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Construction of the first cross-linked double helical polyiodide

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A homobimetallic supramolecular helicate has been used to template the formation of a polyiodide network which adopts an infinite cross-linked double helical structure, topologically analogous to DNA.

In the targeted synthesis of supramolecular frameworks, the construction of helical arrays has been of particular interest. It has been shown that by appropriate combination of metal centres and multidentate ligands, systems ranging from discrete helicates[1] to co-ordination polymers containing infinite helices[2] can be prepared. However, whilst the preparation of discrete binuclear and oligonuclear double helical components is relatively straightforward, infinite double helical arrays have so far proven elusive.

The archetypal double helical structure is of course that of DNA, where two helical strands are cross-linked by the complementary hydrogen bonding between the nucleotide bases. Approaches to re-creating this topology have been varied, with the most important design feature being the mode of linkage between the helical strands. The use of hydrogen-bonding to cross-link the two strands is an obvious and effective starting point.[3] Other interactions which have been exploited to connect the strands include co-ordination bonds,[4] Ag–Ag interactions[5] and π–π aromatic stacking.[6]

One supramolecular synthon which has shown promise in the construction of supramolecular networks is that of polyiodide catenation.[7] The combination of (Lewis acidic) molecular iodine with (Lewis basic) iodide anions to form extended donor–acceptor arrays is a remarkable example of self-assembly, whose flexibility allows templation about a range of cations to produce networks of varying topology. We report herein the formation of a compound containing a helical cation whose polyiodide component displays the same cross-linked double helical topology seen in DNA.

The flexible multimodal ligand (L) has been designed to present two N_3-donor sites to transition metal centres M^{n+} (Fig. 1), resulting in the formation of binuclear metallohelicate complexes of the form $[M_2(L)_2]^{2n+}$. Reaction of one equivalent of yellow $[Zn_2(L)_2][BF_4]_4$ with a mixture of NaI (10 equivalents) and I_2 (15 equivalents) in MeCN, and subsequent diffusion of Et_2O vapour into the reaction solution, affords lustrous, dark red, diffraction-quality crystals.†

Single crystal X-ray diffraction studies‡ established the product as $[Zn_2(L)_2]I_{18}$. The complex crystallises in the centrosymmetric space group $P2/c$, with the asymmetric unit consisting of half of a complex cation and a polyiodide component, formally I_9^{2-}. The complex cation contains two Zn(II) cations co-ordinated by two ligands to give a distorted octahedral geometry about each Zn(II) centre. The Zn···Zn distance in the helicate is 5.409 Å, which is significantly longer than the Ni···Ni distance of 4.167 Å previously reported for the Ni(II) cation $[Ni_2(L)_2]^{4+}$.[8]

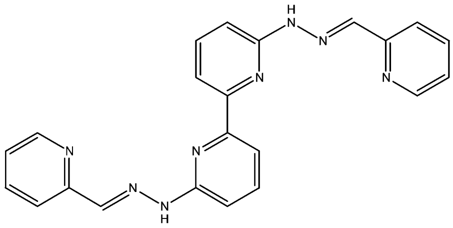

Fig. 1 The ligand L which presents two separate N_3-donor sites.

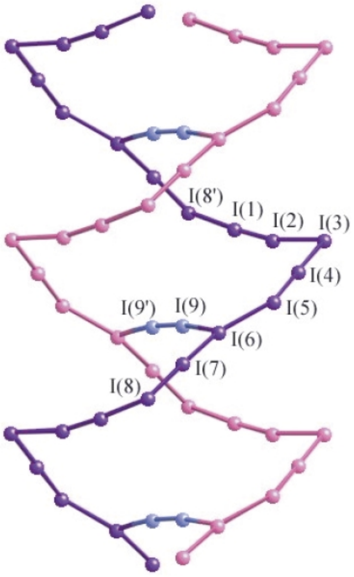

Fig. 2 Partial view of the infinite double helical polyiodide array $\{I_{18}^{4-}\}_\infty$ in $[Zn_2(L)_2]I_{18}$ with numbering scheme. The two helices and the diiodine link are shown in three different colours.

