Molecular tectonics: control of packing of hybrid 1-D and 2-D H-bonded molecular networks formed between bisamidinium dication and cyanometallate anions†

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Upon combining the dicationic bis-amidinium tecton **2** bearing four propyl chains with tetra- and hexa-cyanometallate anions neutral 1- and 2-D hybrid networks were obtained. In the case of $[M(CN)_4]^{2-}$ (M = Ni(II), Pd(II) and Pt(II)), the control of the spacing between consecutive 1-D H-bonded networks by the presence of the propyl chains was demonstrated. For $[M(CN)_6]^{3-}$ (M = Fe(III), Co(III), Cr(III)), 2-D networks presenting hexagonal channels have been obtained. In marked contrast with the case based on the use of **1** for which channels are filled with water molecules, in the case of **2**, as expected, the solvent molecules were replaced by propyl chains.

Introduction

Molecular networks[1] are infinite molecular architectures possessing translational symmetry. These molecular assemblies are generated by combining construction units or tectons[2] containing interaction sites. For some time now, an approach, called molecular tectonics,[3–5] has been developed. The latter is based on the use of concepts, such as molecular recognition, developed in supramolecular chemistry,[6] supramolecular synthesis[6,7] and self-assembly processes[8,9] allowing, through an iterative procedure, the construction of periodic molecular assemblies. Molecular networks are defined by their dimensionality, topology, geometry and their charge.[1,10,11] The three central features governing this approach are: (i) the design of the recognition pattern taking place between a self-complementary or two or several complementary tectons, (ii) geometrical aspects dealing with the localisation of the interaction sites and, (iii) the nature of intermolecular interactions allowing the interconnection of tectons, which, by principle, must be reversible in order to allow self-repairing processes to take place during the construction event. For the latter point, hydrogen bonding is the most often considered interaction.[9–16] A possible reason for the use of this particular interaction is its rather directional nature.[17] In terms of strength, H-bond ranges from weak[18] (a fraction of kcal mol^{-1}) to moderate interactions (5–10 kcal mol^{-1}).[19] In supramolecular chemistry, the possibility of adding several types of interactions is an operational principle. In particular, upon combining directional H-bonding with rather strong charge–charge electrostatic interactions one may increase the overall energy of interaction between tectons.

The majority of molecular networks reported to date are based on non ionic H-bonds.[9–16,20–23] However, several cases of charge assisted hydrogen bonding have also been described.[24–28] In particular, we have shown that protonated bis-amidine based tectons are well suited for the generation of H-bonded molecular networks using anionic moieties such as carboxylate, sulfonate and phosphate derivatives.[29–38]

One of the major issues in molecular tectonics is related to the predictability of the final architecture.[4] It is worth noting that although usually molecular networks are generated in the crystalline phase, mainly because of the possibility of structural characterisation offered by X-ray diffraction methods, the concept of prediction here is not associated with prediction of the crystal structure[39,40] but rather with the connectivity scheme between tectons and thus the general architecture.[4] Although in general, the precise structural prediction of molecular networks still remains a challenge, for rigid and well defined sets of tectons presenting restricted conformational and connection possibilities, prediction of the connectivity and thus the dimensionality may often be achieved. A further even more complex task is the prediction of packing of 1-D (wire type) and 2-D (sheet type) networks. This type of prediction is usually not feasible. However, using a knowledge driven strategy instead of a theory based approach, by taking into account the precise analysis of different factors governing the formation of a characterised architecture, one may control the packing of 1- and 2-D networks by tuning structural features of tectons.

Here, we report on such an approach by describing the control of packing of 1- and 2-D networks using a combination of dicationic organic and anionic inorganic tectons and based on simultaneous use of H-bonding and electrostatic interactions.

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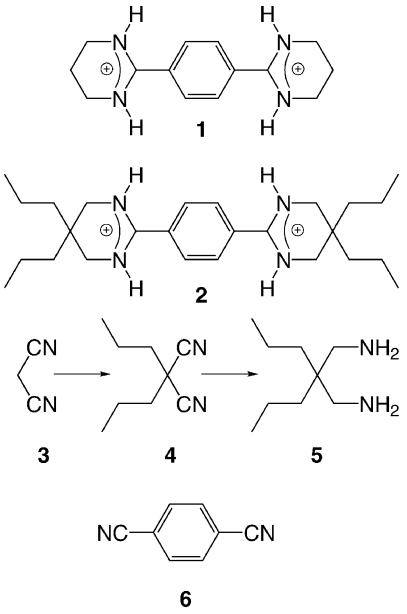
† The HTML version of this article has been enhanced with colour images.



