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Review

Design, synthesis, characterization and utilization of hydrogen bonded networks based on functionalized organometallic sandwich compounds and the occurrence of crystal polymorphism

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Abstract

The design and construction of hybrid organic–organometallic and inorganic–organometallic crystalline materials formed by hydrogen bonded functionalized organometallic sandwich compounds are described. It is shown that the ionic or neutral nature of the building blocks can be exploited to control the strength of intermolecular bonding and the structure–function relationship. The occurrence of crystal polymorphism associated with hydrogen bonded dimers and hydrogen bonded networks is discussed. It is also argued that solid–solid and solid–gas reactions involving preformed hydrogen bonded organometallic molecular crystals provide a viable "green" route to the preparation of novel hybrid molecular crystalline materials.

Keywords: Hydrogen bonded network; Crystal polymorphism; Solid-state chemistry; Organometallic compound

1. Introduction

Making crystals by design is the paradigm of crystal engineering, an area of solid-state chemistry that encompasses molecular crystals and materials [1]. The goal of this field of research is that of assembling "bottom-up" functionalized molecular and ionic components into a target network of supramolecular interactions [2]. The convolution of the physical and chemical properties of the individual building blocks with the periodicity and symmetry operators of the crystal generates *collective* supramolecular properties [3].

The Bolognese molecular crystal-engineering group has been active in the area of solid-state chemistry for more than a decade [4]. At the time of writing, several lines of research were being explored by this group. This review article will deal with one of the most productive of these lines, namely that focused on the design, synthesis, characterization and utilization of hydrogen bonded networks based on functionalized organometallic sandwich compounds. The reader interested to know more about the other research lines is addressed to recent review articles

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produced by the authors in the fields of the solvent-free preparation of crystalline materials [5], and of the investigation of polymorph preparation and interconversion [6].

Our interest in the use of organometallic molecules and ions as building blocks stems from the observation [4] that organometallic molecules combine the supramolecular bonding features of organic molecules (e.g. hydrogen bonding interactions) with the structural variability of coordination compounds (e.g. ligand–metal coordination, coordination geometry, structural flexibly, etc.). On the other hand, the utilization of interactions that are strong and, at the same time, directional is essential for the assembly of molecular components because such types of interactions guarantee transferability and reproducibility, beside strength. For such reasons the hydrogen bond [7] is the interaction of choice in many crystal-engineering experiments where neutral molecules or molecular ions are employed [8]. This is well demonstrated by the plethora of studies on hydrogen bonded molecular or ionic crystals [9].

In this review, we shall deal mainly with hydrogen bonding interactions between "classical" donor and acceptor groups, e.g. –COOH, –OH, –CONHR, etc. present on adequately chosen, or ad hoc prepared, organometallic moieties.

In previous studies, we have dealt with hydrogen-bonded networks formed by organic or inorganic molecules and ions *templated* by non-participating organometallic units (mainly sandwich compounds) [10,11]. The design criterion was based on the idea of *confining* all strong donor/acceptor hydrogen bonding groups on the organic or inorganic (usually anionic) networks while *excluding* the organometallic fragments (usually cationic) from the direct participation in the hydrogen bonds. This strategy led to product crystals characterized by selective self-assembling of the organic/inorganic fragments in hydrogen bonded superstructures, whose topology depended on the size, shape and number and geometry of the –OH/–COOH/$COO^{(-)}$ groups. To this end, cationic sandwich complexes such as $[Co(\eta^5\text{-}C_5H_5)_2]^+$, $[Cr(\eta^6\text{-}C_6H_6)_2]^+$, $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ were found particularly useful. The regular cylindrical shape of the organometallic moiety and the presence of C–H groups allows interactions with the surroundings by means of C–H···O interactions between the acceptor sites on the networks and the C–H groups protruding from the complex surface [12]. For instance, when D,L- and L-tartaric acids were used, the compounds $[Co(\eta^5\text{-}C_5H_5)_2]^+$(D,L-$HO_2CCH(OH)CH(OH)CO_2$) (D,L-$HO_2CCH(OH)CH(OH)CO_2H$)] and $[Co(\eta^5\text{-}C_5H_5)_2]^+$ [(L-$HO_2CCH(OH)CH(OH)CO_2$)]$^-$ were, respectively, obtained [13]. With oxalic acid, compounds $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$ and $[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]\cdot[H_2O]$ were prepared [14], while compounds $[Cr(\eta^6\text{-}C_6H_6)_2][HC_4O_4]$ and $\{[Cr(\eta^6\text{-}C_6H_6)_2]\}_2[C_4O_4]\cdot 6H_2O$ were prepared with squaric acid [15]. With phthalic and terephthalic acids the compounds $\{[Co(\eta^5\text{-}C_5H_5)_2]^+\}_4\{[C_6H_4(COOH)(COO)]^-\}_2$ $[C_6H_4(COO)_2]^{2-}\cdot 4H_2O$, $[Cr(\eta^6\text{-}C_6H_6)_2]^+\{[C_6H_4(COOH)(COO)]^-[C_6H_4(COOH)_2]\}$, and $\{[Co(\eta^5\text{-}C_5H_5)_2]^+\}_2[C_6H_4(COO)_2]^{2-}\cdot 6H_2O$ were prepared [16], while with trimesic acid $[Co(\eta^5\text{-}C_5H_5)_2]^+\{[(C_6H_3(COOH)_3]\,[C_6H_3(COOH)_2(COO)]\}^-\cdot 2H_2O$ [17] was obtained, and with R-binaphtol were prepared $[Co(\eta^5\text{-}C_5H_5)_2]$[(R)-(+)-$(HOC_{10}H_6C_{10}H_6O)]\cdot$[(R)-(+)-$(HOC_{10}H_6C_{10}H_6OH)]$, and $[Co(\eta^5\text{-}C_5H_5)_2]$ [(R)-(+)-$(HOC_{10}H_6C_{10}H_6O)]\cdot$[(R)-(+)-$(HOC_{10}H_6C_{10}H_6OH)]_{0.5}$ [18]. More recently, partially deprotonated inorganic oxoanions derived from sulphuric and phosphoric acids have been used to assemble organometallic cations in inorganic–organometallic hybrid systems by reacting the neutral sandwich compounds with acids such as H_2SO_4 and H_3PO_4 [19]. The anions $HSO_4{}^-$ and $H_2PO_4{}^-$ resulting from partial deprotonation of the neutral acids were shown to assemble into hydrogen bonded mono- and bi-dimensional networks as in the case of organic anions. The structural features of these and several others hybrid organic/inorganic–organometallic superstructures were described before. The reader is addressed to Ref. [20] for further information.

When the donor/acceptor groups are *located on* the organometallic sandwich unit, the organometallic complexes are directly participating in the formation of hydrogen bonded supramolecular aggregates, such as dimers or higher complexity hydrogen bonded networks. This will be the main focus of this article. Besides, the possibility of alternative solutions to the problem of different spatial organization of the same molecular unit in the crystals, i.e. crystal polymorphism [21], will also be discussed whenever necessary [22]. In this respect, since different crystal forms imply the existence of different sets of supramolecular interactions between the same building blocks, polymorphs of the same molecular crystal can be seen as *crystal isomers*. It should also be pointed out that structural flexibility, a key characteristic of organometallic molecules [23], may favour formation of conformational crystal polymorphs, i.e. of different packings of the same molecule in different conformations. A classical example of organometallic conformational polymorphism is provided by ferrocene, for which one room temperature disordered and two low-temperature ordered crystalline forms are known [24].

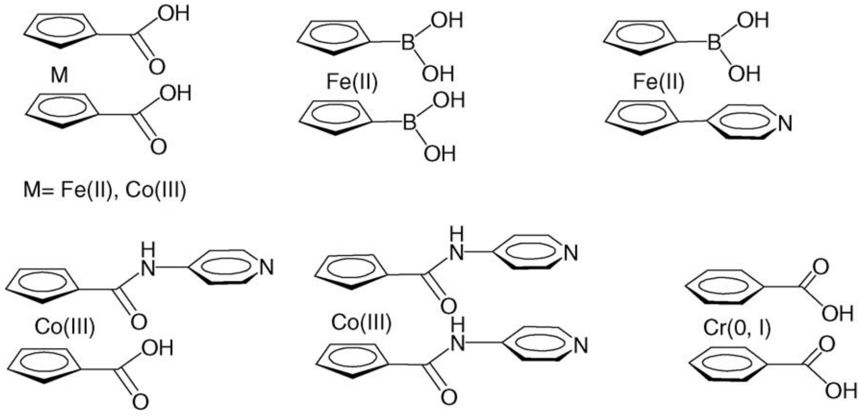
Even though polymorphism is emerging as a fundamental structural and chemical aspect of organometallic solid-state chemistry, rather than devoting a specific section of this review to this phenomenon, the occurrence of polymorphic modifications will be described as we proceed.

2. Hydrogen-bonded dimers and networks formed by organometallic sandwich units and the occurrence of crystal polymorphism

As mentioned in Section 1, the building blocks of choice are sandwich compounds functionalized on the arene or cyclopentadienyl ring by the presence of suitable groups such as carboxylic, amido, boronic groups, etc. (see Scheme 1).

These compounds share some relevant structural features; their understandings are useful to rationalize analogies and differences in their supramolecular behaviour:

(1) Structural flexibility: the sandwich nature allows almost free-rotation of the two moieties coordinated to the metal



Scheme 1. Samples of the hydrogen bonded functionalized sandwich compounds used in this work.

centre about the molecular axis. This feature allows, for example, both the formation of hydrogen bonded dimers when the donor/acceptor groups are eclipsed and that of chains if the donor/acceptor groups are staggered, the two arrangements differing minimally in terms of internal energy.

(2) Charge: when the complex is a charged species the relationship between the presence of an ionic charge on the complex and the formation of intermolecular hydrogen bonds needs to be taken into account. For instance, the possibility of removing a proton in an acid–base process between building blocks may lead to formation of charge-assisted hydrogen bonds.

(3) Oxidation state: contrary to most organic building blocks, organometallic complexes may allow different oxidation states for a same building block, which can bring in the crystal structure important redox properties.

We shall proceed in a logical fashion from the description of supramolecular hydrogen bonded dimeric units to the description of 1D or 2D networks.

The first example of the application of this strategy is provided by the dicarboxylic acid [Fe $(\eta^5\text{-}C_5H_4COOH)_2$]. This molecule has been used by us in the preparation of a series of hybrid organic–organometallic and of organometallic–organometallic crystal architectures, which will be described in the next section. Here, we need to point out that crystalline $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ is known in three polymorphic forms that differ in the relative orientation of the hydrogen bonded molecular pairs (see Fig. 1). The monoclinic (form **I**) and a triclinic (form **II**) crystal forms were determined decades ago [25], while the third polymorphic form **III** has been obtained recently [26]. All three crystal forms are based on dimers of doubly hydrogen bonded carboxylic rings $\{[Fe(\eta^5\text{-}C_5H_4COOH)_2]\}_2$. The simplest way to compare the three crystal structures is by looking at how these dimers are packed within molecular layers. A space-filling representation of a section of the three forms is shown in Fig. 1.

The supramolecular bonding capacity of the diboronic acid complex $[Fe(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)_2]$ has been investigated by two independent groups [27,28]. The main difference between $[Fe(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)_2]$ and $\{[Fe(\eta^5\text{-}C_5H_4COOH)_2]\}_2$ arises from the larger donor/acceptor ratio in the former with respect to the latter. In fact, $[Fe(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)_2]$ does not form dimers but chains as shown in Fig. 2. The chains, however, establish hydrogen-bonding cross-links with lateral protons on the boronic groups.

