Phthalic acid, a versatile building block in organic-organometallic crystal engineering†

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Received (in Montpellier, France) 17th August 1998, Accepted 2nd November 1998

Phthalic acid [C_6H_4-1,2-$(COOH)_2$, H_2PA] and terephthalic acid [C_6H_4-1,4-$(COOH)_2$, H_2TPA] have been reacted with aqueous solutions of the hydroxides $[(\eta^5\text{-}C_5H_5)_2Co]^+[OH]^-$ and $[(\eta^6\text{-}C_6H_6)_2Cr]^+[OH]^-$ produced *in situ* by oxidation of the parent neutral molecules. The acid–base reaction leads to self-assembly of the deprotonated acid anions into honeycomb superstructures held together by hydrogen-bonding interactions of the O—H···O and charged O—H···O^- types. The superanions accommodate the $[(\eta^5\text{-}C_5H_5)_2Co]^+$ and the paramagnetic $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ organometallic cations *via* charge-assisted C—$H^{\delta+}$···$O^{\delta-}$ hydrogen bonds. Four novel organic–organometallic cocrystals, namely $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_4\{[HPA]^-\}_2[PA]^{2-}\cdot 4H_2O$ (**1**), $[(\eta^6\text{-}C_6H_6)_2Cr]^+[HPA]^-[H_2PA]$ (**2**), $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[TPA]^{2-}\cdot 6H_2O$ (**3**) and $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+\}_2[TPA]^{2-}\cdot 6H_2O$ (**4**) have been isolated and structurally characterized by low-temperature X-ray diffraction measurements. It is shown that phthalic acid is a very versatile building block in the formation of hydrogen-bonded networks and unprecedented superanionic architectures. The role played by water molecules in the stabilization of the crystal structures in the absence of all or almost all acidic protons is discussed.

Organometallic crystal engineering is an attractive field of research;[1] early attempts to make crystals based on organometallic components have been mainly directed towards obtaining charge transfer and magnetic systems.[2] Much of the current interest stems from the potential inherent to the utilization of crystal construction strategies developed in the neighboring 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 to the crystals. This objective can be achieved, for example, by controlling the non-covalent interactions established between the ligands, which are most commonly organic in nature, or by using the organometallic moieties to template aggregation of organic components. The intelligent utilization of non-covalent interactions to obtain aggregates that function differently from the separate components is the paradigm of supramolecular chemistry.[4] Hence, crystal engineering, and organometallic crystal engineering of course, may be regarded as being at the crossing point of supramolecular and materials chemistry. A distinction should be made, however, between the engineering of molecular crystals and that of coordination networks or of covalent solids.[5] The distinction is, in essence, in the energetic scale of the interactions: while molecular crystal engineering implies the utilization of intermolecular bonds with energies of the order of a few tens of kJ mol^{-1}, coordination polymers and covalent solids are constructed on the energetic scale of dative ligand-to-metal coordinative bonds and covalent bonds, that is of the order of several hundreds of kJ mol^{-1}.

The principal non-covalent interaction in molecular crystal engineering is the hydrogen bond.[6] The strength and directionality of this three-center four-electron interaction can be tuned by varying the nature of the acceptors and donors and/or the polarity of the groups involved. 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. Negatively charged O—H···O^- bonds have been shown to possess dissociation energies in the range 60–120 kJ mol^{-1}.[6g,h] These interactions are sufficiently strong to control recognition and self-assembly of carboxylic acid/carboxylate anions in robust three-dimensional superstructures. Furthermore, the utilization of polycarboxylic acids permits the simultaneous use of neutral O—H···O and negatively charged O—H···O^- bonding interactions in the construction of complex organic superstructures as shown in the case of D-, L- and L-tartaric acid,[7a] and of trimesic acid.[7b] The same strategy has been successfully applied also to the synthesis of mixed-metal and mixed-valence organometallic crystals from organometallic acids[7c] and to the preparation of charge-transfer salts based on the utilization of squaric acid.[7d] A similar approach has been adopted in the organic crystal engineering field to prepare ionic materials by using L-malic acid and substituted benzylamines[8a,b] and host–guest clathrates based on guanidinium and organosulfonate ions.[8c,d]

