COORDINATIVE FLEXIBILITY OF MONOVALENT SILVER IN [Ag\textsuperscript{I} ← L1]L2 COMPLEXES

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1.1 INTRODUCTION

Monovalent silver, Ag\textsuperscript{+}, is a fifth-period closed-shell d\textsuperscript{10}-ion. It is therefore often considered a pseudo-alkali-metal cation with an ionic radius close to that of Na\textsuperscript{+}, 114 versus 113 pm for coordination number (CN) 4 \cite{1}. Indeed, AgCl crystallizes with an NaCl type of structure, with $a = 554.9$ versus $a = 563.9$ pm \cite{2}. On the other hand, many physical properties are quite different. One striking example is that of AgCl and NaCl solubilities in water, $1.88 \times 10^{-3}$ g/L versus 358 g/L \cite{3}. The solubility of AgCl is enhanced dramatically through the addition of aqueous ammonia, and linear [Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}] cations are formed. Quite obviously, there is a much larger affinity of Ag\textsuperscript{+} toward the N-donor ligand ammonia than toward water or chloride as competing ligands.

There are many complex salts of the [Ag(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}] cation with common inorganic cations, NO\textsubscript{3}\textsuperscript{−} or ClO\textsubscript{4}\textsuperscript{−} (see, e.g., ref. 4). In [Ag(NH\textsubscript{3})\textsubscript{2}](ClO\textsubscript{4}), the [H\textsubscript{3}N–Ag–NH\textsubscript{3}]\textsuperscript{+} complex cation is linear by symmetry in both the high- and low-temperature modifications \cite{4d}. The Ag–N distances are 214 pm, on average, at 170 K. The cations are arranged such that the shortest Ag–Ag contacts are 302 pm, well above the Ag–Ag distance of 288.9 pm in metallic silver but below the sum of the
van der Waals radii of 344 pm. However, argentophilicity [5] (i.e., $d^{10}$–$d^{10}$ bonding interactions at a level of weak hydrogen bonds) may be associated with these short distances. Argentophilicity appears to be a slightly smaller effect than aurophilicity, judging by the $\text{Ag}^+\text{–Ag}^+$ and $\text{Au}^+\text{–Au}^+$ distances in the isostructural compounds $[\text{Ag(NH}_3]_2(\text{ClO}_4)_2$ [4d] and $[\text{Au(NH}_3]_2(\text{ClO}_4)_2$ [6] at the same temperature (170 K): 302.0(2) and 299.0(1) pm, respectively. Much shorter Ag–Ag distances may be seen in constrained systems, of which the dimeric structure of the simple silver acetate is perhaps the most spectacular example, with $d(\text{Ag–Ag}) = 279.4(4)$ to 280.9(3) pm [7].

$\text{Hg}^{2+}$ as a diagonally related $d^{10}$-ion forms analogous linear complexes, $[\text{Hg(NH}_3]_2]^{2+}$, with Hg–N distances of 207.2(16) pm in $[\text{Hg(NH}_3]_2][\text{HgCl}_3]_2$ [8], shorter than $d(\text{Ag–N}) = 212.9(11)$ to 216.0(12) pm in $[\text{Ag(NH}_3]_2(\text{ClO}_4)_2$ [4d] but larger than $d(\text{Au–N}) = 205.2(2)$ in $[\text{Au(NH}_3]_2(\text{ClO}_4)_2$ [6]. Mercuriphilic effects have not been observed, perhaps due to the higher charge. On the other hand, relativistic effects are, for $\text{Hg}^{II}$ as for $\text{Au}^{I}$, much more pronounced than for $\text{Ag}^{I}$. One evidence of these effects in mercuric chemistry is the pronounced preference for linear two-coordinate complexes [9], also termed as characteristic coordination number (CCN) 2 [10].

As relativistic effects are much less important in silver chemistry, $\text{Ag}^{I}$ exhibits a much larger coordinative flexibility, apparent in coordination numbers between 2 and 6 and in typical closed-shell ion coordination polyhedra (as closed as possible). Other than the hard (Pearson acid) alkali-metal ions, the $\text{Ag}^+$ ion is much more polarizable: thus is a much softer Pearson acid with a higher tendency to coordinate to softer Pearson bases, hence with higher covalent bonding contributions.