While no polymorphic modification of $[Fe(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)_2]$ is yet known, its pyridyl derivative $[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]$ has been isolated in three different crystal forms, the two anhydrous forms **I** and **II** and the monohydrate form **III,** the three forms are compared in Fig. 3 [29]. In crystalline form **I** of $[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]$ the molecules form dimers of the type $\{[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]\}_2$ via $(B)OH\cdots N$ bonds, which are then linked in a secondary pattern by the $(B)OH\cdots O(B)$ lateral bonds. This arrangement leads to eclipsing of the $B(OH)_2$ group over the C_5H_4N group. In **II**, on the other hand, the primary motif appears to be the boronic acid ring based on $(B)OH\cdots O(B)$ bonds while dimers are formed by the lateral O–H groups with the pyridyl acceptors. The conformation of the two ligands is *cisoid*. In crystalline **III**, a third, almost intermediate topology is observed.

The topological analogy between the supramolecular dimers $\{[Fe(\eta^5\text{-}C_5H_4COOH)_2]_2\}$ in crystals of the three forms of the dicarboxylic acid as well as in the crystals of $\{[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]\}_2$ can be easily extended to the hydrogen bonded adducts obtained by using other metallocenyl building blocks, such as the cationic complex $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]^+$ [30]. In crystalline $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)][PF_6]$ $(H_2O)_2$ two $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]^+$ units are linked together via a bifurcate $N\text{–}H^{(+)}\cdots O^{(-)}$ hydrogen bond forming the dimer $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]\}_2{}^{2+}$ (Fig. 4), which closely resembles those shown in Figs. 1 and 2. The oxygen atoms of the carboxylate group and the N atom of the amido group are involved in lateral hydrogen bonds with two water molecules. While the dimer in crystalline $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ is formed by neutral molecules, the dimer present in crystalline $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)][PF_6]$ is formed by organometallic cations. This latter system can be described as a supramolecular dication

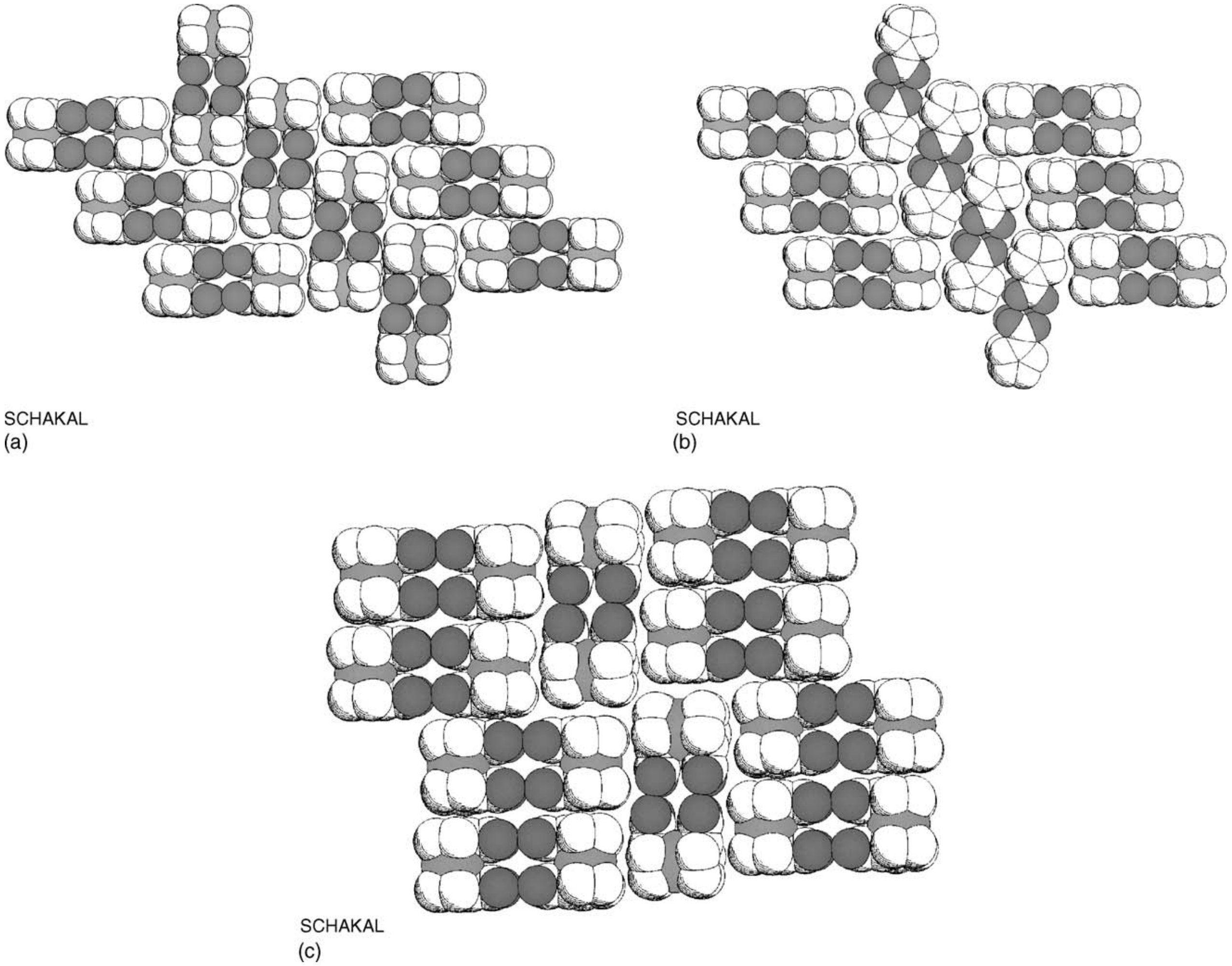


Fig. 1. Space filling representations of the packing in (a) form **I** (monoclinic), (b) form **II** (triclinic) and (c) form **III** of crystalline $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$. Hydrogen atoms omitted for sake of clarity.

$\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]\}_2{}^{2+}$, held together by hydrogen bonding interactions between the protonated pyridine and the deprotonated –COO group.

When the diacid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ is reacted with the diamido molecule $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]$ the cationic heterometallic adduct $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]\}^+$ is obtained [30], as shown in Fig. 5. The two complexes in $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]\}^+$ are linked by O–H···N hydrogen bonds [N···O 2.52(3) Å]. In spite of the structural analogy between $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]\}^+$ and $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]\}_2{}^{2+}$ there are substantial differences in the hydrogen bonding lengths. The inter-dimer separation in $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]\}_2{}^{2+}$ [$N_{pyridine}\cdots O_{COOH/COO^-}$ 2.84(2) and 2.88(2) Å] is, in fact, much longer than in $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$, [$N_{pyridine}\cdots O_{COOH/COO^-}$ 2.52(3) Å].

The crystalline diamido molecule $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$ as its $[PF_6]^-$ anion salt also shows the presence of a tetra-cationic dimers of the type $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]\}_2{}^{4+}$ (see Fig. 6), which are "kept together" by two N–H···N hydrogen bonds.

Supramolecular dimers are present also in crystals of the neutral dicarboxylic acid derivative of bis-benzene chromium(0) $[Cr^0(\eta^6\text{-}C_6H_5COOH)_2]$ (see Fig. 7), which can thus be described, in analogy with the other acids, as crystalline $\{[Cr^0(\eta^6\text{-}C_6H_5COOH)_2]\}_2$ [31]. These dimers are very likely to exist in solution.

On moving to the oxidized form, the paramagnetic cation $[Cr^I(\eta^6\text{-}C_6H_5COOH)_2]^+$, however, the system "switches" to chain formation in spite of the fact that in terms of molecular structure the neutral and cationic complex are almost identical. Besides, the oxidized form $[Cr^I(\eta^6\text{-}C_6H_5COOH)_2][PF_6]$ [31], is known in two crystalline polymorphic modifications, a monoclinic and a triclinic form. Both polymorphs contain cationic chains placed side-by-side and forming a step-ladder superstructure with the $[PF_6]^-$ anions accommodated between the steps, as shown in Fig. 8. The difference between the neutral species $[Cr^0(\eta^6\text{-}C_6H_5COOH)_2]$ and the crystal of the cationic complex may be due to the need, in this latter case of charge distribution in the crystal lattice: the formation of chains with anions in the niches appears to permit an isotropic (or less anisotropic) dis-

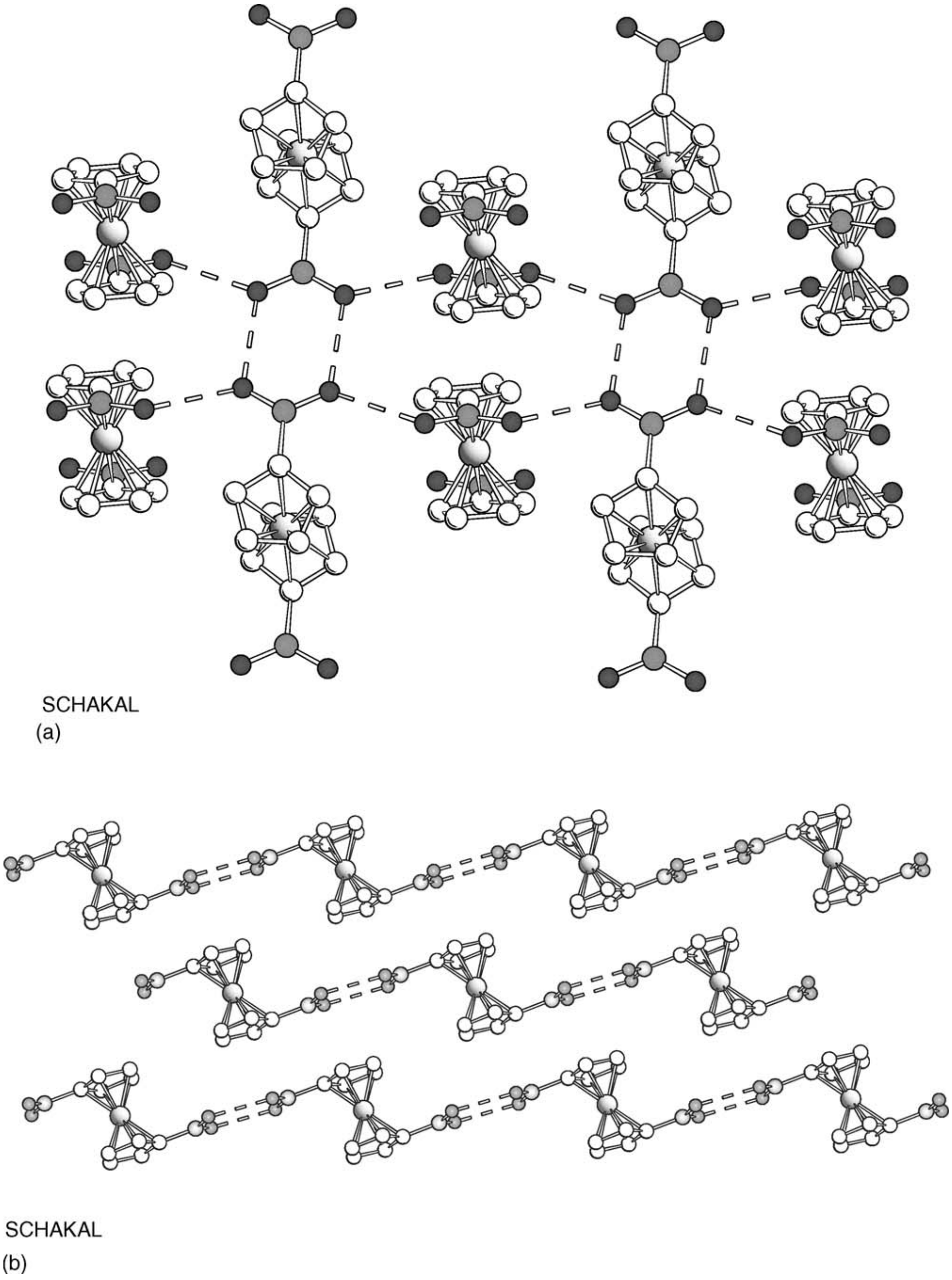


Fig. 2. Two views of compound $[Fe(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)_2]$: (a, top) chains of hydrogen-bonded ferrocenyl moieties in a transoid conformation; (b, bottom) criss-crossing of the chains in the crystal structure and establishment of hydrogen-bonding cross-links with lateral protons. H_{CH} atoms are not shown for clarity.

tribution of charges through the crystal lattice as happen in the crystal structure of $[Co(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$ (Fig. 9).

