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A self-complementary molecular cleft†

David A. McMorran* and Peter J. Steel

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.
E-mail: d.mcmorran@chem.canterbury.ac.nz

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Reaction of silver(I) salts with a new octadentate ligand generates a novel self-complementary molecular cleft which forms dimers in the solid state, stabilised by π-stacking interactions and intermolecular C–H···M interactions.

The designed construction of metallosupramolecular assemblies, constructed from appropriately chosen combinations of metal ions and organic ligands, is a rapidly developing area of chemistry.[1] The goal of this research is the development of rational approaches to the preparation of new metal ion-containing supramolecular species, with novel structural and functional motifs. Such species may in turn find uses as components in molecular devices and sensors. We have been involved in a programme of exploring the consequences of incorporating ligands with inherent flexibility into such assemblies.[2] We recently reported the preparation of the first coordinatively saturated quadruple helicate and showed that this acts as a novel host for polyatomic anions.[3] We now report the preparation of a new type of molecular cleft, with a novel architectural motif, which assembles into organised dimeric pairs in the solid state.

The new ligand 1,2,3,4-tetrakis(3-(2-pyridyl)pyrazol-1-ylmethyl)benzene (**1**) was prepared from 1,2,3,4-tetrakis(bromomethyl)benzene[4] and 3-(2-pyridyl)pyrazole[5] by a phase-transfer-catalysed alkylation[6] (Scheme 1).

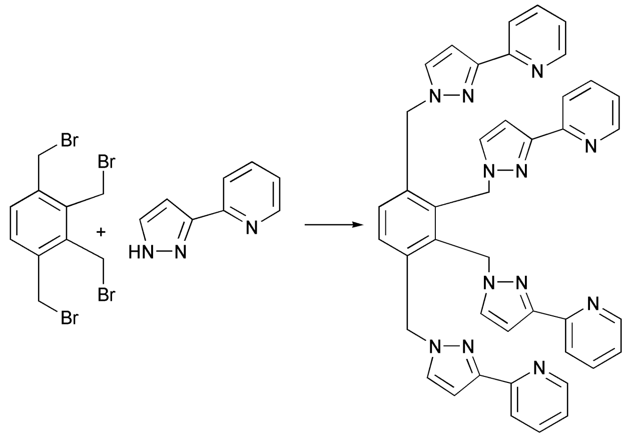
Reaction of **1** with two equivalents of either silver(I) tetrafluoroborate, silver(I) perchlorate or silver(I) triflate in acetonitrile solution gave clear solutions.‡ Diffusion of light petroleum or diethyl ether into these solutions gave colourless crystalline solids. In each case, these solids analysed with a silver to ligand ratio of 2 : 1. This suggested to us that adjacent arms of the ligand were chelating the silver atoms, as we have observed in the related silver complex of hexakis(3-(2-pyridyl)pyrazol-1-ylmethyl)benzene.[7] We were interested to explore the arrangement of the ligand arms of **1** in the current complexes so X-ray structure determinations of $[Ag_2\mathbf{1}](BF_4)_2$, $[Ag_2\mathbf{1}](ClO_4)_2$ and $[Ag_2\mathbf{1}](OTf)_2$ were undertaken.

The structure of $[Ag_2\mathbf{1}](BF_4)_2$ contains two independent M_2L units, each consisting of one ligand and two silver atoms.§ Four tetrafluoroborate anions, two solvate acetonitrile molecules and a water solvate molecule complete the contents of the asymmetric unit.

As suggested by the elemental analysis, each ligand chelates two silver atoms with adjacent arms. In doing so, the ligands adopt the least favoured conformation, such that both silvers lie on the same side of the central benzene ring (Fig. 1). The silver atoms are each coordinated by a pyrazole nitrogen of an exterior arm and a pyridine nitrogen of the adjacent interior arm, with typical Ag–N distances (2.166–2.230 Å) and almost linear geometry (170.26–173.66°). The remaining nitrogen donors arrange themselves into orientations that provide weaker (Ag–N $>$ 2.5 Å) dative interactions with the metal atoms.

