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Helical templating of polyiodide networks at a binuclear metallo complex†

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A homobimetallic supramolecular helicate has been prepared from a new multimodal ligand, and used to template the formation of two polyiodide networks, one containing an unprecedented figure-of-eight polyiodide helix, the other dominated by peripheral C–H···I polyiodide chain interactions.

The construction of novel solid-state frameworks is a major goal in supramolecular inorganic and materials chemistry.[1] One of the few systems utilised for the formation of extended anionic inorganic frameworks is that formed by polyiodides. These are constructed from varying ratios of I_2 and I^- and may result in extended donor–acceptor arrays. Whilst the smaller polyiodides such as I_3^-, I_4^{2-} and I_5^- show a limited range of geometries, larger extended polyiodide anions exhibit a range of topologies,[2] which are highly dependent on the size, shape and charge of the templating cation.[3–6] To date there are no examples of helical cations successfully templating anion networks in which there is a direct translation of geometrical properties from one component to the other. We report herein shape-translation *via* supramolecular contacts, and examine the effect of increasing iodine content on the nature of the resulting interactions.

The new multimodal ligand, bis[6,6′-(*N*-2″-pyridylmethylidenehydrazino)][2,2′-bipyridine] (L) (Fig. 1) forms binuclear complexes with a range of transition metal cations, including Co(II), Ni(II), Cu(II), Cu(I), Zn(II) and Ag(I). The reaction of dark yellow $[Ni_2(L)_2][BF_4]_4$ with a mixture of NaI and I_2 in MeCN and subsequent diffusion of Et_2O vapour into this solution resulted in growth of lustrous dark red crystals of $[Ni_2(L)_2]I_{24}\cdot 4MeCN$, **1**. When the experiment was performed with a five-fold increase in scale, but otherwise identical starting concentrations and diffusion conditions, the crystals produced were found to be of a second material, $[Ni_2(L)_2]I_{13}\cdot 2MeCN$, **2**.

The asymmetric unit of **1** contains half of a $[Ni_2(L)_2]^{4+}$ cation and a polyiodide component, nominally I_{12}^{2-}. The structure of the metal complex cation is a double helix (Fig. 2) with each Ni(II) centre in a distorted octahedral environment of six N-donors from two ligands. The Ni···Ni distance in the complex is 4.167(5) Å, and the torsion angle about the central bipyridyl unit (N–C–C–N) of the ligand is 49.4(1)°. **1** crystallises in the centrosymmetric spacegroup *C*2/*c*, and contains a racemic mixture of the *P* and *M* enantiomers of the complex cation. Despite the shape of the complex, and its extended aromatic surfaces, the cations do not participate in aryl embraces,[3,7,8] the polyiodide array, made up of interacting I_3^- and I_2 molecules, effectively holding the cationic components apart.

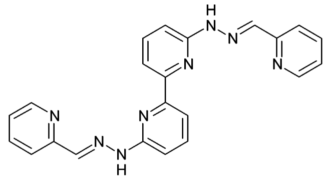

Fig. 1 The hexadentate ligand presenting two N_3 coordination sites.

The structure of the polyiodide repeat unit in **1** (Fig. 3) consists of an infinite chain of iodine atoms with an I_5 repeat unit I(11)–I(8)–I(9)–I(10)–I(12) which propagates through I(11) and I(12) by their symmetry-related equivalents I(11)′ and I(12)′. Appended to this chain are twisted rectangular I_7 arms, which have a van der Waals contact I(1)–I(10) of 3.729 Å to define an I_{10} loop. The infinite chains are of particular interest since they form an unprecedented figure-of-eight helix which runs approximately along the *b* direction. These polyiodide chains form corrugated layers in the *ab* plane with homochiral helices running parallel in the same layer. Adjacent layers contain helices of opposite chirality, which run with an offset angle of approximately 30°. The I_7 arms on each helix are interdigitated and wrap about the complex cations, which lie between the corrugated layers connected in a herringbone net by the infinite polyiodide chains. Within each *ab* layer, the cations are homochiral, but these layers alternate to give an overall racemic structure. Each cation is enveloped within a double helix constructed from two of the infinite polyiodide chains,