In this paper we report the synthesis and structural characterization of four novel organic–organometallic crystalline materials, namely $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_4\{[HPA]^-\}_2$-$[PA]^{2-}\cdot 4H_2O$ (**1**), $[(\eta^6\text{-}C_6H_6)_2Cr]^+[HPA]^-[H_2PA]$ (**2**), $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[TPA]^{2-}\cdot 6H_2O$ (**3**) and $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+\}_2[TPA]^{2-}\cdot 6H_2O$ (**4**). Crystalline **1**–**4** are obtained by reacting the organometallic hydroxides $[(\eta^6\text{-}C_6H_6)Cr][OH]$ and $[(\eta^5\text{-}C_5H_5)_2Co][OH]$,[7b] produced by *in situ* oxidation of the neutral complexes $[(\eta^6\text{-}C_6H_6)Cr]$ and $[(\eta^5\text{-}C_5H_5)_2Co]$ in water or THF, with *ortho*-phthalic acid (H_2PA) (**1** and **2**) or terephthalic acid (H_2TPA) (**3** and **4**). The

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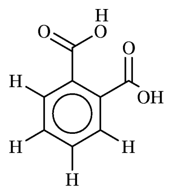
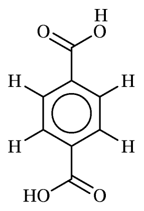
† Part 5 of the series 'Organic–organometallic crystal synthesis'. For part 4 see ref. 7*c*.



H_2PA



H_2TPA

organometallic cations produced by the redox process are very stable so that the arene and cyclopentadienyl ligands cannot be displaced and metal coordination by the carboxylate groups is not possible (but see Experimental). Details of the redox processes and of the effect of the solvent choice have been discussed in previous papers of this series.[7]

It is useful to stress that this seemingly simple reaction *has been devised* to take advantage of the complementary roles of weak and strong hydrogen bonds. The abundance, in organometallic species, of cyclopentadienyl and arene ligands carrying a large number of polarized C—H systems makes C—H···O hydrogen bonding very important in organometallic crystals.[9] As in the case of O—H···O bonds, C—H···O bonds can be reinforced by "adding" polarization to the system, which can be easily achieved if the C—H donors belong to cations and the available acceptor sites belong to anions.[10] In the cases discussed here C—H···O bonds are formed between the organometallic cations and the O atoms belonging to —COOH, —COO$^-$ and to water molecules. Such weak, but charge-assisted and numerous, hydrogen bonds provide a web of interactions that are used to mold the anionic organic frameworks around the organometallic cations.[11] One of the rules of thumb of hydrogen-bond-based crystal engineering is that strong acceptor sites preferentially accept hydrogen bonds from strong donors, leaving all unused lone pairs to the weak donors as a second choice. In this respect, one should note that water molecules may be brought into the crystal if the reaction, or the subsequent crystallization, is carried out in water. When complete deprotonation occurs, water molecules may "compensate the loss" of carboxylic hydrogens, providing alternative strong donors to guarantee crystal cohesion.[7b] In this context, the surprising topological analogy between the crystal structures of **4** and that of the hydrated hydroxide $[(\eta^5\text{-}C_5H_5)_2Co]^+[OH]^- \cdot 4H_2O$[7b] previously determined, will also be discussed.

Experimental

Crystal synthesis

As in the cases discussed in Part 4 and preceding papers,[7] the synthetic aspect of this work is related to the synthesis and crystallization of solid materials. It should be stressed that all usual spectroscopical tools for the characterization of chemical products in solution cannot be used in the context of a crystal synthesis. The products of the synthesis exist only in the condensed phase for which diffraction techniques are essential.

Cobaltocene, and phthalic and terephthalic acid were purchased from Aldrich, bis(benzene)chromium from Strem.

Preparation of the hydroxides $[(C_5H_5)_2Co]^+[OH]^-$ and $[(C_6H_6)_2Cr]^+[OH]^-$. The brown powder of $(C_5H_5)_2Co$ or $(C_6H_6)_2Cr$ (100 mg, 0.53 or 0.48 mmol) was suspended in 20 ml of bidistilled water under stirring at room temperature. Oxygen was bubbled until a clear solution of bright yellow $[(C_5H_5)_2Co]^+[OH]^-$ or $[(C_6H_6)_2Cr]^+[OH]^-$ (pH of the solution >10) was obtained.

