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Second sphere supramolecular chirality: racemic hybrid H-bonded 2-D molecular networks

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Neutral hybrid 2-D networks have been generated using a bis-amidinium capable of chelating $M(CN)_6^{3-}$ anions *via* hydrogen bonds: the packing of the achiral 2-D networks leads to channels which are occupied by water molecules forming polymeric H-bonded chains; furthermore, owing to the dihapto mode of H-bonding, the presence of supramolecular chirality of the Δ' and Λ' types taking place within the second coordination sphere of the metallic centre has been demonstrated.

Molecular tectonics[1a] is an approach based on molecular recognition processes between programmed complementary tectons[1b] and deals with the formation of structurally predicted molecular networks under self-assembly conditions. Among various possible types of reversible interactions, owing to its directional nature, H-bonding has been widely used for the design of a variety of networks.[2] Using charge assisted hydrogen bonds, we have demonstrated that protonated bis-amidine derivatives are interesting tectons for the generation of H-bonded molecular networks using anionic carboxylate, sulfonate and phosphate derivatives.[3]

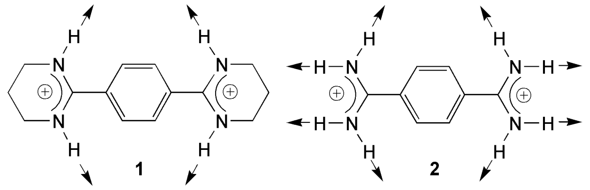
We report here an investigation dealing with the formation of H-bonded molecular networks using the dicationic tecton **1**[4] bearing four acidic protons and $M(CN)_6^{3-}$ anions as H-bond acceptor.

The use of the diprotonated 4,4′-bipyridine as a H-bond donor unit leading to the formation of discrete complexes with $Co(II)Cl_4$[5a] and molecular networks with MCl_4 (M = Pd, Pt, Mn, Cd)[5b] has been reported. The same strategy has also been applied for the generation of infinite networks using the $PtCl_4^{2-}$dianion and 4,4′-bis-piperidinium derivatives.[5c]

Both bis-amidiniums **1** and **2**, differing by their possible mode of H-bonding, were designed as potential tetra- and octa-H-bond donor dicationic tectons respectively (Fig. 1).[4] The connection of the two amidinium units by a phenyl group was achieved in order to reduce the conformational space and furthermore to impose the inter-amidinium distance. Whereas for **2** many H-bonding patterns may be envisaged, for **1** one may impose the unique dihapto mode of interaction upon cyclisation of the amidine units of **2** using two propyl fragments (Fig. 1). An X-ray study carried out on the dichloride salt of **1** revealed a distance of 7.01 Å between the nitrogen atoms located on the same side of **1**.[4] This distance, based on modelling, appeared as appropriate for the binding of octahedral $M(CN)_6^{3-}$ (M = Fe, Co and Cr) anions by a dihapto mode of hydrogen bonding.

In an 8 mm diameter crystallisation tube, upon slow diffusion through a H_2O layer (1 ml) of an aqueous solution (2 ml) of compound **1** (7.5 mM, 8.8 mg) into an aqueous solution (2 ml) of K_3FeCN_6 (5 mM, 3.3 mg) slightly yellowish single-crystals were obtained in quantitative yield overnight at room temperature. X-Ray diffraction† revealed that the crystal (triclinic system, with $P\bar{1}$ as the space group) is composed of three molecules of **1**, two $Fe(CN)_6^{3-}$ anions and eight H_2O molecules (Fig. 2).

For the cationic tecton **1**, owing to the difference in the pK_a values between the $Fe(CN)_6^{3-}$ anion and unprotonated **1**, as expected, all four acidic protons are indeed localised on the nitrogen atoms of **1**. Within each NCN fragment, the C–N distance and N–C–N angle are in the range of 1.31–1.32 Å and 121.4–122.4° respectively. These values are close to average values observed for **1**-2Cl (1.31 Å, 122. 3°).[4] Both 6-membered amidinium cycles adopt a half chair conformation and are almost parallel and coplanar but tilted with respect to the phenyl ring with the NCCC dihedral angle varying between −48.2 and 47.3°. The average distance of *ca* 7.01 Å between nitrogen



1 **2**

Fig. 1 Structures of amidinium **1** and **2**. Arrows indicate the possibility of hydrogen bonding.

