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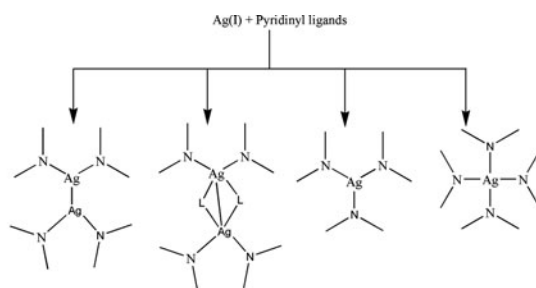
Possible coordination modes of silver(I) by pyridinyl ligands and Ag⋯Ag interactions.

This review highlights some structural features and luminescent properties of homo- and hetero-multinuclear silver(I)–pyridinyl complexes. It focuses on the coordination and geometry of the silver(I) ions to the pyridinyl-nitrogen. For this reason, we have considered only pyridinyl-N–Ag(I) complexes whose crystal data are available. In addition, this review does not consider mononuclear silver(I)–pyridinyl complexes as these have been reviewed elsewhere. This is motivated by the fact that multinuclear silver(I)–pyridinyl complexes have been shown to be more stable in solution, possess enhanced properties, and have fascinating structures compared to their mononuclear counterparts. The introduction highlights pyridinyl ligands used in complexation of silver(I) ions. The main body highlights complexation of silver(I) through pyridinyl nitrogen and the interactions found in the multinuclear silver(I)–pyridinyl complexes as well as the coordination number and geometry of silver(I) centers. Though silver(I) has been flaunted to prefer linear twofold coordination geometry, from this review, it is clear that higher coordination numbers in varied geometries are possible. These include distorted trigonal planar, T-shaped, distorted tetrahedral, trigonal bipyramidal, and octahedral geometries. Coordination of silver(I) to pyridinyl ligands and their metalloligands has been observed to impart or enhance luminescent properties in the ensuing complexes.

Keywords: Silver(I); Pyridinyl; Multinuclear homometallic; Multinuclear heterometallic; Review

1. Introduction

Silver(I) coordination compounds of N-containing ligands have been and still remain a theme of interest; thanks to their structural novelty [1–3] and potential properties, such as

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luminescence [4–8], electrical conductivity [9], nonlinear optical activity [10], electrochemical [11], biological [12], catalytic [13–16], porosity [17], and vapochromic properties [18]. Silver(I) complexes have been comprehensively prepared by coordinating the metal to N-donor heterocyclic ligands, especially five and six membered unsaturated N heterocyclics and their derivatives [19]. This is attributable to the stability of the five and six membered rings compared to rings with fewer atoms [20].

Among the six membered rings, pyridine, which is a borderline soft base, sigma-donor and pi-acceptor monodentate ligand as well as its derivatives, has been extensively utilized to coordinate silver(I) via the pyridinyl-nitrogen. This is due to stability of pyridinyl ligands and their inherent capacity to tolerate fluctuating oxidative and reductive environments. These electronic properties allow complexes of pyridinyl ligands to be utilized in catalytic reactions involving transition metals [21, 22] in the study of excited state dynamics, development of light energy conversion devices and optical sensors [23, 24]. Pyridine-based ligands that have been utilized in complexation of silver(I) include pyridine itself [25], bipyridine [26–30], terpyridine [29], quinquipyridine [31] and their derivatives [32–35], as well as pyridinyl motifs linked by aliphatic and heterocyclic fragments [36–41]. Moreover, pyridine fused to benzene rings yields ligands, such as quinoline [42, 43], isoquinoline [44], 1,10-phenanthroline [45, 46], and hydroxyquinoline [47], that have been utilized in complexation of silver(I). Pyridinyl ligands have been utilized together with ligands bearing other donors such as phosphorus to form heteroleptic silver(I) coordination compounds [48]. Mixed-donor pyridinyl ligands bearing P [49, 50], S, O [51], or non-pyridinyl-nitrogens [52] have been employed in syntheses of silver(I) multinuclear complexes. Depending on the number and orientation of donor sites, these pyridinyl ligands exhibit various coordination modes to silver(I). These modes include monodentate, chelation, and bridging two or more metal centers yielding a diverse range of discrete and polymeric coordination architectures. Syntheses of multinuclear and mixed-metal silver(I)–pyridinyl complexes are inspired by their potential application in medicine, host–guest chemistry, optics, magnetism, electrochemistry, and catalysis.

2. Silver(I) coordination by pyridinyl ligands

Silver(I) is an extremely soft Lewis acid with a good affinity for N-donor ligands. It has a flexible coordinating sphere that accommodates a range of stable coordination numbers, basically from 2 to 6, in various geometries [53]. Upon coordination by pyridinyl ligands, silver(I) can adopt either trigonal [54], tetrahedral [55–57], square-planar [58], trigonal pyramidal [35, 59], T-shaped [60], or octahedral [61] coordination geometry. Furthermore, silver(I) has linear or quasi-linear σ-bonded twofold coordination (N–Ag–N as a bridge between two monodentate ligands) with pyridinyl ligands [62, 63]. This multiplicity in coordination environment of silver(I) is partially due to lack of stereochemical preference by the d^{10} configuration of silver(I). In a case where a ligand has several coordinating sites, the resulting complexes may be: (a) metallamacrocycle [64], (b) coordination polymer, or (c) multinuclear discrete [65, 66] depending on conformation and flexibility of the spacer between the coordinating poles (figure 1).

The assembly process, geometry around the silver(I) ion, and the structure of silver(I)–pyridinyl complexes are influenced to a great deal by secondary effects. These include solvent used in the reaction [32], crystallization process, and metal–ligand ratio [41], presence
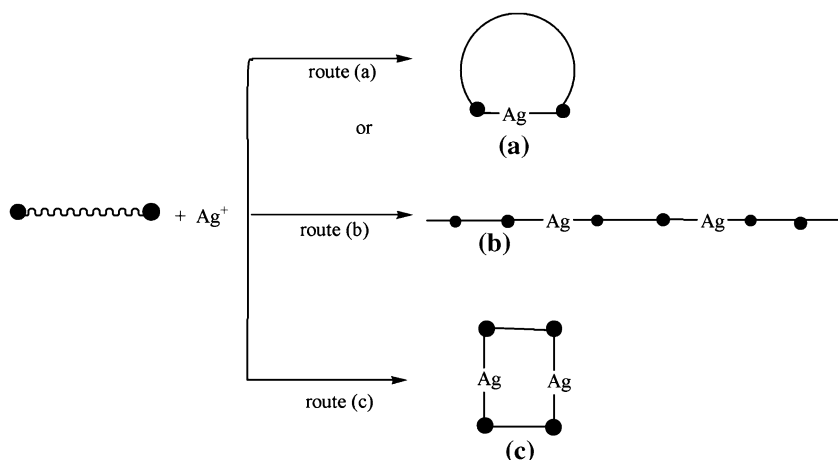
Figure 1. Schematic representation of the formation of (a) metallamacrocycle and (b) an infinite coordination polymer of silver(I) adopting a linear coordination geometry and (c) multinuclear discrete complex upon complexation with a bis-monodentate ligand.

of templates and counter-ions [41, 67], ligand structure and bonding cavity [68] as well as secondary interactions, such as hydrogen bonding and π–π interactions [64, 69]. The pH of solution for reactions in aqueous phase [70], temperature, and number of metal centers as well as the π-acidity of the ligands' central ring [26, 71] also have an effect on the geometry of the metal in silver(I)–pyridinyl complexes. Alteration in any of the aforementioned factors can result in similar or dissimilar complexes with different structures, properties, and functions. For instance, changing solvent from a more coordinating one like CH_3CN to a less interacting solvent like CH_2Cl_2 or THF allows more ligands to coordinate the silver(I) centers, consequently increasing dimensionality and stoichiometry of the ensuing complex [26]. Also, presence of bridging or coordinating anions, such as the halides, pseudo-halides, $CF_3SO_3^-$, ClO_4^-, or NO_3^-, significantly influences the coordination number and geometry around silver(I) centers. Bridging anions and ligands link silver(I) ions in the complexes leading to formation of multinuclear complexes. Multinuclear silver(I) complexes are superior to their mononuclear counterparts with respect to their architecture, properties, stability, and applicability associated with close interactions of the metal centers [72].

Generally, adjacent metal centers in multinuclear silver(I)–pyridinyl complexes have Ag⋯Ag attractions [73, 74]. These attractions are called argentophilic closed shell (d^{10}–d^{10}) interactions and are estimated to have strengths of about 24 kJ mol^{-1}. However, their occurrence was accepted after ligand-unsupported Ag⋯Ag interactions were reported [75]. The metallophilic interactions arise from the overlap of filled 5d orbitals with the empty 6s and 6p orbitals and are thus best described as strong van der Waals attractions. The presence and significance of these interactions in a silver(I) complex are determined in comparison with the van der Waals radii in pure silver. Pure silver has interatomic distance of 2.88 Å, whereas the sum of van der Waals radii of two Ag atoms is 3.44 Å. In a complex, Ag⋯Ag distance of <3.0 Å indicates significant argentophilic interactions while separations >3.3 Å are considered weak interactions, thus insignificant. The argentophilic interactions can either be supported by ancillary ligands and/or anions or may be ligand unsupported. The latter are indicative of a real bond. The strongest Ag⋯Ag interactions are observed in complexes

with bridging ligands (ligand supported). Argentophilic interactions control supramolecular topology, increase dimensionality of the complexes, and contribute in the photophysical properties of the complexes [76, 77]. The argentophilic interactions for instance have been used as a design component to increase structural dimensionality in coordination polymers (though predictability factor is low due to the moderate strength of these interactions coupled with the flexibility of silver(I) coordination) [78].

Silver(I)–pyridinyl heterometallic systems incorporating other d^{10} metals have mixed metal–metal, d^{10}–d^{10}, closed-shell interactions between silver(I) and the second metal [41]. The most frequent is Ag–Au, d^{10}–d^{10}, closed shell interaction and is known as argento–aurophilic. Silver(I)–copper and silver(I)–cobalt complexes [79] as well as silver(I)–iron [80, 81] also portray metal–metal separations that are less than the van der Waals limit. Significant silver(I)–iron interactions ranging between 2.627 and 2.70 Å have been reported. In comparison with either of their homometallic analogs, silver(I) mixed-metal systems have higher metallophilic interactions and consequently, smaller metal–metal separations and higher stability. This is due to the relativistic effects and higher dispersion forces induced by the different metal centers that are also augmented by increase in dipolar interactions from the dissimilar metal centers [82, 83]. Just like the argentophilic interactions, direct closed d^{10}–d^{10} Ag(I)–M interactions have been reckoned to augment some properties such as photoluminescence in the complexes as well as impart structural dimensionality [84]. Silver(I) complexes incorporating metal centers of different elements have been shown to have better physical and chemical properties and a higher stability in solution compared to their corresponding homometallic analogs. These properties are associated with factors such as the nature of the ligand, the heterometal, and the presence or absence of metallophilic interactions. Generally, in compounds with Ag(I)–M, the metallophillic interactions are mainly responsible for the observed heightening of properties [85, 86]. Other interactions observed in multinuclear silver(I)–pyridinyl complexes besides the coordinate covalent bonds are hydrogen bonds, cation–π, anion–π, ligand π–π stacking, and CH–π interactions [20, 73, 74, 87–89] as well as Ag(I)–M dative bonds [90]. Though rare, inter- and intramolecular C–H⋯Ag weak hydrogen bonds have also been observed in polynuclear silver(I)–pyridinyl architectures [91].

Coordination of silver(I) ions by pyridinyl-nitrogen donors induces electron withdrawal from the aromatic ring. Consequently, this increases the electrostatic component of intermolecular π⋯π interactions. These π⋯π interactions have also been found to influence the distance between silver(I) ions in a complex and hence the argentophilicity. The argentophilic and π⋯π interactions can be both "cooperative" and "competitive" in the same supramolecular motif depending on the interplanar distance of two arene moieties. Generally, the "cooperative" interactions occur when the interplanar distance is longer than the equilibrium distance, that is the interplanar distance reaching the energy minimum of the supramolecular system [92]. In the coordination complex of pyridine and AgClO$_4$, the presence of strong π–π interaction was shown to increase the Ag⋯Ag separation (figure 2) [93]. The silver(I)–ligand covalent bond is generally labile. Thus, in solid state, these weak noncovalent interactions and crystal packing forces have a greater influence on the general architecture of silver(I)–pyridinyl complexes than in complexes with strong metal–ligand bonds [93–95].

Multimetallic silver(I)–pyridinyl complexes possess intense, long-lived luminescence in the solid state at ambient temperatures with emission energies spanning the visible spectrum [96]. This makes them potential candidates for application in display technology such as organic light emitting diodes (OLED), as dopant emitters in solar photo-conversion
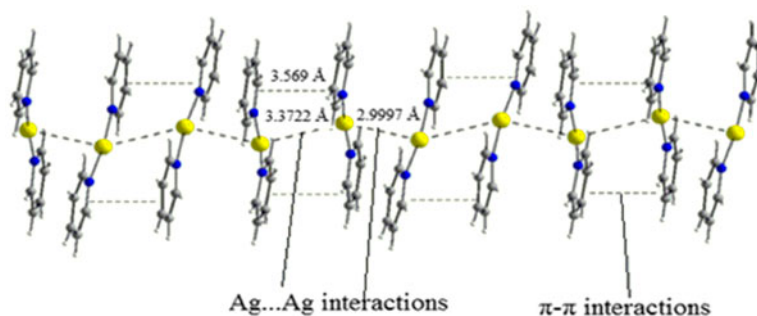
Figure 2. Competition between Ag···Ag and π–π interactions in the cation of a silver(I)–pyridinyl complex resulting in an increase in Ag–Ag distances [93].

chemistry as chromophores and in sensor development for luminescence [97, 98], molecule detection [99] as well as biomolecular and cellular probes [100]. Due to the aforementioned applicability and fascinating structures of the multimetallic silver(I)–pyridinyl complexes, various synthetic approaches have been designed and developed over time to obtain multimetallic silver(I) structures with tailored properties.

The multinuclear silver(I)–pyridinyl complexes discussed in this review are classified based on the metal centers present into: (a) homometallic silver(I) complexes and (b) heterometallic silver(I) complexes where the silver(I) ions are coordinated by pyridinyl-nitrogen. These are further classified based on structure into discrete and polymeric silver(I) pyridinyl complexes. The discussion mainly focuses on the geometry and coordination modes of silver(I) in these complexes in connection to their luminescence properties.

2.1. *Homometallic silver(I) complexes*

Silver(I)–pyridinyl complexes having two or more silver(I) ions have been synthesized via reactions of mono- and polydentate pyridinyl ligands. Depending on the ligand and synthesis conditions, the resulting complex could be discrete or polymeric. Various techniques have been employed in the synthesis of multinuclear homometallic complexes. These include direct mixing of ligand and salt solutions under inert atmosphere or in air followed by agitation via stirring or ultrasonication at ambient or elevated temperatures under reflux, solvothermal techniques where reaction is carried out at high temperatures for several days in Teflon-coated autoclaves followed by controlled cooling [47, 94, 101] and mechanochemical grinding of ligands with silver(I) salts [102]. Crystallization of silver halides from pyridine or substituted pyridines as the solvents has been shown to yield silver (I) pyridine adducts of varying stoichiometry [103].

2.1.1. Discrete homometallic silver(I) complexes. Coordination of silver(I) ions by monodentate pyridine ligands generally yields mononuclear complexes of the type $[Ag(py)_2]^+$ or $[Ag(py)_4]^+$. However, discrete multinuclear silver(I)–pyridinyl complexes are often obtained from pyridine itself and other monodentate ligands such as 3-methylpyridine **L₁** (figure 3), where silver(I) centers are coordinated by the pyridinyl-nitrogen atoms then linked through bridging ligands, anions or argentophilic interactions. In some cases,
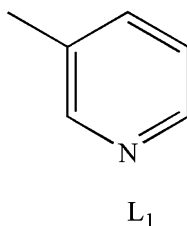
L_1

Figure 3. Chemical structure of monodentate ligand, 3-methylpyridine.

multidentate pyridinyl ligands such as L_2–L_4 (figure 5) that are not capable of iterating to yield coordination polymers due to orientation of donor atoms have resulted in discrete multinuclear silver(I) complexes [104, 105].

Simple dinuclear adducts from pyridine and silver salts bearing anions such as perchlorate, halides, nitrates, and sometimes tetrafluoroborate have been synthesized. For instance, silver (I) perchlorate yields $[Ag(py)_4][Ag(py)_2]_4(ClO_4)_5$, that is $Ag_5(ClO_4)_5(py)_{12}$, in which the per-chlorate ions act as bis-chelating ligands in the complex to form dinuclear complexes [106]. Substituted pyridines give similar adducts, though these substituents affect the Lewis acid–base properties of the pyridine molecule and consequently the type of bond between silver(I) and the pyridinyl-nitrogen. In this regard, methylpyridines (picolines) generally form silver (I) complexes with either n–σ or π–π bonds [107, 108]. The monodentate 3-methylpyridine L_1 yields the dinuclear complex $[(L_1)_2Ag(\mu\text{-Br})_2Ag(L_1)_2]$ (1) upon reaction with AgBr. The complex has each silver(I) bonded to two pyridinyl-nitrogens in a distorted tetrahedral geometry. The silver(I) ions are then bridged to each other via bromides rendering them four-coordinate in a distorted planar geometry (figure 4). The bond angle for N–Ag–N is at 117.4°. Though these complexes have been found to exist in solutions, this was the first sil-ver(I) complex of this stoichiometry to be characterized structurally [109]. Similar dinuclear moieties have since been synthesized where the silver(I) centers are linked by argentophilic interactions like $[Ag_2(L_1)_4]X_2\cdot2H_2O$ (2) (X = 2-amino-5-chlorobenzenesulfonate anion).
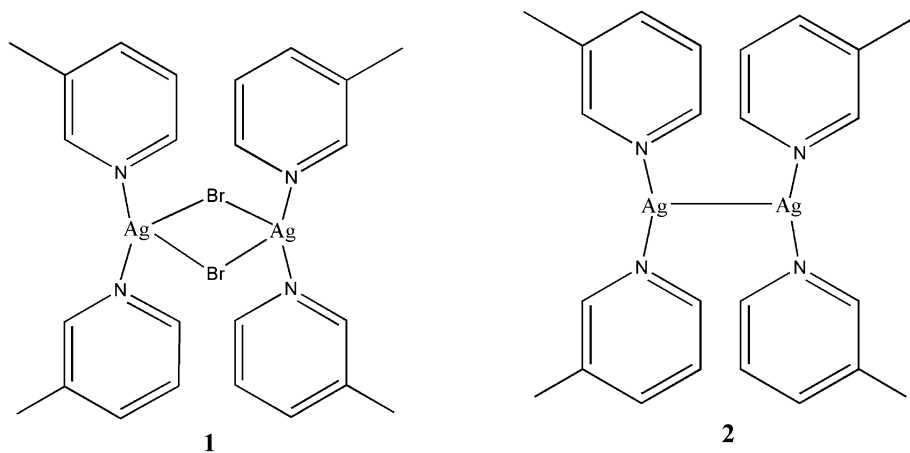

1 **2**

Figure 4. Molecular structures of the cations in **1** [109] and **2** [110] showing the coordination environment in sil-ver(I) centers.

