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Organometallic crystals engineering
Part 7. Construction of mixed-metal crystalline systems via electrostatic interactions and cooperative strong and weak hydrogen bonds

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Abstract

The dicarboxylic organometallic acid $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ ($FeACH_2$) has been used to produce a series of novel mixed-metal mixed-valent crystalline materials by the sequence of reaction steps: (i) oxidation in the air of THF solutions of $[(\eta^5\text{-}C_5H_5)_2Co]$ and $[(\eta^6\text{-}C_6H_6)_2Cr]$ and consequent reduction of O_2 to the strongly basic anion O_2^-; (ii) deprotonation of $FeACH_2$ to yield the anion $FeACH^-$ (or $FeAC^{2-}$); (iii) precipitation of the insoluble organometallic salts formed between the organometallic acidate and the diamagnetic cation $[(\eta^5\text{-}C_5H_5)_2Co]^+$ or the paramagnetic cation $[(\eta^6\text{-}C_6H_6)_2Cr]^+$. The novel materials $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]^-$ (**1**), $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]^-\cdot H_2O$ (**2**), $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+\}_2\text{-}\{[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]_2[(\eta^5\text{-}C_5H_4COOH)_2Fe]\}^{2-}$ (**3**) and $[(\eta^6\text{-}C_6H_6)_2Cr]^+\{[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)\text{-}Fe\}^-\cdot H_2O$ (**4**) have been prepared and structurally characterised by low temperature single-crystal X-ray diffraction. The four species contain different electronic and spin metal centres: 18 electrons Fe^{II} and Co^{III} are present in **1** and **2** whereas Fe^{II} and paramagnetic 17 electrons Cr^{I} are present in **3** and **4**. The crystalline edifices are held together by the complementary contribution of neutral O–H···O and/or negatively charged $O\text{–}H\cdots O^{(-)}$ hydrogen bonding interactions between the acid moieties and of *charge assisted* $C\text{–}H^{\delta+}\cdots O^{\delta-}$ bonds between cations and anions. The structure of the 'heavily hydrated' species $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 7.75H_2O$ (**5**), in which the acid is completely deprotonated, will also be discussed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Organometallic crystal engineering is an attractive field of research [1]; early attempts to make crystals based on organometallic components have been mainly directed to obtain charge transfer and molecular magnetic systems [2]. Much of the current interest in organometallic crystal engineering stems from the potentials inherent to the utilisation of crystal construction strategies developed in the neighbouring field of organic crystal engineering [3] to assemble organometallic molecules or ions in a predesigned way. The ultimate goal is that of preparing novel materials in which the characteristics of transition metal coordination chemistry (e.g. variable valence, oxidation and spin states of the metal atoms) are brought in the crystals. This objective can be achieved by controlling the non-covalent interactions established between the ligands, which can behave as organic functional groups. The intelligent utilisation of non-covalent interaction to obtain aggregates that function differently from the separate components is the paradigm of supramolecular chemistry [4]. Hence, molecular crystal engineering, and organometallic crystal engineering of course, may be regarded as being at the crossing point of supramolecular and materials chemistry.

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The hydrogen bond (HB) is the interaction of choice in molecular crystal engineering because it combines strength (a prerequisite of stability) with directionality (a prerequisite of reproducibility) [5]. Strength and directionality can be tuned by varying the polarity and the geometry of the acceptor and donor groups. The classical O–H···O hydrogen bonds formed by –COOH and –OH groups are among the strongest neutral bonds. It is well known, however, that the O–H···O bond can be further strengthened if the polarity of the acceptor systems is increased via deprotonation. While HB between neutral molecules and anions ($O–H\cdots O^{(-)}$) have been shown [5g,h] to possess dissociation energies in the range 60–120 kJ mol^{-1}, we now know from theory and experiment, that the *function* of $O–H^{(-)}\cdots O^{(-)}$ and of $C–H^{(-)}\cdots O^{(-)}$ HB interactions is that of minimising electrostatic repulsions between anions, thus acting as 'supramolecular organisers' rather than as stable bonds [6]. These 'tug-boat' interactions, however, are extremely efficient in controlling recognition and self-assembly of the ions in supramolecular networks [7].

