

Complementary hydrogen bonds and ionic interactions give access to the engineering of organometallic crystals

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A crystal synthesis strategy based on a sequence of redox/acid–base/self-assembly/crystallisation processes has been devised and successfully applied to prepare a number of mixed organic/organometallic and organometallic/organometallic crystalline materials. An adequate choice of the building blocks permits design and construction of mono-, two- and three-dimensional superanion framework structures encapsulating organometallic cations. The superanions are generated by partial deprotonation of polyprotic acids from the reaction with the organometallic hydroxides $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2][\text{OH}]$ and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2][\text{OH}]$, produced *in situ* by direct oxidation of the neutral complexes $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$. The anionic superstructures are held together by a combination of neutral and interionic O–H \cdots O hydrogen bonds, while the interaction with the organometallic cations is based on a profusion of C–H \cdots O bonds reinforced *via* charge assistance.

1 Introduction

“... in order to achieve the maximum stability, the two molecules must have complementary surfaces, like die and coin, and also a complementary distribution of active groups. The case might occur in which the two complementary structures happened to be identical; however, in this case also the stability of the complex of two molecules would be due to their complementarity rather than their identity” (L. Pauling, M. Delbrück, 1940).¹

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Organometallic crystal engineering is an emerging field of research.² Much of the excitement arises from the idea of being able to combine the plethora of functional group characteristics of organic molecules³ with the co-ordination geometry, ionic charges, valence and spin states typical of organometallic complexes in order to obtain novel crystalline materials.⁴ An intelligent choice of the building blocks may yield materials with magnetic, conducting, superconducting⁵ and non-linear optical properties.⁶

Crystal engineering proceeds *via* the essential steps of analysis, synthesis and application. Analysis is the examination of available information on intermolecular interactions and molecular recognition,⁷ but also nucleation and crystallisation processes.⁸ It relies largely on expert analysis of data repositories, such as the CSD,⁹ on computer graphics and on the utilisation of computational tools. The theoretical generation of crystal structures starting from molecular structure alone can also be seen as a sophisticated kind of crystal structure analysis.¹⁰

2 The energy issue and the target material

Synthesis is where the chemist works on his/her more congenial ground. Crystal synthesis strategies depend on the choice of target materials, hence depend on the energetics of the supramolecular bonding interactions one is planning to master. There is a substantial energetic difference between crystal syn-

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theses involving only non-covalent interactions and those in which covalent bonds are broken and formed to build the crystal edifice. This difference has important methodological consequences. In the construction of non-covalent crystals use is made prevalently of molecular¹¹ or ionic¹² building blocks held together by bonds weaker than those between atoms forming the building blocks. In covalent crystal engineering, on the contrary, use is made of covalent bonds between components that do not have a chemical identity on their own.¹³ Covalent and non-covalent crystal engineering admit an intermediate situation, that is co-ordination crystal engineering¹⁴ where the link between building blocks is provided by polydentate ligands that can join together co-ordination complexes in extended networks ('co-ordination polymers').

This perspective will deal essentially with non-covalent crystal engineering in which the building blocks are molecules or ions. In recent years we have devoted our efforts, also in collaboration with others, to expanding crystal engineering from its cradle, which is organic, to the organometallic chemistry area. The objective is that of bringing the electronic, magnetic, and structural properties of transition metal atoms into crystals that behave very much like organic crystals (but see below).

The role of metal atoms in crystal engineering has been addressed in other reports and will not be dealt with in any great detail here.¹⁵ We have identified five distinct functions of metal atoms.

(i) A topological function: the co-ordination geometry around the metal centres can be used to preorganise in space the extramolecular bonding capacity of the ligands.¹⁶

(ii) An electronic function: the electronics of metal–ligand bonding interactions, such as donation and back donation, permit tuning of ligand polarity and acid/base behaviour.¹⁷

(iii) A (tuneable) electrostatic function: metal atom variable oxidation states and/or the utilisation of non-neutral ligands permit 'charge assistance' to weak bonds (see also below).

(iv) Direct participation of metal atoms in extramolecular bonds: electron deficient metal atoms may accept electron density intermolecularly from suitable Lewis bases, while electron rich metal atoms may have sterically unhindered lone pairs that accept hydrogen bonds.¹⁸

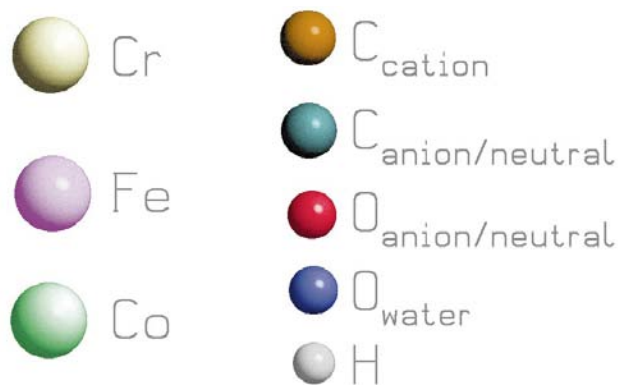
(v) A templating function: organometallic complexes chosen for their size and shape may be used to template self-assembly of organic, inorganic and organometallic molecules or ions into mono- di-, and three-dimensional superstructures.

This article describes how the above functions, in particular (iii) and (v), have been used in our laboratory to produce mixed organic, inorganic and organometallic crystals.

