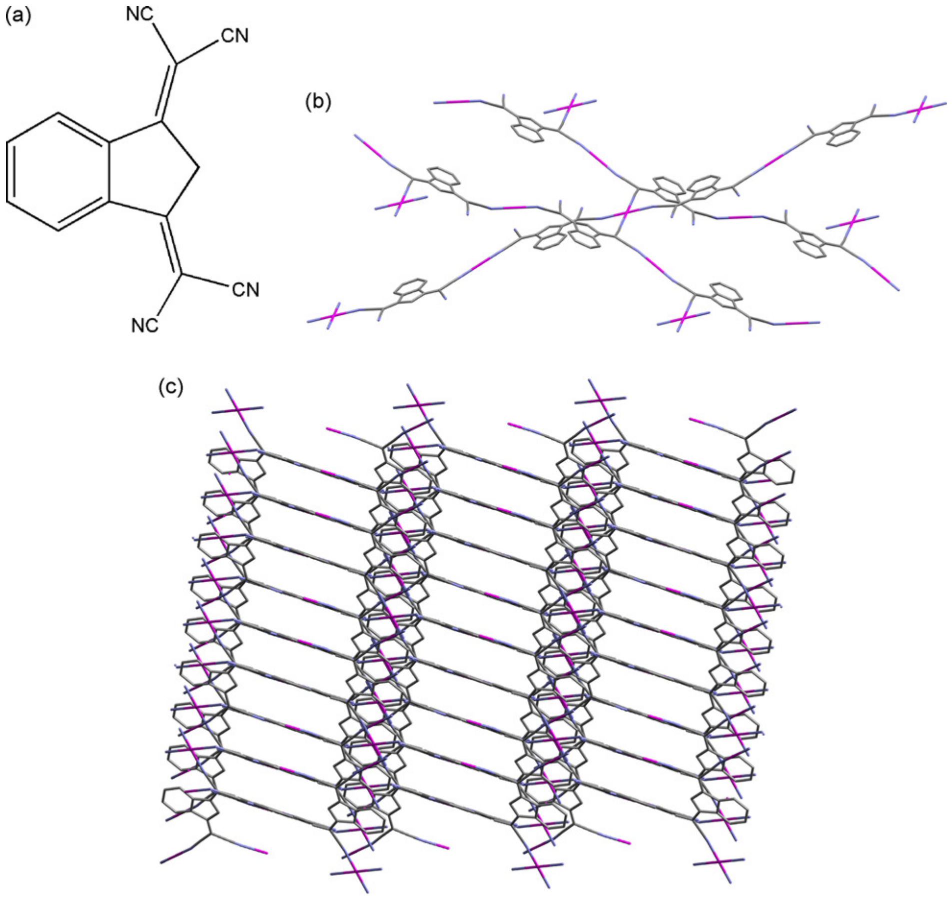


Fig. 49. The ligand **cmi** and the 3D coordination polymer $\{[Ag_2(\mathbf{cmi})_2]\}_\infty$.

tetrahedral and square planar geometry. The last Ag(I) ion has a three coordinate T-shaped stereochemistry. The BF_4^- counter anions and the remaining non-coordinated Me_2CO molecules occupy pores in the network and have no interaction with any of the Ag(I) centres. The authors describe the overall structure as a corrugated sheet and note the loss of solvent molecules upon removal of crystals from the mother liquor (Fig. 50).

6.5. $\{[Ag(\mathbf{dpmi})]ClO_4{\cdot}2H_2O\}_\infty$

The reaction of $AgClO_4$ with $[NC_5H_4(Me)C{=}NCH_2CH_2N{=}C(Me)C_5H_4N]$ (**dpmi**) in MeCN gave the colourless 3D coordination polymer $\{[Ag(\mathbf{dpmi})]ClO_4{\cdot}2H_2O\}_\infty$ [80]. The complex was reported by Patra and Goldberg, and contains two different Ag(I) environments. One Ag(I) ion coordinates four neighbouring ligands via the terminal pyridine N donors in a pseudo-square planar arrangement with a tetrahedral distortion. The other is a distorted tetrahedral stereochemistry binding four imine–N donors from two neighbouring ligands. The pseudo square planar Ag(I) ion sits on a two-fold rotation axis perpendicular to the square plane, and all four of the bond lengths are within experimental error. The ClO_4^- counterions and H_2O molecules are located in pores within the 3D array with ClO_4^- counterions above and below the pseudo square plane with the closest $Ag{\cdots}O{-}ClO_3$ distance being 3.52 Å (Fig. 51).

6.6. $\{[Ag(\mathbf{dpk})]PF_6\}_\infty$

$\{[Ag(\mathbf{dpk})]PF_6\}_\infty$ is yellow and formed from KPF_6 addition to Ag_2SO_4 and di-2-pyridylketone (**dpk**) in aqueous solution. The 1D polymer is described by Yang et al. [81] as $Ag(\mathbf{dpk})^+$ zigzag chains counterbalanced by PF_6^- anions. The ligand acts as a double O, N chelate ligand bridging pairs of Ag(I) ions. The Ag(I) ion sits on an inversion centre and adopts a N_2O_2 square planar geometry. The Ag(I) axial sites are blocked by PF_6^- anions ($Ag{\cdots}F{-}PF_5^-$ distance 3.260(3) Å) which are held in place by H-bonding and no weak axial Ag(I) interactions are present (Fig. 52).

6.7. $\{[Ag(\mathbf{dpk})]BF_4\}_\infty$

$\{[Ag(\mathbf{dpk})]BF_4\}_\infty$ is yellow and is isostructural with $\{[Ag(\mathbf{dpk})]PF_6\}_\infty$. Sommerer et al. [82] consider that the carbonyl O atom plays a prominent role in forming a μ-oxo bridge that helps to maintain the planarity of the extended structure. However, recently the same ligand has been shown to produce non-planar Ag(I) structures whose geometries are sensitive to the nature of the counterion [81]. The Ag(I) axial sites are blocked by disordered BF_4^- anions (shortest $Ag{\cdots}F{-}BF_3^-$ distance 4.113(3) Å) which are held in place by H-bonding and no weak axial Ag(I) interactions are present (Fig. 53).

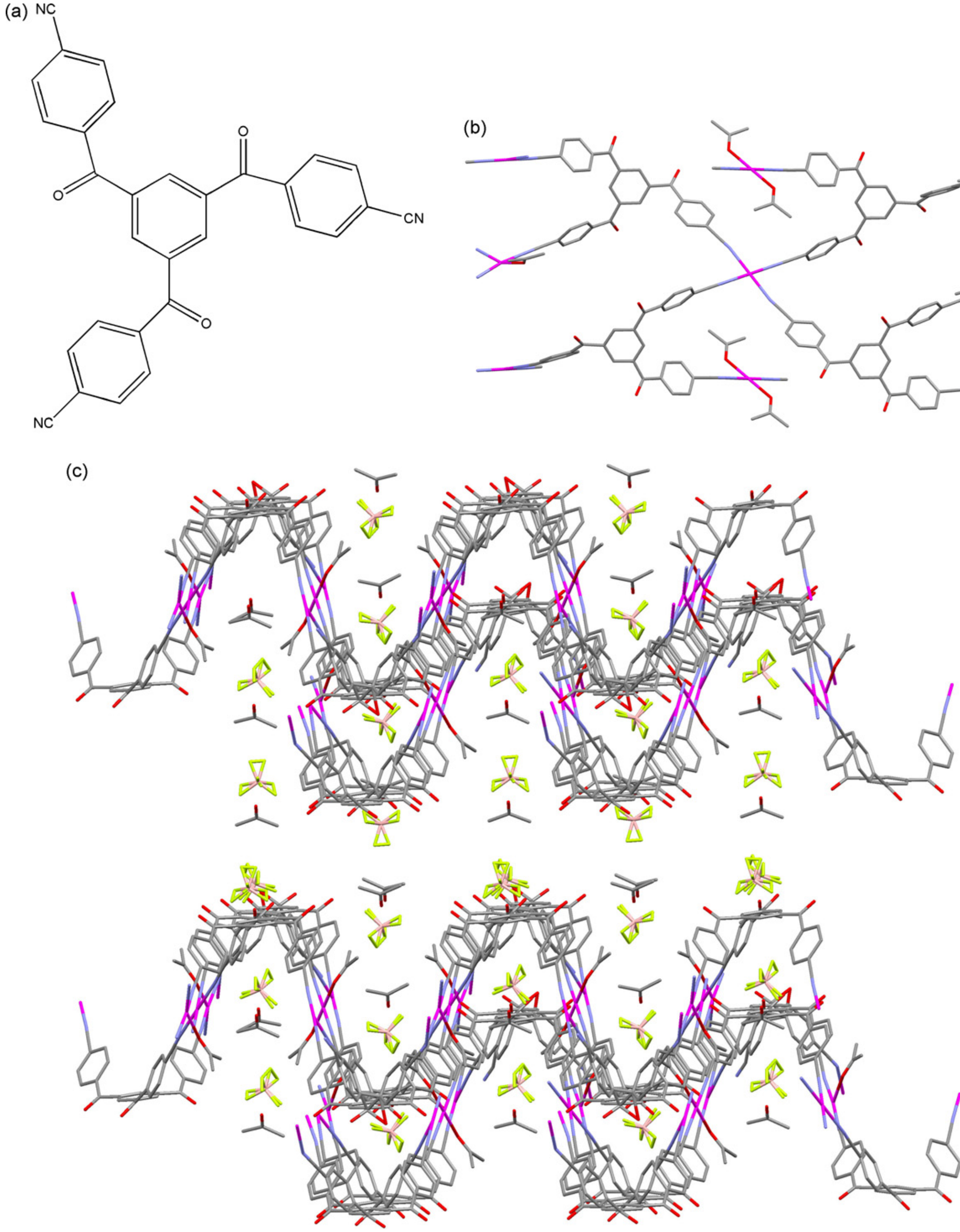


Fig. 50. The ligand **tcbb** and the 2D coordination polymer $\{[Ag_3(\mathbf{tcbb})_3(Me_2CO)](BF_4)_3\cdot 4Me_2CO\}_\infty$. The top view shows the square planar Ag(I) ion coordination spheres with solvent of crystallisation and counter anions omitted for clarity.

6.8. $\{[Ag(\boldsymbol{ptp})]PF_6\}_\infty$

The dark-violet coloured 1D polymer $\{[Ag(\mathbf{ptp})]PF_6\}_\infty$ was formed from the reaction of **ptp** and $AgPF_6$ in MeCN and subsequent diffusion of toluene into the mixture [83]. Schottel et al. describe the centrosymmetric Ag(I) environment as distorted square planar, and the ligands are arranged in an *anti*-orientation which gives rise to the polymer. The bite angles of the ligand result in the deviation of coordination geometry from perfect square planar. The axial sites contain weak interactions to neighbouring PF_6 anions (shortest $Ag\cdots F–PF_5{}^-$ distance 3.029(5) Å) which also display anion$\cdots\pi$ interactions with the tetrazine rings (Fig. 54).