We have successfully used polycarboxylic acids to prepare a number of complex organic and organometallic superstructures [8,9] with predefined architectures and structural features by means of the simultaneous use of neutral O–H···O and negatively charged $O–H\cdots O^{(-)}$ bonding interactions [8]. Our crystal engineering strategy is based on the self-assembly, around the Cr and Co cationic sandwich complexes, $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+$, of the species carrying –COOH and $–COO^-$ groups. The absence on the cations of groups capable of competitive O–H···O interactions allows anion recognition and self-assembly [8]. The $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations are, respectively, paramagnetic and diamagnetic, a feature that allows preparation of mixed-valent and mixed-spin systems. In this paper we discuss the results obtained by using the (rather unconventional) dicarboxylic organometallic acid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ ($FeACH_2$ hereafter) [10]. Part of this work has been the subject of preliminary communications [11]. The reaction sequence proceeds via: (i) oxidation in the air of THF solutions of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+$ and consequent reduction of O_2 to the strongly basic anion O_2^-; (ii) deprotonation of $FeACH_2$ upon reaction with the THF solutions of $[(\eta^5\text{-}C_5H_5)_2Co]^+/O_2^-$ or $[(\eta^6\text{-}C_6H_6)_2Cr]^+/O_2^-$ to yield the anion $FeACH^-$ (or $FeAC^{2-}$ depending on the stoichiometric amount of the sandwich complex); (iii) precipitation of the insoluble organometallic salts formed between the partly deprotonated acid and the sandwich cations. The precipitates are then recrystallized from nitromethane or water. Crystalline **1**, **2**, **3** and **4** have thus been prepared and structurally characterised. The relationship between the hydrated crystalline phases **2** and **4** and those of the related anhydrous compounds **1** and **3** has been investigated. It is worth stressing that the four species contain different electronic and spin metal centres: 18 electrons Fe^{II} and Co^{III} are present in **1** and **2** whereas Fe^{II} and paramagnetic 17 electrons Cr^{I} are present in **3** and **4**.

2. Experimental

2.1. Crystal synthesis

As in the cases discussed in preceding papers in this series [9], the synthetic aspect of this work is related to the synthesis and crystallisation of solid materials. It should be stressed that all usual spectroscopic tools for the characterisation of chemical products in solution can not be used in the contest of a crystal synthesis. The products of the synthesis exist only in the condensed phase for which diffraction techniques are essential. Cobaltocene and ferrocene dicarboxylic acid were purchased from Aldrich, bisbenzene chromium from Strem. The preparation of crystalline **1** and **3** have been already described [11a]. Here we report that **1** and **3** absorb a stoichiometric amount of water when their crystals are ground (a procedure commonly used to prepare samples for powder diffraction). Recrystallization of the samples obtained from **1** and **3** from nitromethane gave single crystals of **2** and **4**. The hydration process relating **1** and **2** has been the subject of a preliminary report [11b].

2.2. Synthesis of 5

$(\eta^5\text{-}C_5H_5)_2Co$ (57 mg, 0.3 mmol) was dissolved in 20 ml of water and stirred until complete oxidation to yellow $[(\eta^5\text{-}C_5H_5)_2Co]^+$. $FeACH_2$ (8 mg, 0.03 mmol) was added to 5 ml of the solution and stirred for 15 min (final pH ca. 6). The yellow-orange solution was filtered and evaporated to dryness and the resulting solid was recrystallized from nitromethane obtaining well formed crystals of **5**.

2.3. Crystal structure characterisation

All X-ray diffraction data collections were carried out on a Nonius CAD-4 diffractometer equipped with an Oxford Cryostream liquid-N_2 device. Crystal data and details of measurements are reported in Table 1. Diffraction data were corrected for absorption by azimuthal scanning of high-χ reflections. SHELXL-97 [12a] was used for structure solution and refinement based on F^2. Fractional atomic co-ordinates and anisotropic displacement parameters are available as Supporting Information. SCHAKAL-97 [12b] was used for the graphical representation of the results. Common to all compounds: Mo–K_α radiation, $\lambda = 0.71069$ Å,