Scheme 1

Results and discussion

The bis-amidinium **1** (Scheme 1) is a dicationic H-bond donor tecton with two sets of two acidic protons oriented in a divergent fashion and located on both sides of the unit. In order to reduce both the conformational mobility and to impose the inter amidinium distance and thus the distance between H-bond donor sites on each face, the two amidinium units are connected by a phenyl spacer. As shown by an X-ray study on the dichloride salt of **1**,[41] the distance of 7.01 Å between the nitrogen atoms located on the same side of **1** is particularly well suited for the recognition, by a dihapto mode of hydrogen bonding, of polycyanometallate anions (Fig. 1).

We have previously demonstrated the ability of tecton **1** to form, by charge assisted H-bonds, 1-D networks with dicyanometallates $M(CN)_2^-$ (M = Au and Ag)[42] and tetracyanometallates $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt)[43] and 2-D networks with pentacyanometallates $[(NO)M(CN)_5]^{3-}$ (M = Fe),[44] hexacyanometallates $[M(CN)_6]^{2-}$ (M = Co, Fe and Cr)[45,46] and $[M(CN)_6]^{4-}$ (M = Fe, Ru).[47] The above mentioned assemblies are all based on the formation of H-bonds of the type NH···N between organic tectons and anionic cyanometallate units. The geometry and dimensionality of the networks described above are the consequences of the structural features (number of H-bonds and localisation) as well as the electrostatic nature of interactions (positive and negative charge distribution). It is worth noting that the above mentioned cases may be regarded as examples of the control of the second coordination sphere around metal centres. This concept has been previously documented in the context of molecular recognition of anionic transition metal complexes by macrocyclic polyammonium receptors.[48–51] The use of the diprotonated 4,4′-bipyridine generating discrete complexes[52] with $[CoCl_4]^{2-}$ and molecular networks with $[MCl_4]^{2-}$ (M = Pd, Pt, Mn, Cd)[53–56] has also been reported. The same strategy has also been applied for the formation of infinite networks combining $[PtCl_4]^{2-}$ dianion with 4,4′-bis-piperidinium derivatives.[57] Further examples of charge assisted assemblies using metal halides and cationic units have also been documented in the literature.[58–61]

Schematic representations of observed patterns for formation of 1-D neutral H-bonded networks between **1** and $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt) and their parallel packing mode are given in Fig. 2a. When analysing the lateral packing of the 1-D network, we thought that one could control the spacing between the networks by modifying the structure of the organic tecton. Thus, the tecton **2** was designed. The latter only differs from **1** by the addition of four propyl chains (see Scheme 1). In principle, since the structural alteration is remote from the recognition site, the tecton **2** should behave in the same manner as the tecton **1** and recognise $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt) anions through a dihapto mode of H-bonding (Fig. 1b). In terms of 1-D network formation, one would expect a similar feature. However, owing to the location of the propyl chains between consecutive 1-D networks, a larger spacing would be expected (Fig. 2b).

The synthesis of **2** (see experimental section) was achieved starting with malononitrile **3**, which was reacted, in anhydrous THF, with 1-bromopropane in the presence of sodium hydride affording the dinitrile **4** in 24% yield.[62] The latter was transformed into the diamine **5** upon treatment with borane in dry THF in 90% yield. The desired compound **2** was obtained in 31% yield as its hydrochloride salt upon reacting the diamino compound **4** with 1,4-dicyanobenzene **6** in the presence of P_2S_5.[63]

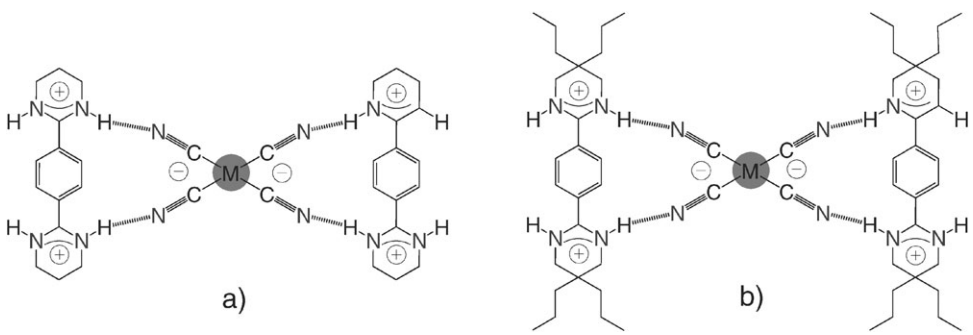


Fig. 1 Schematic representation of the recognition, by a dihapto mode of H-bonding, of square planar $[M(CN)_4]^{2-}$ dianions by tectons **1** (a) and **2** (b).