3. Hybrid organic–organometallic networks

The previous section was focused on the preparation of dimers and chains based on carboxylic or boronic acid rings or on the interaction between a carboxylic acid and another hydrogen bond acceptor. The following section, we will instead provide a series of examples of how some of the building blocks described above can be utilized in acid–base reactions for the construction of supramolecular arrays.

Compounds $[C_8H_{16}N_4][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2$, and $[C_{10}H_{20}N_4]$ $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4\text{'}COO)]_2$, have been obtained by reacting $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ with the bis-amidines $[C_8H_{14}N_4]$, and $[C_{10}H_{18}N_4]$, respectively [33]. The self-assembly of the mono- and di-deprotonated acids with the protonated cations is controlled by the stoichiometric ratio and by the choice of solvent. An acid:base stoichiometric ratio of 2:1 allows partial deprotonation of the acid, thus affording species that show the simultaneous presence of *homo-ionic* $O\text{–}H^{(-)}\cdots O^{(-)}$ and *hetero-ionic* $N\text{–}H^{(+)}\cdots O^{(-)}$ interactions, but do not contain solvent molecules. Crystalline $[C_8H_{16}N_4]$ $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}$

$C_5H_4COO)]_2$ is formed by *homo-ionic* chains of dicarboxylic ferrocenyl anions interacting with the bis-amidine cations in *dihapto* mode. Fig. 10 shows the two-dimensional network present in these crystals: the ionic arrangement can be described as composed of chains of $O–H^{(-)}\cdots O^{(-)}$ interacting $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ anions joined by bis-amidines bridges. Crystalline $[C_{10}H_{20}N_4]$ $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2$ also contains chains of mono-deprotonated $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ anions interacting with the protonated bis-amidine $[C_{10}H_{20}N_4]^{2+}$ in *dihapto* mode (see Fig. 10b). In both compounds $[C_8H_{16}N_4]$ $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2$, and $[C_{10}H_{20}N_4]$ $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2$, the organometallic anions are linked via $O–H\cdots O$ interactions.

In a related experiment we have shown that $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ can be reacted mechanochemically with the solid bases 1,4-diazabicyclo[2.2.2]octane, 1,4-phenylenediamine, piperazine, *trans*-1,4-cyclohexanediamine and guanidinium carbonate, generating quantitatively the corresponding organic–organometallic adducts [34]. In the case of the adduct $[HC_6N_2H_{12}][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, not only the base can be removed by mild treatment regenerating the structure of the starting dicarboxylic acid, but the same product can be obtained also via a (much slower) vapour uptake process (see Fig. 11). The processes imply breaking and reassembling of hydrogen-bonded networks, conformational change from *cis* to *trans* of the –COO/–COOH groups on the ferrocene diacid, and proton transfer from acid to base.

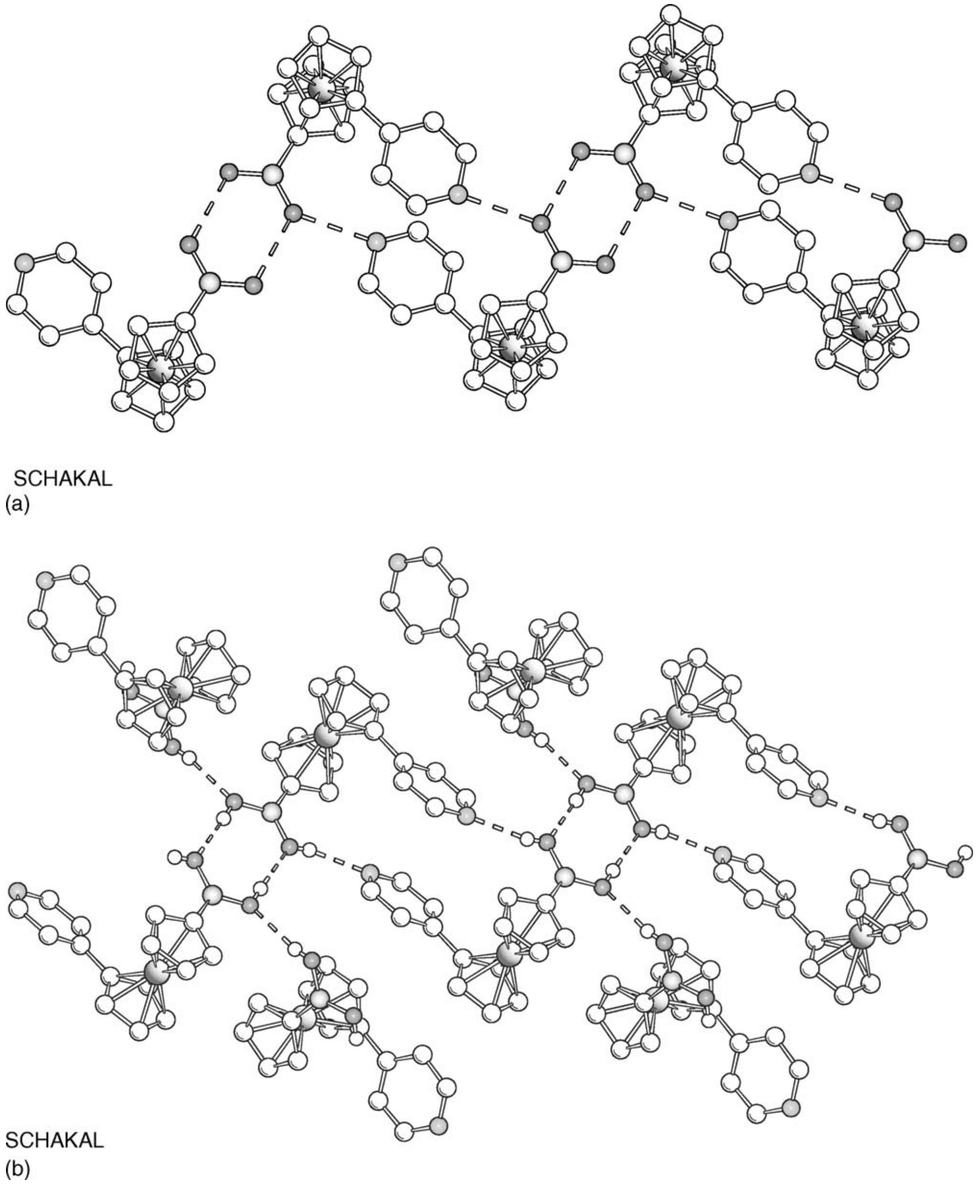


Fig. 3. (a, left) Hydrogen-bonded dimers formed by $(B)OH\cdots N$ interactions in crystalline form **I**. Note how the $\{[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]\}_2$ dimers are connected via $(B)OH\cdots O(B)$ interactions. (b, middle) Hydrogen-bonding pattern in crystalline form **I**. Note how the ligand conformation has changed from eclipsed in form **I** to *cisoid* in form **II**. (c, right) Hydrogen-bonding pattern in crystalline form **III**. H atoms omitted for sake of clarity.

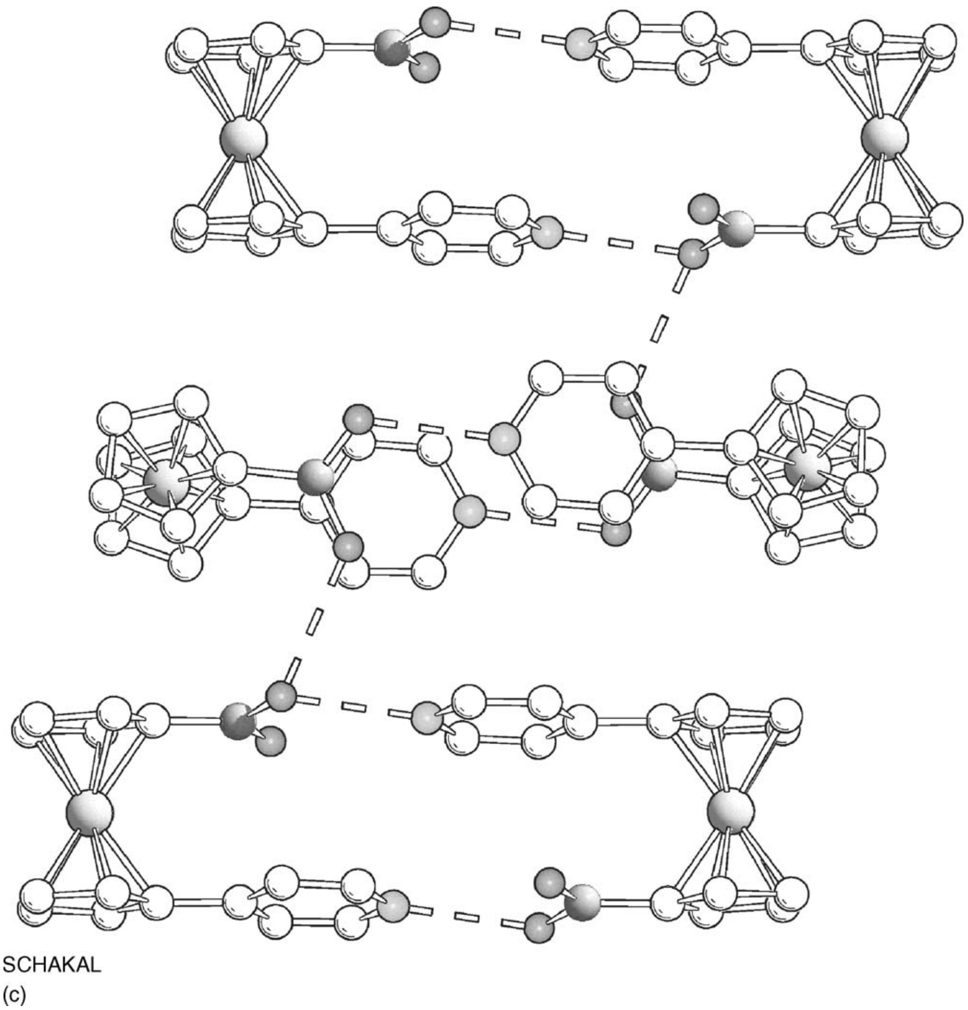


Fig. 3. (*Continued*).

4. Reactions of organometallic sandwich bases with organic acids

The two cases discussed above result from the reactions of an organometallic acid with a base, we shall now look at reactions of organometallic bases with acids. For example, the cationic bis-amide $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$, whose structural features have been described above, has been recently used in a series of reactions with organic dicarboxylic acids, such as fumaric and maleic acids [35]. In the course of the acid–base reaction the complex can be mono- and di-protonated depending on the stoichiometric rations with formation of complex mixed-anions supramolecular salts containing either the dication $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$ or

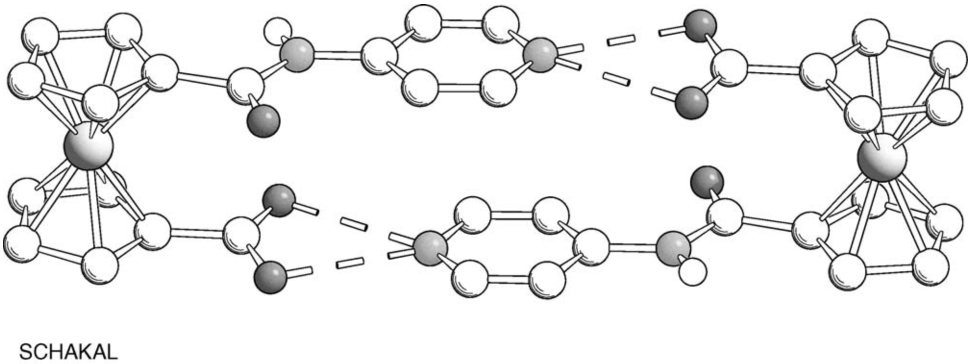


Fig. 4. The dimers $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]^+\}_2$ formed via bifurcate $N{-}H^{(+)}\cdots O^{(-)}$ hydrogen bonding interactions [N···O 2.84(2) and 2.88(2) Å]. H_{CH} omitted for clarity.

