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Crystal engineering *via* negatively charged O–H · · · O$^-$ and charge-assisted C–H$^{\delta+}$ · · · O$^{\delta-}$ hydrogen bonds from the reaction of [Co(η^5-C_5H_5)$_2$][OH] with polycarboxylic acids §

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The polycarboxylic acids $C_6H_3(CO_2H)_3$-1,3,5 (trimesic acid, H_3tma) and O^2,O^3-dibenzoyl-L-tartaric acid (L-H_2bta) reacted in water or thf with [Co(η^5-C_5H_5)$_2$][OH] prepared *in situ* by oxidation of [Co(η^5-C_5H_5)$_2$] to generate organic superanions self-assembled *via* negatively charged O–H · · · O$^-$ and neutral O–H · · · O hydrogen bonds. The resulting organic host accommodates the cations *via* charge assisted C–H$^{\delta+}$ · · · O$^{\delta-}$ hydrogen bonds between organometallic and organic components. Crystalline [Co(η^5-C_5H_5)$_2$]$^+$[(H_3tma)(H_2tma)]$^-$·2H_2O **1** was obtained as the major product from acid and base in a 1 : 2 stoichiometric ratio. Compound **1** contains a complex hydrogen bonded honeycomb-type structure formed by superanions [(H_3tma)(H_2tma)]$^-$ and water molecules. The mixed salt [Co(η^5-C_5H_5)$_2$]$^+$[Co(H_2O)$_6$]$^{2+}$[tma]$^{3-}$ **2** was obtained as a minor product from the same reaction. In crystalline **2** the water molecules of the aqua complex form hydrogen bonds with the three carboxylic groups of the organic anion resulting in a caged structure that encapsulates the [Co(η^5-C_5H_5)$_2$]$^+$ cation. When dibenzoyl-L-tartaric acid was used the chiral crystal [Co(η^5-C_5H_5)$_2$]$^+$[L-Hbta]$^-$ **3** is obtained. The crystal contains chains of O–H · · · O$^-$ hydrogen bonded anions. These results are used to discuss a design strategy for the engineering of organometallic crystals with predesigned structures. Though on a limited data set, the structure of the elusive crystalline hydrate [Co(η^5-C_5H_5)$_2$]$^+$[OH]$^-$·4H_2O **4**, which is liquid at ambient temperature, is discussed.

Crystal engineering is at the intersection of supramolecular chemistry and materials chemistry. For this reason, the experimental[2] and theoretical[3] generation of desired crystal structures is attracting the interest of an increasing number of research groups. The ultimate goal is that of *making crystals with a purpose*. This implies the design, synthesis, characterization and utilization of crystalline materials with predefined assembly of molecules and ions that result in useful collective crystalline properties (magnetism,[4] conductivity and superconductivity,[5] charge transfer,[6] NLO applications,[7] *etc.*).

The synthesis of crystals containing organic and organometallic molecules or ions is a means to *combine* within supramolecular aggregates the intra- and inter-molecular bonding features of organic fragments, whether as ligands or free molecules, with the variable valence state and magnetic behavior of transition metal atoms.[8] An intelligent choice of the organometallic and organic 'partners' allows the rational design of solid materials with predefined arrangements of the component molecules or ions.[9,10]

In Parts 1[11] and 2[1] of this series of papers we have reported the design, synthesis and structural characterization of organic–organometallic crystals obtained from the paramagnetic cations [Cr(η^6-arene)$_2$]$^+$ (arene = benzene or toluene) reacted with cyclohexane-1,3-dione (chd) and from the hydroxide [Co(η^5-C_5H_5)$_2$]$^+$[OH]$^-$ reacted with carboxylic acids. Crystalline aggregates of the type [Cr(η^6-C_6H_6)$_2$]$^+$[(chd)$_2$ − H]$^-$·2chd and [Cr(η^6-C_6H_5Me)$_2$]$^+$[(chd)$_2$ − H]$^-$ have been obtained from the former reaction, whereas crystalline products of chemical formulae [Co(η^5-C_5H_5)$_2$]$^+$[(D,L-Hta)(D,L-H_2ta)]$^-$ and [Co(η^5-C_5H_5)$_2$]$^+$[L-Hta]$^-$ have been obtained by utilizing D,L-tartaric acid and L-tartaric acid and the cobaltocenium cation.

The structural prerequisites of the organic acidic species are the presence of strong donor/acceptor hydrogen bonding groups and a number of acceptor sites larger than the number of donor sites. The organometallic partners, on the other hand, must not possess strong hydrogen bonding donor/acceptor systems which may compete with the organic fragments, but rather a large number of acidic C_{sp}–H groups in the arene and cyclopentadienyl ligands. This is necessary to drive the acid selectively to self-assemble into large hydrogen bonded superanions which can then interact with the organometallic system *via* charge assisted C–H$^{\delta+}$ · · · O$^{\delta-}$ bonds. The importance of charge assistance in the reinforcement of weak hydrogen bonds such as C–H$^{\delta+}$ · · · O$^{\delta-}$, but also C–H$^{\delta+}$ · · · F$^{\delta-}$ (when fluorine is part of inorganic anions such as PF_6^- and BF_4^-) and C–H$^{\delta+}$ · · · $\pi^{\delta-}$ (when the π system of alkynes, alkenes and aromatic carbocycles belongs to organometallic anions), in organometallic crystal chemistry has been assessed and discussed.[12]

In this paper we have taken our strategy to the polycarboxylic acids benzene-1,3,5-tricarboxylic acid (trimesic acid, H_3tma) and O^2,O^3-dibenzoyl-L-tartaric acid (L-H_2bta) and investigated the preparation of new organo–organometallic solids by reaction of the acids with [Co(η^5-C_5H_5)$_2$]$^+$[OH]$^-$. The structure of the crystalline hydrated hydroxide [Co(η^5-C_5H_5)$_2$]$^+$[OH]$^-$·3H_2O is discussed.