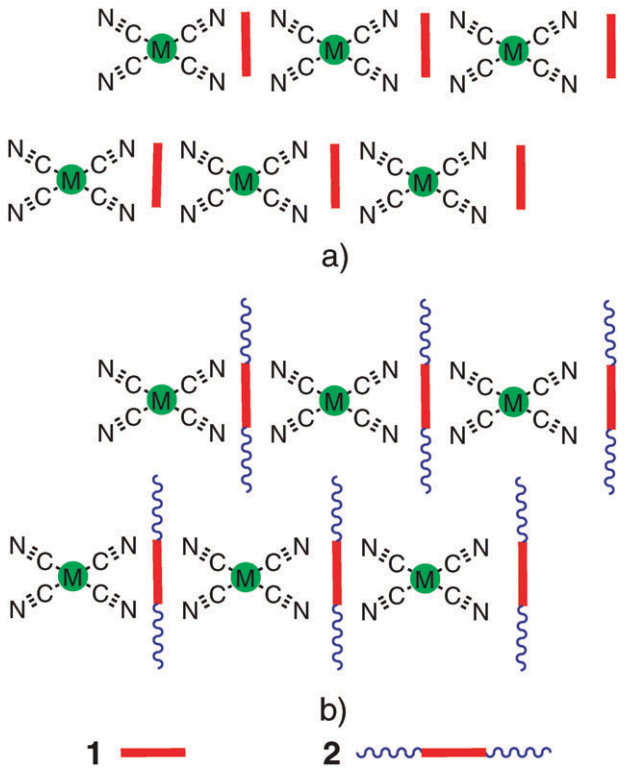


Fig. 2 Schematic representation of lateral packing of 1-D networks formed between $[M(CN)_4]^{2-}$ and tectons **1** (a) and **2** (b).

Solid state structure of the hydrochloride salt of 2

The structure of the hydrochloride salt of **2** was investigated by X-ray diffraction on a single crystal (Table 1) obtained upon slow evaporation of an ethanol solution (Fig. 3).

The crystal was composed of **2**, two Cl^- anions and two water molecules. For the dication **2**, in general position, the C–N distance and N–C–N angle are in the range of *ca.* 1.31 to 1.32 Å and of *ca.* 121.3° to 123.4°, respectively. These values are close to those observed for **1**–2Cl (*ca.* 1.31 Å, 122. 3°).[41] Both six-member amidinium cycles adopt a half chair conformation and are almost parallel and tilted with respect to the phenyl ring with NCCC dihedral angle varying between *ca.* −41.7° and 35.6°. The average distance of *ca.* 7.05 Å between nitrogen atoms belonging to two amidinium units and localised on the same side of the molecule is almost the same as the one observed for **1**–2Cl (7.0 Å).[41] The four propyl chains adopt an extended conformation. In the crystal, in addition to **2** and chloride anions, water molecules are also present. When taking into account the formation of H-bonds between all these three components, the overall structure may be described as a 1-D H-bonded network (Fig. 3). The H_2O molecules and Cl^- anions are located between consecutive dicationic units. The two H_2O molecules are connected through H-bonds (d_{O-O} = 2.805 Å) and thus may be regarded as a pair. They further interact with the Cl^- anions through one H-bond (d_{O-Cl} = 3.173 Å). The water pair bridges the consecutive dicationic tectons **2** by two H-bonds (d_{O-N} = 2.818 Å and 2.900 Å). The Cl^- anions also further interact with the dication through rather weak H-bonds (d_{N-Cl} = 3.106 Å).

Structural analysis of 1-D H-bonded networks based on $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt)

As stated above, the structural features of the dicationic tecton **2** allow the recognition of square planar $[M(CN)_4]^{2-}$ dianions through a dihapto mode of H-bonding (Fig. 1b). Based on charge neutralisation, one would expect the formation of a neutral 1-D network (Fig. 2b) with a 1/1 stoichiometry between the dicationic and dianionic partners. This was indeed observed for $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt). In all three cases, crystals were obtained from a H_2O–MeOH mixture using a 1/1 ratio of **2**/$[M(CN)_4]^{2-}$ (see experimental section).

Table 1 Data collection and refinements for **2**-Cl, **2**-($Ni(CN)_4$), **2**-($Pd(CN)_4$) and **2**-($Pt(CN)_4$). Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 73)

