

Review

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

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Abstract

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

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1. Introduction

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

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

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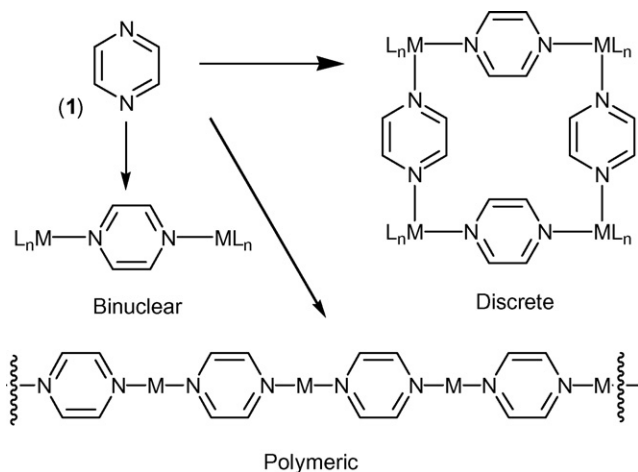


Fig. 1. Representative assemblies derived from pyrazine (1).

2. Discussion

2.1. Assemblies derived from pyrazine (1)

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

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

It is not surprising therefore that when a non-coordinating anion, such as tetrafluoroborate, is used, a more linear polymer results [35]. Thus the 1:1 complex of pyrazine with AgBF_4 has a relatively short Ag–N bond length (2.193 Å) and an N–Ag–N angle of 173.6° . The tetrafluoroborate anions are not bonded to the silver (shortest Ag–F distance > 2.7 Å). This complex is one of four described in a detailed study by Ciani and co-workers [35] where the metal:ligand ratio was varied. Two complexes with 1:2 ratios were isolated and their X-ray structures reported. These both contain planar silver atoms bound to three bridging pyrazine nitrogens with coordination geometry intermediate between trigonal and T-shaped and non-coordinated anions. The

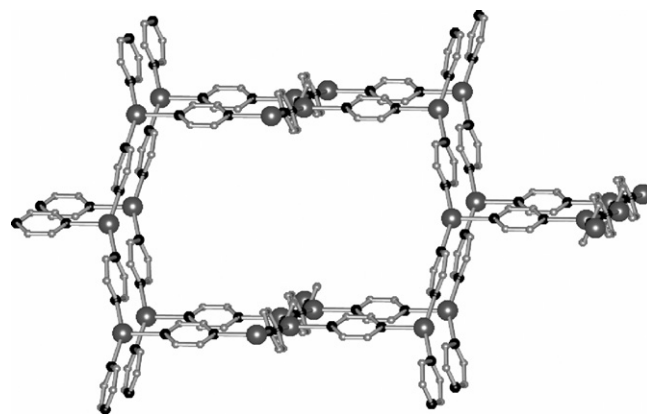


Fig. 2. A section of the (10,3)-b net reported by Ciani and co-workers [35].

first of these complexes is an undulating two-dimensional (2D) sheet with a (6,3) topology, in which the silver atoms represent the three-connecting nodes. The second is a much more complex assembly, consisting of individual 3D triconnected nets with (10,3)-b topology (Fig. 2), which triply interpenetrate. With higher metal:ligand ratios a 1:3 complex was obtained, which has silver atoms bound to two bridging and two monodentate pyrazines. The silver has distorted tetrahedral geometry with N–Ag–N angles spanning the range 92 – 127° . This arrangement results in a 1D zig-zag polymer.

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

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

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

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