Molecular tectonics: polymorphism and enhancement of network dimensionality by a combination of primary and secondary hydrogen bond sites

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A dicationic tecton bearing four NH and two OH groups, as primary and secondary hydrogen bond donor sites, respectively, leads, in the presence of $[M(CN)_4]^{2-}$ anions, to the formation of polymorphic 2- and 3-D hydrogen-bonded networks.

The design and structural studies of periodic architectures or molecular networks in the solid state is a subject of current interest.[1] These molecular assemblies are generated by self-assembly processes between molecular components behaving as building blocks or tectons.[2–4] The interconnection between tectons is ensured by recognition events[5] operating between either self-complementary or complementary units. By considering the recognition patterns as structural nodes, this type of periodic structure can be defined by the number of recognition patterns and their translation in space (1–3-D).[1] A crystalline solid is, by definition, a 3-D arrangement; however, based on the strength of the interactions, one may describe such solids as molecular networks. In terms of design, for 1-D networks, only one direction of space is controlled by pre-designed interactions, whereas for the other two dimensions, the system is non-deterministic. For 2-D networks, only one dimension is non-deterministic. Finally, for 3-D networks, translation of the recognition patterns into all three directions of space is coded within the structure of the tectons.

Here, we report on the design of a dicationic tecton bearing both primary and secondary hydrogen bond donor sites, and its combination with tetracyanometallate anions that leads to the formation of 2- and 3-D hydrogen-bonded molecular networks.

Increasing the dimensionality of hydrogen-bonded networks[6] from 1- to 2-D requires the interconnection of 1-D arrangements. To this end, one may design tectons bearing both primary and secondary hydrogen bond donor or acceptor sites (Fig. 1).

We have previously demonstrated that amidinium-based tectons are interesting construction units for the generation of charge-assisted hydrogen-bonded networks[7] in the presence of anions behaving as hydrogen bond acceptors.[3,8] In particular, the dicationic tecton **1**-$2H^+$ (Scheme 1) was shown to be well suited to the formation of 1-D networks in the presence of cyanometallate anions.[9,10] Hydrogen-bonded networks based on other anionic metal complexes, in particular metal halide species, and protonated tectons have been also reported.[11–13]

Tecton **2**-$2H^+$, an analogue of **1**-$2H^+$, is based on two cyclic amidinium moieties, each bearing an OH group. The choice of a *para*-phenylene group to interconnect the two amidinium units is motivated by the fact that such a rigid spacer leads to the recognition of tetracyanometallate anions on each face of the tecton through a dihapto mode of hydrogen bonding, which takes place between the acidic H atoms of **2**-$2H^+$ and the N atoms of the CN units (Fig. 1). Thus, **2**-$2H^+$ may be regarded as a building block offering four strongly acidic NH groups and two OH moieties as primary and secondary hydrogen bond donor sites, respectively. Consequently, such a unit could allow the interconnection of 1-D networks, based on the association of the primary sites with complex anions, into a 2-D arrangement through hydrogen bonds between the OH groups and cyanometallate units (Fig. 1b).

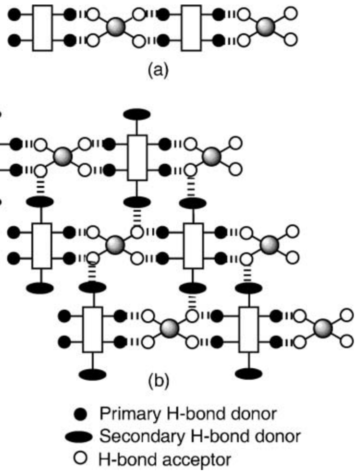
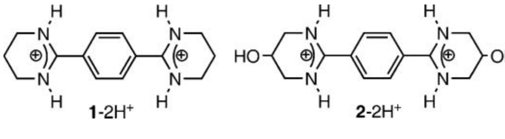


Fig. 1 Schematic representation of (a) the 1-D network formed between **1**-$2H^+$ and $M(CN)_4^{2-}$ anions and (b) the extension to 2-D hydrogen-bonded networks, achieved using **2**-$2H^+$ bearing additional secondary hydrogen bond donor sites.