	2	**2**-($Ni(CN)_4$)	**2**-($Pd(CN)_4$)	**2**-($Pt(CN)_4$)
Empirical formula	$C_{26}H_{44}N_4 \cdot 2\,Cl \cdot 2\,H_2O$	$C_{26}H_{44}N_4 \cdot Ni(CN)_4$	$C_{26}H_{44}N_4 \cdot Pd(CN)_4$	$C_{26}H_{44}N_4 \cdot Pt(CN)_4$
Molecular weight [g mol^{-1}]	519.58	575.44	623.13	711.82
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.1738(6)	8.2020(2)	8.2700(17)	8.2909(2)
b [Å]	9.4718(6)	9.5615(2)	9.5086(19)	9.4857(2)
c [Å]	17.6898(13)	10.9335(3)	10.937(2)	10.9177(2)
α [°]	100.914(3)	68.098(2)	70.10(3)	70.1910(10)
β [°]	92.932(4)	84.4370(10)	85.07(3)	84.9360(10)
γ [°]	103.963(4)	84.4120(10)	85.64(3)	85.7130(10)
V [Å^3]	1457.13(17)	790.07(3)	804.7(3)	803.74(3)
Z	2	1	1	1
Color	Colorless	Colorless	Colorless	Colorless
Crystal size [mm]	0.10 × 0.05 × 0.02	0.20 × 0.10 × 0.07	0.05 × 0.05 × 0.04	0.25 × 0.10 × 0.10
ρ_{calcd} [g cm^{-3}]	1.184	1.209	1.286	1.471
μ [mm^{-1}]	0.251	0.645	0.608	4.396
λ [Å]	0.710 73	0.710 73	0.710 73	0.710 73
Number of reflections collected	13497	12610	9334	15935
Number of data with $I > 2\,\sigma(I)$	6500	4524	4619	4520
R	0.0592	0.0346	0.0299	0.0175
Rw	0.1245	0.0432	0.0323	0.0175
GOF	0.998	1.048	1.086	1.088

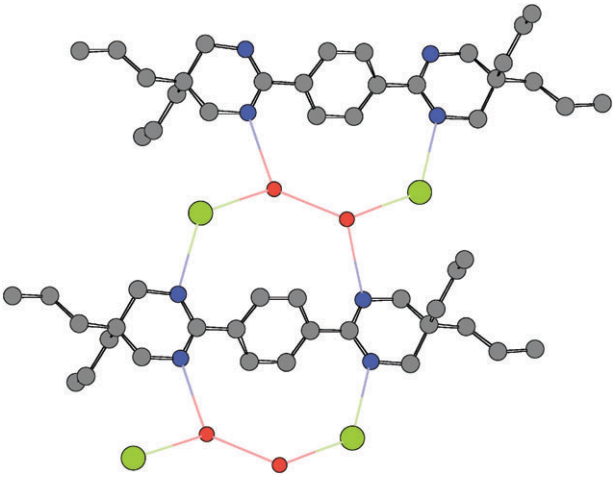


Fig. 3 A portion of the structure of the hydrochloride salt of **2** showing the formation of H-bonds between the dicationic tecton **2**, Cl^- anions and water molecules. H atoms are not represented for clarity. For bond distances and angles see text.

X-ray diffraction studies on single crystals revealed that the three crystalline materials obtained are isomorphous (triclinic system, with $P\bar{1}$ as the space group, see Table 1). For each case, the crystal is composed of one dication **2** and one dianion $[M(CN)_4]^{2-}$. The absence of solvent molecules in the lattice indicates that the cohesion of crystals is ensured by the two components (Fig. 4).

In all three cases, for the dication **2**, lying about an inversion centre, the C–N distance and N–C–N angle are in the range of *ca.* 1.31 to 1.32 Å and of *ca.* 121.9° to 122.0°, respectively. These values are close to average values observed for **1**.[44] Both six-member amidinium cycles adopt a half chair conformation and are almost parallel and tilted with respect to the phenyl ring with the NCCC dihedral angle varying between *ca.* −43.8° and 43.5°. The average distance of *ca.* 7.03 Å between nitrogen atoms belonging to two amidinium units and localised on the same side of the molecule is almost the same as the one observed for **1** (7.02 Å).[43] As in the case of the chloride salt of **2** mentioned above, all four propyl chains adopt an extended conformation. For the $[M(CN)_4]^{2-}$, lying about an inversion centre, the coordination geometry around the M(II) is almost perfectly square planar with M–C distance of 1.87 Å for Ni and of *ca.* 2.00 Å for Pd and Pt and CN distance of *ca.* 1.15 Å. The CMC angle varies between 89.4° and 90.6°. The distance between two metal centres within the 1-D network is in the ranges of 11.53 Å, 11.80 Å for Pd and 11.79 Å for Pt.

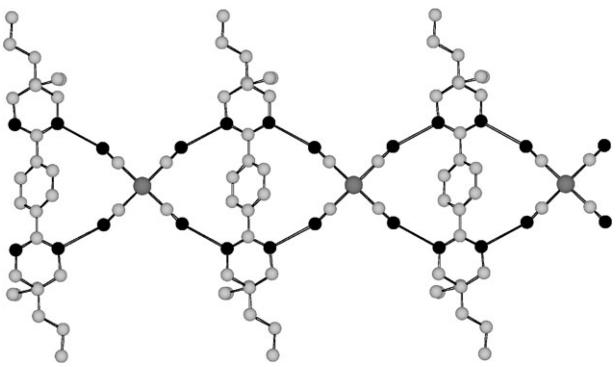


Fig. 4 Portions of the structures of 1-D networks formed between the tecton **2** and $[Ni(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$. All three structures are isomorphous. H atoms are not represented for clarity. For bond distances and angles see text.