6.9. $\{[Ag(\boldsymbol{dpp})_2NO_3]\}_\infty$

Colourless crystals of $\{[Ag(\mathbf{dpp})_2NO_3]\}_\infty$ were obtained from cooling a MeCN solution of $AgNO_3$ and 2,6-

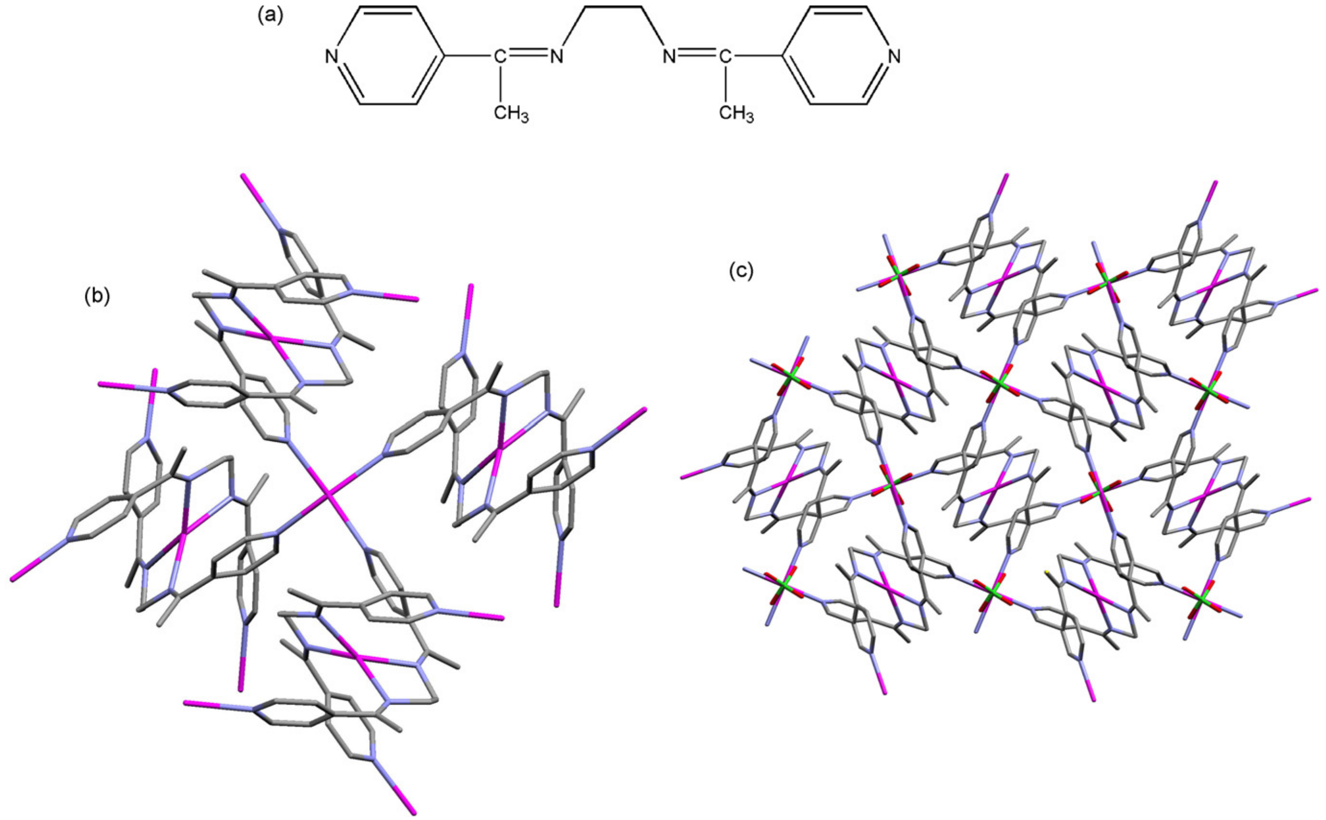


Fig. 51. The ligand **dpmi** and the 3D coordination polymer $\{[Ag(\textbf{dpmi})]ClO_4{\cdot}2H_2O\}_\infty$. The square planar Ag(I) environment is shown to the left and the polymer packing to the right. Waters of crystallisation have been omitted for clarity.

diphenylpyrazine (**dpp**) [66]. Schultheiss et al. describe the centrosymmetric Ag(I) ion as having a pseudo-square planar geometry. Two pyrazine N donors from symmetry related ligands and two nitrate O donors complete the Ag(I) coordination sphere. The Ag–ONO_2 distance of 2.7051(14) Å is at the upper limit of what we consider to be reasonable for a bonding interaction. The Ag(I) axial sites are sterically blocked by a **dpp** phenyl ring bound to the next Ag(I) ion of the polymeric chain, at a closest Ag···C distance of 3.144 Å. The NO_3 counterions bridge adjacent Ag(I) moieties to give a 1D coordination polymer with a zigzag ribbon-like structure. This structure is reported in the same study as that of $[Ag_2(\textbf{dmpp})_4(CO_2CF_3)_2]$ in Section 4.6 above (Fig. 55).

6.10. $\{[Ag(\textbf{bptb})]CF_3SO_3\}_\infty$

Colourless crystals of $\{[Ag(\textbf{bptb})]CF_3SO_3\}_\infty$ were prepared by the 1:1 reaction of 1,4-bis(pyridine-2-ylmethanethio)benzene (**bptb**) and $AgCF_3SO_3$ in Me_2CO [84]. The **bptb** molecule acts as a bis-bidentate ligand adopting

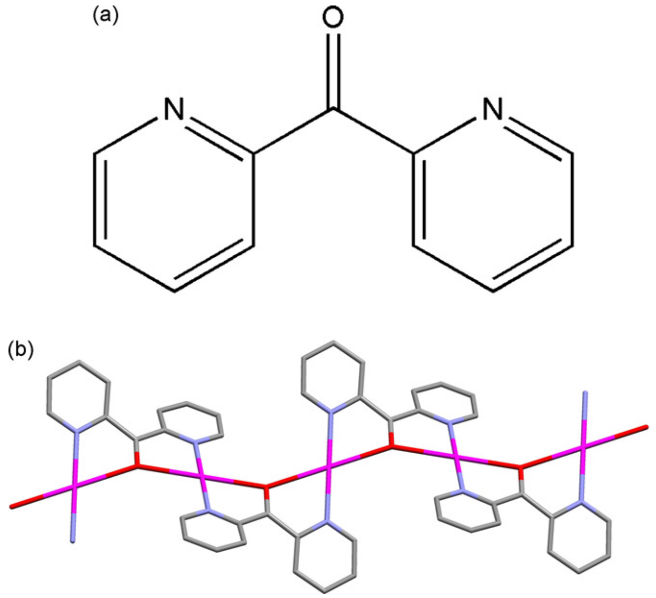


Fig. 52. The ligand **dpk** and the cation chain of the 1D coordination polymer $\{[Ag(\textbf{dpk})]PF_6\}_\infty$.

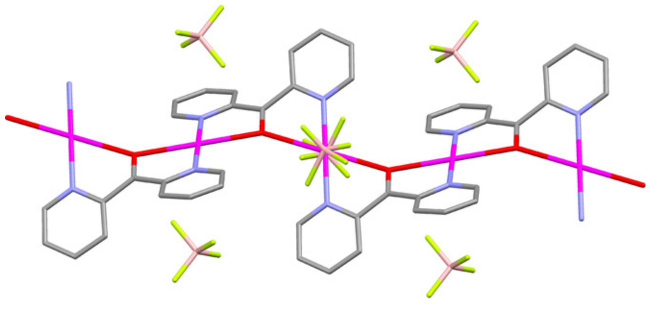


Fig. 53. The 1D coordination polymer $\{[Ag(\textbf{dpk})]BF_4\}_\infty$. The ligand **dpk** is shown in Fig. 52.

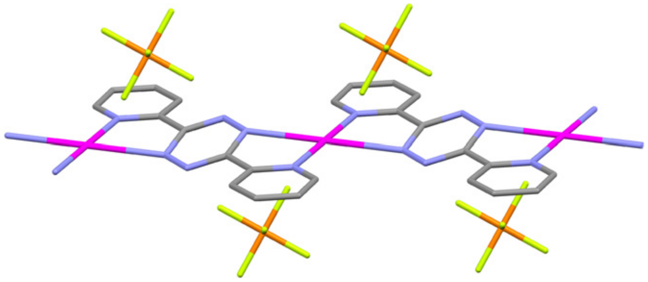


Fig. 54. The 1D coordination polymer $\{[Ag(\mathbf{ptp})]PF_6\}_\infty$. The ligand **ptp** is shown in Fig. 26.

a folded conformation and bridging two unique but chemically very similar Ag(I) ions. Both Ag(I) ions reside on inversion centres and Oh et al. describe their coordination environment as distorted square planar. For each Ag(I) ion, one thioether S donor and one pyridine N donor from two symmetry related ligands complete the Ag(I) square plane. The authors comment that the long Ag–S bond lengths of 2.902 and 2.949 Å represent weak bonding interactions. However, these Ag–S values are typical of those found for other square planar Ag(I) complexes (Table 1). Weak axial interactions with triflate O atoms exist for each Ag(I) ion, at distances of 2.967 and 2.999 Å, respectively. These interactions help encapsulate the triflate anions within the pockets of the polymeric chain. The 1D polymer is described as having a zigzag structure. Interestingly, when the reaction ratio is increased to 3:2 a different 1D polymer containing five coordinate Ag(I) ions using donor atoms from the **bptb** ligand is formed (Fig. 56).

6.11. $\{[Ag_6(\mathbf{pdca})_2(H\mathbf{pdca})_2(H_2O)_4]\}_\infty$

Colourless crystals of $\{[Ag_6(\mathbf{pdca})_2(H\mathbf{pdca})_2(H_2O)_4]\}_\infty$ were prepared by reaction of pyridine-2,3-dicarboxylic acid ($H_2\mathbf{pdca}$) and Ag_2O in aqueous solution, followed by the slow evaporation of solvent [85]. The 1D polymer comprises two very similar chains running along the crystallographic *b* axis, with each chain containing two unique Ag(I) ions. In Fig. 57, the two chains are shown separated for clarity and their location relative to each other can be seen from the crystal-packing diagram. One Ag(I) ion in each chain has a centrosymmetric square planar coordination sphere with a *trans*-bis chelate configuration. Jaber et al. make no comment about the stereochemistry of these two Ag(I) centres, and both are sterically blocked by pyridine N atoms from adjacent polymer chains (Ag···N distances of 3.222 and 3.267 Å, respectively). The remaining Ag(I) centres of each chain are subjectively both either three or four coordinate depending on ones opinion regarding the Ag–Ag interactions which have short distances of 2.843(2) and 2.894(1) Å.

