Anion hydrogen bond effects in the formation of planar or quintuple helical coordination polymers†

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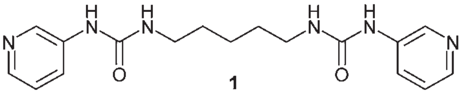
A relatively inflexible 1D coordination polymer is induced to adopt either planar or quintuple helical supramolecular isomers according to the hydrogen bonding demands of the counter anions.

There is growing interest in the design and control of supramolecular helicity in coordination polymer systems[1–7] because of their potential applications in sorption and separation science, and the topic was reviewed in 2005.[8] A single helix is simply a linear strand that has been induced to wind around an axis, turning in a single direction as it moves along that axis. The strand thus develops *M* or *P* chirality according to the direction of that turn. Coordination polymer systems are particularly versatile in generating helicity because of their tremendous synthetic malleability allowing the incorporation of a wide variety of nodes, spacers and secondary functionality that can control the way in which a strand propagates and twists, and how it interacts with neighbouring strands. In their work on hydrogen bonded helical 'molecular braids' Hosseini and co-workers have characterised the assembly of helical structures in terms of first level assembly—molecular conformational effects leading to helix formation, second level assembly—the mutual interbraiding of more than one independent helix and third level assembly corresponding to the lateral association of the braids into a solid network.[9] First level assembly of a helix may be incorporated into molecular design, as in the twisted binaphthyl unit reported by Lin and co-workers,[10] or in more flexible systems it may be imposed by the requirements of the second and third level assembly constraints. Second level assembly is also subject to molecular design since helical braiding, like interpenetration, is related to space filling requirements and thus a long spacer between helical turns will favour highly interbraided systems. Third level assembly should also be subject to manipulation by the use of molecular functionality not directly connected to helix formation that takes part in lateral interactions. Hosseini and co-workers were successful in preparing a remarkable quintuple helical braid using a hydrogen bonded polymer.[9] In coordination polymers, while single, double, triple and even quadruple helices are relatively well known,[8] there are very few examples of quintuple helices.[6,10,11] Among others in the field,[12–14] we have been looking at the influence hydrogen bonding within coordination polymers and hydrogen bonding to anions has on their shape and symmetry.[15–17] We now report a flexible coordination polymer system in which the third level assembly interactions with anions and solvent by means of hydrogen bonding influence the first and second level assembly, leading either to a quintuple helical molecular braid or to its planar supramolecular isomer.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The bifunctional bis(pyridylurea) ligand **1** (an extended version of the ethylene spacer analogue[18,19]) was designed to form a linear strand coordination polymer by coordination to the pyridyl groups while interacting with counter anions *via* the urea functionality.[20,21] The long pentamethylene spacer ensures a large network by creating a large gap between the functional ends. The ligand was prepared as reported elsewhere[19] and reacted with $AgNO_3$ and $AgBF_4$ to produce two new crystalline 1D coordination polymers of formula $[Ag(\mathbf{1})]NO_3{\cdot}MeCN{\cdot}1.75H_2O$ (**2**) and $[Ag(\mathbf{1})]BF_4{\cdot}0.5thf{\cdot}0.5H_2O$ (**3**) which were characterised by X-ray crystallography, elemental analysis and in the case of **3** powder X-ray diffraction (see supplementary data†).‡ In each case the ligand adopts a planar, all-*anti* conformation placing the urea NH donors on the same side of the molecule. Each strand thus has a hydrogen bond donor face comprising four NH groups, and a hydrogen bond acceptor face comprising two urea carbonyl groups. One urea functionality in each ligand in both structures is involved in the formation of the typical $R_2^2(8)$ hydrogen bonded ring synthon to the anion (in graph set nomenclature[22]).[16,23,24] The other urea groups interact with solvent molecules. In the case of **2** this interaction is with the water molecule, forming an $R_2^1(6)$ motif with the water acting as a bifurcated acceptor. The water in turn hydrogen bonds to an adjacent nitrate anion. The $NO_3^-{\cdot}H_2O$ unit is thus nestled between offset pairs of urea groups in the overall polar structure in space group $Pna2_1$, Fig. 1. This co-planar sandwiching of a nitrate anion or $NO_3^-{\cdot}H_2O$ unit is typical for these types of structures and arises because the nitrate anion is a good hydrogen bond acceptor around all edges but not perpendicular to the nitrate plane.[16,23,24] The remaining water OH hydrogen atom hydrogen bonds between planar sheets, while the acetonitrile