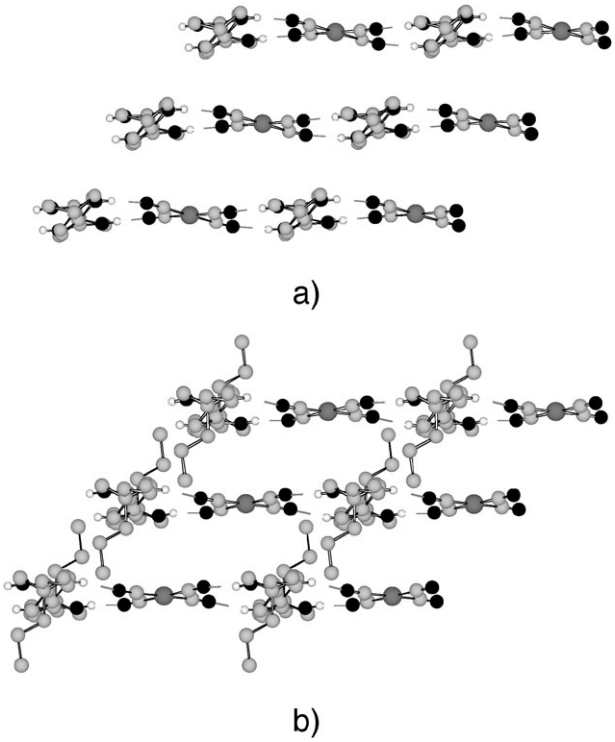


Fig. 5 Portions of the packing of 1-D networks formed between the tecton **1** (a) and **2** (b) and $[M(CN)_4]^{2-}$ in the [*y*0*z*] plane. H atoms are not represented for clarity. For bond distances and angles see text.

As expected, the dicationic and dianionic tectons are interconnected by strong H-bonds through a dihapto mode of interaction leading thus to a neutral 1-D networks. The N–N average distance of *ca.* 2.84 Å is rather short implying strong hydrogen bonds. The 1-D H-bonded networks are packed in a parallel fashion (Fig. 5). Interestingly, as expected by the design of **2**, the presence of propyl chains controls the spacing between the 1-D networks. Indeed, whereas for the 1-D networks obtained when combining $[M(CN)_4]^{2-}$ anions and the tecton **1**, the vertical distance between two consecutive networks in the $>y0z]$ plane is in the range of 6.40–6.44 Å (Fig. 5a), in the case of **2** (Fig. 5b) the spacing is increased and it ranges from 8.41 Å for Ni to 8.28 Å and 8.26 Å for Pd and Pt, respectively.

Structural analysis of 2-D H-bonded networks based on $[M(CN)_6]^{3-}$ (M = Co, Fe, Cr)

We have previously shown that the dicationic unit **1** is also well suited for the recognition of $[M(CN)_6]^{3-}$ (M = Co, Fe, Cr) complex anions and that the recognition again takes place through three dihapto mode of H-bonding (Fig. 6a).[43,45] In principle, since for the tecton **2** the recognition sites are conserved, one would expect the same type of interactions between $[M(CN)_6]^{3-}$ anions and **2** (Fig. 6b).

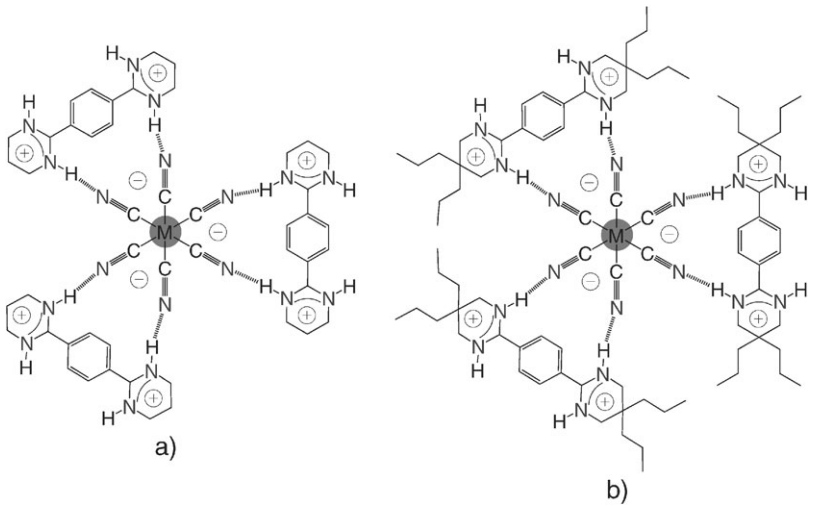


Fig. 6 Schematic representation of the recognition, by a dihapto mode of H-bonding, of octahedral $[M(CN)_6]^{3-}$ anions by tectons **1** (a) and **2** (b).

