Influence of hydrogen bonding on coordination polymer assembly

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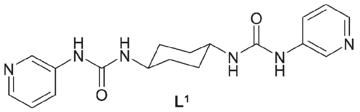
An extended dipyridyl ligand (L^1) capable of hydrogen bonding with guest species *via* urea functionalities has been designed and synthesised. Assembly of a silver(I) coordination polymer of L^1 is dependent on the nature of the hydrogen bond acceptor in a logical extension of the monopyridyl analogue.

Work by Bondy, Gale and Loeb, and by ourselves has resulted in a number of discrete, solution-phase anion binding systems with metal ions at their core.[1–6] Such complexes may be regarded as coordination complex anion hosts,[1,4] or as the result of thermodynamic self-assembly of a metal salt with ligands containing both hydrogen bonding and Lewis basic functionality.[5–8] Thus Loeb and Gale have produced platinum(II) complexes of amide or urea-derived pyridyl species that bind oxoanions. Their work culminated in the recent report of an elegant sulfate binding complex in which the anion is held by four converging urea functionalities.[3] Similarly we have recently reported the $AgNO_3$ templated solution self-assembly of the discrete complexes $[Ag(L^2)_2(S)](NO_3)$ (**1**) (S = MeOH or NO_2Me) which have been characterised crystallographically (Fig. 1).[5,6] Ligand L^2 also forms ML_4 complexes capable of trapping a water square.[9]

In previous work we have shown that the geometry of 1D coordination polymeric species is potentially susceptible to control by inter-strand hydrogen bonding interactions.[10] We reasoned therefore that elaboration of L^2 to form a bidentate, divergent bridging ligand possessing hydrogen bonding functionality would result in coordination polymeric materials with geometry templated by hydrogen bonding interactions with nitrate or other strong hydrogen bond acceptors. In the case of urea derivatives the $R_2^2(8)$ and $R_1^2(6)$ hydrogen bonding motifs (in graph set nomenclature[11]) to oxoanions or monatomic acceptors, respectively, are particularly prevalent and both are found in **1** (Fig. 1).[12] We now report preliminary results of this study in the form of ligand L^1, based on a *trans* 1,4-disubstituted cyclohexyl spacer.



L^1

Ligand L^1 is readily prepared in good yield in a single step from reaction of *trans*-cyclohexane-1,4-diisocyanate with two equivalents of 3-aminopyridine, and has been fully characterised by ^1H and ^{13}C-{^1H} NMR spectroscopy, ESI-MS and elemental analysis. The ligand is sparingly soluble in polar solvents such as DMSO and aqueous methanol. Reaction of L^1 with $AgNO_3$ in DMSO–acetonitrile (50 : 50 v/v) or acetonitrile–methanol–water (3 : 9 : 1 v/v) gave two crystalline 1 : 1 products of formula $[Ag(L^1)]NO_3 \cdot 2DMSO$ (**2**) and $[Ag(L^1)]NO_3 \cdot 3H_2O$ (**3**) both of which have been characterised by X-ray crystallography† and IR spectroscopy in the solid state. Bulk composition has been confirmed by elemental analysis. Both Ag(I) and L^1 represent linear 2-connected tectons[13,14] given the linear geometry usually associated with Ag(I) complexes,[15] and hence complexes **2** and **3** would be expected to be linear 1D coordination polymers since the pyridyl functionalities in L^1 have been chosen to be non-convergent. This connectivity indeed proved to be the case for both **2** and **3**, however, as with **1**, complex **2** exhibits a distorted linear coordination geometry at the Ag(I) centre with the N(1)–Ag–N(6) vector bent to 153.84(4)°. This distortion exposes one face of the Ag^+ ion to long range interactions to the two DMSO oxygen atoms and the nitrate anion. This result is in keeping with **1** which is even more bent (*ca.* 130–133°; several independent molecules). The significant deviation from linearity noted for **1** is a result of the wrapping of the urea groups around the nitrate anion. Compound **2**, exhibits convergent hydrogen bonding of the urea groups further along the ligand (farthest from to the metal linking the ligand pair) to the oxygen atoms of the included DMSO molecules that, in turn, form long range interactions to a symmetry equivalent Ag(I) complex, Fig. 2. The formally zwitterionic DMSO is clearly the best hydrogen bond acceptor and the resultant coordination polymer adopts a highly pleated structure (Fig. 3) in order to envelop the guest complex in what amounts to self-inclusion of one polymer chain in another.