Table 1
Crystal data and details of measurements for **1**, **2**, **3**, **4** and **5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{22}H_{19}CoFeO_4$	$C_{22}H_{21}CoFeO_5$	$C_{30}H_{26}CrFe_{1.5}O_6$	$C_{24}H_{23}CrFeO_5$	$C_{32}H_{43.5}Co_2FeO_{11.75}$
Molecular weight	462.15	480.17	618.28	499.27	789.88
Temperature (K)	213(2)	223(2)	223(2)	223(2)	223(2)
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	Cc	$P\bar{1}$
a (Å)	9.792(6)	12.251(5)	15.421(8)	34.102(5)	11.675(5)
b (Å)	9.249(4)	17.276(6)	9.998(5)	8.431(5)	12.087(2)
c (Å)	10.338(8)	18.083(7)	16.208(6)	14.375(5)	25.125(4)
α (°)	90	90	90	90	85.60(1)
β (°)	98.70(6)	91.56(3)	97.39(4)	90.480(10)	77.27(1)
γ (°)	90	90	90	90	82.67(1)
V (Å^3)	925.5(10)	3825.8(25)	2478(2)	4133(3)	3425.8(4)
Z	2	8	4	8	4
F(000)	472	1968	1268	2056	1638
Min. and max. transmission	0.84–1.00	0.87–1.00	0.92–1.00	0.85–1.00	0.89–1.00
μ(Mo–K$_\alpha$) (mm^{-1})	1.706	1.658	1.351	1.263	1.435
Measured reflections	1726	6933	4135	5703	9023
Unique reflections	1629	6710	3974	3414	8754
Refined parameters	112	454	292	235	724
GoF on F^2	0.859	0.981	1.000	0.976	1.080
R_1 (on F, $I>2\sigma(I)$)	0.0449	0.0456	0.0360	0.0605	0.0707
wR_2 (on F^2, all data)	0.1386	0.1457	0.1016	0.1758	0.2499

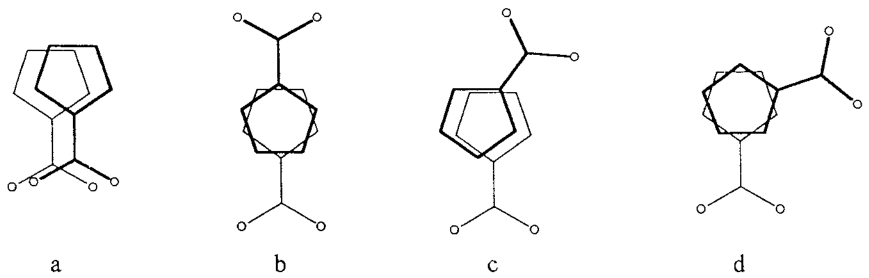
monochromator graphite. All non-H atoms were refined anisotropically. The positions of the $H_{(COOH)}$ hydrogen atoms in **1** and **2** and of the water hydrogens in **3** and (partly) in **4** have been observed in the Fourier maps and were not refined. The remaining H atoms bound to C atoms were added in calculated positions in all compounds and refined riding on the corresponding C-atoms. The water hydrogens in **5** could not be located, no attempt was made to model their positions. The computer program PLATON [12c] was used to analyse the geometry of the hydrogen bonding patterns. In order to evaluate C–H···O bonds the C–H distances were normalised to the neutron derived value of 1.08 Å. Diffraction data have all been measured at 223 K. Atomic co-ordinates and full listing of bond angles and distances as well as all details of intermolecular structural parameters are provided as 'supplementary material' and are available from the authors upon request.

3. Results and discussion

Since the focus of this paper is on the supramolecular features of the crystalline materials, details of the structures of the ions will not be described while some attention will be given to the conformational geometry of the anions derived from ferrocene dicarboxylic acid. The data collected in Table 2 indicate that O–H···O and O–H···O$^{(-)}$ hydrogen bonding distances are comparable to those formed by other polycarboxylic acidates discussed previously, irrespective of the 'organic' or 'organometallic' nature of the ions. The effect of charge is notable on all interactions. Water–water hydrogen bonds are, in general, longer than water–carboxylates. Because of the structural relationship between the cobalt and chromium derivatives the pairs