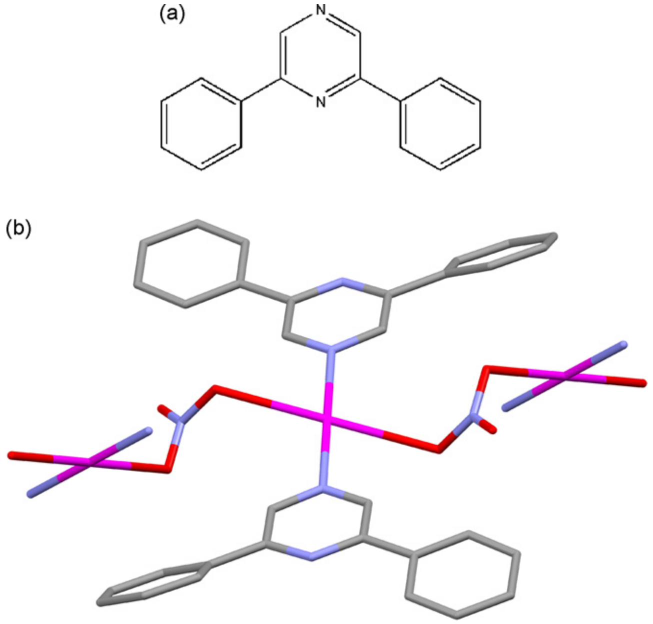


Fig. 55. The ligand **dpp** and the 1D coordination polymer $\{[Ag(\mathbf{dpp})_2NO_3]\}_\infty$.

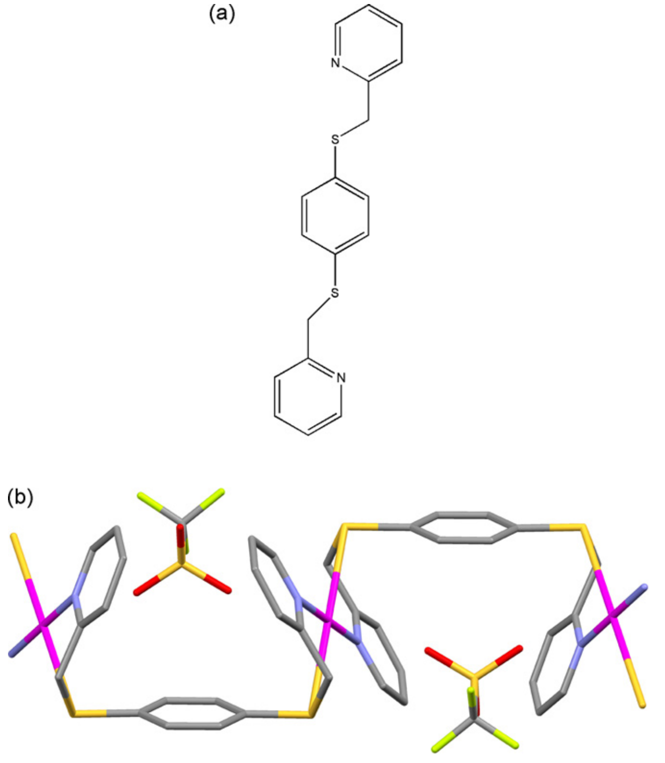


Fig. 56. The ligand **bptb** and the 1D coordination polymer $\{[Ag(\mathbf{bptb})]CF_3SO_3\}_\infty$.

6.12. $\{[Ag_3(\mathbf{bipy})_2(\mathbf{phnz})_2(Mo_8O_{26})]H_3O\}_\infty$

Yellow crystals of $\{[Ag_3(\mathbf{bipy})_2(\mathbf{phnz})_2(Mo_8O_{26})]H_3O\}_\infty$ were obtained via a hydrothermal reaction of $(NH_4)_6Mo_7O_{24}\cdot 2H_2O$, $AgNO_3$, 2-2′-bipyridine (**bipy**), and phenazine (**phnz**) in aqueous solution [86]. Shi et al. describe the 1D coordination polymer as chains constructed from β-octamolybdate bridged by **bipy** and **phnz** coordinated Ag(I) fragments. Two different Ag(I) environments are present in this compound. The first is centrosymmetric and the coordination sphere is completed by **phnz** N atoms from two ligands (Ag–N distance of 2.364(5) Å) and terminal O atoms from two β-octamolybdate clusters (Ag–O distance of 2.405(5) Å). The authors describe

Table 1
Reported complexes containing square planar Ag(I) ions with their space group, bond lengths and crystallographic symmetry.

No.	Complex name	Space group	Ag bond atoms	Ag bond lengths (Å)	Ag symmetry	Reference
1	{[Rh$_2$(**dfpma**)$_2$(MeCN)$_4$]$_2$[Ag(MeCN)$_4$]}(PF$_6$)$_5$	*C*2/*m*	Ag–N	2.290(6)	2/*m*	[49]
			Ag–N	2.409(6)		
2	[Ag(Pt(NH$_3$)$_2$**omuc**)$_4$](NO$_3$)$_5$·5H$_2$O	*P*2$_1$/*c*	Ag–O	2.35(2)	*i*	[50]
			Ag–O	2.43(2)		
3	[Ag(**mnso**)$_2$]PF$_6$	*C*2/*c*	Ag–S	2.654(2)	*i*	[51]
			Ag–S	2.717(1)		
4	[Ag(OH$_2$)$_2$(**pz**Co(NH$_3$)$_5$)$_2$](NO$_3$)$_7$·4H$_2$O	*C*2/*c*	Ag–N	2.320(5)	*i*	[52]
			Ag–OH$_2$	2.585(5)		
5	[Ag(**dptpb**)$_2$]PF$_6$	*P*-1	Ag–N	2.398(2)	*i*	[53]
			Ag–N	2.279(2)		
6	[Ag(**pbdb**)$_2$]PF$_6$ (two components of disorder)	*P*-1	Ag–N	2.293(10)	*i*	[53]
			Ag–N	2.427(7)		
			Ag–N	2.293(5)		
			Ag–N	2.495(2)		
7	[Ag(**dbdp**)$_2$]PF$_6$·Me$_2$CO	*P*-1	Ag–N	2.356(2)	*i*	[54]
			Ag–N	2.367(2)		
8	[{(**hbtp**)Rh(PPh$_3$)(μ-Cl)$_2$}$_2$Ag]BF$_4$	*C*2/*c*	Ag–Cl	2.619(2)	*i*	[12]
			Ag–Cl	2.6588(19)		
9	[Ag(**adpo**)$_4$]SbF$_6$	*P*4/*ncc*	Ag–P	2.612(1)	4	[55]
10	[Ag$_7$(**bmimen**)$_6$](ClO$_4$)$_7$·MeCN	*C*2/*c*	Ag–N(imine)	2.218(5)	*i*	[45]
			Ag–N(imid.)	2.615(6)		
11	[Ag$_4$(**oesq**)(**odsq**)(NO$_3$)$_4$]·H$_2$O (two different square planar Ag(I) centres in same molecule)	*Pbcn*	Ag–S	2.6807(12)	2	[56,57]
			Ag–N	2.351(3)		
			Ag–S	2.6157(13)		
			Ag–N	2.297(3)		
12	[{Ag(**tpy**)(MeCN)}$_2$](PF$_6$)$_2$ (two different square planar Ag(I) molecules in unit cell)	*P*2$_1$/*c*	Ag–N(py)	2.392(6)	None	[58]
			Ag–N(py)	2.415(7)		
			Ag–N(py)	2.401(7)		
			Ag–N	2.222(8)		
			Ag–N(py)	2.377(6)		
			Ag–N(py)	2.389(8)		
			Ag–N(py)	2.443(7)		
			Ag–N	2.211(9)		
13	[Ag(**dptpy**)(MeCN)](BF$_4$)·MeCN	*P*2$_1$/*c*	Ag–N(py)	2.310(6)	None	[58]
			Ag–N(py)	2.467(6)		
			Ag–N(py)	2.435(6)		
			Ag–N	2.174(8)		
14	[Ag$_3$(**tpy**)$_4$][(MeCN)Ag(**tpy**)](ClO$_4$)$_4$ (two different square planar Ag(I) molecules in unit cell)	*P*-1	Ag–N(py)	2.331(5)	None	[59]
			Ag–N(py)	2.399(7)		
			Ag–N(py)	2.433(7)		
			Ag–N	2.174(7)		
			Ag–N(py)	2.198(5)		
			Ag–N(py)	2.188(5)		
			Ag–N(py)	2.624(5)		
			Ag–N(py)	2.818(5)		
15	[Ag(**tpyp**)(MeCN)]PF$_6$·MeCN	*P*2$_1$/*n*	Ag–N(py)	2.348(5)	None	[26]
			Ag–N(py)	2.378(4)		
			Ag–N(py)	2.470(5)		
			Ag–N	2.187(6)		
16	[Ag(**tpysm**)(MeCN)]PF$_6$·MeCN	*Cc*	Ag–N(py)	2.343	None	[60]
			Ag–N(py)	2.352		
			Ag–N(py)	2.438		
			Ag–N	2.155		
17	[Ag(**tpyor**)(MeCN)]PF$_6$·Et$_2$O (two different molecules in unit cell)	*P*-1	Ag–N(py)	2.318	None	[61]
			Ag–N(py)	2.403		
			Ag–N(py)	2.483		
			Ag–N	2.230		
			Ag–N(py)	2.317		
			Ag–N(py)	2.418		
			Ag–N(py)	2.479		
			Ag–N	2.230		

Table 1 (*Continued*)

