

## A modular, self-assembled, separated ion pair binding system

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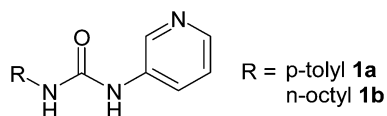
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**Assembly of a silver(I) complex of a simple pyridyl ligand containing a urea derivative is templated by nitrate; analogous complexes of Ag<sub>2</sub>SO<sub>4</sub> and AgCF<sub>3</sub>SO<sub>3</sub> exhibit radically different geometries.**

A holistic view of ion-binding systems requires a full consideration of the overall charge neutrality requirement. A neutral ion receptor must contain *a priori* binding sites for both anion and cation either as a contact or separated ion pair, as exemplified by the elegant receptors designed by Smith and Atwood.<sup>1,2</sup> Charged receptors effectively replace, and compete with counter-ions, usually forming new contact ion paired host-guest systems.<sup>3,4</sup> In both cases the host is generally a covalently bonded organic molecule assembled under kinetically controlled conditions in the absence of the target guest. Recently, work by both Gale and Loeb<sup>5</sup> and ourselves<sup>6</sup> has highlighted the preparation of coordination complexes in which a relatively inert metal cation such as Pt(II) or Ru(II) acts as a core linking together two or more anion-binding arms bearing hydrogen bonding functionality. These 'semi-labile' coordination complex host systems are conceptually analogous to organic podands in which the core is an arene ring, for example, and indeed we have applied the same pyridyl-terminated arms in both contexts.<sup>7,8</sup> Taking the inorganic core concept to extremes, there is no reason why the same species may not be formed using a highly labile metal ion in a fully thermodynamically controlled self-assembly regime.<sup>9</sup> Thus it should be conceptually possible to replace the thermodynamic equilibrium involving association of a covalent host and a guest ion or ion pair with a multi-component templated thermodynamic self-assembly in which the guest anion and cation play an intimate part by templating the overall assembly. Such assemblies might potentially prove more effective sensors for particular salts than their traditional covalent counterparts since changes in colour or electrochemical or photochemical properties should result from different self-assemblies.

In order to test this concept we have designed and prepared a series of simple pyridyl-urea ligands (R = *p*-tolyl **1a**, *n*-octyl **1b**) readily synthesised in 90–95% yields from 3-aminopyridine and the appropriate isocyanate. The pyridine nitrogen atoms are capable of binding a metal cation while the urea groups are known to bind strongly to anions.<sup>10,11</sup> Reaction of **1a** with labile Ag(I) as the nitrate, triflate and sulfate salts in methanol-water (50 : 50) results in the isolation of a series of complexes of 1 : 2 stoichiometry, namely [Ag(**1a**)<sub>2</sub>](NO<sub>3</sub>)·MeOH **2**, [Ag(**1a**)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)·0.5H<sub>2</sub>O **3** and [Ag(**1a**)<sub>2</sub>]<sub>2</sub>(SO<sub>4</sub>) **4**, all of which have been characterised

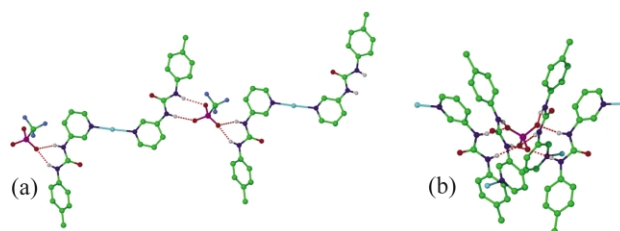


crystallographically. †It is to be expected from Etter's rules that the urea NH donors should interact with the anions in each case since the anion oxygen atoms are the strongest hydrogen bond acceptors. In the case of complexes **3** and **4** these interactions result in infinite hydrogen bonded assemblies in the solid state in which each anion is surrounded by an array of two or four urea groups (in the case of **3** and **4** respectively) all of which come from ligands attached to

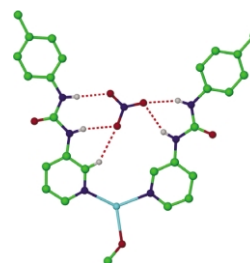
different metal centres. Thus in complex **3** triflate anions bridge between pairs of Ag(**1a**)<sub>2</sub><sup>+</sup> cations exhibiting both R<sub>2</sub><sup>2</sup>(8) and R<sub>1</sub><sup>2</sup>(6) motifs, Fig. 1a. In contrast, only the non-bifurcated R<sub>2</sub><sup>2</sup>(8) motif is observed for **4** with the double negative charge of the SO<sub>4</sub><sup>2-</sup> anion necessitating the surrounding of the anion by four urea groups instead of two, Fig. 1b.