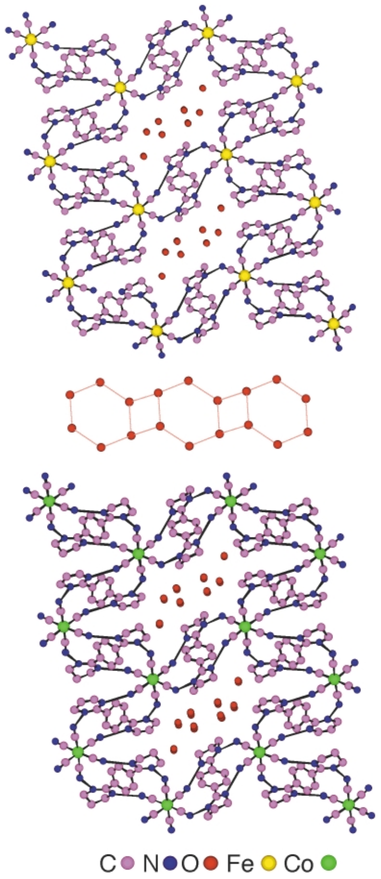


Fig. 2 Portion of the X-ray structure of the 2-D H-bonded network obtained upon self-assembly of the dicationic tecton **1** and $Fe(CN)_6^{3-}$ (top) or $Co(CN)_6^{3-}$ (bottom) anion showing the alternate positioning of Δ' and Λ' supramolecular enantiomers and the inclusion of water molecules and a view of the H-bonded water polymer (middle). For bond distances and angles see text. H atoms are omitted for clarity.

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atoms belonging to two amidinum units and localised on the same side of the molecule is almost the same as the one observed for **1**-2Cl (7.0 Å).[4]

For the anionic tecton Fe(CN)$_6^{3-}$, the coordination geometry around the Fe(III) centre is a slightly distorted octahedral with Fe–C and C–N distances varying between 1.93 and 1.95 Å and 1.15 and 1.16 Å respectively. These values are close to those observed for Cs$_2$KFe(CN)$_6^{3-}$ (average values of 1.92 and 1.14 Å respectively).[7] The slight deviation with respect to the Cs$_2$KFe(CN)$_6^{3-}$ salt (*cis* C–Fe–C angle varying between 89.7 and 90.3°, and *trans* C–Fe–C angle of 180.0°)[7] is reflected by the *cis* and *trans* C–Fe–C angles which are in the range of 83.6–93.2° and 175.5–176.4° respectively.

All the dicationic and trianionic tectons are interconnected through strong H-bonds and electrostatic charge–charge interactions leading thus to a 2-D H-bonded hybrid network, *i.e.* all Fe(CN)$_6^{3-}$ anions are surrounded by three dications **1**. The molecular recognition process between **1** and Fe(CN)$_6^{3-}$ takes place through a dihapto or chelate mode of H-bonding between two acidic protons localised on the same side of **1** and two anionic CN fragments of Fe(CN)$_6^{3-}$ in a mutually *cis* position with the N···N distance varying between 2.86 and 2.99 Å. Owing to the disposition of the other two remaining equivalent acidic protons of **1**, by an iterative process into two directions of space the 2-D network of 63 topology is generated. The latter may be regarded as either anionic Fe(CN)$_6^{3-}$ tectons interconnected by dications **1**, or conversely as dicationic tectons **1** interconnected by anionic Fe(CN)$_6^{3-}$ units.

It is worth noting that because of the dihapto or chelate mode of H-bonding between **1** and Fe(CN)$_6^{3-}$ anions, every single node of the network, *i.e.* an octahedral complex surrounded by three H-bonded chelates localised within the second coordination sphere of the metal, presents a supramolecular chirality (chirality occurring within the second coordination sphere through non-covalent reversible interactions) of the Δ and Λ types which one may note as Δ′ and Λ′ (Fig. 3). The 2-D network obtained in the present case is composed of both Δ′ and Λ′ enantiomers with an alternate distribution. Thus, the overall network is achiral. The molecular recognition of anionic transition metal complexes by macrocyclic polyammonium cations through the use of the second coordination sphere has been previously demonstrated.[8]

The packing of the neutral 2-D networks leads to channels which are filled with H-bonded 1-D molecular networks exclusively composed of water molecules (Fig. 2). The network is formed by hexagons of H$_2$O molecules with an average O···O distance of *ca.* 2.84 Å, interconnected through the formation of tetragons with an O···O distance of 2.845 Å. In other words, one of the two oxygen atoms involved in the interconnection of the hexagon is further hydrogen bonded to another H$_2$O molecule not taking part in the formation of the network with a rather long O···O distance of 3.048 Å.