In this chapter we report on a number of recently discovered $\text{Ag}^{I}$ complexes with multi-N donor ligands [11] but do not consider this work a comprehensive review. The fact that silver coordination chemistry [12] is presently a rather hot topic may also be seen from a series of leading-edge research papers which have recently been published in the Australian Journal of Chemistry [13]. Silver complexes may have a number of functionalities; they may conduct electric current or luminesce, or they may have antimicrobial activity [14], to name only two.

As ammonia (NH$_3$) is the parent of all N-donor ligands, Ag–N distances as short as, say, 210 pm are considered the landmark for the strongest $\text{Ag}^{I} \leftrightarrow \text{N}$ interactions (“bonds”) possible in $[\text{Ag}^{I} \leftrightarrow \text{L}_1]\text{L}_2$ coordination compounds. L1 is usually a neutral N-donor ligand and L2 is an auxiliary ligand (co-ligand) with a negative charge competing with the L1 ligand for space in the coordination sphere of $\text{Ag}^{I}$.  

### 1.2 Ligands L1 with 1,2 N-donor Functions

1,2-Pyrazole has two directly neighboring nitrogen functions. As competing L2 ligands, triangular (NO$_3^−$), tetrahedral (BF$_4^−$, ClO$_4^−$, SO$_4^{2−}$), and octahedral anions (PF$_6^−$) as well as trifluoroacetate (CF$_3$COO$^−$ = Tfa$^−$) were attempted. In all of these, pyrazole coordinates as a neutral ligand with N2, which bears no hydrogen atom.
In Ag(Pyz)$_2$(BF$_4$)$_2$ (1), [Ag(Pyz)$_3$](Tfa) (5), and [Ag(Pyz)$_4$]$_2$(SO$_4$)$_2$ (6), we observe truly linear N–Ag–N environments (Fig. 1.1), whereas in [Ag(Pyz)$_2$]$_2$(PF$_6$)$_2$(Pyz) (4) the N–Ag–N angle is bent by a few degrees (see Table 1.1). Cations and anions seem to be independent of each other in 1, 2, and 4, which all have 1:2:1 (Ag:L1:L2) stoichiometries. In the nitrate (3), with its unusual 1:1:1
<table>
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<tr>
<th>Compound</th>
<th>CN</th>
<th>Coordination Geometry</th>
<th>d(Ag–N)/pm, d(Ag–O)/pm</th>
<th>&lt;(N–Ag–N)/°</th>
<th>CCDC No.</th>
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<tr>
<td><a href="BF(_4)">Ag(Pyz)(_2)</a> (1)</td>
<td>2</td>
<td>Linear, isolated</td>
<td>212.0(3), 213.1(3)</td>
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<td>214.4(7), 216.4(7)</td>
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<td>Ag(Pyz)(NO(_3)) (3)</td>
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<td>212.6(3), 240.3(4)</td>
<td>180</td>
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<td><a href="PF(_6)">Ag(Pyz)(_2)</a>(Pyz) (4)</td>
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<td>Linear, isolated</td>
<td>211.7(5)–212.8(5)</td>
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<td><a href="Tfa">Ag(Pyz)(_3)</a> (5)</td>
<td>3</td>
<td>Trigonal, isolated</td>
<td>220.1(3)–227.5(3)</td>
<td>107.4(1)–142.7(1)</td>
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<td><a href="SO(_4)">Ag(Pyz)(_4)</a> (6)</td>
<td>4</td>
<td>Tetrahedral, isolated</td>
<td>223.9(1)–239.9(1)</td>
<td>96.5(3)–125.5(3)</td>
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<td>Ag(Dcp)(OAc) (7)</td>
<td>2</td>
<td>Linear + tetrahedral, double chain</td>
<td>218.4(3), 249.2(4), 218.2(4), 244.1(4)</td>
<td>172.2(2), 93.8(2)</td>
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<td>227.6(3)</td>
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<tr>
<td>Ag(Dcp)(Tfa) (8)</td>
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<td>Linear + tetrahedral, double chain</td>
<td>218.2(4), 244.1(4), 228.9(4)</td>
