A coordination polymer strategy for anion encapsulation: anion–π interactions in (4,4) nets formed from Ag(I) salts and a flexible pyrimidine ligand†

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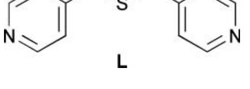
Anions encapsulated by a uniform mode of anion–π binding in isomorphous (4,4) nets formed from Ag(I) salts and bis(4-pyrimidylmethyl)sulfide appear to be structurally directing.

Supramolecular chemistry relies on the utilisation of intermolecular non-covalent interactions for the design and development of functional materials. It is only recently that the interaction between an anion and an electron deficient π-acidic ring system has been considered feasible in this context. Intuitively, anions are not expected to interact with neutral aromatic π clouds because any interaction between them should be repulsive. Some experimental and extensive theoretical studies have confirmed that π-acidic systems as diverse as halo-,[1,2] nitro- and cyano-substituted benzenes,[3] calixarenes,[4] cyanuric acids,[5,6] tetrazines[7,8] and triazines[2,6,9,10] can interact with simple anions such as halides or more charge delocalised multi-atomic anions such as NO_3^- and BF_4^-.

If anion–π interactions are to be exploited in synthetic anion receptors, it is necessary to design systems incorporating sufficient π-acidity. Metal–ligand interactions involving heterocyclic rings based on triazine and tetrazine have already shown potential in this area. The presence of a number of heteroatoms perturbs the π-electron density of the ring, which is further polarized upon coordination to a positively-charged metal ion.[11] In addition, if the ring can potentially bridge between metal ions, a more π-acidic heterocyclic ring centre will result. Coordination polymer systems are likely to be useful in this respect. However, a subtle balance is required between electron deficiency and donor ability because electron deficient heterocycles such as triazines and tetrazines are weak donors and, as a result, are more inclined to form discrete complexes. Coordination polymers have another advantage, as through careful ligand design or as a result of packing effects, they often form cavities bounded by arene rings, in which the anion may be situated.[12] In certain circumstances, these cavities are reminiscent of the π-acidic interiors of some molecular containers that are used as anion receptors.[13]


L

Our strategy was to design a flexible multimodal ligand, bis(4-pyrimidylmethyl)sulfide (**L**), based on a 4-substituted pyrimidine moiety. This moiety is able to provide both suitably strong N-donors and sufficiently π-acidic ring centres. Furthermore, the particular arrangement of N-donors was considered conducive to the formation of more open coordination polymer networks. Previously, pyrimidine-thioether ligands have included 2-substituted pyrimidine moieties. This substitution often results in only one of the N_{pym}-donors coordinating to a metal ion, thus presenting a less favourable arrangement for the formation of higher dimensional polymers.

Ligand **L** was prepared by the reaction of 4-(chloromethyl)pyrimidine[14] with thioacetamide under basic conditions.† The reaction of **L** with AgX (X = BF_4, ClO_4 and PF_6) in a 1 : 1 molar ratio afforded tan coloured precipitates, which gave analyses consistent with 1 : 1 metal-to-ligand ratios. X-Ray quality crystals of $\{[AgL]X\}_\infty$ [X = BF_4 (**1**), ClO_4 (**2**) and PF_6 (**3**)] were grown by the slow diffusion of **L** in $MeNO_2$ into a solution of AgX in MeCN.‡

Structural analyses§ of **1–3** revealed all three complexes to be isomorphous with two-dimensional sheet structures. The complexes crystallised in the chiral orthorhombic space group $P2_12_12$. The two-dimensional sheets (Fig. 1) had a (4,4) topology.[15] The net was uninodal with each nodal point corresponding to the Ag(I) centre. The structure of the sheets consisted of 16-membered metallomacrocyclic rings, which were represented as 4-gons in the topological nets (Fig. 1). The asymmetric unit contained half a ligand molecule, half an Ag(I) ion and half a counterion. The structure was generated by 2-fold rotations about the special positions for S(1), Ag(1) and the central atom of each respective