In this complex, silver(I) is three-coordinate in a T-shaped geometry courtesy of two N atoms from the 3-methylpyridine ligands and the metal–metal bond. The N–Ag–N bond in this complex deviates significantly from linearity to 168° [110].

Multidentate pyridine-azine ligands, such as L_2, L_3, and L_4, shown in figure 5, have been extensively employed in syntheses of silver(I) multinuclear systems. This is in the quest to find complexes with unique structures as well as magnetic, electronic, and spectroscopic traits. For instance, 2-pyridinealdazine L_2 forms a dinuclear silver(I) complex $[Ag_2(L_2)_2]$ $(CH_3SO_3)_2$ (**3**), where the metal ions are in an approximate T-shaped geometry, courtesy of three N atoms from two ligand molecules (figure 6). The N–Ag–N angles in this complex range from 175.91 to 71.00° [60]. This ligand also gives a dimeric silver(I) complex (**4**) with AgOTf. The silver(I) ions in the dimer are in an octahedral geometry via the four N atoms from the ligands and two oxygens from triflate (figure 6) [33]. Reaction of pyridyl-methylketazine, L_3, with silver(I) gave a fascinating dinuclear triple helix silver(I) complex, $[Ag_2(L_3)_3][PF_6]_2$ (**5**), in which the silver(I) centers are in an infrequent five-coordinate distorted trigonal bipyramidal environment. One ligand uses all four donors to coordinate as a bis-bidentate ligand to the two metal centers, while the other two ligands use only three donors and coordinate bidentate to one metal and monodentate to the other with a non-co-ordinated imine residue acting as a spacer between the binding sites. Ag–N bond lengths are 2.32–2.49 Å [33].

The multidentate 3,6-bis(2′-pyridyl)-1,2-pyridazine L_4, while in *syn* orientation, chelates two silver(I) ions to form dinuclear complexes $[Ag_2(L_4)_2(CH_3CN)_2]X_2$ (X = PF_6 (**6**) or AsF_6 (**7**)). The silver(I) ions in these complexes are in square-pyramidal geometry through N atoms from the pyridine and pyrazine units and the fifth position occupied by a solvent (CH_3CN) molecule as shown in figure 6 [71]. This ligand and its substituted derivatives also yields complexes where the silver(I) centers are in trigonal prismatic arrangement and distorted tetrahedral, as well as pseudo-square planar geometries [111].

The quinoline derivatives 1,5-bis(8-quinolylsulfanyl)-3-oxapentane L_5, 1,8-bis(8-quino-lyl-sulfanyl)-3,6-dioxaoctane L_6, and 8-[(pyridin-3-yl)methylthio]quinoline L_7 (figure 7) are examples of pyridinyl heterodonor ligands that have been employed in the syntheses of multinuclear silver(I) complexes.

L_5 and L_6 upon reaction with $AgNO_3$ gave tetranuclear super molecules $[Ag_2(L_5)(NO_3)_2]$ (**8**) and $[Ag_2(L_6)(NO_3)_2]$ (**9**), respectively (figure 8). The metal centers in the complexes portray different coordination geometries where one pair of the silver(I) centers shows a square planar geometry courtesy of two quinoline nitrogens. The N–Ag–N bond angles are 165.0° in **8** and 172.08° in **9** and two thioether sulfurs of the same ligand while the second pair of silver(I) ions have a square pyramidal geometry via two thioether sulfurs of two different ligands and three oxygens of two nitrates, one η^1 and the other η^2
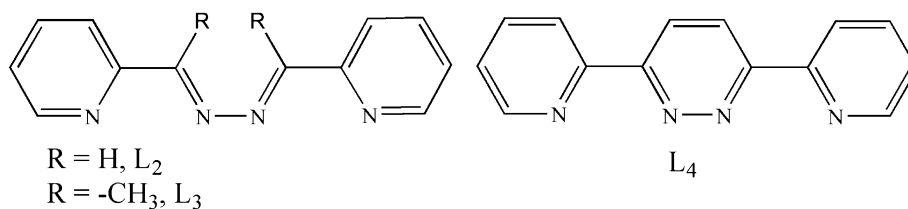

R = H, L_2
R = -CH_3, L_3

L_4

Figure 5. Chemical structures of the monodentate ligands L_2–L_4.
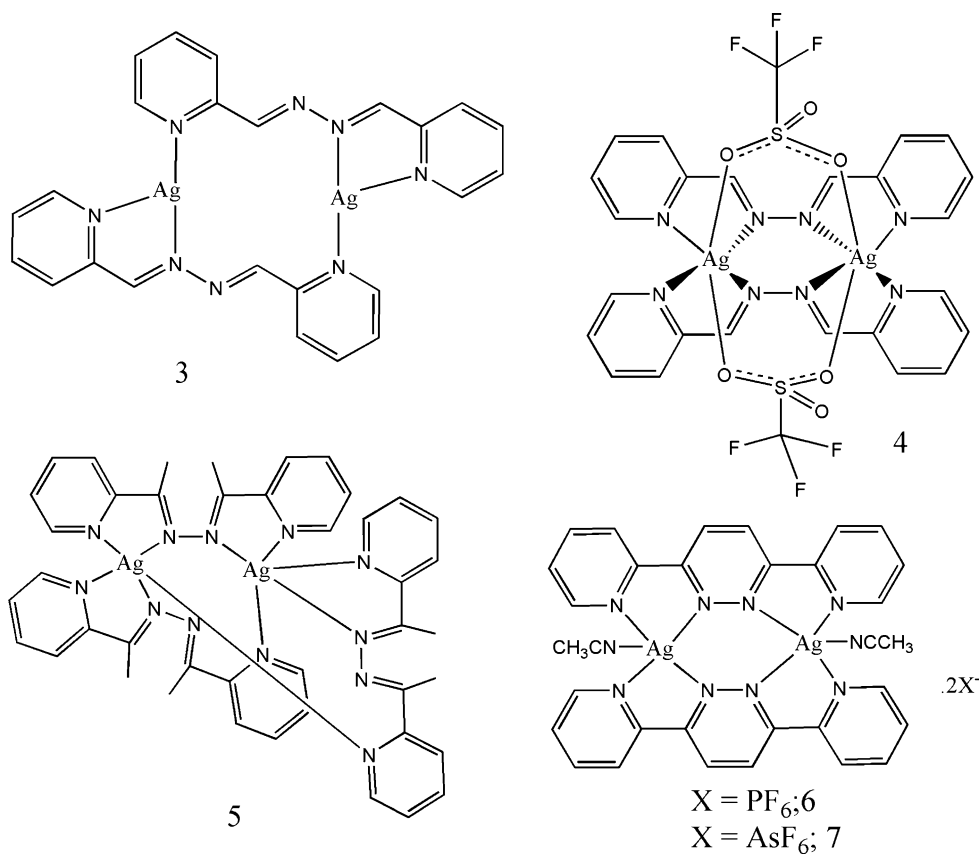
Figure 6.   Chemical structures showing silver(I) coordination environment in **3** [60], **4** and **5** [33] as well as **6** and **7** [71].
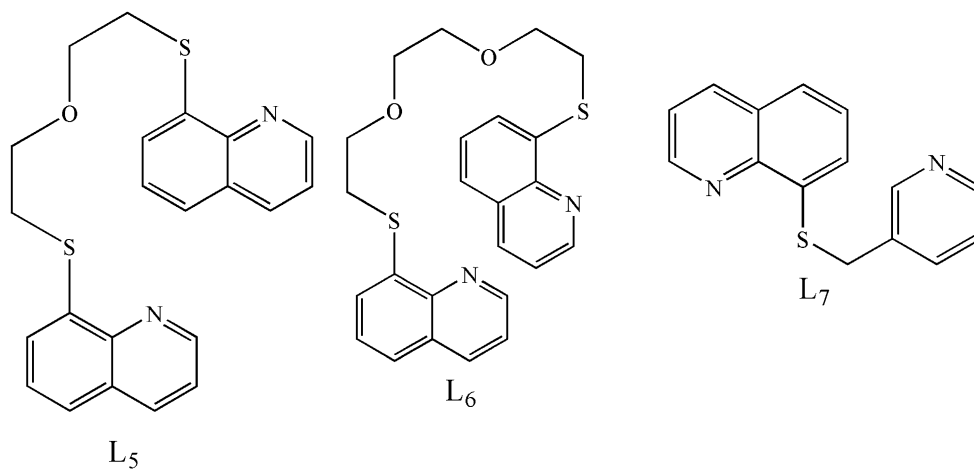

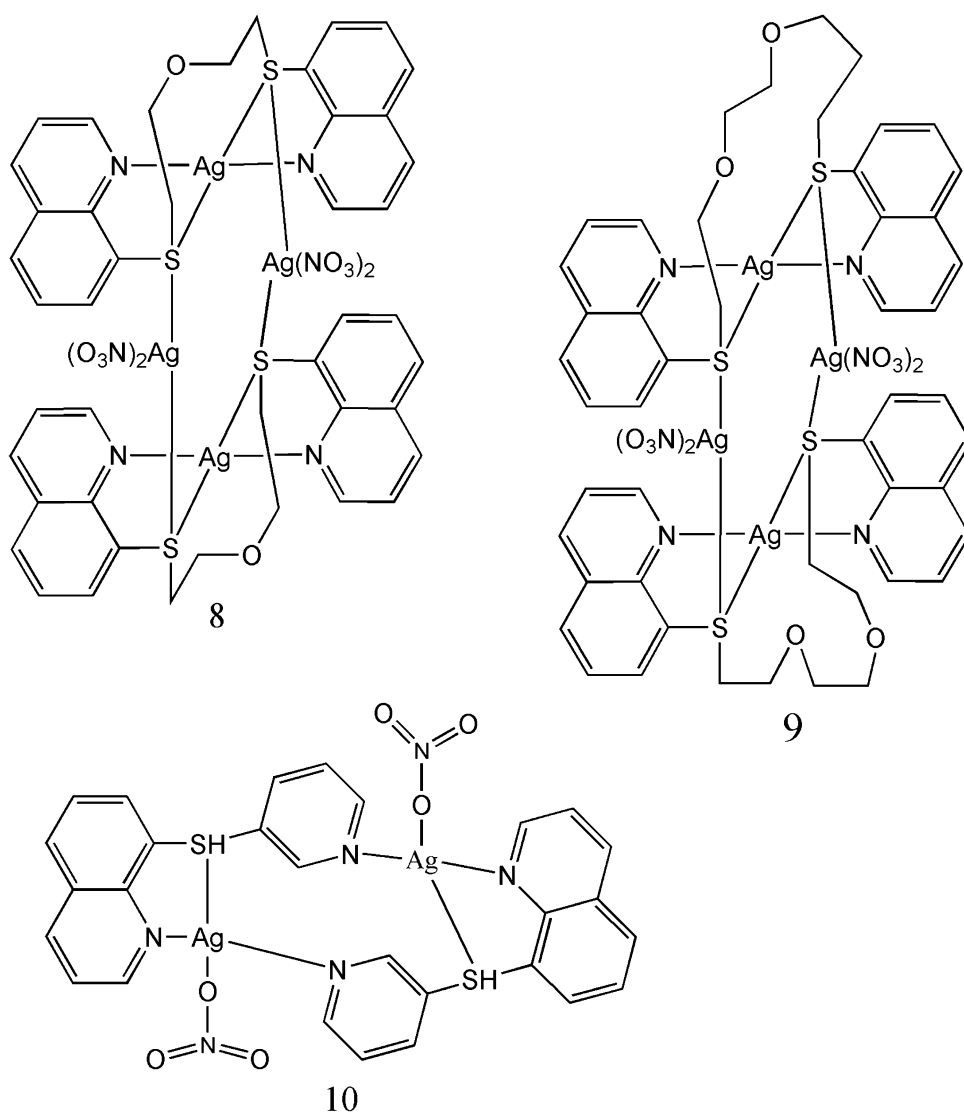Figure 7.   Chemical structures of the heterodonor ligands **L₅–L₇**.

Figure 8. Molecular structures of cations in **8**, **9** [112] and **10** [113] showing the geometry of silver(I) centers.

coordination. Each sulfur is a bridge to assemble the dinuclear monomer into a tetranuclear dimer as shown in figure 8 [112]. Similar complexes from pyridinyl ligands that incorporate S donors in the structure show a high tendency of silver(I) to have higher coordination numbers. For example, the linear tridentate ligand 8-[(pyridin-3-yl)methylthio]quinoline, L_7 (figure 7) yields a bimetallic structure $[Ag_2(L_7)_2(NO_3)_2]$ (**10**) in which the silver(I) centers are distorted tetrahedral through coordination to two N atoms, one from the quinoline ring and the other from pyridine of a different ligand, and one sulfur and an oxygen from the nitrate where the N–Ag–N angle is bent at 121.3° [113].
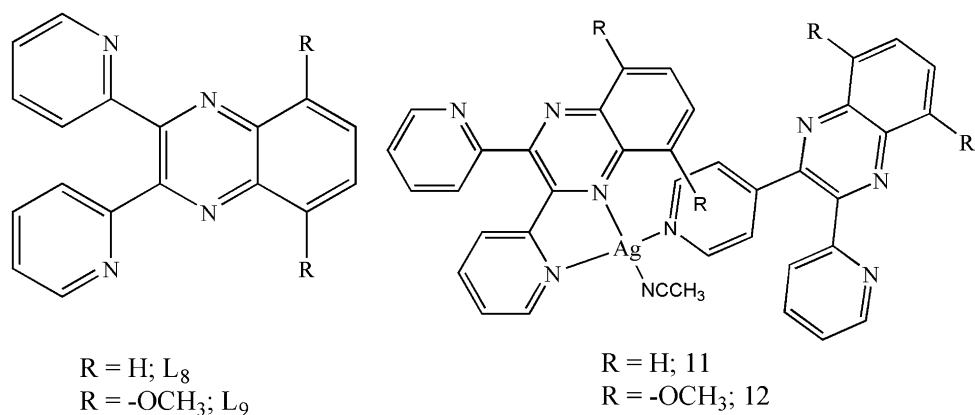
Figure 9. Molecular structures of **L8** and **L9** and cations in **11** and **12**, respectively [11].

L8 and **L9** (figure 9) are multidentate with both pyridine and pyrimidine N donors. Upon reaction of **L8** with AgBF$_4$ and **L9** with AgClO$_4$, the dinuclear cyclic dimeric complexes [Ag(**L8**)(CH$_3$CN)]$_2$[BF$_4$]$_2$·2CHCl$_3$ (**11**) and [Ag(**L9**)(CH$_3$CN)]$_2$·2ClO$_4$ (**12**) were obtained. In each of these dinuclear complexes, silver(I) ions are four-coordinate in a distorted tetrahedral environment as shown by random values of N–Ag–N, ranging from 70.2 to 149.9°. This is by virtue of coordination to three nitrogens, one from the pyrazine ring and one from a pyridine ring of same ligand molecule and a pyridinyl-nitrogen from a second ligand molecule as well as the nitrogen of an acetonitrile. This arrangement yields discrete 'boxlike' dimers where two of the potentially tetradentate ligands jointly coordinate to silver(I) centers by using three nitrogens of each ligand and by rotating the pyridyl rings out
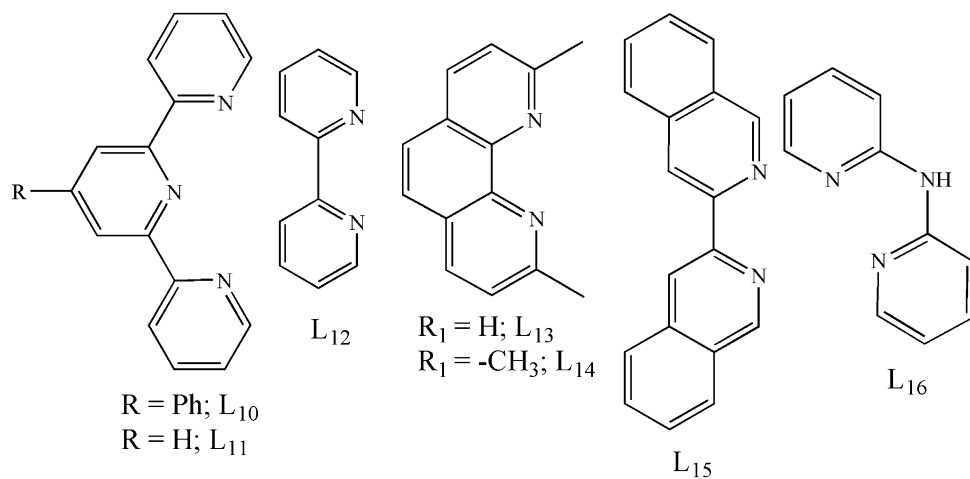

Figure 10. Chemical structures of the multidentate pyridinyl ligands **L10**–**L16**.
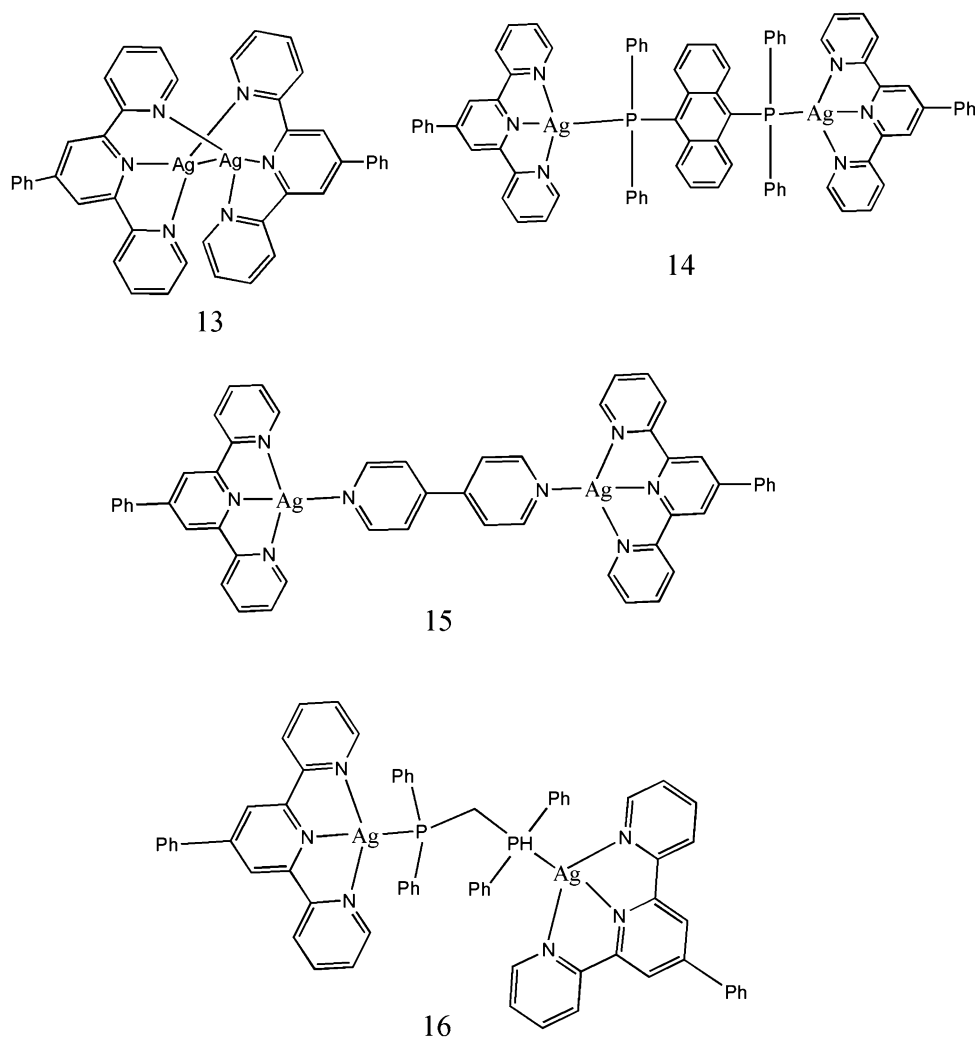
Figure 11.   Molecular structures of cations in **13–16** showing the coordination environment in silver(I) centers [114].

of the plane of the quinoxaline system. This coordination mode and ligand arrangement ultimately precludes the formation of infinite end-on structures [11].