Synthesis of crystalline $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_4\{[HPA]^-\}_2[PA]^{2-}\cdot 4H_2O$ (1), $[(\eta^6\text{-}C_6H_6)_2Cr]^+[HPA]^-[H_2PA]$ (2), $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[TPA]^{2-}\cdot 6H_2O$ (3) and $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+\}_2[TPA]^{2-}\cdot 6H_2O$ (4). Acid-to-hydroxide stoichiometric ratios of 1 : 1 and 2 : 1 were used for the reaction of H_2PA and H_2TPA with cobaltocenium and bis(benzene) chromium hydroxides. The white powder of phthalic and terephthalic acid (21.6 mg, 13 mmol and 43.2 mg, 26 mmol for the stoichiometric ratios 1 : 1 and 1 : 2, respectively) was added to 5 ml (0.13 and 0.12 mmol for the cobalt and the chromium hydroxides, respectively) of the hydroxide solution. Powders of **1–4**, were obtained by evaporation of the filtered aqueous solution. The powders were then dissolved in CH_3NO_2 and crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature on a watch glass. Yields were almost quantitative. When bis(benzene)chromium hydroxide was used the formation of undesired green material, probably resulting from overoxidation of chromium, was

Table 1 Crystal data and details of measurements for **1–4**[a]

	1	2	3	4
Formula	$C_{64}H_{62}Co_4O_{16}$	$C_{28}H_{23}CrO_8$	$C_{28}H_{36}Co_2O_{10}$	$C_{32}H_{40}Cr_2O_{10}$
Mol wt	1261.72	539.46	650.43	688.64
T/K	213(2)	223(2)	223(2)	223(2)
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	*Pbcn*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
a/Å	28.534(8)	7.952(2)	8.937(6)	25.066(4)
b/Å	15.244(8)	11.592(3)	14.084(8)	9.615(3)
c/Å	12.982(8)	13.970(10)	23.760(10)	13.945(8)
α/°	90	67.77(4)	99.27(4)	90
β/°	90	88.13(4)	100.71(5)	112.69(3)
γ/°	90	84.30(2)	90.21(5)	90
U/Å^3	5647(5)	1186(1)	2898(3)	3101(2)
Z	4	2	4	4
F(000)	2728	558	1352	1440
Min. and max. transmission	0.76–1.00	0.85–1.00	0.80–1.00	0.84–1.00
μ(MoKα) mm^{-1}	1.228	0.536	1.198	0.758
Measd reflect	7178	5195	10089	4106
Unique reflect	4939	4834	9822	3773
Unique reflect [$I > 2\sigma(I)$]	2698	2483	7019	1623
Refined parameters	313	407	667	186
GOF on F^2	0.988	0.957	0.864	0.964
R_1 [on F, $I > 2\sigma(I)$]	0.0844	0.0404	0.0557	0.0513
wR_2 (on F^2, all data)	0.2938	0.1340	0.1755	0.1818

[a] Common to all compounds: MoKα radiation, $\lambda = 0.71069$ Å, graphite monochromator.

sometimes observed. In these cases, the preparation was repeated. The correspondence between the structure of the bulk material and that of the crystalline materials subjected to single crystal diffraction experiments (see below) has been checked by measuring powder spectra and by comparing the spectra with those calculated on the basis of the single crystal structures.

Crystal structure characterization

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. SHELX86[12a] and SHELXL92[12b] were used for structure solution and refinement based on F^2. Fractional atomic coordinates and anisotropic displacement parameters are available as Supporting Information. SCHAKAL97[12c] was used for the graphical representation of the results. All non-H atoms, except for the disordered C_{Cp} and the O_{water} atoms in **1**, were refined anisotropically. The positions of the H_{COOH} hydrogen atoms in **1** and **2** and of 13 water hydrogens in **3** have been observed in the Fourier maps. The remaining H atoms bound to C atoms were added in calculated positions in all compounds. The computer program PLATON[12d] 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. Diffraction data have all been measured at 223 K. The Cp ligands bound to Co(2) in **1** and one of the Cp rings bound to Co(3) in **3** have been found to be disordered over two sites with occupancy factors of 0.70 : 0.30, 0.50 : 0.50 and 0.50 : 0.50 for the three rings, respectively. One of the water molecules [O(9)] in **1** is also affected by disorder, and has been refined over two distinct positions with occupancy factors of 0.60 and 0.40. CCDC reference number 440/080. See http://www.rsc.org/suppdata/njc/1999/17/for crystallographic data in .cif format.