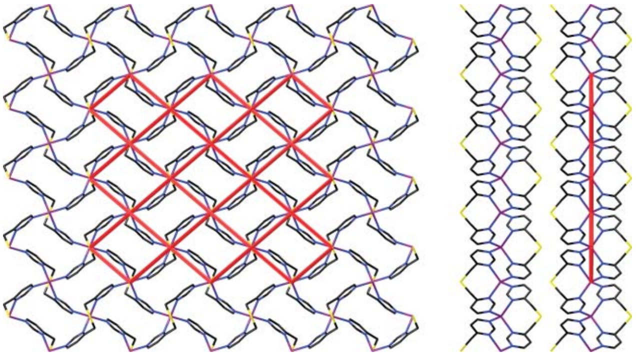


Fig. 1 Left: View (ab plane) of the two-dimensional sheet of **1–3** with an overlay (red) of the (4,4) topological net (hydrogen atoms and anions omitted for clarity). Right: Side view (ac plane) showing the stacking of the sheets.

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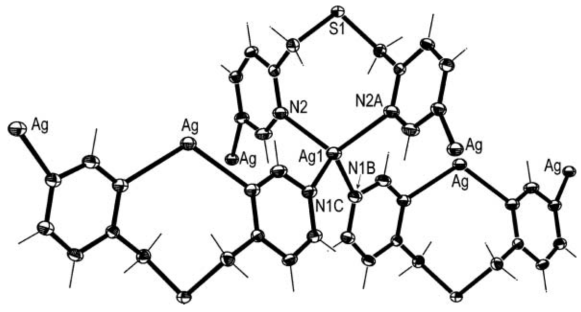

Fig. 2 View of **1** representing the coordination environment and endo-*anti* ligand conformation found in **1–3**. BF_4^- anions are omitted for clarity (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.2988(19), Ag(1)–N(2) 2.3112(19); N(1B)–Ag(1)–N(1C) 112.87(9), N(1B)–Ag(1)–N(2) 103.45(7), N(1B)–Ag(1)–N(2A) 112.14(7), N(1C)–Ag(1)–N(2) 112.14(7), N(1C)–Ag(1)–N(2A) 103.45(7), N(2)–Ag(1)–N(2A) 113.12(9) (symmetry codes A: $1 - x$, $1 - y$, z; B: $x + ½$, $½ - y$, $-z$; C: $½ - x$, $y + ½$, $-z$).

anion. The ligand adopted a stretched-out endo-*anti* conformation,[16] in which the rings were tilted by 22.3, 32.0 and 24.2° with respect to each other (**1**, **2** and **3**, respectively). The Ag(I) ion was coordinated in a distorted tetrahedral fashion by a NNN′N″ donor set from one chelating and two monodentate ligands (Fig. 2). This arrangement meant that all the available pyrimidine N-donors were used in generating the structure. Each ligand was able to bridge these Ag ions, and in this way enhanced the π acidity of the ring centre. The formation of an eight-membered chelate ring assisted with the generation of a more opened-out framework. The Ag(I)–N distances were within the normal range (2.11–2.63 Å), as determined by a search of the CSD (version 5.27).[17] The S-donor was oriented away from the centre of the sheets and was not coordinated (Fig. 2). The only interactions that the S atoms were involved in were weak S···H–C contacts [2.86 Å, **1**; 2.87 Å, **2** and 3.00 Å, **3**] between adjacent sheets.

The open nature of the two-dimensional structures and the stabilisation provided by anion–π interactions allowed the anions to be situated in cavities formed within the sheets rather than being located between adjacent sheets. The cavities were bounded by pyrimidine rings, and the embedded anions were all held in place by four complementary π–anion–π sandwich interactions with two pyrimidine rings (Fig. 3; Table 1). The anion interactions with the rings were asymmetric in nature and consisted of one short and one moderate anion-to-centroid distance (Fig. 3). Recently, the influence of the number of heteroatoms in rings has been examined in a comparative study using Ag(I) complexes of tetrazine- and pyridazine-substituted ligands.[7] The study shows that the less π-acidic pyridazine systems have weaker anion–π interactions than the analogous tetrazine systems. In **1–3**, the anion–π distances were comparable to values found in such pyridazine systems, but on average were slightly longer than those observed in metal triazine[9,18] or tetrazine[7,19] systems, which have more heteroatoms in the rings.