L₁₀–L₁₆ (figure 10) are all pyridinyl multidentate ligands. **L₁₀, L₁₁, L₁₂, L₁₅,** and **L₁₆** are relatively flexible; the N donor sites could either be in *syn-* or *anti-*orientations, compared to **L₁₃** and **L₁₄**, whose coordination sites are fixed in *syn-*position.

The terpyridine derivative 4′-phenyl-terpyridine **L₁₀**, when reacted with AgSO₃CF₃, gave a double helicate dinuclear silver(I) complex [Ag₂**L₁₀**](SO₃CF₃)₂ (**13**) (figure 11). Each of the silver(I) ions in this complex is coordinated by three N-atoms, two from one of the ligands and the third from the second ligand, giving a distorted trigonal geometry when the Ag–Ag bonds are ignored. This complex reacts with bidentate ligands, such as 9,10-bis(diphenylphosphino) anthracene (PAnP), 4,4′-bipyridine (4,4′-Bipy), or bis(diphenylphosphino)methane (dppm), to

give the corresponding bridged dinuclear heteroleptic complexes [Ag$_2$(**L$_{10}$**)$_2$(PAnP)](SO$_3$CF$_3$)$_2$ (**14**), [Ag$_2$(**L$_{10}$**)$_2$(4′,4-Bipy)](SO$_3$CF$_3$)$_2$ (**15**) and [Ag$_2$(**L$_{10}$**)$_2$(dppm)](SO$_3$CF$_3$)$_2$ (**16**) (figure 11). The silver(I) ions are in distorted tetrahedral geometries in the three heteroleptic complexes courtesy of three nitrogens from the terminal terpyridiyl ligand and one donor of the bridging ligand [114].

Other heteroleptic discrete multinuclear silver(I)–pyridinyl complexes of these ligands, **L$_{10}$**–**L$_{16}$**, incorporating ligands, such as phosphines, arsines, or a second pyridinyl ligand, have been studied and reveal the versatile coordination of silver(I). Generally, complexes involving phosphines or arsines have a ratio of 2 : 1 : 2 with respect to pyridinyl ligands to phosphine/diarsine to silver(I), respectively. In these complexes, the phosphines or arsines bridge two silver(I) centers while the multidentate pyridinyl ligand caps the metal centers and effectively stops formation of polymer chains. Heteroleptic dinuclear silver(I) complex of 2,2′-bipyridine [Ag$_2$(**L$_{12}$**)$_2$(dppb)](BF$_4$)$_2$ (**17**) (where dppb is 1,4-bis(diphenylphosphino)-butane) has the silver(I) chelated by a bipyridine ligand forming a five membered ring with N–Ag–N angle of 72.08° and then two chelated silver(I) moieties joined by dppb ligand (figure 12). The silver(I) in this case is in a distorted trigonal geometry and tetrafluoroborate is not involved in coordination [30].

Similar heteroleptic binuclear silver(I) complexes from N,N′-bidenate ligands (ter-pyridine, 2,2′-bipyridine **L$_{11}$**, 1,10-phenanthroline **L$_{13}$**, 2,9-dimethyl-1,10-phenanthroline **L$_{14}$**, 2,2′-biquinolyl **L$_{15}$**, bis(2-pyridyl)amine **L$_{16}$**), figure 10, with phosphines or arsine heteroligands have been comprehensively studied by Marchetti *et al.* [29]. Reaction of AgClO$_4$ with the respective bidentate ligands and diphenylphosphinomethane (dppm) gave complexes [Ag$_2$(**L$_{12}$**)$_2$dppm]2ClO$_4$ (**18**), [Ag$_2$(**L$_{13}$**)$_2$dppm]2ClO$_4$ (**19**), [Ag$_2$(**L$_{14}$**)$_2$dppm]2ClO$_4$ (**20**), [Ag$_2$(**L$_{15}$**)$_2$dppm]2ClO$_4$ (**21**) and [Ag$_2$(**L$_{16}$**)$_2$dppm]2ClO$_4$ (**22**) whose molecular structures are shown in figure 12. All these complexes have tricoordinate silver(I) centers in quasi-planar trigonal geometry courtesy of two N atoms from the bidentate pyridinyl ligands and P from dppm heteroligand [29]. These complexes have similar Ag–N distances (averaging at 2.3 Å), argentophilic interactions at 3.073–3.7380 Å and bite angles (ranging from 71.6 to 74.1°) except for **22** that has a larger N–Ag–N at 84.5°. However, the heteroleptic complex [Ag(**L$_{11}$**)$_2$dppm]2ClO$_4$ (**23**) involving the terpyridine (**L$_{11}$**) has four-coordinate silver(I) ions where all three N atoms are coordinating in a distorted planar geometry [29].

Higher coordination number by silver(I) ions is also observed in dinuclear [Ag$_2$(dppm)$_2$(**L$_{17}$**)$_2$](CF$_3$SO$_3$)$_2$ (**24**) (figure 13) from monodentate isoquinoline **L$_{17}$** and bis(diphenylphosphanyl)methane (dppm) ligands in a single-pot reaction with AgCF$_3$SO$_3$. Each silver(I) is coordinated by two P atoms from the dppm and one N from isoquinoline, consequently adopting a T-shaped geometry [115].

As the polymethylene chain in the heteroligands increases, steric crowding and straining around the coordination site decreases. Consequently, this enhances flexibility in the bridging ligand. This allows coordination of solvent molecules or anions to silver(I) in complexes as depicted in **25**–**29** (figure 14). This coordination of anions or solvents to the silver(I) centers does not affect N–Ag–N angles which basically remain within the same ranges as those of **18**–**23** [29]. Relevant data of complexes discussed in this section are summarized in table 1.

Though silver(I) has been reputed to have a pronounced tendency to exhibit linear two-fold co-ordination (due to the ds hybridization effects) [116], in the discrete complexes reviewed here, it is noted that the overwhelming majority of structures adopt higher coordination numbers and lower coordination numbers are only achieved in sterically
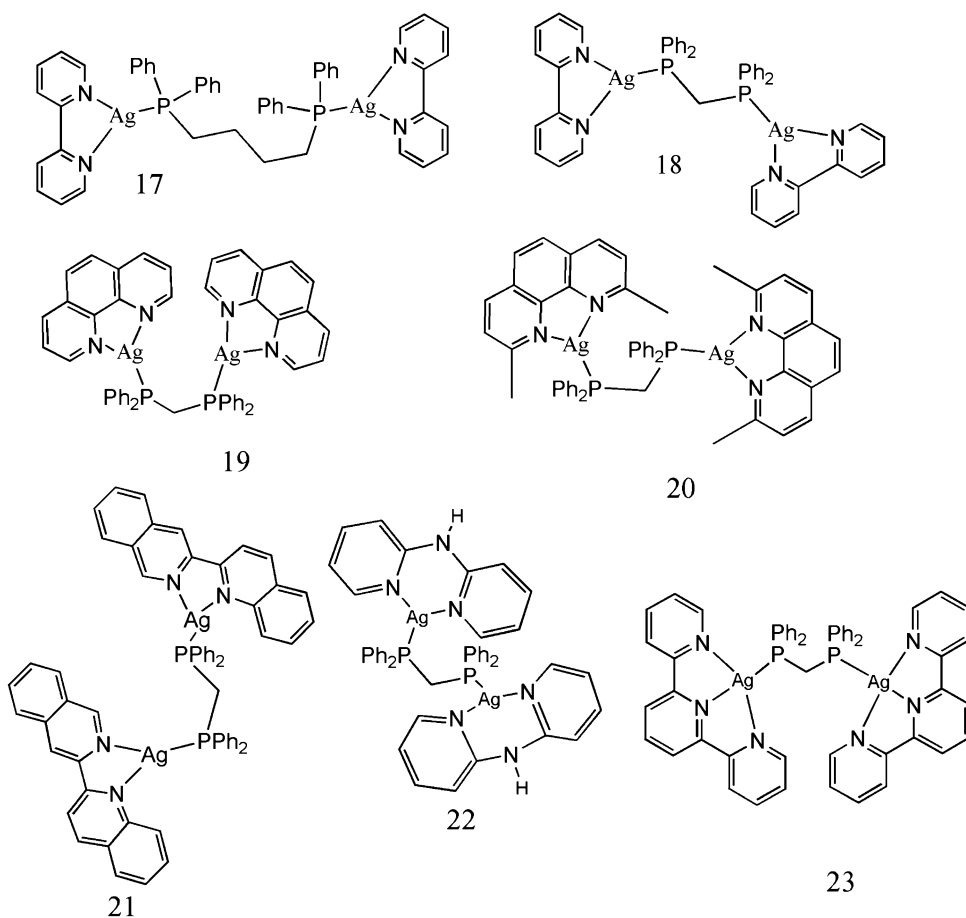
Figure 12.   Molecular structures of cations of silver(I) heteroleptic complex cation in **17** [30] and in **18–23** showing the silver coordination and bridging by the second ligands [29].
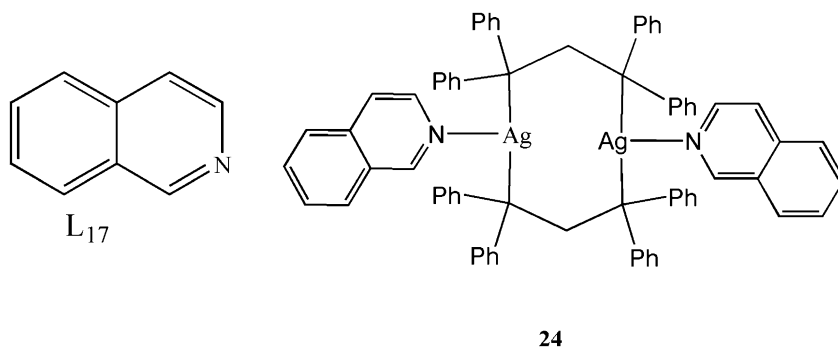

Figure 13.   Molecular structure of **L₁₇** and its heteroleptic dinuclear silver(I) complex **24** with dppm showing the coordination of silver(I) [115].
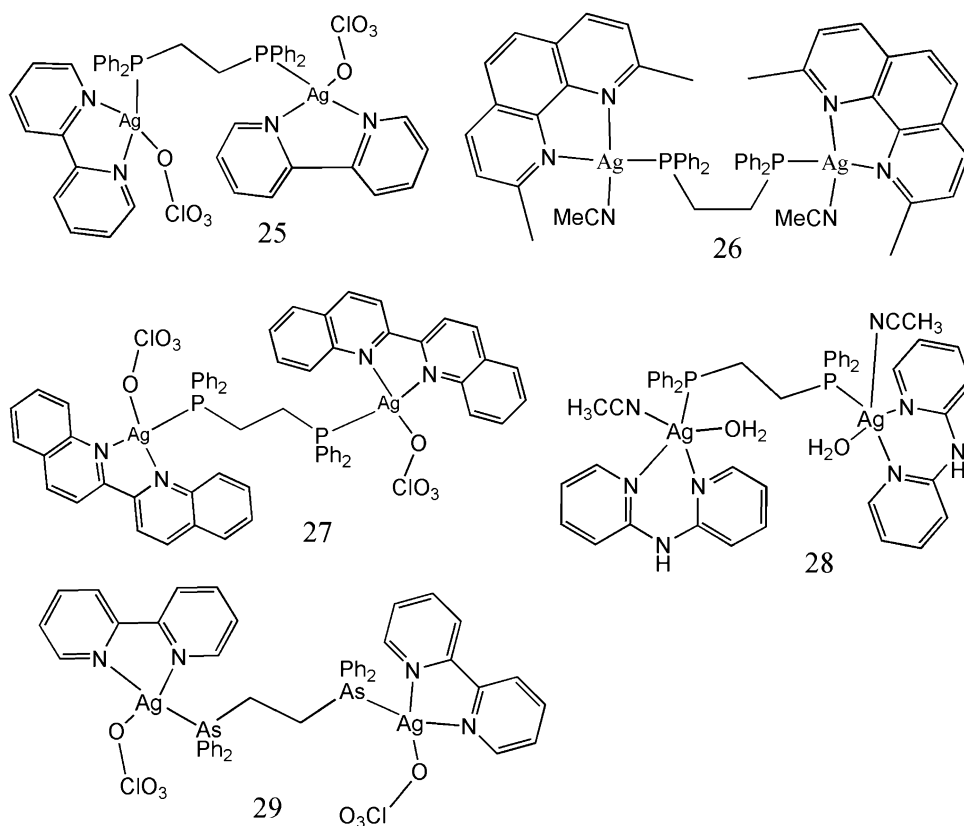
Figure 14.   Structures of cations of silver(I) heteroleptic complexes **24–29** showing coordination around silver(I) centers [29].

crowded situations. The geometry around the silver(I) is also variable and not necessarily linear as has been postulated elsewhere.

2.1.2. Homometallic silver(I) coordination polymers. The basic requirement for synthe-ses of silver(I)–pyridinyl polymers is a multidentate pyridinyl ligand whose donors are strategically oriented to allow creation of protracted chains involving the metal and the ligand. The N donors could all be pyridinyl [117] or a mixture of pyridinyl and non-pyridinyl [118]. Ligands bearing pyridinyl-nitrogens together with other donors such as O [119, 120], S [113], or P [50] in the same molecule have also been employed in synthesis of silver(I) coordination polymers. Heteroleptic silver(I) pyridinyl coordination poly-mers have also been reported and shown to have fascinating architectures [94, 121, 122]. Monodentate pyridinyl ligands yield silver(I) discrete asymmetric units that are linked through anion bridging to form polymeric architectures [123]. Reaction of silver(I) salt with these multidentate ligands often results in coordination polymers that could be single, dou-ble, or triple strands or circular helicates with coordinated silver(I) ions incorporated in the chains. These coordination polymers have captivated attention of researchers due to the

Table 1. The Ag···Ag bond distances, N–Ag–N angles, and geometry of Ag(I) in selected homometallic discrete complexes.

S. No.	Formula	Anion	N–Ag–N bond angle (°)	Ag···Ag bond length (Å)	Geometry	Refs.
1	$[(L_1)_2Ag(\mu\text{-}Br)_2Ag(L_1)_2]$	Br^-	117.4	3.167	Distorted tetrahedral	[109]
2	$[Ag_2(L_1)_4]$	NO_3^-	168.81	3.123	T-shaped	[110]
3	$[Ag_2(L_2)_2]$	$CH_3SO_3^-$	175, 110, 72	–	T-shaped	[60]
4	$[Ag_2(L_2)_2]$	$CF_3SO_3^-$	165.0		Distorted tetrahedral	[60]
5	$[Ag_2(L_3)_3]$	$[PF_6]_2^-$	172.1		Distorted trigonal pyramidal	[33]
6	$[Ag_2(L_4)]$	NO_3^-	165	–	Square planar/ pyramidal	[112]
7	$[Ag_2(L_5)]$	NO_3^-	172	–	Square planar/ pyramidal	[112]
8	$[Ag_2(L_6)_2]$	NO_3^-	121.3	–	Distorted tetrahedral	[113]
9	$[Ag_2(L_7)_2]$	$CF_3CO_2^-$	118.3	–	Distorted tetrahedral	[113]
10	$[Ag_2(L_7)_2(CH_3CN)_2]$	PF_6^-	67–108.3	–	Square pyramidal	[111]
11	$Ag(L_8)(CH_3CN)]_2$	$[BF_4]_2^-$	–	70.2–149.9	Distorted tetrahedral	[11]
12	$[Ag(L_9)(CH_3CN)]_2$	ClO_4^-	–	169	Distorted tetrahedral	[11]
18	$[Ag_2(L_{12})_2dppm]^-$	ClO_4				[29]
19	$[Ag_2(L_{13})_2dppm]$	ClO_4	71.6–74.1		Quasi-planar trigonal	[29]
20	$[Ag_2(L_{14})_2dppm]$	ClO_4	73.06–73.08		Quasi-planar trigonal	[29]
22	$[Ag_2(L_{16})_2dppm]$	ClO_4	82.8–84.5		Quasi-planar trigonal	[29]
28	$[Ag_2(L_{12})_2dpae]^-$	ClO_4	89.3−92.16		Trigonal planar	[29]

high flexibility of silver(I) coordination sphere and geometries of corresponding complexes. Silver(I)–pyridinyl coordination polymers possess interesting properties such as antimicrobial activity [124, 125], enhanced luminescence [126], liquid crystalline properties [127], and silver(I) induced emissions in condensed phases [128]. Most common pyridinyl ligands that have been used to prepare silver(I) coordination polymers include bipyridines, pyridinyltetrazines, 2,2′-biquinolines, terpyridines and their derivatives where the pyridinyl-nitrogen donor sites are separated by alkyl or aryl spacers. Multidentate mixed-donor pyridinyl ligands incorporating N (non-pyridinyl), O, P, or S such as pyridyl-pyrimidinyl disulfide derivatives, L_{20}–L_{22} [129], 1,2-bis(4-pyridylmethyl-amino)ethane L_{23} [130], N,N'-bis(3-pyridylmethyl)-1,4-benzenedimethylene-imine L_{25} [38], 2-{5,5-dimethyl-3-[2-(pyridin-3-yl)-ethenyl]cyclohex-2-enylidene}propane-dinitrile L_{26} and 2-{5,5-dimethyl-3-[2-(pyridin-2-yl)-ethenyl]cyclohex-2-enylidene}propane-dinitrile L_{27} [8] in figure 15, have been employed in synthesis of silver(I) coordination polymers. In several of these coordination polymers, silver(I) is a bridge (L–Ag–L) linking several ligand molecules to form infinite chains [65, 131, 132]. In the structures, silver(I) tends to show linear or quasi-linear geometries (with respect to the N–Ag–N angle) when not coordinated to anions or solvent molecules [133, 134]. The geometry around silver(I) and long range structure of the polymers are influenced to a great deal by anion bridging, metal–metal interactions, metal–π interactions, and other non-covalent interactions [20].