Results and discussion

Since the focus of this paper is on the supramolecular features of the four crystalline materials, details of the structures of the ions will not be described. Table 2 collects some important average structural parameters, whereas Table 3 collects all relevant hydrogen bonding parameters. O—H···O and $O—H···O^-$ hydrogen-bonding distances are comparable to those formed by other polycarboxylic acidates discussed previously,[7] with the notable exception of the intramolecular O···O separation in one of the phthalates in crystalline **2**, which is affected by disorder (see below). The effect of charge is notable on all interactions. Water—water hydrogen bonds are, in general, longer than water—carboxylate bonds. The $C—H^{\delta+}···O^{\delta-}$ hydrogen bond interactions between the cations and the organic framework and between the cations and the water molecules follow the same general trend: the former are shorter, on average, than the latter distances. C—H···O distances are also shorter when the completely deprotonated dianions in **1**, **3**, and **4**, are involved.

The crystalline edifice of $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_4\{[HPA]^-\}_2[PA]^{2-}\cdot 4H_2O$ (1)

The species is obtained when cobaltocenium hydroxide and H_2PA are reacted in a 1 : 1 stoichiometric ratio. The crystal architecture is remarkable: the hydrated organic superstructure recalls a brick wall, with large rectangular channels extending along the *c* axis [see Fig. 1(*a*)]. The channels are occupied by pairs of columns of $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations [see Fig. 1(*b*)]. The "small" and "large" walls of the rectangular channels have different chemical compositions. The *bc*

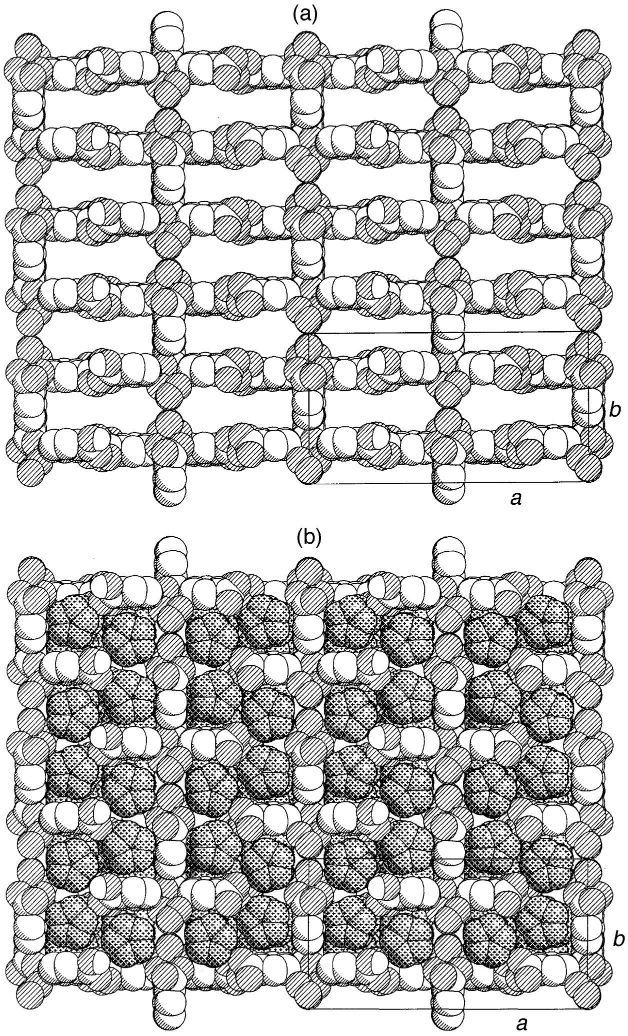


Fig. 1 (a) Space-filling representation of the brick-wall type anionic organic superstructure present in crystalline **1**. (*b*) The cations are arranged in pairs of columns along the *c* axis. H atoms are omitted for clarity. Line-shaded spheres are the oxygen atoms.

Table 2 Relevant average intramolecular bonding parameters (in Å) for **1**–**3**

	1	**2**	**3**	**4**
Mean M—C (M = Cr, Co)	2.033_{20}	2.134_9	2.028_{19}	2.131_7
Mean $C_{Cp}—C_{Cp}/C_{Bz}—C_{Bz}$	1.42^b	1.396_7	1.42^b	1.39^b
Mean $C_{ring}—C_{ring}$	1.39_1	1.38_1	1.39^b	1.39^b
Mean $C_{ring}—C_{COO}$	1.499_4	1.50_1	1.514_3	1.526(6)
Mean C—O	1.291_6	1.29_2	—	—
Mean C—O	1.205_6	1.21_1	—	—
Mean C$\overset{\cdot\cdot}{-}$O (dianion)[c]	1.24_1	—	1.250_{10}	1.247_{11}

[a] e.s.d.s on the mean values are given as subscripts. [b] Cp, Bz or phthalate rings refined as rigid groups. [c] C—O and C═O groups are not distinguishable on the basis of bond distances.