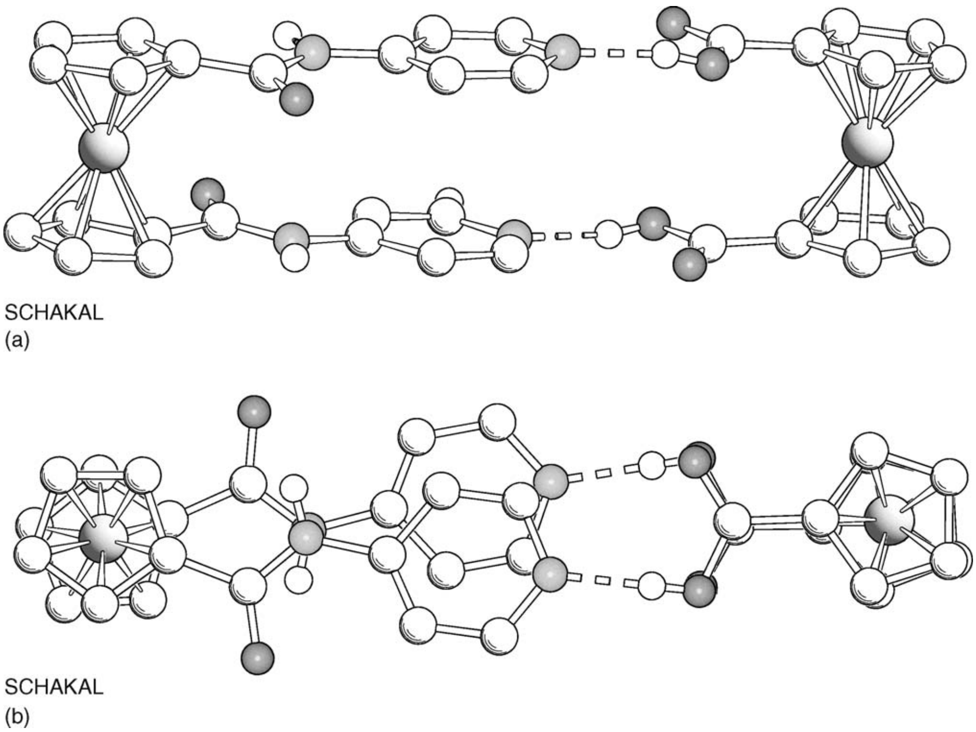


Fig. 5. The ferrocene dicarboxylic acid molecule and the diamido molecule $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^+$ in $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$ are linked via O—H···N hydrogen bonds [N···O 2.52(3) Å] (top). Note how Cp rings of the ferrocene dicarboxylic acid are eclipsed, while those in the cobalt complex are staggered; furthermore, the pyridyl groups are almost eclipsed and in *cisoid* conformation, while the amido oxygens point in opposite directions (bottom). H_{CH} omitted for clarity.

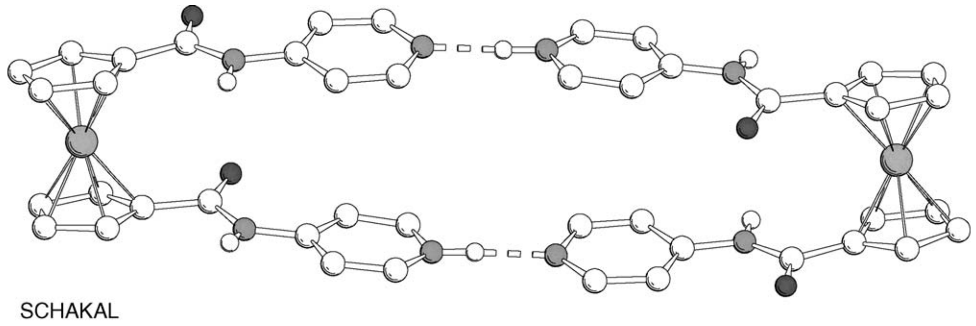


Fig. 6. The supramolecular aggregate $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]\}_2{}^{4+}$ present in the hydrated crystal $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]\}_2[PF_6]_4\cdot H_2O$. The tetra-cation is "kept together" by two N—H···N [2.715(4) and (2.738(6) Å] hydrogen bonds. H_{CH} omitted for clarity.

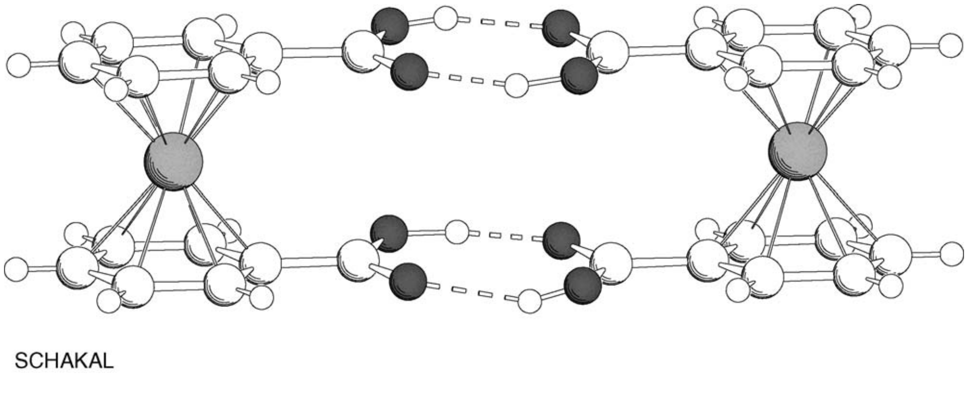


Fig. 7. The hydrogen bonded dicarboxylic dimer $\{[Cr^0(\eta^6\text{-}C_6H_5COOH)_2]\}_2$ in crystals of the neutral bis-benzene dicarboxylic acid complex.

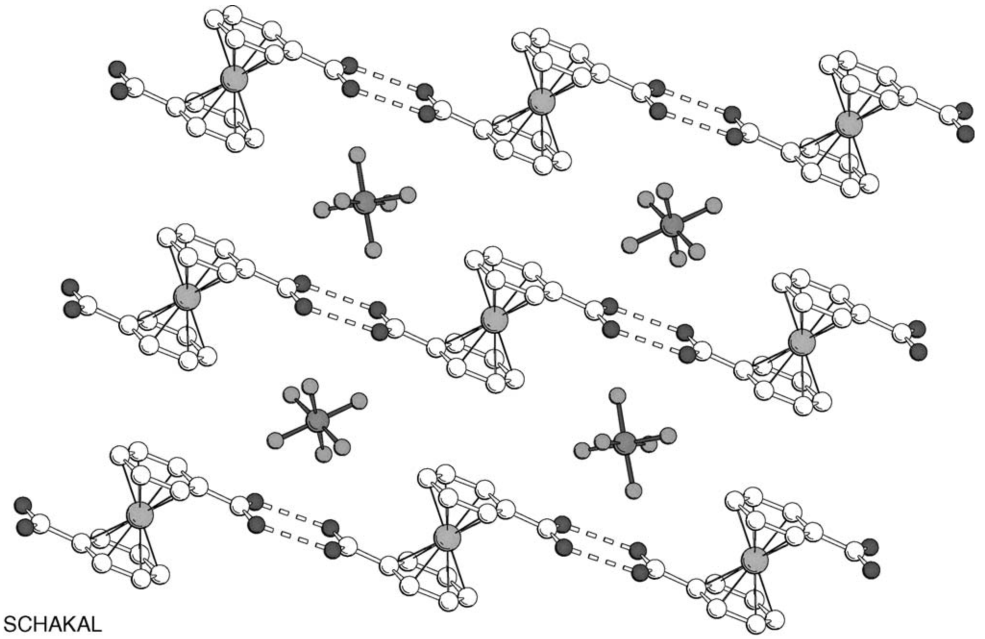


Fig. 8. Both polymorphs of the oxidized form $[Cr^{I}(\eta^6\text{-}C_6H_5COOH)_2][PF_6]$ contain cationic chains placed side-by-side and forming a step-ladder superstructure with the $[PF_6]^-$ anions accommodated between the steps. H atoms omitted for clarity.

the three-cation $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}$. This is shown schematically in Scheme 2.

The products of the reaction of the bis-amide $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$ with fumaric acid, namely $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]^-\cdot[(C_4H_2O_4)_{1/2}]^-$, and $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot H_3O^+\cdot[PF_6]^-\cdot(C_4H_2O_4HC_4H_2O_4)^{3-}$ contain the fumarate dianion $(C_4H_2O_4)^{2-}$ and a hydrogen bridged supramolecular three-anion $(C_4H_2O_4HC_4H_2O_4)^{3-}$, respectively. The structure of crystalline $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)\ (\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]^-\cdot[(C_4H_2O_4)_{0.5}]^-$ is shown in Fig. 12.

The possibility of formation of intra-molecular hydrogen bonds in the hydrogen maleate anion with respect to the hydrogen fumarate anion, allows formation of the salts $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\ \{[PF_6]_{3/2}[C_4H_2O_4H]_{1/2}\}^{2-}$, $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\{[PF_6]_{5/2}(C_4H_2O_4H)_{1/2}\}^{3-}\cdot H_2O$, and $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4$

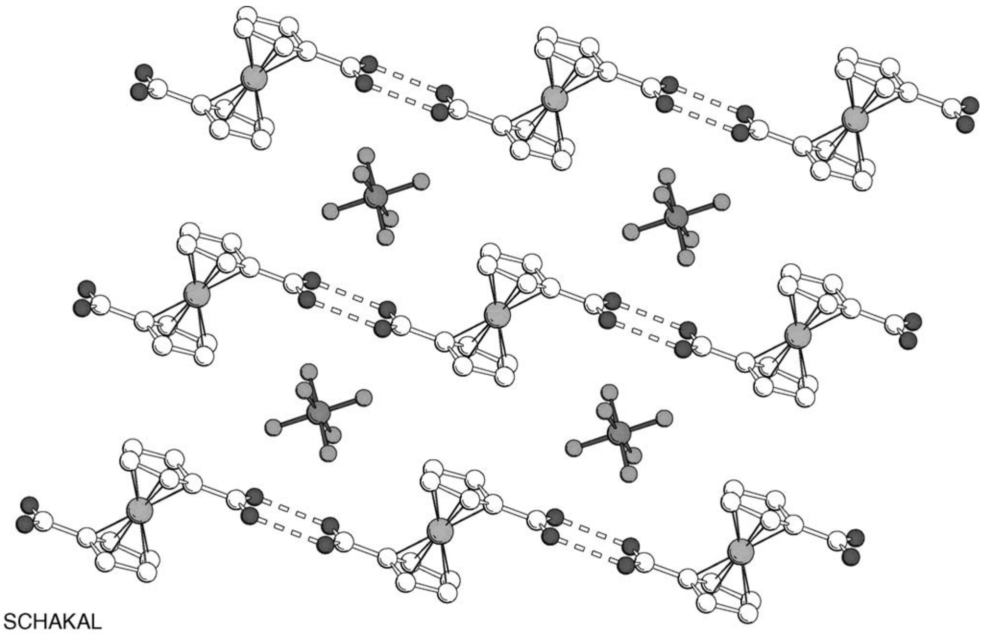


Fig. 9. Hydrogen bonded chains in crystalline $[Co(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$. H atoms omitted for clarity.