Experimental

Crystal synthesis

As in the cases discussed in Parts 1 and 2, the synthetic aspect of this work is related to the synthesis and crystallization of solid materials. All reagents were commonly available organic and organometallic substances.

[Co(η^5-C_5H_5)$_2$]$^+$[(H_3tma)(H_2tma)]$^-$ 1, [Co(η^5-C_5H_5)$_2$]$^+$[Co(H_2O)$_6$]$^{2+}$[tma]$^{3-}$ 2, [Co(η^5-C_5H_5)$_2$]$^+$[L-Hbta]$^-$ 3 and [Co(η^5-C_5H_5)$_2$]$^+$[OH]$^-$·4H_2O 4. Brown powder of [Co(C_5H_5)$_2$] (100 mg, 0.53 mmol) was suspended in bidistilled water (20 cm^3) with stirring at room temperature. Oxygen was bubbled until a clear solution of bright yellow [Co(C_5H_5)$_2$]$^+$[OH]$^-$ (pH of the solution >10) was obtained. White powder of benzene-1,3,5-

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§ Organic-organometallic crystal synthesis. Part 3.

tricarboxylic acid (H_3tma) (56 mg, 0.26 mmol) was mixed with cobaltocenium hydroxide (5 cm^3, 0.13 mmol) to obtain in almost quantitative yield bright yellow crystals of complex **1** after evaporation of water at room temperature in the air. Among the yellow crystals, however, a few well shaped light orange crystals were also found. These were later identified as **2**.

Crystals of complex **3** were obtained in the same way as those of **1** by mixing a basic solution of $[Co(C_5H_5)_2]^+[OH]^-$ (5 cm^3, 0.13 mmol) with white powder of L-O^2,O^3-dibenzoyltartaric acid (L-H_2bta) (46.5 mg, 0.13 mmol) followed by evaporation of water at room temperature in the air. The reaction to produce **3** gave almost quantitative yield. Benzene-1,3,5-tricarboxylic acid, L-O^2,O^3-dibenzoyltartaric acid and cobaltocene were from Aldrich. Compound **4** was obtained by evaporation of the bright yellow solution resulting from prolonged stirring in the air of a suspension of brown powder of $[Co(C_5H_5)_2]$ (100 mg, 0.53 mmol) in bidistilled water (20 cm^3). Tetrahydrofuran was distilled from sodium–benzophenone and stored under argon.

Crystallography

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. The programs SHELXS 86[13a] and SHELXL 92[13b] were used for structure solution and refinement based on F^2; SCHAKAL 92[13c] was used for the graphical representation of the results. Common to all compounds: Mo-Kα radiation, $\lambda = 0.710\,69$ Å, graphite monochromator. All non-H atoms, except for the O atoms in **4**, were refined anisotropically. The positions of all hydrogen atoms in **1**, of the water hydrogens in **2**, and of the carboxylic hydrogen atoms in **3** have been observed in the Fourier maps. The remaining H atoms bound to C atoms were added in calculated positions in **2**, **3** and **4**. The computer program PLATON[13d] was used to analyze the geometry of the hydrogen bonding patterns. In order to evaluate C–H···O bonds the C–H distances were normalized to the neutron derived value of 1.08 Å. In **2** the C_5H_5 ligands were found to be disordered over two sites of occupancy ratio 1 : 1.

The water molecules and the OH groups in crystals of compound **4** are affected by disorder. There are five independent oxygen atoms in the hydrogen bond network. Two of these oxygens are disordered over two positions with equal occupancy related by a centre of inversion (O4) and a two-fold axis (O6), whereas O1, O2 and O3 are close to a crystallographic two-fold axis and form almost flat hexagons interconnected *via* atom O5 in general position. The very large thermal motion of the oxygen atoms perpendicular to the hexagon plane is a clear indication that the hexagonal six-water systems are puckered as usually observed in water clathrates and in the structure of ice and that the flat hexagon results as an average of the oxygen atoms displaced above and below the ring. As mentioned above, all attempts to obtain better behaving crystalline material have failed. Crystals of **4** are only formed at low temperature by slow evaporation and cooling of the solution. This procedure often results in an enamel-like material covering the surface of the container from which solid particles were obtained and used for measurement at low temperature.

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Results and Discussion

As described in Part 2 of this series,[1] the crystal synthesis is based on a direct acid–base reaction followed by self-assembly of the partially deprotonated organic acids into organic superanions which then host the organometallic cations in cavities or channels. Crystalline compounds **1**, **2** and **3** have been obtained in three steps: (i) oxidation of cobaltocene to the cobaltocenium cation and consequent formation of a basic solution as the final product of oxygen reduction in solution is the OH^- anion (see below), (ii) acid–base reaction between $[Co(C_5H_5)_2][OH]$ and the organic acid and (iii) precipitation of the crystalline aggregate. The preparation can be carried out in water or thf but, while in water the hydroxide $[Co(C_5H_5)_2][OH]$ can be prepared first and then treated with the organic acid, in thf the oxidation must occur in the presence of the organic acid. In both cases the oxidant is molecular oxygen and the oxidation is indicated by the bright yellow color of the solution due to the presence of cobaltocenium cation.

Though simple it may appear, the formation of the desired product depends not only on the difference in solubility in water or thf between the organic acid and the organic–organometallic aggregate, but also on the acid–base equilibria controlling first, second (and third in the case of trimesic acid) deprotonations of the polycarboxylic acid. The crystallization conditions are also different: while crystals from water are obtained by slow evaporation of the reaction mixture, crystallization from thf never gives crystalline products but only powder materials. It is necessary to solubilize the precipitates in water and allow recrystallization. The precipitation from thf is somewhat cleaner than that from water as unchanged cobaltocene may remain in solution.

Structural characterization

Relevant intramolecular and intermolecular bonding parameters are reported in Tables 2 and 3, respectively. For clarity the following conventional description of hydrogen bonding structural parameters has been adopted: X(H)···O (X = C, O) indicates the distance between a donor C or O atom and acceptor O atom, (X)H···O the distance between a donor hydrogen atom bound to X and acceptor, while X–H···O indicates the angle.

