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Short communication

Silver(I) complexes of 2,6-bis(4-pyridylsulfenyl)pyrazine: Interplay of anion coordination and argentophilic interactions

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ABSTRACT

Reaction of 2,6-bis(4-pyridylsulfenyl)pyrazine ($\mathbf{L_1}$) with Ag(I) salts gives a series of $[Ag_2(\mathbf{L_1})_2]^{2+}$ rectangles. Where the anion is NO_3^- or OTf^-, bridging of the two Ag(I) cations by the anion brings them close enough to support a Ag(I)···Ag(I) interaction. Where the anion is ClO_4^- or PF_6^-, bridging by the anion is not observed; in the case of the ClO_4^- complex, no Ag(I)···Ag(I) interaction results whereas in the PF_6^- complex, a coordinated acetonitrile acts as the bridge instead, supporting the Ag(I)···Ag(I) interaction.

As research into the structural characteristics of coordination polymers continues to mature, a feature continues to be the unpredictability of the structures of silver(I)-containing systems. While there are many attractive features associated with Ag(I)-pyridine based systems in particular, not least of which being the readiness with which they tend to crystallise, the coordinative flexibility associated with silver's d^{10} configuration, both in terms of its coordination geometry and number, means that finding reliable factors which can be used to drive rational structural design remains elusive. To this end, a number of studies have explored the influence of the anion, the solvent and weak interactions such as π-π stacking interactions and hydrogen bonding [1]. Another weak interaction which has also received increasing attention is the argentophilic interaction. Such closed shell d^{10} attractive interactions, which are well known for Au(I), have become increasingly well understood for Ag(I) and many examples of both supported (the interaction being reinforced by bridging ligands) and unsupported Ag(I)···Ag(I) interactions have now been reported [2]. A commonly used indicator of such an interaction is a Ag(I)···Ag(I) distance below 3.44 Å, the sum of the van der Waals radii. While in many cases the presence of an Ag(I)···Ag(I) interaction is serendipitous, there have now been a number of examples reported which suggest that the ability of the anion to bridge the two Ag(I) ions can play a role in directing its formation. In particular, Jung et al. have reported a series of $[Ag_2(\mathbf{L_1})_2]^{2+}$ rectangles where the presence of an Ag(I)···Ag(I) interaction appears to be directly related to the bite size of the anion [3]. NO_3^-, with the smallest bite size, gave a rectangle with a Ag(I)···Ag(I) distance of 3.20 Å, while ClO_4^-, with a larger bite angle, gave a rectangle with a Ag(I)···Ag(I) distance of 3.41 Å. PF_6^- and triflate (OTf^-), with larger bite angles again, had Ag(I)···Ag(I) distances beyond 3.44 Å. These observations are also in line with the reported strengths of the Ag-anion bond [4]. The observation that NO_3^- can bridge Ag(I) ions such that a Ag(I)···Ag(I) interaction results has been reliably used to assemble pyridyl acrylic acid and related molecules for subsequent photodimerisation reactions [5–8]. However, other cases have been reported where the NO_3^- anion does not bridge two Ag atoms and a Ag(I)···Ag(I) interaction is still observed [9]. Similarly examples have been reported where OTf^- and ClO_4^- sometimes reinforce a Ag(I)···Ag(I) interaction [10,11] and sometimes play no role [12–14]. And, in some cases, the nature of the ligand used means that π-π stacking interactions also appear to reinforce the Ag(I)···Ag(I) interaction [11,12,14]. Similar results have been reported for Ag(I) coordination polymers [15–20]. Thus, there still seems to be a lack of clarity into the role of the anion in such systems.

Previously, we have reported the preparation of 2,6-bis(3-pyridyloxy)pyrazine ($\mathbf{L_2}$) (Scheme 1) and explored its coordination chemistry with silver(I), copper(I) and copper(II) salts. Upon reaction with $AgNO_3$, the ligand utilised both the pyridine and one of the pyrazine nitrogen donors to generate a chiral [6:3] coordination polymer. By contrast, reaction with copper(I) or copper(II) both resulted in rectangular 2 + 2 metallocycles, in which NO_3^- (Cu(II)) or iodide (Cu(I)) anions bridged the metal cations; in neither case were the pyrazine nitrogen atoms utilised for coordination to the copper ion.