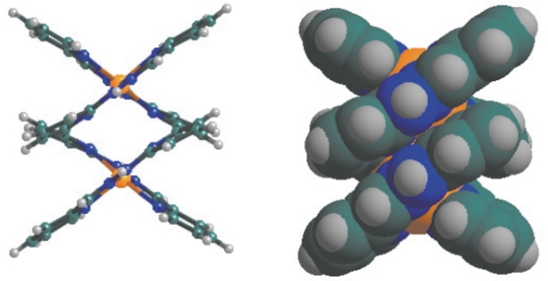

Fig. 2 The helical cation $[Ni_2(L)_2]^{4+}$, shown in ball-and-stick view and space-filling representations. Carbon, green; nitrogen, blue; nickel, orange; and hydrogen, grey.

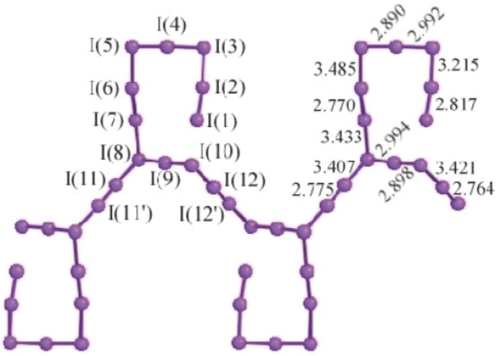

Fig. 3 The polyiodide component with atom numbering scheme shown on the left and iodine···iodine distances (Å) on the right.

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† Electronic supplementary information (ESI) available: synthetic details, crystal data (CCDC 198624 and 198625 in CIF format) and views of the C–H···I and H···I interactions between I_6^{2-} and I_3^- and the cationic component in **2**. See http://www.rsc.org/suppdata/cc/b2/b211743f/.

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rather like a sweet in a wrapper (Fig. 4). The remaining exposed front and back surfaces of the cation are covered by I_7 loops originating from the adjacent interdigitating polyiodide layers. Each cation is, therefore, encapsulated by six polyiodide chains, two from its nearest-neighbour layers, and four fragments from subsequent layers.

The FT-Raman spectrum of **1** shows three bands at 108, 136 and 170 cm^{-1}. The first two are indicative of the presence in the polyiodide unit of two slightly asymmetric I_3^- [I(3)–I(4)–I(5), I(8)–I(9)–I(10)] and can be assigned to the symmetric and antisymmetric stretching modes, respectively. The remaining polyiodide is made up of I_2 molecules with slightly different degrees of elongation with *d*(I–I) ranging from 2.764 to 2.817 Å. This results in a single broad band observed at 170 cm^{-1} with the absorptions due to the *ν*(I–I) stretching vibrations for the four fragments falling within this envelope. These vibrations occur, as expected, at a lower frequency than that for pure I_2 (180 cm^{-1} in the solid state[4,6]).

The single crystal structure of **2** shows the asymmetric unit to contain one complex cation and a polyiodide consisting of four asymmetric I_3^- moieties and half of an I_2 molecule. The cation is found to have the same form as that of **1**, but is slightly asymmetric in shape, with two larger N–C–C–N bipy torsion angles of 68.79(6) and 62.64(6)° leading to a longer Ni···Ni distance of 4.586(2) Å. **2** crystallises in the centrosymmetric space group *P*1, and, like **1**, contains a racemic mixture of *P* and *M* helicate cations.

The polyiodide fragments in **2** combine to give the overall stoichiometry $[Ni_2(L)_2](I_3)(I_6)(I_8)_{0.5}$ (Fig. 5). The structure is dominated by weak C–H···I and N–H···I interactions. Taking the van der Waals radii of H and I to be 1.20 and 2.15 Å, respectively, any H···I contact less than 3.35 Å and C–H···I angle >130° may therefore potentially be considered significant. The structure of **2** shows many contacts which fulfill these distance and angle criteria, and furthermore displays a unique alignment of polyiodide fragments with respect to the ligand peripheries, with each cation having 29 C–H···I and N–H···I interactions. In comparison, complex **1**, despite its higher iodine content, shows only 11 C–H···I and N–H···I contacts per cation which meet the same criteria.