Crystalline $[Co(\eta^5\text{-}C_5H_5)_2]^+[(H_3tma)(H_2tma)]^-\cdot 2H_2O$ **1** represents the first example of an organometallic salt of trimesic acid. Trimesic acid[14a] is a kind of prototypical system in crystal engineering studies. Thanks to the highly symmetrical distribution of the three carboxylic groups, trimesic acid should, in principle, be able to form a very stable two-dimensional hydrogen bond network by in plane arrangement of molecules. This is not so, and the pure organic material forms pseudo-catenane structures by interpenetration of condensed six-molecule hydrogen bonded rings. One hydrated form of trimesic acid is also known.[14b] A few cocrystals have also been obtained.[15] Crystalline salts of trimesic acid as well as co-ordination compounds in which the carboxylic groups bind to metal atoms are also known.[16]

The salient structural features of crystalline compound **1** can be summarized as follows. (i) There are two units derived from trimesic acid forming a dimeric superanion of formula $[(H_3tma)(H_2tma)]^-$ from which only one acidic proton has been removed. The superanion is held together by a strong negative hydrogen bond between one CO_2H system of one formally neutral acid molecule and the deprotonated CO_2 unit from a formally anionic $[H_2tma]^-$ system [see A in Fig. 1(a)].

(ii) The $[H_3tma] + [H_2tma]^-$ description can only be formal and approximate as the 'inter-trimesic' hydrogen atom is shared between the two trimesic acid units, so that the organic repeating unit is more correctly described as formed by a deprotonated dimeric system of two trimesic acid moieties.

(iii) This basic unit is left with a grand total of four CO_2H groups to employ in hydrogen bonding systems with the surrounding anions; this is done with the intermediacy of two water molecules which appear to play a crucial role in the stabilization of the hydrogen bond network.

(iv) The water molecules bridge pairs of CO_2H units by forming 10-atom rings *via* insertion of one O_wH group within the carboxylic ring [B in Fig. 1(a)], while the other O_wH group of the same water molecules links the free oxygen atoms on the

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

	1	**2**	**3**	**4**
Formula	$C_{28}H_{25}CoO_{14}$	$C_{19}H_{25}Co_2O_{12}$	$C_{28}H_{23}CoO_8$	$C_{10}H_{19}CoO_5$
M	644.41	563.24	546.39	277.93
T/K	223(2)	223(3)	223(2)	253(2)
System	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_12_12_1$	$C2/c$
a/Å	7.874(4)	11.058(4)	10.522(10)	22.28(2)
b/Å	8.964(9)	19.393(8)	13.053(6)	8.805(9)
c/Å	10.967(9)	10.880(10)	17.58(1)	13.81(1)
α/°	97.92(8)			
β/°	107.44(6)	101.97(6)		101.55(9)
γ/°	110.84(7)			
U/Å^3	644(1)	2283(2)	2414(3)	2654(4)
Z	1	4	4	8
Minimum, maximum transmission	0.83, 1.00	0.74, 1.00	0.81, 1.00	0.77, 1.00
μ(Mo-Kα)/mm^{-1}	0.724	1.515	0.763	1.25
Measured reflections	2603	2121	1938	1837
Unique reflections	2450	1994	1917	1602
Unique reflections [$I > 2\sigma(I)$]	1726	807	1229	892
Goodness of fit on F^2	1.035	0.974	0.997	0.897
$R1$ [on F, $I > 2\sigma(I)$]	0.0341	0.0628	0.0440	0.1055
$wR2$ (on F^2, all data)	0.1362	0.1815	0.1344	0.3559

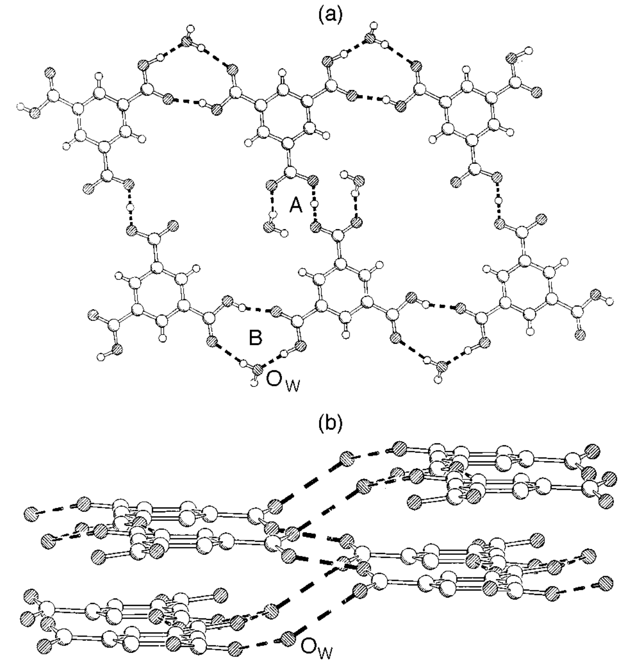

Fig. 1 (a) Ball and stick representation of the hydrogen bonding patterns in crystalline compound **1** showing the complex mixing of negatively charged hydrogen bonds between the two trimesic acid units (A) and the hydrogen bonds involving the water molecules forming 10-atom rings *via* insertion of one OH group within the carboxylic ring (B). (b) The water hydrogen bonds propagate the structure in the third dimension forming layers of trimesic acid anions (H atoms omitted for clarity)

deprotonated inter-trimesic CO_2–H–O_2C system. In such a way, although the ions and molecules depicted in Fig. 1(a) do actually lie almost coplanar, the water molecules propagate the structure in the third dimension by expanding to layers above and below the reference plane. This is easy to appreciate from Fig. 1(b). The benzene rings lie flat on the next layer at a graphitic distance of 3.30 Å. This arrangement recalls closely that observed in crystals of trimesic acid.