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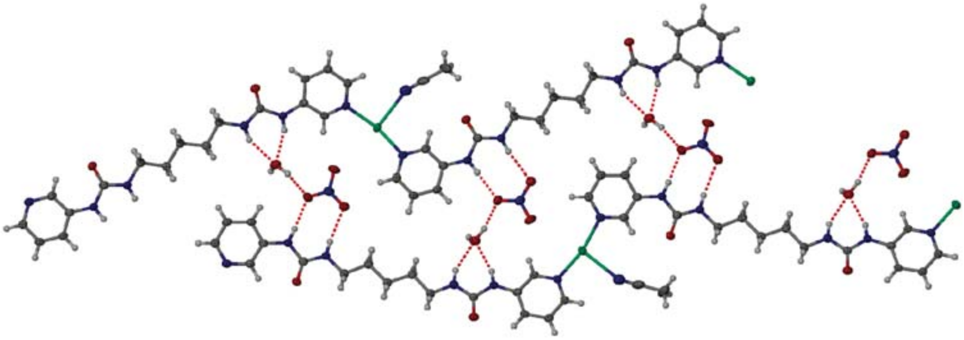

Fig. 1 Co-planar interactions between the coordination polymer strands, water and nitrate anions in **2**. Selected hydrogen bond distances (Å) $NH\cdots O_3N^-$ 2.846(4) and 3.008(4) Å, $NH\cdots OH_2$ 2.853(4) and 2.917(4) Å, $OH_2\cdots O_3N$ 2.735(4) and 2.790(5) Å.

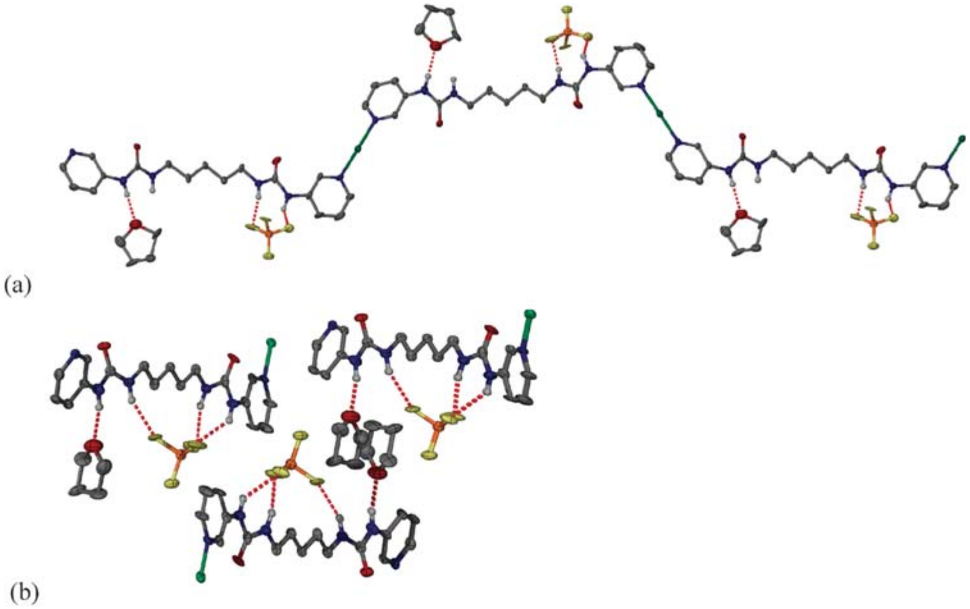

Fig. 2 Hydrogen bonding to BF_4^- anions and thf in **3** (a) part of a single strand, (b) stacks of strands showing the third interaction with the anion perpendicular to the chain direction. Selected hydrogen bond distances (Å) $NH\cdots F_4B^-$ 3.05(3), 2.90(3), 2.78(3), 3.11(5), 3.01(4) Å, $NH\cdots O$ 2.83(2) Å.