Owing to the dihapto (chelate) mode of H-bonding between **1** or **2** and the octahedral $[M(CN)_6]^{3-}$ anions, this type of recognition leads to the generation of supramolecular chirality of the type Δ' and Λ'.[43–45]

The combination of the tecton **1** with $[M(CN)_6]^{3-}$ (M = Co, Fe, Cr) leads in all three cases to the formation of isostructural neutral 2-D networks. As expected, the latter are achiral since they contain both Δ' and Λ' stereoisomers. The packing of the neutral 2-D networks leads to the formation of channels filled with H-bonded 1-D water polymers (Fig. 7a). The analysis of the inclusion of solvent molecules within the channels suggested that upon substitution of the tecton **1** by **2**, one could replace the water molecules by the propyl chains (Fig. 7b).[45]

The combination of **2** with $[M(CN)_6]^{3-}$ (M = Co, Fe, Cr) afforded crystalline materials (see experimental section), which were analysed by X-ray (see Table 2).

In all three cases, single crystals (trigonal system, with $P\bar{3}$ as the space group) are isostructural and exclusively composed of the dicationic tecton **2** and $[M(CN)_6]^{3-}$ anions. In marked contrast with the case of **1**, no water molecules are present in the lattice (Fig. 8). As expected, for charge neutrality reasons, the ratio of **2**/$[M(CN)_6]^{3-}$ is 3/2. For the tecton **2**, lying about an inversion centre, within each NCN fragment, the C–N distance and N–C–N angle are in the range of *ca.* 1.31–1.32 Å and 121.8–121.9°, respectively. These values are almost identical to those observed for the combination of **2** and $[M(CN)_4]^{2-}$ mentioned above. Again both six-member amidinium cycles adopt a half chair conformation and are almost parallel, coplanar and tilted with respect to the phenyl ring (NCCC dihedral angle of 45.0° and 46.4°). The average distance of *ca.* 7.03 Å between nitrogen atoms belonging to two amidinium units and localised on the same side of the molecule is again almost the same as the one observed for the hydrochloride salt of **2** and for the 1-D networks formed between **2** and $[M(CN)_4]^{2-}$ mentioned above.

For the anionic unit $[M(CN)_6]^{3-}$, lying on a threefold axis, the coordination geometry around the M(III) centre is a weakly distorted octahedron with CMC angles varying between 87.0° and 93.4° (*cis*) and 174.4° and 174.9° (*trans*). The average M–C distance is 1.90 Å for Co, 1.94 Å for Fe and 2.07 Å for Cr.

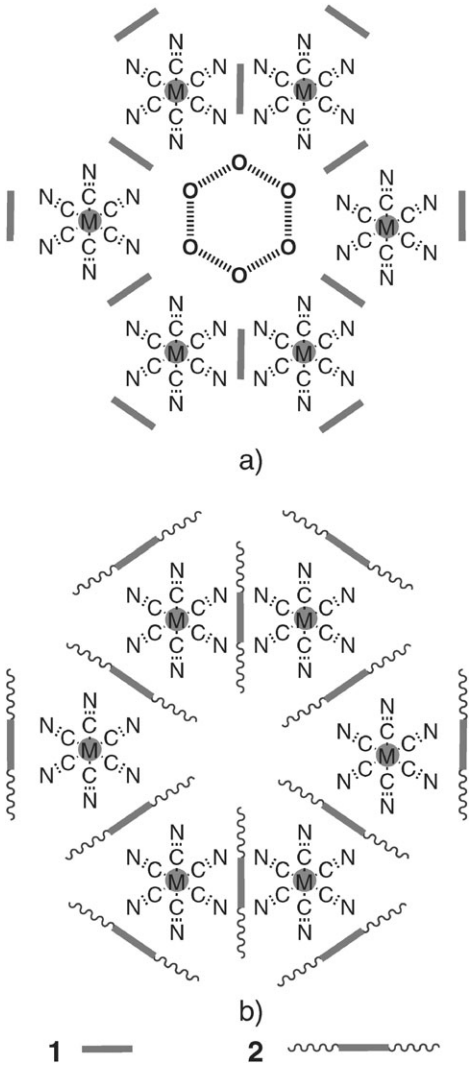


Fig. 7 Schematic representation of the arrangement of cationic and anionic units within 2-D networks formed between $[M(CN)_6]^{3-}$ and tectons **1** (a) and **2** (b). Whereas in the case of **1** water molecules (a projection presented in (a)) occupy the channels, in the case of **2** the voids are occupied by propyl chains of **2** (b).