We now report the preparation of the related ligand 2,6-bis(4-pyridylsulfenyl)pyrazine ($\mathbf{L_1}$) (Scheme 1). $\mathbf{L_1}$ has a similar structure to $\mathbf{L_2}$ but possess a thioether linkage between the central pyrazine and

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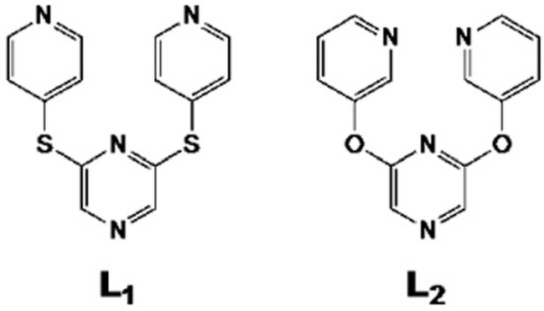


Scheme 1. The ligand $\mathbf{L_1}$ discussed in this work, and $\mathbf{L_2}$ [21].

the pendent 4-pyridyl group. We supposed that the larger sulfur linker might offer even more flexibility than the ether linkage [21]. However, in its reaction with Ag(I) salts, rectangular $[Ag_2(\mathbf{L_1})_2]^{2+}$ complexes were obtained in each case.

$\mathbf{L_1}$ was prepared in 71% yield by a double nucleophilic substitution reaction between 4-mercaptopyridine and 2,6-dichloropyrazine (Scheme 2) in hot DMF under an inert atmosphere and was isolated as a red-brown solid. Its composition was fully characterized by elemental analysis, infrared spectroscopy, high resolution electrospray mass spectrometry and ^{1}H NMR spectroscopy.

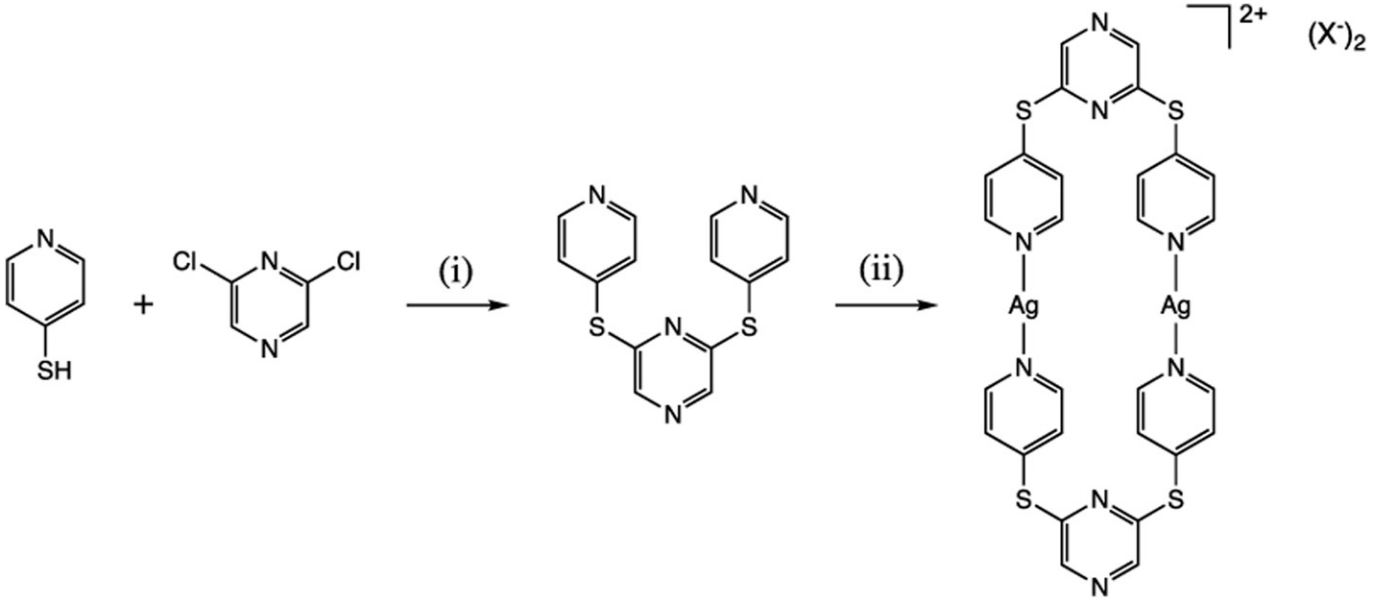
Reaction of $\mathbf{L_1}$ with Ag(I) salts in hot methanol yielded yellow solids in high yields. Microanalyses showed a 1:1 Ag:$\mathbf{L_1}$ ratios in all cases and IR spectra contained peaks characteristic of $\mathbf{L_1}$ and the different anions. The complexes are sparingly soluble in common solvents. They are sufficiently soluble in acetonitrile to enable ESI-MS spectra to be obtained and, in each case, a set of peaks corresponding to $[Ag(\mathbf{L_1})]^+$, $[Ag(\mathbf{L_1})_2]^+$ and $[Ag_2(\mathbf{L_1})_2X]^+$ were observed, but attempts to obtain ^{1}H NMR spectra in MeCN-d_3 were unsuccessful, with peaks corresponding to free $\mathbf{L_1}$ being the only ones observed. However, X-ray quality crystals of the complexes were able to be obtained by slow diffusion of diethyl ether into MeCN solutions of AgX and $\mathbf{L_1}$, yielding large yellow crystals.

