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Review

Metallosupramolecular silver(I) assemblies based on pyrazine and related ligands

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Abstract

Assemblies obtained by reactions of silver(I) salts with ligands that contain a pyrazine subunit are surveyed. A diverse range of discrete and one-, two- and three-dimensional polymeric species are described. Many complexes of pyrazine itself have been reported, as have compounds derived from substituted pyrazines and benzofused ligands, such as phenazine. Ligands that contain more than one pyrazine ring are also covered and these tend to lead to assemblies of higher dimensionality.

Keywords: Silver; Pyrazine; Metallosupramolecular; Coordination polymer; Bridging ligand

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1. Introduction

Bridging *N*-heterocyclic ligands are extensively used in coordination and metallosupramolecular chemistry [1–3]. The simplest such ligand is pyrazine (**1**) which has two nitrogen donors that can be used to form simple binuclear complexes, such as the Creutz–Taube mixed-valence complex [4], or larger discrete assemblies, such as molecular squares [5], or even larger coordination polymers (Fig. 1) [6–12]. Such metallosupramolecular assemblies have been the subject of much study in recent years [13–21].

Over the last decade, one of the most popular metals employed in the construction of such assemblies has been silver(I) [22–25]. This d^{10} metal is particularly versatile in its coordination number and geometry. In this review we survey the chemistry of silver(I) complexes of over 50 ligands that contain a pyrazine subunit. This reveals a remarkably rich array of discrete and polymeric structures, within which silver atoms are not only involved in coordination to the pyrazine nitrogens, but also participate in many other types of interactions, notably with anions and solvent molecules. Other weak associations, such as Ag–Ag, π–π, CH–N, CH–π and anion–π interactions, further help to provide diversity to the architectures of the assemblies formed. Silver complexes of ligands containing non-coordinated pyrazines are not, in general, included.

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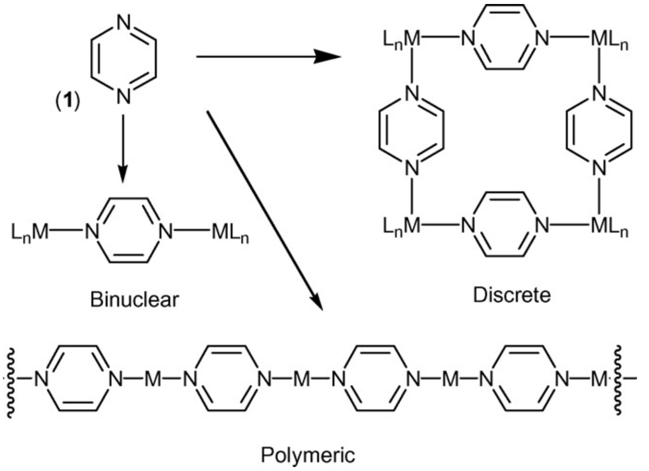


Fig. 1. Representative assemblies derived from pyrazine (**1**).

2. Discussion

2.1. Assemblies derived from pyrazine (*1*)

There have been many reports of the use of pyrazine itself as a synthon for coordination to silver in the preparation of metallosupramolecular assemblies. A large range of structures has been reported with variety resulting from the use of different metal:ligand ratios, different anions and different reaction conditions.

The coordination chemistry of pyrazine with silver(I) began more than a century ago with two early reports of the preparation of the 1:1 complex with silver nitrate [26,27]. This compound has since been the subject of various studies, including measurements of stability constants [28,29], infrared spectra [30] and mass spectra [31]. It was unambiguously shown to be a linear coordination polymer when its X-ray crystal structure was reported in 1966 [32]. The structure of this compound has recently been redetermined with a considerably higher level of precision [33]. Within the polymeric chain the N–Ag–N is significantly bent at an angle of 159°, due to the presence of weakly coordinating oxygen atoms of nearby nitrate anions. Using a search of the Cambridge Crystallographic Database for silver nitrate complexes of nitrogen ligands, Abu-Youssef et al. have recently shown that such deviations from linearity correlate with the distance of approach of the nitrate anions to the silver atom [34].

It is not surprising therefore that when a non-coordinating anion, such as tetrafluoroborate, is used, a more linear polymer results [35]. Thus the 1:1 complex of pyrazine with $AgBF_4$ has a relatively short Ag–N bond length (2.193 Å) and an N–Ag–N angle of 173.6°. The tetrafluoroborate anions are not bonded to the silver (shortest Ag–F distance > 2.7 Å). This complex is one of four described in a detailed study by Ciani and co-workers [35] where the metal:ligand ratio was varied. Two complexes with 1:2 ratios were isolated and their X-ray structures reported. These both contain planar silver atoms bound to three bridging pyrazine nitrogens with coordination geometry intermediate between trigonal and T-shaped and non-coordinated anions. The first of these complexes is an undulating two-dimensional (2D) sheet with a (6,3) topology, in which the silver atoms represent the three-connecting nodes. The second is a much more complex assembly, consisting of individual 3D triconnected nets with (10,3)-b topology (Fig. 2), which triply interpenetrate. With higher metal:ligand ratios a 1:3 complex was obtained, which has silver atoms bound to two bridging and two monodentate pyrazines. The silver has distorted tetrahedral geometry with N–Ag–N angles spanning the range 92–127°. This arrangement results in a 1D zig-zag polymer.

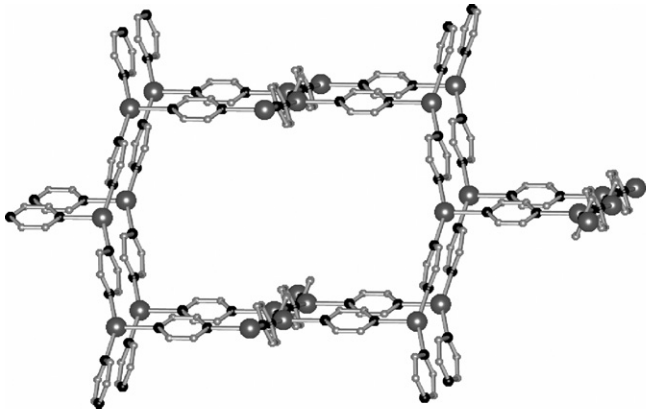


Fig. 2. A section of the (10,3)-b net reported by Ciani and co-workers [35].

In contrast to the complicated 1:2 metal:ligand complexes described above, the corresponding 1:2 silver:pyrazine complex with a hexafluorophosphate counterion has four-coordinate silvers bound to four bridging pyrazines [36]. This leads to undulating 2D sheets. The corresponding 1:1 complex with a PF_6^- counterion is a simple linear 1D polymer in which the N–Ag–N angle is crystallographically restrained to exactly 180° [37,38]. In one form of this compound the PF_6^- anions were disordered with hydroxide counterions. Another series of silver hexafluorophosphate complexes of pyrazine are more complicated [38]. These have an unusual 3:7 metal:ligand ratio and have a wafer-like polymeric structure consisting of alternating layers of different nature and composition. One layer consists of tessellated face-shared cubes with five-coordinate square-pyramidal silver atoms bridged by pyrazines with PF_6^- anions in the interior. The other layer is a flat square grid with square-planar silvers bridged by four pyrazines. Solvent molecules and counterions separate the alternating layers. Interestingly, the corresponding SbF_6^- complex has a 1:3 ratio and is a simple cubic framework of silver atoms lying on special positions with 222 symmetry. These are octahedrally coordinated to six bridging pyrazine ligands with relatively long Ag–N bond lengths.

There have been two reports of silver triflate complexes of pyrazine with a 2:3 metal:ligand ratio [37,39]. These are both ladder-like structures (Fig. 3) with T-shaped silver atoms as the three connecting unit and bridging pyrazines providing the sides and rungs of the ladder. The silver atoms have additional weak interactions with a triflate oxygen and, in one form, a water molecule.

An interesting series of three structures was reported by Ma and co-workers using arylsulfonates as the counterions

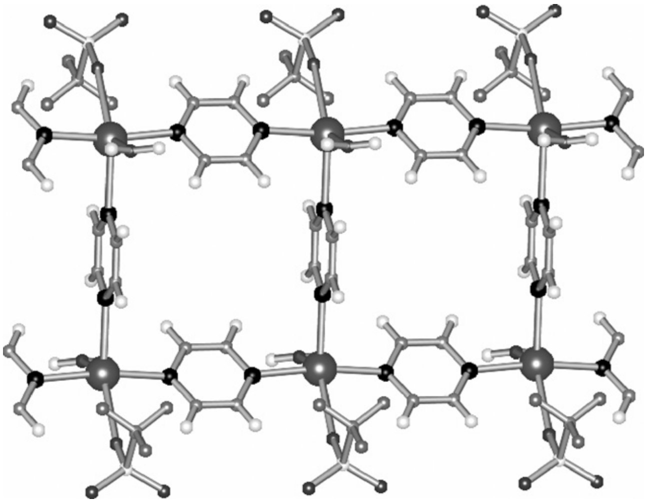


Fig. 3. A section of the silver triflate 1D ladders of (**1**) [37,39].

[40]. With 1-naphthalenesulfonate and *para*-toluenesulfonate two similar 1:1 silver:pyrazine coordination polymers were formed. These consist of two parallel linear chains (N–Ag–N angles of 175° and 177°, respectively) which are bridged by pairs of coordinated sulfonate groups to form eight membered rings (Fig. 4). With 1,3,6,8-pyrenetetrasulfonate a more complex 2D network resulted. This consists of parallel chains, similar to those described above, but with additional bridging involving all four sulfonate groups of the tetraanion acting as μ_2-bridges to connect the chains into a 2D-net. In this case there are two independent silver atoms, one with N_2O_2 square-planar geometry and the other with N_2O_3 square-pyramidal geometry, due to additional coordination by a water molecule.

In a similar fashion silver carboxylates can be used as bimetallic synthons for the formation of higher order assemblies. Brammer et al. reported the synthesis and X-ray structure of the silver trifluoroacetate complex of pyrazine [41,42]. This consists of the usual silver–pyrazine zig-zag chains (N–Ag–N angle = 134°) which are crosslinked by the carboxylate bridged Ag_2 dimeric units to produce 2D polymeric layers containing Ag_8L_4 rhomboids, which further link into a 3D network. Wang and Mak [43] also used trifluoroacetate as the anion in the synthesis of an interesting 3D network, in which columns of fused Ag_6 polyhedra containing encapsulated acetylide dianions are crosslinked by bridging pyrazine units. The non-coordinated trifluoroacetate anions reside in channels within the network.

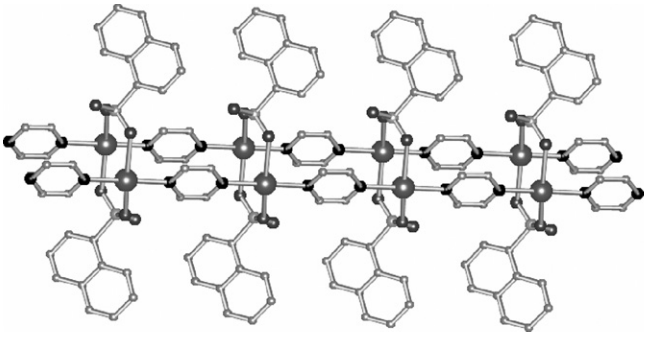


Fig. 4. A section of the parallel 1D chains bridged by arylsulfonates [40].