Reaction of silver salts with monodentate pyridinyl ligands normally yields simple adducts of 1 : 1, 1 : 2, and 1 : 4 metal–ligand stoichiometry. These adducts can further be used in construction of coordination polymers. This is done via multiple sets of ligand supported or unsupported argentophilic interactions as well as anion bridging and π–π interactions to form 1D, 2D, or 3D infinite networks [135]. Stoichiometries of the adducts are highly pegged on nature of the silver(I) salt and ligand solution. For instance, saturated
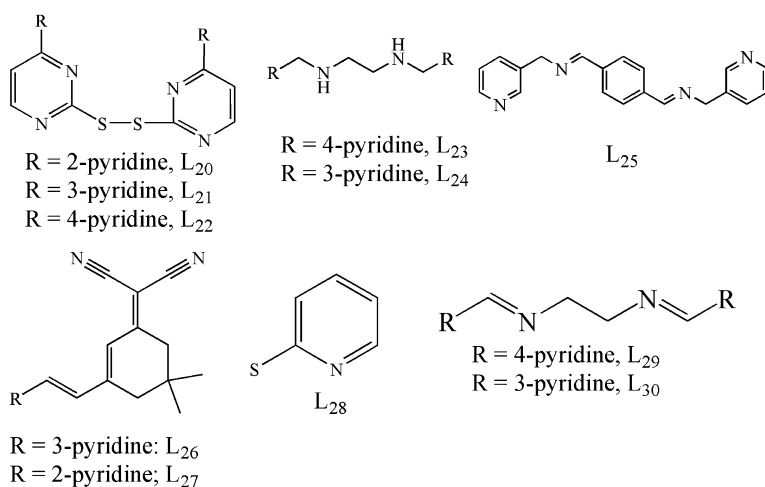
Figure 15.   Chemical structures of **L$_{20}$–L$_{31}$**.

pyridine solutions of the silver(I) salts yield 1 : 2 adducts while pyridine/water solutions yield 1 : 4 adducts [135]. More often, crystallization of silver(I) halides from neat pyridine, methylpyridines, or quinoline yields adducts of 1 : 1 stoichiometries further link (via argentophilic bonds or anion bridging) to form infinite polymeric chains [103]. Recrystallization of silver(I) bromide from 3- and 4-methylpyridine (3Me-py, and 4Me-py, respectively) gives adducts with silver(I) bromide-base ratios of 1 : 1 [(AgBr(3Me-py)}$_n$] (**30**) and [(AgBr(4Me-py)}$_n$] (**31**), respectively. Notably, 3-methylpyridine and 4-methylpyridne form protracted chains, whereas their positional isomer 2-methylpyridine (2Me-py) forms a discrete dimer (**1**). The adduct from 3-methylpyridine aggregates via the anion to form a tube polymer while those of 4-methylpyridine form a step polymer. The AgBr(4Me-py) polymer has significant Ag⋯Ag separation at 3.162 and 3.167 Å while in AgBr(3Me-py) they are weak and insignificant, ranging from 4.365 to 4.091 Å [109].

Unlike in **30** and **31** above, the silver(I) adducts [Ag(Py)$_2$]X (X = ClO$_4^-$ (**32**); BF$_4^-$ (**33**)) have 1 : 2 stoichiometries, where each [Ag(Py)$_2$] unit is joined to the next via anion bridging in a chelate fashion. Each of these pairs of adducts are joined by extended ligand unsupported argentophilic interactions buttressed by π–π stacking of pyridyl rings to yield 1D zigzag polymeric coordination polymers. The silver(I) centers are in distorted linear geometries at 173.83 and 174.81°, respectively. These bond lengths are significantly shorter than those observed for adducts involving the halides in **30** and **31**. The Ag⋯Ag separations within [Ag(Py)$_2$]$^{2+}$ adducts are 2.999 and 3.000 Å for **32** and **33**, respectively, while between pairs of adducts the metal–metal distance is 3.3722 Å in **32** and 3.3443 Å **33**. It is observed that π–π interactions between adjacent aromatic systems of the ligands in **32** and **33** reduce the argentophilic interactions between pairs of adducts (figure 16). Influence of anion on the assembly of the coordination polymers is evident as the coordination polymers **32** and **33** (with tetrahedral ClO$_4^-$ and BF$_4^-$ anions) have isomorphous structures bearing an infinite 1D chain formed via ligand-supported argentophilic interactions. In contrast, the coordination polymer {[Ag(Py)$_2$]$_2$PF$_6$}$_n$ (**34**) having an octahedral PF$_6^-$ has pairs of [Ag
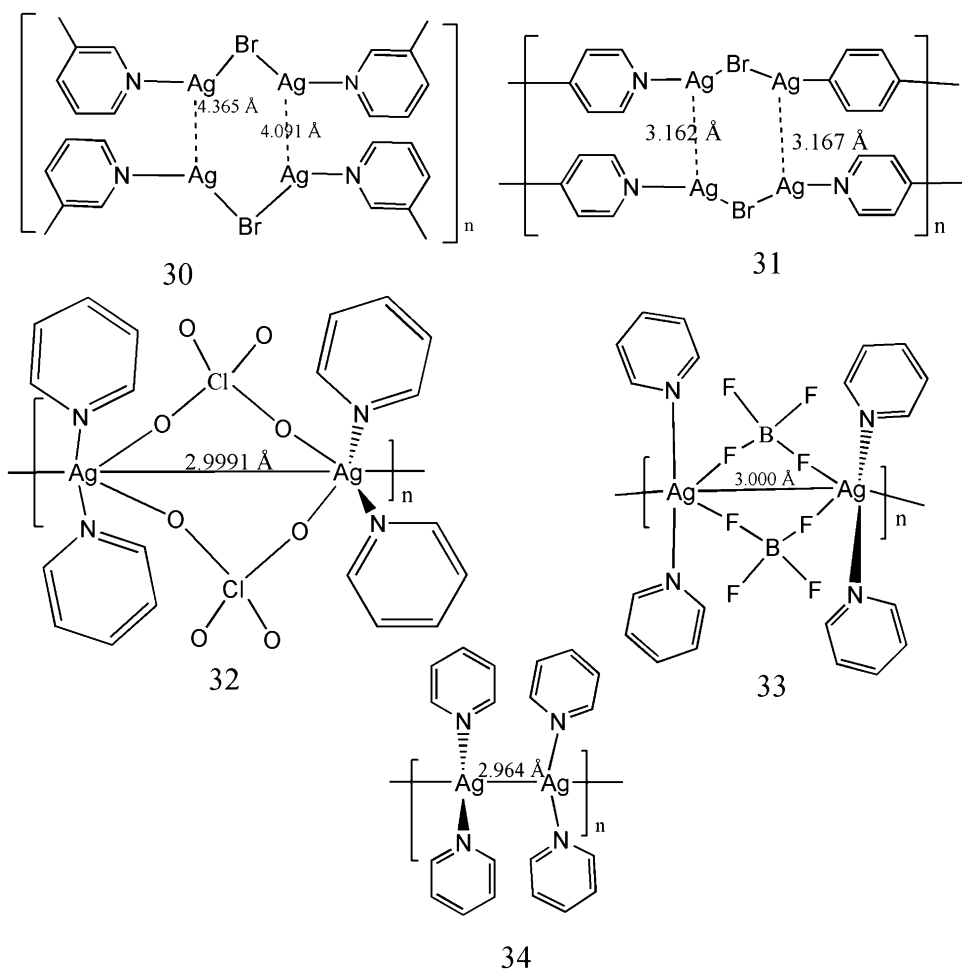
Figure 16. Structures of cations of repeating units in coordination polymers **30**, **31** [109] and **32-34** [93], each showing coordination around the silver(I) centers.

$(Py)_2]_2^{2+}$ adducts linked by the anion to form a 3D network. In **34**, the N–Ag–N is nearly linear, 178.1°. The Ag···Ag separation within the adducts is similar at 2.964 Å [93].

Silver(I) coordination polymers from mixed-donor pyridinyl ligands such as mono- and dithiolate ligands have also been investigated, where the ligands chelate to produce infinite 1D chain structures and 3D networks [136, 137]. For instance, the mercaptopyridine, pyridine-2-thionate $\mathbf{L_{28}}$ (figure 15) forms a neutral silver(I) polymeric complex, $[Ag_6(L_{28})_6]_n$ (**35**), where the repeating units are joined by Ag–S and Ag···Ag interactions to form the 1D coordination polymer shown in figure 17 [136]. The silver(I) centers are in a distorted tetrahedral coordination courtesy of three S and an N of the mercaptopyridine ligands. This coordination polymer has some significant metal–metal interactions as indicated by Ag···Ag separations that range from 2.959 to 3.369 Å [109].

Mixed-donor pyridinyl ligands with oxygen in same molecule have been utilized in synthesis of silver(I) polymeric architectures. The most common examples are the nicotinate
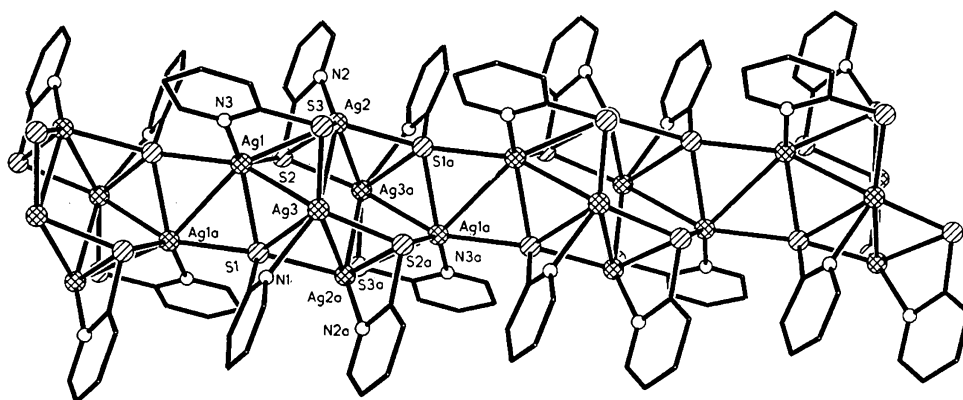
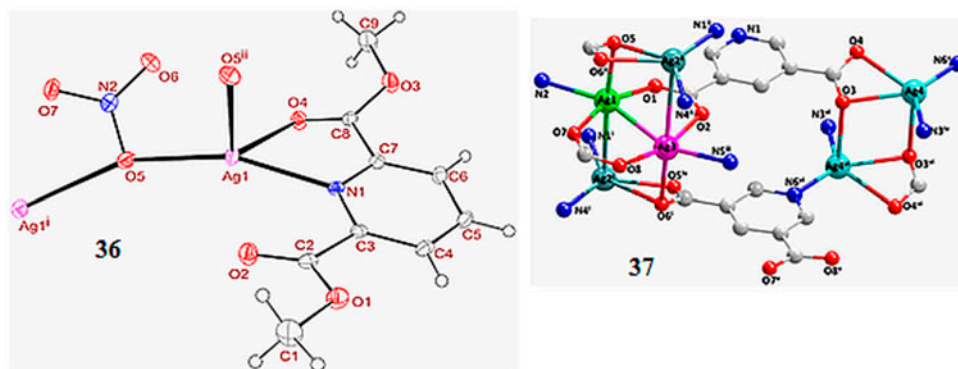Figure 17. Chemical structure showing the coordination of silver(I) in 1D coordination polymer **35** [136].

Figure 18. ORTEP diagrams for molecular structures of repeat units in [Ag(L)NO$_3$]$_n$ (**36**) [123] and [Ag$_4$(μ-pydc)$_2$(μ-pm)$_2$]$_n$ (**37**) [138].

(pyridinecarboxylate) ligands. For instance, dimethylpyridine-2,6-dicarboxylate **L$_{31}$** reacted with AgNO$_3$ to give the polymer [Ag(**L$_{31}$**)NO$_3$]$_n$ (**36**) shown in figure 18. In this silver(I) coordination polymer, the silver(I) centers are in distorted tetrahedral geometries courtesy of two oxygens from nitrates, one nitrogen and one carboxylate O from **L$_{31}$**. In this arrangement, the nitrates bridge two adjacent silver(I) centers via one O yielding 1D polymeric chains [123]. Heteroleptic silver(I) coordination polymer from 3,5-pyridinedicarboxylic acid (3,5-PyCOO) and pyrimidine (pm), [Ag$_4$(μ-(3,5-PyCOO)(μ-pm)$_2$] (**37**), figure 18, has four crystallographically different silver(I) centers in distinct coordination environments. In this polymer, all the silver(I) centers are four coordinate in distorted tetrahedral environment, albeit to different magnitude and also coordinated to different donors [138].

Heteroleptic silver(I) coordination polymers of pyridinecarboxylates in conjunction with triphenyl phosphine are shown in figure 19. These were obtained by reacting silver(I) phosphine complexes [Ag(PPh$_3$)CH$_3$COO] with 2,3-pyridinedicarboxylic acid (2,3-pyCOO) to yield [Ag(PPh$_3$)(2,3-pyCOO)]$_n$ (**38**), 3-pyridinecarboxylic acid (3-pyCOO) to yield [Ag$_2$(PPh$_3$)$_2$(3-pyCOO)$_2$]$_n$ (**39**) and with 4-pyridinecarboxylic (4-PyCOO) to yield the
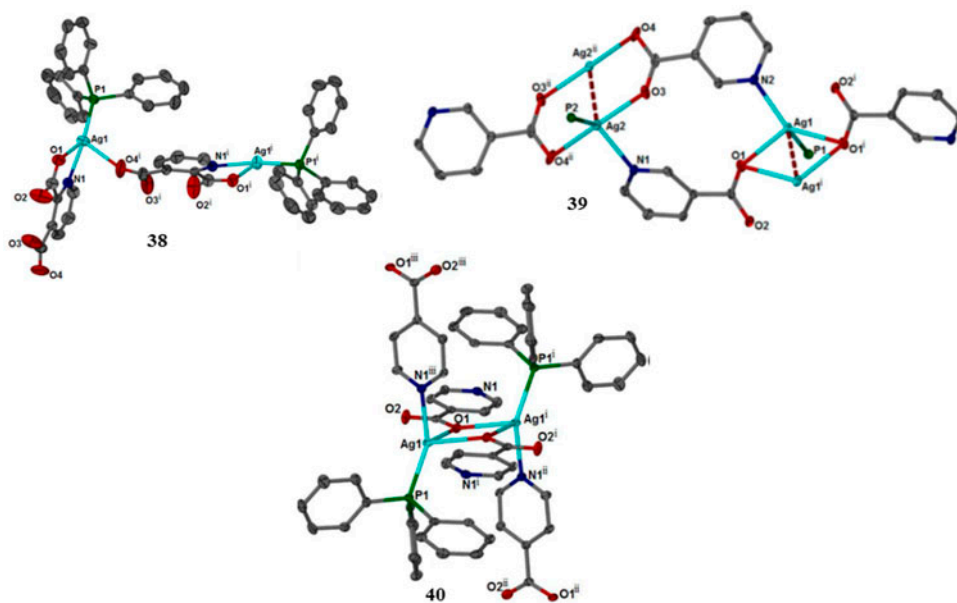
Figure 19.   ORTEP diagrams in chemical structures of repeating units showing silver(I) coordination environment in $[Ag(PPh_3)(2,3\text{-}py(COO)]_n$ (**38**), $[Ag_2(PPh_3)_2(3\text{-}pyCOO)_2]_n$ (**39**) and $[Ag(PPh_3)(4\text{-}pyCOO)]\cdot EtOH$ (**40**) [139].

solvated $[Ag(PPh_3)_2(4\text{-}PyCOO)]_n.EtOH$ (**40**) [139]. In **38,** each silver(I) center is four coordinate tetrahedral courtesy of N and O from one ligand, an O from the second ligand and P from the phosphine. Consequently, the 2,3-PyCOO ligand bridges two Ag(I) ions via two doubly deprotonated carboxylates yielding a 1D zigzag chain. In **39,** the silver(I) centers have tetrahedral geometry via two O, one P from PPh$_3$, and a N atom from the pyridine ring as shown in figure 19. The compound also shows significant argentophilic interactions between adjacent metal centers. Pairs of silver(I) centers are bridged by two 3-pyCOO$^-$ ligands in two different coordination modes leading to a 1D ladder-like structure. In **40**, silver(I) also has tetrahedral geometry and is coordinated to N and O, all from different 4-PyCOO ligands and a P from the phosphine ligand. The 4-pyCOO$^-$ ligand shows only one bridging mode, bridging three silver(I) ions via O from the carboxylate and pyridinyl-nitrogen (unlike 3-pyCOO$^-$ in **39**) yielding a 2-D network [139]. The repeating units in these coordination polymers depicting ligand coordination are shown in figure 19.