(v) Hydrogen bonding distances grouped in Table 3 are comparable to those formed by other negative $O_{CO_2H}\cdots O_{CO_2}$ and neutral $O_{CO_2H}\cdots O_{CO_2H}$ hydrogen bonds.[1,11]

(vi) The distribution of trimesic acid moieties and water molecules results in a large anionic organic superstructure which folds around the cobaltocenium cations as shown in Fig. 2(a). A view of the whole three-dimensional organic superanion is shown in Fig. 2(b). Note the honeycomb type structure with channels extending along the *a* axis, reminiscent of the superstructures obtained from D,L- and L-tartaric acid.[1]

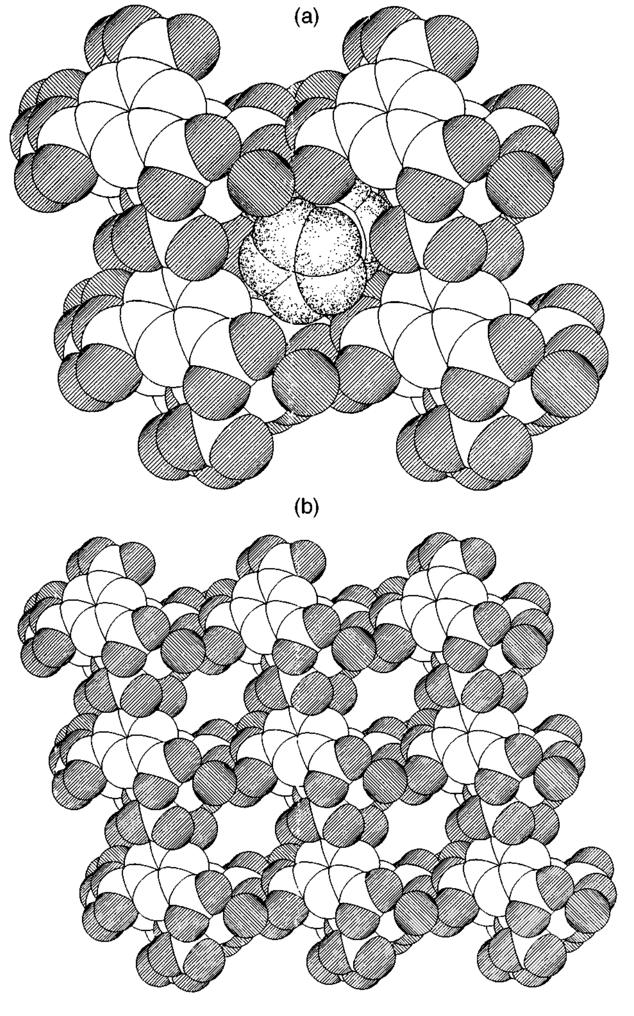

Fig. 2 (a) Space filling representation of the anionic organic superstructure folding around the cobaltocenium cation in crystalline compound **1**. (b) The honeycomb type anionic organic superstructure formed by trimesic acid and water molecules

Table 2 Relevant bonding distances (Å) for compounds **1**, **2** and **3**[a]

		2[b]				**4**[c]	
	1	**A**	**B**	**3**		**a**	**b**
Co–C	2.022(4)	2.03(2)	2.11(2)	2.010(7)	2.029(7)	2.029(11)	2.017(9)
	2.013(5)	2.04(2)	2.09(2)	2.017(8)	2.036(7)	2.020(11)	2.035(9)
	2.016(5)	2.03(2)	2.02(2)	2.020(7)	2.032(7)	2.004(11)	2.040(8)
	2.022(5)	2.02(2)	1.98(2)	2.022(7)	2.039(7)	2.004(11)	2.024(8)
	2.022(4)	2.02(2)	2.04(2)	2.024(7)	2.035(7)	2.019(12)	2.010(8)
mean	2.019_4	2.04_4		2.026_9		2.015_9	
Co–O		2.081(6)					
		2.063(6)					
		2.104(6)					
C–C in C_5H_5	1.396(7)	1.42[d]		1.42[d]		1.42[d]	
	1.409(6)						
	1.403(7)						
	1.402(7)						
	1.403(7)						
mean	1.403_4						
tma				bta			
mean C_{ring}–C_{ring}	1.390_4			mean C–C_{chain}	1.538_{23}		
mean C_{Ph}–C_{CO_2}	1.498_6	1.383_7		mean C–C_{Ph}	1.462_4		
mean C–O	1.298_{18}	1.509_{11}		mean C–O	1.272_1		
mean C=O	1.214_{11}	1.254_{11}[e]		mean C–$O_{benzoyl}$	1.349_{15}		
				mean C=O	1.201_{10}		

[a] Estimated standard deviations on the mean values are given as subscripts. [b] A and B are the two disordered images of the C_5H_5 ring (occupancy factor 0.5 for both images). [c] Two half independent cations in the asymmetric unit. [d] C_5H_5 rings defined as rigid groups. [e] The C–O and C=O groups are not distinguishable on the basis of bond distances.

Table 3 Relevant intermolecular hydrogen bonding parameters in crystalline compounds **1**, **2** and **3** (distances in Å, angles in °)

Interaction type	**1**	**2**		**3**	
$O\cdots(H)\cdots O^-$	2.448			2.415	
$O(H)\cdots O$	2.609				
$O\cdots O_w$	2.567	2.656	2.729		
	2.887	2.777	2.745		
	2.769	2.666	2.771		
$(C)H^{\delta+}\cdots O^{\delta-} < 2.6$	2.529	2.532[a]		2.299	2.556
	2.548	2.527[a]		2.343	2.496
	2.473	2.382[b]		2.484	2.487
				2.516	2.367
$C–H^{\delta+}\cdots O^{\delta-}$	140.32	143.50[a]		136.17	139.95
	141.66	145.60[a]		133.48	155.76
	127.91	150.58[b]		148.40	124.95
				129.34	163.60
$(C)H^{\delta+}\cdots O_w < 2.6$		2.397[a]			
		2.519[b]			
$C–H\cdots O_w$		152.90[a]			
		164.27[b]			

[a] Interaction involving ring A. [b] Interaction involving ring B.

The cobaltocenium cations are accommodated within the channels.