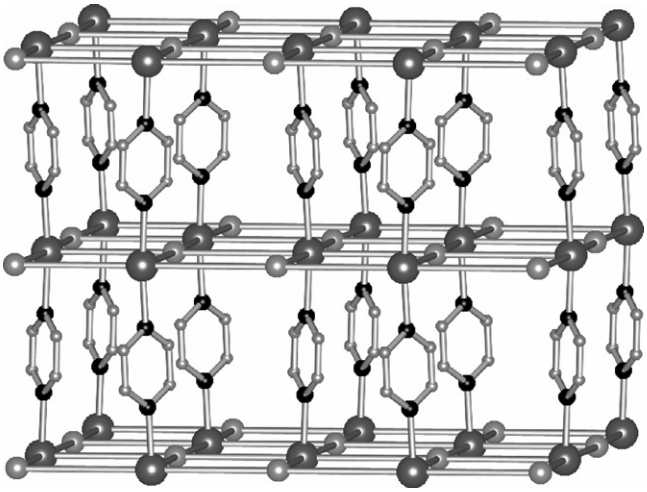


Fig. 5. Checkerboard sheets of silvers and carborane anions (represented here as small balls) connected by pillars of bridging pyrazines [44].

Complexes with much larger anions have been the subject of recent studies. Hardie and co-workers reported two silver–pyrazine structures with carborane anions [44]. The complex with $(CB_{11}H_{12})^-$ is a linear 1D polymer (N–Ag–N angle = 175°) which extends into a 3D network by virtue of the fact that each carborane anion forms BH–Ag interactions with four surrounding silver atoms. Thus, each silver binds to two bridging pyrazines and four BH groups from different anions in an octahedral coordination environment. This leads to checkerboard sheets of silvers and anions that are connected by pillars of bridging pyrazines (Fig. 5). With the larger $[Co(C_2B_9H_{11})_2]^-$ anion 1D chains are formed in which each silver atom is coordinated to two bridging pyrazines and two acetonitrile molecules with flattened tetrahedral geometry around the silver. These large anions do not interact directly with the silvers but reside in the spaces between the chains. Ren et al. recently reported the structure of a complex with a polyoxometallate anion [45]. This structure has two independent silver atoms that are bridged by pyrazines to form zig-zag polymer chains (N–Ag–N angles of 142° and 151°), which further assemble into a 3D network through weak interactions between the silver atoms and oxygens of the large $(PW_{12}O_{40})^{3-}$ anions.

In contrast to the almost linear 1D polymer formed with silver nitrate, the corresponding complex with silver nitrite is a zig-zag polymer due to the fact that the nitrite anion acts as a strongly chelating ligand [46]. The resulting N–Ag–N angle is reduced to 126°. Furthermore, the chains themselves assemble into an interesting 3D network by means of additional, albeit weak, Ag–Ag interactions (Fig. 6). The complex with the strongly coordinating dimesylamido anion is also a 1D zig-zag polymer (N–Ag–N angle = 99°) and has distorted tetrahedral silver atoms bound to two bridging pyrazines, the nitrogen of the $[N(SO_2Me)_2]^-$ anion and an acetonitrile molecule [47]. Robson and co-workers reported the synthesis and X-ray structure of an interesting complex with the tricyanomethanide (tcm) anion [48]. This is a strongly coordinating trigonal bridging ligand and leads to pla-

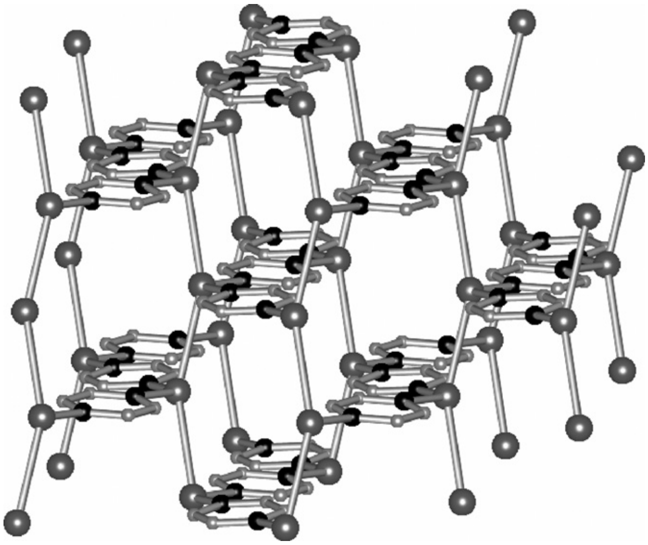


Fig. 6. The 3D network obtained with silver nitrite [46].

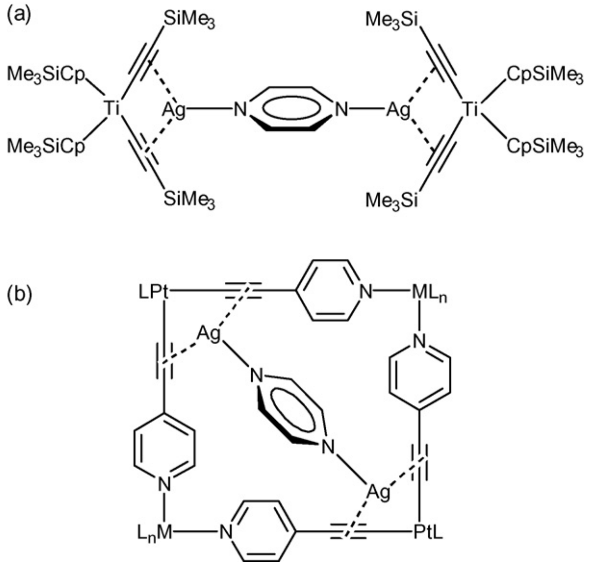


Fig. 7. Use of the "π–tweezer effect" to incorporate pyrazine–disilver units [50–52].

nar hexagonal arrays of silver atoms bridged by tcm anions as (6,3)-nets, which are then interconnected by bridging pyrazine ligands. This leads to five-coordinate trigonal-bipyramidal silver atoms as part of a 3D framework. Furthermore, two of these frameworks then interpenetrate.

Maggard and co-workers recently reported the syntheses and X-ray structures of two intriguing pyrazine pillared compounds with bridging metal-containing anions [49]. The perrhenate complex consists of linear pillars of silver–pyrazine chains (N–Ag–N angle = 170°) which are crosslinked into a 3D network through weaker coordination of the silver to oxygen atoms of three adjacent ReO_4^- anions. Correspondingly, each tetrahedral perrhenate coordinates to three different silver atoms. A similar, but more complex, assembly results from the use of the $[Mo_2O_4F_7]^{3-}$ anion, wherein π–π stacked cofacial linear silver–pyrazine chains are crosslinked into a 3D network by the molybdate anions. In this case there are two independent silver atoms, with $N_2O_2F_2$ and N_2O_2F coordination environments.

Lang and co-workers have reported two studies of complexes in which pyrazine bridges two silver atoms that are further bound to organometallic titanium tweezer units via silver–alkyne interactions [50,51]. The X-ray structure of one of these discrete complexes (Fig. 7a) was reported [51]. In a related context, Stang and co-workers have used this "π–tweezer effect" to incorporate an Ag_2(**1**) unit as a guest within organometallic molecular squares [52] (Fig. 7b).

Pyrazine has also been employed as a bridge between silver and a different metal for the formation of both discrete and polymeric heterometallic assemblies. The first X-ray structure of such a compound was a trinuclear mixed cobalt-silver compound, in which a central silver atom is bound to two pyrazines that bridge to octahedral pentaamminecobalt units [53]. Lippert and co-workers recently reported an interesting 1D polymer (Fig. 8) in which planar silver atoms are weakly coordinated (Ag–N distances = 2.586 Å) to four pyrazines, each of which bridges to a platinum atom that acts as a two-connecting unit to another pyrazine [54]. Carlucci et al. have described the preparations and X-ray structures of three fascinating Ru-Ag mixed-metal assemblies obtained by reactions of *trans*-$[RuCl_2(\mathbf{1})_4]$ with silver salts [55]. Reaction with silver triflate gave two products depending on the reaction conditions. The first of these has 1:1 stoichiometry and consists of molecular squares (Fig. 9) with alternate Ru and Ag corners, where two of the pyrazines on each ruthenium act as bridges and the other two are hypodentate. These squares then join together by means of chloride bridges, two per metal corner, leading to distorted tetrahedral silver atoms. The resulting extended structure has a double honeycomb layer arrangement. The second example has a 1:2 Ru:Ag ratio and consists of a single 3D bimetallic network of alternating six-connected Ru centres and three-connected Ag centres. The ruthenium starting material uses all four pyrazines, as well as the two chlorides, as bridging units and the silver atoms have distorted tetrahedral geometry with coordination to two pyrazines, a bridging chloride and a terminal O-bonded triflate anion. The third example results from reaction with silver nitrate and is a 3D tetragonal network with alternating six-connected Ru and Ag octahedral centres (Fig. 10). The six-coordinate silver atoms have relatively long bonds to four pyrazine nitrogens and two bridging chlorides.

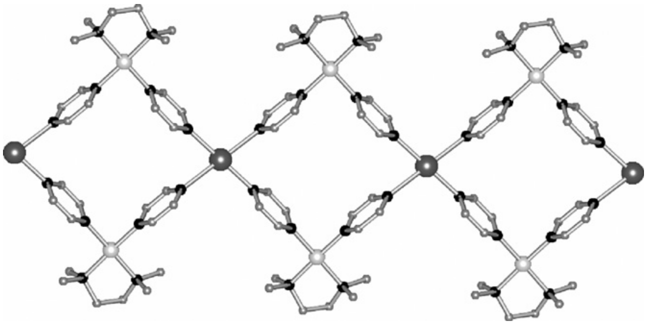


Fig. 8. A section of a mixed silver–platinum 1D polymer [54].

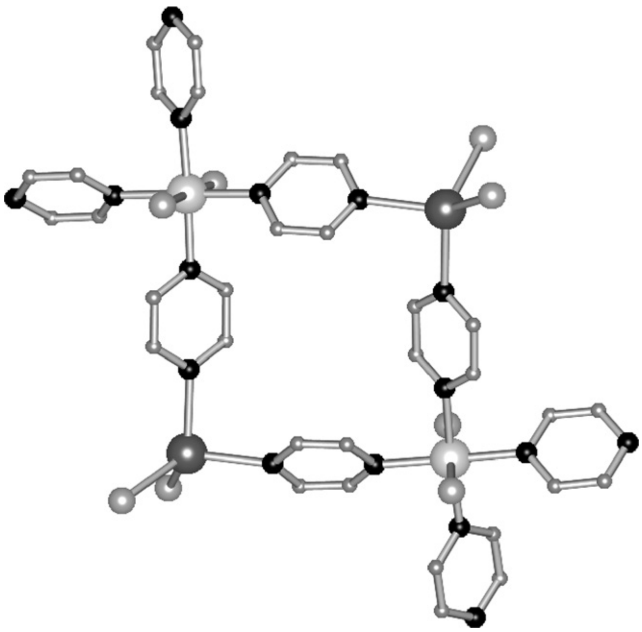


Fig. 9. A discrete silver–ruthenium molecular square [55].

Finally, we note that an early paper [56] suggested that pyrazine was able to stabilise silver in the +2 oxidation state and that the resulting polymeric peroxydisulfate complex has square-planar silver atoms bound to bridging pyrazines. Such compounds have been the subject of subsequent solution [57] and gas phase [58] studies.