<td>172.2(2), 93.8(2)</td>
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<td>Ag(Dcp)(_2)](BF(_4)) (9)</td>
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<td>83.3(1)–137.6(1)</td>
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<td>Ag(Mel)(_2)](Tfa)(H(_2)O) (13)</td>
<td>4 + 1</td>
<td>Pyramidal, chain</td>
<td>229.7(6), 232.8(6), 229.7(6), 232.8(6), 245.4(6)</td>
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<td>Ag(Mel)(NO(_3)) (14)</td>
<td>2 + 2</td>
<td>Bent, chain</td>
<td>225.3(5), 229.0(4), 225.3(5), 229.0(4), 257.6(6)</td>
<td>126.6(2)</td>
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<td><a href="NO(_3)">Ag(Dpt)(_2)</a>(_2) (15)</td>
<td>2 + 2</td>
<td>Bent, dimer</td>
<td>220.6(4), 221.9(6), 220.6(4), 221.9(6), 282.6(4)</td>
<td>145.4(2)</td>
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<td>Dihedral Angles</td>
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<tr>
<td>[Ag(Dpt)$_2$(OAc)]$_2$ (16)</td>
<td>Tetrahedral, dimer</td>
<td>230.1(4), 235.3(5), 237.4(3)</td>
<td>122.8(2)</td>
<td>662489</td>
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<tr>
<td>Ag(Dpt)(H$_2$O)(ClO$_4$) (17)</td>
<td>Bent, chain</td>
<td>228.2(5), 240.2(5), 240.1(7)</td>
<td>111.2(2)</td>
<td>662490</td>
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<td>Ag(Bpy)$_2$(ClO$_4$) (18)</td>
<td>Square, monomer</td>
<td>227.6(3)–243.0(3)</td>
<td>71.4(1)–159.2(1)</td>
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<td>Ag(Bpy)(Tfa) (19)</td>
<td>Trigonal, weak dimer</td>
<td>229.7(4), 232.2(4), 218.2(3)</td>
<td>72.0(1)</td>
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<td>Ag(Bpq)$_2$(Tfa) (20)</td>
<td>Trigonal prism, monomer</td>
<td>240.5(12)–248.7(13), 233.9(10)–267.8(13)</td>
<td>68.2(4)–153.0(4)</td>
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<td>Ag$_2$(Bpq)(NO$_3$)$_2$ (21)</td>
<td>Chain</td>
<td>227.9(3), 238.2(2)–252.2(2)</td>
<td>70.3(1)</td>
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<td>Ag(Tpt)(NO$_3$) (22)</td>
<td>Winding chain</td>
<td>242.7(4)–261.3(4), 236.1(4)</td>
<td>63.9(1)–136.0(2)</td>
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<td>Ag$_4$(Tpt)$_2$(Tfa)$_4$(H$_2$O) (23)</td>
<td>Tetramers, stairs</td>
<td>238.6(7)–253.1(9), 225.6(7), 276.0(2)</td>
<td>65.9(3)–133.8(2)</td>
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<tr>
<td><a href="BF$_4$">Ag(Pip)</a> (24)</td>
<td>Linear, isolated</td>
<td>216.6(7), 217.4(9)</td>
<td>174.1(2)</td>
<td>662497</td>
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<td><a href="Tfa">Ag$_2$(Pip)$_3$</a>$_2$(H$_2$O)$_6$ (25)</td>
<td>Trigonal, layer</td>
<td>226.3(2), 229.1(2), 239.2(2)</td>
<td>104.6(1), 116.9(1), 137.6(1)</td>
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<td><a href="NO$_3$">Ag(Pip)$_2$</a> (26)</td>
<td>Tetrahedral, waved layer</td>
<td>238.6(4), 239.4(4), 245.2(4), 245.6(5)</td>
<td>89.9(2)–116.6(2)</td>
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stoichiometry, however, there are two symmetrically and functionally independent Ag$^+$ ions. One is, as above in 1, 2, and 4, incorporated in the linear [Ag(Pyz)$_2$]$^+$ cation. The second Ag$^+$ ion has four contacts to C3 and C4 of pyrazole with $d$(Ag–C) = 249.4(4) and 281.8(5) pm and to two oxygen atoms of two nitrate ions at $d$(Ag–O) = 240.3(4) pm, such that a chain of the stoichiometry Ag(Pyz)$_2$Ag(NO$_3$)$_2$ is created (see Fig. 1.2). [Ag(Pyz)$_3$](Tfa) (5) and [Ag(Pyz)$_4$]$_2$(SO$_4$)$_2$ (6) exhibit triangular and tetrahedral environments, respectively, as the 1 : 3 and 1 : 4 stoichiometries of