The synthesis of **2**-2HCl was achieved upon heating under argon at 120 °C for 1.5 h a 1 : 2 mixture of 1,4-dicyanobenzene and 1,3-diamino-2-propanol with a catalytic amount of P_2S_5.[14] The resulting solid bisamidine was acidified with HCl and stored as its hydrochloride salt.†



Scheme 1

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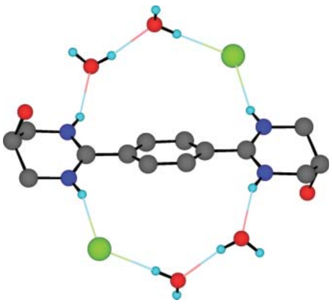

Fig. 2 A portion of the structure of **2**-2HCl showing the hydrogen bonds between **2**-$2H^+$, and Cl^- anions and H_2O molecules. H atoms, except for those engaged in hydrogen bonds, are omitted for clarity. For bond distances and angles, see the text.

The structure of the latter was elucidated by XRD on a single crystal,‡ and revealed that for the centrosymmetric **2**-$2H^+$ unit, the two planes containing the amidinium groups ($d_{C–N}$ of *ca.* 1.32 Å and NCN angle of 121.0°), tilted by *ca.* 27.5° with respect to the *para*-phenylene spacer, are parallel and coplanar (Fig. 2). Both amidinium cycles adopt a half-chair conformation, with the OH groups in axial positions. On each side of the unit, the acidic NH groups are either hydrogen-bonded to a Cl^- anion ($d_{N–Cl}$ = 3.096 Å) or to a H_2O molecule ($d_{N–O}$ = 2.817 Å). Two hydrogen-bonded H_2O molecules ($d_{O–O}$ = 2.742 Å and $d_{O–Cl}$ = 3.069 Å) bridge the amidinium and chloride anion.

Upon mixing, at r.t., an aqueous solution (5 mL) of tecton **2**-2HCl (20 μmol) with an aqueous solution (5 mL) of either $BaM(CN)_4{\cdot}nH_2O$ (M = Ni^{2+}, Pt^{2+}) or $K_2M(CN)_4{\cdot}nH_2O$ (M = Ni^{2+}, Pd^{2+}, Pt^{2+}) (20 μmol), colourless crystals were obtained overnight. In the case of $[Ni(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$, plate-shaped crystals (α-phase) were obtained (Fig. 3(a)); whereas for $[Pt(CN)_4]^{2-}$, a mixture of plate (Fig. 3(a)) and prismatic-shaped (β-phase) (Fig. 3(c)) crystals were observed.

For the α-phase, in all three cases, the crystals are isomorphous (triclinic, space group *P*-1). The crystals are composed of **2**-$2H^+$ dications and $[M(CN)_4]^{2-}$ (M = Ni^{2+}, Pd^{2+} and Pt^{2+}) dianions, without any solvent molecules. Considering the hydrogen bonds formed between the primary NH sites and the CN groups, as expected and as previously observed for **1**-$2H^+$ dications,[10] the cationic and anionic components form a neutral 1-D network through a dihapto mode of hydrogen bonding ($d_{N–N}$ in the range 2.83–2.90 Å) (Fig. 4). Owing to the OH groups behaving as secondary hydrogen bond donor sites, the overall structure is a 2-D network. Indeed, the two OH groups, again in axial positions, interconnect the 1-D networks through hydrogen bonds of the OH···N≡C type ($d_{N–O}$ in the range 2.95–2.98 Å). Among the four CN groups connected to the metal centre, only two are involved in hydrogen bonding with the OH groups (Fig. 3b).

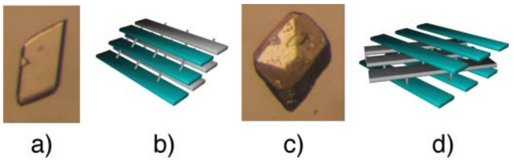

Fig. 3 Pictures of (a) polymorph α, obtained from the combination of tecton **2**-$2H^+$ with $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt), and (c) polymorph β, obtained only for (**2**-$2H^+$, $[Pt(CN)_4]^{2-}$). (b) and (d) represent schematically the arrangement of the networks in the α- and β-phases, respectively.