We have entered the field with the initial objective of building organometallic (OM hereafter) systems that would mimic the packing of organic (OR hereafter) crystals through bringing in the solid transition metal complexes. The first step was the preparation of a bis(benzene) chromium analogue of Etter's cyclohexane-1,3-dione (CHD) inclusion compound (see Scheme 1 and Fig. 1).¹⁹ We succeeded only partially because $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ is easily oxidised to $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ which then forms ionic systems.²⁰ Etter's benzene cyclamer and our bis(benzene) chromium analogue $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+ \cdot [(\text{CHD})_2]^- \cdot 2\text{CHD}$ present many analogies and differences: (i) benzene and $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ have similar discoidal shape, (ii) in both systems the diones are linked *via* O–H...O hydrogen bonds and here is where they are similar, (iii) the interaction between $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ and the surrounding superanion is chiefly coulombic in nature and here is where the two systems are fundamentally diverse.

3 The crystal synthesis strategy

The dione/ $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ experiment showed us that the bis(benzene) chromium hydroxide could provoke self-assembly of



Scheme 1 Colour scheme adopted for all figures, which have been produced with the computer graphic program SCHAKAL 97 (E. Keller, University of Freiburg, Germany).

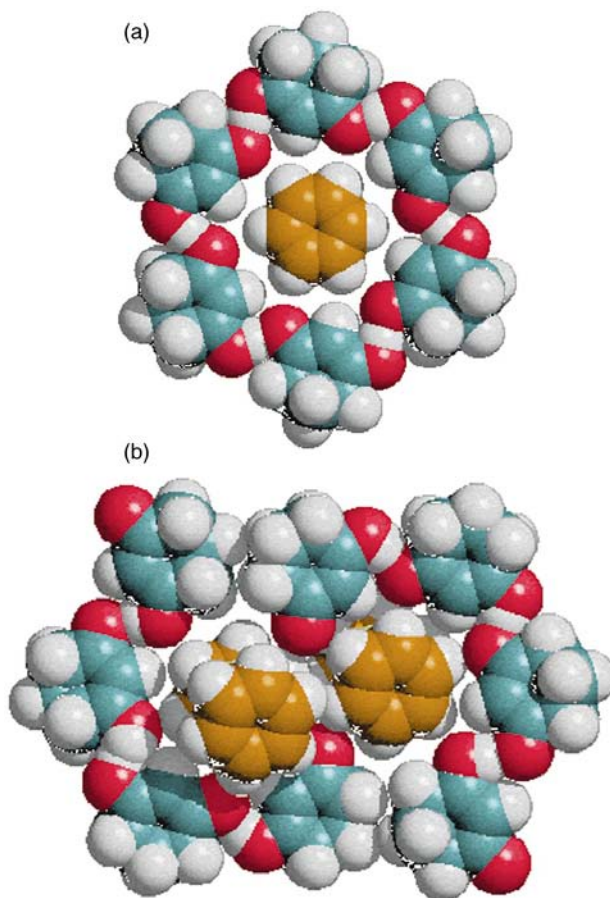


Fig. 1 Space filling representation of Etter's crystalline $(\text{CHD})_6(\text{C}_6\text{H}_6)$ cyclamer (a) and of the organometallic inclusion compound $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+ \cdot [(\text{CHD})_2]^- \cdot 2\text{CHD}$ (b).

the deprotonated dione into superanions *via* formation of negatively charged O–H...O[−] hydrogen bond interactions. The step from the dione to polycarboxylic OR acids came quite naturally with the realisation that the reproducibility of the self-assembly strategy was controlled by two factors: (i) the absence of hydrogen bond acceptors on the cation that could compete with the acid itself and (ii) the complementary role of strong and weak hydrogen bonds reinforced by coulombic contributions. Many novel crystalline materials have been prepared based on the combination of redox processes, acid–base and solubility equilibria as summarised below.

<i>Oxidation of neutral sandwich OM molecules to the corresponding cations</i>
<i>Reduction of O₂ to strongly basic O₂⁻ Deprotonation of the acid and generation of OR/OM anions</i>
⇒ The OM cations are stable ⇒ The metal atoms are not available for co-ordination ⇒ Neutral species are insoluble in water or polar solvents and soluble in thf ⇒ In water the solutions are those of hydroxides
<i>The anions form O–H···O, O–H⁻···O⁻ and O–H···O⁻ interactions and self-assemble into supramolecular anions</i>
<i>The cations mould the O–H···O hydrogen bonded frameworks via charge assisted C–H^{δ+}···O^{δ-} bonds</i>
⇒ The strongly basic CO ₂ ⁻ groups seek strong donors which are only available on the neutral or partially deprotonated acid itself ⇒ The supramolecular salts are insoluble in low polarity solvents while they are soluble in water ⇒ The aggregates precipitate immediately in apolar solvents and can be recrystallised from water or nitromethane

This, of course, does not imply a temporal sequence, rather serves the scope of describing the chemical and physical processes that lead from the initial neutral OR and OM molecular building blocks to the desired OR/OM or OM/OM crystalline solids.

In the first step of the crystal synthesis sequence the highly basic O₂⁻ anion is produced by oxidation of the OM cation. Redox potentials for many OM sandwich complexes are available and have recently been reviewed.²¹ Two distinct processes occur in water and in less polar solvents (*e.g.* thf) because reactants and products have inverse solubility in the two types of solvent. In water the neutral OM species, namely [Cr(η⁶-C₆H₆)₂] and [Co(η⁵-C₅H₅)₂], are insoluble while the acid is usually (from very to fairly) soluble. In thf, on the contrary, the neutral OM species is soluble while the acid is usually only sparingly (if at all) soluble. Hence, in water oxidation of the OM species occurs in the heterogeneous phase (*e.g.* the solid neutral OM goes into solution as a cation together with the reduced oxygen species), whereas the acid deprotonation and formation of carboxylate anions occurs in the homogeneous phase. On the contrary, in thf OM oxidation occurs in the homogeneous phase, but the subsequent acid–base reaction is heterogeneous (*e.g.* in the presence of the solid acid) and the product is insoluble and precipitates, as soon as it is formed, as a powder material which then needs to be recrystallised from water or nitromethane. This is an important point because one may wonder if the aggregation in highly organised superstructures (see below) occurs as the product is formed or only upon recrystallisation from polar solvents. We do not have a definitive answer to this question. Although in most cases powder diffraction spectra of the bulk materials obtained from thf could be assigned on the basis of the experimental single crystal structure, we have also observed differences which may indicate the occurrence of polymorphic forms or different degrees of solvation for the same crystalline materials.