The validity of the approach was further confirmed by using the Co(CN)$_6^{3-}$ anion. As expected, the same type of network was again obtained under the same conditions.† In addition to the same H-bond pattern between the cationic and anionic tectons, the number as well as the connectivity pattern for the H$_2$O molecules are the same as in the case of Fe(CN)$_6^{3-}$. In other terms, both cases are perfectly isostructural. Furthermore, the same type of network was obtained for **1**:Fe(CN)$_6^{3-}$ ratios of 1:1, 3:2 and 2:3 demonstrating the robustness of the self-assembling process. Moreover, after *ca.* 2 h at room temperature, the same solid may be obtained in large quantity and quantitative yield as a microcrystalline powder upon mixing the two components in water. The identity of the polycrystalline and monocrystalline material was confirmed by elemental analysis.

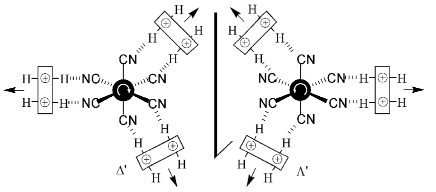

Fig. 3 Schematic representation of the supramolecular chirality of the Δ′ and Λ′ types obtained upon binding within the second coordination sphere of the octahedral M(CN)$_6^{3-}$ anion by dicationic tecton **1** capable of a dihapto mode of H-bonding.

In conclusion, we have demonstrated that by using a dicationic organic tecton capable of interconnecting through a dihapto mode of H-bonding octahedral anions such as M(CN)$_6^{3-}$ (M = Fe or Co), a 2-D H-bonded hybrid network may be formed. Furthermore, we have demonstrated, for the first time to the best of our knowledge, the presence of the supramolecular chirality of the Δ and Λ types taking place within the second coordination sphere of the metallic centre. In the context of generating chiral networks using the same concepts, the synthesis of chiral analogues of **1** and their self-assembly with M(CN)$_6^{3-}$ (M = Fe or Co, Cr) is under current investigation.

Notes and references

† *Crystal data* for (3**1**-2FeCN$_6^{3-}$)$_n$·8H$_2$O: (yellow, 173 K), 3(C$_{14}$H$_{20}$N$_4$)·3FeC$_6$N$_6$·8H$_2$O: M = 1301.06, triclinic, space group $P\bar{1}$, a = 7.1092(2), b = 12.4303(4), c = 17.9853(6) Å, α = 83.443(5), β = 87.583(5), γ = 84.059(5)°, U = 1569.73(8) Å^3, Z = 2, D_c = 1.38 g cm^{-3}, Mo-Kα, μ = 0.534 mm^{-1}, 4100 data with $I > 3\sigma(I)$, R = 0.049, R_w = 0.073.

For (3**1**-2CoCN$_6^{3-}$)$_n$·8H$_2$O: (colorless, 173 K), 3(C$_{14}$H$_{20}$N$_4$)·3CoC$_6$N$_6$·8H$_2$O: M = 1307.22, triclinic, space group $P\bar{1}$, a = 7.1082(2), b = 12.3899(5), c = 17.8711(6) Å, α = 83.424(5), β = 87.389(5), γ = 84.108(5)°, U = 1554.38(9) Å^3, Z = 2, D_c = 1.40 g.cm^{-3}, Mo-Kα, μ = 0.606 mm^{-1}, 4180 data with $I > 3\sigma(I)$, R = 0.049, R_w = 0.073. Data were collected on a Nonius Kappa CCD and structural determination was achieved using the Nonius OpenMolenN package.[6]

CCDC reference numbers 175756 and 178504. See http://www.rsc.org/suppdata/cc/b1/b111207b/ for crystallographic data in CIF or other electronic format.

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