Given that adjacent flexible substituents about a central benzene platform tend to organise themselves in an alternating pattern on opposite faces of the benzene ring,[8] it is remarkable that, in this structure, the four arms of the ligand self-organise about one side. As a consequence, a cleft is generated between the arms. The dimensions of the cleft can be defined by the distances between pairs of interior arms (4.455 (a) and 4.601 Å (b)), the distances between pairs of exterior arms (7.249 (a) and 7.517 Å (b)) and the angle between pairs of adjacent arms (44.6 (a) and 49.8° (b)).¶

These dimensions are such that the cleft might be expected to be able to recognise suitable aromatic guest species *via* π-stacking and/or π-cation interactions. As such, it is perhaps not surprising that the cleft of molecule **a** is found to be occupied by one of the arms of molecule **b** and, in complementary fashion,



(**1**)

Scheme 1

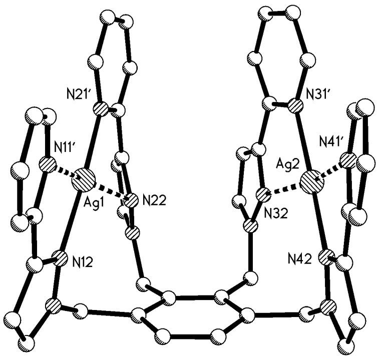


Fig. 1 Selected bond lengths (Å) and angles (°) for $[Ag_2\mathbf{1}]_2(BF_4)_4$: Molecule **a** [Molecule **b**]: Ag1–N12 2.211(3) [Ag3–N52 2.226(3)], Ag1–N21′ 2.210(3) [Ag3–N61′ 2.216(3)], Ag1–N11′ 2.586(3) [Ag3–N51′ 2.566(3)], Ag1–N22 2.807(3) [Ag3–N62 2.808(3)] Ag2–N31′ 2.231(3) [Ag4–N71′ 2.224(3)], Ag2–N42 2.187(3) [Ag4–N82 2.166(3)], Ag2–N32 2.651(3) [Ag4–N72 2.620(3)], Ag2–N41′ 2.766(4) [Ag4–N81′ 2.808(4)]; N12–Ag1–N21′ 173.67(11) [N52–Ag3–N61′ 171.71(12)], N11′–Ag1–N22 170.83(10) [N51′–Ag3–N62 169.41(10)], N31′–Ag2–N42 173.05(12) [N71′–Ag4–N82 170.24(12)], N32–Ag2–N41′ 167.93(10) [N72–Ag4–N81′ 166.95(10)].

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† Electronic supplementary information (ESI) available: assignment of the ^1H NMR spectrum of $[Ag_2\mathbf{1}](BF_4)_2$ in CD_3CN solution. See http://www.rsc.org/suppdata/cc/b2/b205831f/

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the cleft of molecule **b** is occupied by one of the arms of molecule **a**. The two molecules thus form a dimeric structure, with one slotted into the other, with the angle between the two central benzene rings being 45.3° (Fig. 2).

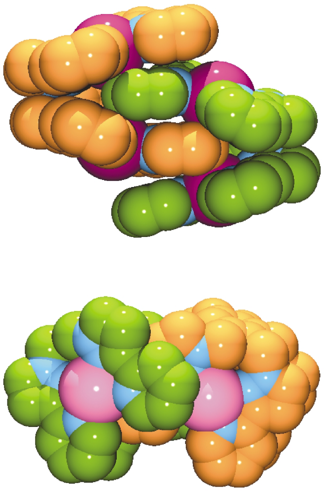

Fig. 2 Space-filling diagram of the [Ag_2**1**] dimer.

This supramolecular assembly is stabilised by two cooperating sets of interactions. First, the pyridine rings of the exterior arms of the two molecules form three π–π interactions, with closest inter-ring distances of 3.62, 3.63 and 3.66 Å (Fig. 3).

While a similar arrangement has been reported in organic molecular cleft species[9] we believe this to be the first example in a metallosupramolecular system.[10] Secondly, examination of the intermolecular distances further shows the presence of four intermolecular C–H···M interactions, between the silver atoms and the pyridine ring H4 hydrogens, with Ag···H distances of 2.944–3.032 Å and C–H–Ag angles of 92.0–94.1° (Fig. 3). This is, to our knowledge, only the second identified example of an *intermolecular* C–H···M interaction, the other being a pair of Pd···H interactions in the dimer of *cis*-[$PdCl_2(TPA)_2$].[11]

The X-ray structure of [Ag_2**1**](ClO_4)$_2$ was found to be isomorphous with that of [Ag_2**1**](BF_4)$_2$, with the ClO_4^- anions occupying the same sites in the lattice as the structurally similar BF_4^- anions. The X-ray structure of [Ag_2**1**](OTf)$_2$, although in a different crystal system with a different packing arrangement of the molecules, was found to also have a similar structure, although in this case, the two component molecules of the dimer fitted together somewhat less tightly, due to slight structural differences.