4 The organometallic hydroxides [Cr(η⁶-C₆H₆)₂][OH]·3H₂O and [Co(η⁵-C₅H₅)₂][OH]·4H₂O

The possibility of using oxygen as oxidant is the beauty and limitation of the process described above. Oxidation with oxygen is clean and does not produce undesired anions that

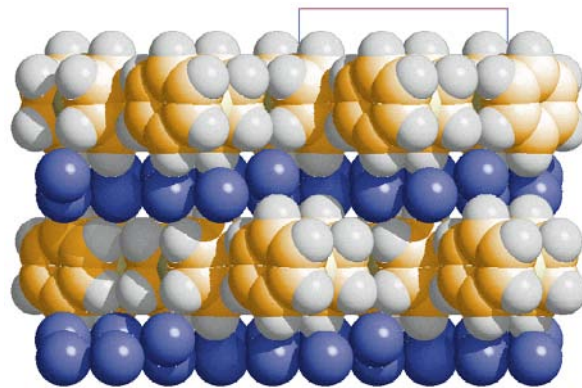


Fig. 2 Space filling representation of crystalline [Cr(η⁶-C₆H₆)₂][OH]·3H₂O. The crystal is constituted of a stacking sequence of layers containing [Cr(η⁶-C₆H₆)₂]⁺ cations intercalated with ([OH]⁻·3H₂O)_n layers of hydrogen bonded water molecules and OH⁻ groups.

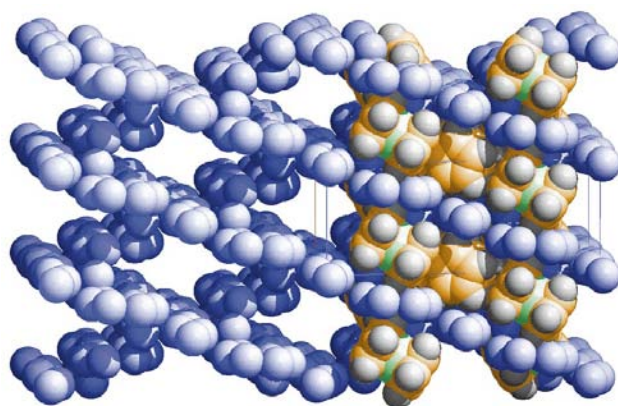


Fig. 3 Space filling representation of crystalline [Co(η⁵-C₅H₅)₂]⁺[OH]⁻·4H₂O. The [OH]⁻·4H₂O system forms a three-dimensional structure based on hydrogen bonded zigzagged chains of disordered 'ice-like' hexagonal rings interconnected *via* oxygen atoms.

may compete with those obtained from the acid molecules by deprotonation. Furthermore, it generates *in situ* the strongly basic O₂⁻ anion which deprotonates the acid. Of course, if the acid is the water used as solvent, the reaction simply leads to formation of bright yellow solutions of the hydroxides [Cr(η⁶-C₆H₆)₂][OH] and [Co(η⁵-C₅H₅)₂][OH], which we have been able to isolate and characterise in their hydrated crystalline forms.^{22,23}

The crystal of the hydroxide [Cr(η⁶-C₆H₆)₂][OH]·3H₂O is constituted of a stacking sequence of layers containing [Cr(η⁶-C₆H₆)₂]⁺ cations intercalated with layers of hydrogen bonded water molecules and OH⁻ groups. Therefore, the layers carry opposite ionic charge and result in a system with crystal faces of completely different chemical composition (see Fig. 2). The ([OH]⁻·3H₂O)_n layer is formed of a slightly puckered hexagonal network containing three water molecules and one OH⁻ group per formula unit, with the oxygen atoms hydrogen bonded to three neighbours.

Contrary to [Cr(η⁶-C₆H₆)₂][OH]·3H₂O, which is solid at room temperature and fairly stable in the air, crystals of the analogue cobaltocenium hydroxide [Co(η⁵-C₅H₅)₂][OH] have been, thus far, obtained at temperatures below 273 K where it solidifies with a variable number of water molecules. Successful structural characterisation has been possible for the hydrated form [Co(η⁵-C₅H₅)₂][OH]·4H₂O.²³ The [OH]⁻·4H₂O system forms a three-dimensional structure (see Fig. 3) based on hydrogen bonded zigzag chains of disordered 'ice-like' hexagonal rings interconnected *via* oxygen atoms.²⁴

Both crystals show that the interaction between the OM cations and the negatively charged hydrogen bonded water/OH⁻ superstructures is based on several C–H···O bonds