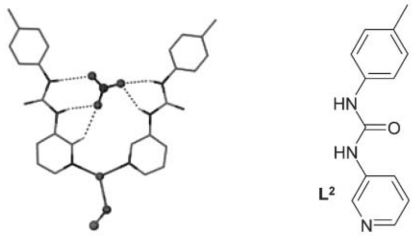


Fig. 1 The discrete complex $[Ag(L^2)_2(MeOH)](NO_3)$ **1** formed from monodentate ligand L^2.[5,6]

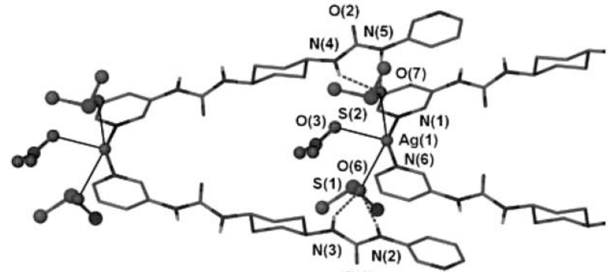


Fig. 2 Convergent self-inclusion in adjacent units of **2** mediated by DMSO molecules weakly interacting with the Ag(I) centre (thin black lines). Selected bond lengths (Å): Ag–N(1) 2.198(1), Ag–N(6) 2.190(1), Ag–O(3) 2.549(1), Ag–O(6) 2.816(1), Ag–O(7) 2.639(1).

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The DMSO oxygen atoms are held by $R_1^2(6)$ motifs,[12] one of which (involving N(2) and N(3)) is more symmetrical than the other, and is included in a pocket formed between pairs of ligands coordinated to the same Ag(I) centre, fig. 2. The situation is thus a reverse of that in **1** in which nitrate templates the formation of the structure and the neutral solvent molecules take advantage of the exposed metal ion surface. The nature of the coordination polymer propagation is shown in Fig. 3.

While interesting, this result is highly dependent on the properties of the serendipitously included DMSO and we sought to avoid DMSO inclusion by a change of ligand solvent medium to a less strongly hydrogen bond accepting methanol–water mixture (9 : 1 v/v). This resulted in the isolation and characterisation of complex **3** which has the same $[Ag(L^1)]NO_3$ formula for the metal complex and same connectivity as **2** but exhibits a radically different and much more open structure controlled by hydrogen bonding of the urea groups to the nitrate anions and water molecules, Fig. 4. While the ratio of two urea functionalities to one nitrate anion suggests that nitrate could be chelated by two urea functionalities, in fact an open geometry is adopted in which one urea group forms a $R_2^2(8)$ motif to a nitrate anion while the other takes part in a $R_1^2(6)$ unit involving a water molecule. The opposite face of the nitrate anion is involved in a large $R_8^6(16)$ unit involving two anions and four water molecules, including two that accept hydrogen bonds from the urea as part of the $R_1^2(6)$ units (Fig. 4). The remaining unique water molecule forms a long interaction with the Ag^+ ion, Ag(1)–O(6) 2.728(4) Å and hydrogen bonds to a urea carbonyl group and one of the nitrate oxygen atoms. Overall, the inclusion of water allows a relatively unstrained structure with a comparatively linear N–Ag–N vector of 168.97(14)°, compared to the much more distorted geometry seen for **1**. This result also contrasts to the distortion induced by the stronger acceptor DMSO in **2** which also involves the coordination of the nitrate anion, a phenomenon also observed in solution.[6]

