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Molecular squares, rectangles and infinite helical chains utilising the simple 'corner' ligand 4-(2-pyridyl)-pyrimidine

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The ligand 4-(2-pyridyl)-pyrimidine forms multinuclear Ag(I) complexes by a combination of chelating and bridging coordination modes; molecular shape (square or rectangle) and degree of aggregation depend on the anion used.

Sophisticated polydentate nitrogen ligands based on pyridine, pyrazine, pyrimidine and pyradizine units have become the scaffold of choice for designing and assembling novel metal–ligand architectures.[1] Interestingly, a very simple ligand that has been essentially ignored is 4-(2-pyridyl)-pyrimidine, **1**. To date, only the free ligand,[2] **1**, and $[Ru(bipy)_2(L)][PF_6]_2$ where L = 2-methyl-4-(2-pyridyl)-pyrimidine, have been characterised by X-ray crystallography.[3] A few structural reports have appeared on complexes of the symmetrical ligands 4,4′-bipyrimidine and 2,2′-dimethyl-4,4′-bipyrimidine, but the symmetrical nature of these species makes direct comparson to the coordination chemistry of **1** peripheral.[4,5]

As shown below (Fig. 1), **1** has two sites for metal–ligand interaction; a simple chelating site analogous to 2,2′-bipyridyl and an exo N-donor site for bridging. Since these two sites are oriented ~90° to each other, we reasoned that this ligand could be used to assemble simple molecular polygons. There are, of course, two very simple planar polygons that can be generated using four ML units with 90° corners; a square and a rectangle. Which of these is formed depends upon whether the building blocks are arranged head-to-tail (square) or head-to-head (rectangle). What might dictate the formation of either of these molecular motifs is difficult to predict and may be quite subtle.

4-(2-Pyridyl)-pyrimidine, **1**, was prepared in 90% yield using the published method.[2] 2-[3-(*N*,*N*-dimethylamino)-1-oxoprop-2-en-1-yl]pyridine, prepared from 2-acetylpyridine and *N*,*N*-dimethylformamidine dimethylacetate, was reacted with 3 equivalents of formamidine and 3 equiv. of sodium ethoxide. As a way of initially probing the coordination preferences of **1**, we reacted equivalent amounts of the Ag(I) salts $AgBF_4$, $AgCF_3SO_3$ or $AgNO_3$ and **1** in a non-coordinating solvent, $MeNO_2$.[6] In each case, X-ray quality crystals were grown from the reaction mixture and the solid state structure determined.†

A complex with a 1:1 metal to ligand ratio was formed from the reaction of **1** with $AgBF_4$. The X-ray structure showed this complex to be the square tetramer $\{[\mathbf{2}][BF_4]\}_4$; Fig. 2(A). The head-to-tail aggregation of four corner residues requires that the Ag(I) ions each bond to **1** in a pseudo-trigonal planar geometry with respect to the N-donors of **1**. The tetra-cationic unit is essentially planar[7] and forms alternating layers with the BF_4^- anions as shown in Fig. 2(B). The asymmetric trigonal geometry and layered structure are stabilized by interactions between the large flat cation and non-coordinating BF_4^- anions; closest contact is 2.86 Å between Ag(2) and F(2).

A compound with the same 1:1 ligand to metal ratio and basic tetrameric formula was formed when $AgCF_3SO_3$ was reacted with **1** in $MeNO_2$. The X-ray structure showed this complex to be the rectangular isomer $\{[\mathbf{3}][CF_3SO_3]\}_4$; Fig. 3(A). The head-to-head plus tail-to-tail aggregation requires that the Ag(I) ions adopt different coordination geometries. Ag(1) is bonded in a distorted square planar geometry to the chelating sites of two different ligands while Ag(2) adopts a linear geometry by coordinating to the bridging N-donors from two different molecules of **1**. The cationic unit in $[\mathbf{3}]^{4+}$ is also flat but not as planar as the cation in $[\mathbf{2}]^{4+}$.[7] As is shown in Fig. 3(B), the rectangular tetrameric cations also form alternating layers with the $CF_3SO_3^-$ anions. The greater distortion from planarity is a result of the tetrahedral distortion about Ag(I). It is