Table 2
O–H···O hydrogen bonding interactions in crystalline **1**, **2**, **3**, and **4** [O–H···O$^{(-)}$ and O–H$^{(-)}$···O$^{(-)}$ in bold]

Donor–H···accceptor	O–H	H···O	O···O	O –H···O
1. (Estimated S.D.s 2)				
O(1)–H(101)···O(1)	**1.23**	**1.23**	**2.45**	**180.0**
2. (Estimated S.D.s 2)				
O(4)–H(100)···O(7)	**1.14**	**1.40**	**2.49**	**157.4**
O(2)–O(5)	**–**	**–**	**2.52**	**–**
O(9)–H(101)···O(2)	0.85	1.97	2.81	168.2
O(9)–H(102)···O(8)	0.87	1.89	2.73	160.6
O(10)–H(103)···O(1)	0.95	1.89	2.83	172.9
3. (Estimated S.D.s 2)				
O(3)–H(100)···O(1)	**1.11**	**1.48**	**2.57**	**168.5**
O(5)–H(101)···O(1)	**1.01**	**1.56**	**2.57**	**171.3**
4. (Estimated S.D.s 2)				
O(2)–H(200)···O(4)	**1.16**	**1.30**	**2.46**	**173.4**
O(6)–H(600)···O(8)	**1.19**	**1.25**	**2.44**	**174.1**
O(1)···O(9)	–	–	2.82	–
O(3)···O(9)	–	–	2.75	–
O(5)···O(10)	–	–	2.82	–
O(5)···O(10)	–	–	2.85	–



Scheme 1. Different conformations of the 'Fe(CpCOO)$_2$' unit found in the crystals structure of the dicarboxylic acid (a); in crystalline **1**, **2**, **3** (b); in crystalline **2** (c); and in the crystalline **5** (d). Hydrogen atoms and double bond are omitted for clarity.

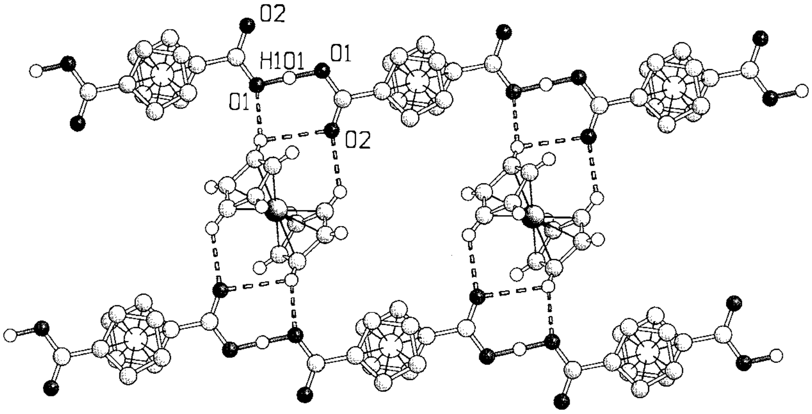


Fig. 1. In crystalline **1** the FeACH$^-$ anions form parallel chains enclosing the [(η^5-C$_5$H$_5$)$_2$Co]$^+$ cations. Schematic representation of the patterns of O···H···O interactions connecting the FeACH$^-$ anions and of the charge enhanced C–H$^{\delta+}$···O$^{\delta-}$ hydrogen bonds (broken lines) between the FeACH$^-$ anions and the cobalticinium cations. Note how the two sets of three C–H$^{\delta+}$···O$^{\delta-}$ hydrogen bonds are directed precisely towards the 'unused' lone pairs on the carboxylic oxygen atoms. For O–H···O interactions refer to Table 2, H-atoms of the FeACH$^-$ anions omitted for clarity.

of systems **1–2**, and **3–4**, will be discussed together while the structure of the hydrated species **5**, in which the acid is completely deprotonated, will be discussed separately.

As it will become apparent through the following discussion the acid FeACH$_2$ is very versatile not only because it can participate in hydrogen bonded networks as neutral, mono- and di-deprotonated species but also because of the conformational freedom due to a seemingly low-energy rotational barrier of the two C$_5$ rings about the coordination axis. Scheme 1 shows the conformations in the four compounds and should help the following discussion.