2.2. *Assemblies derived from substituted pyrazines*

There are six methyl-substituted pyrazines, (**2**)–(**7**), all of which have been used to form silver complexes (Scheme 1).

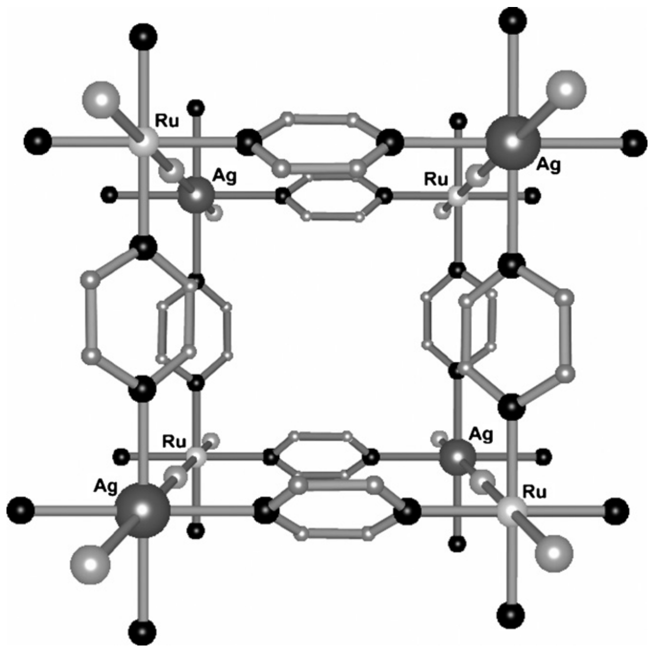
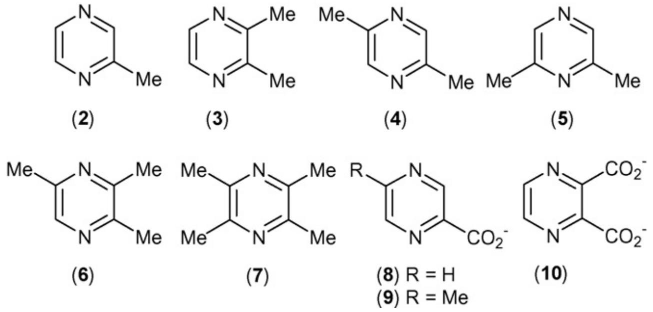


Fig. 10. A 3D network with alternating Ru and Ag octahedral centres [55].



Scheme 1.

There were some early studies of the synthesis and stability constants of simple 1:1 silver nitrate complexes of several of these ligands [28,59–61]. The X-ray structure of the silver nitrate complex of 2,5-dimethylpyrazine (**4**) has recently been reported [34]. It consists of 1D zig-zag chains with two independent silver atoms, each with trigonal geometry (N–Ag–N angle = 127°) and bound to two bridging pyrazines and a strongly coordinated monodentate nitrate. This compound was shown to have weak antimicrobial activity. The X-ray structure of the silver nitrate complex of tetramethylpyrazine (**7**) has also been reported recently [33]. It also has two independent silver atoms, but in this case they are quite different. One has a bent two-coordinate geometry (N–Ag–N angle = 157°) being bound only to two bridging tetramethylpyrazine groups, while the other has six-coordinate octahedral geometry with two pyrazine nitrogens (N–Ag–N angle = 91°) and two chelating nitrate anions. Weaker Ag–O interactions involving the two coordinate silver atoms further crosslink the chains into 2D sheets.

The X-ray structure of the 1:1 complex of silver trifluoroacetate and methylpyrazine (**2**) has been reported twice [62,63]. It also has two independent silver atoms each having tetrahedral geometry with two bridging pyrazines (N–Ag–N angles = 121°) and two bridging trifluoroacetate ligands. The double bridging leads to a 3D network. The structures of silver trifluoroacetate complexes of the four other methyl-substituted pyrazines have been reported by Brammer et al. [41]. Whereas 2,5-dimethylpyrazine (**4**) forms a network very similar to that described above for the parent ligand (**1**), 2,6-dimethylpyrazine (**5**), trimethylpyrazine (**6**) and tetramethylpyrazine (**7**) all form tiled 2D networks in which the trifluoroacetates bridge silvers using a single oxygen atom (Fig. 11). The 1:1 complex between silver hexafluoroantimonate and ethylpyrazine contains M_4L_4 squares that further link into “double crankshaft ribbons” that are interpenetrated [64]. A complex of silver iodide with ethylpyrazine has recently been reported [65]. It is a (6,3) 2D network with μ_3-iodides and monodentate pyrazine ligands coordinated through the less hindered N4 nitrogen.

The silver tricyanomethanide (tcm) complex of methylpyrazine (**2**) has a 2:3 silver:pyrazine ratio and exists as a 1D ladder (Fig. 12), which has bridging tcm groups providing the sides to the ladder and bridging methylpyrazine ligands providing the rungs [66]. The tetrahedral coordination of the silver atoms is completed by monodentate methylpyrazine ligands, which interestingly coordinate through the more sterically

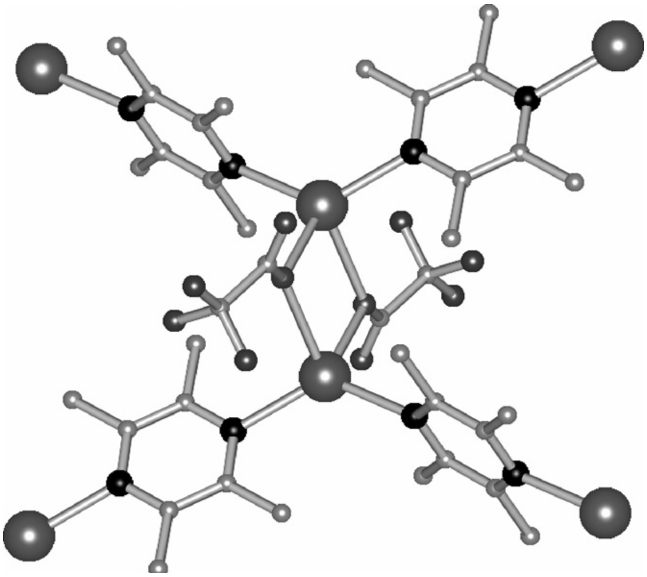


Fig. 11. Part of the 2D network obtained from ligand (**7**) and silver trifluoroacetate [41].

hindered, but more electron rich, nitrogen. The corresponding complex with tetramethylpyrazine (**7**) is different again and has 2:1 silver:pyrazine stoichiometry. It consists of rectangular tubes of Ag(tcm) bridged by tetramethylpyrazine ligands to form 2D sheets [66]. Stang and co-workers have also used tetramethylpyrazine (**7**) with two attached silver atoms as a guest within a molecular square [67]. Recently, Kong et al. [68] reported a fascinating structure with a (6,3)-net of trigonal silver atoms bridged by 2,3-dimethylpyrazine (**3**) ligands with a $(SiW_{12}O_{40})^{4-}$ counterion. The polyoxometallate tetraanion fill the voids in the 2D network.

Pyrazine carboxylic acids have been extensively used as ligands, primarily because of their ability to act as N,O-chelating ligands, and these are usually employed in their deprotonated form as anionic ligands. The simplest such ligand is pyrazinecarboxylate (**8**). The structure of its complex with silver was reported by Jaber et al. [69] and is a 3D polymer, wherein distorted tetrahedral silver atoms are bound to two pyrazine ligands, one of which is N,O-chelated. The coordinated oxygen further bridges to a symmetry related silver, thereby completing the coordination sphere of the silver. Seemingly unaware of the earlier report, Qin et al. have since redetermined this structure [70]. Zhao and Mak have recently used this ligand as an anionic bridging ligand in two 3D complexes with polyhedral silver cages having encapsulated acetylenedianions and additional nitrate or trifluoroacetate bridges [71].

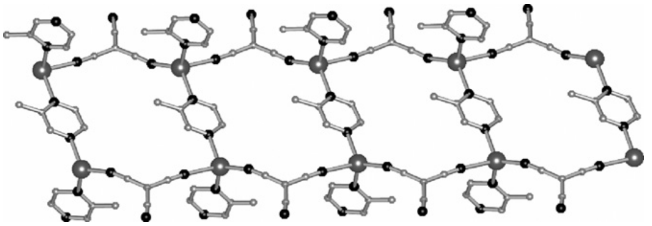


Fig. 12. The 1D ladder from silver tricyanomethanide and methylpyrazine [66].

Ligand (**8**) has also been used to make a number of heteronuclear mixed-metal assemblies. Dong et al. [72] reported the structure of a mixed copper(II)–silver(I) 3D network within which linear chains of alternating coppers and silvers are bridged by ligand (**8**) with N,O-chelation to copper and silver bound to the other nitrogen. These chains are crosslinked by water molecules to form sheets that are further joined by inter-layer $Ag–NO_3–Cu$ bridges. Two similar polymers, with nitrate and tetrafluoroborate anions, were also prepared from the methyl substituted ligand (**9**) and their X-ray structures reported [73]. Ciurtin et al. reported a similar Ag-Co mixed-metal linear polymer containing (**8**) that linked into a 3D network through other weak interactions [74]. Maggard and co-workers [75] used ligand (**8**) to prepare mixed silver–metal (Co, Ni) species in which the ligand bridges in a similar manner between octahedral chelated metals and $AgReO_4$ units to assemble pillared hybrid solids. The corresponding anhydrous copper complex is chiral [76].

2,3-Pyrazinedicarboxylate (**10**) is also a well-studied ligand. In addition to some early synthetic work [56,77], the structures of several silver complexes have been reported. The neutral 2:1 silver:pyrazine complex is surprisingly complicated [78]. It has two independent silver atoms, one of which is tetrahedral and coordinated to three oxygens and one nitrogen of four different molecules of (**10**). The other has trigonal coordination to two oxygens and one nitrogen of three different ligands, as well as two short axial Ag–Ag interactions between symmetry equivalent silvers which results in helical silver chains. Each molecule of (**10**) is bound to seven silver atoms leading to a complex 3D assembly. The monohydrate of this compound has a completely different structure, again with two independent silver atoms [78]. One is tetrahedral with an N,O-chelate, an oxygen of the other carboxylate of another molecule of (**10**) and a water molecule as ligands. The other has trigonal geometry with a nitrogen and two oxygens of three different molecules of (**10**), which this time is coordinated to five silvers. Once again there are short Ag–Ag interactions which lead to hexagonal Ag_4O_2 rings. The complete structure is a 3D polymer which also features π–π stacking of the pyrazine rings (Fig. 13). These compounds are photoluminescent.

The 2:1 complex of (**10**) with an additional coordinated ammonia molecule has also been reported [69]. It has two trigonal silver atoms, one being coordinated to two oxygens and one nitrogen of three different ligands, while the second is bonded to an N,O-chelated ligand and the ammine. The 1:1 complex of (**10**), as an ammonium salt, has a less complicated 2D sheet structure with silver coordinated in a trigonal manner to two oxygens and one nitrogen of three different molecules of (**10**), each of which coordinates to three silvers [79]. The only report of other isomeric pyrazinedicarboxylates are of the 2,5- and 2,6-isomers, whose silver complexes have been reported to possess antibacterial and antifungal properties in the patent literature [80].