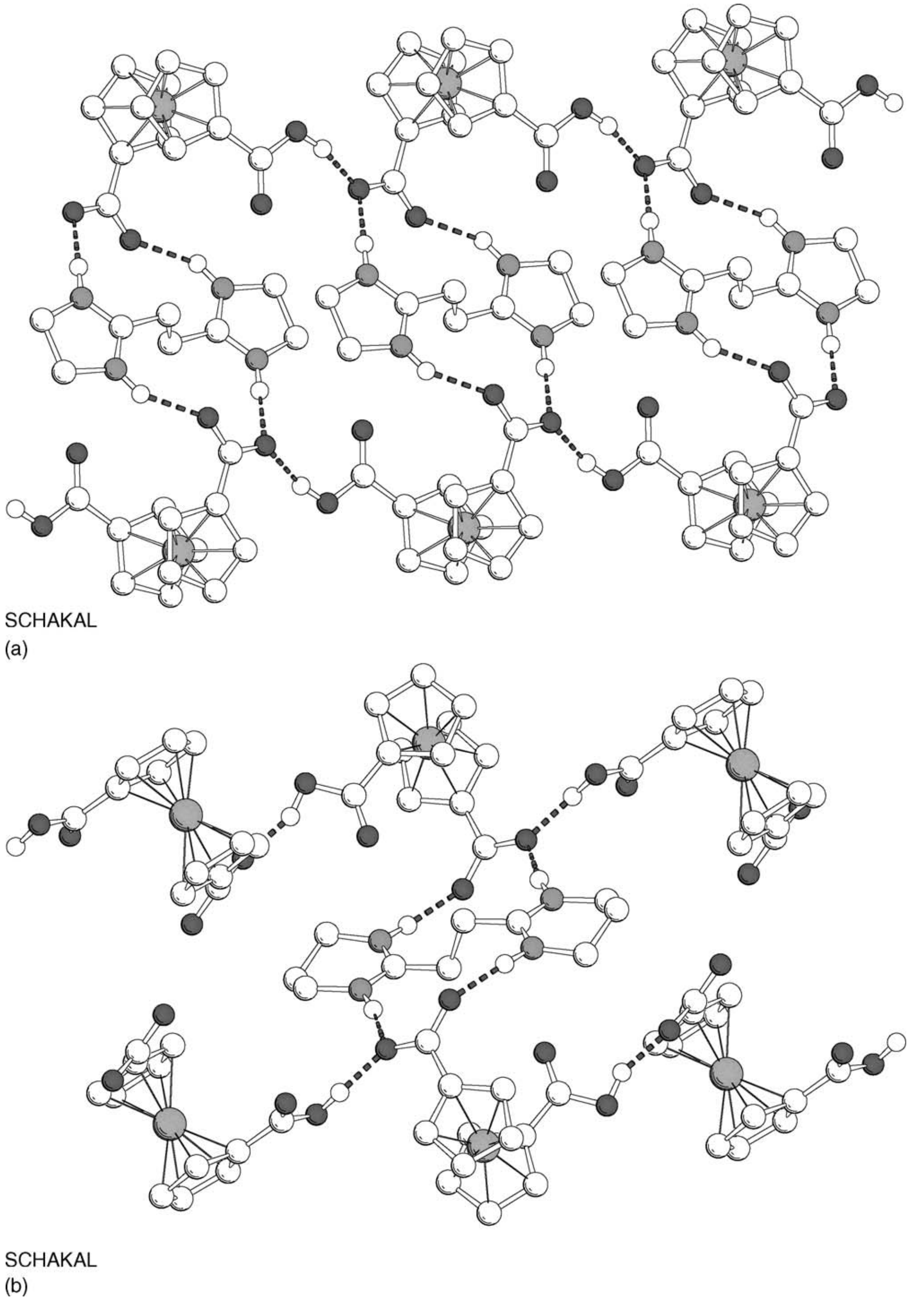


Fig. 10. (a) The ribbons formed by two chains of $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ interacting with the dication $[C_8H_{16}N_4]^{2+}$ via hydrogen bonds in $[C_8H_{16}N_4][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2$. (b) Portion of the three-dimensional network, formed by the monoanion $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ chains interacting with the dication $[C_{10}H_{20}N_4]^{2+}$ in $[C_{10}H_{20}N_4]$ $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2$. Only $H_{(NH)}$ and $H_{(COOH)}$ atoms shown for clarity.

$NH)_2]^{3+}\cdot[PF_6]_2^-\cdot(C_4H_2O_4H)^-\cdot H_2O$. In all these crystals, the hydrogen maleate anion acts as a bridge between the protonated bis-amido organometallic sandwiches (see Fig. 13).

5. Mixed-metal hydrogen bonded networks

The dicarboxylic organometallic acid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ has also been used to produce a series of mixed-metal, mixed-valent crystalline materials by reacting directly the diacid in with the neutral complexes $[Co(\eta^5\text{-}C_5H_5)_2]$ and $[Cr(\eta^6\text{-}C_6H_6)_2]$ in solution. The reactions produce the strongly basic anion O_2^-, which is able to deprotonate $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ to yield the anions $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ or $[Fe(\eta^5\text{-}C_5H_4COO)_2]\}^{2-}$ [36]. The resulting organometallic salts contain the partially de-protonated organometallic acid anion and the diamagnetic cation $[Co(\eta^5\text{-}C_5H_5)_2]^+$ or the paramagnetic cation $[Cr(\eta^6\text{-}C_6H_6)_2]^+$.

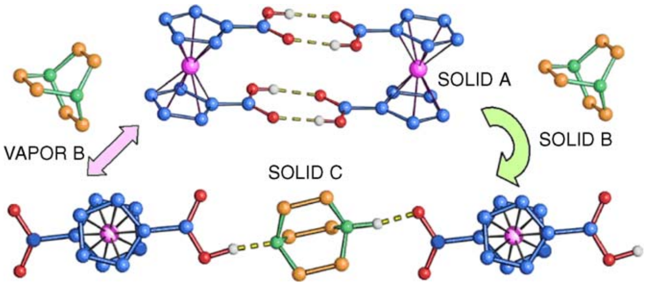
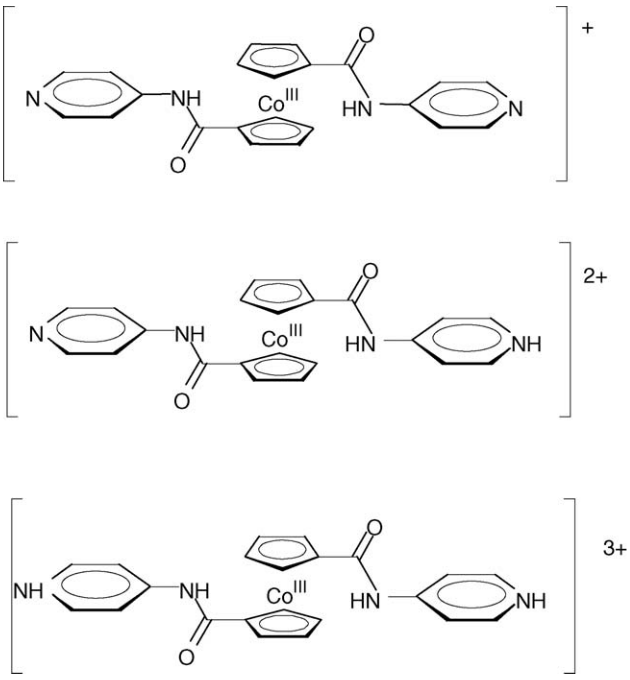


Fig. 11. In compound $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ the $[HC_6H_{12}N_2]^+$ cations act as bridges between acid sandwich molecular anions in transoid conformation. The adduct can be prepared both by co-grinding of the crystalline base $[C_6H_{12}N_2]$ and acid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ or via (a much slower) vapour uptake. The process is reversible. Reprinted from Ref. [5(a)] with permission.



Scheme 2. The different states of protonation of the bis-amide $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$ upon reaction with a suitable protic acid.

In such a way, the materials $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot H_2O$, $[Cr(\eta^6\text{-}C_6H_6)_2]_2[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ and $[Cr(\eta^6\text{-}C_6H_6)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot H_2O$ have been prepared and structurally characterized [36,37]. The four species contain different electronic and spin metal centres: 18 electrons Fe^{II} and Co^{III} metal atoms are present in $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ and $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot H_2O$, whereas, 18-electrons Fe^{II} and paramagnetic 17 electrons Cr^I are present in $[Cr(\eta^6\text{-}C_6H_6)_2]_2[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ and $[Cr(\eta^6\text{-}C_6H_6)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot H_2O$. The crystalline edifices are held together by the complementary contribution of neutral O–H···O and/or negatively charged

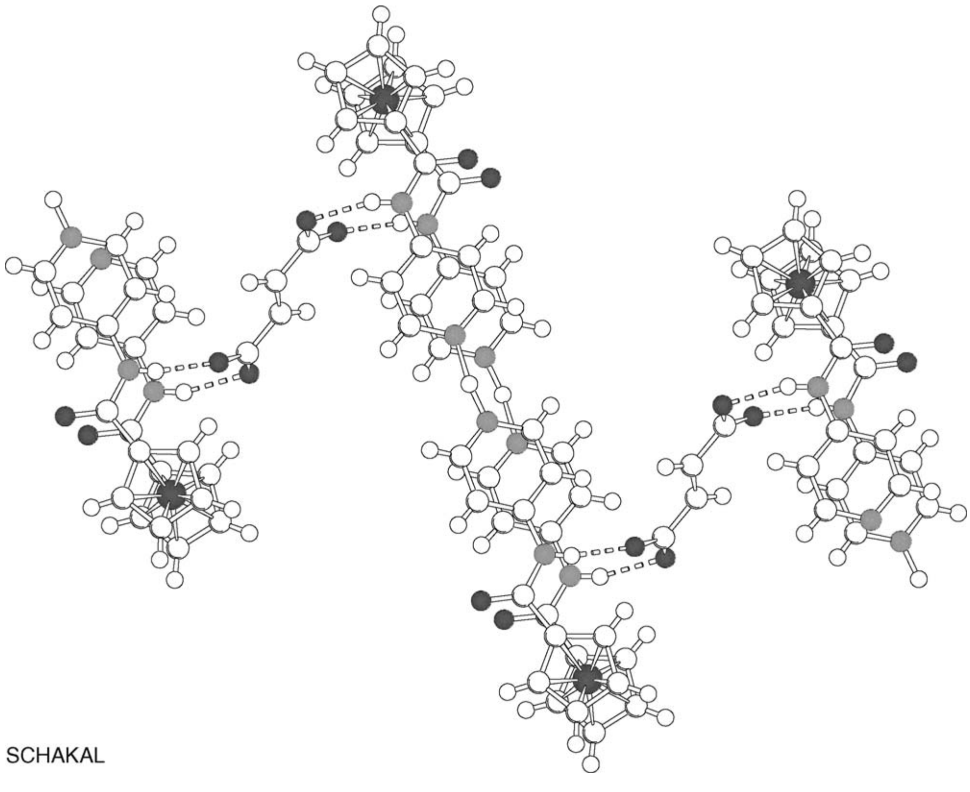


Fig. 12. Crystalline $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]^-\cdot[(C_4H_2O_4)_{1/2}]^-$. The hydrogen bridged amide dimers [N(3)···N(4) 2.669(7) Å] are linked together in a zigzag fashion via the interaction of the deprotonated fumarate dianions and the outer amido N—H groups. Each fumarate dianion interacts with the organometallic cations via four N—H···O bonds.

