Molecular tectonics: polymorphism and enhancement of networks dimensionality by combination of primary and secondary H-bond sites

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Receipt/Acceptance Data [DO NOT ALTER/DELETE THIS TEXT]

Publication data [DO NOT ALTER/DELETE THIS TEXT]

DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

A dicationic tecton bearing four NH and two OH groups as primary and secondary H-bond donor sites respectively leads in the presence of $[M(CN)_4]^{2-}$ anions to the formation of polymorphic 2- and 3-D H-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 events⁵ operating between either self-complementary or complementary tectons. 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 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 predesigned 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, the 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 H-bond donor sites and its combination with tetracyanometallate anions leading to the formation of 2- and 3-D H-bonded molecular networks.

Increasing the dimensionality of H-bonded networks⁶ from 1- to 2-D requires the interconnection of 1-D arrangements. To this end, one may design tectons bearing both primary and secondary H-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 H-bonded networks⁷ in the presence of anions behaving as H-bond acceptors.^{3,8} In particular, the dicationic tecton **1-2H⁺** (scheme 1) was shown to be well suited for the formation of 1-D networks in the presence of cyanometallate anions.^{9,10} H-bonded networks based on other anionic metal complexes, in particular metal halide species, and protonated tectons have been also reported.¹¹⁻¹³

The tecton **2-2H⁺**, an analogue of **1-2H⁺**, is based on two cyclic amidinium moieties bearing each a OH group. The choice of the *p*-phenylene to interconnect the two 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 H-bonding taking place between the acidic H atoms of **2-2H⁺** and 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 H-bond donor sites respectively. Consequently, such unit could allow to interconnect the 1-D networks that are based on association of the primary sites with complex anion, into a 2-D arrangement through H-bonds between the OH groups and cyanometallate units (Fig. 1b).

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

The synthesis of **2-2H⁺-2Cl⁻** was achieved upon heating under argon at 120 °C for 1.5 hours a 1/2 mixture of 1,4-dicyanobenzene and 1,3-diamino-2-propanol with a catalytic amount of P_2S_5 .¹⁴ The resulted solid bisamidine was acidified with HCl and stored as its hydrochloride salt.

Scheme 1

The structure of the latter was elucidated by XRD on single crystal which 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 *p*-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

H-bonded to a Cl⁻ anion ($d_{\text{N-Cl}} = 3.096 \text{ \AA}$) or to a H₂O molecule ($d_{\text{N-O}} = 2.817 \text{ \AA}$). Two H-bonded H₂O molecules ($d_{\text{O-O}} = 2.742 \text{ \AA}$, $d_{\text{O-Cl}} = 3.069 \text{ \AA}$) bridge the amidinium and the chloride anion.

Fig. 2: A portion of the structure of 2-2HCl showing the H-bonds between 2-2H⁺ and Cl⁻ anions and H₂O molecules. H atoms, except those engaged in H-bonds, are omitted for the sake of clarity. For bond distances and angles, see text.

Upon mixing at r.t. an aqueous solution (5 mL) of the tecton 2-2HCl (20 μmol) with an aqueous solution (5 mL) of either BaM(CN)₄·nH₂O (M = Ni²⁺, Pt²⁺) or K₂M(CN)₄·nH₂O (M = Ni²⁺, Pd²⁺, Pt²⁺) (20 μmol) colourless crystals were obtained overnight. Whereas in the case of [Ni(CN)₄]²⁻ and [Pd(CN)₄]²⁻, plate shape crystals (α-phase) were obtained (Fig. 3a), for [Pt(CN)₄]²⁻, a mixture of plate (Fig. 3a) and prismatic shape (β-phase) (Fig. 3c) crystals were observed.

Fig. 3: Pictures of the polymorph α (a) obtained for the combination of tecton 2-2H⁺ with [M(CN)₄]²⁻ (M = Ni, Pd and Pt) and of polymorph β (c) obtained only for (2-2H⁺, [Pt(CN)₄]²⁻). b) and d) represent schematically the arrangement of networks in α- and β-phase respectively.