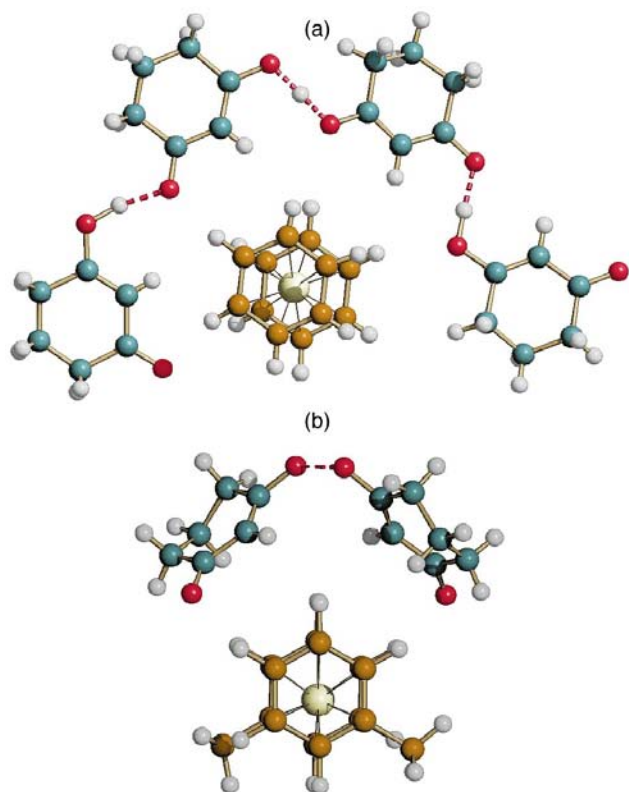


Fig. 4 The analogy between (a) $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+[(\text{CHD})_2]^- \cdot 2\text{CHD}$ and (b) $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]^+[(\text{CHD})_2]^-$. Note how the structure of the bis-(toluene)chromium differs from that of the bis(benzene)chromium by the absence of the two pendant neutral CHD.

between oxygen atoms and the C–H systems of the ligands (see also below).

5 Horseshoes and clamps

As mentioned in the Introduction, the crystals obtained from cyclohexane-1,3-dione were the first to be prepared. In a similar way, the aggregate $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]^+[(\text{CHD})_2]^-$ has been obtained starting from $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]$.²⁵ While in crystalline $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+[(\text{CHD})_2]^- \cdot 2\text{CHD}$ the dione “horseshoes” are related by a centre of inversion resulting in a large nearly planar system formed by two $[(\text{CHD})_4]^-$ systems that embrace two bis(benzene)chromium cations [Fig. 1(b)], substitution of one methyl group for a hydrogen atom on the cation changes the overall shape of the fragment. The “arms” of the toluene ligands are not compatible with a tetrameric unit and the superanion $[(\text{CHD})_2]^-$ acts as a “clamp” around the OM cation. The relationship between $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+[(\text{CHD})_2]^- \cdot 2\text{CHD}$ and $[\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]^+[(\text{CHD})_2]^-$ is shown in Fig. 4.

6 Ribbons, sheets, honeycombs and boxes

The experiments with the dione systems taught us that self-assembly in supraanionic structures can be attained (i) if the metal centres on the OM species are “protected” from coordination and do not carry ligands which can compete in strong hydrogen bonding formation, and (ii) if the anions have a “reserve” of strong proton donors for O–H \cdots O bonding. These simple design criteria have been exploited to prepare a number of new crystalline materials based on polyprotic organic and organometallic acids. These will be briefly described in the following.

Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione, H_2SQA) has been treated with cobaltocenium hydroxide in 1 : 1 and 2 : 1 stoichiometric ratios obtaining two different crystalline materials. The 1 : 1 system is constituted of $([\text{HSQA}]^-)_n$ ribbons and of ribbons of cobaltocenium cations, see Fig. 5.²⁶ The good

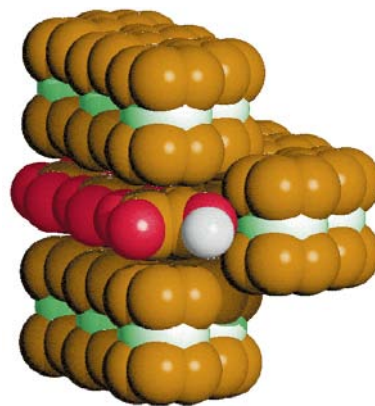


Fig. 5 Ribbons of $[\text{HSQA}]^-$ monoanions bonded *via* negatively charged O–H \cdots O hydrogen bonds and ribbons of cobaltocenium cations form the crystal of the 1 : 1 system.

matching in size and shape between the cyclopentadienyl ligands and the $[\text{HSQA}]^-$ ions leads to a superstructure in which the squarate ribbons intercalate between cobaltocenium cations (Fig. 5). The π – π distance is *ca.* 3.35 Å. The oxygen atoms from the rims of the $([\text{HSQA}]^-)_n$ ribbons interact with the $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations *via* charge-assisted C–H δ^+ \cdots O δ^- hydrogen bonds (five H \cdots O distances in the range 2.272–2.500 Å). What is more, the packing arrangement is chiral in space group $P2_1$. The unusual orange colour suggests formation of a charge transfer complex, whose properties are under investigation.

On changing the stoichiometry to 2 : 1 the unusual orange colour is lost, and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{HSQA})(\text{H}_2\text{SQA})]^-$ is obtained as yellow crystals. The crystals contain supramolecular monoanions $[(\text{HSQA})(\text{H}_2\text{SQA})]^-$ resulting from the loss of one proton for every two squaric acid molecules bonded *via* interanion O–H \cdots O hydrogen bonds (O \cdots O distances 2.440 and 2.436 Å). The monoanions form ribbons *via* O–H \cdots O hydrogen bond interactions, with formation of ten-membered ring systems (O \cdots O distances in the range 2.539–2.574 Å) reminiscent of the carboxylic rings. The ribbons are stacked in such a way that squarate moieties overlap hydrogen bonded rings, resulting in layers with oxygen atoms protruding above and below the layer surface. The cobaltocenium cations lie side-on to the layer and interact *via* charge-assisted C–H δ^+ \cdots O δ^- hydrogen bonds.