No.	Complex name	Space group	Ag bond atoms	Ag bond lengths (Å)	Ag symmetry	Reference
18	[Ag$_2$(**ptp**)$_2$](CF$_3$SO$_3$)$_2$	*P*-1	Ag–N(py)	2.403(9)	None	[25,62]
			Ag–N(py)	2.323(9)		
			Ag–N(pz)	2.417(7)		
			Ag–N(pz)	2.552(8)		
19	[Ag(**ppp**)$_2$]CF$_3$SO$_3$	*P*-1	Ag–N(py)	2.336(2)	None	[10]
			Ag–N(py)	2.352(2)		
			Ag–N(pz)	2.366(2)		
			Ag–N(pz)	2.325(2)		
20	[Ag$_2$(**tipm**)$_2$](BF$_4$)$_2$	$P2_1/c$	Ag–N(py)	2.366(4)	None	[63]
			Ag–N(py)	2.487(4)		
			Ag–N(pz)	2.298(3)		
			Ag–N(pz)	2.373(3)		
21	[Ag(**mpp**)]$_4$(CF$_3$SO$_3$)$_4$	*P*-1	Ag–N(py)	2.335(5)	None	[64]
			Ag–N(py)	2.413(5)		
			Ag–N(pm)	2.378(5)		
			Ag–N(pm)	2.423(5)		
22	[Ag(**dpbipy**)$_2$]BF$_4$·(11/3)DMF·(1/3)Me$_2$O (two different square planar Ag(I) centres in unit cell)	*C*2/*c*	Ag–N	2.240(4)	*i*	[65]
			Ag–N	2.591(5)		
			Ag–N	2.325(4)	None	
			Ag–N	2.339(4)		
			Ag–N	2.400(5)		
			Ag–N	2.424(5)		
23	[Ag$_2$(**dmpp**)$_4$(CO$_2$CF$_3$)$_2$]	*P*-1	Ag–N	2.2045(14)	None	[66]
			Ag–N	2.2164(15)		
			Ag–O	2.5584(13)		
			Ag–O	2.5742(13)		
24	[Ag(**fmip**)]BF$_4$·CHCl$_3$	$P2_1/c$	Ag–N(py)	2.277(7)	None	[67]
			Ag–N(py)	2.472(8)		
			Ag–N(imine)	2.308(7)		
			Ag–N(imine)	2.521(8)		
25	(NBu$_4$)$_4$[Ag$_2$(Mo$_5$O$_{13}$(OMe)$_4$NO)$_2$]	*Pbca*	Ag–O	2.342(8)	None	[68]
			Ag–O	2.346(7)		
			Ag–O	2.362(7)		
			Ag–O	2.477(7)		
26	[Ag$_4$(**odsq**)$_2$(NO$_3$)$_4$]	*Pcab*	Ag–N	2.308(5)	None	[56]
			Ag–N	2.336(5)		
			Ag–S	2.6757(17)		
			Ag–S	2.7071(17)		
27	[Ag(**acp**)NO$_3$]	$P2_1/n$	Ag–N	2.196(8)	None	[69]
			Ag–O	2.293(8)		
			Ag–O	2.553(9)		
			Ag–O(C=O)	2.552(9)		
28	[Pd(**nhc**)$_2$]$_2$(Ag$_2$X$_6$)·2Me$_2$CO (X = Cl, Br) (two different square planar Ag(I) centres in same molecule)	$P2_1/c$	Ag–X	2.298	None	[70]
			Ag–X	2.355		
			Ag–X	2.402		
			Ag–X	2.409		
			Ag–X	2.337		
			Ag–X	2.359		
			Ag–X	2.400		
			Ag–X	2.415		
29	{[Ag(**htsb**)]PF$_6$}$_\infty$	$P2_1/c$	Ag–S	2.6813(6)	None	[8]
			Ag–S	2.6618(6)		
			Ag–S	2.6203(6)		
			Ag–S	2.5999(6)		
30	{[Ag(**dpk**)]ClO$_4$}$_\infty$ (three different square planar Ag(I) centres in unit cell)	*Cc*	Ag–N	2.14(1)	None	[21]
			Ag–N	2.21(1)		
			Ag–O	2.59(1)		
			Ag–O	2.59(1)		
			Ag–N	2.16(1)		
			Ag–N	2.19(1)		
			Ag–O	2.57(1)		
			Ag–O	2.59(1)		
			Ag–N	2.17(1)		
			Ag–N	2.20(1)		

Table 1 (*Continued*)

No.	Complex name	Space group	Ag bond atoms	Ag bond lengths (Å)	Ag symmetry	Reference
			Ag–O	2.56(1)		
			Ag–O	2.60(1)		
31	$\{[Ag(urea)_2]ClO_4\}_\infty$	$P2_1/a$	Ag–N	2.323(3)	None	[71]
			Ag–N	2.351(3)		
			Ag–O	2.552(2)		
			Ag–O	2.492(2)		
32	$\{[Ag_5(\mathbf{nopca})_4]NO_3\}_\infty$	$P2/c$	Ag–O	2.209(2)	None	[72]
			Ag–O	2.218(2)		
			Ag–O	2.507(2)		
			Ag–Ag	2.9093(3)		
33	$\{[Ag_8(\mathbf{ttba})_2(MeOH)_{1/2}(H_2O)_{(3/2)}]\cdot 4MeOH\cdot 4H_2O\}_\infty$ (four different square planar Ag(I) centres in unit cell)	$P2_1/n$	Ag–O(ether)	2.707	None	[73]
			Ag–O(ether)	2.591		
			Ag–O(RCO$_2$)	2.304		
			Ag–O(RCO$_2$)	2.266		
			Ag–O(ether)	2.586		
			Ag–O(ether)	2.688		
			Ag–O(RCO$_2$)	2.271		
			Ag–O(RCO$_2$)	2.286		
			Ag–O(ether)	2.584		
			Ag–O(ether)	2.593		
			Ag–O(RCO$_2$)	2.292		
			Ag–O(RCO$_2$)	2.306		
			Ag–O(ether)	2.730		
			Ag–O(ether)	2.880		
			Ag–O(RCO$_2$)	2.210		
			Ag–O(RCO$_2$)	2.257		
34	$\{[Ag(\mathbf{sac})\mathbf{py}]\}_\infty$	$P3_121$	Ag–N(py)	2.116(2)	None	[74]
			Ag–N(sac)	2.084(2)		
			Ag–Ag	2.909(2)		
			Ag–Ag	2.985(1)		
35	$\{[Ag(\mathbf{dpms})]CF_3SO_3\}_\infty$	$P2_1/n$	Ag–N	2.328(8)	None	[75]
			Ag–N	2.324(8)		
			Ag–S	2.893(2)		
			Ag–S	2.913(2)		
36	$\{[Ag(\mathbf{bipy})H_2O][Ag(\mathbf{bipy})(\mathbf{ndc})H_2O]\cdot H_2O\}_\infty$	P-1	Ag–N(py)	2.163(2)	None	[76]
			Ag–N(py)	2.166(2)		
			Ag–OH$_2$	2.831(3)		
			Ag–O	2.826(3)		
37	$\{[Ag(\mathbf{tsa})\mathbf{pz}]\}_\infty$	P-1	Ag–N	2.197(3)	None	[77]
			Ag–N	2.203(4)		
			Ag–O	2.675(3)		
			Ag–O	2.707(3)		
38	$\{[Ag(\mathbf{nsa})\mathbf{pz}]\cdot H_2O\}_\infty$	R-3	Ag–N	2.243(4)	None	[77]
			Ag–N	2.269(4)		
			Ag–O	2.567(3)		
			Ag–O	2.568(3)		
39	$\{[Ag(\mathbf{pz})_2][Ag_2(\mathbf{pz})_5](PF_6)_3\}_\infty$	$P4/mbm$	Ag–N	2.32(2)	*mmm*	[4]
			Ag–N	2.45(2)		
40	$\{[Ag(\mathbf{miax})NO_3]\}_\infty$	$C2/c$	Ag–O	2.484(6)	*i*	[13]
			Ag–N	2.294(6)		
41	$\{[Ag_2(\mathbf{cmi})_2]\}_\infty$	P-1	Ag–N	2.280(4)	*i*	[78]
			Ag–N	2.427(6)		
42	$\{[Ag_3(\mathbf{tcbb})_3(Me_2CO)](BF_4)_3\cdot 4Me_2CO\}_\infty$ (two different square planar Ag(I) centres in unit cell)	$P2_1/c$	Ag–NC	2.158	*i*	[79]
			Ag–NC	2.652		
			Ag–NC	2.205		
			Ag–O	2.479		
43	$\{[Ag(\mathbf{dpmi})]ClO_4\cdot 2H_2O\}_\infty$	$Pnn2$	Ag–N	2.382(6)	2	[80]
			Ag–N	2.386(6)		
44	$\{[Ag(\mathbf{dpk})]PF_6\}_\infty$	$C2/c$	Ag–O	2.5878(12)	*i*	[81]
			Ag–N	2.161(3)		
45	$\{[Ag(\mathbf{dpk})]BF_4\}_\infty$	$C2/c$	Ag–O	2.552(1)	*i*	[82]
			Ag–N	2.180(3)		

Table 1 (*Continued*)

No.	Complex name	Space group	Ag bond atoms	Ag bond lengths (Å)	Ag symmetry	Reference
46	{[Ag(**ptp**)]PF$_6$}$_\infty$	*P*-1	Ag–N(py)	2.218(5)	*i*	[83]
			Ag–N(tz)	2.564(5)		
47	{[Ag(**dpp**)$_2$NO$_3$]}$_\infty$	*Pbcn*	Ag–N	2.2052(14)	*i*	[66]
			Ag–O	2.1051(14)		
48	{[Ag(**bptb**)]CF$_3$SO$_3$}$_\infty$ (two different square planar Ag(I) molecules in unit cell)	*P*2$_1$/*c*	Ag–N	2.205	*i*	[84]
			Ag–S	2.902		
			Ag–N	2.205		
			Ag–S	2.949		
49	{[Ag$_6$(**pdca**)$_2$(H**pdca**)$_2$(H$_2$O)$_4$]}$_\infty$ (two different square planar Ag(I) centres in unit cell)	*P*-1	Ag–N	2.166(5)	*i*	[85]
			Ag–O	2.705(4)		
			Ag–N	2.172(4)		
			Ag–O	2.706(5)		
50	{[Ag$_3$(**bipy**)$_2$(**phnz**)$_2$(Mo$_8$O$_{26}$)]H$_3$O}$_\infty$	*P*-1	Ag–N	2.364(5)	*i*	[86]
			Ag–O	2.405(5)		
51	{[Ag(C$_{10}$N$_7$)]}$_\infty$	*C*2/*c*	Ag–N	2.30(1)	*i*	[9]
			Ag–N	2.32(1)		
52	{[Ag$_7$(**tpst**)$_4$(NO$_3$)$_5$](ClO$_4$)$_2$·(DMF)$_2$}$_\infty$	*C*2/*c*	Ag–N	2.25	*i*	[87]
			Ag–S	2.871		
53	{[Ag(**psdbf**)$_2$]NO$_3$}$_\infty$	*P*-1	Ag–N	2.5059(14)	*i*	[3]
			Ag–N	2.3062(15)		
54	{[Ag(**psdbf**)$_2$]ClO$_4$}$_\infty$	*P*-1	Ag–N	2.308(2)	*i*	[3]
			Ag–N	2.578(2)		
55	{[Ag{(CN)$_2$}$_2$]AsF$_6$}$_\infty$	*C*2/*m*	Ag–N	2.364(7)	*i*	[88]
			Ag–N	2.399(6)		
56	{[Ag(Pt(**pz**)$_2$**tmeda**)$_2$](ClO$_4$)$_5$·2H$_2$O}$_\infty$	*C*2/*c*	Ag–N	2.320(4)	*i*	[89]
			Ag–N	2.586(4)		
57	{[Ag(**tpsa**)]}$_\infty$	*I*-4	Ag–O	2.377(2)	S4	[90,91]
58	{[Ag$_4$(**pyts**)(**pz**)$_4$(H$_2$O)$_2$]}$_\infty$	*Fddd*	Ag–N	2.202(4)	2	[77]
			Ag–O	2.666(4)		
59	{[Ag(**pmit**)]ClO$_4$}$_\infty$	*C*2/*c*	Ag–N(py)	2.247(5)	*i*	[11]
			Ag–N(imine)	2.543(5)		

the Ag(I) stereochemistry as distorted square planar. Axial sites experience weak intramolecular interactions with H atoms of **phnz** at distances of 2.89 and 2.94 Å, and with a terminal β-octamolybdate O atom at a Ag···O distance of 2.929 Å. The other Ag(I) ion is connected to the first by a bidentate bridging **phnz** ligand and has a trigonal pyramidal coordination geometry through additional coordination to a chelating **bipy** and a terminal β-octamolybdate O atom. The authors state that protonated water molecules interact with adjacent chains extending the structure, and have no interactions with the Ag(I) ion. This compound is intensely fluorescent. Further, polymeric structures based on similar molybdenum clusters have also been reported by An et al. [96] from the same research institution (Fig. 58).