![Diagram of a chain of Ag(Pyz)$_2$Ag(NO$_3$)$_2$](image)

**FIGURE 1.2** (a) Part of a $\cdots$Ag(Pyz)$_2$Ag(NO$_3$)$_2$$\cdots$ chain as observed in the crystal structure of Ag(Pyz)(NO$_3$)$_2$ (3); (b) the surrounding of (SO$_4$)$_2^-$ by four [Ag(Pyz)$_4$]$^+$ cations stabilized by N–H•••O hydrogen bonding in the crystal structure of [Ag(Pyz)$_4$]$_2$(SO$_4$)$_2$ (6).
Ag : L1 suggest (see Fig. 1.1). Distances increase steadily with coordination numbers (see Table 1.1). Angles in the AgN₃ triangles and AgN₄ tetrahedra of 5 and 6 cover a rather wide range (Table 1.1); hence, these coordination polyhedra are rather distorted. The sulfate ion in 6 is surrounded by four [Ag(Pyz)₄]⁺ cations and appears to form hydrogen bonds to N–H hydrogen atoms with d(N–H···O) between 193 and 207 pm (see Fig. 1.2).

1.3 LIGANDS L1 WITH 1,3 N-DONOR FUNCTIONS

Although pyrazole has two possible nitrogen functions, –Nl and –N–H, the free pair of electrons of the –Nl function binds only to Ag⁺ with distances dependent on the coordination number.

Pyrimidine (1,3-diazine, Pym) has two –Nl functions in the 1,3 positions. Both functions are used to form coordination polymers in the pyrimidine derivative 2,4-diamino-6-chloropyrimidine (Dcp) when acetate (OAc⁻) or trifluoroacetate (Tfa⁻) are the competing L2 ligands [15]. As chelating anions, these are incorporated as bridging ligands in the essentially isostructural compounds Ag(Dcp)(OAc) (7) and Ag(Dcp)(Tfa) (8). There are two crystallographically and functionally independent Ag⁺ cations in the structures, both of which are coordinated by two –Nl functions of Dcp. These –Nl functions are different, as one (N3) is neighboring the C4–Cl function and the other one is opposite it (N1). Ag1 is almost linearly coordinated by two N3 atoms at d(Ag–N) = 218.4(4) pm and <(N–Ag–N) = 170.08(2)°. Ag2 has two N1 atoms as neighbors, although at a distance of 249.1(4) pm with two oxygen atoms of two acetate anions at 227.5(3) pm; N–Ag2–N and O–Ag2–O are 94.95(9)° and 154.34(1)°, respectively. Thus, dimers Ag2(Dcp)₄(OAc)₂ are formed with rather close Ag–Ag contacts of 321.33(8) pm. These dimers can, however, not be isolated [note that the stoichiometry is Ag(Dcp)(OAc)!]. Rather, they are bridged via N1 and N3 functions to zigzag chains (see Fig. 1.3).

In Ag(Dcp)(OAc) (7) the amino groups are not involved in the coordination sphere of Ag⁺. This is, however, the case in the isostructural compounds Ag(Dcp)₂(BF₄) (9) and Ag(Dcp)₂(ClO₄) (10). Each Ag⁺ has two nitrogen atoms of pyrimidine functions (N3) and two amino-nitrogen atoms (N2') as nearest neighbors at distances of, for 9, 233.3(3) and 250.7(3) pm, respectively. This leads to a chain with Ag–Ag distances of 485.8(1) pm (see Fig. 1.3).