Tartaric acids

Similarly to the squarate systems, different stoichiometries lead to isolation of different crystalline systems when D,L-tartaric acid (D,L- H_2TA) is used. In crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{D,L-HTA})(\text{D,L-H}_2\text{TA})]^-$ the acid forms an anionic organic honeycomb framework [see Fig. 6(a)].²⁷ The superanion $[(\text{D,L-HTA})(\text{D,L-H}_2\text{TA})]^-$ is formally the result of the loss of one proton for every two tartaric acid molecules, with the two units bonded *via* a short –C(O)O–H \cdots O(O)C– hydrogen bond [2.434(1) Å]. The dimers are then linked in the honeycomb framework *via* O–H \cdots O bonds involving the two external carboxyl groups and the hydroxyl groups. The interaction between the supraanionic network and the encapsulated $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations occurs *via* C–H δ^+ \cdots O δ^- hydrogen bonds between the staggered cyclopentadienyl ligands of the cations and the CO and the OH groups of the anionic framework [Fig. 6(b)]. If the stoichiometric ratio between $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2][\text{OH}]$ and tartaric acid in the acid–base reaction is changed from 1 : 2 to 1 : 1, the hydrated crystalline salt $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{D,L-HTA})]^- \cdot \text{H}_2\text{O}$ is obtained.

Trimesic acid

When the acid $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ -1,3,5-(H_3TMA) is treated with

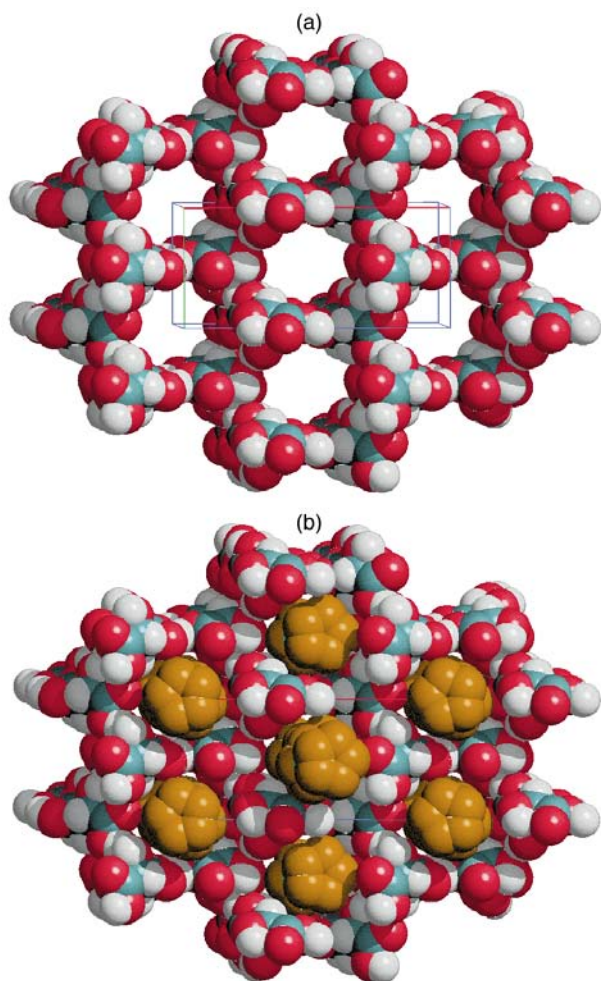


Fig. 6 The honeycomb arrangement of D,L-tartaric acid in crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{D,L-HTA})(\text{D,L-H}_2\text{TA})]^-$ (a) and a view of the honeycomb type structure with the cobaltocenium cations occupying the channels (b).

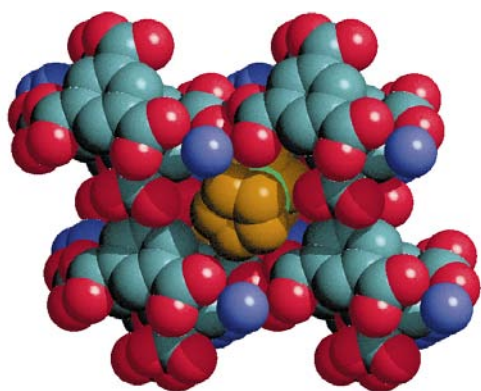


Fig. 7 The anionic organic superstructure which folds around the cobaltocenium cation in crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{H}_3\text{TMA})(\text{H}_2\text{TMA})]^- \cdot 2\text{H}_2\text{O}$.

$[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{OH}]^-$ crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{H}_3\text{TMA})(\text{H}_2\text{TMA})]^- \cdot 2\text{H}_2\text{O}$ is obtained²³ in which (formally) one mono-deprotonated and one neutral acid molecule form a dimeric superanion held together by an $\text{O-H} \cdots \text{O}$ hydrogen bond interaction. The superanion can be described as formed by a deprotonated dimeric system of two trimesic acid moieties which maintains four CO_2H groups to employ in hydrogen bonding systems with the surrounding anions. The distribution of trimesic acid moieties results in a large anionic organic superstructure which folds around the cobaltocenium cation as shown in Fig. 7. Two water molecules also participate in the hydrogen bond network.