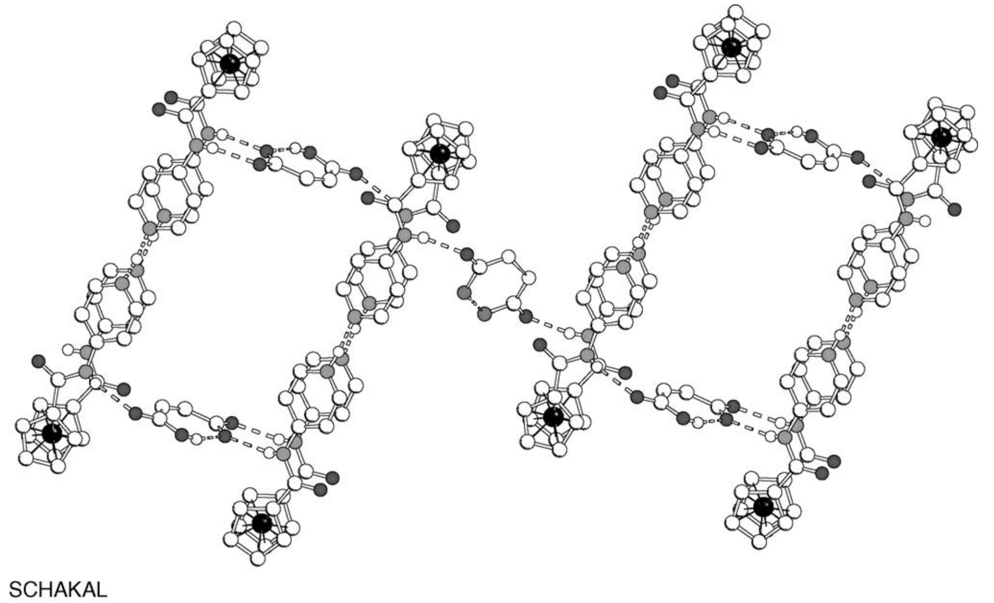


Fig. 13. The structure of $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$ $\{[PF_6]_{3/2}\ [C_4H_2O_4H]_{1/2}\}^{2-}$ shows the presence of hydrogen bond dimers in the solid state of the type observed for $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]_2{}^{2-}\cdot(H_2O)_{1/2}$ as well as the hydrogen fumarate salts $[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]^-\ [(C_4H_2O_4)_{1/2}]^-$. The "dimers of dimers" are held together by a bridge formed of hydrogen maleate anions. H_{CH} omitted for clarity.

$O\text{–}H\cdots O^{(-)}$ hydrogen bonding interactions between the acid moieties and of *charge assisted* $C\text{–}H^{\delta+}\cdots O^{\delta-}$ bonds between cations and anions.

In crystalline $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ the $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ anions, derived from mono-deprotonation of the neutral acid, form chains via symmetric O–H–O interactions between ligands in *transoid* conformation (see Fig. 14a). Charge assisted $C\text{–}H^{\delta+}\cdots O^{\delta-}$ hydrogen bonds link then the cobalticinium cations to the $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ chains. The compound $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot H_2O$ can also be obtained by *grinding* solid $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ in air [38].

The formula unit in crystalline $[Cr(\eta^6\text{-}C_6H_6)_2]_2[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ contains both neutral ferrocene diacid molecules and anions. The neutral molecule acts as a bridge between hydrogen bonded dimers formed by two $[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^-$ anions (see Fig. 14b). In a way $[Cr(\eta^6\text{-}C_6H_6)_2]_2[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ recalls the situation observed for $[Co(\eta^5\text{-}C_5H_5)_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot H_2O$ with the neutral molecule acting as a buffer (a spacer) between the anionic units (Fig. 14c). The neutral-anion $O\text{–}H\cdots O^{(-)}$ hydrogen bond is of the same length as that between the two mono-anions [2.570(5) Å versus 2.569(5) Å]. All "unused" acceptor sites on the O-atoms are directed outwards along the chain to attain the maximum number of $C\text{–}H^{\delta+}\cdots O^{\delta-}$ interactions with the $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ cations. These values are again indicative of a substantial electrostatic reinforcement of the weak bonds. The presence of pairs of $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ cations in the packing of $[Cr(\eta^6\text{-}C_6H_6)_2]_2[Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ is noteworthy.

6. Preparation of crystals by solvent-free reactions between crystals and between crystals and vapours

The water soluble dicarboxylic cationic acid $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ has proven to be an extremely versatile building block for the construction of hydrogen bonded networks [32]. What is more, the networks formed by the complex in cationic or zwitterionic form can be made *react* in solid–solid and solid–gas processes (see below).

Removal of one proton from $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ leads to formation of the neutral zwitterion $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, while further deprotonation leads to formation of the dicarboxylate monoanion $[Co(\eta^5\text{-}C_5H_4COO)_2]^-$ (see Scheme 3). The cationic form $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ has been characterized in different crystalline salts, namely $[PF_6]^-$, Cl^-, as well as in its co-crystal with urea, and with the zwitterionic form $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ in $\{[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\ [Co(\eta^5\text{-}C_5H_4COOH)_2]\}[PF_6]$ [39].

If water solutions of this latter complex $\{[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\ [Co(\eta^5\text{-}C_5H_4COOH)_2]\}[PF_6]$ are treated with alkali metal or ammonium hydroxides MOH ($M = K^+$, Rb^+, Cs^+, $[NH_4]^+$) in 1:1 stoichiometric ratio, the acid cation is partially deprotonated and a series of nearly isomorphous supramolecular aggregates co-crystallized with the inorganic salts MPF_6 ($M = K^+$, Rb^+, Cs^+, $NH_4{}^+$) are obtained. The same compounds can be obtained by treating water solutions of [Co(η^5-C_5H_4COOH)(η^5-C_5H_4COO)] with a stoichiometric amount of the appropriate salt. In these complex structures the cations are encapsulated via either $M^+\cdots O$ interactions, in the cases of metals, or N–H···O hydrogen bonds, in the case of the NH_4^+ cation, within a strongly nucleophilic cage formed by four molecules of [Co(η^5-C_5H_4COOH)(η^5-C_5H_4COO)]. All the species are *quasi* isostructural and isomorphous (see Fig. 15).

A much faster and quantitative way to prepare adducts of the type [Co(η^5-C_5H_4COOH)(η^5-C_5H_4COO)]$_2$ [M][PF_6] is, however, that based on solid–solid reaction, that is to say on the co-grinding of stoichiometric amounts of the organometallic zwitterions in the crystalline form together with the solid MX salts (M = K^+, Rb^+, Cs^+, NH_4^+; X = Cl^-, Br^-, I^-, PF_6^-) [40]. In some cases (M = Rb^+, Cs^+, X = Cl^-, Br^-, I^-) it was necessary to recur to *kneading* by adding a few drops of water to the solid mixture in order to obtain the desired product. This class of compounds is characterized by the presence of a supramolecular cage formed by four zwitterionic molecules encapsulating the alkali or ammonium cations. The cage is sustained by O–H···O hydrogen bonds between carboxylic –COOH and carboxylate –$COO^{(-)}$ groups, and by C–H···O bonds between –CH_{Cp} and –CO groups, while the anions are layered in between the cationic complexes, as shown in Fig. 15. It is fascinating to think of the process leading to formation of the cages as a kind of sophisticated solvation based operated by the organometallic complex.

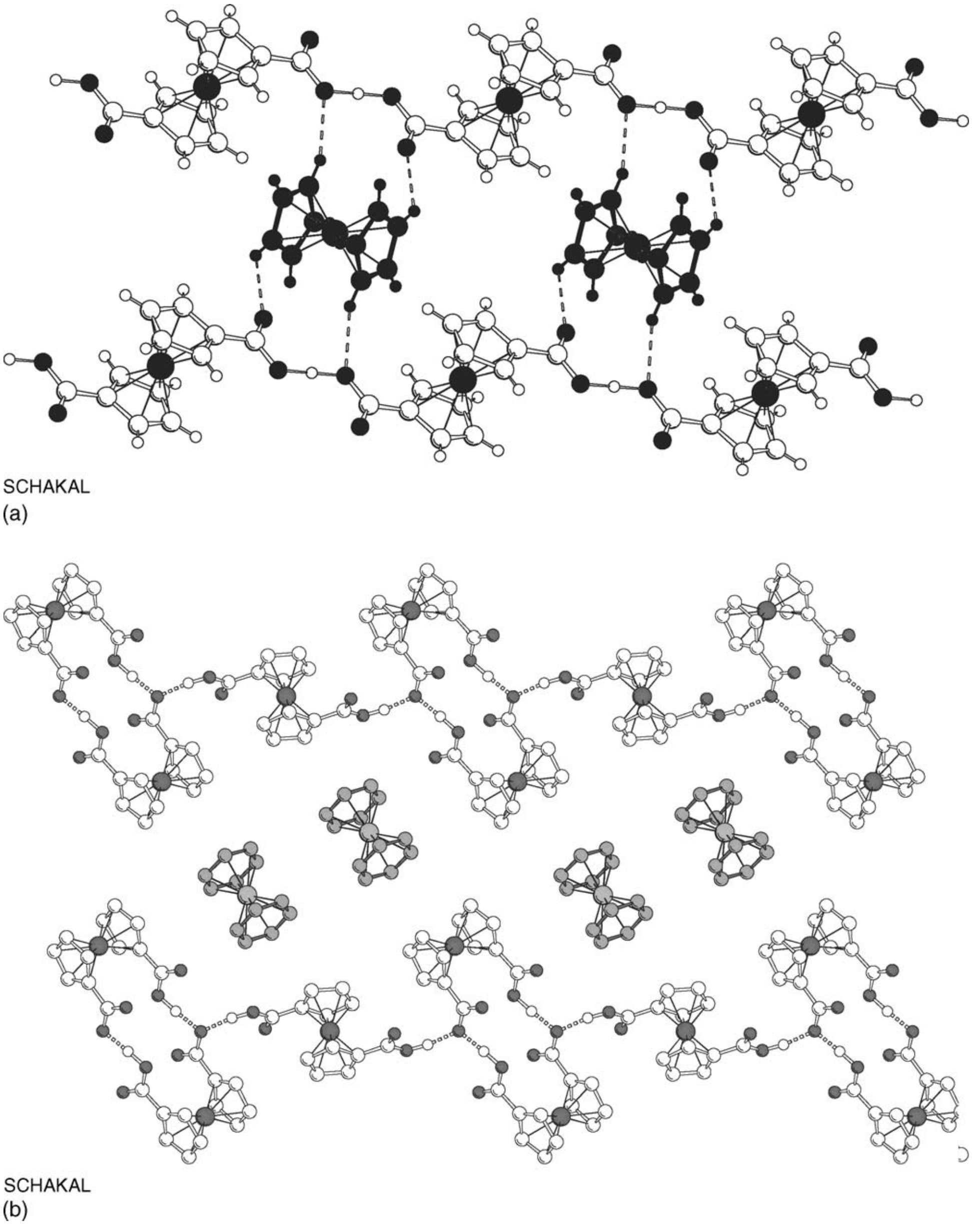


Fig. 14. (a) The chains of anions [Fe(η^5-C_5H_4COOH)(η^5-C_5H_4COO)]$^-$ linking the cations via C—H···O hydrogen bonds. (b) In crystalline [Cr(η^6-C_6H_6)$_2$]$_2$[Fe(η^5-C_5H_4COOH)(η^5-C_5H_4COO)]$_2$[Fe(η^5-C_5H_4COOH)$_2$] neutral ferrocene diacid molecules act as bridges between hydrogen bonded dimers formed by two [Fe(η^5-C_5H_4COOH)(η^5-C_5H_4COO)]$^-$ anions. (c) In solid [Co(η^5-C_5H_5)$_2$][Fe(η^5-C_5H_4COOH)(η^5-C_5H_4COO)]·H_2O the neutral molecules act as bridges between the anionic units. In (a) and (b) H_{CH} omitted for clarity.