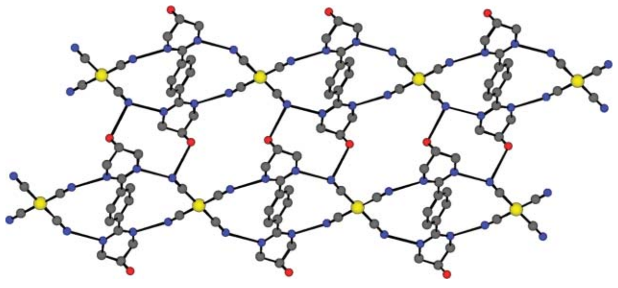

Fig. 4 A portion of the 2-D hydrogen-bonded networks (α-phase) formed between the tecton **2**-$2H^+$ and $[M(CN)_4]^{2-}$(M = Ni, Pd and Pt). H atoms are omitted for clarity. For bond distances and angles, see the text.

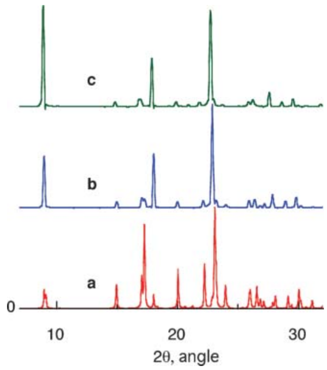

Fig. 5 XRPD patterns for (**2**-$2H^+$, $[Ni(CN)_4]^{2-}$): (a) simulated and (b) observed; (c) observed for (**2**-$2H^+$, $[Pd(CN)_4]^{2-}$).

This description is consistent with our IR study on powder samples, which indeed revealed the presence of two vibration bands for the nitrile group (2110 and 2130 cm^{-1} for $[Ni(CN)_4]^{2-}$, and 2124 and 2144 cm^{-1} for $[Pd(CN)_4]^{2-}$).

The 2-D-formed planes pack in a parallel fashion along the *a* axis, with *ca.* 4.60 Å distances between the metal centres in consecutive layers (Fig. 3(b)). Both in the case of Ni (Fig. 5(b)) and Pd (Fig. 5(c)), the XRPD study indicates the presence of a single phase (α-phase) and is consistent with the simulated pattern (Fig. 5(a)) obtained from XRD investigations on single crystals.

As stated above, in the case of $[Pt(CN)_4]^{2-}$, in addition to the α-phase, another morphology (β-phase) is observed (Fig. 3(c)). Again, when only considering the hydrogen bonds occurring between the primary NH sites and CN^- groups, a neutral 1-D network, identical to the one observed for the α-phase, is obtained ($d_{N–N}$ in the range 2.90–2.95 Å). In marked contrast to the previous case discussed above, the second type of hydrogen bond is of OH···O type and takes place between OH moieties belonging to consecutive planes ($d_{OH\cdots O}$ = 2.88 Å).

Furthermore, again in marked contrast to the α-phase, consecutive planes are tilted by *ca.* 60° (Fig. 6). Because of this particular orientation of consecutive layers, the overall architecture is a 3-D hydrogen-bonded network (Fig. 3(d)).

Although we were able to select single crystals of either plate or prismatic shape morphology and determine their structures by XRD, we have investigated the possibility of forming pure α or β phase. Two parameters, *i.e.* the nature of the counterion (Ba^{2+} or

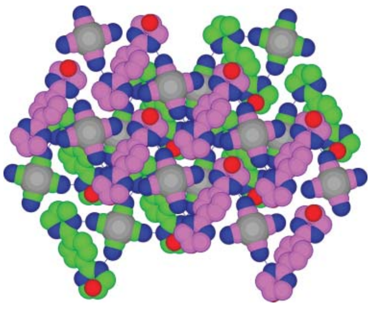

Fig. 6 A portion of the 3-D hydrogen-bonded network (β-phase) formed between the tecton **2**-2H$^+$ and $[Pt(CN)_4]^{2-}$, showing the orientation of two consecutive planes. H atoms are omitted for clarity. For bond distances and angles, see the text.