Reaction of $AgNO_3$ and $\mathbf{L_1}$ gives complex **1**, which crystallises in the triclinic space group *P*-1 with the asymmetric unit containing one Ag(I) cation, one NO_3^- anion, one $\mathbf{L_1}$ ligand and one acetonitrile solvent molecule. The Ag(I) ion is linearly coordinated by the N_{py} donors of two $\mathbf{L_1}$ ligands as well as by an oxygen of the NO_3^- anion, giving a distorted T-shaped geometry. The remaining pyridine donors of the two $\mathbf{L_1}$ ligands coordinate similarly to a second Ag(I) ion, giving a [2 + 2] 28-membered macrocycle (Fig. 1a). The resulting distance between the Ag(I) ions is 3.117 Å, well inside the distance required for a Ag(I)···Ag(I) interaction. If this interaction is included in the coordination sphere, then each Ag(I) ion can be considered to adopt a seesaw coordination geometry ($\tau_4 = 0.66$) [22]. Perhaps surprisingly, given that silver complexes of pyrazine-based ligands are well known [23], neither donor from the pyrazine ring is involved in bonding to the Ag ions.

Reaction of $AgClO_4$ and $\mathbf{L_1}$ gives complex **2**, which crystallises in the monoclinic space group $P2_1/c$ with the asymmetric unit containing one Ag(I) cation, one ClO_4^- anion, one $\mathbf{L_1}$ ligand and one acetonitrile solvent molecule. The Ag(I) ion again adopts a T-shaped coordination geometry, being linearly coordinated by one N_{py} from each of the $\mathbf{L_1}$ ligands and, in this case, the nitrogen of the acetonitrile molecule. The closest Ag···$OClO_3$ distance is 2.835 Å, too far for the ClO_4^- anion to be considered to be coordinating. The remaining pyridine donors of the two $\mathbf{L_1}$ ligands coordinate similarly to a second Ag(I) ion, giving a [2 + 2] macrocycle (Fig. 1b). The Ag cations in this case are 3.585 Å apart — too far to be considered a Ag(I)···Ag(I) interaction. Again, neither of the pyrazine nitrogen atoms are coordinated.

Reaction of AgOTf and $\mathbf{L_1}$ gives complex **3**, which crystallises in the monoclinic space group $P2_1/c$ with the asymmetric unit containing two Ag(I) cations, two OTf^- anions and two $\mathbf{L_1}$ ligands. Centres of inversion generate two independent $[Ag_2(\mathbf{L_1})_2]^{2+}$ macrocycles, with the Ag cation in each being linearly coordinated to an N_{py} donor from each $\mathbf{L_1}$ ligand, along with an oxygen donor from a triflate anion, giving a T-shaped geometry. In one of the macrocycles, the Ag(I)···Ag(I) distance of 3.359 Å, giving the Ag ion a *pseudo*-seesaw geometry, with $\tau_4 = 0.65$ (Fig. 1c). The Ag cations in the second molecule lie at a distance of 3.686 Å to each other (Fig. 1d). Again, in neither case are the nitrogen donors on the pyrazine rings coordinated.

Reaction of $AgPF_6$ and $\mathbf{L_1}$ gives complex **4**, which crystallises in the triclinic space group *P*-1 with the asymmetric unit containing one Ag(I) cation, one PF_6^- anion, one $\mathbf{L_1}$ ligand and one acetonitrile solvent molecule. The Ag(I) ion is linearly coordinated by N_{py} donors from each of two $\mathbf{L_1}$ ligands and also by the nitrogen atom of the acetonitrile molecule, giving a T-shaped geometry. The distance between the two Ag(I) cations is 3.289 Å, within the sum of the van der Waals radii and so each Ag(I) ion can be considered to adopt a *pseudo*-seesaw coordination geometry ($\tau_4 = 0.65$) [22]. The PF_6^- is present as a counterion only — the closest Ag···FPF_5 distance is 3.183 Å. The remaining pyridine



Scheme 2. Preparation of ligand $\mathbf{L_1}$ and complexes **1**–**4** (i) Cs_2CO_3, DMF, 110 °C, Ar, 18 h, 71%; (ii) AgX, MeOH, 55 °C, 30 min, 81–91%.