Melamine (2,4,6-triamino-1,2,3-triazine; Mel) is a highly symmetrical ligand with three –Nl and three –NH₂ functions. There are a small but increasing number of transition metal–melamine complexes. A molecular, zwitterionic complex has been found with divalent mercury in [MelH⁺HgCl₃⁻](Mel) [16]. The Hg–N separation in this molecule is 233.6(6) pm, pretty close to that in the HgII–pyridine complex Hg(Pyr)₂Cl₂ [9,17].

With Ag⁺, two sorts of melamine complexes have been observed with a variety of competing ligands, with CN 2 and higher, respectively [18]. In Ag(Mel)₂(BF₄) (11) and in the isostructural Ag(Mel)₂(ClO₄) (11a) [19], melamine also acts as a monodentate μ₁ ligand with one of the three –Nl functions forming somewhat bent
cations with Ag–N distances of 215.4(3) pm and an N–Ag–N angle of 170.7(1)°. This angle might be due to a weak attraction to one fluorine atom of the (BF₄)⁻ anion, d(Ag–F) = 284.4(3) pm (Fig. 1.4). An analogous almost linear cation [Ag(Mel)₂]⁺ with even slightly smaller Ag–N distances [213.1(2), 213.6(2) pm] is seen in [Ag(Mel)₂](BF₄)(Mel)₂ (12). Two solvent molecules of melamine are very loosely attached to the [Ag(Mel)₂]⁺ cations with amino functions at distances of 287.3(3) and 302.0(3) pm (see Fig. 1.4).
With the somewhat stronger ligands trifluoroacetate and nitrate, chain structures are formed with melamine acting as a bridging $\mu_2$ ligand. The coordination environment around Ag$^+$ in Ag(Mel)$_2$(Tfa)(H$_2$O) (13) is a (distorted) square pyramid with four $-\text{N}1$ functions of four melamine molecules forming the base at Ag–N distances of 229.7(6) and 232.8(6) pm and an apical oxygen atom of one Tfa$^-$ anion at $d(\text{Ag}–\text{O}) = 245.4(6)$ pm. The Ag(Mel)$_4$(Tfa) units bridge via neighboring $-\text{N}1$ functions to chains with the Ag$\text{N}_4\text{O}$ pyramids directed alternately up and down.

**FIGURE 1.4** (a) [Ag(Mel)$_2$]$^+$ cations to which $X = (\text{BF}_4)^-/(\text{ClO}_4)^-$ are loosely attached in the crystal structure of [Ag(Mel)$_2$]X (11); (b) the [Ag(Mel)$_2$]$^+$ cation to which two melamine molecules are loosely attached in [Ag(Mel)$_2$](\text{BF}_4)(\text{Mel})$_2$ (12).
The nitrate ligand influences the coordination sphere around Ag\(^{+}\) much more than does trifluoroacetate. This is documented more clearly by the much more bent N–Ag–N part \([126.6(2)^\circ]/C14\) than by the Ag–N distances (see Table 1.1 and ref. 20). The 1:1:1 stoichiometry also affords a chain structure with neighboring –Ni functions of melamine ligand bridging (see Fig. 1.5).

A similar \(\mu_2\) bridging coordination mode was recently found in Cu\(_2\)(Mel)Br\(_2\). In Cu\(_3\)(Mel)Cl\(_3\) melamine even acts as a \(\mu_3\) bridging ligand using all three –Ni functions [21]. Hydrogen bonding between the amino-H atoms and the halogen atoms is made responsible for the formation of two- and three-dimensionally extended structures.

In the ligand 2,4-diamino-6-phenyl-1,3,5-triazine (Dpt), one amino ligand of melamine is substituted by a phenyl ring. With nitrate as L2 and the stoichiometry...
1:2:1, a dinuclear complex \([\text{Ag(Dpt)}_2(\text{NO}_3)]_2\) is formed in (15) with bent \([\text{Ag(Dpt)}_2]^+\) cations \(<(\text{N–Ag–N}) = 145.4(2)^\circ\) and still rather short Ag–N distances of 220.6(4) and 221.9(6) pm, respectively. The cations are bridged by two nitrate ions with rather long Ag–O distances of 282.2 (14) pm (Fig. 1.6).