(vii) The interaction between the cobaltocenium cations and the organic framework is based on charge assisted $C–H^{\delta+}\cdots O^{\delta-}$ hydrogen bonds between the positively charged CH groups of the cations and the oxygen atom lone pairs left 'free' by the stronger hydrogen bonded network with carboxylic groups or water molecules (see Table 3).

Crystalline $[Co(\eta^5\text{-}C_5H_5)_2]^+[Co(H_2O)_6]^{2+}[tma]^{3-}$ **2** can only be obtained as a minor product accompanying the preparation of **1** in water. Its formation is very likely due to decomposition of the cobaltocene or of the cobaltocenium cation upon reaction with the acid. Although admittedly serendipitous, the formation and stability of such a crystalline aggregate indicate the possibility of forming even more complex crystals by cocrystallization of different ions. Strictly speaking, crystalline **2** is an example of organic–inorganic–organometallic co-crystallization. The most relevant structural features are as follows.

(i) The crystal is formed by hexaaquacobalt(II) cations $[Co(H_2O)_6]^{2+}$ which co-crystallize together with cobaltocenium cations and one fully deprotonated trimesic acid unit per formula, *e.g.* corresponding to the formula $[Co(\eta^5\text{-}C_5H_5)_2]^+$-$[Co(H_2O)_6]^{2+}[tma]^{3-}$. The aqua complex shows three independent Co–O distances of length 2.081(6), 2.063(6) and 2.104(6) Å.

(ii) To our knowledge this is the first example of a fully deprotonated trimesate $[tma]^{3-}$ anion; salts of this anion have not been observed before, all the other examples being derived from partially deprotonated acid molecules.[16]

(iii) Diffraction data were of sufficient quality to allow location of all water hydrogen atoms. The knowledge of these atomic positions permits a clear understanding of the hydrogen bonds linking the anions and cations, as well as the two types of cations.

(iv) Fig. 3 shows how the trimesate anions interact with the aqua complexes with each oxygen atom taking part in a bifurcated interaction with two water molecules co-ordinated to two cations.

(v) The $[Co(H_2O)_6]^{2+}$ cations are arranged in columns through the crystal architecture as shown in Fig. 4. Each $[Co(H_2O)_6]^{2+}$ column is completely surrounded by six columns formed by an A/B/A/B stacking of $[Co(\eta^5\text{-}C_5H_5)_2]^+$ cations intercalated between the benzene rings of the trimesic acid anions [see Fig. 5(a)]. The distance between the cyclopentadienyl planes and those of the C_6 rings ranges from 3.4 to 3.8 Å.

(vi) The $\{[Co(\eta^5\text{-}C_5H_5)_2]^+[tma]^{3-}\}_n$ columns are arranged so

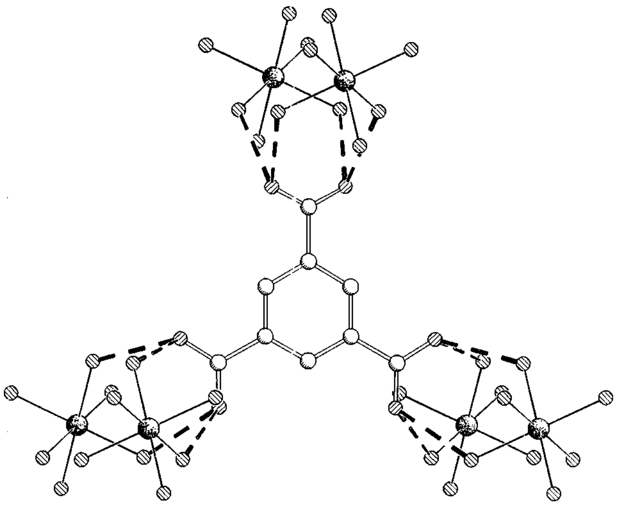

Fig. 3 The trimesate anions in crystalline $[Co(\eta^5\text{-}C_5H_5)_2]^+$-$[Co(H_2O)_6]^{2+}[tma]^{3-}$ **2** interact directly with the $[Co(H_2O)_6]^{2+}$ cations, each oxygen atom taking part in a bifurcated interaction

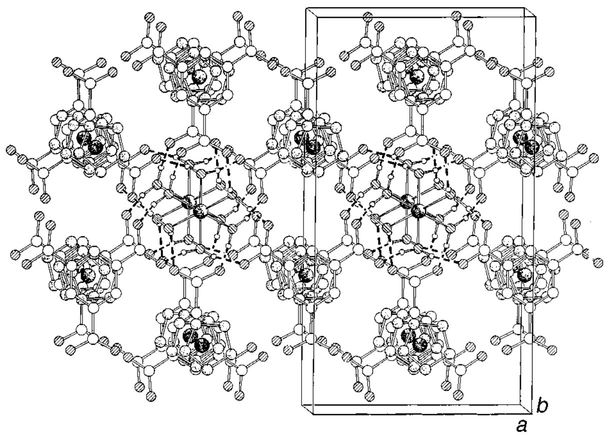

Fig. 4 The $[Co(H_2O)_6]^{2+}$ cations are arranged in columns through the crystal and completely surrounded by piles of alternating $[Co(\eta^5\text{-}C_5H_5)_2]^+$ and $[tma]^{3-}$ ions. Only H(water) atoms are shown for clarity

that each $[Co(\eta^5\text{-}C_5H_5)_2]^+$ cation of one column is effectively embraced by three trimesate anions of neighboring columns [see Fig. 5(b)].

(vii) The C–H $\cdots$ O hydrogen bonds are formed between the C–H groups of the cyclopentadienyl ligands and the water or trimesic acid moieties. The cyclopentadienyl ligands are disordered over two orientations of identical occupancy (see Experimental section). Both orientations allow C–H $\cdots$ O hydrogen bonds to be established in almost equal number and distribution of C–H $\cdots$ O lengths so that the orientation of the C_5H_5 ligand is indifferent for crystal cohesion.