Table 2 Data collection and refinements for $\mathbf{2}_3$-$(Cr(CN)_6)_2$, $\mathbf{2}_3$-$(Fe(CN)_6)_2$ and $\mathbf{2}_3$-$(Co(CN)_6)_2$. Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 73)

	$\mathbf{2}_3$-$(CrCN)_6)_2$	$\mathbf{2}_3$-$(Fe(CN)_6)_2$	$\mathbf{2}_3$-$(CoCN)_6)_2$
Empirical Formula	$[C_{26}H_{44}N_4]_3 \cdot [Cr(CN)_6]_2$	$[C_{26}H_{44}N_4]_3 \cdot [Fe(CN)_6]_2$	$[C_{26}H_{44}N_4]_3 \cdot [Co(CN)_6]_2$
Molecular weight [g mol^{-1}]	1654.20	1661.90	1668.06
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$P\bar{3}$	$P\bar{3}$	$P\bar{3}$
a [Å]	18.1638(1)	17.9242(4)	17.8434(6)
b [Å]	18.1638(14)	17.9242(4)	17.8434(6)
c [Å]	8.5506(12)	8.6140(4)	8.6540(6)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	120	120	120
V [Å3]	2443.1(4)	2396.71(13)	2386.2(2)
Z	1	1	1
Color	Colorless	Pale yellow	Orange
Crystal size [mm]	0.10 × 0.09 × 0.08	0.10 × 0.10 × 0.05	0.10 × 0.10 × 0.05
ρ_{calcd} [g cm^{-3}]	1.124	1.151	1.161
μ[mm^{-1}]	0.276	0.357	0.403
λ [Å]	0.710 73	0.710 73	0.710 73
Number of reflections collected	19843	16699	15160
Number of data with $I > 2\ \sigma(I)$	3753	3684	4646
R	0.0512	0.0435	0.0566
Rw	0.1019	0.0747	0.1050
GOF	1.072	1.056	1.019

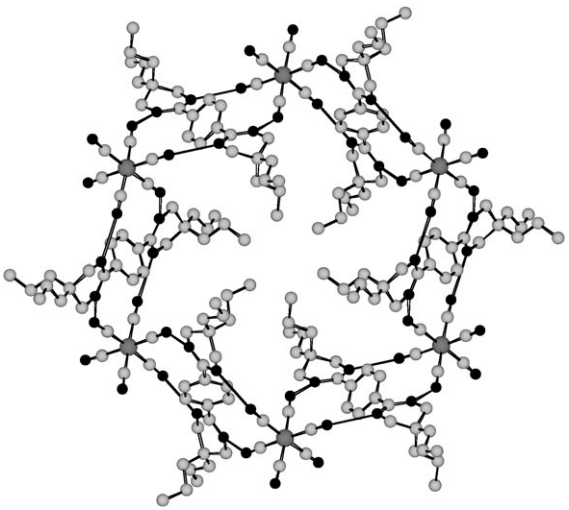


Fig. 8 Portions of the structures of 2-D networks formed between the tecton **2** and $[Co(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Cr(CN)_6]^{3-}$. All three structures are isomorphous. H atoms are not represented for clarity. For bond distances and angles see text.

For all three cases, dicationic and trianionic tectons are interconnected through strong H-bonds and electrostatic charge–charge interactions leading thus to 2-D H-bonded networks (N···N distance varying between *ca.* 2.83 to 2.92 Å). The honeycomb type arrangement is formed because each $[M(CN)_6]^{3-}$ anion is surrounded by three dications **2** and conversely each dication **2** is in interaction with three $[M(CN)_6]^{3-}$ anions. Each anionic centre presents a supramolecular chirality of the type Δ′ and Λ′. The overall 2-D network containing both enantiomers in an alternate mode is achiral.

Conclusions

In conclusion, on one hand, we have demonstrated through the design of the new tecton **2**, an analogue of **1** bearing four propyl chains, the possibility of tuning the packing distance between 1-D networks generated upon combining the tecton **2** with square planar $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) anions. On the other hand, we have shown that in the case of octahedral $[M(CN)_6]^{3-}$ (M = Co, Fe, Cr) anions, the substitution of the tecton **1** by **2** leads to the replacement of water molecules filling the channels in the case of **1** by the propyl chains of the tecton **2**. This study demonstrates the robustness of the design principles followed. Similar investigations on other analogous tectons bearing different alkyl chains are currently under progress.