In contrast, the nitrate complex **2** displays a much more interesting, discrete 1 : 1 assembly in which the nitrate anion is asymmetrically chelated by two ligands attached to the same metal centre, Fig. 2, forming a highly complementary cavity. The metal is approximately trigonal pyramidal with the third coordination site occupied by methanol. The deviation from linearity of the Ag...O–N vector is extremely interesting. Exact linearity would give two R<sub>2</sub><sup>2</sup>(8) motifs<sup>12</sup> as observed intermolecularly for **4**. In contrast, the rotation away from 180° (155°, 156° or 165° in three independent molecules) results in formation of the two motifs observed for **3** and allows the formation of an extra CH...O interaction. The crystal packing in **2** is also fascinating with 3.5 independent molecules.<sup>13</sup> The extra half is situated on a two-fold rotation axis and hence exhibits an apparently linear Ag...O–N vector since all atoms lie on the rotation axis. In fact the anisotropic displacement ellipsoids indicate that this apparent symmetry is a disorder average of two orientations that are similar to those observed for the other three independent molecules. The whole [Ag(**1a**)<sub>2</sub>](NO<sub>3</sub>)·MeOH in **2** is almost exactly planar. The solid state structure comprises discrete, π-stacked seven-molecule aggregates (Fig. 3) held together by OH...O interactions from the coordinated methanol to the urea carbonyl and, in the centre, long Ag–O bonds to urea carbonyls (2.53 Å). The heptamer is terminated by CH...O interactions.

Complexes **3** and **4** also exhibit remarkable crystal packing arrangements. Complex **3** exists as discrete, helical trimers linked



**Fig. 1** Infinite solid state arrays mediated by hydrogen bonding (a) R<sub>2</sub><sup>2</sup>(8) and R<sub>1</sub><sup>2</sup>(6) (bifurcated acceptor) in complex **3** and (b) non-bifurcated interactions in **4**.



**Fig. 2** The discrete [Ag(**1a**)<sub>2</sub>](NO<sub>3</sub>)·MeOH in **2** showing the slight tilt of the nitrate anion.

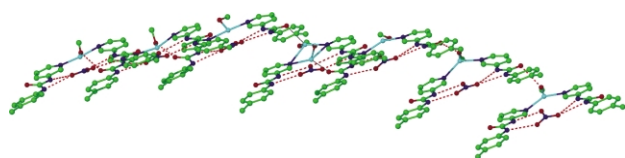


Fig. 3 One of the discrete heptameric assemblies in **2**.

by long range Ag–O and CH...O interactions, while **4** possesses linear, polar chains in which the Ag(**1a**)<sub>2</sub> units interdigitate, Fig. 4.

Infinite assemblies such as found in **3** and **4** are not expected to persist in solution, and indeed all species are distinctly insoluble once crystalline. However, a series of <sup>1</sup>H NMR experiments were carried out on supersaturated samples (which are relatively slow to nucleate) in order to probe the possibility of the discrete assembly in **2** forming and persisting in solution. Fig. 5 shows the <sup>1</sup>H NMR spectrum of ligand **1a** in acetone solution (A) alone, (B) following addition of half an equivalent of NBu<sub>4</sub>(NO<sub>3</sub>), (C) following addition of half an equivalent of Ag(CF<sub>3</sub>SO<sub>3</sub>) and (D) addition of half an equivalent of NBu<sub>4</sub>(NO<sub>3</sub>) to a solution of **1a** + ½Ag(CF<sub>3</sub>SO<sub>3</sub>) as in 'C'. The spectra clearly indicate that in the presence of nitrate or Ag<sup>+</sup> and a non-coordinating counter ion (NBu<sub>4</sub><sup>+</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) there is little change in the chemical shift of **1a**. However, when both Ag<sup>+</sup> and NO<sub>3</sub><sup>-</sup> are present a very marked change is observed with Δδ 1.2 ppm for the NH protons of **1a**. This result is consistent with solution self-assembly of complex **2**. Precipitation of **2** over periods of ca. 10 min makes NMR titration a difficult task, however, a titration curve and Job plot were obtained by addition of NBu<sub>4</sub>(NO<sub>3</sub>) to solutions of **1a** containing one equivalent of

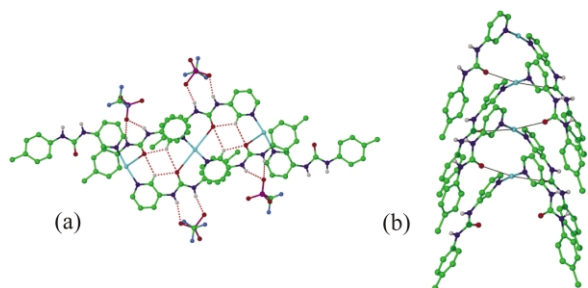


Fig. 4 Crystal packing (a) a discrete trimer in **3** and (b) an infinite polymer in **4**.