The I_8^{2-}component in **2** has only three C–H···I contacts and nestles within the groove formed by the helicate ligand surface. Each I_8^{2-} anion interacts with four cations and shows remarkable shape-complementarity in the solid-state packing (Fig. 6). The overall crystal packing of **2**, therefore, shows segregation of the cations into polyiodide-lined channels with the anionic chains running parallel to ligand edges and filling ligand grooves.

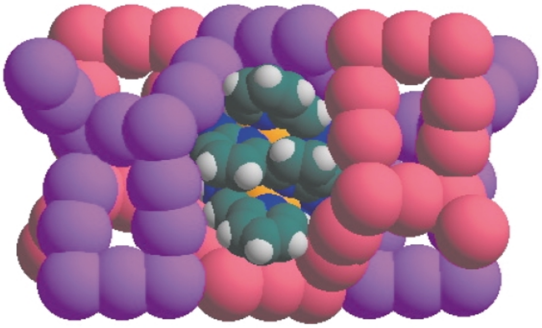

Fig. 4 View of a complex cation in **1** enveloped in a double helix constructed from two polyiodide chains.

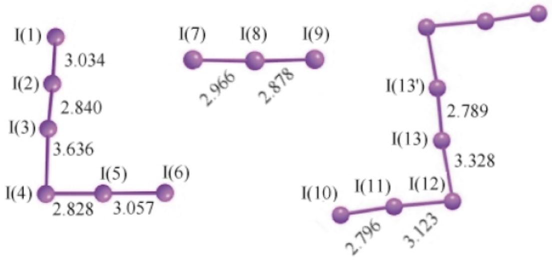

Fig. 5 The polyiodide components of **2** with atom numbering scheme and bond distances.

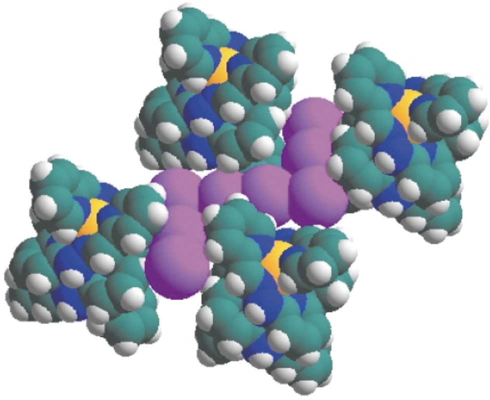

Fig. 6 A view of an I_8^{2-} fragment interacting with the four neighbouring cations in **2**. Note the shape-complementarity between the nestling iodine chain and the ligand surfaces.

The FT-Raman spectrum of **2** shows one very broad band centred at 153 cm^{-1}, with a shoulder at 138 cm^{-1} and a further broad band at 109 cm^{-1}. The bands centred at 109 and 138 cm^{-1} are consistent with the presence of differently asymmetric I_3^- units [I(1)–I(2)–I(3), I(4)–I(5)–I(6), I(7)–I(8)–I(9)] within the polyiodide matrix. The very broad band at 153 cm^{-1} (half-width of about 20 cm^{-1}) accounts for all the I–I stretching vibrations from the differently elongated diiodine molecules present in the structure [I(10)–I(11), I(13)–I(13')]. This is consistent[6] with a diiodine molecule with an I–I distance of around 2.8 Å, as is found in this complex structure.

An interesting point of comparison between **1** and **2** is that as the iodine content decreases the peripheral C–H···I interactions rather than I···ligand facial contacts are retained. The relatively energetically favourable C–H···I interactions are, therefore, present even at low iodine content, and as the iodine content increases, crystal packing affords more intimate wrapping of each cation leading to facial covering of the cationic aromatic surface.

This work has shown that by providing a helical template and by utilising the preference of polyiodides for mutually orthogonal interactions, two unique anionic supramolecular networks have been constructed. **1** displays tight-wrapping of cations by a complex polyiodide inducing a helical anionic strcuture, while **2** is dominated by peripheral C–H···I interactions.

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