Table 3 Relevant intermolecular hydrogen-bonding parameters in crystalline **1**–**4** (distances in Å, angles in degrees)

Interaction type	**1**	**2**	**3**	**4**
$O_{COOH}\cdots O_{COO^-}$	—	2.605, 2.652	—	—
$O_{COOH^-}\cdots O_{COO^-}$	2.493	2.356 (intra)[a]	—	—
$O_{COO^-}\cdots O_W$	2.753, 2.591	—	2.774, 2.763 2.828, 2.831 2.778, 2.743 2.745, 2.770 2.728, 2.736 2.830, 2.817 2.767, 2.772	2.741, 2.744 2.738
$O_W\cdots O_W$	2.876, 2.762	—	2.839, 2.788 2.773, 2.737 2.770, 2.745 2.792	2.767, 2.739 2.764
$(C)H^{\delta+}\cdots O < 2.6$	—	2.354, 2.207	—	—
$C—H^{\delta+}\cdots O$	—	172.54, 158.28	—	—
$(C)H^{\delta+}\cdots O^{\delta-} < 2.6$	dianion 2.308, 2.099 2.141, 2.451 monoanion 2.325, 2.229 2.437, 2.129 2.559	monoanion 2.351, 2.446 2.486, 2.573 2.498, 2.504	dianion 2.579, 2.563 2.225, 2.229 2.365, 2.381 2.362, 2.383	dianion 2.384, 2.442
$C—H^{\delta+}\cdots O^{\delta-}$	dianion 163.89, 173.30 155.96, 177.79 monoanion 158.22, 171.80 111.79, 145.49 113.39	dianion 165.83, 132.26 124.05, 119.65 125.65, 124.24	dianion 137.80, 138.87 165.14, 164.56 139.86, 139.97 139.90, 139.4	dianion 156.31, 133.17
$(C)H^{\delta+}\cdots O_W < 2.6$	2.576, 2.589	—	2.158, 2.173 2.163, 2.156 2.509, 2.437 2.453, 2.251 2,300, 2.293 2.275, 2.368 2.535	2.402
$C—H^{\delta+}\cdots O_W$	133.62, 130.89	—	169.95, 167.46 169.08, 167.46 141.60, 136.20 168.30, 167.86 162.06, 161.61 167.94, 148.58 154.50	164.24

[a] See text for a discussion of the disorder affecting the atoms involved in this bond.

planes are formed by fully deprotonated PA^{2-} dianions interlinked by O—H···O hydrogen bonds [see Fig. 2(*a*)] involving the water molecules as donors, whereas the *ac* planes are formed by mono-deprotonated HPA^- anions linked by negatively charged $O—H\cdots O^-$ hydrogen-bonding interactions [see Fig. 2(*b*)]. Although the acceptor oxygen atoms belong exclusively to the anions, it is worth noting that the $O—H\cdots O_W$ bonds are appreciably longer than the $O—H\cdots O^-$ ones but shorter than in ice (see Table 2).[13]

In summary, **1** contains two well distinct building blocks, resulting from complete and partial deprotonation of H_2PA that play different structural roles in the construction of the crystal edifice. The two hydrogen bond arrangements in **1** represent two "options" for phthalic acid. A third one will be seen in the structure of **2**.

The crystalline edifice of $[(\eta^6\text{-}C_6H_6)_2Cr]^+[HPA]^-[H_2PA]$ (2)

When bis(benzene) chromium is employed, a different arrangement of the acceptor and donor groups derived from H_2PA is observed. The crystal of **2** contains chains formed by an alternation of mono-deprotonated anions and of neutral H_2PA acid molecules (see Fig. 3). Interestingly, the —OH group of the HPA^- anion is used in intramolecular hydrogen bonding, so that the two outer oxygen atoms of the monoanion can accept hydrogen bond donation on both sides by two molecules of neutral H_2PA. Neutral molecules and monoanions form chevron-type patterns that "embrace" pairs of bis(benzene) chromium cations as shown in Fig. 4(*a*). We have found an interesting structural analogy between this packing motif and the arrangement observed previously in the case of the derivatives obtained from cyclohexane-1,3-dione $[(\eta^6\text{-}C_6H_6)_2Cr]^+(CHD)_2^-\cdot(CHD)_2$[1a] [compare Fig. 4(*a*) and (*b*)]. As in the case of **1** there are several short charge-assisted $C—H^{\delta+}\cdots O^{\delta-}$ interactions between the benzene ligands and the O atoms (see Table 3). The overall packing arrangement in **2** is shown in Fig. 5.