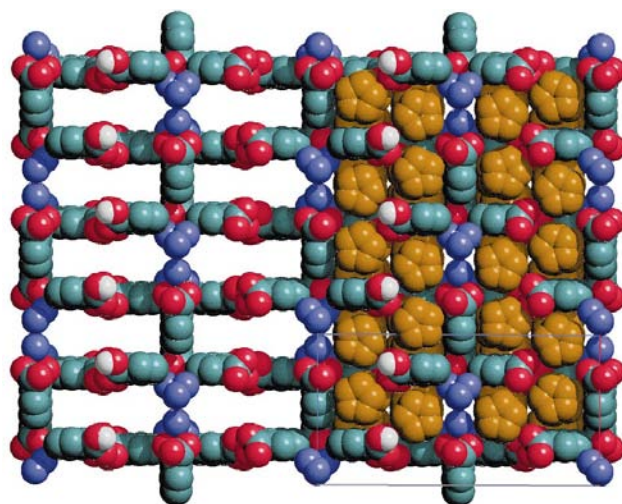


Fig. 8 Space filling representation of $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\}_4[\text{HPA}^-]_2[\text{PA}^{2-}] \cdot 6\text{H}_2\text{O}$ which contains ribbons formed by hydrogen bonded mono-deprotonated anions and ribbons formed by fully deprotonated anions interlinked by water molecules forming, respectively, the “ceiling and floor” and “walls” of the crystalline edifice.

Phthalic acid

The acid $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ -1,2-(H₂PA) has been used to produce $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\}_4[\text{HPA}^-]_2[\text{PA}^{2-}] \cdot 6\text{H}_2\text{O}$.^{28a} The interest in this particular building block stems from the possibility for phthalic acid of forming both intra- and inter-molecular hydrogen bonds. The crystal of $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\}_4[\text{HPA}^-]_2[\text{PA}^{2-}] \cdot 6\text{H}_2\text{O}$ contains ribbons formed by mono-deprotonated anions and ribbons formed by fully deprotonated anions interlinked by water molecules (see Fig. 8). The two types of ribbons form, respectively, the “ceiling and floor” and “walls” of the crystalline edifice.

Chiral acids: L-tartaric and dibenzoyl-L-tartaric acid

The idea of using commercially available enantiomerically pure OR acids to build up chiral frameworks is a logical progression of the results described above. The possibility of reproducible strategies for the preparation of chiral frameworks in which dipolar electronic systems could be accommodated is of primary importance in the search for efficient second harmonic generation materials.

When enantiomerically pure L-tartaric acid is employed the chiral crystal $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{L-HTA}]^-$ is obtained.^{28b} The crystal is constituted of a three-dimensional OR superanion. The honeycomb-type structure is no longer based on hexagonal channels as in the previous case but on square ones (see Fig. 9). The monodeprotonated L-HTA⁻ ions form chains that are cross-linked by other neutral $\text{-OH} \cdots \text{O}=\text{C}$ hydrogen bonds.

An analogous preparation can be carried out with enantiomerically pure dibenzoyl-L-tartaric acid (L-H₂BTA).^{28b} The crystal structure of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{L-HBTA}]^-$ is (obviously) chiral in space group $P2_12_12_1$. Since the acid is mono-deprotonated, as in the case of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{L-HTA}]^-$, one “untouched” CO_2H group forms a COO-H-OOC hydrogen bond with the carboxylate system CO_2^- of another anion thus forming ribbons through the crystal. However, since the (L-HBTA⁻), anionic chains have no additional donor groups to use in cross-links, the construction of a connected hydrogen bonded three-dimensional network is not possible. The interaction between the anionic chain and OM cations takes advantage of a large number of charge-assisted $\text{C-H}^{\delta+} \cdots \text{O}^{\delta-}$ interactions.

7 The organometallic acid $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})_2]$

More recently, the redox/acid–base strategy outlined above has

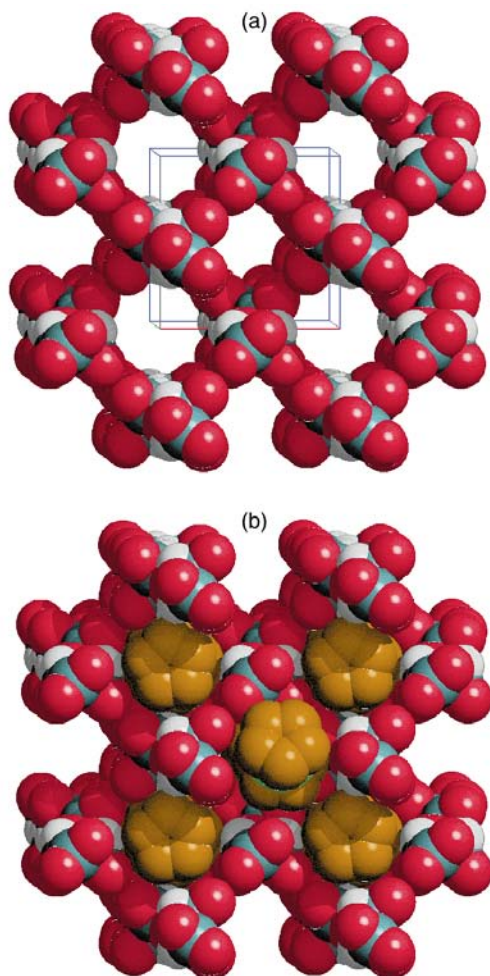


Fig. 9 (a) Space-filling representation of the *L*-tartaric acid framework in crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{L-HTA}]^-$ with the cations occupying the channels (b); H atoms bound to C atoms are omitted for clarity.