**FIGURE 1.6** Dimers in the crystal structures of (a) \([\text{Ag(Dpt)}_2(\text{NO}_3)]_2\) (15) and (b) \([\text{Ag(Dpt)}_2(\text{OAc})]_2\) (16).
Acetate also functions as a bridging ligand in the crystal structure of Ag(Dpt)$_2$(OAc) (16), such that, again, dimeric units are formed. While nitrate acts as a monodentate ligand, acetate functions as a bidentate bridging ligand (Fig. 1.6). Acetate acts as a much stronger ligand, which is demonstrated by the much smaller N–Ag–N angle, shorter Ag–O distance, and longer Ag–N distance (see Table 1.1).

The crystal structure of Ag(Dpt)(H$_2$O)(ClO$_4$) (17) is special in that Ag$^+$ has a coordination number of $1 + 1 + 1$ with bridging Dpt ligands forming a chain and one water molecule coordinating with the central Ag$^+$ ion. One Ag–N distance is rather short [228.2(5) pm]; the other is equal to the Ag–OH$_2$ distance [240.1(7) pm]. The chains run down the $b$-axis and are arranged such that layers appear between which the ClO$_4^-$ ions and the coordinating water molecules are included (Fig. 1.7).

1.4 LIGANDS L1 WITH 1,4 N-DONOR FUNCTIONS

2,2'-Bipyridine (Bpy) is one of simplest ligands, with a cisoid N–C–C–N function; hence it usually acts as a bidentate ligand. In Ag(Bpy)$_2$(ClO$_4$) (18) [22], Ag$^+$ has an unusually squarelike environment with rather strong deviations of the N–Ag–N angles from 90° (see Table 1.1), subject mainly to the bite distance, d(N–N) = 271.4 (13) pm in the Bpy ligand and to the torsion angle between the two pyridyl rings of 12.6(5)°. The [Ag(Bpy)$_2$]$^+$ cations form a chain in the crystallographic [0 1 0] direction with Ag–Ag distances of 366.6(1) pm and an Ag–Ag–Ag angle of 152.4(1)°, where some π–π stacking interactions might be involved [23] (Fig. 1.8). The (ClO$_4$)$^-$ anions act as “noncoordinating” anions; they provide electroneutrality and are not really involved in coordination with Ag$^+$, the shortest Ag–O distance being 496.8(5) pm.

In Ag(Bpy)Tfa (19) [22], a very similar five-membered ring to that of Ag(Bpy)$_2$(ClO$_4$) is observed, with Ag–N distances of 229.7(4) and 232.2(4) pm and an N–Ag–N angle of 72.0(1)°. However, in contrast to 18, 19 forms a molecular, triangular complex Ag(Bpy)Tfa. These complexes are stacked to dimers with surprisingly short Ag–Ag distances of 303.73(9) pm (see Fig. 1.8). Hydrogen bonding between the fluorine atoms of the trifluoromethyl substituents and phenyl-H atoms appears to be further stabilizing, with d(F⋯H) = 294 and 299 pm.

Judging from these two Ag–Bpy complexes, with a very weakly coordinating (ClO$_4$)$^-$ ligand and a considerably stronger Tfa$^-$ ligand competing with 2,2'-bipyridine, Ag$^+$ appears to prefer rather small coordination numbers with rather strong Ag–N bonding interactions. Recently, we have also been investigating Mn$^{II}$ complexes with bipyridine and a variety of other N-donor ligands [24]. In all of these, Mn$^{II}$ prefers an octahedral coordination environment: for example, in the simple Mn(Bpy)$_2$cis-Br$_2$, with Mn–N distances around 230 pm. With a 1 : 1 : 2 stoichiometry in Mn(Bpy)Br$_2$, zigzag chains of edge-sharing MnN$_2$Br$_4$ octahedra are formed with d(Mn–N) = 226.3(3) pm. However, despite the different coordination numbers, the
FIGURE 1.7  (a) Cationic [Ag(Dpt)$_2$(H$_2$O)]$^+$ chains in the crystal structure of Ag(Dpt) (H$_2$O)(ClO$_4$) (17); (b) a projection of the structure onto (010).
FIGURE 1.8 (a) Cationic $[\text{Ag(Bpy)}_2]^+$ chains in the crystal structure of $\text{Ag(Bpy)}_2(\text{ClO}_4)$ (18); (b) connection between $\text{Ag(Bpy)}\text{Tfa}$ molecules and dimers in $\text{Ag(Bpy)}\text{Tfa}$ (19).
very similar Ag–N and Mn–N distances in the five-membered C–N–M–N–C rings (M = Ag, Mn) attest to the fact that it is mainly the ring geometry and the similar ionic radii (Ag$^+$ : 129, Mn$^{2+}$ : 97 pm for CN 6 [1]) that is responsible for the respective M–N distances.