For the α-phase, in all three cases the crystals are isomorphous (*triclinic*, space group *P-1*). Crystals are composed of 2-2H⁺ dications and [M(CN)₄]²⁻ (M = Ni²⁺, Pd²⁺ and Pt²⁺) dianions without any solvents molecules. When considering H-bonds formed between the primary NH sites and CN groups, as expected and previously observed for 1-2H⁺ dications,¹⁰ the cationic and anionic components form a neutral 1-D network through a dihapto mode of H-bonding ($d_{\text{N-N}}$ in the range of 2.83 Å and 2.90 Å) (Fig. 4). Owing to OH groups, behaving as secondary H-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 H bonds of the OH-N≡C type ($d_{\text{N-O}}$ in the range of 2.95 Å, and 2.98 Å). Among the four CN groups connected to the metal centre, only two are involved in H-bond with the OH groups (Fig. 3b).

Fig. 4: A portion of the 2-D H-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 the sake of clarity. For bond distances and angles, see text.

This description is consistent with the 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⁻, 2124 and 2144 cm⁻¹ for [Pd(CN)₄]²⁻).

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

Fig. 5: XRPD patterns for (2-2H⁺, [Ni(CN)₄]²⁻): simulated (a), observed (b) and observed (c) for (2-2H⁺, [Pd(CN)₄]²⁻).

As stated above, in the case of the [Pt(CN)₄]²⁻, in addition to the α-phase, another morphology (β-phase) was observed (Fig. 3c). Again, when only considering the H-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 ($d_{\text{N-N}}$ in the range of 2.90 Å and 2.95 Å). In marked contrast with the previous case discussed above, the second type of H-bond is of OH-O type and takes place between OH moieties belonging to consecutive planes ($d_{\text{OH-O}} = 2.88 \text{ \AA}$).

Fig. 6: A portion of the 3-D H-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 the sake of clarity. For bond distances and angles, see text.

Furthermore, again in marked contrast with 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 H-bonded network (Fig. 3d).

Although we were able to select single crystals with either plate type or prismatic-shape morphologies 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 counter ion (Ba²⁺ or K⁺) and the concentration of the two components, were studied. Using as reference both simulated patterns from the XRD data obtained on single crystals of α-phase (Fig. 7a) and β-phase (Fig. 7c), 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 the concentration of the components in the range of 0.5 and 8 mM was more informative. Indeed, an increase of the β -phase was visually observed at low concentration.

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

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

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

Université Louis Pasteur, Institut Universitaire de France, the CNRS and the Ministry of Education and Research are acknowledged for financial support and for a scholarship to P. D. We also thank G. Laugel for kindly performing XRPD measurements.

Notes and references

Synthesis of $2\text{-}2\text{HCl}$: 2.00 g (1 eq., 15.6 mmol) of 1,4-dicyanobenzene, 2.91 g (2 eq., 31.2 mmol) of 1,3-diamino-2-propanol and 15 mg of P_2S_5 were mixed together and heated at 120°C with a gentle flux of argon during 1.5 hours. The resulted solid was cooled and acidified with an aqueous solution of HCl (1N) until pH 5 was reached. After 15 min of stirring, the mixture was filtered and the filtrate evaporated. The pure compound $2\text{-}2\text{HCl}$ was obtained in 80 % yield as a slightly yellowish solid upon crystallisations from distilled water. Colourless monocystals were obtained by slow diffusion of acetone into an aqueous solution of $2\text{-}2\text{HCl}$. $^1\text{H-NMR}$ ($\text{D}_2\text{O} + t\text{BuOH}$, 300 MHz, 25 °C, δ ppm): 3.67 (m, 8H, $\text{CH}_2\text{-NH}$); 4.57 (t, 2H, $J = 2.8$ Hz, CH-OH); 7.92 (s, 4H, CH arom.); $^{13}\text{C-NMR}$ ($\text{D}_2\text{O} + t\text{BuOH}$, 75 MHz, 25 °C, δ ppm): 45.7 ($\text{CH}_2\text{-NH}$); 57.8 (CH-OH); 129.0 (CH arom.); 133.3 (C arom.); 160.5 (N-C-N). mp = 300 °C decomp., $\text{C}_{14}\text{H}_{20}\text{Cl}_2\text{N}_4\text{O}_2 \cdot 2\text{H}_2\text{O}$ 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 $\text{Mo-K}\alpha$ ($\lambda = 0.71073$) radiation. For the structure, diffraction data were corrected for absorption and structural determination was achieved using SHELEXL-97. All hydrogen atoms have been calculated except those connected to disordered atoms. CCDC 335 ??? contains the supplementary crystallographic data for this paper.