The dibenzoyl-L-tartaric acid derivative **3** will now be discussed. Although the stoichiometry is much simpler than that of **1** and **2** and the crystal architecture less striking, **3** is somewhat more interesting because the crystal is chiral in space group $P2_12_12_1$ (see Experimental section). This was to be expected as the starting material is enantiomerically pure dibenzoyl-L-tartaric acid. No water of crystallization is present.

The use of enantiomerically pure chiral acids is at the basis of the development of our crystal engineering strategy. As mentioned in the introduction our scope is that of gaining control over the crystallization of chiral materials with the objective of introducing dipolar organometallic molecules (which, of course is not the case of the cobaltocenium cation!) for optoelectronic applications. However, crystallization of chiral objects in a non-centrosymmetric space group is generally more difficult than that of racemic mixtures or of non-chiral molecules. We

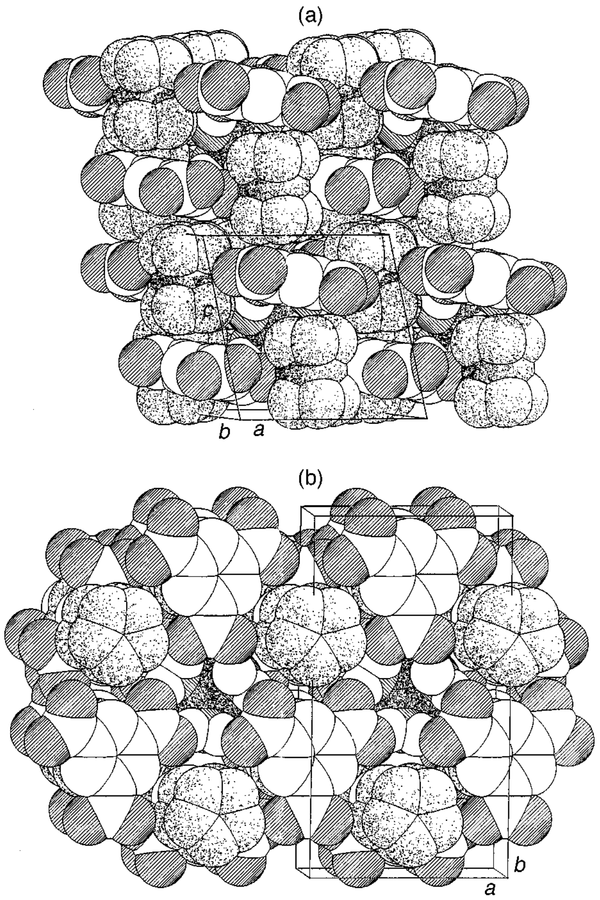

Fig. 5 (a) Each $[Co(H_2O)_6]^{2+}$ column in crystalline **2** is completely surrounded by six columns formed by an A/B/A/B stacking of $[Co(\eta^5\text{-}C_5H_5)_2]^+$ cations sandwiched between trimesic acid anions. (b) Each $[Co(\eta^5\text{-}C_5H_5)_2]^+$ cation of one $\{[Co(\eta^5\text{-}C_5H_5)_2]^+[tma]^{3-}\}_n$ column is embraced by three trimesate anions of neighboring columns

have previously succeeded only with L-tartaric and dibenzoyl-L-tartaric acids, but in this latter case only *via* the serendipitous isolation of an (extremely interesting though) undecahydrate crystalline material obtained from complete deprotonation of the L-H_2bta acid.[1]

The existence of compound **3** now demonstrates that it is possible to obtain a chiral crystal of L-H_2bta without water molecules. The important characteristics of **3** can be summarized as follows.

(i) The acid is deprotonated only once, *i.e.* one CO_2H group remains untouched whereas the second one forms the carboxylate system CO_2^- which becomes a strong hydrogen bond acceptor.

(ii) The L-Hbta anions are linked in chains through the crystal by CO_2–H–O_2C interactions [see Fig. 6(a)]. Contrary to **1**, the hydrogen atom position along this bond has not been observed and the hydrogen bond feature needs to be judged from the O $\cdots$ O distance which is 2.415 Å, *i.e.* towards the shortest values for negatively charged hydrogen bonds of this type (see Table 3).

(iii) The (L-Hbta$^-$)$_n$ anionic chains have no means to interlink *via* hydrogen bonds as the only available hydrogen atom is used along the chain. Small channels, generated along the *a* axis [see Fig. 6(b)], accommodate a *snake-like* arrangement of cobaltocenium cations [see Fig. 7(a)]. The resulting packing arrangement is shown in Fig. 7(b). Although the dibenzoyl-L-tartaric acid is very bulky compared with the cobaltocenium cation the flexibility of the tartaric acid skeleton allows folding about the cations and efficient packing.

(v) As observed in all previous cases, the interaction between the organometallic guest and the large organic host is based on charge assisted C–H$^{\delta+}$ $\cdots$ O$^{\delta-}$ interactions (there are eight

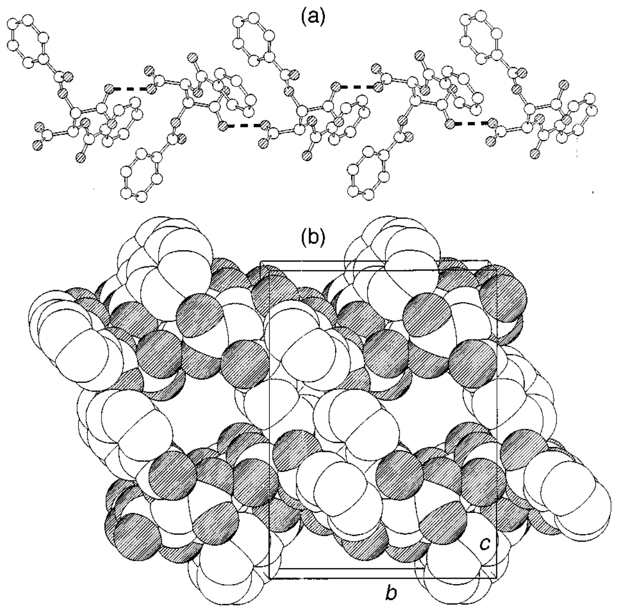

Fig. 6 (a) The L-$Hbta^-$ anions in crystalline compound **3** are linked in chains through the crystal by CO_2–H–O_2C interactions. (b) Space filling representation of the organic chains. Note that small channels are generated in which the cobaltocenium cations are accommodated. Hydrogen atoms are omitted for clarity