2-Pyridylpyrazines can also act as chelating ligands, although as neutral rather than the anionic ligands of pyrazine carboxy-

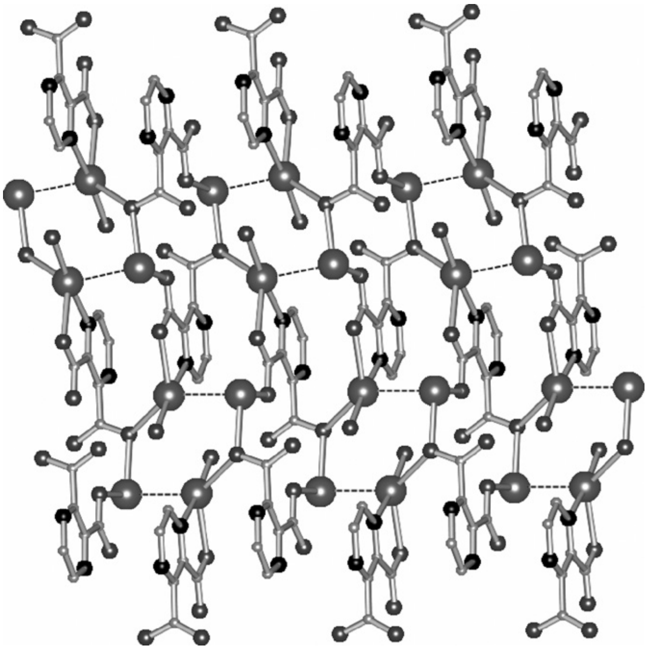


Fig. 13. Part of the 3D polymer obtained from ligand (**10**) [78].

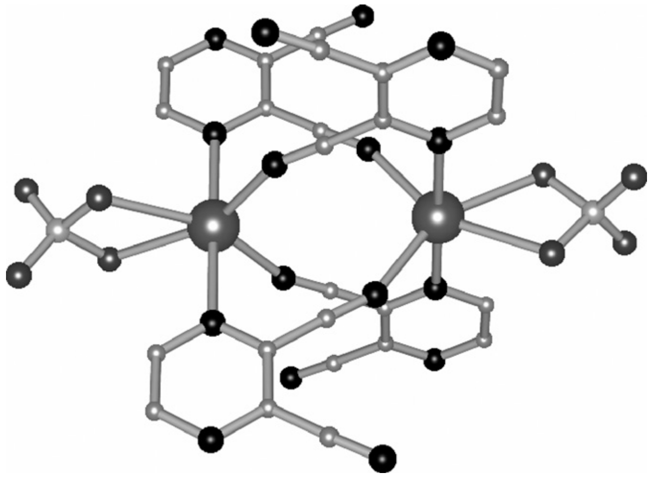
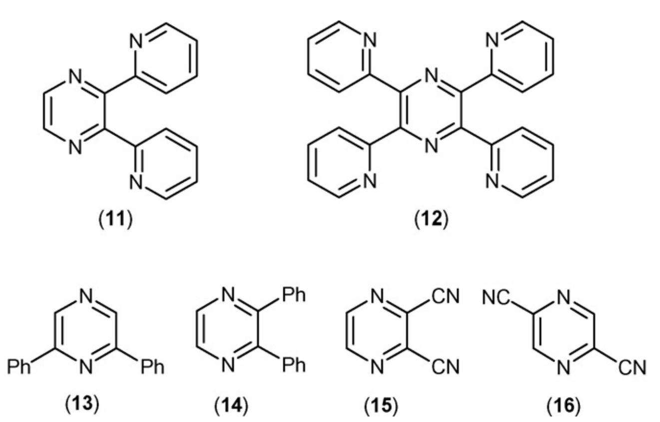


Fig. 14. Part of the 1:1 complex between silver perchlorate and ligand (**15**) [88].

lates [81]. 2,3-Bis(2-pyridyl)pyrazine (**11**) (Scheme 2) reacts with [Ag(MeCN)$_4$]BF$_4$ to form a 1D helical polymer, but in this case only the pyridine rings are coordinated to the silvers [82]. Hardie and co-workers have reported an interesting 1D chain formed from the reaction of (**11**) with a silver cobalticarborane [44]. It has two types of four coordinate silvers and two types of bridging ligand. One of these uses only the pyridine nitrogens to bridge, while the other uses three of the four available nitrogens and includes an N,N-chelating moiety. The $[\mathrm{Co(C_2B_9H_{11})_2}]^-$ anions fill the spaces between the chains, leading to a checkerboard arrangement. More recently, two silver complexes with phenylcarborane anions were reported [83]. These are both 1D chains; in one the ligand uses both chelation sites, while in the other each silver is bound to three ligands with only one chelating interaction. Wang and Mak also used this ligand as a bridge in their studies of linked silver cages with enclosed acetylenediide dianions [43]. A related ligand with 4-pyridyl substituents forms a linear coordination polymer with silver acetate, but only uses the pyridine nitrogens for coordination [84]. Tetrakis(2-pyridyl)pyrazine (**12**) has been used to form a 2D bimetallic oxide constructed from Ag$_4$(**12**)$_2$(OH$_2$) chains linked through $\mathrm{Mo_8O_{26}}^{4-}$ clusters [85]. There are three silver environments in the chains, one coordinated to four nitrogens, one to two nitrogens and a water and the other to three nitrogens and an oxygen of the anion.

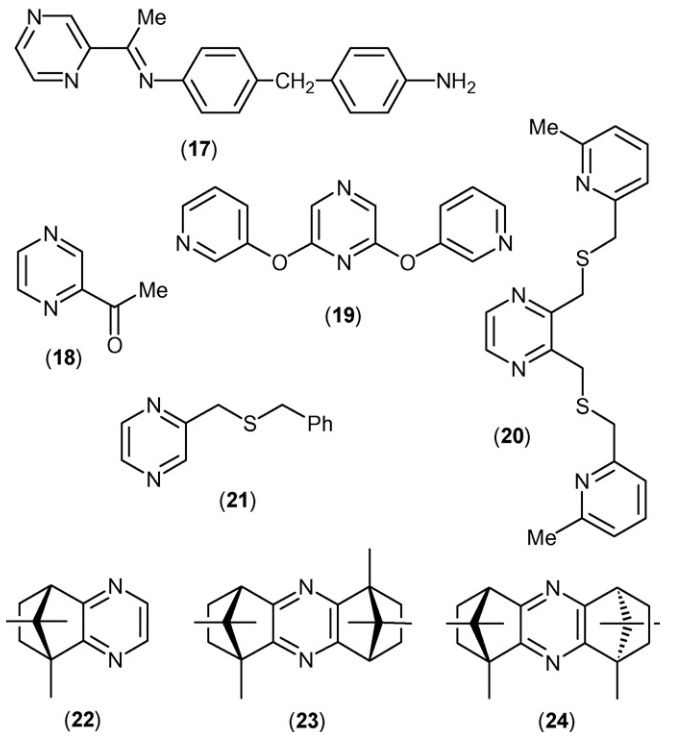


Scheme 2.

In a related context, Bosch and co-workers have reported two interesting studies involving the use of diarylpyrazines as bridging ligands. Both discrete and polymeric species were formed from reactions of various silver salts with 2,6-diarylpyrazines [86]. In the simplest case of 2,6-diphenylpyrazine (**13**) (Scheme 2), reactions with silver nitrate and silver tetrafluoroborate lead to 1:2 silver:ligand complexes in which only the less hindered N4 nitrogen coordinates because the phenyl rings lie in the same plane as the pyrazine ring. The silver atoms are square-planar (N–Ag–N angle = 180°) and additional π–π stacking and silver anion interactions led to a more complex superstructure. Introduction of methyl substituents into the *ortho* positions of the phenyl rings served to twist these rings out of the plane of the pyrazine ring, thereby exposing the N1 nitrogen for coordination. This leads to polymeric complexes with silver trifluoroacetate in which the ligands act as bridges and additional Ag–anion and/or Ag–π interactions occur. In a subsequent study with 2,3-diarylpyrazines, such as (**14**), the two nitrogens are equivalent and 1D coordination polymers formed with various silver salts [87].

Suenaga et al. [88] reported an intriguing 1:1 complex between silver perchlorate and 2,3-pyrazinedicarbonitrile (**15**). It has each of the four nitrogens coordinated to four different silver atoms and each silver coordinated to four nitrogens and a weakly chelating perchlorate (Fig. 14). This results in a square mesh network with internal channels. The corresponding product with 2,5-pyrazinedicarbonitrile (**16**) has a related structure but with square-pyramidal silver atoms that produces a different type of 3D framework that is maintained in the analogous silver triflate complex [89].

Hannon and co-workers obtained an AgBF$_4$ complex containing the pyrazinylketimine ligand (**17**) (Scheme 3) which



Scheme 3.

acted as a triply bridging ligand to three silvers [90]. Each silver atom is five-coordinate, bonded to an N,N-chelating unit, the N4 pyrazine nitrogen and the amino group of three different ligands. The coordination sphere was completed by a THF molecule. Dong et al. reported the structure of a silver triflate complex of 2-acetylpyrazine (**18**) in which the ligand bridges silver atoms, acting as an N,O-chelate and monodentate bridge [91]. The resulting 1D zig-zag chains are crosslinked by weak Ag–O interactions with the triflate anions. An X-ray structure of the silver nitrate complex of 2-phenylethenylpyrazine has been reported and has five-coordinate silver atoms with four attached ligands bound through the less hindered N4 nitrogen and a monodentate nitrate [92]. Further weak Ag–O interactions link these units into linear chains.

We have described the reaction of silver nitrate with ligand (**19**), which leads to a 1:1 complex in which the ligand acts as a Y-shaped bridge to three silver atoms using the two pyridine nitrogens and the less hindered of the two pyrazine nitrogens [93]. The tetrahedral silver atoms are also bound to a monodentate nitrate, which results in the formation of 2D sheets.

Hanton and co-workers have described a number of ligands containing a pyrazine ring with appended groups that contain additional coordination sites. For example reaction of silver perchlorate with the 2,3-disubstituted ligand (**20**) led to an intriguing 2:1 silver:ligand complex containing a single stranded helix that underwent spontaneous resolution [94]. Each molecule of (**20**) bridges four silver atoms, each with distorted trigonal geometry and bound to an N,S-chelating group and a pyridine nitrogen (Fig. 15). Subsequent work with the analogous 2,5-disubstituted ligand lacking the two methyl groups led to coordination polymers with both silver perchlorate and silver nitrate [95]. The silver perchlorate complex is a 1D polymer with five-coordinate silvers bound to two pyrazine nitrogens, two sulfurs and one pyridine nitrogen; the other pyridine is not coordinated. The silver nitrate complex is more complicated and has two isomeric polymer chains coexisting within the same crystal. These differ in the donor atoms on the silver and the arrangement of adjacent ligands along the chain. More recently, a series of simpler ligands, such as (**21**), were prepared [96]. This ligand was shown to form three silver complexes all of which were 2D sheets with considerable π–π stacking interactions. The related ligands in which the phenyl group is replaced by 2-, 3- or 4-pyridyl groups display very rich coordination chemistry with silver, leading to discrete dimers, 1D chains, 2D sheets and 3D networks [96].