Experimental

Syntheses

Dinitrile 4. Although this compound has been previously described, we used the following method for its preparation.[62] A solution of malononitrile **3** (2.00 g, 30.3 mmol) in anhydrous THF (30 ml) was added dropwise to a suspension of sodium hydride (1.60 g, 66.6 mmol) in THF (30 ml) at 0 °C and the mixture stirred for 30 min. 1-Bromopropane (7.45 g, 60.6 mmol) was then added and the reaction mixture was refluxed for 24 h under argon. The excess of sodium hydride was quenched with MeOH (15 ml) and the solvents were evaporated. The product was extracted with CH_2Cl_2 (2 × 120 ml) and the organic layer washed with H_2O before it was dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (SiO_2, cyclohexane/CH_2Cl_2 2/1) affording the desired compound **4** in 24% yield as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C), ppm: 1.04 (t, 6H, J = 7.2 Hz, CH_3); 1.70 (m, 4H, CH_2–CH$_2$–C); 1.89 (m, 4H, CH_2–C).

Diamine 5. A BH_3 solution in THF (1N, 50 ml) was added dropwise to a solution of compound **4** (1.4 g, 9.33 mmol) in anhydrous THF (50 ml). The reaction mixture was refluxed for 22 h under argon. The excess of BH_3 was quenched with 20 ml of water and the solvents were evaporated. To the residue was

added to 150 ml of a solution (MeOH 50%, H_2O 25%, HCl (12N) 25%) and the mixture was refluxed for 20 h. After evaporating the solvents, an aqueous solution of NaOH was added dropwise until the pH 13 was reached. The product was extracted several times into CH_2Cl_2 (3 × 100 ml). The organic layer was further washed with H_2O (20 ml), dried over $MgSO_4$ and evaporated to dryness affording the diamine **5** in *ca.* 90% yield as a colorless oil and was directly used in the next step. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C) δ ppm: 0.89 (t, 6H, J = 6.6 Hz, CH_3); 1.19 (m, 8H, CH_2 *n*-propyle); 2.56 (s, 4H, CH_2–NH_2).

Hydrochloride salt 2. 600 mg (3.80 mmol) of the compound **5**, 243 mg (1.90 mmol) of dicyanobenzene **6** and 20 mg of P_2S_5 as catalyst[62] were mixed under argon and the temperature raised to 130 °C for 3 h. The mixture was dissolved in MeOH and acidified with HCl (6N). The solvents were evaporated and the residue was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 97/3). After recrystallisation in EtOH, compound **2** was obtained as a white solid in 31% yield. M.p. >310 °C, ^{1}H NMR (CD_3OD, 300 MHz, 25 °C) δ ppm: 0.97 (t, 12H, J = 6.1 Hz, CH_3); 1.40 (m, 16H, CH_2 *n*-propyl); 3.38 (s, 8H, CH_2–NH_2); 7.98 (s, 4H, C*H* arom.); ^{13}C NMR (CD_3OD, 75 MHz, 25 °C) δ ppm: 13.6 (*C*H_3); 15.7 (*C*H_2–CH_3); 30.7 (*C*–$(CH_2)_4$); 35.3 (C–*C*H_2–C_2H_5); 47.6 (*C*H_2–NH_2); 128,3 (*C*H phenyl); 132.6 (C phenyl); 159,0 (N–*C*═N). Elemental analysis: $C_{26}H_{44}N_4Cl_2 \cdot H_2O$, calculated: C = 62.26%; H = 9.24%; N = 11.17%, found: C = 63.04%; H = 9.10%; N = 10.90%. Due to the vacuum drying of the polycrystalline sample, the percentage of water slightly differs between the elemental analysis and X-ray diffraction study.

Crystals of 2-[Ni(CN)$_4$], 2-[Pd(CN)$_4$] and 2-[Pt(CN)$_4$]. In a 4 mm diameter crystallisation tube, upon slow diffusion at room temperature, through a layer of MeOH (0.5 ml), of a solution of **2** (1 mM) in MeOH (0.25 ml) into an aqueous solution (0.25 ml) of $K_2Ni(CN)_4$, $K_2Pd(CN)_4$ or $BaPt(CN)_4$ (1 mM), colorless crystals were obtained in quantitative yield after *ca.* one week. M.p. >310 °C.

Crystals of 2-[Fe(CN)$_6$], 2-[Co(CN)$_6$] and 2-[Cr(CN)$_6$]. In a 4 mm diameter crystallisation tube, upon slow diffusion at room temperature, through a layer of MeOH (0.5 ml), of a solution of **2** (0.8 mM) in MeOH (0.25 ml) into an aqueous solution (0.25 ml) of $K_3M(CN)_6$ (0.5 mM), crystalline materials suitable for X-Ray diffraction were obtained in quantitative yield after *ca.* two weeks. Whereas in the case of Fe crystals were yellowish, in the case of Co and Cr crystals were colorless. For **2**-[Fe(CN)$_6$] and **2**-[Co(CN)$_6$], crystals were air dried prior to data collection. M.p. >270 °C.

Crystallography

Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ = 0.710 73) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. All hydrogen atoms have been calculated except those connected to disordered atoms. CCDC 611940–611947. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606265m.

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