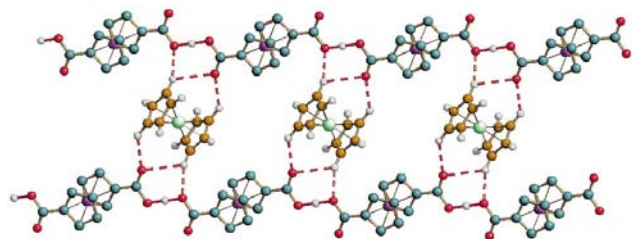


Fig. 10 Ribbons of hydrogen bonded $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})(\eta^5\text{-C}_5\text{H}_4\text{CO}_2)]^-$ anions interacting with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations *via* charge-assisted $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ bonds.

been extended to the use of OM carboxylic acids as building blocks. Although polycarboxylic OM acids are not as common as organic ones, the neutral OM complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})_2]$ (FeACH_2 hereafter) has proved to be extremely versatile.²⁹ The reaction with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$ and $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ in *thf* proceeds similarly to the ones leading to OR/OM systems, with the non-trivial difference that the result is an OM/OM mixed system which contains metal atoms in different oxidation and/or spin states. Crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})(\eta^5\text{-C}_5\text{H}_4\text{CO}_2)]^-$ and $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})(\eta^5\text{-C}_5\text{H}_4\text{CO}_2)]^-$ have been prepared.²⁹ The two species contain different electronic and spin metal centres: 18 electron Fe^{II} and Co^{III} are present in the former whereas 18 electron Fe^{II} and paramagnetic 17 electron Cr^{I} are present in the latter crystalline material. In the Fe/Co crystal the FeACH_2^- anions form ribbons *via* interanion $\text{O-H}\cdots\text{O}^-$ bonds between ligands in *transoid* conformation (see Fig. 10). In the Fe/Cr system, on

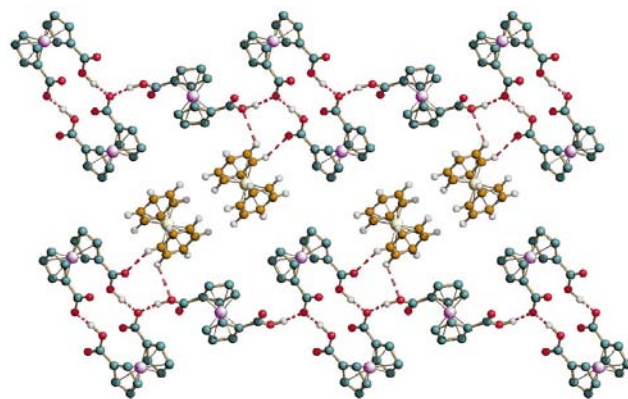


Fig. 11 Ribbons of $\{[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})(\eta^5\text{-C}_5\text{H}_4\text{CO}_2)][\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})_2]_{0.5}\}^-$; note how the neutral molecule acts as a bridge between hydrogen bonded dimers formed by two FeACH_2^- anions. Charge-assisted $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ bonds link the pair of encapsulated $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ cations.

the other hand, there is one neutral FeACH_2 molecule per two FeACH_2^- anions. The neutral molecule acts as a bridge between hydrogen bonded dimers formed by two FeACH_2^- anions (see Fig. 11). It is noteworthy that this latter species contains pairs of paramagnetic $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ cations, a packing feature observed already with the cyclohexanedione derivative.

8 Heavily hydrated species

Rather serendipitously, “heavily hydrated species” are sometimes obtained. Although formation of these compounds is likely to be mainly under kinetic control, we have observed that it is only when a stoichiometric defect of the acid is used that species with a large number of water molecules are obtained. With dibenzoyl-*L*-tartaric acid the crystalline material $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\}_2[\text{L-BTA}]^{2-}\cdot 11\text{H}_2\text{O}$ is obtained. Since the acid is completely deprotonated, no hydrogen bonding donor group is available for the twelve potential hydrogen bonding acceptor sites. The eleven water molecules, therefore, play a twofold function: not only they fill space efficiently, but also, and more importantly, they provide a large number of OH donor groups which are able to stabilise the crystal structure *via* hydrogen bonding. Crystallisation from water of the $\text{Co}(\text{C}_5\text{H}_5)_2\text{-FeACH}_2$ system prepared in 2:1 ratio leads to complete deprotonation of the dicarboxylic acid and to crystallisation of $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\}_2[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2)_2]^{2-}\cdot 7.75\text{H}_2\text{O}$.²⁸

9 Co-operative strong and weak hydrogen bonds and charge assistance

The hydrogen bond is the principal non-covalent interaction in the synthesis of molecular crystals, because it combines strength with directionality.³⁰ Directionality means predictability and reproducibility, properties which are essential in any synthetic strategy. The classical $\text{O-H}\cdots\text{O}$ hydrogen bonds formed by CO_2H and OH groups are among the strongest neutral bonds. When neutral molecules are involved the strength of this three-centre four-electron interaction can be tuned by varying the nature of the acceptors and donors and/or the polarity of the groups involved. In addition to this, the $\text{O-H}\cdots\text{O}$ bond can be strengthened if the polarity of the acceptor systems is increased *via* deprotonation. Negatively charged $\text{O-H}\cdots\text{O}^-$ bonds have been studied extensively and shown to possess dissociation energies in the range 60–120 kJ mol^{-1} .³¹ The hydrogen bond has been subjected to numerous theoretical studies.³²

The utilisation of polycarboxylic acids permits the simultaneous use of neutral $\text{O-H}\cdots\text{O}$ and charged $\text{O-H}\cdots\text{O}^-$ bonding interactions, including the participation of water