3.1. Ion organisation in crystalline **1** and **2**

In crystalline **1** the FeACH$^-$ anions, derived from mono-deprotonation of the neutral acid, form chains via symmetric O···H···O interactions between ligands in *transoid* conformation. Charge assisted C–H$^{\delta+}$···O$^{\delta-}$ hydrogen bonds link then the cobalticinium cations to the FeACH$^-$ chains. The two sets of three C–H$^{\delta+}$···O$^{\delta-}$ hydrogen bonds on both sides of the cations are directed towards the 'unused' lone pairs on the carboxylic oxygen atoms. There are two very short (C)H···O distances (2.192 and 2.254(3) Å) and a longer one (2.523(3) Å) in the bifurcated bond as shown in Fig. 1. The FeACH$^-$ chain extends in the *a*-direction establishing a markedly anisotropic packing arrangement. The anionic superstructure can be described as an arrangement of parallel rows of anions forming channels in which the cations are accommodated.

Although the stoichiometry of compound **2** corresponds to the formula [(η^5-C$_5$H$_5$)$_2$Co]$^+$[(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)Fe]$^-$·H$_2$O the distribution of –COOH groups indicates that the asymmetric unit is composed of one fully protonated ferrocenedicarboxylic acid FeACH$_2$ unit in general position and of two 'half' dianionic, i.e. completely deprotonated, FeAC^{2-} units, in addition to two cobalticinium cations and two water molecules. All hydrogen atoms involved in hydrogen bonds (see below), except one, were located in the final Fourier maps. Although location of H-atom positions in X-ray diffraction experiments is not always trustworthy, it is useful to note that the assignment of neutral and anionic units to the ferrocene moieties is in agreement with the distribution of bond length relative to the carboxylic/carboxylate groups. With the caveat on the

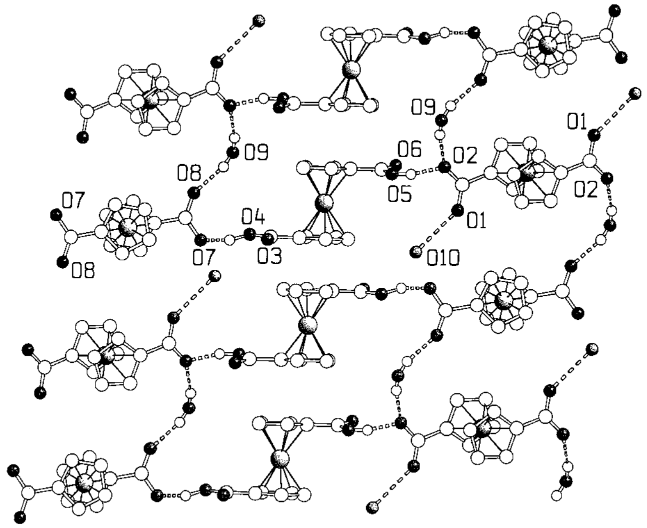


Fig. 2. In crystalline **2** the $FeACH_2$ and the $FeACH^{2-}$ anions form chains of the type $\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots$ via O–H···O hydrogen bonding interactions (refer to Table 2). Parallel chains are linked by the water molecules. Cations are not shown. H-atoms bound to the C-atoms are omitted for clarity.

reliability of the structural information, the chains shown in Fig. 2 can be described as resulting from the neutral/dianion alternation $\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots$ (see Fig. 2). The hydrogen bond interaction along the chains in **2** are 2.49(2), and 2.52(2) Å, i.e. slightly longer than in **1** (2.45(2) Å). The separations between the iron centres in the two crystals is almost the same (9.79 versus 9.78 and 9.65 Å in **1** and **2**, respectively). Therefore the hydration process from **1** to **2** implies only minor changes in the fundamental packing motifs in the crystals, with a redistribution of the H-atoms along the HB sequence and the water molecules acting as inter-chains linkers.