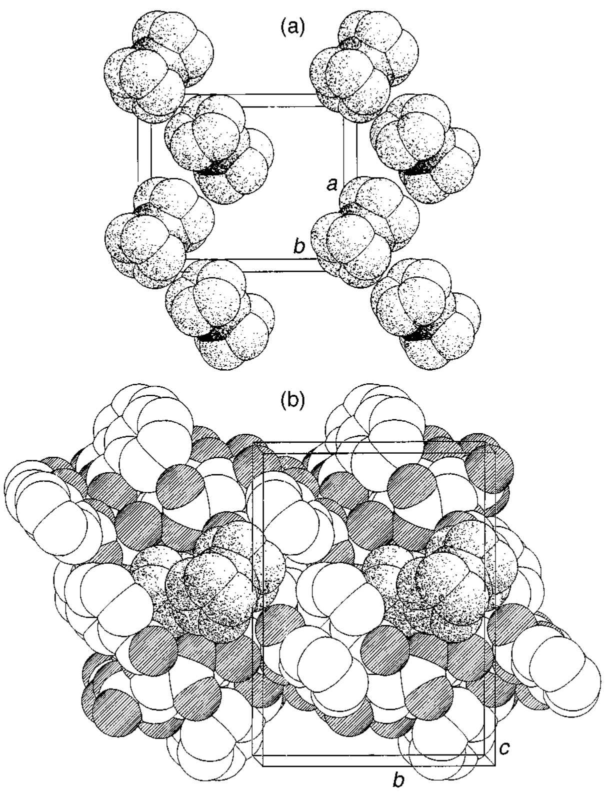

Fig. 7 (a) The snake-like arrangement of the cobaltocenium cations in crystalline compound **3**. (b) Space filling representation of the overall packing arrangement. Hydrogen atoms are omitted for clarity

H···O distances in the range 2.299–2.496 Å, three of which are shorter than 2.370 Å. The C–H···O distances involving phenyl hydrogens of the organic anions are in general longer.

It is worth recalling that, contrary to compound **3**, in the crystalline material $2[Co(\eta^5\text{-}C_5H_5)_2]^+[\text{L-bta}]^{2-}\cdot 11H_2O$[11] the acid was completely deprotonated, hence no hydrogen bonding donor group was available to cope with the presence of twelve potential hydrogen bonding acceptor sites. In that compound the eleven water molecules appear to play a twofold function: they fill space efficiently, but also, and more importantly, they provide a large number of O–H donor groups to stabilize the crystal structure. Based on this consideration it is interesting to consider the role of water in crystalline **2**, which, is the undecahydrate crystal,[11] contains only fully deprotonated anions derived from the organic acid and six water molecules, though co-ordinated to the cobalt(II) center. One may speculate that, though co-ordinated to the Co^{2+} cations, the water molecules play the same role of compensation towards a highly unbalanced hydrogen bonding donor/acceptor ratio.

Finally, the crystal structure of the hydrated hydroxide $[Co(\eta^5\text{-}C_5H_5)_2]^+[OH]^-\cdot 4H_2O$ **4** will be described. As mentioned in the Experimental section, this crystalline material is easy to prepare but crystals suitable for X-ray diffraction are very hard to get. It seems that the hydroxide solidifies with a variable number of water molecules at a temperature around 0 °C. While solid materials can, of course, always be obtained by decreasing the temperature, only in four distinct cases small fragments with some diffracting power could be rescued from the solid mass. In all four cases the number of observed reflections is far from desirable, and only in two cases the same unit cell could be attributed and the structure solved. Here we discuss the best results of such efforts, with the awareness that some reader (or referee) may object to the reporting of diffraction data of low quality. The crystalline hydroxide is however extremely interesting. It is worth stressing, that, after the bis(benzene)chromium species $[Cr(\eta^6\text{-}C_6H_6)_2]^+[OH]^-\cdot 3H_2O$,[11] crystalline **4** is only the second case of an organometallic sandwich complex hydroxide to be structurally characterized.

As in the case of the chromium complex, the $[OH]^-$ groups are indistinguishable from the water molecules. The $[OH]^-\cdot 4H_2O$ system forms a three-dimensional structure that closely resembles some of the structural types obtained with polycarboxylic acids [see Fig. 8(a)]. The oxygen atoms form zigzagged chains of disordered hexagonal rings (see Experimental section for a description of the disorder) interconnected *via* two oxygen atoms disordered over two positions (O4 and O6) and the one in general position (O5). This disordered arrangement is shown schematically in Fig. 8(b). A space filling representation of how the water/OH^- hydrogen bonded superstructure hosts the cobaltocenium cations is shown in Fig. 8(c).

Conclusion and Perspectives

With this study we have demonstrated that common polycarboxylic organic acids can be used to construct complex chiral and achiral organic superstructures by ‘forcing’ self-assembly of the organic moieties *via* strong hydrogen bonds between carboxylic or carboxylate groups. This can easily be achieved by partially deprotonating the organic acid with a base whose conjugate acid is unable to interact directly with the carboxylate groups, as would otherwise be the case if an alkali or an alkaline earth metal had been used. The organometallic cations obtained from $[Cr(\eta^6\text{-}C_6H_6)_2]$ and from $[Co(\eta^5\text{-}C_5H_5)_2]$ are well suited for this purpose; the latter has been used in Part 2 and in this work. The oxidation of both sandwich complexes is spontaneous in the presence of oxygen in water, tetrahydrofuran or nitromethane solutions and leads to the simultaneous formation of the hydroxide anion to deprotonate the acid and of the cations for crystallization of the organic–organometallic aggregate.