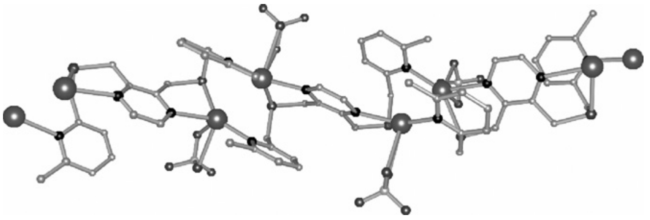


Fig. 15. A section of the single stranded helix obtained from ligand (**20**) [94].

We have recently synthesised a series of chiral pyrazine derivatives (**22**)–(**24**), which are derived from the readily available monoterpene (+)-camphor. These homochiral ligands all have bornane units fused to a pyrazine ring. The C1-symmetric ligand (**22**) reacts with silver nitrate to form a linear 1D polymer within which the ligands faithfully assemble in a regular fashion to form a unidirectional chiral coordination polymer [97]. The two doubly bornane-fused ligands (**23**) and (**24**) both have C2 symmetry but differ in a subtle way. Ligand (**23**) has the C2 axis perpendicular to the plane of the pyrazine ring, such that the two nitrogens are symmetrically equivalent. As a result the chiral coordination polymer formed from reaction with silver nitrate is non-directional (Fig. 16a) [98]. In contrast, ligand (**24**) has the C2 axis lying in the plane of the pyrazine ring and has two different nitrogens, one being considerably more sterically hindered than the other. Upon reaction with silver nitrate this ligand also faithfully assembles into a chiral coordination polymer (Fig. 16b) that is unidirectional [99].

2.3. Assemblies derived from benzofused pyrazines

The benzofused pyrazines, phenazine (**25**) and quinoxaline (**26**), have both been used to form silver complexes (Scheme 4). Early investigations focused on their use in emulsions with silver salts as sensitisers, desensitisers and developing agents for photography [100]. Silver salts have also been used extensively in the purification and characterisation of sulfonic acid and carboxylic acid derivatives of (**25**) and (**26**) [101,102].

Phenazine has been used more extensively than quinoxaline to form silver complexes, perhaps due to its higher symmetry. Munakata and co-workers reported the first examples of X-ray structures of silver complexes of (**25**) with different counterions [103]. Non-coordinating perchlorate gives a 1D

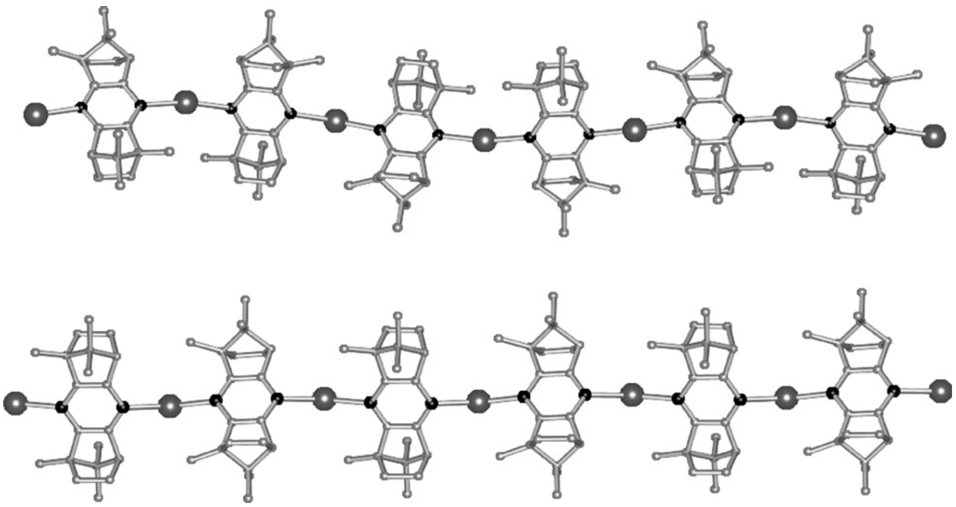
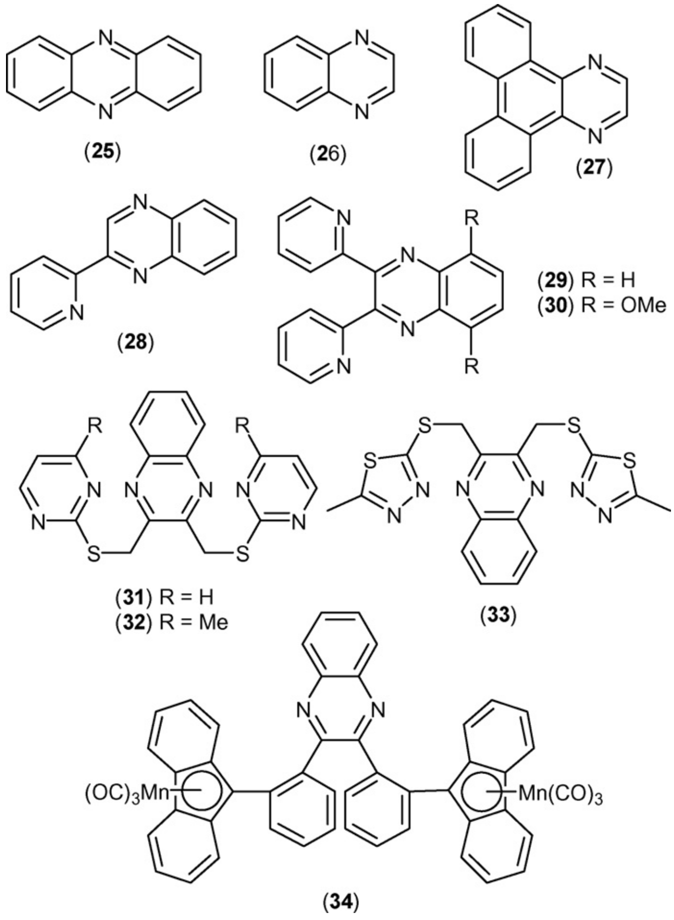


Fig. 16. Sections of the non-directional (a, top) and unidirectional (b, bottom) chiral coordination polymers from ligands (**23**) [98] and (**24**) [99].

polymeric structure where the silver atoms have almost linear coordination geometry, bridging two phenazine ligands with an N–Ag–N angle of 178.6°. The more coordinating nitrate counterion completely disrupts the bridging by silver atoms, which now coordinate to only one bridging molecule of (**25**) and two bridging nitrate counterions, thereby creating a 2D network structure (Fig. 17). The large aromatic surface area of (**25**) increases the likelihood of π–π stacking, and this is observed in both complexes. In two separate studies, Khmelevskaya and co-workers prepared discrete 1:2 metal:ligand complexes, where two phenazine molecules coordinate silver through one nitrogen atom. The silver atoms are also coordinated by water ligands, with the number controlled by the nature of the counterion, with triflate having one coordinated water [104] and tetrafluoroborate having two [105].



Scheme 4.

Phenazine can be utilised as a bridge between silver and other metal fragments. Siedle and co-workers observed the coordination of silver triflate to an organometallic platinum phenazine complex. No structural information was given, with the complex shown to exist as a discrete unit in solution by conductivity measurements [106].

Phenazine represents a more hindered analogue of pyrazine, and as such has been used extensively in comparative structural studies. In their investigation of silver complexes of tricyanomethanide Robson and co-workers also utilised (**25**) [48]. In contrast to the pyrazine structure described above, the bridging phenazine ligands restrict the silver atoms to a dis-

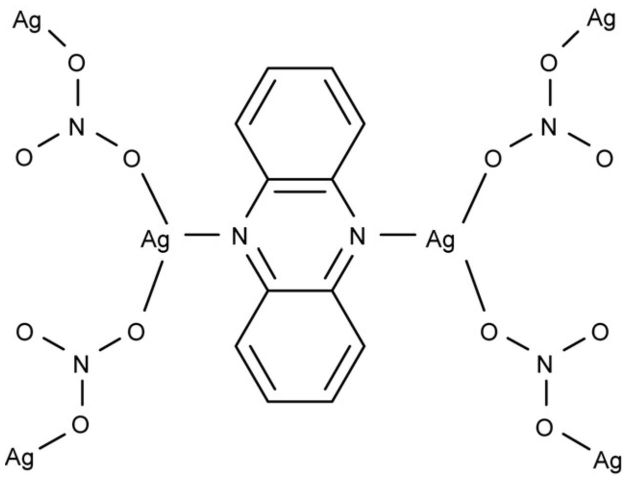


Fig. 17. Representation of part of the 2D network from phenazine and silver nitrate [103].

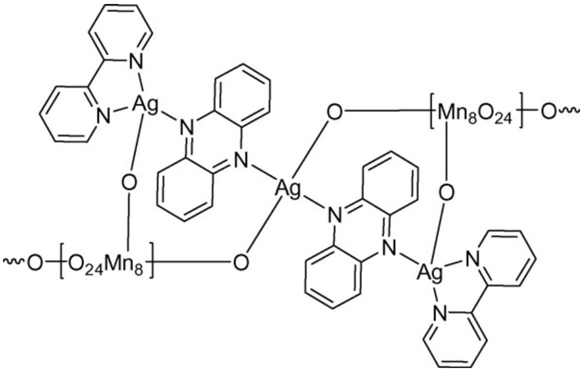


Fig. 18. Representation of part of the 1D polymer involving silver phenazine subunits bridged by β-octamolybdate clusters [107].

torted tetrahedral geometry, and prove too large to penetrate the (6,3)-net structure of silver tcm. Interestingly, however, the network remains interpenetrated, with silver tcm forming interwoven undulating layers that are bridged by molecules of (**25**). Stang and co-workers [52,67] have used (**25**) in a similar manner to pyrazine (**1**) and tetramethylpyrazine (**7**) in multimetallic complexes investigating the "π–tweezer effect" to localise a guest heterocycle within the host cavity of an organometallic molecular square using π-bound silver atoms.

Peng and co-workers recently reported the preparation, X-ray structure and luminescent properties of an interesting 1D polymer consisting of discrete silver phenazine subunits bridged by β-octamolybdate clusters [107]. The subunits are constructed from two molecules of phenazine, three silver atoms and two 2,2′-bipyridine cap units as shown in Fig. 18. These discrete units are bridged by β-octamolybdate clusters (Mn_8O_{26}) through the central silver atoms, which have a square-planar geometry. The clusters also coordinate to the peripheral silver atoms giving them a trigonal pyramidal geometry, and causing an intriguing pyramidalisation of the nitrogen atoms of (**25**). The solid shows strong photoluminescent behaviour with emission at 517 nm, in contrast to the weak luminescent behaviour of the ligands [107].

Quinoxaline (**26**) forms a 1D structure with silver perchlorate, as reported by Ito and co-workers [108]. It consists of two separate 1D chains, one with perchlorate coordinated and an N–Ag–N angle of 173°, and one with weaker Ag–O interactions and an N–Ag–N angle of 179°. The structure of the silver nitrate complex was reported by Abu-Youseff et al. as part of the study involving 2,5-dimethylpyrazine described above [34]. It consists of a 1D polymeric chain with the silver atom having slightly distorted linear geometry bound to two bridging quinoxalines (N–Ag–N angle = 164°). The silver atom interacts with an adjacent nitrate counterion (Ag· · ·O distance = 2.58 Å), which causes the non-linearity. This complex was also found to have antimicrobial activity.

Lu and co-workers recently used hydrothermal synthesis to prepare a mixed inorganic and coordination framework material that they characterised by X-ray crystallography [109]. The complex consists of a 1D polymer based on a polyoxomolybdate framework bridged by a 1D silver–quinoxaline polymer to give a 3D-network structure. The silver atoms bridge quinoxaline ligands with a distorted linear geometry (N–Ag–N angle = 152°) and are coordinated to two oxygen atoms of the complex anion.