The simultaneous presence in **2** of fully deprotonated anions derived from a carboxylic acid, viz. of supposedly strong bases, together *with* fully protonated acid molecules may appear in contradiction with the ‘common-sense’ behaviour of acids and bases. However, one should keep in mind that the acid-strength concept is relative to the strength of the proton acceptor, usually the solvent. In the solid state this concept does not hold and can not be applied because the interactions at work are of different nature than in solution. It can be argued that dianion–neutral alternation within the chains in **2** achieves the important result of decreasing the electrostatic repulsion between anionic species. A monoanionic chain $\cdots[FeACH^-]\cdots[FeACH^-]\cdots[FeACH^-]\cdots$ as in **1** with respect to the chain $\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots$ in **2** possesses exactly the same *number of hydrogen bonds* but should pay a larger electrostatic repulsion than in the latter where the neutral molecule may act as a *buffer* between the two anions. The balance must be subtle and the overall difference in energy not very large. It is interesting, however, to note that this situation is not unique of **1** and **2**: similar alternations of dianions and neutral molecules have been observed by us in the case of the crystal constructed with phthalic acid [9d] and also in the crystal of barium oxalate [13].

The ferrocene moieties in **2** also possess two different conformations: in projection the ligands in $FeAC^{2-}$ are *transoid* with the C_5 ring *staggered* while in the neutral $FeACH_2$ molecule the conformation can be described as *pseudo transoid* with the C_5 rings *eclipsed* in projection. The dianions $FeAC^{2-}$ are tilted respect to the molecule of $FeACH_2$ (see Fig. 3), probably to allow the hydrogen bonds with the water molecules. The role of these molecules is clear to see, they act as a bridge between the chains $\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots$ forming a two-dimensional anionic layer structure (O–O_w distances, 2.733, 2.814, 2.835(3) Å). The interaction between the supra-anionic network and the cobalticinium cations occurs via C–H···O hydrogen bonds between the *staggered* cyclopentadienyl ligands of the cations and the oxygen of the carboxylic/carboxylate group and the oxygen of the water. There are 12 (C)H···O distances shorter of 2.5 Å.

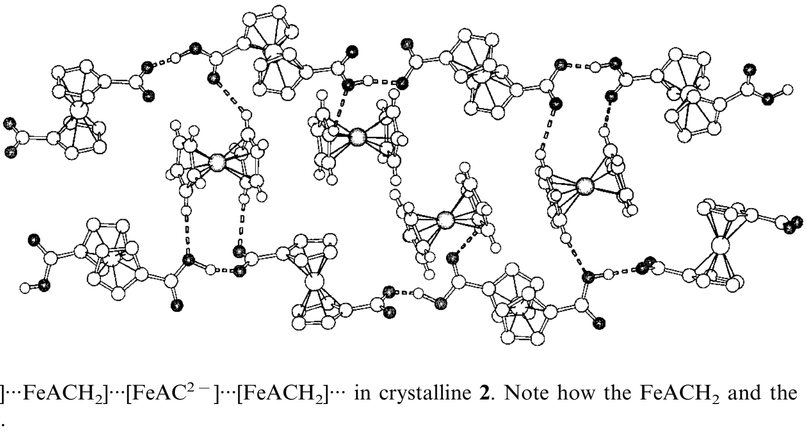


Fig. 3. Chains of $\cdots[FeAC^{2-}]\cdots FeACH_2]\cdots[FeAC^{2-}]\cdots[FeACH_2]\cdots$ in crystalline **2**. Note how the $FeACH_2$ and the $FeACH^{2-}$ units are rotated one with respect to the other.