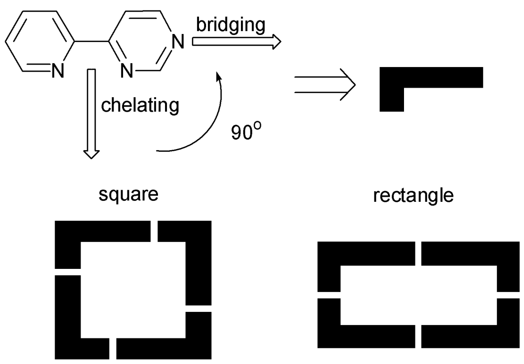

Fig. 1 The ~90° angle 'corner' provided by **1** could produce either a molecular square complex (left) *via* head-to-tail aggregation or a molecular rectangle complex (right) from head-to-head aggregation.

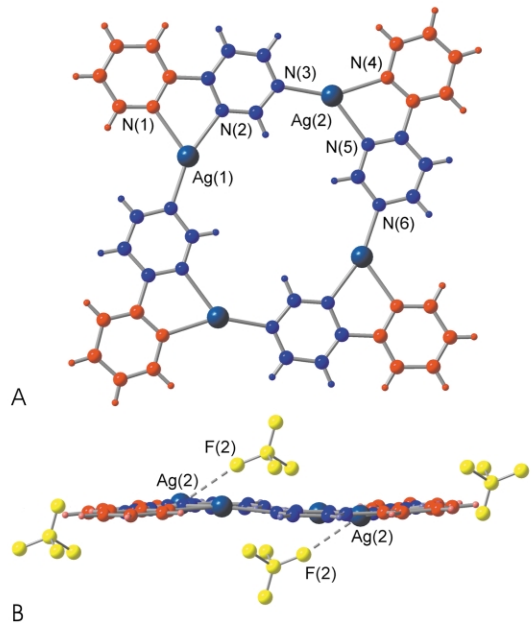

Fig. 2 Ball-and-stick representations of the X-ray structure of the cationic square $[\mathbf{2}]^{4+}$. There is a crystallographic inversion centre at the centre of the square. Colour key: pyridine ring, red, pyrimidine ring, blue, BF_4^- anions, yellow. Top view (A) shows the cationic tetramer with a basic numbering scheme. Bottom view (B) shows an edge-on view with four closest anions of the intervening layers. Selected distances (Å) and angles (°): Ag(1)…Ag(1)′ 9.83, Ag(2)…Ag(2)′ 7.84, Ag(1)…Ag(2) 6.39, Ag(1)…Ag(2)′ 6.18, Ag(1)–N(1) 2.270(8), Ag(1)–N(2) 2.356(7), Ag(1)–N(6)′ 2.184(7), Ag(2)–N(3) 2.141(8), Ag(2)–N(4) 2.372(8), Ag(2)–N(5) 2.276(7), N(1)–Ag(1)–N(2) 71.8(3), N(1)–Ag(1)–N(6)′ 150.8(3), N(2)–Ag(1)–N(6)′ 135.3(3), N(3)–Ag(2)–N(4) 126.8(3), N(3)–Ag(2)–N(5) 160.8(3), N(4)–Ag(2)–N(5) 70.8(3).

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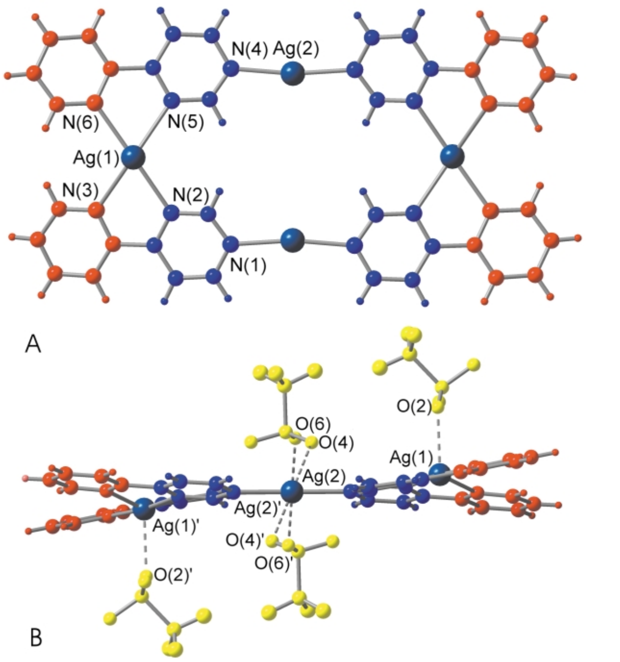