1,4-Diazatriphenylene (**27**) further increases the steric bulk around the nitrogen atoms of the ligand, and was utilised by Williams and co-workers to form two intriguing complexes [110]. In both cases the complexes have 1D polymeric structures with the ligand bridging silver atoms. With the use of non-coordinating perchlorate, the silver atom has a distorted linear geometry (N–Ag–N angle = 158°). In an interesting contrast, the usually non-coordinating tetrafluoroborate anion was found to be bound to the silver atom through one fluorine atom (Ag–F distance = 2.63 Å, N–Ag–N angle = 161°). Interestingly, the molecules of (**27**) in the structure display significant twisting away from planarity, with N–C–C–C torsion angles of ∼13° for the four bay regions within the complexes (Fig. 19).

Pyridyl-substituted quinoxalines, (**28**) and (**29**), are potential chelating ligands. The monosubstituted derivative (**28**) was used by Fun and co-workers to form an undulating linear polymeric structure. Each silver atom bridges the chelating section of one ligand and the remaining less hindered quinoxaline nitrogen. A nitrate counterion also weakly coordinates to the silver atom, which has a trigonal pyramidal geometry [111].

2,3-Dipyridylquinoxaline (**29**) has two symmetrically equivalent chelating sites and has been employed, along with several derivatives, as a bridging ligand with silver salts. The ligand reacts with silver tetrafluoroborate to form a discrete M_2L_2 box structure (Fig. 20). Interestingly, only three of the nitrogen atoms are utilised out of the four possible, with only one of the quinoxaline nitrogens coordinating; acetonitrile also coordinates giving a distorted tetrahedral geometry to the silver. One of the pyridyl groups does not chelate, and is splayed out of the plane of the quinoxaline ring, allowing the formation of the discrete box, rather than a polymeric structure. This complex was isolated independently by the groups of Bu and Yam [112], and Jung [113], with the only difference being the crystallisation solvents; chloroform/acetonitrile and acetonitrile, respectively. As part of their study Bu et al. showed that the 5,8-dimethoxy derivative (**30**) also forms a similar M_2L_2 box with silver perchlorate, with no coordination by the methoxy groups. The 5-nitro derivative of (**29**) also forms an M_2L_2 box with silver perchlorate, where

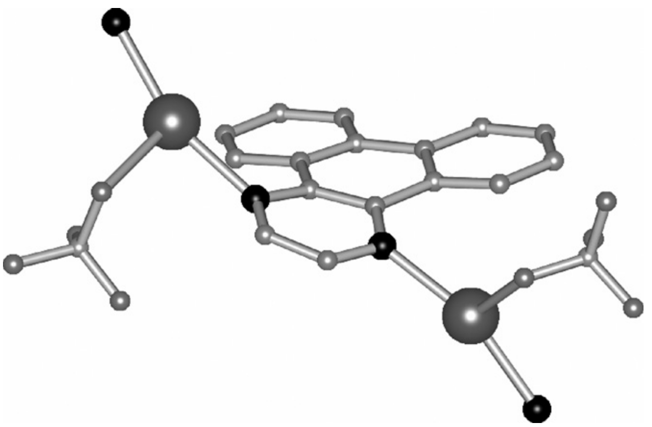


Fig. 19. Part of the 1D polymeric structure incorporating the twisted ligand (**27**) [110].

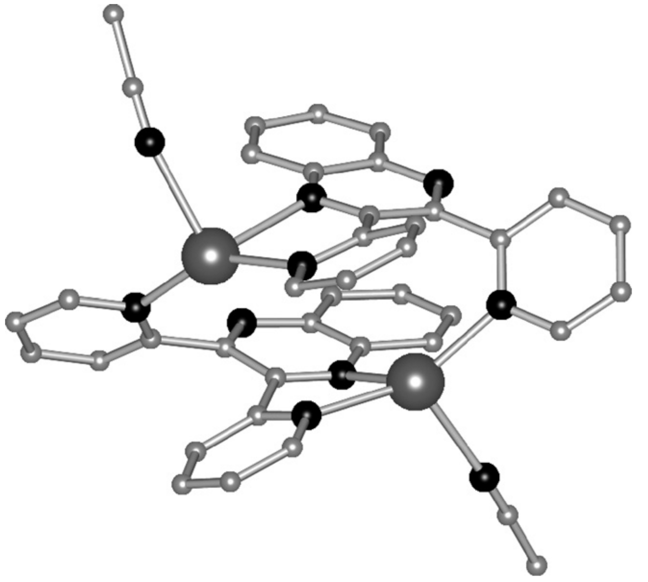


Fig. 20. The discrete M_2L_2 box structure from silver tetrafluoroborate and ligand (**29**) [112,113].

the steric environment around the quinoxaline nitrogen with the adjacent nitro group precludes coordination to silver [114].

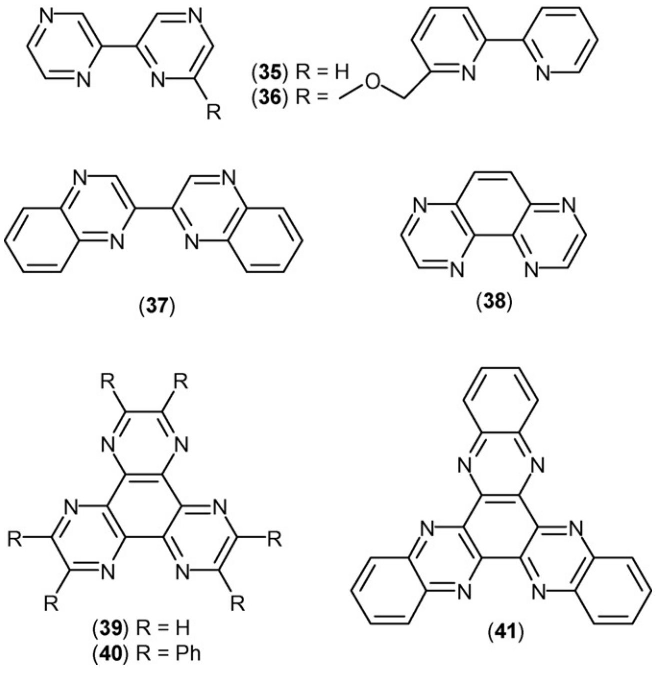
A series of flexible ligands containing a 2,3-disubstituted quinoxaline ring appended with groups containing additional coordination sites have been used to form polymeric complexes. Hong and co-workers prepared two dipyrimidyl thioether ligands, with different substituents in the pyrimidine ring (R = H (**31**) [115] and R = Me (**32**) [116]). Despite the small difference in the ligands, the silver nitrate complexes of these ligands have quite different structures. Ligand (**31**) coordinates to three independent silver atoms to form a complex 2D network. Two of the silver atoms are chelated by the ligand through the quinoxaline nitrogens and sulfur atoms of (**31**), and other silver atoms through bridging nitrate counterions. One of these silver atoms is also coordinated by one of the nitrogens of a pyrimidine ring. The third silver is coordinated to two pyrimidine nitrogens of two different ligands. The silver nitrate complex of (**32**) has a much simpler structure, with only two distinct silver atoms. These are both chelated by the ligand through the sulfur atoms and quinoxaline ring nitrogens and coordinated to the less hindered nitrogen of the pyrimidine rings of adjacent molecules, giving a 1D polymeric tape-like structure. The silver atoms differ in the ancillary ligand, one coordinating a nitrate counterion and the other a dimethylformamide molecule. Hong and co-workers also prepared the related 4-pyridyl substituted ligand and formed a linear coordination polymer with silver perchlorate; however, this ligand only coordinates through the pyridine nitrogens.

Bu and co-workers used the 1,3,4-thiadiazole based ligand (**33**) with silver to form linear polymeric structures [117]. Interestingly, in all these structures the silver atoms are not coordinated to the thioether sulfur. The structure of the perchlorate salt consists of a 1D polymer, where each ligand coordinates to silver through two thiadiazole nitrogens and one quinoxaline nitrogen. There is also a weak nitrogen to silver interaction, which gives an overall double stranded structure. The hexafluorophosphate salt has two different silver atoms and the ligand coordinates through all of its nitrogen atoms. Both silver atoms form N_4Ag_2 macrocycles with the thiadiazole groups of different ligands; one is also coordinated by a methanol solvent molecule. The 1D polymer has a linear tape structure. In a subsequent study, these authors prepared the silver tetrafluoroborate complex and found it to have the same supramolecular topology as the perchlorate salt [118].

Pfeffer and co-workers have reported the formation of a 1D linear silver complex, where the metal atoms bridge the dimanganofluorenyl ligand (**34**) [119,120]. Appending large groups adjacent to the quinoxaline locks these rings in a helical arrangement, and in the silver complex only molecules of one hand are observed. Individual crystals form in the chiral space group $P2_12_12_1$. Presumably, however, the bulk solid consists of crystals containing building blocks of either M- or P-helicity. Despite the bulky groups near to the coordination site of the silver, the Ag–N bond lengths are both about 2.26 Å. The silver is also coordinated by a methanol solvent molecule, which assists the formation of the helical polymeric structure.

2.4. Assemblies derived from ligands containing two or more pyrazine rings

The simplest ligand containing two pyrazine rings is 2,2′-bipyrazine (**35**) (Scheme 5), which is a well-studied ligand in coordination chemistry [1,121]. However, its 1:2 complex with silver nitrate is somewhat unusual as it involves an unprecedented μ_4-bridging mode for the ligand, wherein each of the four nitrogen atoms of (**35**) is bonded to a different silver [122]. The two rings of the ligand are twisted at an angle of 35.4° and the two silver atoms bonded to the N1 and N1′ nitrogens are involved in a relatively strong Ag–Ag interaction (Fig. 21). Each



Scheme 5.

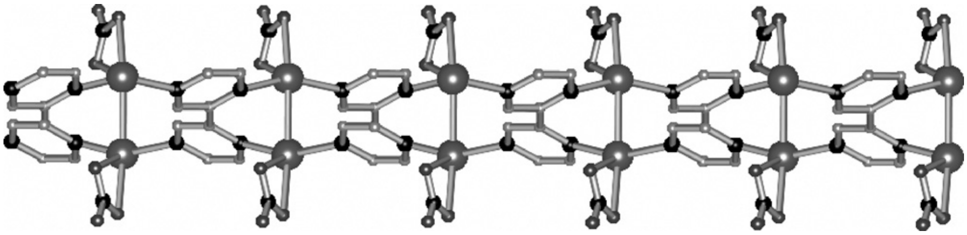


Fig. 21. The 1D polymer of ligand (**35**) displaying a μ_4-bridging mode [122].

silver atom is bonded to an N1 and N4 nitrogen of two different ligands, three oxygens of two nitrates and the adjacent silver. The nitrates serve to crosslink chains into a complex 2D network. This compound is photoluminescent at room temperature.