oxygens as donors or acceptors. The “charged” interactions can be grouped in two distinct categories: the $\text{O-H}\cdots\text{O}^-$ interactions when the donor belongs to a neutral molecule and the acceptor is an anion, and (ii) the interanion $\text{O-H}^-\cdots\text{O}^-$ when both donor and acceptor groups belong to an anion. In all cases the $\text{O}\cdots\text{O}$ distances are considerably shorter than the sum of the van der Waals radii and there is a marked preference for linearity. Importantly, $\text{O-H}\cdots\text{O}^-$ and $\text{O-H}^-\cdots\text{O}^-$ interactions, although possessing the same geometrical properties as neutral $\text{O-H}\cdots\text{O}$ bonds, are generally associated to $\text{O}\cdots\text{O}$ distances shorter than in the case of neutral systems (roughly 2.45 against 2.65 Å).^{30b} Since we are dealing with $\text{O-H}\cdots\text{O}$ interactions, which are commonly regarded as prototypes of “strong” hydrogen bonds, the decrease in $\text{O}\cdots\text{O}$ distance is usually taken as indicative of a substantial increase in hydrogen bond strength. The relationship between length and strength of the interactions involving ions had recently been begun to be investigated by theoretical methods with intriguing results.³³ For instance, it has been demonstrated that the short $\text{O-H}^-\cdots\text{O}^-$ interactions (2.52 Å) present in crystalline KHC_2O_4 are not associated with stable interanion interactions. In this and similar cases, the $\text{O-H}^-\cdots\text{O}^-$ interaction should be regarded as a supramolecular organiser of anions rather than as a stable bond. A discussion of this aspect, albeit important, is beyond the scope of this article. The interested reader is addressed to recent preliminary communications published by us in collaboration with J. J. Novoa.^{33,34}

It is useful to stress that all interactions of the $\text{O-H}\cdots\text{O}$ type stabilise the supraanionic aggregates. Whether the stabilisation is on a relative energy scale (as in the case of purely interanion $\text{O-H}^-\cdots\text{O}^-$ interactions) or on an absolute scale (as would be the case of “conventional” neutral $\text{O-H}\cdots\text{O}$ and of neutral-anion $\text{O-H}\cdots\text{O}^-$ interactions) it is not of crucial importance for the design strategy. It is clear that the most relevant contribution to crystal cohesion is of electrostatic rather than of covalent nature, *e.g.* the superstructures are stable because of the anion-cation interplay.

The cations are sandwich complexes that do not carry donor/acceptor groups in competition for hydrogen bond formation with interanion self-assembly. This brings about the question of weak $\text{C-H}\cdots\text{O}$ hydrogen bonds.^{17,35} The sandwich cations participate in a large number of $\text{C-H}\cdots\text{O}$ interactions with most (but not all) arene or cyclopentadienyl H atoms at a short distance from an oxygen acceptor on the supramolecular anion. In these cases, $\text{H}\cdots\text{O}$ distances are some 0.01–0.03 Å shorter than when the same molecular fragments form $\text{C-H}\cdots\text{O}$ bonds in neutral crystals. One can look at the shortening effect as another consequence of the strong ionic field generated by the ionic charges, with the far from trivial difference that the ionic charge assists the hydrogen bond. The positive charge carried by the cation decreases the shielding of the proton on the donor C-H groups and makes it more acidic; if this occurs simultaneously to the presence of a negative charge on the acceptor, which increases its nucleophilicity, the net result is a strengthening of the weak bonds. Similar behaviour has been observed when the acceptor is a fluorine atom belonging to anions such as PF_6^- and BF_4^- ,³⁶ or a π system belonging to phenyl groups carried by anions.³⁷

In summary, while the electrostatic field generated by the presence of ions may be said to provide most of the cohesion, the hydrogen bonds (or hydrogen bond like³³) $\text{O-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{O}$ interactions provide directionality, selectivity and reproducibility. Since ionic solids are much more stable than most molecular solids, crystalline materials based on charged hydrogen bonded systems involving ions are expected to be much more robust than molecular networks constructed with neutral hydrogen bonds. One may say that charged hydrogen bonds confer directionality to coulombic interactions thus behaving as supramolecular tugboat interactions that organise the ions in space.

10 Conclusions and outlook

This article has been devoted to describing a simple, reproducible, and transferable strategy to build crystalline materials. The forces we have exploited are sufficiently strong to generate stable and robust edifices with clearly defined two- and three-dimensional superstructures. The classification of the crystalline materials described herein in terms of the covalent, ionic, co-ordination solids is not straightforward. It is much easier to state what they are not. The supraanionic hydrogen bonded salts are not extended covalent networks because the basic linker is not a covalent bond but a hydrogen bond and they are not co-ordination networks because the metal centres are unavailable for co-ordination since they are protected by stable π ligands. Although formed of charged particles, they are not, strictly speaking, ionic salts (*e.g.* alkali metal carbonylates) because of the high dimensionality of the ionic components. The anions are linked in two- or three-dimensional networks and are more appropriately described as superanions. On the other hand, they are not molecular crystals because the components do actually carry ionic charges and the anionic frameworks would fall apart if the counter ions were removed.

What are they then? They could be considered “organometallic super-salts” which own their cohesion and stability mainly to electrostatic forces, but that possess the shape they have and can be built and rebuilt the way they can thanks to the directionality, predictability and reproducibility of the strong and weak hydrogen bonds. Similar to “conventional” salts, these super-salts are expected to have high melting points and high solubility in polar solvents, such as water or nitromethane, while the presence of extended networks introduces anisotropy in the ion arrangements (*e.g.* the squarate salts above) and characteristics that are typical of hydrogen bonded molecular crystals. This understanding has implications in crystal engineering studies when ionic building blocks are involved.

The utilisation and combination of organometallic acids or bases allow the preparation of crystals that contain metal atoms in different oxidation, charge and spin states. It is also possible to construct non-centrosymmetric crystals, and this is one of the goals of NLO materials chemistry.⁵ The alignment of dipoles in a polar crystal so that centrosymmetric pairs do not cancel each other is one of the prerequisites of the construction of materials with potential for efficient second-harmonic generation effects. The goal is now that of using dipolar OM ions in place of the symmetric sandwich systems to obtain dipole alignment within the chiral frameworks. This project is still at an embryonic stage of development but initial results have been extremely promising. The preparation of hydrogen bonded superstructures hosting metal atoms in different oxidation and/or spin states is also a challenging development of our crystal synthesis strategy.

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