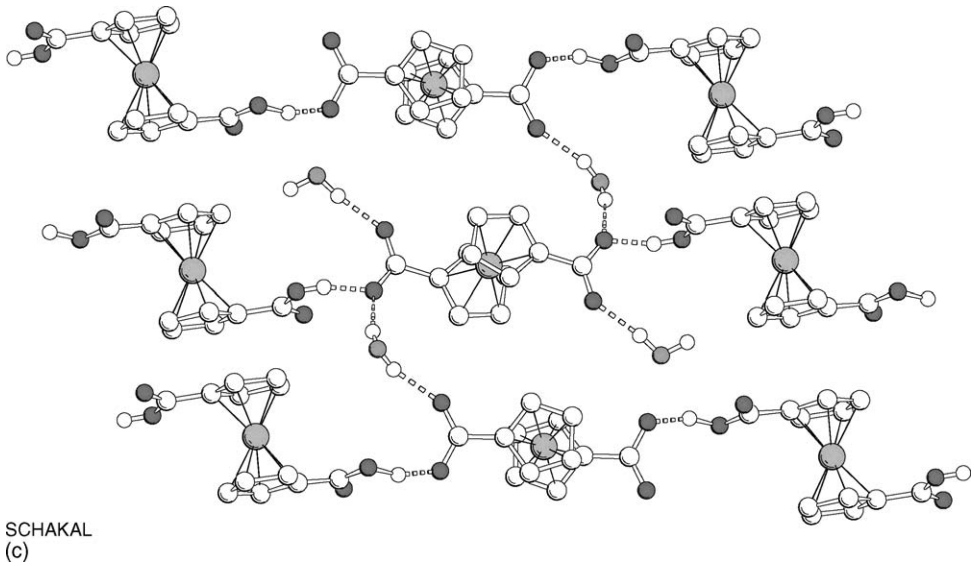
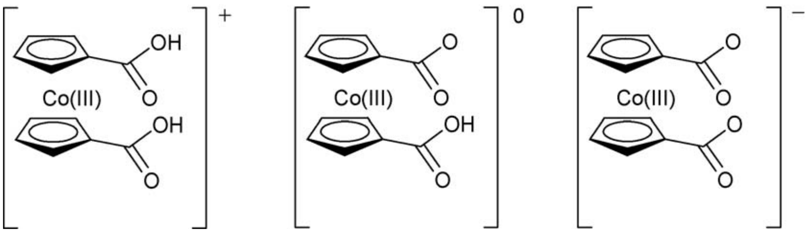


Fig. 14. (*Continued*).



Scheme 3. Removal of one proton from the cation $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ leads to formation of the neutral zwitterion $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, while further deprotonation leads to formation of the dicarboxylate monoanion $[Co(\eta^5\text{-}C_5H_4COO)_2]^-$.

The zwitterion is able of "extracting" via $O\cdots X^-$ interactions the alkali cations from their lattice while the anions are "extruded" and left to interact with the peripheral C–H groups via numerous $C–H\cdots X$ interactions. The solid–solid process can be described as the dissolution of one solid (the alkali salt) into a *solid solvent*.

It should be mentioned that the zwitterion is usually obtained from a water solution as a three-hydrated species [Co(η^5-

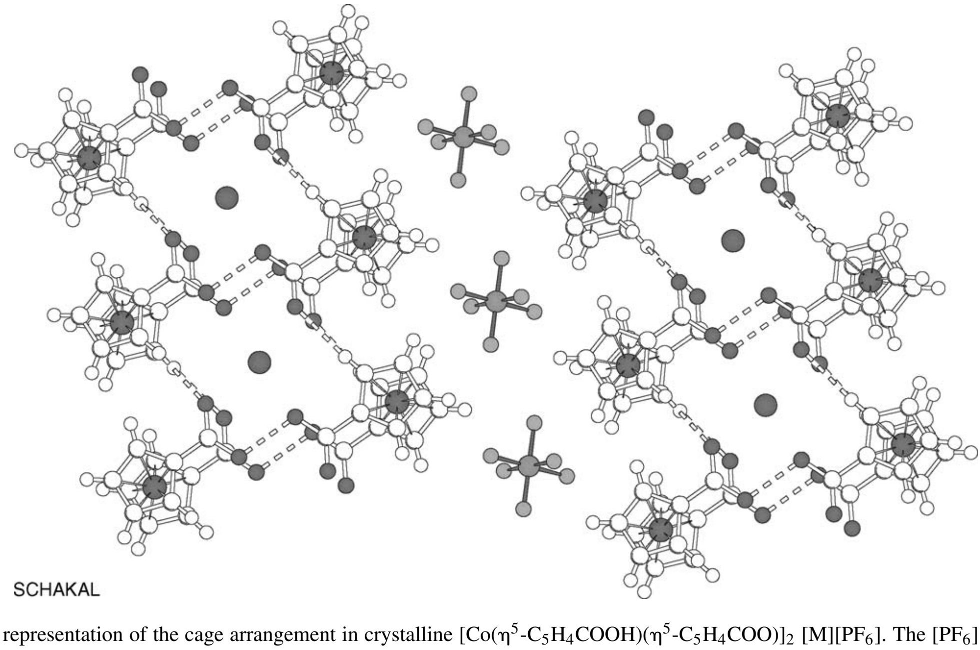


Fig. 15. Ball and stick representation of the cage arrangement in crystalline $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\,[M][PF_6]$. The $[PF_6]^-$ anions pile up on both sides of the supramolecular cages and interact via $C–H\cdots F$ hydrogen bonds with the zwitterion molecules.

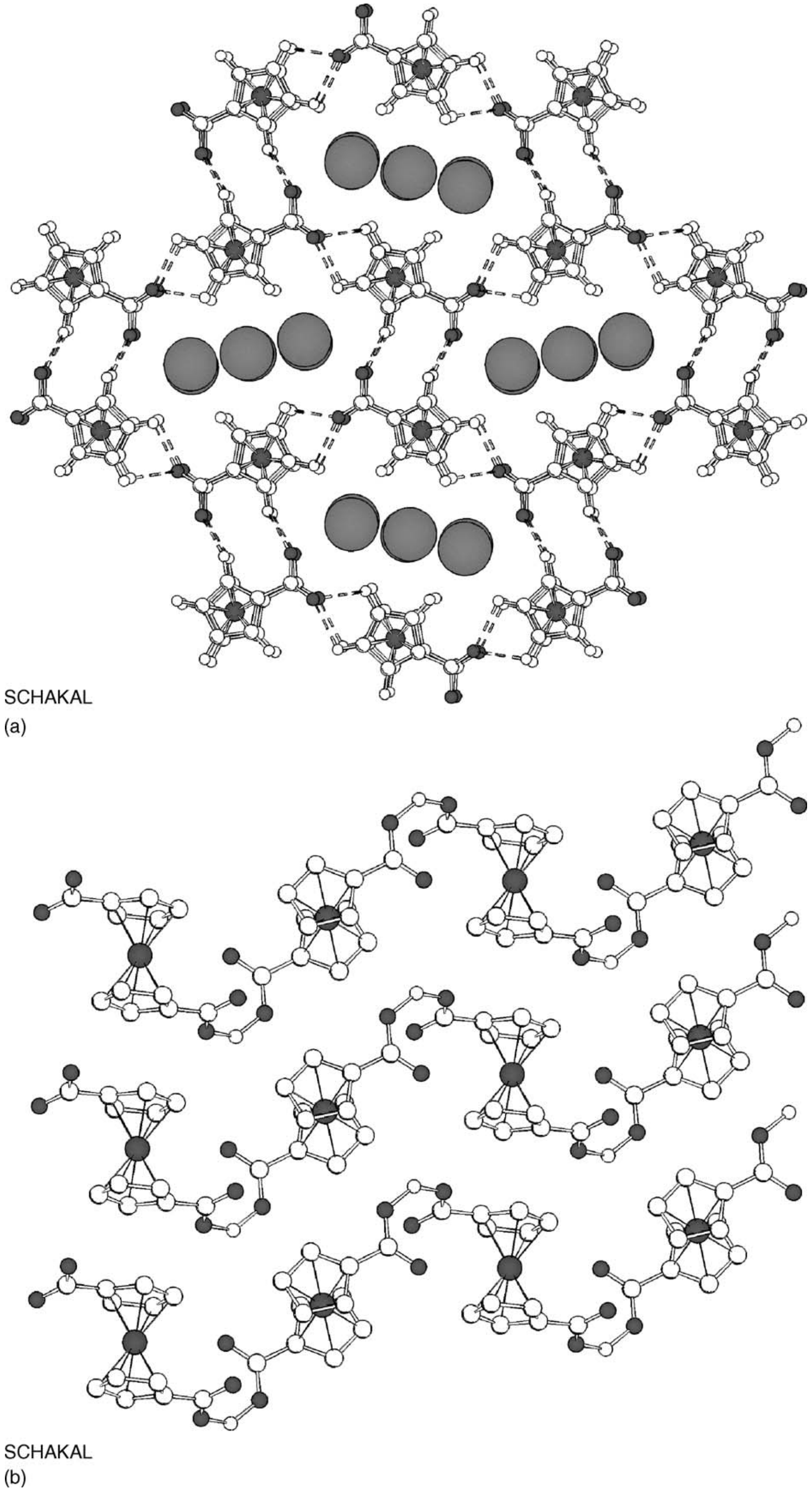


Fig. 16. (a) Comparison of the zwitterion arrangement in crystals of the hydrated species $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot 3H_2O$ and (b) the anhydrous $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ obtained by *seeding* the starting solution with *seeds* prepared by step-wise dehydration and subsequent phase transition of the hydrated species, In (b) H_{CH} omitted for clarity.

$C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot 3H_2O$, from which the anhydrous compound can be obtained by thermal/vacuum dehydration, a process which leads to a polycrystalline product. Single crystals of the anhydrous modification of $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ can, however, be prepared by *seeding* water solutions of the zwitterion with *seeds* prepared by step-wise dehydration and subsequent phase transition of the hydrated species $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot 3H_2O$ [41]. The structure of $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ is based on a one-dimensional network of O–H···O bonded zwitterion molecules (see Fig. 16).

Compound $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ has also been extensively exploited by us in reactions with gaseous substances. Thanks to its amphoteric behaviour the complex undergoes reversible gas-solid reactions (Fig. 17a) with hydrated vapours of a variety of acids (e.g. HCl, CF_3COOH, CCl_3COOH, CHF_2COOH, HBF_4, HCOOH), and bases (e.g. NH_3, NMe_3, NH_2Me) [42]. The salts resulting from the heterogeneous reactions contain the organometallic moiety either in its fully protonated form $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ (in the reaction with acids) or in its fully deprotonated form $[Co(\eta^5\text{-}C_5H_4COO)_2]^-$ (in the reaction with bases). The two types of reactions imply the interconversion between neutral O–H···O hydrogen bonding interactions and $^{(+)}O\text{–}H\cdots X^{(-)}$ and $^{(-)}O\cdots H\text{–}N^{(+)}$ interactions, respectively. Some examples are summarized in Fig. 17.

The processes depicted above are all fully reversible. Crystalline $[Co(\eta^5\text{-}C_5H_4COOH)_2]Cl\cdot H_2O$ can be converted back to neutral $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ by heating the sample for 1 h at 440 K under low pressure (10^{-2} mbar). The behaviour of the zwitterion towards NH_3 is similar to that towards HCl but obviously opposite in terms of proton exchange. $[Co(\eta^5\text{-}C_5H_4COO)_2][NH_4]\cdot 3H_2O$ upon thermal treatment (1 h at 373 K, ambient pressure) the salt converts quantitatively into the starting material. While crystals of $[Co(\eta^5\text{-}C_5H_4COOH)_2]Cl\cdot H_2O$ and $[Co(\eta^5\text{-}C_5H_4COO)_2][NH_4]\cdot 3H_2O$ contain the fully protonated cation and fully deprotonated anion derived from the zwitterions, the case of the reaction with formic acid is more intriguing. When formic acid vapours are absorbed the co-crystal $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][HCOOH]$ is obtained [43]. Contrary to the other compounds of this class, no proton transfer from the adsorbed acid to the organometallic moiety is observed as confirmed by ^{13}C CPMAS NMR spectroscopy. Conversion to the starting material is attained by leaving the sample at room temperature in the air for few days or by mild heating.