In pursuit of silver(I) coordination polymers with tailored structural arrangements and higher optical properties, Jin *et al.* utilized positional isomers L_{26} and L_{27} (figure 15) [8]. Silver(I) perchlorate reacts with L_{26} to give a trinuclear 1D polymer $\{[Ag_3(L_{26})_2(H_2O)](ClO_4)_3\}_n$ (**41**). In the repeating unit of the coordination polymer, a pair of ligands bridge two silver(I) ions in a head-to-tail fashion through Ag–N coordination bonds essentially generating a dinuclear $[Ag_2(L_{26})_2]^{2+}$ metallacycle with metal centers far apart (Ag⋯Ag distance of 8.512 Å). One silver(I) ion is two-coordinate through two N atoms, one cyano from one ligand and the second, a pyridinyl-nitrogen from the second ligand with O of ClO_4^- only weakly coordinating. The N–Ag–N deviates from linearity to 167°. The second silver(I) shows square planar coordination geometry via two O and two N atoms coordinated by nitrogen of cyano groups and oxygen from H$_2$O molecules. Consequently, two

neighboring $[Ag_2(L_{26})_2]^{2+}$ are bridged into metallacycle units forming an infinite chain through Ag1–N1 bonds. In contrast, L_{26} with AgNO$_3$ gives zigzag 1D infinite chains that are linked by hydrogen bonds into a 2D coordination polymer $\{[Ag(L_{26})(NO_3)]0.5C_6H_6\}_n$ (**42**). The repeating unit has two silver(I) ions that are in two different coordination environments. The first silver(I) ion is in a distorted tetrahedral geometry courtesy of two O atoms from two nitrates and two N from two cyano groups of two different ligands while the second is in perfect linear two coordinate via two pyridinyl-nitrogens from two different ligands (N–Ag–N 180°). The Ag–N$_{pyridinyl}$ at 2.159 Å is shorter than the one in **41** [8]. These differences in coordination polymers **41** and **42** further buttresses the significance and influence of anions and solvents in controlling structures of polymeric silver(I) complexes. On the other hand, the isomer L_{27} gives a 2D coordination polymer $\{[Ag(L_{28})$ $(NO_3)]\cdot0.5C_6H_6\}_n$ (**43**) (figure 20) bearing two geometrically equivalent silver(I) ions in the repeating unit. The silver(I) centers are in distorted tetrahedral O$_2$N$_2$ coordination geometry. The two O are from two NO$_3^-$ anions, one N is from a pyridyl moiety and the other from a cyano group of a different ligand. The coordination of a ligand to different silver(I) ions leads to extended 2D structure [8]. The ligand, N,N′-bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine L_{25} reacts with AgNO$_3$ in acetonitrile to give silver(I) complex catena-((μ_2-N,N′-bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine)-silver(I) nitrate dihydrate) $[Ag(L_{25})]NO_3\cdot2H_2O)$ (**44**) (figure 20). The silver(I) ions are two coordinate via two pyridinyl-nitrogens from different ligands in a quasi-linear environment (N–Ag–N bond angle = 174°). The ligand molecules are joined by silver(I) ions to give the infinite 1D zigzag structure [38].

The versatility of the coordination sphere in silver(I) as well as the influence of the size and flexibility of the spacer and position of the donor in multidentate pyridinyl ligands on the holistic structure of coordination polymers frameworks has been studied using the multidentate bipyridine analogs 1,2-bis(3′-pyridylmethylamino)ethane, L_{23} and 1,2-bis(4′-pyridylmethylamino)ethane L_{24} [140], N,N′-bis(3-pyridylmethyl)-1,4-benzenebis (methyl-amine) L_{25} [141], 1,2-bis(4′-pyridyl)ethylenediamine L_{29}, and 1,2-bis(3′-pyridyl) ethylenedi-amine L_{30} [142] (figure 15). The silver(I) coordination polymers from these ligands have infinite 1D chain structures that are further linked via non-covalent interactions into a 2D structure. In these structures, silver(I) ions within the repeating units of the coordination polymers show different coordination numbers (2, 3, and 4) and geometries courtesy of two different ligand methods.

The dinuclear complex $[Ag_2(OTf)_2(\mu\text{-PPh}_2py)_2]$ (**45**) (PPh$_2$py = 2-(diphenylphosphino)-pyridine) has a bridging P, N unit forming an eight-membered ring. The two silver(I) ions are in different coordination environment, the first in trigonal pyramidal geometry via P and N atoms from different ligands, an O atom from the triflate and a metal–metal bond (figure 21). The Ag···Ag bond length is 3.044 Å. The second silver(I) is in a tetrahedral environment with the four sites occupied by two O from different triflate ions; P and N from different ligands. In both cases, the Ag coordination angles deviate from linear geometry where the N–Ag–P angles are 156.61 and 160.92°. A triflate ion further bridges two silver(I) centers leading to formation of a zigzag polymer [50].

2.1.3. Luminescence in homometallic silver(I) complexes. Multidentate π-conjugated polypyridinyl donor ligands have excellent optical traits and coordinate to silver(I) centers in various modes as observed in preceding sections. Silver(I)–pyridinyl complexes possess long-lived excited states. Subsequently, these complexes have applications as photosensitizers
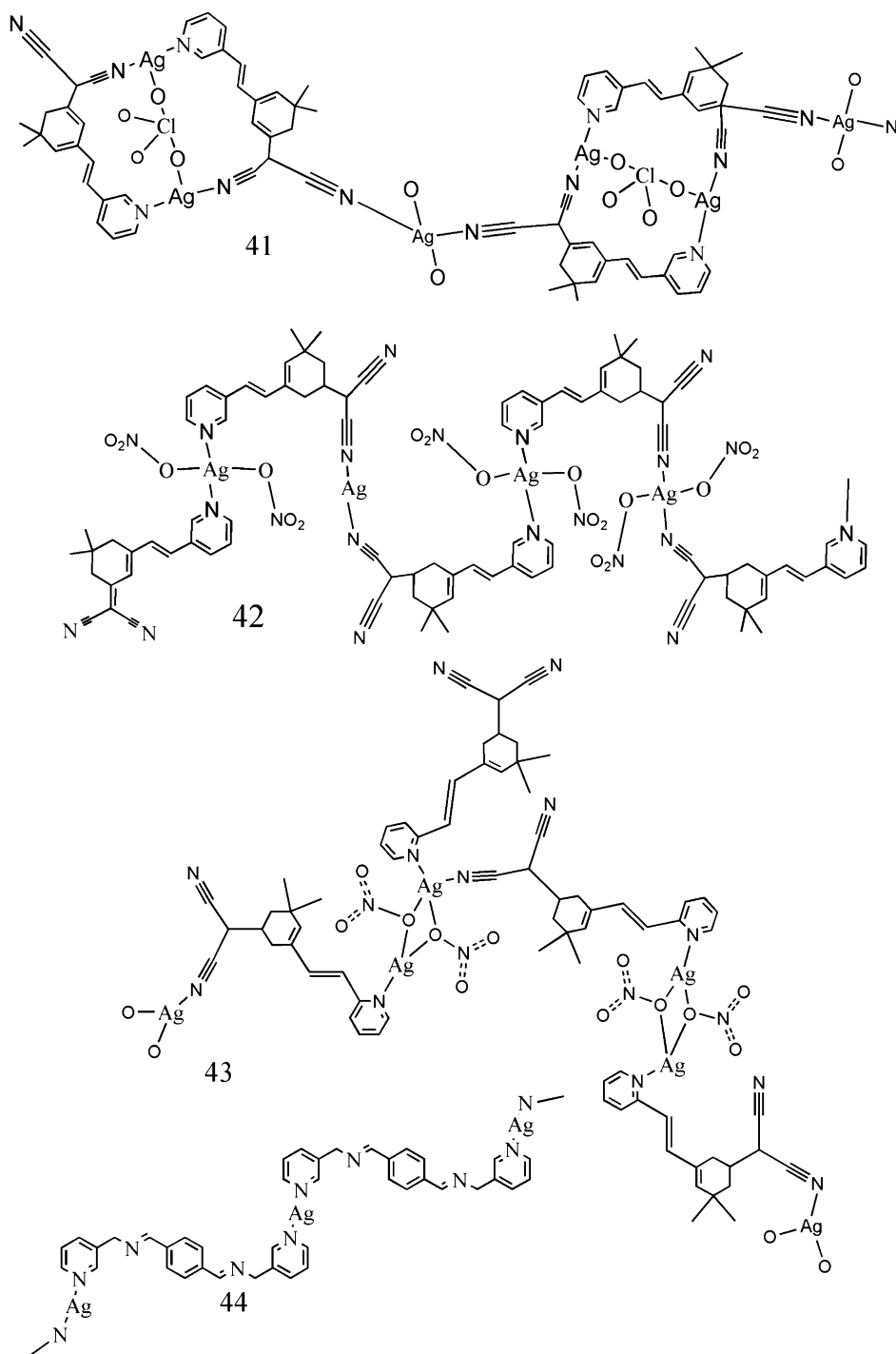
Figure 20.   Molecular structures of repeating units in coordination polymers **41–43** [8] and **44** [38].
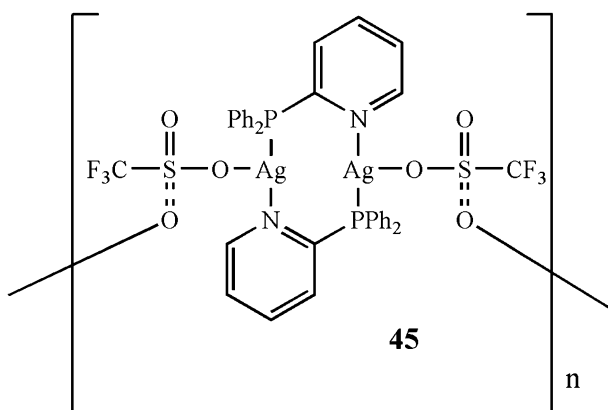
Figure 21. Molecular structure of repeating unit in coordination polymer **45** [50].

in energy conversions and electron transfer processes [11, 143, 144] as well as in biomolecular and cellular probes [100]. Coordination of silver(I) in conjugated organic molecules increases the latter's conformational rigidity and decreases symmetry within the ligand molecules. The net result is a reduction in energy loss by intramolecular vibrational and rotational motions. This enhances or imparts remarkable luminescence in the resulting complexes [145, 146]. Use of substituted ring systems also reduces π–π interactions and molecular packing and this augments luminescent properties in the solid state at ambient temperature. Luminescence in silver(I)–pyridinyl multinuclear complexes is assigned either as metal-to-ligand charge transfer (MLCT) [147], intraligand charge transfer (ILCT) [148], or ligand–metal charge transfer (LMCT) [149]. In complexes containing significant argentophilic interactions, the luminescence may originate from the short metal–metal contacts [150–152]. The nature of observed luminescence is determined by the structure of the ligand employed in coordination as well as the nature of the complex formed [8]. At room temperature, silver (I) coordination polymers show feeble luminescence [153] but are known to be greater emitting materials at low temperatures (where they have enhanced emitting intensity) [154] and/ or a shift of the emission wavelength [155]. These macrocyclic silver(I)–pyridine polymers also portray solid state and solution luminescence originating from intermetallic silver–silver interactions. The polymers are known to fluoresce in solution and solid state at room temperature [152].

A photoluminescent hexanuclear silver(I) discrete cluster synthesized by reacting AgNO$_3$ with 2,6-dimethylpyridine in the presence of anthracene-9-carboxylic acid, synthesized by Liu *et al.*, shows silver(I) enhanced luminescence [57]. The complex shows stable, intense and enhanced room-temperature luminescence emission at λ_{max} = 449 nm, upon excitation at 413 nm in the blue region compared to free ligands' solid-state greenish-blue luminescence at λ_{max} = 510 nm upon excitation at λ = 410 nm. The enhancement of luminescence is attributed to coordination of the ligand to silver(I), which effectively increases the rigidity of the ligand and reduces the loss of energy by non-radiation decay, consequently facilitating intraligand π^*–π transitions of anthracene-9-carboxylate ligand [57]. The dinuclear cyclic dimers [Ag(L$_8$)(CH$_3$CN)]$_2$[BF$_4$]$_2$·2CHCl$_3$ (**11**) and [Ag(L$_9$)(CH$_3$CN)]$_2$·2ClO$_4$ (**12**) show solid-state luminescence at 77 K originating from metal-perturbed IL excited states. The emission maxima for the two are 585 and 598 nm, respectively [11]. Complex **13** from

4′-phenyl-terpyridine is photoluminescent in various solvents and also shows strong fluorescence in the solid state with its excitation band appearing at 383.5 nm and the maximum emission band at 535.5 nm [114]. This shift in maximum emission upon coordination of silver(I) is also evident in coordination polymers as well, where red shifts are common [8]. Coordination polymer **45** shows mixed IL and LMCT luminescence at room temperature with a maximum emission at 497 nm and at 77 K, 479 nm. The metallophillic interactions in the complex also contribute to the luminescence observed. In **45**, the ligand plays a critical role in facilitating intramolecular metallophillic bridging and consequently enhancing the luminescent properties of the ensuing complex [50]. Reaction of $AgNO_3$ and pyridine-3,5-dicarboxylic (pydc) acid yields 3D coordination polymers $[Ag_5(pydc)_2(CN)]_n$ and $\{[Ag_4(pydc)_2]CH_3CN\}_n$ that exhibit blue/green photoluminescence at room temperature with the emission maximum at 527 and 488 nm upon excitation at 387 and 332 nm, respectively [101]. Luminescence intensity is much stronger in complexes that have high argentophilic interactions and those lacking π–π interactions and strong auxiliary ligand coordination.

2.2. *Heterometallic silver(I) complexes*

Though polynuclear silver(I)–pyridinyl complexes are dominated by homometallic analogs, prudent ligand design and varying metallic partners have permitted creation of a variety of discrete and polymeric silver(I) heterometallic architectures where the silver(I) is coordinated by a pyridinyl-nitrogen donor. Heterometallic assemblies are infrequent since their syntheses are more tedious and challenging on account of difficulties in controlling the relative arrangement of the different metal centers. Nevertheless, these challenges have been successfully prevaricated through a stepwise approach, where metalloligands are employed in creation of heterometallic silver(I)–pyridinyl coordination complexes [17, 156]. Pyridinyl metalloligands have, for instance, been obtained by linking pyridinyl ligands to preformed metallocenes, such as ferrocene. The pyridinyl moiety could be linked to the ferrocene directly or through rigid or flexible spacers to either one or both cyclopentadienyl rings generating iron-based metalloligands that can be applied in coordinating silver(I) ions via the peripheral pyridinyl-nitrogen [157–160]. Alternatively, mixed-donor multidentate pyridinyl ligands bearing different coordination sites having dissimilar binding propensity toward different metals have also been utilized in creation of silver(I)–pyridinyl mixed-metal complexes. This entails exploiting the hierarchy of binding between the different donor sites that is primary and secondary, where the ligand is reacted with an appropriate metal that reacts preferentially with other sites leaving the pyridine site uncoordinated. Consequently, a metal complex bearing peripheral uncoordinated pyridinyl-nitrogen is generated. Subsequent coordination of these complexes with a silver(I) cation via the free peripheral pyridinyl sites leads to heterometallic architectures that are either discrete or protracted depending on the number and orientation of available peripheral coordination sites [157, 161–165]. This not only permits the assembly of heterometallic complexes but also enables predictability and precise control over the relative location of the two different metal centers with high degree of confidence [166]. Neutral homoleptic pyridinyl metalloligands of transition metals, such as copper [79], cobalt [79], ruthenium [51, 167], rhodium [168], gold [169], platinum [170], rhenium [171] as well as those of lanthanides such as europium, terbium, and neodymium [172], have been synthesized. These metalloligands have successively been used to coordinate silver(I) ions, yielding heterometallic architectures (discrete

Cp = cyclopentadienyl ring

ML1

R = 4-pyridine; ML2
R= 3-Pyridne; ML3

ML4

M = Fe; ML5
M = Ru; ML6

ML7

R = 3-pyridine; ML8
R = 4-pyridine; ML9

R = 3-pyridine; ML10
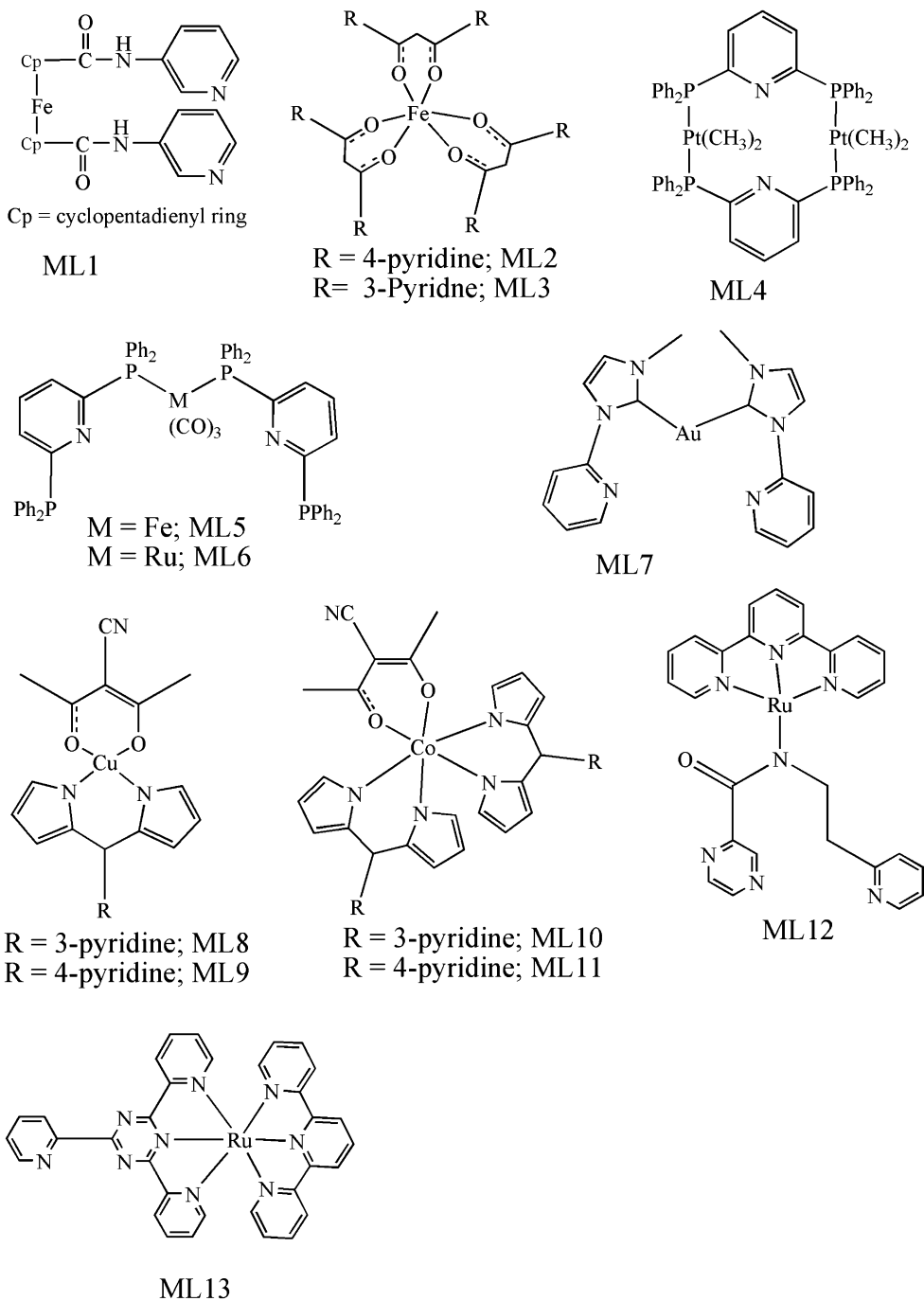R = 4-pyridine; ML11