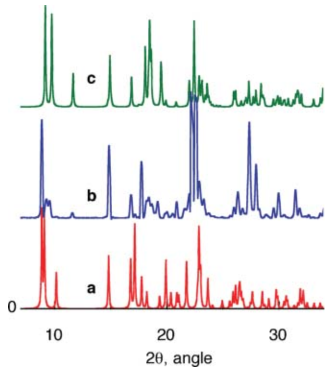

Fig. 7 XRPD patterns for (**2**-2H$^+$, $[Pt(CN)_4]^{2-}$): (a) simulated for α-phase, (b) observed for a mixture and (c) simulated for β-phase.

K$^+$) and the concentration of the two components, were studied. Using as references both simulated patterns from the XRD data obtained by single crystals of α- (Fig. 7(a)) and β- (Fig. 7(c)) phase, no influence of the cation could be observed. Indeed, in the case of K$^+$ and Ba^{2+}, both α- and β-phases were obtained (Fig. 7b). The variation of component concentration in the range 0.5–8 mM was more informative. Indeed, an increase in β-phase was visually observed at low concentration. However, it was not possible to obtain pure α- or β-phase.

The possible thermal interconversion of the two polymorphs was investigated by DSC measurements, revealing the absence of such a process in the 30–350 °C temperature range. No phase transition between room temperature and decomposition was observed for the α-phase obtained with Ni and Pd.

In conclusion, the dicationic tecton **2**-2H$^+$ offers six hydrogen bond donor sites, four primary of NH type and two secondary of OH type. When compared to tecton **1**-2H$^+$, lacking the secondary sites, based on the design of **2**-2H$^+$, the increase in the dimensionality of the network from 1-D to 2-D was predicted and indeed observed for all three $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt) complex anions. However, the observation of two polymorphs (α- and β-phases) in the case of $[Pt(CN)_4]^{2-}$ could not be anticipated.

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Notes and references

† Synthesis of **2**-2HCl: 2.00 g (1 equiv., 15.6 mmol) of 1,4-dicyanobenzene, 2.91 g (2 equiv., 31.2 mmol) of 1,3-diamino-2-propanol and 15 mg of P_2S_5 were mixed together and heated at 120 °C under a gentle flux of argon for 1.5 h. The resulted solid was cooled and acidified with an aqueous solution of HCl (1 M) until pH 5 was reached. After 15 min of stirring, the mixture was filtered, and the filtrate evaporated. Pure compound **2**-2HCl was obtained in 80% yield as a slightly yellowish solid upon crystallisation from distilled water. Colourless monocrystals were obtained by the slow diffusion of acetone into an aqueous solution of **2**-2HCl. ^{1}H NMR (D_2O + *t*BuOH, 300 MHz, 25 °C, δ/ppm): 3.67 (m, 8H, CH_2–NH), 4.57 (t, 2H, J = 2.8 Hz, C*H*–OH) and 7.92 (s, 4H, C*H* arom.). ^{13}C NMR (D_2O + *t*BuOH, 75 MHz, 25 °C, δ/ppm): 45.7 (CH_2–NH), 57.8 (*C*H–OH), 129.0 (*C*H arom.), 133.3 (C arom.) and 160.5 (N–*C*–N). mp = 300 °C (decomp.). $C_{14}H_{20}Cl_2N_4O_2 \cdot 2H_2O$ calc. C, 43.87; H, 6.31; N, 14.62; found C, 43.01; H, 6.22; N, 14.16%.

‡ XRD 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-K$_\alpha$ (λ = 0.71073 Å) radiation. For the structure, diffraction data were corrected for absorption, and structural determination was achieved using SHELXL-97. All hydrogen atoms have been calculated, except for those connected to disordered atoms.

XRPD diagrams were collected on a Scintag XDS 2000 diffractometer using monochromatic Cu-K$_\alpha$ radiation with a scanning range (2θ) between 5 and 90° using a scan step size of 2° min^{-1}. CCDC 650826–650830. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708997j

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