molecule coordinates weakly to the Ag(I) ion. Sheets are linked back-to-back by an additional disordered water molecule that interacts with the carbonyl acceptors. In contrast to **2**, in compound **3**, the urea unit that is not bound to the BF_4^- anion interacts 50% of the time with a water molecule and 50% of the time with a molecule of thf. The presence of thf or water in this site is correlated to a twofold disorder of the BF_4^- anion allowing it to form one of two equivalent $R_2^2(8)$ motifs with the other urea group. The opposite face of the BF_4^- anion forms moderately strong $CH\cdots F$ interactions with an adjacent polymer strand but does not interact with the urea groups. The water, thf and BF_4^- anions overall are held in a pocket in between columns of coordination polymer interacting with urea groups on adjacent columns in a nearly-orthogonal fashion, Fig. 2. This orthogonal inter-stack interaction is reflected by the mutually near-orthogonal arrangement of the ligands within the stacks which causes them to form a twofold helical arrangement of pitch 37.0 Å. The space left within this arrangement by the long pentamethylene chain results in the mutual intertwining of five such helices to give a quintuple helical molecular braid, Fig. 3.

The robustness of the planar $R_2^2(8)$ hydrogen bonding motifs from urea to NO_3^- and BF_4^- was addressed by a search of the Cambridge Structural Database. In the case of nitrate 20 structures exhibiting the $R_2^2(8)$ urea–NO_3^- motif were found containing 33 instances of the interaction of which just eleven examples exhibited significant non-planarity. In the case of the BF_4^- anion there are fewer examples, with the search only finding three structures and six independent motifs of which just one contains a non-coplanar $O{=}C(NH)_2\cdots F_2B$ unit.

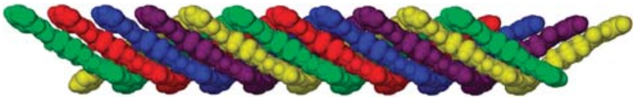

Fig. 3 Quintuple helical molecular braid. Independent strands are shown in different colours.

Work is in progress on the synthesis of related compounds with other anions. Preliminary data indicate that the silver(I) acetate complex exhibits near-planar chains related to the nitrate complex **2**, consistent with the planarity of the acetate anion (see supplementary information†).

In conclusion, therefore, we can regard the ligand **1** and the linear two-coordinate Ag(I) ion as essentially rigid tectons because the conformation of **1** is dominated by the strong preference for intramolecular CH···O interactions from pyridyl to carbonyl[19] and the tendency towards adopting an all-*anti* conformation along the oligomethylene chain. There is thus only freedom to change crystal packing by rotation about the Ag–N bonds adopting either a planar arrangement (as in **2**) or a twisted helical arrangement as in **3**. Which of these supramolecular isomers is adopted depends purely on the hydrogen bonding to the anions and solvent and hence their geometry.

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Notes and references

‡ Crystal data for **2**: $C_{19}H_{28.50}AgN_8O_{6.75}$, $M = 584.87$, $0.32 \times 0.27 \times 0.14$ mm^3, orthorhombic, space group $Pna2_1$ (No. 33), $a = 34.975(3)$, $b = 12.5607(11)$, $c = 5.7537(5)$ Å, $V = 2527.7(4)$ Å^3, $Z = 4$, $D_c = 1.537$ g cm^{-3}, $F_{000} = 1198$, SMART6000, MoKα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 55.0°$, 14 617 reflections collected, 5580 unique ($R_{int} = 0.0353$). Final $GooF = 1.037$, $R1 = 0.0375$, $wR2 = 0.0919$, R indices based on 4842 reflections with $I > 2\sigma(I)$ (refinement on F^2), 334 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 0.850$ mm^{-1}. Absolute structure parameter = −0.03(3).[25] Crystal data for **3**: $C_{19}H_{26}AgBF_4N_6O_3$, $M = 581.14$, $0.23 \times 0.17 \times 0.13$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 15.4790(17)$, $b = 7.3940(8)$, $c = 21.154(2)$ Å, $\beta = 96.132(4)°$, $V = 2407.2(4)$ Å^3, $Z = 4$, $D_c = 1.604$ g cm^{-3}, $F_{000} = 1176$, SMART 1000, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 50.0°$, 22 311 reflections collected, 4204 unique ($R_{int} = 0.0601$). Final $GooF = 1.220$, $R1 = 0.1264$, $wR2 = 0.2940$, R indices based on 3735 reflections with $I > 2\sigma(I)$ (refinement on F^2), 351 parameters, 72 restraints. Lp and absorption corrections applied, $\mu = 0.901$ mm^{-1}.

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