ML12

ML13

Figure 22.   Molecular structures of some metalloligands that have been used in synthesis of silver(I) heterometallic complexes.

or coordination polymers) [32, 173–175]. Molecular structures of some of these metalloligands that have been utilized in coordination of silver(I) are shown in figure 22. Mixed-metal silver(I)–pyridine complexes have also been obtained by reacting silver(I)–pyridinyl metalloligands with a second metal [176], electrochemical oxidation of a metalloligand [177], or through the reaction of a mixed-donor polydentate ligand that have predetermined coordination sites with silver(I) and a second metal simultaneously in one-pot reaction (self-assembly) [178]. Heterometallic silver(I)–pyridinyl complexes possess structural diversity and novelty as well as tailored properties imposed by combining unlike metal centers with diverse geometries. For instance, they have been found to yield porous materials that in turn find application in gas storage, carbon capture and catalysis [173, 179]. These mixed-metal silver(I) complexes have also been found to have superior luminescence properties, with respect to excited state times. The majority of silver(I)–transition metal heterometallics are obtained through solvent diffusion techniques or mechanical agitation under inert atmosphere (Schlenk technique) under normal conditions of pressure and temperature. On the other hand, the majority of silver(I)–lanthanide complexes are synthesized through solvothermal techniques in Teflon-lined steel/autoclave vessels or in a microwave.

2.2.1. Discrete heterometallic silver(I) complexes. Silver(I)–iron mixed-metal complexes are obtained by use of mixed-donor ligands, often having pyridine moieties and O donor in the ligand skeleton or by linking pyridinyl substituents in one or both cyclopentadienyl rings of ferrocene. For instance, in the quest to find novel heterometallic architectures with tailored properties, the ferrocene-based pyridinyl bidentate metalloligand 1,1′-bis[(4-pyridylamino)carbonyl]ferrocene, **ML1**, has been employed in complexation of silver(I) ions. This metalloligand yielded silver(I)–iron heterometallic complexes $[Ag_2(ML1)_2](CF_3SO_3)_2 \cdot 3H_2O$ (**46**) and $[Ag_2(ML1)_2](CF_3COO)_2 \cdot 2CH_3CN_3 \cdot C_6H_6$ (**47**) (figure 23) upon reaction with silver(I) trifluoromethanesulfonate and silver(I) trifluoroacetate, respectively [92]. The two silver(I) centers in each complex are equivalent and have ligand supported Ag⋯Ag interactions. However, in the trifluoroacetate complex **47**, the dimers are linearly arranged generating a 2-step structure linked through O of trifluoroacetate to form 1D chains that are further linked into a 2D network via C–H⋯O hydrogen-bonding between host intrapolymer and guest-benzene molecule.
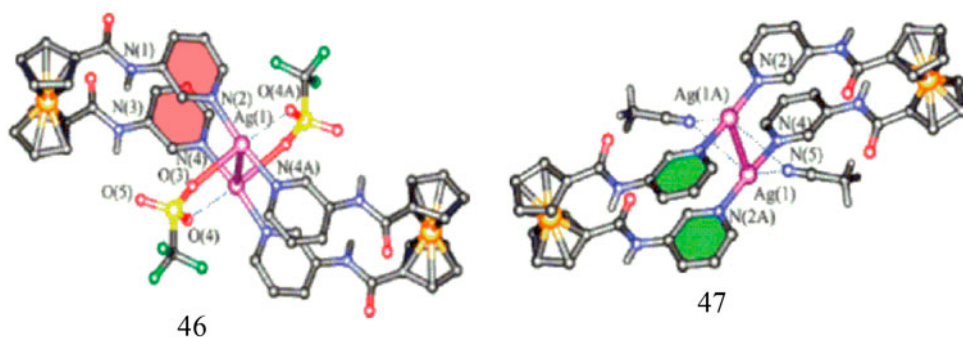

Figure 23. Molecular structure of the dimeric units of **46** and **47** showing the silver(I) coordination environment [92].

Complex **46** has each silver(I) center coordinated by two nitrogens from two different metalloligands, in an almost linear fashion where the N–Ag–N bond angle is 172.86°. As portrayed in figure 23, the two silver(I) centers bind to two $CF_3SO_3^-$ anions located on different sides of the dimer. Consequently, two silver(I) ions are wrapped up by four different support ligands to form a 'gear-wheel-like' structure [92]. The Ag⋯Ag distance in the pair which forms the axis of the dimer gear structure is 3.22 Å. The discrete units are in turn linked via weak cation–π (Ag–Cp) interactions to build 2D frameworks. In this case, the cyclopentadienyl ring coordinates to silver(I) in adjacent units via π–cation yielding a rare bimetallic sandwich-of-sandwich structure. On the other hand, the dimer structure in **47** has the two silver(I) centers coordinated by two **ML1** in head-to-head mode as portrayed in figure 23. The N–Ag–N bond angle is 173.95° (close to that of **46**) and the Ag⋯Ag distance is 3.19 Å, slightly shorter than that in **47**. Unlike the anion coordination in **46**, two guest acetonitrile molecules bond weakly to the silver(I) centers. The coordination dimers in **47** are arranged linearly and generate a ladder-like chain structure which is stabilized by Ag–O interactions. The Ag–O interaction between dimer units constructs a 1D chain, in which the Ag⋯Ag distance between two adjacent dimers is 5.54 Å. Weak hydrogen bonds link these 1D chains to form a 2D network.

Other ferrocene pyridinyl silver(I) complexes include the macrocyclic **48** [180] and **44** [181] (figure 24). In these complexes, the silver(I) centers bridge the ligands through coordination to the pyridine nitrogens in an almost linear fashion where the N–Ag–N bond angle is 178.1° for both silver(I) centers in **48** and 175.1 and 172.9° in **49**. The Ag⋯Ag interaction in **48** is insignificant [180] while in **49** it is 3.2469 Å [181]. The differences could be due to the different orientation of the pyridinyl-nitrogens in the two metalloligands. As observed in **46–49**, silver(I) bridges 1,1-pyridinyl ferrocene metalloligands via the pyridinyl-nitrogens when the substituents on the cyclopentadienyl rings are in *syn*-orientation, yielding discrete complexes. Also, the silver(I) ions tend to show linear coordination geometry as observed for **46–49**, albeit with or without coordination by solvent or anions.

Iron salts also form mixed-metal complexes with silver(I) as observed in the single-pot reaction of multidentate pyrazolate-bipyridine **L31** with Fe(B4)2 followed by AgBF4, giving a diferric-tetrasilver complex $[(L_{31})_4Fe(Ag_2)_2](BF_4)_6$ (**50**) in a rhomboid structure (figure 25). The complex has short Ag⋯Ag distances ranging from 2.93 to 2.88 Å, indicating strong metal–metal interactions. When the Ag⋯Ag interaction is neglected, the coordination environments of the silver(I) ions are four-coordinate via three pyrazolates arranged almost in same plane, and a pyridinyl-nitrogen that is out of the plane and forms a weak asymmetric bridge to the apical position of a neighboring silver(I) atom. The silver(I)
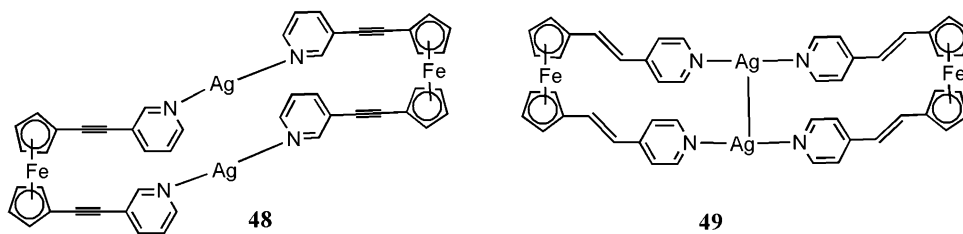

Figure 24. Molecular structures of the cations in mixed-metal complexes **48** [180] and cation of **49** revealing the silver(I) coordination environment [181].
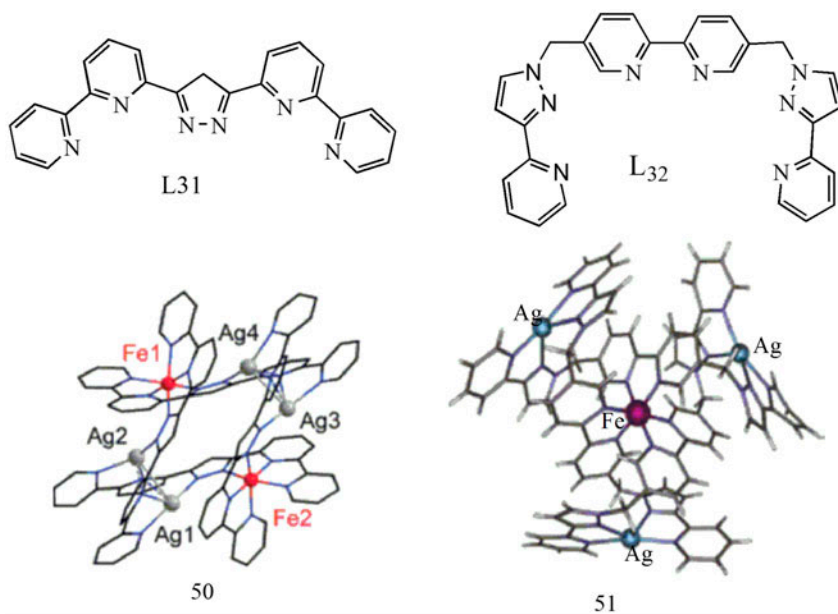
Figure 25. Molecular structures of cations in **50** and **51** showing silver(I) coordination [183].

atoms are stabilized by close contacts ranging from 3.12 to 2.99 Å with the π system of a proximate bipyridine unit that is bound to iron(II) [182]. Moreover, the heteronuclear silver (I) metallomacrocycle $[Ag_3Fe(\mathbf{L_{32}})_3H_2O](ClO_4)(PF_6)_4\cdot3EtOH$ (**51**) from multidentate N donor $\mathbf{L_{32}}$ has iron(II) coordinated in an octahedral geometry to the bipyridine units, while the pyridylpyrazole units coordinate the silver(I) ions (figure 25). Within the crystal structure, the metallomacrocycles link through argentophilic interactions to form chiral 1D supermolecules [183].

Iron(III) metalloligands **ML2** and **ML3** have been applied in preparation of Fe–Ag(I) complexes [173, 179]. The metalloligands yield mixed-metal silver(I) complexes whose structural arrangements depend heavily on the counter-anion and solvents used in the reaction. However, the coordination number and geometry of silver(I) are the same in all the complexes and there is also close similarity in the Ag–N–Ag bond angles. The general molecular structure of complexes from these metalloligands is shown in figure 22. In [Ag(ML2)$_3$]BF$_4$·DMSO (**52**) (figure 26), the geometry around the silver(I) centers is tetrahedral courtesy of four pyridinyl-nitrogens from three ligands; one ligand coordinates via two pyridinyl-nitrogens and the other two ligands via one nitrogen each [173]. The N–Ag–N bond angles range between 100.81 and 134.39°. Solvent effect on structure of the complexes are evident since the analogous complex [Ag(ML2)$_3$]BF$_4$·4THF, synthesized by Carlucci *et al.* [179], has an undulated layer structure that is markedly different from that of **52** that bears a DMSO molecule in lieu of the THF.

Similarly, in [Ag(ML2)$_3$]PF$_6$·3.28DMSO (**53**), the silver(I) centers display distorted tetrahedral geometry from four pyridinyl-nitrogens [150]. The N–Ag–N bond angles lie between 95.1 and 135.5°. Coordination of the equatorial nitrogens to silver centers connects the metalloligands into chains that are further cross-linked into corrugated 2D layers by coordination of the axial nitrogens to silver(I) centers [173]. The differences in the structure
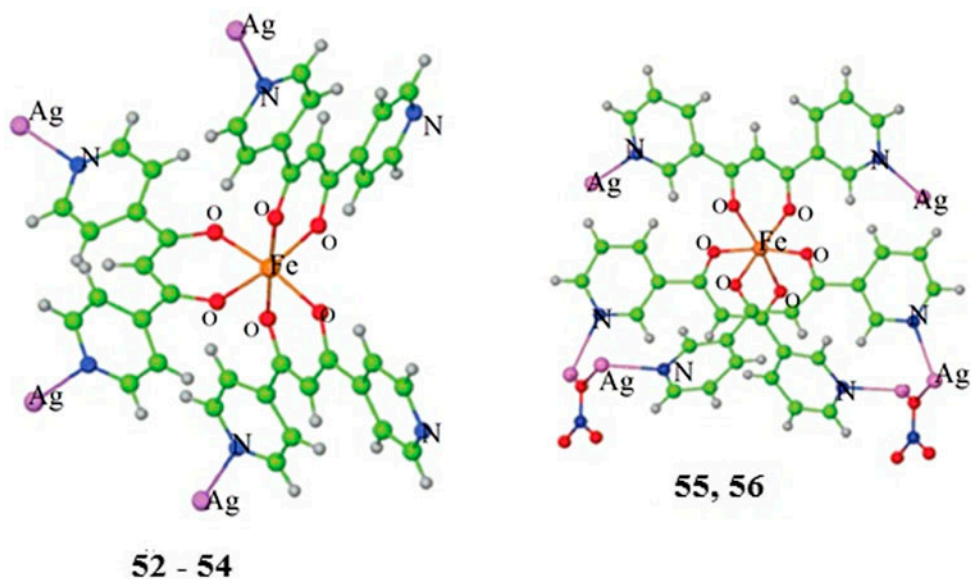
Figure 26.　General molecular structure showing the coordination of metal centers in cations of **52–56** [173].

of **52** and **53** arise from the anion effects. The complex [Ag(ML2)$_3$]SbF$_6$·1.25DMSO (**54**) is similar to **53** with the only differences being in the degree of corrugation, within the layers **53** being considerably more undulated than those in **54** [173]. In contrast, **ML3** position isomer with 3-pyridine donor sites yields [Ag$_2$(ML3)$_3$(ONO$_2$)]NO$_3$·MeCN·CH$_2$Cl$_2$ (**55**) and [Ag$_2$(ML3)$_3$(O$_2$CCF$_3$)]CF$_3$CO$_2$·2MeCN·0.25CH$_2$Cl (**56**) [173], in figure 26. In these complexes, all pyridinyl-nitrogens are coordinated to silver(I) centers and one oxygen from nitrate bridges two silver(I) centers leading to formation of chains. Therefore, silver(I) centers are in a distorted tetrahedral environment. The N–Ag–N bond angles in **55** lie between 83.8 and 120.1° while in **56**, N–Ag–N bond angles range between 84.30 and 134.44° [173].

Ligands with P as an addition donor to the pyridinyl-nitrogens have also been used as building blocks for syntheses of mixed-metal silver(I)–pyridine complexes. This involves initial synthesis of metalloligands using phosphinopyridyl ligands, where the primary metal is coordinated by P, while the N atom remains uncoordinated. Reaction of the ensuing metalloligands with silver(I) salts yields mixed-metal complex. The ligand 2,6-bis(diphenylphosphino)pyridine gives trinuclear mixed-metal complexes in which the silver(I) is bound to the phosphinopyridine ligand through N in linear fashion (N–Ag–N). For instance, when Pt(II) is reacted with 2,6-bis(diphenylphosphino)pyridine, it gives the platinum metalloligand **ML4**. Reaction of this metalloligand **ML4** with silver(I) gave [(CH$_3$)$_2$Pt(μ-ML4)$_2$Ag$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$CH$_3$CN (**57**) (figure 27) [90]. This complex has the silver(I) in a trigonal bipyramid geometry where Pt and Ag occupy axial positions and two pyridyl rings and the CH$_3$CN lie in the equatorial plane; the sum of the three N–Ag–N angles is almost 360° [90]. The Ag···Ag separation is 2.9061 Å, suggesting a significant argentophilic interaction between the silver(I) centers. The Pt-Ag distance of 2.819 Å is slightly shorter than the sum of the metallic radii of the two metals (2.83 Å), suggesting the existence of strong Pt(II)···Ag(I) dative bonding. The Pt–Ag–Ag chain has a bond angle of
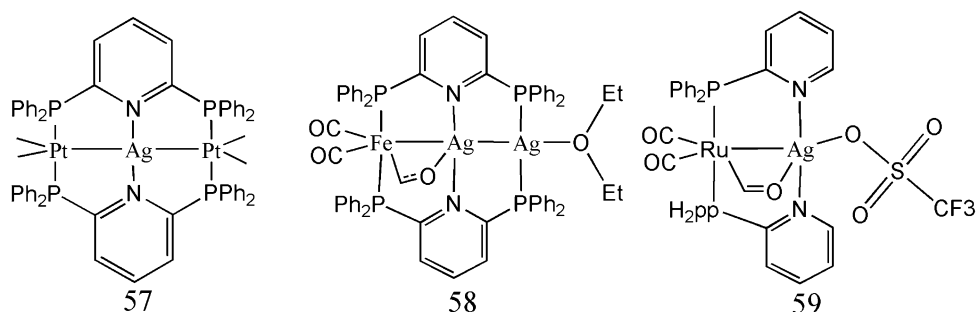
Figure 27. Molecular structures of cations in **57**, **58** [90], and **59** [49] showing the coordination around silver(I) centers.