6.13. {[Ag(C$_{10}$N$_7$)]}$_\infty$

The complex {[Ag(C$_{10}$N$_7$)]}$_\infty$ was prepared from AgNO$_3$ and the cyano-dienide ligand, Et$_4$N(C$_{10}$N$_7$), in water/Me$_2$CO solution and subsequently red–violet crystals were obtained by recrystallization from water/Me$_2$CO/MeCN [9]. Decoster et al. describe the 3D polymer as successive planes of centrosymmetric pseudo-square planar Ag(I) ions and C$_{10}$N$_7$$^-$ ligands, linked by pseudo tetrahedral Ag(I) ions sitting on a two fold axis. Each C$_{10}$N$_7$$^-$ ligand is strongly bound to four separate Ag(I) ions via external cyano N donors. The authors identify very long axial Ag···N interactions (3.36(1) Å) with neighbouring planes. They establish through electrochemical and ESR measurements that the Ag cation is diamagnetic and a genuinely Ag(I) ion. The authors attribute the unusual square planar coordination to steric effects. Initial tetrahedral Ag(I) coordination of these rigid C$_{10}$N$_7$$^-$ ligands would seem to give rise to parallel planes such that the only possible coordination environment with four N donors linking adjacent ligands must be square planar (Fig. 59).

6.14. {[Ag$_7$(**tpst**)$_4$(NO$_3$)$_5$](ClO$_4$)$_2$·(DMF)$_2$}$_\infty$

Reaction of a 2:1 molar ratio of AgNO$_3$ and an exotridentate N donor ligand 2,4,6-tris[(4-pyridyl)methylsulfanyl]-1,3,5-triazine (**tpst**) in MeOH/DMF solution and subsequent addition of AgClO$_4$ gave the colourless complex {[Ag$_7$(**tpst**)$_4$(NO$_3$)$_5$](ClO$_4$)$_2$·(DMF)$_2$}$_\infty$ [87]. It is a single stranded 1D coordination polymer containing nanosized tubes. These short tubes consist of face-to-face tetramers where each **tpst** ligand binds three Ag(I) ions through the two other arms with approximate linear coordination and in turn each of these Ag(I) ions bridges two **tpst** ligands. Adjacent tetramers are linked through further Ag(I) ions via a triazine N and thioether S donors on different ligands. Hong et al. describe these cen-

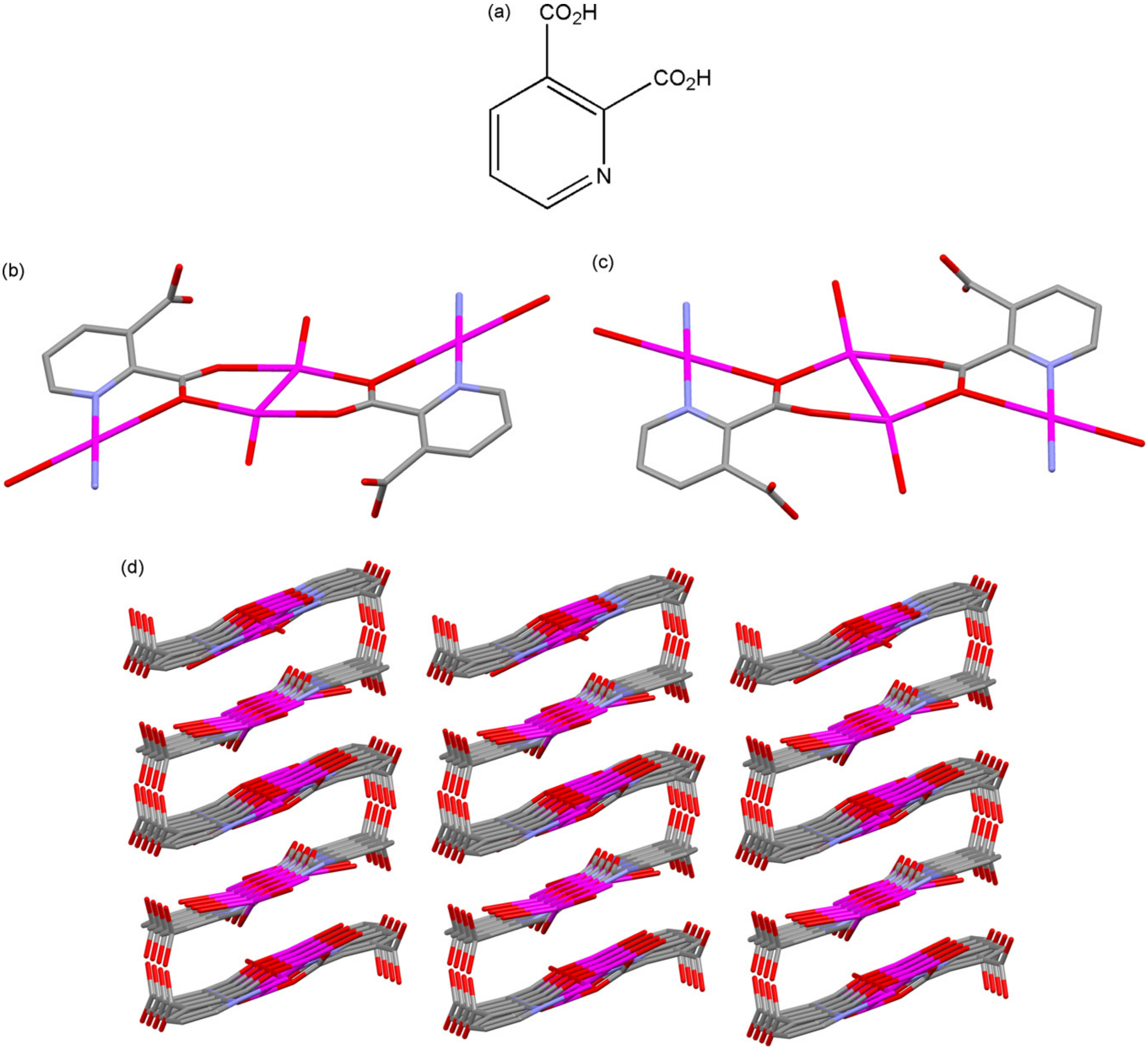


Fig. 57. The ligand H_2**pdca** and the complex $\{[Ag_6($**pdca**$)_2($H**pdca**$)_2(H_2O)_4]\}_\infty$. The two crystallographically different 1D polymeric chains of the dimer are shown separately for clarity. In reality, the dimers are neatly stacked in a planar manner, as is shown in the polymer packing diagram on the below.

trosymmetric Ag(I) ions as having a seldom observed, slightly distorted, square planar coordination. Four adjacent non-bound thioether sulfur atoms block the axial sites of this Ag(I) ion at distances of 3.24 and 3.34 Å (Fig. 60).

6.15. *$\{[Ag($**psdbf**$)_2]NO_3\}_\infty$*

Hanton and Young prepared colourless crystals of $\{[Ag($**psdbf**$)_2]NO_3\}_\infty$ by the diffusion of a $CHCl_3$ solution of **psdbf** into an MeCN solution of $AgNO_3$, and subsequent slow evaporation [3]. The 1D polymer contains square planar Ag(I) ions coordinated by four pyridine arms from two dibenzofuran derivatized ligands, with the ligands adopting a helical conformation. The Ag(I) axial sites have weak interactions to neighbouring disordered NO_3^- counterions at a distance of 3.01 Å. Interestingly, $\{[Ag($**psdbf**$)_2]NO_3\}_\infty$ and $\{[Ag($**psdbf**$)_2]ClO_4\}_\infty$ were found to have isomorphous crystal structures. Given that both a coordinating and non-coordinating anion gave the same structure it would appear the π-bound motif is very robust and most likely the reason for the square planar environment adopted in this case. BVS calculations (Section 1) were used to support the assignment of the square planar Ag(I) stereochemistry in these two isomorphous complexes (Fig. 61).