The deprotonation generates negatively charged $O_{CO_2H}\cdots O_{CO_2^-}$ hydrogen bonds that constitute a robust backbone for the three-dimensional aggregation of the organic fragments. Negatively charged bonds are amongst the strongest hydrogen bonds and have been shown to possess dissociation energies in the range 60–120 kJ mol^{-1},[17] hence they are very well suited for the construction of robust hydrogen bonded frameworks. The O···O distances involving the negatively charge assisted hydrogen bond present in crystalline **1** and **3** are comparable to

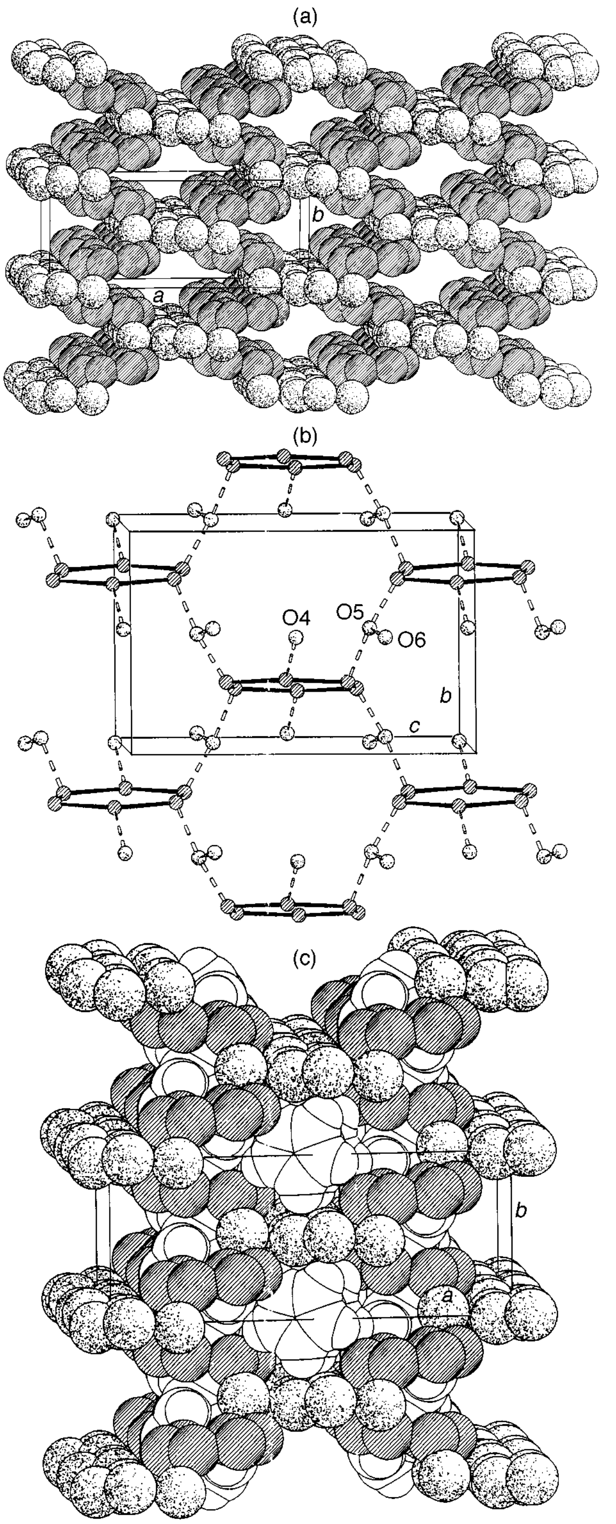

Fig. 8 (a) Space filling arrangement of the water molecules in crystalline compound **4**. (b) Schematic representation of the disordered hexagons of water molecules. (c) Space filling representation of the overall packing in the hydroxide $[Co(\eta^5\text{-}C_5H_5)_2]^+[OH]^-\cdot 4H_2O$

the values observed in the cyclohexanedione derivatives of $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ and in the derivatives of tartaric acid reported in Parts 1 and 2.

The second design criterion is based on the possibility of taking advantage of the abundance of weakly polarized C–H groups present on the cyclopentadienyl ligands. These ligands have been shown to be able to participate in weak hydrogen bonds of the C–H···O type when suitable acceptors are present in the crystals.[18] These interactions are strengthened when the acceptor atom belongs to an anionic system and the ligand belongs to a cationic complex. The 'charge assistance' is reflected in an appreciable decrease of the C–H···O distances with respect to the values commonly observed with neutral species.

Similar approaches have been developed in the organic crystal engineering field. For example, L-malic acid and substituted benzylamines have been employed by Aakeroy and Nieuwenhuyzen[19] to prepare ionic materials *via* hydrogen bonding interactions of the O–H···O type between the deprotonated acid and of the N–H···O type between anions and cations. The strategy adopted by Hosseini *et al.*[20] to build one-, two- and three-dimensional networks in mixed organic crystals is also based on the interaction between acids and bases. In both cases, however, the building blocks are chosen so that there is preferential hydrogen bond formation between anions and cations rather than forced self-assembly of the organic part. The use of electrostatic interactions to template and sustain crystalline aggregates with predefined arrangements of the ionic components has also been exploited by Ward and co-workers[21] to prepare crystalline materials for charge transfer applications and caged structures in which molecules could be trapped.

Trimesic acid appears to be a versatile building block in organic–organometallic crystal engineering. Species **1** and **2** demonstrate that it is possible to achieve a progressive deprotonation of the acid, which, in turn, allows one to vary the number of acceptor sites on the organic moiety and the interaction with other hydrogen bond donors. The structure of **3** demonstrates that the use of enantiomerically pure derivatives of L-tartaric acid is a viable and easy route to chiral crystals.

Work is in progress to isolate and characterize other crystalline aggregates based on the utilization of chiral acids including natural amino acids, and of other organometallic molecules and ions. We will also investigate the possibility of using organometallic acids as hydrogen bond 'carriers' to be employed with organic bases.

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