169.63°. The Fe–Ag(I) analogous complex **58** (figure 27) has slightly bent silver(I) as the N–Ag–N angle deviates from linearity to 161.4°. The complex shows significant argentophilic interactions at 2.9267 Å and strong Fe–Ag dative bond at 2.7135 Å [90]. The ruthenium metalloligand **ML6** upon reaction with $AgCF_3SO_3$ yields Ru $(ML6)_2(CO)_3AgCF_3SO_3$ (**59**) (figure 27). The silver(I) center coordinates to two pyridinyl-nitrogens linearly. Silver(I) is also coordinated to an O of triflate and forms a bond with Ru (Ru–Ag is 2.7132 Å). Thus, essentially the silver(I) is four-coordinate and adopts a distorted tetrahedral geometry [49].

In the Ag–Au gold cluster $[Au_6Ag_2(Ph_2PPy)_6C](BF4)_4$ (**60**) [184] as well as in the complexes with a general formula $[Au_3(\mu_3$-E)Ag-(Ph_2PPy)_3](BF_4)_2$ (where Ph_2PPy = 2-(diphenylphosphino)pyridine and E = O (**61**); S, (**62**); Se (**63**), and $[Au_3(\mu_3$-S)Ag-(Ph_2PMePy)_3](BF_4)_2$ (Ph_2PMePy = 5-methyl2-(diphenylphosphino)pyridine) (**64**) (figure 28) [185], each silver(I) center is coordinated by three N atoms from different ligands in T-shaped geometry. These complexes exhibit metallophilic interactions, where the Au–Ag distances are 2.9134–3.0164 Å in **61** and **62** while in **63** and **64**, the distances are slightly longer, between 3.1150 and 3.4616 Å. Besides metallophilic interactions, all the metal ions are linked by bridging ligands as well.

The gold metalloligand $[Au(CH_3impy)_2]PF_6$ **ML7**, obtained from the precursor 1-methyl-3-(2-pyridinyl)-1H-imidazolium hexafluorophosphate, $[H(CH_3impy)]PF_6$, was employed in synthesis of Ag–Au bimetallic iso-structural tetrametallic complexes **65**, **66,** and **67** shown in figure 29 [74]. These complexes have four-coordinate silver(I) centers, neglecting metallophilic interactions, in a distorted tetrahedral environment through two pyridinyl-nitrogens of two ligands and two oxygens from different benzoates as shown in figure 29. The Au–Ag interactions average at 3.000 Å [74]. Dimetallic complex **68** of **ML8**, on the other hand, has two-coordinate silver(I) through pyridinyl-nitrogens of two ligands. The N–Ag–N bond angle in this complex deviates from linearity to 154.6° [162].

2.2.2. Polymeric heterometallic silver(I) complexes. Pyridinyl metalloligands that contain suitably oriented *exo*-donor groups capable of directing formation of desired polymeric architectures have been designed and synthesized. Subsequent reaction with silver(I) ions yields polymeric architectures of various topologies.
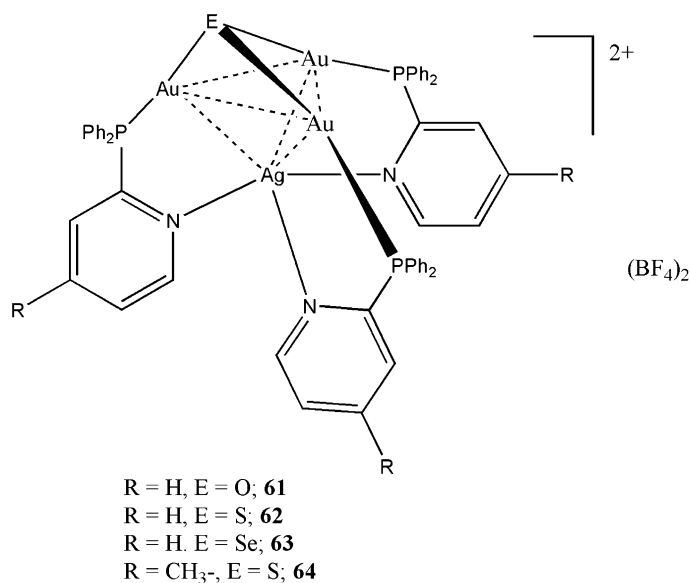
R = H, E = O; **61**
R = H, E = S; **62**
R = H. E = Se; **63**
R = CH₃-, E = S; **64**

Figure 28. Molecular structure of cations in **61–64** showing coordination of the metal centers [185].

2.2.2.1. Silver(I)–transition metal polymers. Carlucci *et al.* reacted metalloligand **ML2** with a series of silver(I) salts to form polymeric complexes [Fe(ML2)₃Ag]X (X = BF_4^- (**69**); ClO_4^- (**70**); PF_6^- (**71**); AsF_6^- (**72**); SbF_6^- **73**; $CF_3SO_3^-$ **74**; NO_3^- **75;** and tosylate **76**) [179]. The structures of the polymers from the metalloligand are greatly influenced by the counter-ions, especially due to their size, coordination ability, and shapes. The polymers with BF_4^-, ClO_4^-, PF_6^-, AsF_6^-, and SbF_6^- as counter-anions are 2D polymeric species where only four out of the six pyridinyl-nitrogens bind to silver(I) ions as shown in figure 30. The reaction of $Ag(CF_3SO_3)$ with **ML2** affords a quite different 2D polymeric framework, where only four pyridinyl nitrogens are involved in silver(I) coordination. Using $AgNO_3$ gives [Fe₂(ML2)₆Ag₃](NO₃)₃ (**74**) in a 3D framework, comprising double layers connected via Ag bridges on both sides to produce an interpenetrated network. Finally, reaction of metalloligand **ML2** with silver *p*-toluene sulfonate produces a complex having a 3D nano-porous network [Fe₃(ML2)₉Ag₅](tosylate)₅ (**75**) with six connected metalloligands, three silver(I) centers and four counter-ions [179].

Metalloligand [Ru(L₃₄)₂][PF₆]₂ reacts with excess AgClO₄ to yield the trinuclear helicate [RuAg₂(L₃₄)₂][ClO₄]₄ (**77**). The structure is a trinuclear double helicate containing six-coordinate Ru(II) in the central cavity and four Ag(I) ions at the two peripheral sites in irregular four-coordinate geometries as revealed in figure 31. The helical structures are characterized by extensive stacking between the two intertwined ligands, which form a five-layer stack on one side of the complex involving terminal pyridyl/pyrazoles of one ligand coordinated to silver(I), phenyl spacer groups of the second ligand and the central ruthenium(II)-bound pyridinyl-nitrogen of another ligand. The Ru···Ag separation in the asymmetric unit is 8.65 Å [186].

2.2.2.2. Silver(I)–lanthanide mixed-metal polymers. The synthesis of silver(I)–lanthanide (a 4d–4f combination) heterometal coordination polymers is, however, hampered by myriad
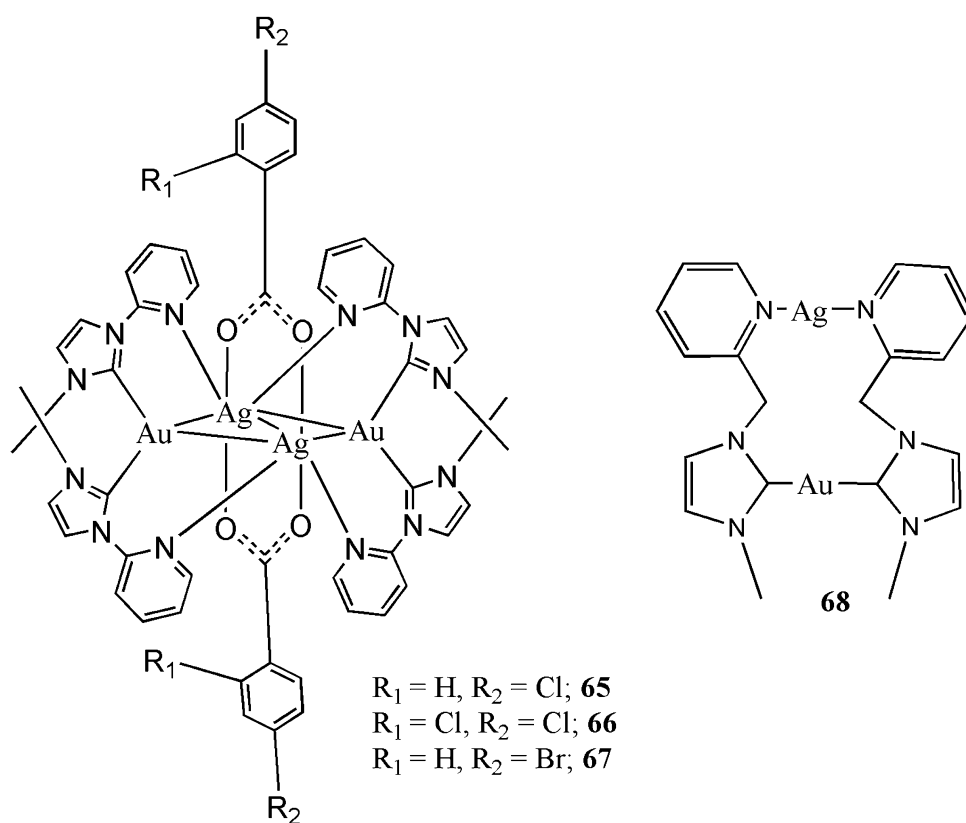
Figure 29.   Molecular structures in cations of **65–67** [74] and **68** [162] showing the coordination environment of silver(I).

challenges and consequently, few of them have been synthesized compared to their 3d–4d counterparts. These challenges include: (i) snags in design and synthesis of appropriate ligands with favorable structure for formation of silver(I)–lanthanides heterocomplexes, (ii) competitive reaction between lanthanides and transition metal ions that favors formation of homometallic networks, (iii) the adaptability of coordination spheres and the variable coordination numbers in 4d and 4f ions that lead to lack of stereochemical preferences, (iv) the flexibility of lanthanide cations (that makes targeted oriented design an uphill task), high coordination number of the lanthanides due to their large ions, (v) low coordination number of silver(I) (when compared with the lanthanides), (vi) ligands having low chelating positions, and (vii) a prolonged span where there was lack of design strategies for 4d–4f heterometallic coordination polymers [8, 187–189]. Nevertheless, silver(I) and lanthanides have dissimilar Lewis acidities and affinities for O and N donors, providing a unique opportunity that has been functional in synthesis of the of the silver(I)–Ln heteronuclear coordination polymers [190, 191]. Accordingly, the majority of pyridinyl–silver(I)–Ln heteronuclear coordination polymers have been obtained through O and N mixed-donor ligands such as pyridine carboxylic acids [192–195]. In these ligands, silver(I) ion is coordinated by the soft nitrogen-donor (exhibiting coordination numbers varying from 2 to 4),
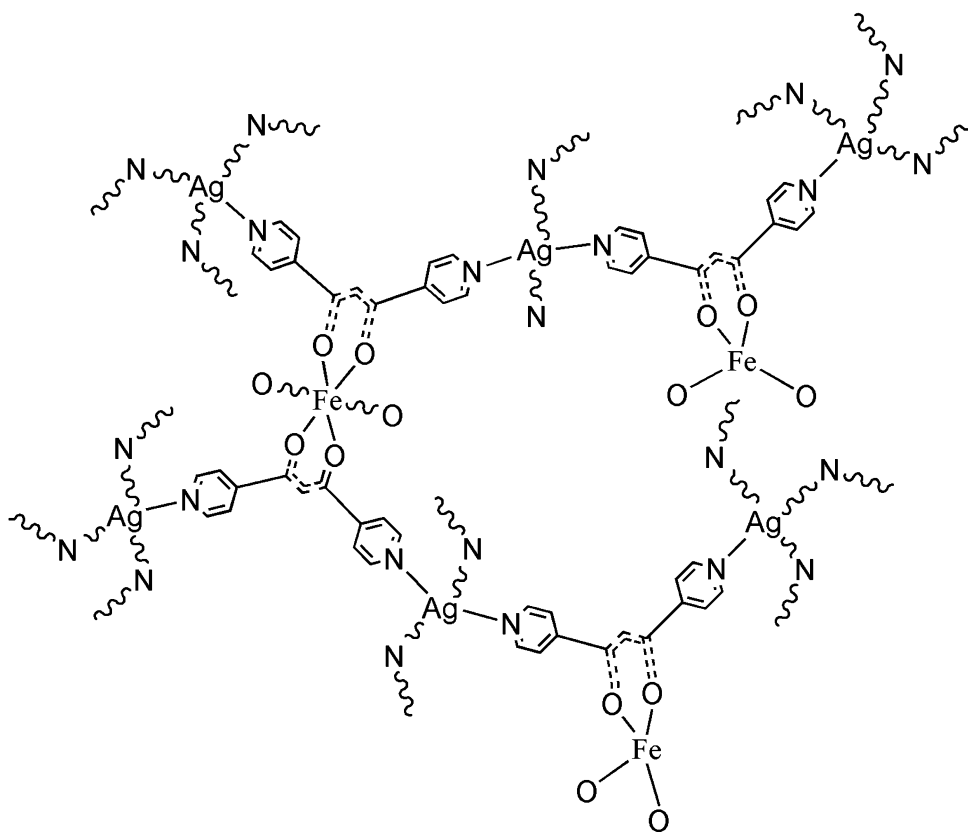
Figure 30. General molecular structure showing the four-coordination around silver(I) ions in the polymeric frameworks **69–76** [179].

while the lanthanide ions have high oxo-affinity and thus coordinated to O [196]. In this arrangement, the silver(I) bridges two ligands via the pyridinyl-nitrogen while the secondary metal (lanthanide) coordinates to oxygen in a chelation or bis-monodentate fashion, hence generating a drawn-out complex (figure 32). Nicotinic acids have thus been extensively employed in the synthesis of these compounds where the carboxylate O bind lanthanides and pyridinyl-nitrogen to silver(I) giving 1-, 2-, and 3D architectures as well as microporous coordination polymers [197–199].

The iso-structural homochiral silver(I)–lanthanide coordination polymers $[Nd_4(H_2O)_2Ag(1,3-bdc)_4(inic)_5]\cdot0.25H_2O$ (**78**) and $[Eu_4(H_2O)_2Ag(1,3-bdc)_4(inic)_5]$ (**79**), obtained from Hinic = isonicotic acid and bdc = 1,3-benzenedicarboxylic acid, have the silver(I) ions with distorted tetrahedral geometry. This is by virtue of coordination by four nitrogens from four crystallographically unique isonicotinic ligands as shown in figure 33. The N–Ag–N bond angles are 96.94–119.98°. The Ag–N distances range from 2.304 to 2.354 Å. These polymers have potential applications in enantioselective separations [198].

Microwave assisted reaction affords the iso-structural 3D bimetallic coordination polymers $[AgLnL_2(H_2O)_3](NO_3)_2(H_2O)_4$ (Ln = Eu (**80**), Tb (**81**), Nd (**82**); L = 3-pyridine-propionate). The general coordination mode of the metal centers is depicted in figure 34. In the
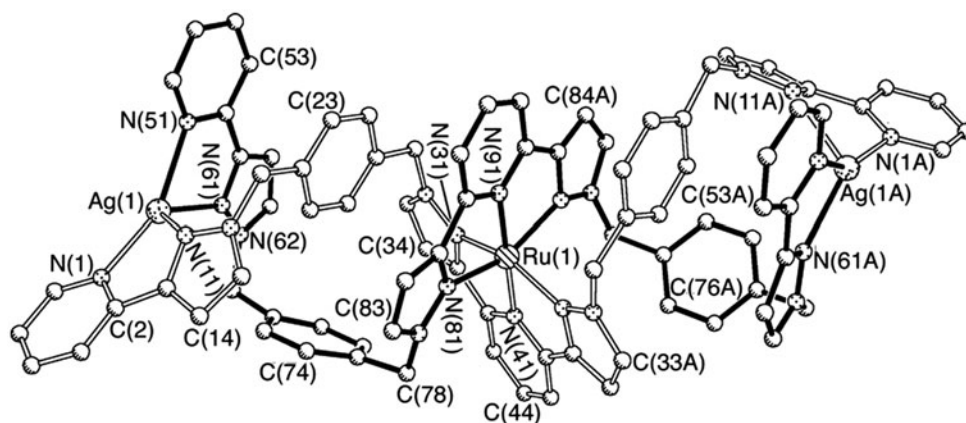
Figure 31.   Molecular structure of the complex cation of **77** showing coordination environment of silver(I) [186].
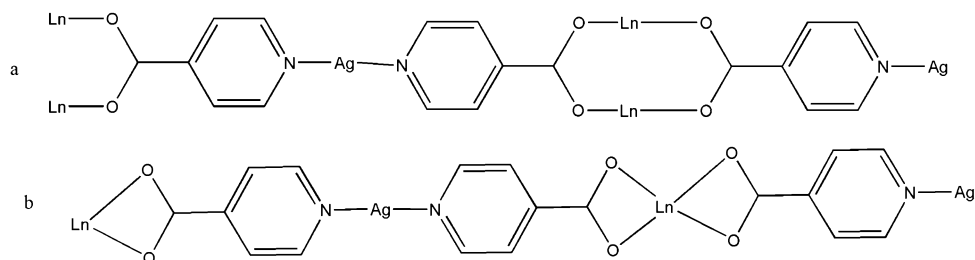

Figure 32.   Illustration of possible coordination modes of isonicotinate ligands with silver(I) and lanthanides leading to polymeric coordination polymers.

polymers, silver(I) ions are two-coordinate via the pyridinyl-nitrogens. However, weak Ag⋯Ag interaction (Ag–Ag bond 3.3699 Å) imposes a T-shaped environment on the silver (I) atoms. The N–Ag–N bond angle averages at 170° [172].

In the coordination polymers [LnAg₂(IN)₄(OAC)·5H₂O]·2H₂O (Ln = Gd (**83**) or Eu (**84**); HIN = isonicotinic acid; HOAC = acetic acid) the silver(I) centers show similar coordination modes where the N–Ag–N deviates from linearity averaging at 169°, as shown in figure 35. The inter-chain Ag⋯Ag distance in these complexes averages at 3.3181 Å [200].