6.16. *$\{[Ag\{(CN)_2\}_2]AsF_6\}_\infty$*

Roesky et al. prepared $\{[Ag\{(CN)_2\}_2]AsF_6\}_\infty$ which is colourless and formed by the reaction of $AgAsF_6$ and excess cyanogen $(CN)_2$, in liquid SO_2 [88]. The 2D polymer contains a very rare example of a bridging cyanogen ligand. Each centrosymmetric Ag(I) ion is bound by four cyanogen N donor atoms in a square planar arrangement. The authors point out that

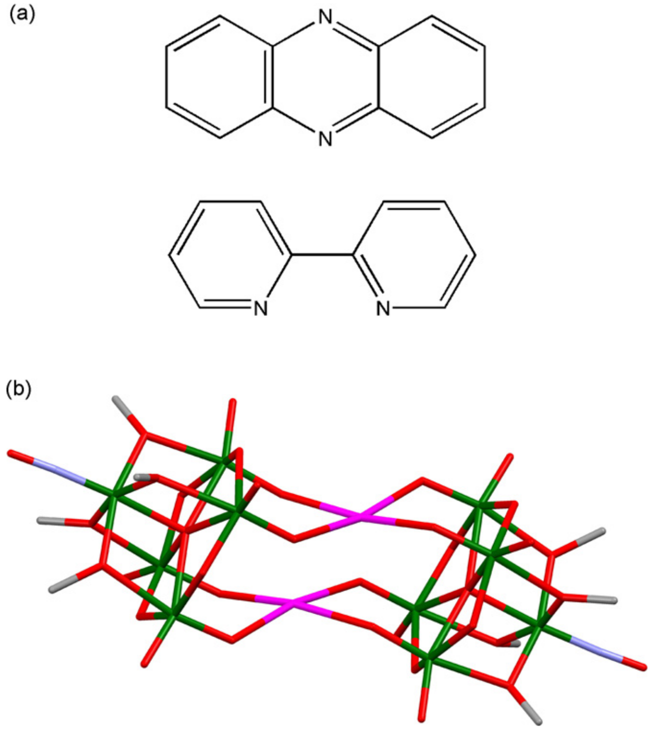


Fig. 58. The ligands **phnz** and **bipy**, and the 1D chain of the coordination polymer $\{[Ag_3(\mathbf{bipy})_2(\mathbf{phnz})_2(Mo_8O_{26})]H_3O\}_\infty$.

there are further weak axial Ag···F–AsF$_5$ interactions (Ag···F distance of 2.76 Å) completing a distorted octahedral coordination about the Ag(I) ion (Fig. 62).

6.17. $\{[Ag(Pt(\mathbf{pz})_2\mathbf{tmeda})_2](ClO_4)_5{\cdot}2H_2O\}_\infty$

Colourless crystals of $\{[Ag(Pt(\mathbf{pz})_2\mathbf{tmeda})_2](ClO_4)_5{\cdot}2H_2O\}_\infty$ (where **tmeda** = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; **pz** = pyrazine) were prepared by reaction of $[Pt(\mathbf{pz})_2(\mathbf{tmeda})](NO_3)_2{\cdot}2H_2O$ and AgClO$_4$ and then subsequent cooling of the aqueous solution [89]. Willermann et al. make no comment on the Ag(I) coordination stereochemistry which has a strictly planar donor set. A weak interaction with a ClO_4^- counterion is present at a Ag···O–ClO$_3$ distance of 2.920 Å. Numerous other disordered anions are present in the network (Fig. 63).

6.18. $\{[Ag(\mathbf{tpsa})]\}_\infty$

The white crystalline 3D polymer $\{[Ag(\mathbf{tpsa})]\}_\infty$ was first reported by Charbonnier et al. in 1983 [91] and subsequently by Makinen et al. in 2001 [90] with no reference to the earlier work. Makinen et al. prepared $\{[Ag(\mathbf{tpsa})]\}_\infty$ by sonication of two equivalents of 3-pyridinesulfonic acid (H**tpsa**) and one equivalent of Ag$_2$CO$_3$ in a MeOH solution, and subsequent solvent diffusion of isopropyl ether. $\{[Ag(\mathbf{tpsa})]\}_\infty$ contains ribbons of Ag(I) ions in three different environments in 2:1:1 ratio. The first environment is of highly distorted tetragonal geometry (or nearly linear according to Charbonnier et al.) of two trans N pyridine donors (Ag–N(py) 2.143(2) Å), two weakly interacting *trans*-sulfonate O atoms (Ag–O, 2.710(2) Å) and two possible weak axial interactions to adjacent Ag(I) ions (Ag···Ag, 3.0148(4) Å). The second Ag(I) environment is described by Makinen et al. as a less distorted tetragonal geometry and by Charbonnier et al. as a nearly square planar arrangement. The Ag(I) ions bind four equivalent sulfonate O donors in the plane (Ag–O, 2.377(2) Å) and have axial contacts to two further Ag(I) ions (Ag···Ag, 2.9878(7) Å). These two “tetragonal” Ag(I) environments form the above mentioned ribbon. The remaining Ag(I) environment is tetrahedrally coordinated to four equivalent sulfonate O donors (Ag–O, 2.380(2) Å). Interestingly, Makinen et al. have found the diffu-

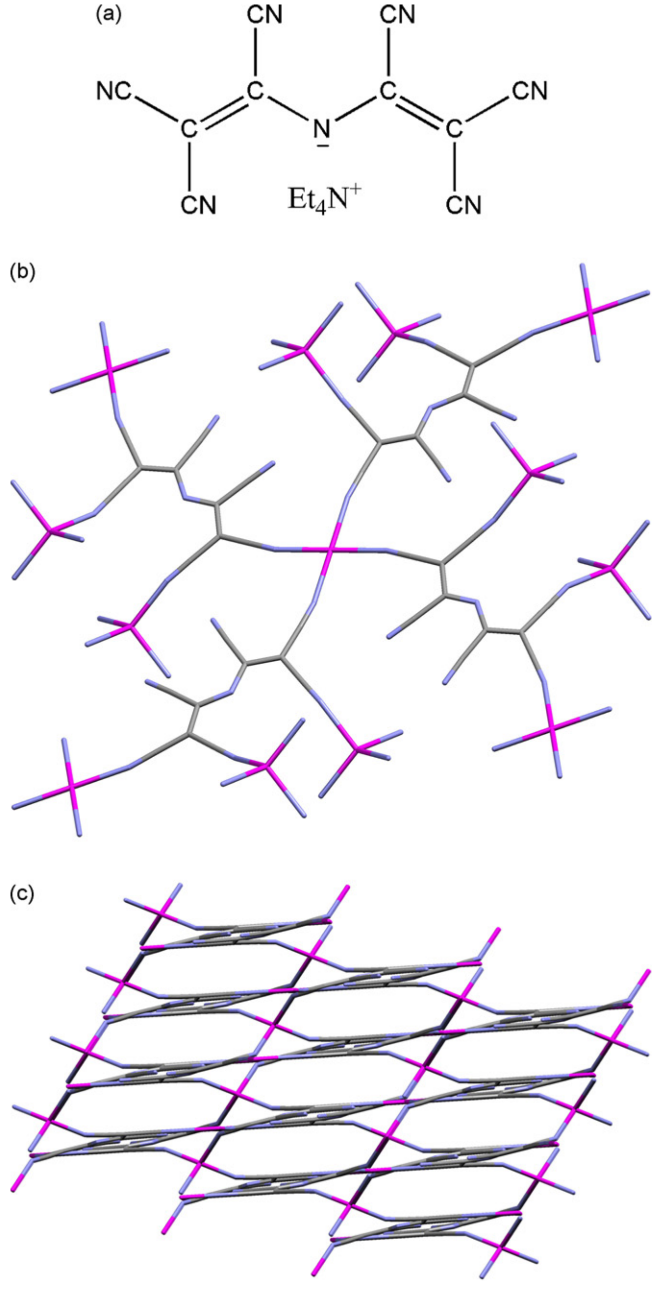


Fig. 59. The ligand Et$_4$N(C$_{10}$N$_7$) and the 3D coordination polymer $\{[Ag(C_{10}N_7)]\}_\infty$. The square planar Ag(I) environment is shown in the top image and the polymer packing is shown below.

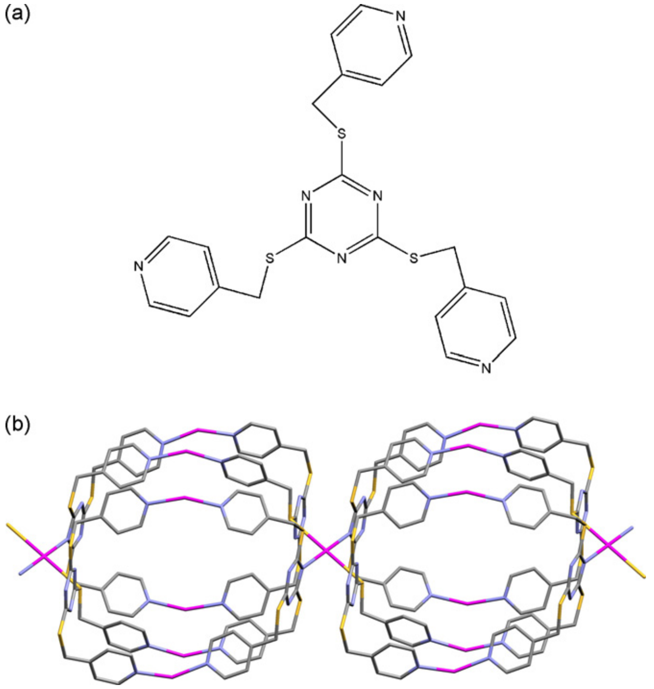


Fig. 60. The ligand **tpst** and the cationic chain of the 1D coordination polymer $\{[Ag_7(\mathbf{tpst})_4(NO_3)_5](ClO_4)_2{\cdot}(DMF)_2\}_\infty$.

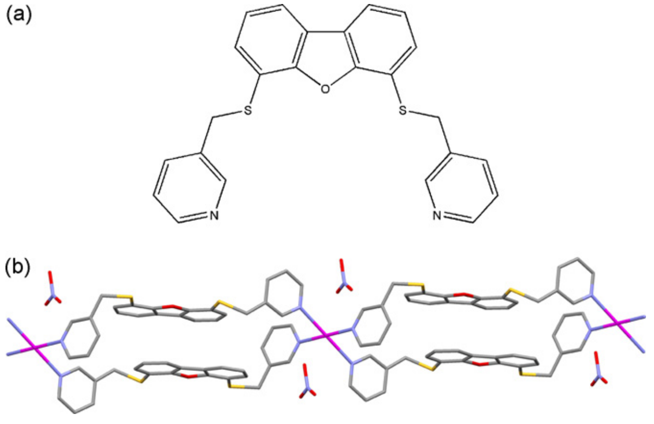


Fig. 61. The ligand **psdbf** and the 1D coordination polymer $\{[Ag(\mathbf{psdbf})_2]NO_3\}_\infty$.

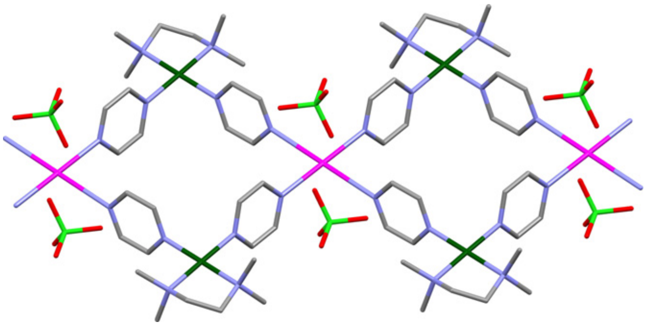


Fig. 63. The 1D polymer $\{[Ag(Pt(\mathbf{pz})_2\mathbf{tmeda})_2](ClO_4)_5{\cdot}2H_2O\}_\infty$. Waters of crystallisation and some counter anions have been removed for clarity.

sion of EtOAc into a MeCN solution of the sonicated polymer gave a new white polymer $\{[Ag(\mathbf{tpsa})(MeCN)_{1/2}]\}_\infty$. This is comprised of linked 24-membered rings with distorted linear and tetrahedral Ag(I) geometries. Polymers $\{[Ag(\mathbf{tpsa})]\}_\infty$ and $\{[Ag(\mathbf{tpsa})(MeCN)_{1/2}]\}_\infty$ can be interconverted by the reversible binding of MeCN with a rare space group change from tetragonal to triclinic (Fig. 64).