Champness and co-workers have reported a fascinating array of silver complexes of (**35**) with non-coordinating anions [123,124]. The solvent and anion dependence of the assemblies formed were investigated. In an initial report of 1:1 metal:ligand complexes with silver tetrafluoroborate, the complex obtained from nitromethane solution had a tetrahedral silver chelated to one molecule of (**35**) and further bonded to the N4 nitrogens of two other molecules, which led to a chiral 3D network. When the solvent was changed to acetonitrile, coordination of the solvent produced a complex with five-coordinate silvers and a 2D sheet array [124]. In a subsequent paper [123], the hexafluorophosphate salt produced a similar 3D assembly but with an expanded pitch to the helical array. Interestingly, when benzonitrile was employed as the solvent, the assembly collapsed into a 1D polymeric form.

Lippert and co-workers have used silver salts to expand the architecture of trinuclear, triangular assemblies of platinum complexes of (**35**). In one paper [125], they prepared mixed-metal complexes with platinum atoms bound to the N4 nitrogens and silver chelated to the N1, N1′ nitrogens to afford higher-nuclearity Pt_6Ag_2 and Pt_6Ag_3 compounds, the latter involving the encapsulation of a silver atom and five nitrate anions within its interior. In a subsequent report [126], they described a 1D polymeric assembly with Pd(en) units chelated to (**35**) and silver atoms bridging through the N4 nitrogens to form a loop-like array. Mathieu et al. described the reaction of a segmental ligand (**36**) containing a bipyrazine subunit linked by a flexible spacer to a 2,2′-bipyridine unit [127]. On the basis of NMR studies and the X-ray structure of the analogous copper(I) complex they proposed that this formed a binuclear double helicate.

2,2′-Biquinoxaline (**37**) is a benzofused derivative of (**35**) that has been shown by us to form a 2D network with silver nitrate [128]. In contrast to the analogous complex with 2,2′-bipyrazine (**35**) described above, the ligand only coordinates through the two least hindered nitrogens, and its heterocyclic rings are coplanar and transoid. The silver atoms bridge two ligands and are in turn bridged by nitrate counterions, giving them a distorted tetrahedral geometry.

1,4,5,8-Tetraazaphenanthrene (**38**) is a conformationally constrained derivative of (**35**), and when reacted with silver nitrate forms a discrete 2:1 complex where each silver atom is chelated by two ligand molecules and one nitrate counterion [129]. Unfortunately, the space group for this structure was misassigned, and represents one of the “perils of *Cc*”, which was subsequently reinterpreted in the more symmetrical monoclinic space group *C*2/*c* by Marsh [130]. As part of their study of silver complexes of (**35**) with non-coordinated counterions, Champness and co-workers also formed a 1:1 tetrafluoroborate complex with (**38**) [123]. This forms a 3D network with each silver chelating one ligand molecule, and bridging two others in a distorted tetrahedral geometry. Unlike the tetrafluoroborate complex with (**35**), this structure is not diamondoid and is achiral, a difference assigned by the authors to the distortions required by the silver atom on chelating (**38**). Interestingly, when the reaction is carried out in acetonitrile or benzonitrile a discrete 2:1 complex is formed, with each silver chelated by two ligand molecules.

Fusing three pyrazine rings together gives the potentially triply chelating ligand 1,4,5,8,9,12-hexaazatriphenylene, or HAT (**39**), a well-studied ligand [131]. Robson and co-workers were able to use HAT to synthesise a remarkably robust network with silver perchlorate [132]. The silver atoms are hexacoordinate, bridging three ligands, and each ligand chelates three silver atoms, giving a (10,3)-a network structure where both ligand and silver are three connected nodes. The regular framework contains significant solvent accessible void space occupied by nitromethane solvate and perchlorate counterions. Intriguingly, nitromethane molecules could be removed and replaced with atmospheric water while maintaining the crystallinity; indeed throughout several solvent-removal and replacement cycles (water/nitromethane) the AgHAT framework was retained. The hexaphenyl-HAT derivative (**40**) was used by Lehn and co-workers in their construction of supramolecular molecular cylinders [133]. This combined rigid bridging components containing 2,2′-bipyridine units acting as the walls and molecules of (**40**) to form lids. The silver atoms are tetrahedral and bridge the components as shown in Fig. 22.

The silver nitrate complex of the tribenzofused ligand (**41**), a more extended analogue of HAT (**39**) has a 3D network structure, as reported by Bu and co-workers [134]. However, due to the increased steric hindrance of the chelating bays, the silver atoms are only coordinated by two ligands. This extends the size of the cavities allowing two (10,3)-a networks to interpenetrate, with non-coordinating nitrate counterions occupying the remaining spaces. Remarkably, in a subsequent paper, the same workers observed a 2D network structure with silver nitrate and (**41**) [135]. The only differences in synthesis methodology were an increase of the metal:ligand ratio, from 3:2 to 2:1, and replacement of CH_2Cl_2/MeCN solvent for $CHCl_3$/MeCN. In the later case, there are three independent silver atoms, one bridges two

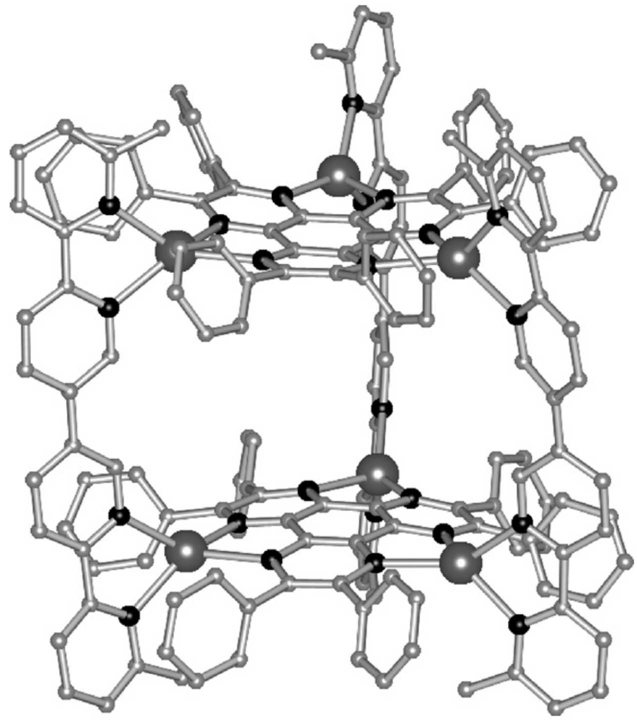
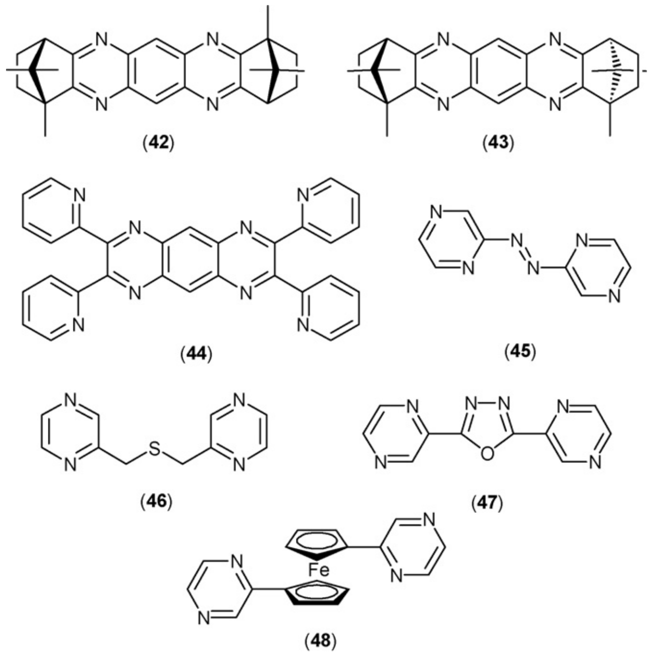


Fig. 22. A molecular cylinder capped with ligand (**40**) [133].

ligand molecules, while the remaining two are chelated by one ligand molecule and bridged by disordered nitrate counterions.

Curiously, no silver complexes have been reported of ligands containing two pyrazine rings separated by a single atom spacer. This is in contrast to the common use of di-2-pyridyl-methane, -ketone, -amine, -ether and -sulfide as ligands in coordination chemistry. Although 1,4,5,8-tetraazaanthracene itself has not been reacted with silver, we have prepared the two chiral derivatives (**42**) and (**43**) which have fused bornane units (Scheme 6). These isomeric ligands have the same symmetry relationship as the simpler ligands (**23**) and (**24**) discussed above. Reactions of these ligands with silver nitrate lead to chiral ladder-like silver coordination polymers, wherein ligand (**42**) produces a bidirectional polymer (Fig. 23), whereas the isomer (**43**) produces a unidirectional polymer [99]. The tetra-2-pyridyl derivative (**44**) is effectively two superimposed molecules of ligand (**29**), and as such upon reaction with silver nitrate the M_2L_2 box motif is retained, but in this case extended to form a 1D polymeric structure (Fig. 24) [112].

The only ligand with a two atom spacer between two pyrazine rings that has been studied with silver is 2,2′-azopyrazine (**45**). This was the subject of a detailed report by Carlucci et al. in 2003, which described the crystal structures of a fascinating array of coordination frameworks formed from reactions of (**45**) with three different silver salts with varying stoichiometric ratios [136]. 1D helical chains, 2D sheets and a complex 3D network were described in which ligand (**45**) was bound to up to four silver centres, using between two and all six of the available nitrogen donors. Within the structures the silver centres exhibit high (up to six) coordination numbers. A representative example is shown in Fig. 25.



Scheme 6.

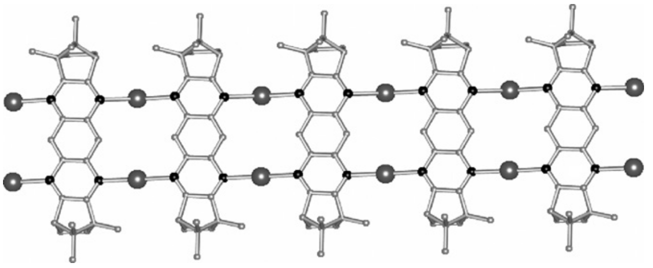


Fig. 23. A section of the chiral bidirectional polymer from ligand (**42**) [99].

The Hanton group has reported two studies of ligand (**46**), which has a three atom spacer that includes a potentially coordinating sulfur atom [137,138]. Once again, this ligand was shown to lead to a remarkable array of complexes depending on the anion, solvent and reaction stoichiometry. In the first study [138], which used tetrafluoroborate and hexafluorophosphate anions, a 1D ladder, a 2D sheet and a 3D network were reported. In a second report perchlorate, nitrate and triflate were used as anions to

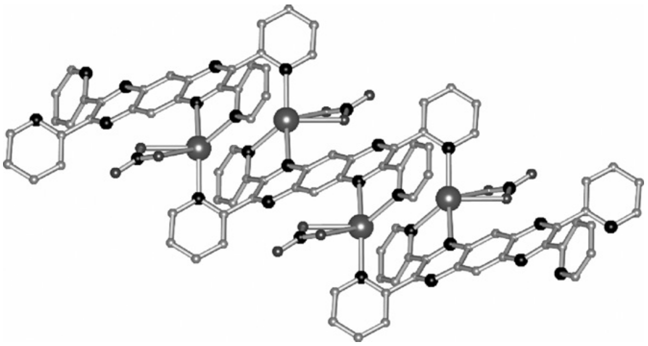


Fig. 24. 1D polymeric structure obtained from ligand (**44**) with silver nitrate [112].