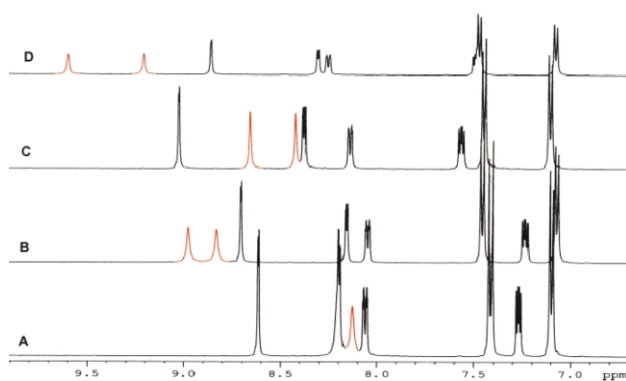


Fig. 5 <sup>1</sup>H NMR spectrum of ligand **1a** (A) alone, (B) following addition of half an equivalent of NBu<sub>4</sub>(NO<sub>3</sub>), (C) following addition of half an equivalent of Ag(CF<sub>3</sub>SO<sub>3</sub>) and (D) addition of half an equivalent of NBu<sub>4</sub>(NO<sub>3</sub>) to a solution of **1a** + ½Ag(CF<sub>3</sub>SO<sub>3</sub>). NH peaks highlighted in red.

Ag(CF<sub>3</sub>SO<sub>3</sub>). The Job plot reaches a clear maximum at 0.33 indicating 1 : 2 stoichiometry ([Ag(**1a**)<sub>2</sub>] : NO<sub>3</sub>), while the titration data give nitrate binding constants, K<sub>11</sub>, of 17000 M<sup>-1</sup> and K<sub>12</sub> of 1660 M<sup>-1</sup> for Ag(**1a**)<sub>2</sub> in the presence of triflate. Thus, while [Ag(**1a**)<sub>2</sub>](NO<sub>3</sub>) is extremely stable, in the presence of excess nitrate there is gradual formation of an additional 1 : 2 complex in which each urea group interacts with a different nitrate anion.

In summary, the simple highly labile Ag<sup>+</sup>–**1a** system is templated in both the solid state and solution by NO<sub>3</sub><sup>-</sup> to give a discrete host–guest assembly. Non-complementary anions such as CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> do not form analogous species. This result, in a labile, thermodynamic self-assembly regime highlights the modularity<sup>7,8,14–16</sup> of hydrogen bonding pyridine based systems. The same ligand **1a** may also be used in a covalent anion binding host.<sup>17</sup>

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## Notes and references

† Crystal data: for compound **2**: C<sub>27</sub>H<sub>30</sub>AgN<sub>7</sub>O<sub>6</sub>, *M* = 656.45, monoclinic, *a* = 49.675(4), *b* = 13.4895(10), *c* = 33.477(3) Å, *U* = 18996(3) Å<sup>3</sup>, *T* = 120(2) K, space group *C2/c* (no. 15), *Z* = 28, μ(Mo–Kα) = 0.799 mm<sup>-1</sup>, 57083 reflections measured, 18601 unique (*R*<sub>int</sub> = 0.0613) which were used in all calculations. The final *R*1 and *wR*2 were 0.0660 and 0.1593 [*I* > 2σ(*I*)]. For compound **3**: C<sub>27</sub>H<sub>26.67</sub>AgF<sub>3</sub>N<sub>6</sub>O<sub>5.33</sub>S, *M* = 717.47, triclinic, *a* = 7.1774(5), *b* = 16.7930(15), *c* = 19.6054(18) Å, α = 107.586(3), β = 93.998(3), γ = 91.066(4), *U* = 2245.2(3) Å<sup>3</sup>, *T* = 120(2) K, space group *P1* (no. 2), *Z* = 3, μ(Mo–Kα) = 0.810 mm<sup>-1</sup>, 7417 reflections measured, 5223 unique (*R*<sub>int</sub> = 0.0531) which were used in all calculations. The final *R*1 and *wR*2 were 0.0566 and 0.1255 [*I* > 2σ(*I*)]. For compound **4**: C<sub>52</sub>H<sub>52</sub>Ag<sub>2</sub>N<sub>12</sub>O<sub>8</sub>S, *M* = 1220.86, tetragonal, *a* = 17.4146(6), *c* = 8.2655(6) Å, *U* = 2506.7(2) Å<sup>3</sup>, *T* = 150(2) K, space group *P4<sub>2</sub>c* (no. 114), *Z* = 2, μ(Mo–Kα) = 0.892 mm<sup>-1</sup>, 21760 reflections measured, 3055 unique (*R*<sub>int</sub> = 0.0299) which were used in all calculations. The final *R*1 and *wR*2 were 0.0307 and 0.0749 [*I* > 2σ(*I*)]. CCDC 233238, 233239 and 238925. See <http://www.rsc.org/suppdata/cc/b4/b402882a/> for crystallographic data in .cif or other electronic format.

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