Crystallographic data for $2\text{-}2\text{H}^+\text{-}2\text{Cl}^-$: Colourless, 173 K, $\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_4$, $M = 383.27$, monoclinic, $a = 13.0888(8)$, $b = 4.5837(3)$, $c = 15.0058(10)$ Å, $\beta = 99.515(4)^\circ$, $U = 887.89(10)$ Å³, $Z = 2$, space group $P2(1)/n$, $DC = 1.434$ g.cm⁻³, $\text{Mo-K}\alpha$, $\mu = 0.392$ mm⁻¹, 2038 independent data with $I > 2\sigma(I)$, $R = 0.0344$, $R_w = 0.0541$.

$(2\text{-}2\text{H}^+, [\text{Ni}(\text{CN})_4]^{2-})$ (α -phase): Colourless, 173 K, $\text{C}_{18}\text{H}_{20}\text{N}_8\text{NiO}_2$, $M = 439.13$, triclinic, $a = 4.6008(4)$, $b = 10.3677(10)$, $c = 10.3677(10)$ Å, $\alpha = 110.610(2)^\circ$, $\beta = 99.751(2)^\circ$, $\gamma = 90.156(2)^\circ$, $U = 469.02(8)$ Å³, $Z = 1$, space group $P-1$, $DC = 1.555$ g.cm⁻³, $\text{Mo-K}\alpha$, $\mu = 1.068$ mm⁻¹, 2973 independent data with $I > 2\sigma(I)$, $R = 0.0358$, $R_w = 0.0476$.

$(2\text{-}2\text{H}^+, [\text{Pd}(\text{CN})_4]^{2-})$ (α -phase): Colourless, 173 K, $\text{C}_{18}\text{H}_{20}\text{N}_8\text{PdO}_2$, $M = 486.82$, triclinic, $a = 4.6215(2)$, $b = 10.5270(4)$, $c = 10.8108(4)$ Å, $\alpha = 111.288(2)^\circ$, $\beta = 99.763(2)^\circ$, $\gamma = 89.328(2)^\circ$, $U = 482.25(3)$ Å³, $Z = 1$, space group $P-1$, $DC = 1.676$ g.cm⁻³, $\text{Mo-K}\alpha$, $\mu = 0.996$ mm⁻¹, 2717 independent data with $I > 2\sigma(I)$, $R = 0.0247$, $R_w = 0.0258$.

$(2\text{-}2\text{H}^+, [\text{Pt}(\text{CN})_4]^{2-})$ (α -phase): Colourless, 173 K, $\text{C}_{18}\text{H}_{20}\text{N}_8\text{PtO}_2$, $M = 575.51$, triclinic, $a = 4.6482(2)$, $b = 10.4381(5)$, $c = 10.8458(4)$ Å, $\alpha = 111.0191(10)^\circ$, $\beta = 99.3081(10)^\circ$, $\gamma = 88.850(2)^\circ$, $U = 484.32(4)$ Å³, $Z = 1$, space group $P-1$, $DC = 1.973$ g.cm⁻³, $\text{Mo-K}\alpha$, $\mu = 7.276$ mm⁻¹, 2810 independent data with $I > 2\sigma(I)$, $R = 0.0176$, $R_w = 0.0176$.

$(2\text{-}2\text{H}^+, [\text{Pt}(\text{CN})_4]^{2-})$ (β -phase): Colourless, 173 K, $\text{C}_{18}\text{H}_{20}\text{N}_8\text{PtO}_2$, $M = 575.51$, triclinic, $a = 10.0141(3)$, $b = 10.0141(3)$, $c = 10.7497(10)$ Å, $\alpha = 67.893(2)^\circ$, $\beta = 67.893(2)^\circ$, $\gamma = 69.861(2)^\circ$, $U = 969.85(6)$ Å³, $Z = 2$, space group $P-1$, $DC = 1.971$ g.cm⁻³, $\text{Mo-K}\alpha$, $\mu = 7.267$ mm⁻¹, 5654 independent data with $I > 2\sigma(I)$, $R = 0.0356$, $R_w = 0.0797$.

XRPD diagrams were collected on a Scintag XDS 2000 diffractometer using monochromatic $\text{Cu K}\alpha$ radiation with a scanning range (2 θ) between 5° and 90° using a scan step-size of 2° min⁻¹.

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The combination of a dicationic tecton bearing four NH and two OH groups as primary and secondary H-bond donor sites respectively with $[\text{M}(\text{CN})_4]^{2-}$ anions leads to the formation of two polymorphs.