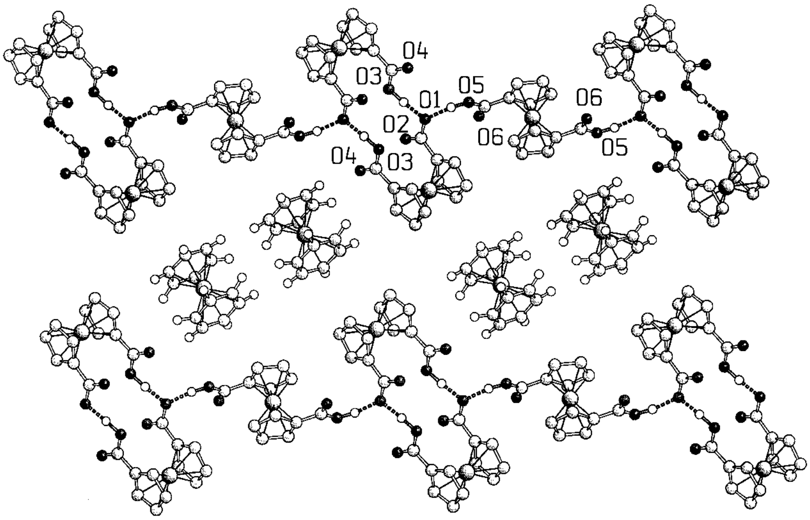


Fig. 4. In crystalline **3** the neutral $FeACH_2$ molecule acts as a bridge between hydrogen bonded dimers formed by two $FeACH^-$ anions. There are two types of O–H···O hydrogen bonding interactions, those within the $\{[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]_2\}^{2-}$ unit and those between these units and the neutral $FeACH_2$ spacer (refer to Table 2 for structural parameters). H-atoms bound to C-atoms of the anions are omitted for clarity.

*3.2. Ion organisation in crystalline **3** and **4***

The formula unit in crystalline **3** contains one neutral $FeACH_2$ molecule every two $FeACH^-$ anions. The neutral molecule acts as a bridge between hydrogen bonded dimers formed by two $FeACH^-$ anions. In a way **3** recalls the situation observed for **2** with the neutral undeprotonated molecule acting as a buffer (a spacer) between the anionic units (see Fig. 4). It is also interesting to note that **3** is the only compound that contains a dimeric unit similar to that observed in neutral $FeACH_2$; the O···O separations are shorter than in the neutral molecule (2.570(5) versus 2.600(5) Å). The neutral-anion $O–H\cdots O^{(-)}$ hydrogen bonds (see the bifurcated interaction in Fig. 4) is of the same length as that between the two mono-anions (2.570(5) 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 $C–H^{\delta+}\cdots O^{\delta-}$ interactions with the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations. There are as many as six (C)H···O distances shorter than 2.5 Å, with one as short as 2.072(5) Å. These values are again indicative of a substantial electrostatic reinforcement of the weak bonds [14]. The presence of pairs of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations in the packing of **4** is noteworthy. Similar characteristic has been observed before in the case of the cyclohexanedione derivative $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+[(CHD)_2]^-(CHD)_2\}_2$ [15]. Since the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cation is paramagnetic, one may wonder if the presence of pairs of the bis-benzene chromium cations may be seen as a manifestation of the well-known McConnell's model which predicts the presence of intermolecular ferromagnetic interactions between neighbouring paramagnets [16].

Crystalline **4** presents two mono-deprotonated $FeACH^-$ units in general position, two $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations and two water molecules. The carboxylic hydrogens were located in the Fourier map and they are almost midway between the two oxygens involved in the $O–H\cdots O^{(-)}$ HBs. The length of the two independent $O–H\cdots O^{(-)}$ HB is similar (2.461 and 2.438 (3) Å) and comparable to that commonly found in anionic HB [6a]. The $FeACH^-$ are in *pseudo-transoid* conformation with the C_5 ring *eclipsed* and form a zigzag chain. The water molecules act as bridges between the chains ($O\cdots O_w$ distances, 2.747, 2.815, 2.821, 2.847(3) Å). It is worth noting that all oxygen atoms are involved in O–H···O hydrogen bonds as shown in Fig. 5. The interaction between the supramolecular anionic network and the cobalticinium cations occurs via charge assisted $C–H^{\delta+}\cdots O^{\delta-}$ hydrogen bonding interactions between the *staggered* cyclopentadienyl ligands of the cations and the oxygen of the carboxylic/carboxylate group and the oxygen of the water. There are ten (C)H···O distances shorter of 2.5 Å.