Fig. 3 Ball–and–stick representations of the X–ray structure of the cationic rectangle $[\mathbf{3}]^{4+}$.[9] There is a crystallographic inversion centre at the centre of the rectangle. Top view (A) shows the cationic tetramer with a basic numbering scheme. Bottom view (B) shows an edge-on view with four closest anions of the intervening layers. Selected distances (Å) and angles (°): Ag(1)…Ag(1)′ 11.22, Ag(2)…Ag(2)′ 5.87, Ag(1)…Ag(2) 6.34, Ag(1)…Ag(2)′ 6.33, Ag(1)–N(2) 2.423(5), Ag(1)–N(3) 2.335(5), Ag(1)–N(5) 2.378(5), Ag(1)–N(6) 2.413(5), Ag(2)–N(1) 2.203(5), Ag(2)–N(4) 2.206(5), N(2)–Ag(1)–N(3) 69.5(2), N(2)–Ag(1)–N(5) 110.5(2), N(2)–Ag(1)–N(6) 154.2(2), N(3)–Ag(1)–N(5) 174.9(2), N(3)–Ag(1)–N(6) 108.7(2), N(5)–Ag(1)–N(6) 69.0(2), N(1)–Ag(2)–N(4)′ 171.7(2).

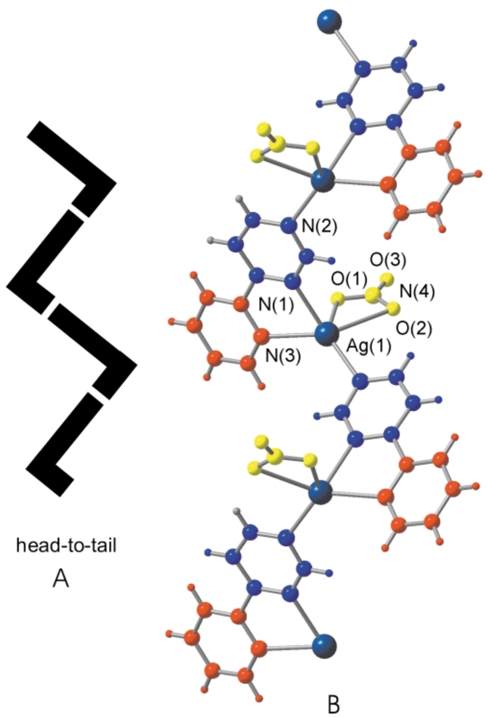

Fig. 4 An illustration (left) of $[Ag(\mathbf{1})]^+$ units linked head-to-tail into a 1D polymer. A ball-and-stick representation (right) of the X–ray structure of the 1D helical polymer $\{[\mathbf{4}]\}_n^{n+}$ Selected distances (Å) and angles (°): Ag(1)…Ag(1)′ 6.02, Ag(1)–N(1) 2.347(3), Ag(1)–N(2) 2.204(3), Ag(1)–N(3) 2.374(3), Ag(1)–O(1) 2.468(3), Ag(1)–O(2) 2.810(3), N(1)–Ag(1)–N(2)′ 134.4(1), N(1)–Ag(1)–N(3) 70.0(1), N(2)′–Ag(1)–N(3), 126.6(1) N(1)–Ag(1)–O(1) 90.4(1), N(2)′–Ag(1)–O(1) 129.4(1), N(3)–Ag(1)–O(1) 84.8(1), N(1)–Ag(1)–O(2) 110.3(1), N(2)′–Ag(1)–O(2) 89.7(1), N(3)–Ag(1)–O(2) 130.5(1), O(1)–Ag(1)–O(2) 46.3(1).

not possible to form a strictly square planar $[M(2,2'\text{-bipy})_2]^{n+}$ complex without some degree of tetrahedral distortion even when the metal ion strongly prefers this geometry.[8] The linear two-coordinate geometry at Ag(2) defines the short side of the rectangle. This Ag…Ag distance is spanned by bridging $CF_3SO_3^-$ anions and is probably the reason why a rectangle is preferred with this anion; contacts are Ag(2)…O(6) 2.57, Ag(1)…O(2) 2.83, Ag(2)…O(4) 2.59 Å.