Another ligand with two –Nl functions in the 1,4 positions as in 2,2′-bipyridine and with two further –Nl functions in the pyrazine rings is bis(pyrazino)[2,3-f]quinoxaline (Bpq). In Ag(Bpq)$_2$(Tfa) (20), two Bpq ligands and the two oxygen atoms of the Tfa$^-$ carboxylate group build up a distorted trigonal prism (Fig. 1.9a). These complex
FIGURE 1.10  (a) One complex Ag(Tpt)(NO$_3$) (22) “molecule”; (b) its connection through pyridyl-N atoms to a winding chain, with (c) rather effective space filling.
molecules are arranged such that, again, hydrogen bonds between the phenyl-H and the trifluormethyl-F atoms stabilize the three-dimensional structure.

With nitrate as the auxiliary ligand, Bpq acts as a bridging ligand in Ag₂(Bpq)(NO₃)₂ (21), in contrast to Ag(Bpq)₂(NO₃) [25], where molecules of this composition are formed. In 21, one type of Ag⁺ is coordinated by Bpq in the same manner as in 20, with two oxygen atoms of nitrate adding to the coordination sphere, while the second type of Ag⁺ is coordinated by an opposite pyrazine-N with a rather short Ag–N bond [227.9(3) pm]. Three oxygen atoms of nitrate ions add to a heavily distorted tetrahedral coordination. The Ag₂(Bpq)(NO₃)₂ chains (Fig. 1.9b) are connected further to layers via nitrate-O.

2,4,6-Tris-(2-pyridyl)-1,3,5-triazine (Tpt) is a flexible 6N ligand with three 1,4-bipyridyl functions and the ability to act as a tridentate ligand. This is observed in Ag(Tpt)(NO₃) (22), where nitrate coordinates bidentately, although with rather long Ag–O distances. More important, Ag⁺ is also coordinated by one neighboring complex with a pyridyl-N, with the shortest Ag–N distance in this compound, only 236.1(4) pm. Thus, through the bridging Tpt ligand, an unusual winding chain is created with rather efficient space filling (Fig. 1.10).

In Ag₄(Tpt)₂(Tfa)₄(H₂O) (23), tetrameric complexes are formed with two functionally distinct Ag⁺ atoms. The two inner silver atoms are three-coordinate by Tpt in the same manner as in 22 and are connected by two bridging Tfa⁻ anions (Fig. 1.11). The two outer silver atoms are included in a bipyridyl-like five-membered ring and are further coordinated by water and Tfa⁻ anions, which bridge to further tetramers such that a staircase-like coordination polymer is created (Fig. 1.11).

Again, Ag⁺ shows a high level of coordinational flexibility in these Tpt complexes, in fair contrast to Mn⁺. Here we always observe octahedral MnN₃L₃ environments with the Tpt ligand in meridional conformation [24]; for example, in Mn(Tpt)Cl₂(H₂O) or in the trimeric Mn₃(Tpt)₂(OAc)₆ (see Fig. 1.12).

Piperazine (Pip) is a nonaromatic 1,4 transoid N–C–C–N ligand, as the chair conformation of Pip is more stable. It therefore also tends to form coordination polymers with Ag⁺. With the weakly coordinating (BF₄⁻) ion, zigzag chains are built in [Ag(Pip)](BF₄) (24). Both opposite N–H functions of Pip coordinate to Ag⁺, which exhibits strong, almost linear N–Ag–N bonding with d(Ag–N) = 216.6(7) and 217.4 (9) pm and <(N–Ag–N) = 174.1(2)° (Fig. 1.13). Tetrahedral coordination is seen in [Ag(Pip)₂](BF₄) [26], with d(Ag–N) ranging from 231.6(8) to 243.9(6) pm and with the Pip molecules bridging to “undulated” layers.