*3.3. The 'heavily hydrated' species **5***

Although somewhat unrelated to the four crystalline systems discussed above, we need to mention that when the cation:anion ratio is 2:1 or higher, viz. complete deprotonation is likely to occur, crystallisation from water of 'heavily hydrated species' is often observed [8]. 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 (leading to complete removal of the acidic protons) that species with a large number of water molecules are obtained. We have previously prepared a derivative of

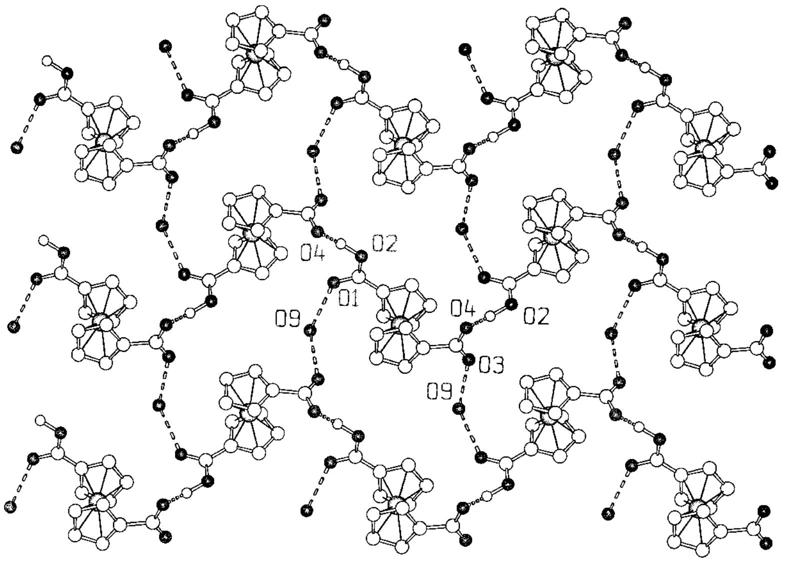


Fig. 5. In crystalline **4** the $FeACH^-$ anions form zigzag $FeACH^-\cdots FeACH^-\cdots FeACH^-$ chains via O–H···O hydrogen bonding interactions (see Table 2). These chains are linked to each other by water molecules as observed in **2** forming a two-dimensional network. H-atoms bound to C-atoms are omitted for clarity; cations are not shown, only one portion of the asymmetric unit is shown.

dibenzoyl-L-tartaric acid (L-H_2BTA) with the cobalticinium cation, yielding the crystalline material $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[\text{L-BTA}]^{2-}\cdot 11H_2O$ [9a]. As in this case, crystallisation from water of the $(C_5H_5)_2Co{:}FeACH_2$ system prepared in 2:1 ratio leads to complete deprotonation of the dicarboxylic acid and to crystallisation of $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 7.75H_2O$. In **5** the acid $FeACH_2$ is completely deprotonated, hence no hydrogen bonding donor group is available to cope with the presence of the 12 potential hydrogen bonding acceptor sites.

The 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. In **5** the completely deprotonated $FeAC^{2-}$ anion has no –O–H hydrogen bonding donor groups available, and the water molecules form hexameric units which are linked together in ribbons and interact with the $-COO^{(-)}$ groups.

4. Conclusions

We have shown that novel hydrogen bonded organometallic architectures can be obtained by utilising organometallic carboxylic acids as building blocks for the construction of anionic hydrogen bonded frameworks. The acid $FeACH_2$ is very versatile thanks to both the conformational freedom about the coordination axis (that permits the orientation in space of the $-COOH/-COO^-$ groups which optimises HB formation) and the possibility of participating in HB as mono- and di-deprotonated anion. The *eclipsed* conformation, which is present in the neutral acid, is maintained in the monodeprotonated dimer in **3**. In all the other crystals the $FeACH^-$ anion is in the *transoid* conformation but the rings can be *eclipsed* or *gauche*. Moreover, the carboxylic/carboxylate group can loose the planarity with the cyclopentadienyl ring to allow the maximum number of hydrogen bonds. The acid–base reaction allows to conceive the preparation of a great variety of hydrogen bonded organometallic crystals in which metal atoms in different oxidation and spin states can be combined within robust hydrogen bonded superstructures. Furthermore, the abundance of polarised C–H systems on metal co-ordinated ligands, such as C_5H_5 and C_6H_6, make the use of $C\text{–}H^{\delta+}\cdots O^{\delta-}$ interactions also profitable, in particular since they may be reinforced when donors and acceptors belong to cations and anions, respectively.

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