Similar behaviour is shown towards other volatile acids. Exposure of the zwitterion to vapours of CF_3COOH and HBF_4, for instance, quantitatively produces the corresponding salts of the cation $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$, viz. $[Co(\eta^5\text{-}C_5H_4COOH)_2][CF_3COO]$ (see Fig. 18) and $[Co(\eta^5\text{-}C_5H_4COOH)_2][BF_4]$ (see Fig. 18).

Exposure of the solid zwitterion to vapours of CHF_2COOH quantitatively produces the corresponding salts of the cation $[Co(\eta^5\text{-}C_5H_4COOH)_2][CHF_2COO]$ (see Fig. 18). The solid–gas reaction implies a profound rearrangement of the hydrogen bonding patterns with formation of ionic pairs between

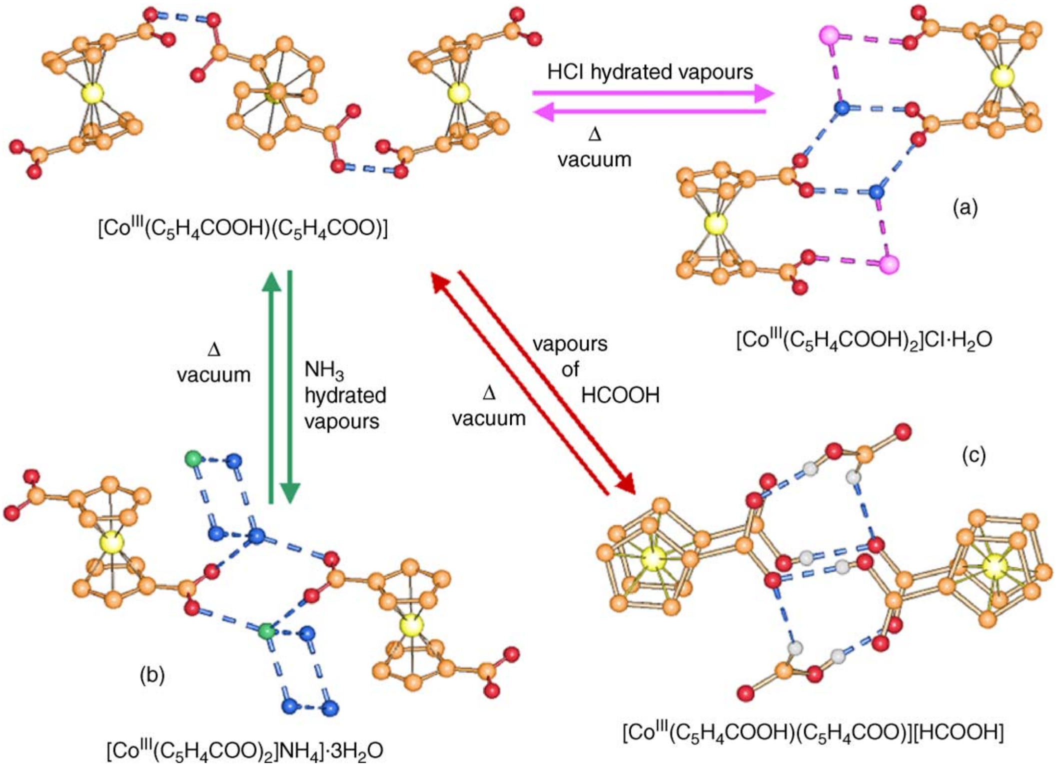


Fig. 17. The reversible reactions between anhydrous $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ and HCl (a), NH_3 (b), and HCOOH (c) leading to formation of $[Co(\eta^5\text{-}C_5H_4COOH)_2]Cl\cdot H_2O$, $[Co(\eta^5\text{-}C_5H_4COO)_2][NH_4]\cdot 3H_2O$, and $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][HCOOH]$, respectively (reprinted from Ref. [5(a)] with permission).

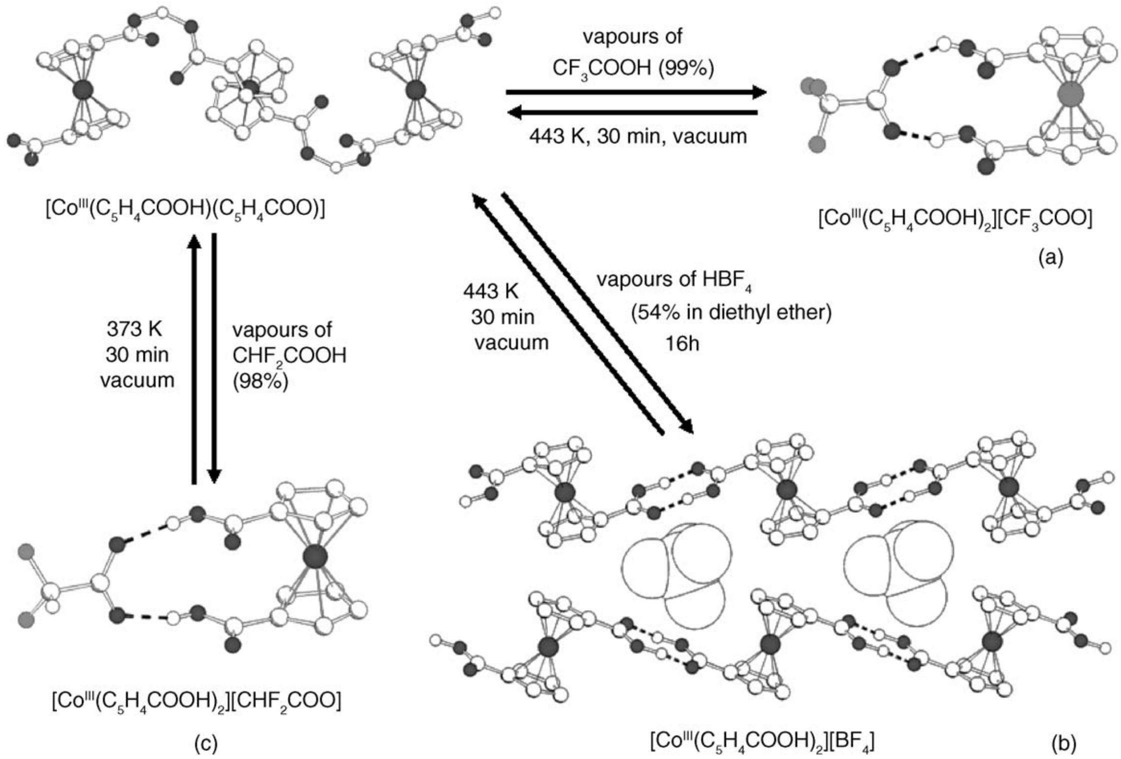


Fig. 18. (a) The structure of $[Co(\eta^5\text{-}C_5H_4COOH)_2][CF_3COO]$, (b) the structure of $[Co(\eta^5\text{-}C_5H_4COOH)_2][BF_4]$, (c) the structure of $[Co(\eta^5\text{-}C_5H_4COOH)_2][CHF_2COO]$.

organometallic and organic moieties. The reaction with hydrated vapours of $CH_2ClCOOH$ produces the hydrated salt $[Co(\eta^5\text{-}C_5H_4COOH)_2][CH_2ClCOO]\cdot H_2O$.

The organometallic dicarboxylic acid cation $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ has also been used with the di-hydrogen phosphate acid anion $[H_2PO_4]^-$ to form the hydrated crystal $[Co(\eta^5\text{-}C_5H_4COOH)_2][H_2PO_4]\cdot H_2O$ and the anhydrous $[Co(\eta^5\text{-}C_5H_4COOH)_2][H_2PO_4]\cdot[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]\cdot[H_3PO_4]_2$; which can also be formulated as, $[Co(\eta^5\text{-}C_5H_4COOH)_2]_2$ $[H_2PO_4]_2\cdot[H_3PO_4]$, because of the competition in the possession of the proton in the O–H···O hydrogen bond between the organometallic and inorganic moieties [44].

7. Conclusions and outlook

In this review article, we have shown that organometallic building blocks functionalized with classical hydrogen bonding donor/acceptor groups (e.g. –COOH, $–B(OH)_2$, pyridine, amides, etc.) can be successfully utilized in a broad range of crystal engineering exercises for the formation of supramolecular adducts and hydrogen bonded networks. The building block of choice in this report is a sandwich compound (whether bis-arene of bis-cyclopentadienyl sandwich) carrying hydrogen bonding functional groups. We have shown in the first section that most dicarbocylic acids utilize the twin intermolecular hydrogen bonding to form cyclic dimers, which are then *maintained* in the crystal structures as supramolecular units of packing. The packing of such dimeric units is then that of supramolecular van der Waals objects capable, to the most, of weak C–H···O interactions. The existence of three polymorphs of such dimers in the case of $\{[Fe(\eta^5\text{-}C_5H_4COOH)_2]\}_2$ is noteworthy. Interestingly, compounds such as the dicarboxylic acids $\{[Fe(\eta^5\text{-}C_5H_4COOH)_2]\}_2$, $\{[Co(\eta^5\text{-}C_5H_4COOH)_2]\}_2$ and $\{[Cr(\eta^6\text{-}C_6H_5COOH)_2]\}_2$ or, just as well, the dication $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]^+\}_2$ and the supramolecular adduct $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]\}^+$, which forms dimers, show an important topological difference from the relative "organic-only" compounds (i.e. organic dicarboxylic acids, bis-amides, etc.) because these latter compounds are, in general not "allowed" the conformational freedom of sandwich compounds and, therefore, cannot dimerize. In fact, dicarboxylic organic acids tend to form chains in the solid state, rather than self-assemble in dimeric units. The chain formation, on the other hand is not precluded to the organometallic sandwich acids. Not only the chain motif is also possible for a same species, as in the case of form **II** of $[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]$, but it is also the motif of choice in all cases of cationic acids, e.g. the two polymorphs of $[Cr(\eta^6\text{-}C_6H_5COOH)_2][PF_6]$ and $[Co(\eta^5\text{-}C_5H_4COOH)_2]X$ ($X = PF_6{}^-$, $BF_4{}^-$). In these cases, the chain structure might be favoured because of the need to optimize simultaneously the Coulombic interactions between ions of opposite charge as well as the hydrogen bonds in between anions.

We have put the emphasis on the structural and supramolecular features of the sandwich compounds, but it should made clear that, *before* these building blocks can be used in supramolecular bonding they *have to be made*. In many instances, it was necessary to synthesize ab initio, the building block of choice because only few of the starting materials are commercially available. Details of the solution chemistry that precedes the crystal engineering steps are available in the original papers quoted through the review.

We have also shown that the preparation of molecular crystals of the type described in this contribution is not confined to traditional crystallization from solution. Solvent-free methods, such as solid–solid reactions, vapour uptake from a solid, *kneading* of crystalline solids with small amount of solvent or liquid reactant can be exploited to prepare novel compounds, some of which cannot be otherwise obtained by traditional solution methods. These methods, widely used in the organic solid-state chemistry field [45], can be predicted to have an important future also in the neighbouring field of solid-state organometallic chemistry [46].

Beside the preparation of crystalline materials based on hydrogen bonds, we are currently investigating the use of some of the building blocks described above, such as pyridine and amido ferrocenyl and cobalticinium complexes, in the preparation of complexes of complexes [47], the exploitation of mechanochemical methods to prepare coordination networks [48], and the preparation of supramolecular adducts based on acid salts [49]. These results will constitute the subject matter of future reports.

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