6.19. $\{[Ag_4(\mathbf{pyts})(\mathbf{pz})_4(H_2O)_2]\}_\infty$

Brown crystals of $\{[Ag_4(\mathbf{pyts})(\mathbf{pz})_4(H_2O)_2]\}_\infty$ were produced by the reaction of sodium 1,3,6,8-pyrenetetrasulfonate (Na_4**pyts**) and $AgNO_3$ in aqueous solution, followed by addition firstly of pyrazine (**pz**) in MeOH and then of aqueous NH_3 [77]. Two crystallographically unique Ag(I) ions are present, both residing on two-fold axes. The first is described by Li et al. as a nearly buckled square plane geometry, with the plane consisting of longer bonds from two sulfonate O donors and shorted bonds from two **pz** N donors. Interestingly, two related structures $\{[Ag(\mathbf{tsa})\mathbf{pz}]\}_\infty$ and $\{[Ag(\mathbf{nsa})\mathbf{pz}]{\cdot}H_2O\}_\infty$ from the same study (Sections 5.9 and 5.10) with similar bond angles were described as having flattened tetrahedral coordination geometry. This reflects the confusion surrounding the assignment of such stereochemistries. The Ag(I) axial sites are blocked by a tetrasulfonate C atom from a neighbouring sheet of the 2D polymer, and a Ag ion from within the same sheet at distances of 3.692 and 3.843 Å, respectively. The second unique Ag(I) ion is five

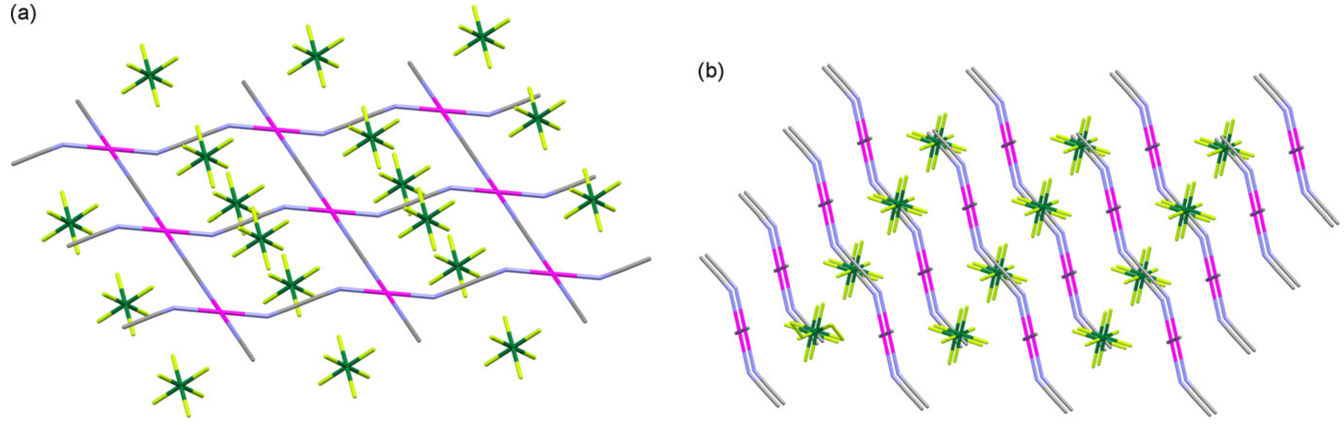


Fig. 62. The 2D coordination polymer $\{[Ag\{(CN)_2\}_2]AsF_6\}_\infty$.

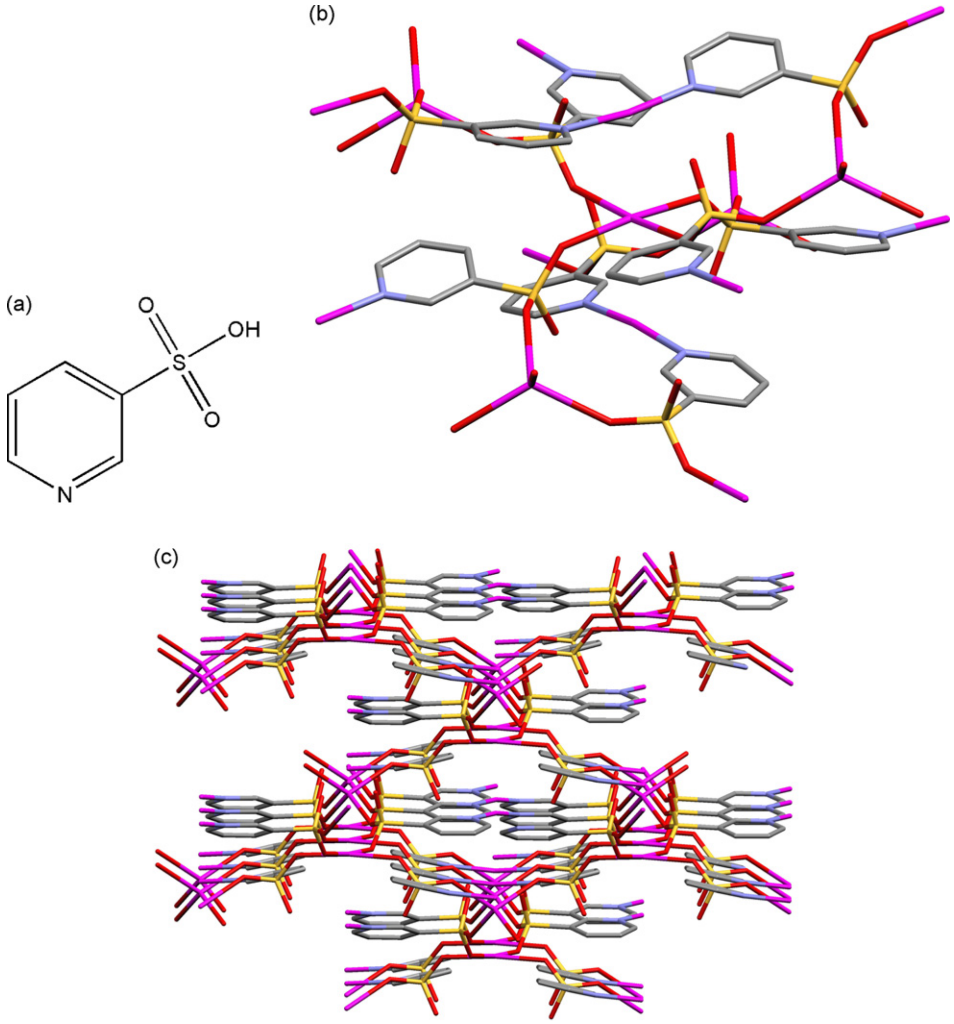


Fig. 64. The ligand **tpsa** and the 3D coordination polymer $\{[Ag(\mathbf{tpsa})]\}_\infty$. The square planar Ag(I) environment is shown above and the polymer packing is shown below.

coordinate and has a distorted square pyramidal geometry made up of bonds from two sulfonate O donors, two **pz** N donors, and a water molecule disordered equally over two sites (Fig. 65).

6.20. $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$

In this example, four-coordinate Ag(I) is stabilised in a square planar geometry by the acyclic N-donor ligand, **pmit**. Chowdhury et al. [11] attempt to rationale this less common Ag(I) geometry. The yellow polymeric complex $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$ was formed by the reaction of **pmit** and $AgClO_4$, and subsequent recrystallization from MeCN/Et_2O. $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$ consists of a 1D chain of $[Ag(\mathbf{pmit})]^+$ units where each ligand backbone is essentially planar and binds two symmetry related square planar Ag(I) ions in a chelated manner. The ClO_4^- counterions do not interact with the Ag(I) ion and its axial sites are sterically shielded by the methyl groups and by the adjacent polymer chains. A very different complex, $\{[Ag_2(\mathbf{ppit})_2](ClO_4)_2\}_{1.5}\cdot(MeOH)_{3.5}$, of the closely related ligand **ppit** is also reported. This yellow discrete complex was formed by the reaction of **ppit** and $AgClO_4$, and subsequent recrystallization from CH_2Cl_2/*n*-hexane. It consists of the dimeric cation $[Ag_2(\mathbf{ppit})_2]^{2+}$ and non-coordinating ClO_4^- anions. Each ligand backbone is helical and binds two tetrahedrally coordinated Ag(I) ions in a similar chelating manner to $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$ (Fig. 66).

The change from tetrahedral to square planar Ag(I) geometry from $\{[Ag_2(\mathbf{ppit})_2](ClO_4)_2\}_{1.5}\cdot(MeOH)_{3.5}$ to $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$ is accompanied by the conformational change of the ligand backbone from helical to planar. A conformation calculation study of the free ligands **ppit** and **pmit** revealed the lowest energy conformations being helical and planar, respectively. The crystal structure of the free ligand **ppit** is very similar to the calculated lowest energy structure. The crystal structure of **pmit** has not been obtained. The major conformational change is the *trans–cis* rotation in **ppit** required by formation of the five-membered chelate ring during Ag–N bond formation. $\{[Ag_2(\mathbf{ppit})_2](ClO_4)_2\}_{1.5}\cdot(MeOH)_{3.5}$ also contains strong π–π stacking interactions (3.45 Å) between one phenyl ring of a ligand and another pyridine ring of an adjacent ligand in the same complex, which further stabilises the helical backbone over its planar conformational alternative. The authors also