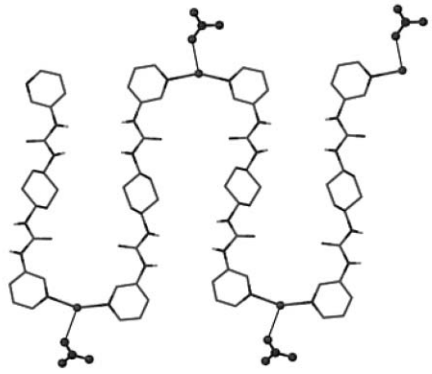

Fig. 3 The polymeric structure of **2**.

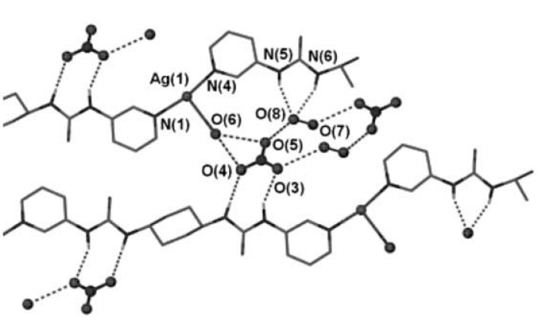

Fig. 4 Two parallel polymer chains in **3** showing the hydrogen bonding arrangement including the $R_8^6(16)$ unit involving two nitrate anions and four water molecules. Selected bond lengths (Å): Ag–N(1) 2.128(3), Ag–N(4) 2.138(3), Ag–O(6) 2.728(4).

In conclusion, by analogy to the discrete system **1**, we have generated a topologically predictable 1D coordination polymer in which the degree of folding is controlled by hydrogen bonding interactions to the hydrogen bond donor groups positions on the ligand spacer. Hydrogen bonding to the nitrate anion is dominant as for the monomeric system **1**, except in the presence of the strong hydrogen bond acceptor DMSO. This effect is echoed in our recent work on the reproducibility of the $R_1^2(6)$ urea···Cl–M synthon in metal chloride complexes of **1** and its *para* analogue.[12] A range of analogues of L^1 exhibiting varying length, degree of curvature and substitution pattern are currently under development.

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Notes and references

† Crystal data for **2**: $C_{22}H_{34}AgN_7O_7S_2$, M = 680.55, monoclinic, space group $P2_1/c$ (No. 14), a = 12.9266(5), b = 13.3289(5), c = 16.5474(7) Å, β = 105.3550(10)°, V = 2749.30(19) Å^3, Z = 4, D_c = 1.644 g cm^{-3}, F_{000} = 1400, Bruker Proteum-M with Bede Microsource, MoKα radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 61.0°, 35951 reflections collected, 8354 unique (R_{int} = 0.0190). Final *GooF* = 1.050, *R1* = 0.0254, *wR2* = 0.0648, *R* indices based on 7542 reflections with $I > 2\text{sigma}(I)$ (refinement on F^2), 372 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.940 mm^{-1}. CCDC 259231. Crystal data for **3**: $C_{18}H_{28}AgN_7O_8$, M = 578.34, colourless plate, triclinic, space group $P\bar{1}$ (No. 2), a = 9.4135(7), b = 10.9132(9), c = 12.3810(10) Å, α = 110.4250(10), β = 95.5680(10), γ = 102.5200(10)°, V = 1142.69(16) Å^3, Z = 2, D_c = 1.681 g cm^{-3}, F_{000} = 592, MoKα radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 61.1°, 14718 reflections collected, 6835 unique (R_{int} = 0.0421). Final *GooF* = 1.135, R_1 = 0.0575, *wR2* = 0.1536, *R* indices based on 5952 reflections with $I > 2\text{sigma}(I)$ (refinement on F^2), 340 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.942 mm^{-1}. CCDC 259232. See http://www.rsc.org/suppdata/cc/b4/b419216h/ for crystallographic data in CIF or other electronic format.

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