Trigonal coordination is observed in [Ag₂(Pip)₃](Tfa)₂(H₂O)₆ (25), with Ag–N distances ranging from 226.3(2) to 239.2(2) pm and N–Ag–N angles between 104.62(9) and 137.58(9)°. As the composition Ag : Pip = 2 : 3 suggests, Pip acts as a μ₂ bridging ligand, and a layer structure with 6 + 6-membered rings is formed (Fig. 1.14). (Tfa⁻) and noncoordinating water molecules lie between these layers. The anhydrous compound Ag₂(Pip)₄(Tfa)₂ [27] is built from dimeric complexes of that composition, with the Tfa⁻ anions bridging with d(Ag–Ag) = 400.1(2) pm.
FIGURE 1.11  (a) The tetrameric complexes of \( \text{Ag}_4(Tpt)_2(Tfa)_{4}(\text{H}_2\text{O}) \) (23); (b) their arrangement as a staircase coordination oligomer.

FIGURE 1.12  Acetate-bridged trimers in the crystal structure of \( \text{Mn}_3(Tpt)_2(\text{OAc})_6 \).
In the crystal structure of $\text{[Ag(Pip)$_2$(NO$_3$)$_2$]}^+$, Ag$^+$ is tetrahedrally coordinated by piperazine molecules which produce heavily waved layers through $\mu_2$ bridging (see Fig. 1.15). Their stacking in the third direction, [001], produces channels that are occupied by nitrate anions. Ag–N distances of 238.6(4)/239.4(4) and 245.2(4)/245.6(5) pm attest to rather strong bonding within the AgN$_4$ tetrahedra such that the nitrate anions cannot act as ligands in $\text{[Ag(Pip)$_2$(NO$_3$)$_2$]}^+$, much the same as in $\text{[Ag(Pip)(BF$_4$)$_2$]}$ and $\text{[Ag$_2$(Pip)$_3$(Tfa)$_2$(H$_2$O)$_6$]}$.

1.5 CONCLUSIONS

In $\text{[Ag}^\dagger \leftarrow \text{L}_1] \text{L}_2$ complexes, L1 as a (neutral) (multi-)N-donor ligand competes with an auxiliary negatively charged ligand (co-ligand) L2 for space in the coordination sphere of Ag$^+$. As a closed-shell d$^{10}$-cation, Ag$^+$ exhibits a rather strong tendency for small coordination numbers and low-dimensional structures. This tendency is, however, not as pronounced as in Hg$^{II}$ chemistry, where relativistic effects have a much greater influence on coordinative bonding. Therefore, coordination geometries surrounding Ag$^+$ are more flexible and range from isolated complex cations via oligomers to chains and layers. Strong N-donor ligands such as pyrazole, melamine, or piperazine coordinate Ag$^+$ linearly in cationic complexes, or with trigonal or tetrahedral environments, depending on the strength of the competing ligand and upon stoichiometry. Multi-N donor ligands lead to chelating coordinations [e.g., with 2,2′-bipyridine (Bpy) or with 2,4,6-tris-(2-pyridyl)-1,3,5-triazine (Tpt)]. Ag$^+$–Ag$^+$
interactions ("argentophilicity") seem to play only a minor role, comparable to hydrogen bonding. Chelating ligands such as Bpy seem to be necessary for special coordinations, such as (almost) square planar in Ag(Bpy)$_2$(ClO$_4$), which bring the Ag$^+$ cations close together.

**FIGURE 1.14** (a) [Ag$_2$(Pip)$_3$]$^{2+}$ layers in the crystal structure of [Ag$_2$(Pip)$_3$](Tfa)$_2$(H$_2$O)$_6$ (25); (b) their stacking and separation by (Tfa)$^-$ anions and water molecules.
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FIGURE 1.15 (a) Projection of [Ag(Pip)$_2$]$^+$ layers in the crystal structure of [Ag(Pip)$_2$] (NO$_3$) (26); (b) the stacking of these waved layers with (NO$_3$)$^-$ anions in between.

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