Despite containing anions of different volume, the three structures are isomorphous. This invariance in structure indicated that either the sheets were robust enough to accommodate the guest anions or that the anion–π interactions were strong enough to engender the same overall structural arrangement. If space filling was the major determinant, different overall network structures might be expected, as such Ag–heterocyclic systems are especially difficult to direct. Therefore, it appeared in this case that the anion–π interactions were structurally directing. These

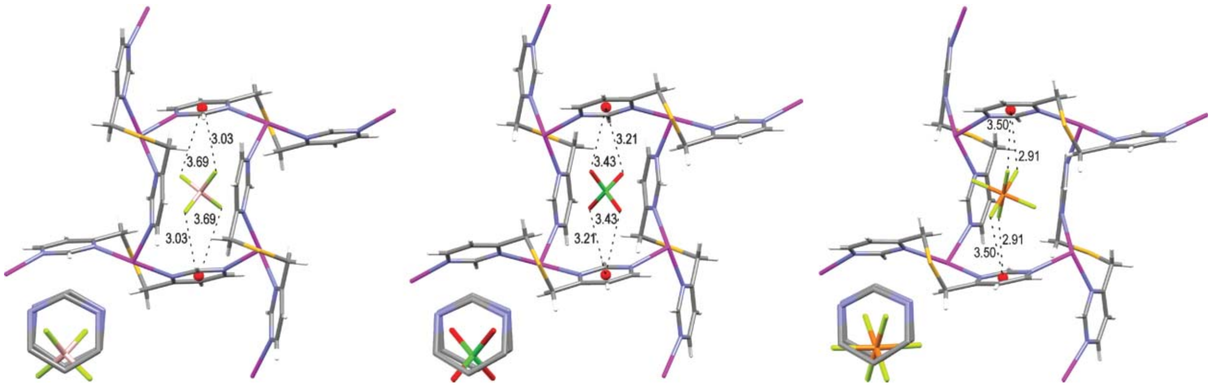

Fig. 3 View (ab plane) of the uniform mode of BF_4^-, ClO_4^- and PF_6^- anion–π interactions in **1–3** (left to right). A top down view of the π–anion–π sandwich interaction is shown as an inset for each structure.

Table 1 Analysis of anion–π interactions for **1–3**

Compound	Interaction	X = ring centroid/Å	X = ring plane/Å	Angle between F/O···X axis and ring plane (X = ring centroid)/°	X = closest ring atom/Å
1	B(1)–F(11)···X	3.027(3)	2.97	79.0	3.067(4) (C4)
	B(1)–F(12)···X	3.692(3)	3.27[a]	62.4	3.301(3) (C1)
2	Cl(1)–O(1)···X	3.432(11)	3.19	68.2	3.189(11) (C1)
	Cl(1)–O(2)···X	3.206(11)	3.05	72.0	3.062(12) (C4)
3	P(1)–F(1)···X	3.500(5)	3.25[a]	68.2	3.252(7) (C3)
	P(1)–F(2)···X	2.910(5)	2.79	73.2	2.820(7) (C1)

[a] Contact with the plane was <0.7 Å outside of the pyrazine ring.

three structures **1–3** represent only the second examples demonstrating anion–π interactions using π-acidic pyrimidine ring centres.[20]

Anion coordination is an important and challenging aspect of contemporary supramolecular chemistry. Our investigation has provided further experimental evidence for the usefulness of diazines in the design of anion receptors by demonstrating the ability of pyrimidine to interact with anions through multiple anion–π interactions. In addition, both the structural consistency displayed by these networks and the uniform mode of anion binding demonstrate the potential for the use of anion–π interactions in a structurally directing role. These are important characteristics to be considered in the design of receptors with enhanced selectivity for non-coordinating anions. Finally, our work bolsters the concept of anion–π interactions as another type of important supramolecular interaction.