There is a crystallographic detail that needs some attention. Judging from the data in Table 2, the intramolecular O···O distance of 2.356(2) Å in the mono-deprotonated anion HPA^- may be regarded as very short, even shorter than in the case of lithium hydrogen phthalate (2.40 Å), which has been subjected to a neutron diffraction study.[14] Fig. 6 shows the orientation of the anisotropic displacement parameters (adps) for the monoanion. It is apparent that the O atoms of the two carboxylic groups possess an extensive additional motion, roughly perpendicular to the ring plane, which is indicative of some degree of orientational disorder. A reasonable model for

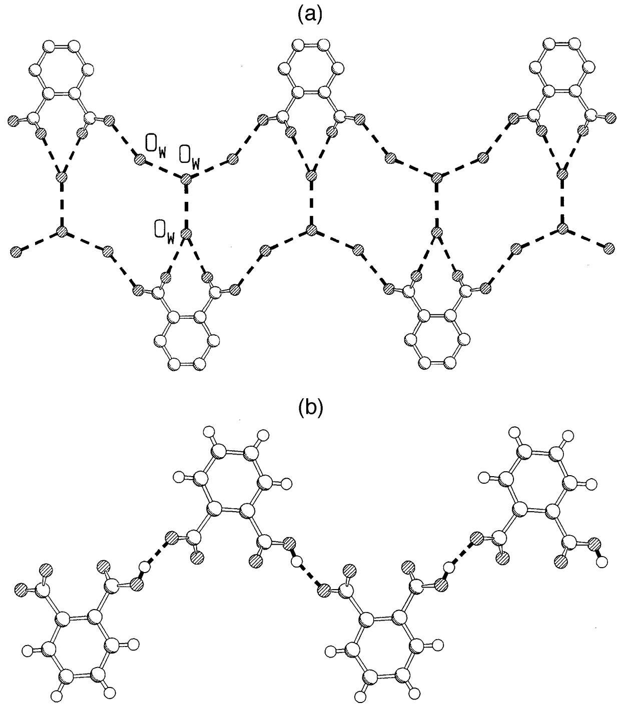


Fig. 2 (*a*) The *bc* planes in crystalline **1** are formed by fully deprotonated PA^{2-} dianions interlinked by O—H···O hydrogen bonds involving the water molecules as donors. (*b*) The *ac* planes are formed by mono-deprotonated HPA^- anions linked by negatively charged $O—H\cdots O^-$ hydrogen-bonding interactions.

the disorder implies that the two —COO groups are displaced alternatively above and below the plane of the ring with the H atom (located from the Fourier map) almost in the center of the system. An intramolecular O···O separation of 2.4 Å, in agreement with the neutron data, can be easily accommodated by oxygen atoms occupying two alternate sites along the adps. Unfortunately the positions of the O atoms of the same —COO groups are too close to be treated separately in the refinement so that the disorder results in the large anisotropic displacement shown in Fig. 6.

In summary, there are as many as four different structural arrangements of phthalic acid or its deprotonation products. **1** contains one fully deprotonated PA^{2-} unit that accepts hydrogen-bond formation from water molecules, and one mono-deprotonated HPA^- unit that forms chains *via* $O—H\cdots O^-$ hydrogen-bonding interactions. **2** contains one neutral H_2PA molecule acting as a bridge between mono-deprotonated HPA^- units. These monoanions, however, differ from those in **1** because of the presence of an intramolecular O—H···O hydrogen bond. In this way the HPA^- unit in **2** is more likely the fully deprotonated unit in **1** since it may accept twin donation of O—H···O bonds from neutral H_2PA as it does in **1** with respect to water. There is an additional difference, though. The intramolecular bond makes possible an "all-flat" geometry for the monoanion, whereas the two $—COO^-$ groups in **1** repel each other and generate a twist geometry.