The nine iodines in the asymmetric unit consist of two asymmetric triiodide anions and one and a half di-iodine molecules. These are further linked by I···I contacts of between 3.414 and 3.664 Å to form a helical chain with the repeat unit I(1)–I(2)–I(3)–I(4)–I(5)–I(6)–I(7)–I(8), which runs parallel to the *b* direction in the crystal. Two of these chains are then cross-linked by the I_2 molecule I(9)–I(9′), which is itself bound to I(6) and I(6′) by contacts of 3.417 Å. The double helical polyiodide arrangement is shown in Fig. 2, and iodine–iodine distances are given in Table 1.

The crystal contains a racemic mixture of both cationic helicates and anionic polyiodide helices, which pack in an arrangement which fully utilises the shape-complementarity of the complex polyiodide with the ligand surfaces. Layers

Table 1 Iodine–iodine bonded and contact distances (Å)

I(1)–I(2)	2.743 (2)
I(2)–I(3)	3.518 (2)
I(3)–I(4)	3.009 (2)
I(4)–I(5)	2.853 (2)
I(5)–I(6)	3.664 (2)
I(6)–I(7)	2.870 (2)
I(7)–I(8)	3.029 (2)
I(8′)–I(1)	3.414 (2)
I(6)–I(9)	3.417 (2)
I(9)–I(9′)	2.730 (2)

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comprising one enantiomer of cationic helicate with the opposite enantiomer of polyiodide helix alternate (in the *ac* plane) with layers of opposite chirality (Fig. 3): thus each *P*-helicate cation is firmly wrapped by two *M*-helices of polyiodide, and *vice versa* (Fig. 4). The tendency of polyiodides to exhibit angles of around 90° complements the orthogonality within the coordinated ligand, allowing the polyiodide to wrap intimately around the cations, with the pitch of the polyiodide helix corresponding to the repeat required to fit one cation, 11.280(1) Å.§

The wrapping of the helicate cations occurs by interaction of the polyiodide chains with the aromatic ligand surfaces, with only three peripheral C–H···I and N–H···I interactions in the expected range (H···I < 3.35 Å and Y–H···I > 130°).[8,9] Indeed, the polyiodide chains generally run parallel to the ligand faces (Fig. 4.), with C–I distances of between 3.6 and 3.9 Å. It is noteworthy that the crystal contains no solvent molecules, thus confirming the high complementary and efficient packing of the flexible polyiodide about the cations. The role of diethyl ether in forming this product is, therefore, as an antisolvent.

The FT-Raman spectrum of the compound agrees very well with the assignment of the $\{I_{18}{}^{4-}\}_\infty$ double helical polyiodide array as $[\{(I_3)_4\cdot(I_2)_3\}^{4-}]_\infty$. Of the three bands observed at 106, 146 and 176 cm^{-1}, the first two can be assigned to the symmetric and asymmetric stretching modes, respectively, of the two very similar $I_3{}^-$ ions I(3)–I(4)–I(5) and I(6)–I(7)–I(8), while the third can be assigned to the stretching vibrations of the two slightly elongated I_2 molecules I(1)–I(2) and I(9)–I(9′). It is worth noting that all polyiodides lose I_2 at varying rates. Usually, the higher the $I_2 : I^-$ ratio, the faster this loss is. In $[Zn_2(L)_2]I_{18}$, the $I_2 : I^-$ ratio is only 1.75 : 1, so it should lose iodine at a rate slower than that of a simple $I_5{}^-$ salt. Indeed, repeated elemental analysis taken a few months after structure determination confirms no loss of I_2. In addition, the FT-Raman spectrum does not change upon long exposure of the compound to the laser excitation source and upon changing the power of the laser source, thus confirming the general stability of this polyiodide species.