The silver(I)–europium coordination polymer [EuAg(OX)(IN)₂]ₙ·H₂O (**85**) (where OX is oxalic acid and IN is isonicotinic acid) each has silver(I) ions in a T-shaped geometry, defined by two N from two IN ligands and O from one oxalate ligand [201]. In the polymeric structure of this complex, the carboxylate groups of the isonicotinic ligands and the oxalate ligands are connected to Eu(III) ions to form a Eu-carboxylate layered network. These layers are further connected via the pyridinyl nitrogen and oxygen from oxalate ligands coordinating silver(I) ions to form a 3-D network. A Ag(I)–Eu(III) coordination polymer from isonicotinate and oxalate shows a similar coordination environment for the metal centers, bond distances and angles. The silver(I) bridges two ligands via the N of isonicotinate which then coordinate the europium(III) via the carboxylate units [202].
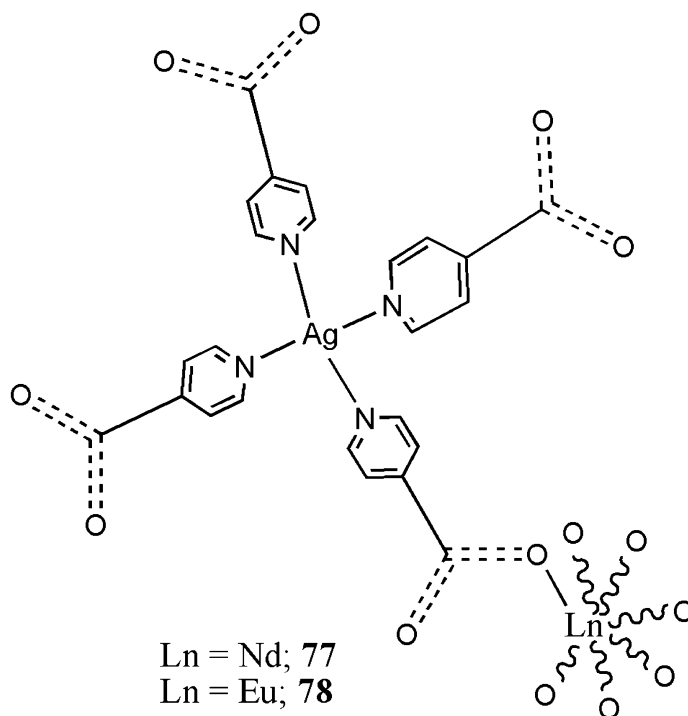
Figure 33.   Chemical structures showing coordination mode of silver(I) in the Nd and Eu coordination polymers.

Reaction involving Pr_6O_{11} or La_2O_3 with $AgNO_3$, perchloric acid and nicotinic acid affords the 1D coordination polymers $\{[Ag_2Pr(C_6H_4NO_2)_4(H_2O)_4]ClO_4 \cdot H_2O_n$ (**86**) [203] and $[Ag_2La(C_6H_4NO_2)_4(ClO_4)(H_2O)_5]_n$ (**87**) [204], respectively (figure 36). In these mixed-metal coordination polymers, the lanthanides (praseodymium(III) and lanthanum(III)) are coordinated by eight oxygens, four from four nicotinate ligands and four waters, giving it distorted square-antiprismatic coordination geometry. On the other hand, silver(I) are two-coordinate in an almost linear fashion via two pyridinyl-nitrogens from two nicotine ligands, bolstered by Ag···O interactions. Silver(I) ions also exhibit long range argentophilic interaction, at 3.357 Å in the Pr(III) complex and 3.3340 Å in the La(III) complex. In the two complexes, two lanthanide ions link two $Ag(nicotine)_2^+$ units into a ring, which are further extended into infinite zigzag chains by sharing a common Pr(III) and La(III). These chains are further connected into a 3-D network via weak Ag···O interactions, O-H···O hydrogen bonds, weak Ag···Ag interactions and π–π interactions occurring between the pyridyl rings of neighboring nicotine ligands.

The polymer $[AgGd(PDC)_2]_2H_2O$ (**88**) (H_2PDC = pyridine-3,5-dicarboxylic acid), shown in figure 37 has two independent silver(I) ions that bridge two ligands via the N atoms in a linear fashion. The Ag–N bonds are 2.228 and 2.202 Å. Each of the silver ions is also coordinated by two water molecules [205].

2.2.3. Luminescence in heterometallic silver(I) complexes. Silver(I)–transition metal heterometallic complexes, such as those involving Au, Cu, and Co, possess attractive

Ln = Eu; **79**
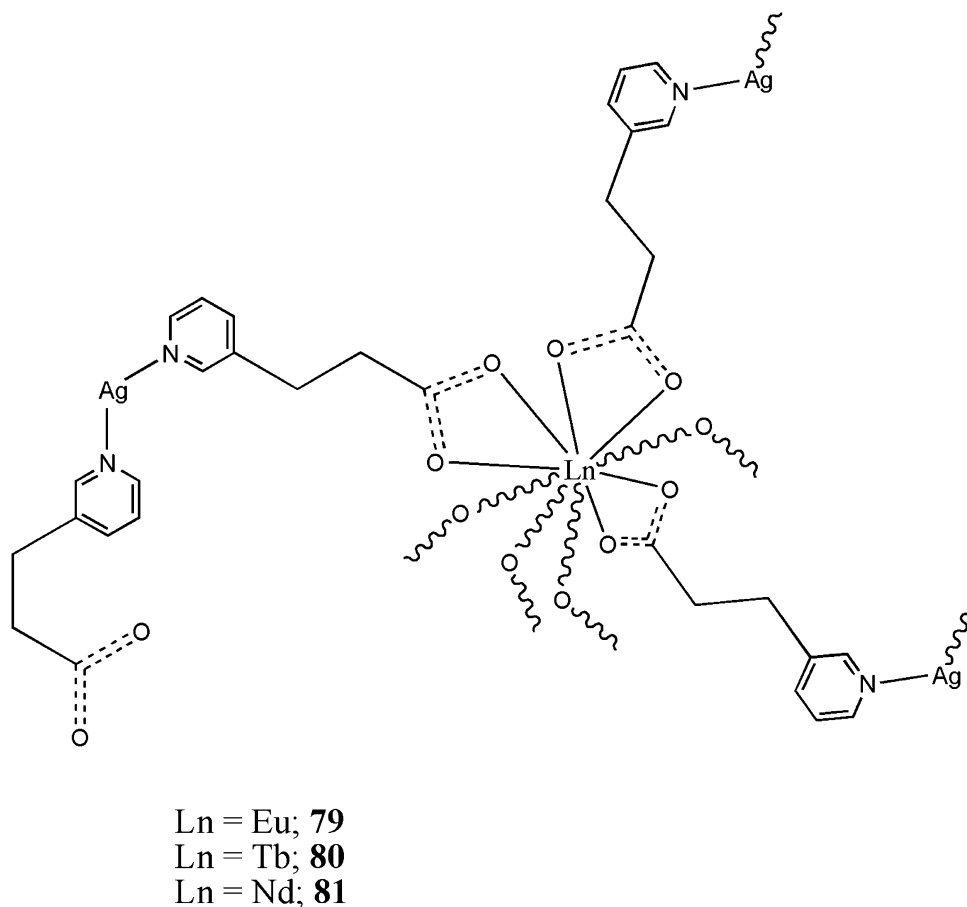Ln = Tb; **80**
Ln = Nd; **81**

Figure 34. Chemical structures showing local coordination of silver(I) in coordination polymers **80–82** [172].

photochemical properties. Complexes that have short Au–Ag metallophilic interactions are brightly luminescent in the solid state, at room and low temperatures or in frozen solutions with lifetimes in the microsecond range [206, 207]. The Au–Ag bimetallics have efficient luminescence whose color is rapidly switched by short exposure to solvent vapors, induced sheer stress or partial amorphization via grinding of the complexes [208]. The Ag–Au complex **60** has a strong green emission in the solid state and an extremely bright luminescence in solution at room temperature. This is attributed to the heightened rigidity induced by silver(I) coordination which effectively precludes the diphenylphosphinopyridine ligands from moving [184]. Luminescence in Ag–Au complexes is mostly pegged on the donors to which the metals are coordinated. Complexes **61–63** for instance show an intense solid-state luminescence at room temperature and 77 K with emission maxima lying between 460 and 700 nm [185].

Due to strong luminescence in the visible region of Ag(I) coordination complexes, silver (I) has been used to sensitize the NIR luminescence from lanthanides such as the Er(III) complexes [209, 210]. Studies have shown that Ag–Ln heterometallic complexes have
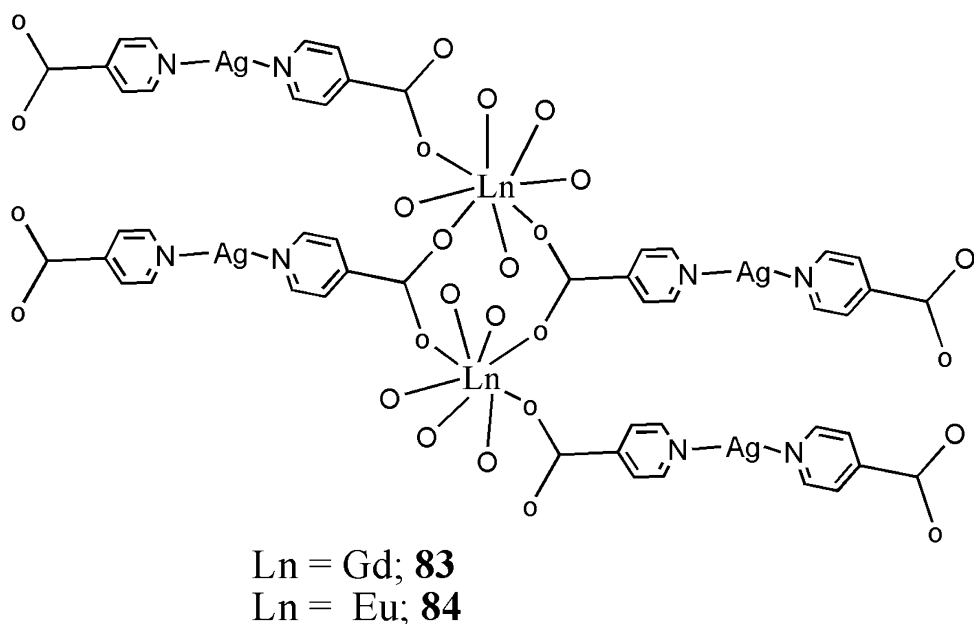
Ln = Gd; **83**
Ln = Eu; **84**

Figure 35. Molecular structure of the repeating unit in coordination polymers **83** and **84** showing silver(I) coordination [200].

improved luminescent properties over the ligands and their homometallic analogs. For instance, the coordination polymers **81** [200] and **87** [205] show blue fluorescence with maximum emission occurring at wavelengths 423 and 428 nm, respectively. The free ligand molecules on the other hand display a very weak emission at 431 nm in the UV region, corresponding to the excited light at 320 nm. The enhanced fluorescence efficiency of the complexes is attributed to coordination of the ligand to the Ag(I) and Gd(III), that effectively intensifies the rigidity of the ligand and the subsequent reduction in energy loss via radiationless thermal vibrations. The blue shift of the emission from UV light to the blue region is due to energy differences in Ag and Gd ions arising from their different coordination environments [205].

The Ag(I)–Eu(III) coordination polymers show luminescence at wavelengths above 600 nm. The Ag(I)–Eu(III) coordination polymer **83** shows intense photoluminescence at room temperature with maximum emission occurring at 615 nm upon excitation at 395 nm at room temperature [201]. The coordination polymer **84** also shows a similar trend where it has solid-state emission at room temperature with intense emissions at 614 and 618 nm upon excitation at 396 nm [202].

Strong luminescence especially in the visible region, from mixed-metal complexes discussed here, unearths their potential to be exploited in applications such as lighting and display devices such as fluorescent light and OLEDs. These complexes could also be applied in sensors in which the luminescence intensity and/or lifetime are sensitive to specific substrates, biological imaging and assays based on resonance energy transfer between a chromophore and the metal ions.
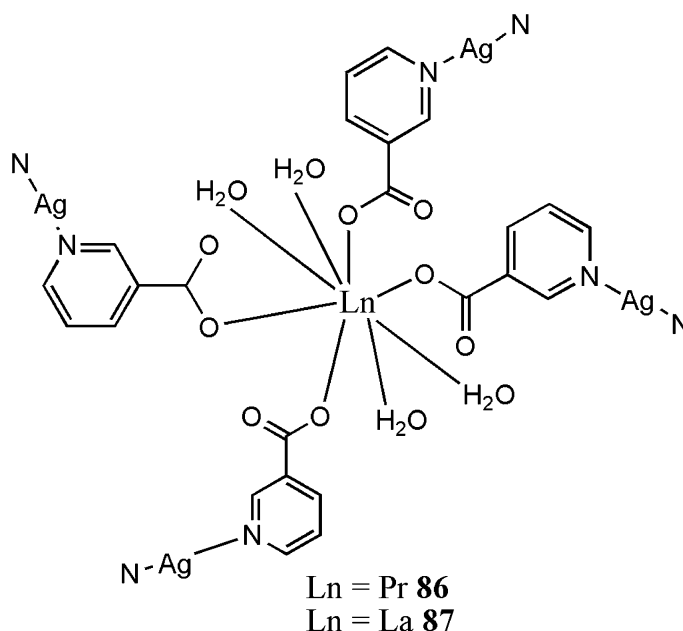
Ln = Pr **86**
Ln = La **87**

Figure 36. Molecular structures of the repeating units in **86** [203] and **87** [204] revealing coordination environments of the metal ions.

2.3. *Other applications of silver(I)–pyridinyl complexes*

2.3.1. Biological activity. Silver(I) complexes have been used as antiseptics [211], antifungal, anti-inflammatory [212], and antitumor agents [213]. Silver(I)–N complexes have broad spectrum antimicrobial activity as compared to the Ag–S, Ag–P complexes or silver salts, attributed to the weak Ag–N bond [214, 215]. Besides the nature of Ag–N bonds, the activity of pyridinyl silver(I) complexes is also dependent on substitutions on the ligands [216]. Biologically benign and active molecules such as nicotinic acid and nicotinamides have been used as ligands in synthesizing silver(I) complexes with remarkable antimicrobial activity [217]. Quinolone sulfonyl complex with silver(I) ions yield biologically active polynuclear silver(I) complexes. For instance, silver(I) complexes of the asymmetric tridentate ligand 8-((pyridin-3-yl)methylthio)quinolone (TQMP3), namely $[Ag_2(TQMP3)_2(NO_3)_2]$, and $[Ag_2(TQMP3)_2(CF_3CO_2)_2]$ have shown considerable antibacterial, antifungal and pesticide activities [113]. The ligand 8-(2-pyridinylmethylthio)quinoline (Q1) forms silver(I) complexes $[Ag_2(Q1)_2(ClO_4)_2]$ and $[Ag_2(Q1)_2(NO_3)_2]$ that are active against bacteria, fungi, and pesticides [218]. Also, the mercaptonicotinate complex $[Ag(mna)]_6^{6-}[Na^+]_4[(HOCH_2)_3CNH_3^+]_2$ has high antibacterial and antifungal properties [219]. Heteroleptic silver(I) pyridinyl complexes have shown broad antimicrobial activities also [138].

2.3.2. Catalytic silver(I) complexes. Based on the ability of silver(I) to form silver(I) acetylide complexes with terminal alkynes, it has been applied in catalysis of alkyne
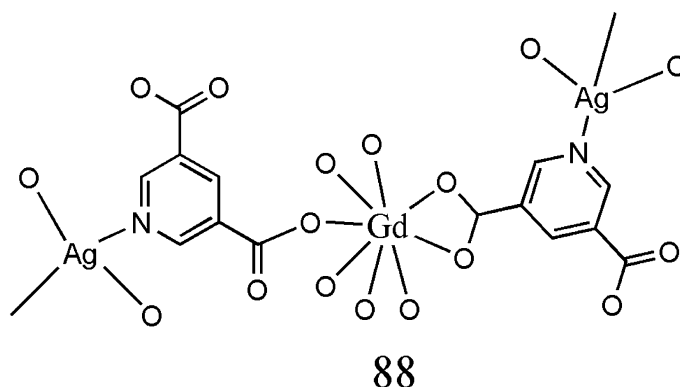
Figure 37.   Molecular structure of the repeating unit in coordination polymer **88** showing Ag(I) and Gd(III) coordination environments [205].

reactions to yield various functional groups [220]. However, only a few silver(I) pyridinyl complexes have been studied for catalytic activity, such as the dinuclear silver(I) compound $[Ag_2-(tBu_3tpy)_2(NO_3)](NO_3)$. The complex has two four-coordinate silver(I) centers through the pyridinyl-nitrogens and also shows strong Ag–Ag interactions. The complex was prepared through reaction of $AgNO_3$ and t-Bu_3tpy (4,4′,4″-tri-$tert$-butyl-2,2′ : 6′,2″-terpyridine). This dinuclear silver(I) complex shows non-radical aziridination of terminal alkenes [13], stereospecific intramolecular amidation, and intermolecular amination of sp^3 C–H bonds [14] as well as imination of sulfoxides [15]. Though silver(I) complexes of other ligands have been studied for their catalytic activity as reviewed by Naodovic and Yamamoto [221], investigation of pyridinyl silver(I) complexes in catalysis is lacking.

3. Conclusion

In this review, the rich variety of polynuclear silver(I)–pyridinyl complexes has been highlighted. The diverse coordination numbers and geometries of silver(I) and their dependency on combination of factors such as shape and size of the building blocks, anions, non-covalent interactions, as well as solvent effects have been recorded. Though silver(I) ions have been stated as having higher preference for linear twofold geometry, from the complexes reviewed, it is evident that silver(I) ions also give three-coordinate trigonal planar or T-shape or four-coordinate distorted tetrahedral geometries with ease. Other geometries recorded here are trigonal bipyramidal and octahedral. The ability of silver(I) to impart or enhance luminescence in organic molecules and other metal complexes has been recorded. The silver(I)–pyridinyl complexes reviewed here, especially the homometallic analogs, have also been investigated and shown to have appreciable biological activity. However, the catalytic potential of silver(I)–pyridinyl complexes is yet to be explored. Biological activity studies of mixed-metal silver(I)–pyridinyl complexes are also lagging.

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