While the complexes are stable in acetonitrile solutions, they appear to exist as discrete [Ag_2**1**]$^{2+}$ species. Electrospray MS shows the [Ag_2**1**]$^{2+}$ ion to be the major species present, while the ^{1}H NMR spectrum is also consistent with a monomeric structure. Complete assignment of the ^{1}H NMR spectrum was achieved by HSQC and 2D ROESY experiments, which show it to be consistent with the molecular cleft structure. In particular, comparison with the ^{1}H NMR spectrum of **1** shows that, upon coordination to silver, signals for the protons on the inner arms are shifted upfield by *ca*. 0.2 ppm, consistent with the enforced proximity of the inner arms in the cleft structure. The observation that the monomer is favoured in solution may result from unfavourable electrostatic interactions between the two dicationic cleft species. However, the presence of the metal ions in the walls of the cleft may enhance the binding of other aromatic species.

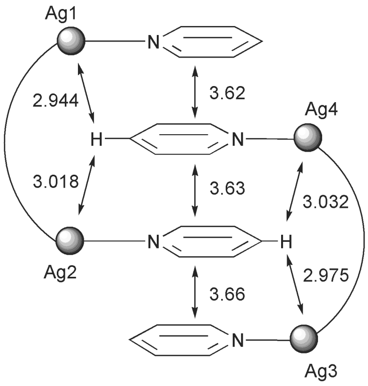

Fig. 3 Intermolecular interactions between molecules **a** and **b** (distances in Å).

In summary, reaction of various silver salts with the new ligand **1** generates a self-complementary metallosupramolecular cleft, which forms dimers in the solid state which are stabilised by a combination of intermolecular π-stacking and C–H···M interactions. This cleft represents a novel architectural motif for potential host systems for aromatic guest species. We are currently trying to prepare clefts with other metal ions, such as copper(II), and exploring the ability of such clefts to recognise suitable aromatic species in solution.

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Notes and references

‡ *Preparation* of [Ag_2**1**]$_2$(BF_4)$_4$: $AgBF_4$ (13.8 mg, 7.1 × 10^{-5} mol) was dissolved in acetonitrile (1 mL) and added to **1** (25 mg, 3.5 × 10^{-5} mol) dissolved in acetonitrile (2 mL), giving a clear, pale brown solution. Light petroleum (bp = 60–80 °C) was diffused into the solution to give colourless crystals, yield 20 mg (50%), mp 234–235 °C. Analysis: Calc. for $C_{42}H_{34}N_{12}Ag_2B_2F_8\cdot 3H_2O$: C, 43.86; H, 3.50; N, 14.60. Found: C, 43.70; H, 3.17; N, 14.62%. ^{1}H NMR (500 MHz, CD_3CN), δ 5.67 (s, 4H, $CH_{2\ out}$), 5.73 (s, 4H, $CH_{2\ in}$), 6.88 (s, 2H, H_4 pz_{in}), 7.13 (s, 2H, H_4 pz_{out}), 7.26 (s, 2H, H_5, H_6), 7.50 (s, 2H, H_5 pz_{in}), 7.59 (t, 2H, H_5 py_{in}), 7.61 (t, 2H, H_5 py_{out}), 7.87 (d, 2H, H_3 py_{in}), 8.03 (m, 6H, H_5 pz_{out}, H_3 py_{out}, H_4 py_{in}), 8.07 (t, 2H, H_4 py_{out}), 8.65 (s, 2H, H_6 py_{in}), 8.84 (d, 2H, H_6 py_{out}). ES-MS: 461.1 [Ag_2**1**]$^{2+}$.

§ *Crystal data*: $C_{44}H_{38}Ag_2B_2F_8N_{13}O_{0.5}$, M = 1146.23, monoclinic, space group $P2_1/n$, a = 15.177(5), b = 24.188(9), c = 25.010(9) Å, β = 102.044(5)°, V = 8979(5) Å^3, Z = 8, D_c = 1.696 Mg m^{-3}, μ = 0.957 mm^{-1}, $F(000)$ = 4584, colourless plate 0.60 × 0.37 × 0.06 mm, $2\theta_{max}$ 52°, Mo-Kα (λ = 0.7107 Å), T = 168 K, 114722 reflections, 18010 unique (97.8% completeness), 1282 parameters, $wR2$ = 0.0944 for all data, R = 0.0385 for 9381 data with $I > 2\sigma(I)$. CCDC reference number 188027. See http://www.rsc.org/suppdata/cc/b2/b205831f/ for crystallographic data in CIF or other electronic format.

¶ Distances measured between the centroids of the pyridine rings.

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