Since two different anions (BF_4^- and $CF_3SO_3^-$) with different shapes and arguably (slightly) different coordinating abilities gave two very different shaped aggregates it was of interest to examine the effect of using a coordinating oxyanion such as nitrate. A compound with a 1 : 1 metal to ligand ratio was prepared from $AgNO_3$ and **1** in $MeNO_2$. As shown in Fig. 4(B), the X-ray structure revealed that for $AgNO_3$ the complex formed was a linear 1D helical coordination polymer $\{[\mathbf{4}][NO_3]\}_n$. Each molecule of ligand **1** propagates an $[ML]_n$ chain by alternately chelating and bridging to two different Ag(I) ions. The remainder of the coordination sphere of each Ag(I) ion is occupied by 2 O atoms from a nitrate ion. This infinite 1D motif is, of course, one of two alternate ways of linking 90° corners; the head-to-tail version as illustrated in Fig. 4(A).

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Notes and references

† ^1H NMR spectra (VT, $MeNO_2$-d_3) showed no features that could be used to assign structure. Only crystalline material was isolated and data crystals selected randomly from the bulk. *Crystal data*, $\{[\mathbf{2}][BF_4]\}_4$: $C_{36}H_{28}Ag_4B_4F_{16}N_{12}$, M = 1407.4, triclinic, *P-1*, a = 7.841(2), b = 9.214(2), c = 17.007(3) Å, α = 102.984(3), β = 94.837(3), γ = 101.366(3)°, U = 1163.1(4) Å³, T = 289(2) K, Z = 1, μ = 1.768 mm^{-1}, 4067 independent reflections (R_{int} = 0.0179). R_1 = 0.0712, wR_1 = 0.0724, (2402 reflections, $I > 2\sigma I$), R_2 = 0.2352, wR_2 = 0.2396, (all data), GoF(F^2) = 1.134. $\{[\mathbf{3}][CF_3SO_3]\}_4$: $C_{40}H_{28}Ag_4F_{12}N_{12}O_{12}S_4$, M = 1656.5, triclinic, *P-1*, a = 10.127(1), b = 10.453(1), c = 13.504(2) Å, α = 81.403(2), β = 72.533(2), γ = 89.410(2)°, U = 1347.3(3) Å³, T = 293(2) K, Z = 1, μ = 1.699 mm^{-1}, 5794 independent reflections (R_{int} = 0.0091). R_1 = 0.0486, wR_1 = 0.0539, (3834 reflections, $I > 2\sigma I$), R_2 = 0.1365, wR_2 = 0.1422, (all data), GoF(F^2) = 1.068. $\{[\mathbf{4}][NO_3]\}_n$ $C_9H_7AgN_4O_3$, M = 327.1, monoclinic, $P2_1/n$, a = 5.432(2), b = 10.860(5), c = 18.009(8) Å, β = 98.486(6)°, U = 1050.7(8) Å³, T = 289(2) K, Z = 4, μ = 1.920 mm^{-1}, 4381 independent reflections (R_{int} = 0.0200). R_1 = 0.0279, wR_1 = 0.0299, (1490 reflections, I > $2\sigma I$), R_2 = 0.0741, wR_2 = 0.0764 (all data), GoF(F^2) = 1.085. Data were collected on a Bruker APEX CCD instrument and solutions performed using the SHELXTL 5.03 Program Library, Bruker Analytical Instrument Division, Madison, WI, USA, 1997. CCDC numbers 191503, 191504, 191505. See http://www.rsc.org/suppdata/cc/b2/b206989j/ for crystallographic data in CIF or other electronic format.

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