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Notes and references

‡ *Synthesis of complexes* $\{[\mathrm{Ag}(\mathbf{L})](\mathrm{X})\}_\infty$ (X = BF_4, ClO_4 and PF_6): In a typical synthesis, AgX (0.30 mmol) dissolved in MeCN (25 mL) was added to **L** (0.30 mmol) dissolved in MeCN (25 mL). The solution was stirred overnight and concentrated to 10 mL. 1-Butanol (10 mL) was added and the solution was further concentrated, resulting in the formation of a tan precipitate (66%). X-Ray quality crystals were grown from the slow diffusion of a $MeNO_2$ solution of **L** layered with benzene into a MeCN solution of AgX.

$\{[\mathrm{Ag}(\mathbf{L})](\mathrm{BF_4})\}_\infty$: Anal. calc. for $C_{10}H_{10}N_4SAgBF_4$: C, 29.09; H, 2.44; N, 13.57. Found: C, 29.50; H, 2.41; N, 12.88%. Selected IR (KBr)/cm^{-1}: 1593 (s) (**L**), 1551 (m) (**L**), 1397 (m), 1055 (s) (BF_4^-) and 597 (w).

$\{[\mathrm{Ag}(\mathbf{L})](\mathrm{ClO_4})\}_\infty$: Anal. calc. for $C_{10}H_{10}N_4SAgClO_4$: C, 28.22; H, 2.37; N, 13.16; S, 7.53. Found: C, 28.44; H, 2.33; N, 13.17; S, 7.50%. Selected IR (KBr)/cm^{-1}: 1586 (s) (**L**), 1552 (s) (**L**), 1320 (m) (**L**), 1107 (s, br) (ClO_4^-) and 624 (s) (ClO_4^-).

$\{[\mathrm{Ag}(\mathbf{L})](\mathrm{PF_6})\}_\infty$: Anal. calc. for $C_{10}H_{10}N_4SAgPF_6\cdot H_2O$: C, 24.56; H, 2.47; N, 11.45; S, 6.56. Found: C, 24.49; H, 2.17; N, 11.19; S, 6.41%. Selected IR (KBr)/cm^{-1}: 1583 (s) (**L**), 1551 (m) (**L**), 1471 (m), 1390 (m), 1313 (w) (**L**), 1163 (w) (**L**), 835 (s, br) (PF_6^-) and 557 (s) (PF_6^-).

§ *Crystal data* for **1**: $C_{10}H_{10}AgBN_4F_4S$, M = 412.97, orthorhombic, $P2_12_12$, a = 7.608(5), b = 8.883(5), c = 9.914(5) Å, V = 670.7(7) Å^3, Z = 2, T = 88(2) K, 2133 unique reflections. Refinement of 97 parameters converged at final R_1 = 0.0207, wR_2(all data) = 0.0517.

2: $C_{10}H_{10}AgN_4O_4SCl$, M = 425.60, orthorhombic, $P2_12_12$, a = 7.7198(3), b = 9.1284(3), c = 9.7867(4) Å, V = 689.66(5) Å^3, Z = 2, T = 123(2) K, 2018 unique reflections. Refinement of 97 parameters converged at final R_1 = 0.0335, wR_2(all data) = 0.0907.

3: $C_{10}H_{10}AgN_4F_6PS$, M = 471.12, orthorhombic, $P2_12_12$, a = 7.8018(16), b = 9.0824(17), c = 9.9020(19) Å, V = 701.6(2) Å^3, Z = 2, T = 93(2) K, 1291 unique reflections. Refinement of 106 parameters converged at final R_1 = 0.0290, wR_2(all data) = 0.0703.

CCDC 639720–639722. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703522e

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