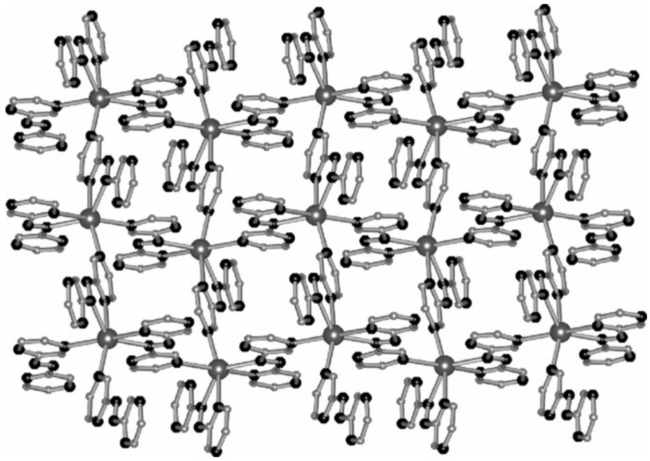
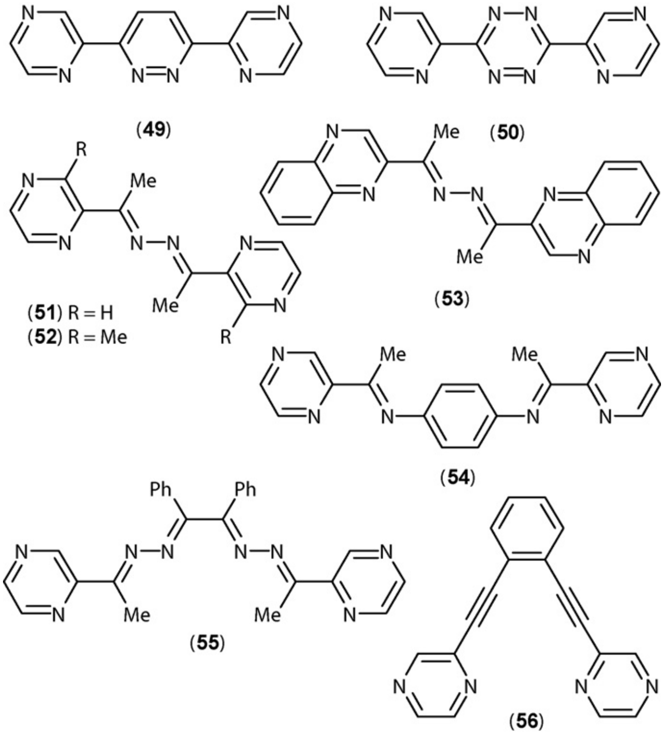


Fig. 25. One of the polymeric structures formed by 2,2′-azopyrazine (**45**) [136].

form a variety of 1D coordination polymers, including ladders, chains and fused loops [137]. In these studies ligand (**46**) showed various coordination modes in which it was bound to between two and four silver atoms, all of which involved coordination by the central sulfur atom.

The oxadiazole-containing ligand (**47**) was used by Du et al. to form a series of 3D open coordination networks with various silver salts [139]. In all cases ligand (**47**) binds to four silver centres using two chelating sites and two monodentate sites. Each silver is bound to four ligands and is therefore six-coordinate. Interestingly, two topological 3D networks resulted, depending upon whether the two chelating sites were *cis* or *trans* to one another. The dipyrazinylferrocene ligand (**48**) was recently used by Mochida and co-workers to prepare a number of silver-bridged diferrocenes [140]. Silver perchlorate, nitrate and hexafluorophosphate all led to dimeric structures in which (**48**) acted as a bidentate bridging ligand using only the N4 nitrogens of the pyrazine rings.



Scheme 7.

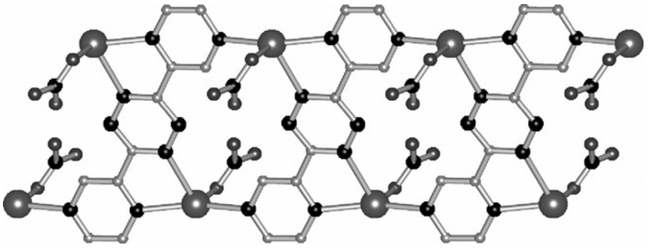


Fig. 26. The ladder-like structure from reaction of silver nitrate with ligand (**50**) [141].

Champness and co-workers have reported the reaction of the dipyrazinylpyridazine (**49**) (Scheme 7) with silver nitrate [141]. This forms a 2D grid in which each silver is bound to four different ligands and a monodentate nitrate anion. Each molecule of (**49**) uses all six nitrogen donors to coordinate to four silvers, with two chelating and two monodentate sites, similar to the situation displayed by the structurally related ligand (**47**). The same authors used the analogous tetrazine ligand (**50**) to form complexes with various silver salts [141,142]. The silver nitrate complex has a ladder-like structure wherein ligand (**50**) provides the rungs that connect to four silver atoms with the two chelating units now on opposite sides of the tetrazine ring (Fig. 26). With non-coordinating anions a series of 2D coordination frameworks with unusual network topologies were obtained along with a 1D “tubular ribbon”. In these structures the silver atoms have high coordination numbers and ligand (**50**) bridges two to four silver atoms.

There have been a number of studies of ligands containing two pyrazines separated by spacers that are hydrazones or imines derived from 2-acetylpyrazine. Dong and co-workers [143] reported two interesting structures of silver assemblies derived

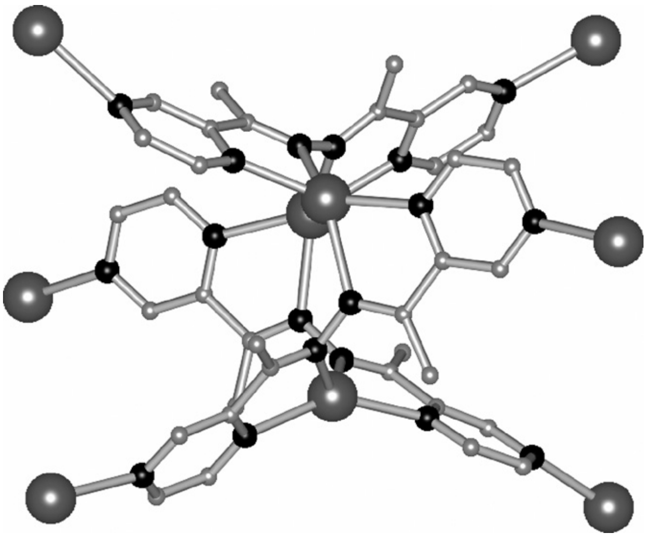


Fig. 27. The circular helicate unit present in the network formed from ligand (**51**) [143].

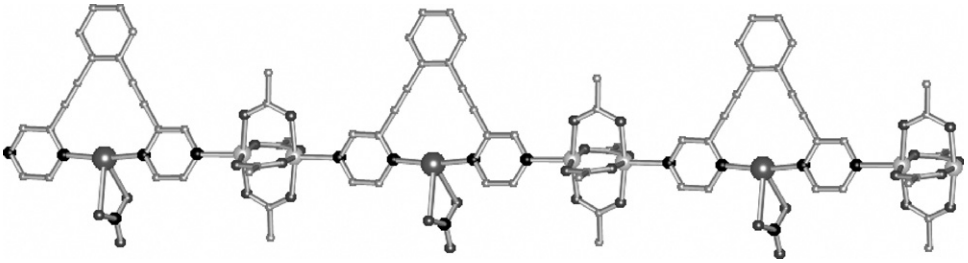


Fig. 28. A mixed-metal coordination polymer from ligand (**56**) [146].

from ligand (**51**). The first is a remarkable structure obtained from reaction with silver nitrate. It is a non-interpenetrated 3D network consisting of an inorganic $[Ag(NO_3)_3]^{2-}$ honeycomb net which encapsulates metal-organic tubes with $[Ag_5(\mathbf{51})_3(NO_3)_3]^{2+}$ stoichiometry which in turn acts as a host to organic chloroform molecules. In this network, the ligand (**51**) forms an M_3L_3 circular helicate unit (Fig. 27), and bridges two independent silver atoms using its two remaining nitrogen donors. The related complex with silver hexafluoroantimonate is less complex and exists as 1D tubes in which the ligand is hypodentate. In a subsequent report [91] a related $AgPF_6$ complex was reported along with several isomorphous and isostructural 3D zeolite-like networks obtained from reactions of silver salts with the methyl substituted ligand (**52**). Hannon and co-workers subsequently reported [90] a similar $AgPF_6$ complex of (**51**) and drew particular attention to the double helical nature of the bridging by the ligand in this structure and in the more complex silver nitrate assembly.

The analogous quinoxaline based ligand (**53**) was used by Dong and co-workers to form a series of silver complexes with non-coordinating anions [144]. The tetrafluoroborate complex forms a 2D network of double helical building blocks. The ligand (**53**) chelates only one silver atom through quinoxaline and hydrazone nitrogens, with the other possible chelating site remaining unoccupied. The least hindered nitrogen atoms of adjacent ligands occupy the other two coordination sites of the pentacoordinate silver atoms. The complexes with perchlorate, hexafluorophosphate and hexafluoroantimonate all contain the circular M_3L_3 building block observed for the pyrazine ligand (**51**). In the perchlorate structure the remaining nitrogens are coordinated to silvers, each of which bridges three circular helicate units, giving a 3D network structure. In the hexafluorophosphate and hexafluoroantimonate, the circular helicate units bridge disordered silver atoms giving a 2D network and 1D polymer, respectively.

The Hannon group also reported [90] an $AgBF_4$ complex of the *para*-phenylene linked imine ligand (**54**). This has two separate six-coordinate silver centres with one chelated to three ligands and the other bound in a monodentate fashion to six different ligands. This leads to a 3D network with a cube-like architecture. The flexible ligand (**55**) with a more extended eight-atom linker was reported [145] to react with silver nitrate to give single stranded helical chains that further assembled into a doubly interpenetrated 3D network.

Finally, the *ortho*-phenylene ligand (**56**) was employed by Bosch and co-workers to prepare four interesting silver-containing assemblies [146]. The first is a 1:1 mononuclear complex with silver nitrate in which the ligand simply chelates to a silver atom using the two N2 nitrogens, forming an eleven-membered chelate ring. Reaction with two equivalents of silver nitrate led to a coordination polymer in which the above mononuclear units were bridged by silver atoms coordinated to the N4 nitrogens. They also prepared two mixed-metal assemblies using combinations of silver(I) nitrate and copper(II) acetate. The first is a discrete tetranuclear complex in which two of the above mononuclear units are bridged by a dicopper(II) tetraacetate moiety. By varying the stoichiometry of the reactants this was then extended into a mixed-metal coordination polymer (Fig. 28).

3. Conclusion

The study of silver complexes of ligands containing a pyrazine ring has been the subject of numerous reports over the last decade. As described above, this has led to a rich diversity of both discrete and polymeric assemblies. Pyrazine itself has produced a wide array of discrete, as well as 1D-, 2D- and 3D-polymeric, species depending on the counterion, the stoichiometry and reaction conditions. Numerous substituted pyrazines have been studied, many of which have substituents that are capable of chelating to silver centres. Benzo-fused pyrazines have also been much studied and these are especially prone to exhibit π–π stacking interactions. Also popular have been ligands containing more than one pyrazine subunit, which tend to form assemblies of higher dimensionality. No doubt, many more new pyrazine-containing ligands will appear in the future that will further extend the plentiful array of metallosupramolecular architectures that result from reactions with silver(I).

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