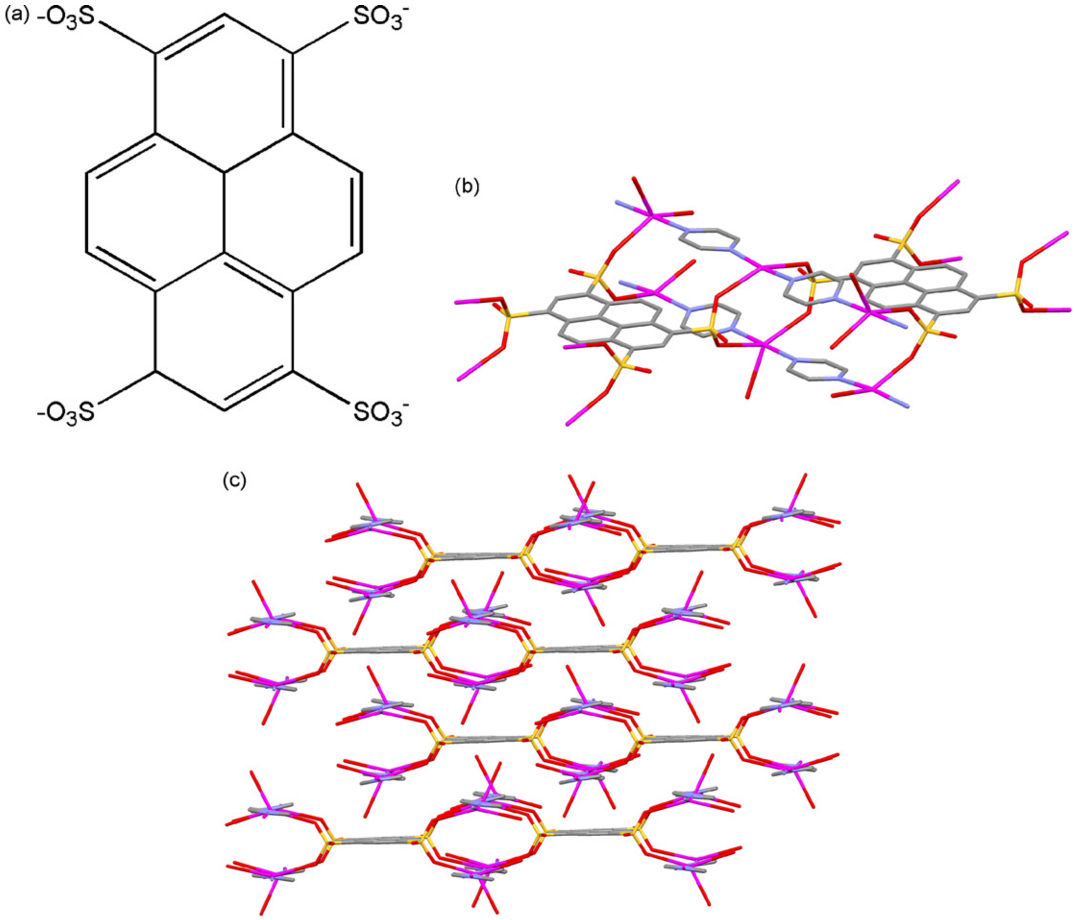


Fig. 65. The ligand **pyts** and the 2D coordination polymer $\{[Ag_4(\textbf{pyts})(\textbf{pz})_4(H_2O)_2]\}_\infty$. The top view shows the Ag(I) coordination sphere and the bottom view shows the polymer packing. For simplification, only one form of the disordered water ligand is shown.

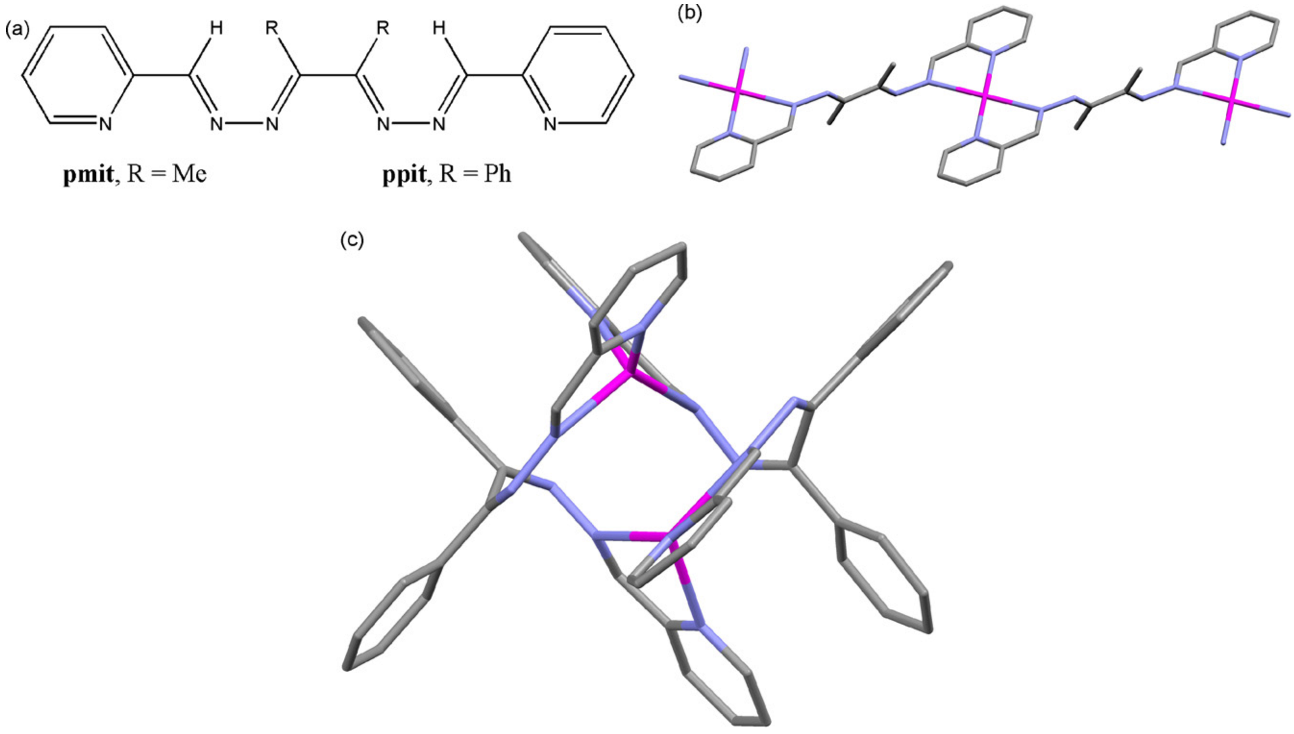


Fig. 66. The ligands **pmit** and **ppit**, the cationic chain of the 1D coordination polymer $\{[Ag(\textbf{pmit})]ClO_4\}_\infty$, and the cation of the discrete complex $\{[Ag_2(\textbf{ppit})_2](ClO_4)_2\}_{1.5}\cdot(MeOH)_{3.5}$ containing tetrahedral Ag(I) centres.

estimated the energy difference in coordination sphere of the tetrahedral and square planar motifs, using the simplified model compound 2-pyridinemethanimine. DFT calculations produced a difference of 11.2 kcal mol^{-1} as an approximate measure of the energy required to persuade Ag(I) to become square planar instead of tetrahedral in $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$. This suggests the linear polymer formation in $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$ is another important factor, as the above energy difference is considerably larger than the energy difference of the conformations in **pmit** of 2.53 kcal mol^{-1}. The complex $\{[Ag(\mathbf{pmit})]ClO_4\}_\infty$ was used for the BVS analysis in Section 1 of this review.

6.21. Section summary and comments

These 20 complexes (excluding three further isomorphous occurrences) are polymers with a range of dimensionalities, that contain a square planar Ag(I) centre with crystallographically imposed symmetry. The ligands employed vary considerably and collectively involve N, O, and S donor atoms. Four of these square planar Ag(I) centres have bond lengths within experimental error, while the remainder have two longer and two shorter *trans* bonds. All the square planar Ag(I) centres have axial sites that either contain weak interactions or are sterically blocked. In all but one case, the weak axial interactions involve neighbouring counter anions, while the axial steric blocking occurs from a large variety of groups that show no apparent trends. In the case of $\{[Ag(C_{10}N_7)]\}_\infty$, the authors comment on weak axial interactions to neighbouring polymer chains at a distance of 3.36. This distance is more likely to indicate blocking than a weak interaction.

7. Conclusion

Square planar Ag(I) complexes remain rare with only ∼2% of all silver complexes adopting this stereochemistry. There are currently around 65 well-characterised examples and with the growing interest in crystal engineering and coordination polymer synthesis this number will slowly increase. However, predicting the precise requirements for the formation of a square planar Ag(I) centre remain difficult.

In general, we have found that a large variety of seemingly unrelated ligands with a range of donor atoms give rise to square planar environments about a Ag(I) ion. This has more to do with the soft accommodating nature of the Ag(I) ion and its susceptibility to crystal packing forces than to any structural directing influences on the part of the ligands. The obvious exception is those ligands based on the terpyridine moiety (Section 3) which almost always produce a four coordinate planar system with Ag(I) salts. Associated with the plastic coordination character of Ag(I) is the empirical observation from the above occurrences of the prevalence of two longer and two shorter *trans* Ag(I)–ligand bond lengths. Our DFT calculations indicated that the origin of this is probably due to imposed crystallographic symmetry or crystal packing forces rather than any electronic effects associated with the Ag(I) centre. It is also possible that this apparent disparity in bond lengths results from the relatively small number of occurrences of the square planar geometry and as more structures are reported this apparent statistical anomaly may even out.

Interestingly, about half of the identified square planar structures were coordination polymers and as such have only been reported in the last 12 years. One possible reason for this is that the Ag(I) ion is located in an extended polymer structure. The specific orientation of the polymer structure means that the Ag(I) ion is affected by the steric congestion arising from the ancillary supramolecular interactions holding the polymer networks together. This steric congestion can protect the planar environment of the Ag(I) ion by blocking the vacant axial sites. The blocking of axial sites is a crucial element in forming square planar Ag(I) environments and not only are coordination polymers effective at this but also certain flexible ligands with ancillary bulky groups in close proximity to the ligand donor atoms. A number of discrete square planar complexes arise from complexation with a disparate range of ligands which all have this feature (Section 2). Our analysis shows that if the axial sites are not blocked in some way through steric measures there is almost invariably a weak interaction with a counter anion. Our statistical analysis (Section 1) of the Ag(I)$\cdots$anion distance for the typically used salts NO_3^-, ClO_4^- and BF_4^- suggests that 2.70–2.72 Å represents the boundary between a formal Ag(I) ligand bond and a weak axial interaction.

Our CSD search parameters included all four coordinate Ag(I) structures where *trans*-bond angles were in the range $175 \pm 5^\circ$ and $165 \pm 15^\circ$. However, in practice the unambiguous assignment of the square planar geometry is often complicated by a progressive distortion towards a tetrahedron. The square planar geometry is intrinsically dependent upon a planar arrangement of ligands and even small deviations from planarity may cause the stereochemistry to appear more tetrahedral than planar. This subtle distinction is open to subjective interpretation because as yet no simple designator exists for four coordination in the way that the τ value does for five coordination [97].

Finally, the square planar Ag(I) stereochemistry will continue to be of use to crystal engineers as a right angle node in network building and will always remain of interest to chemists due to its rarity which despite the number of occurrences we reviewed is still not threatened.

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