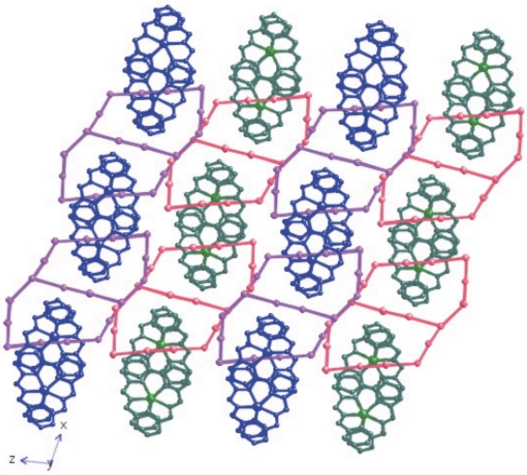

Fig. 3 View down the polyiodide helices, showing sections of opposite chirality. *P*-helicates shown in blue, *M*-helicates shown in green, *P*-polyiodide helices shown in pink, *M*-polyiodide helices shown in purple.

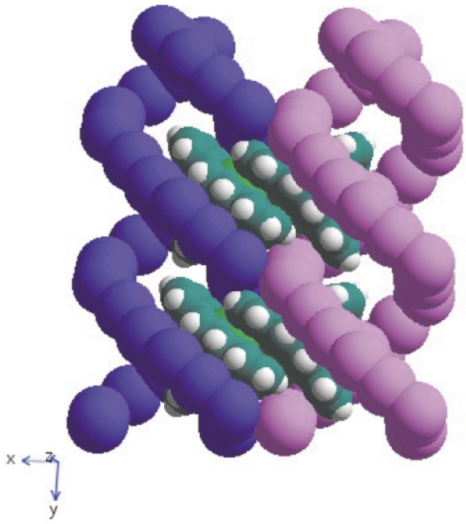

Fig. 4 View of two *M*-polyiodide double helices wrapping two *P*-metallohelicate cations. Note that close facial wrapping of cations by polyiodide is favoured over the formation of C–H···I contacts.

We have successfully constructed and characterised an infinite double helix containing only one type of atom. This unique arrangement was achieved by using the flexible supramolecular synthon of polyiodide catenation templated at a rigid helical cation. This system illustrates the direct transfer of geometrical properties (in this case helicity) from one crystal component to the other. This study demonstrates the great versatility of polyiodides and confirms their ability to undergo specific templating in the presence of cations. We are currently pursuing a vigorous study of the effect of cation geometry, hydrogen-bonding and π–π interactions upon polyiodide array formation.

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Notes and references

† Synthesis: The ligand L was prepared by reaction of 6,6′-dihydrazino-2,2′-bipyridine with 2 molar equivalents of pyridine-2-carbaldehyde in methanol solution. $[Zn_2(L)_2][BF_4]_4$ was prepared by reaction of $Zn[BF_4]_2\cdot 6H_2O$ with one equivalent of L in acetonitrile solution, then precipitated by addition of diethyl ether. Crystals of $[Zn_2(L)_2]I_{18}$ were prepared by the slow diffusion of diethyl ether vapour into a reaction mixture containing one molar equivalent of $[Zn_2(L)_2][BF_4]_4$, 10 molar equivalents of NaI and 15 molar equivalents of I_2 in acetonitrile. Anal. Calc. for $C_{44}H_{36}N_{16}Zn_2I_{18}$: C 16.49, H 1.13, N 6.99%. Found: C 16.67, H 1.02, N 6.81%.

‡ Crystal data: $C_{44}H_{36}N_{16}Zn_2I_{18}$, M = 3203.87, monoclinic, a = 15.505(2), b = 11.280(1), c = 21.938(2) Å, β = 107.268(2)°, U = 3664(1) Å^3, T = 150(2) K, space group $P2/c$ (No. 13), Z = 2, μ(Mo–Kα) = 8.281 mm^{-1}, 22871 reflections measured, 8505 unique (R_{int} = 0.029). Final R_1 [$I > 2\sigma(I)$] = 0.0361, $wR2$ [all data] = 0.0871. CCDC reference number 207149. See http://www.rsc.org/suppdata/cc/b3/b303289b/ for crystallographic data in .cif format.

§ This is the distance between an iodine atom I(x) and its symmetry equivalent I(x') which lies one unit cell away along the b axis.

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