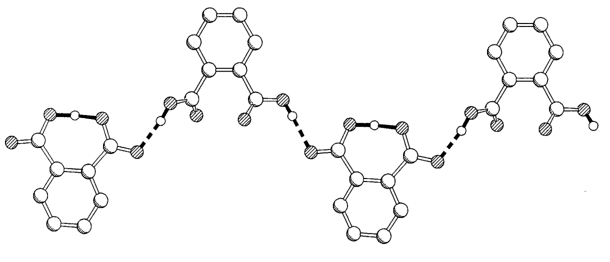


Fig. 3 Chains formed by an alternation of mono-deprotonated anions and of neutral H_2PA molecules in crystalline **2**. Note how the —OH group of the HPA^- anion is used in intramolecular hydrogen bonding, so that the two outer oxygen atoms of the monoanion can accept hydrogen bond donation on both sides by two molecules of neutral H_2PA. H atoms were observed from the Fourier maps (see Experimental).

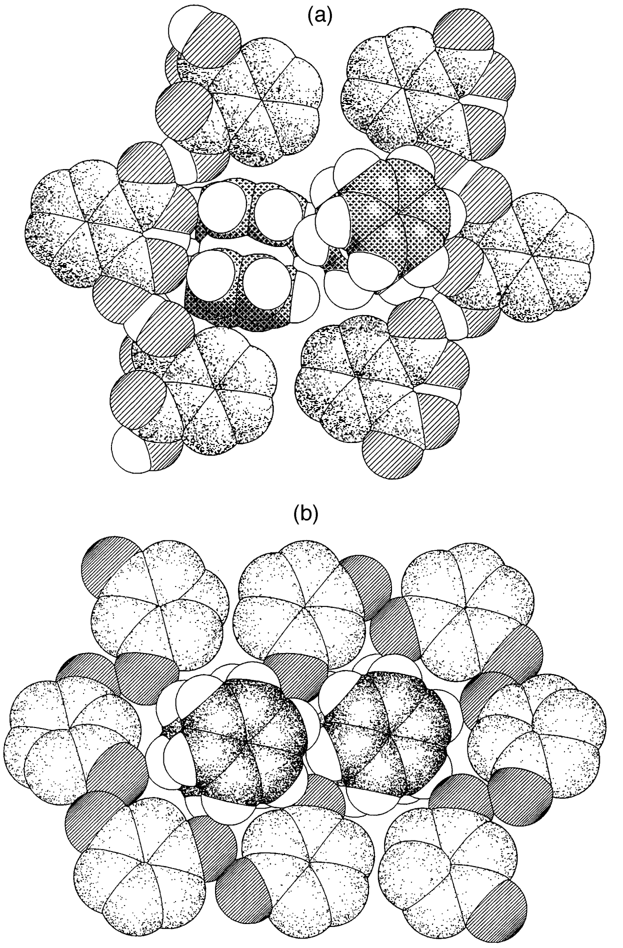


Fig. 4 Comparison between the "cation embrace" in (*a*) crystalline **2** and in (*b*) derivatives obtained from cyclohexane-1,3-dione $[(\eta^6\text{-}C_6H_6)_2Cr]^+(CHD)_2^-\cdot(CHD)_2$. Note how, in both cases, a pair of bis(benzene)chromium cations are embraced by the superanions. Available O atom lone pairs are directed towards the benzene ligands to optimize C—H···O interactions.

The crystalline edifice of $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[TPA]^{2-}\cdot 6H_2O$ (3)

Though chemically similar, phthalic and terephthalic acid differ substantially in topology. The position of the two —COOH groups on opposite sides of the benzene moiety, beside making impossible the intramolecular utilization of hydrogen bond donor and acceptor sites, renders the terephthalate building block longer than wider with respect to the phthalate unit. This difference in shape is well-reflected in the packing patterns in which the TPA^{2-} unit can take part.

As in the cases of **1** and **2** discussed above, when terephthalic acid is used with the cobaltocenium and bis(benzene)-chromium hydroxides, two different crystalline products are obtained.

Crystalline **3** is constituted of TPA^{2-} anions, resulting from complete deprotonation of the H_2TPA acid, joined by hydrogen bonds with the six water molecules of the unit formula. The water-bridged TPA^{2-} system forms a fascinating anion superstructure [see Fig. 7(*a*)] that can be described as constituted of large, almost rectangular, channels delimited on the left and right sides (with respect to the orientation in Fig. 7) by water molecules only and above and below (floor and ceiling) by the terephthalate anions. The large-channeled

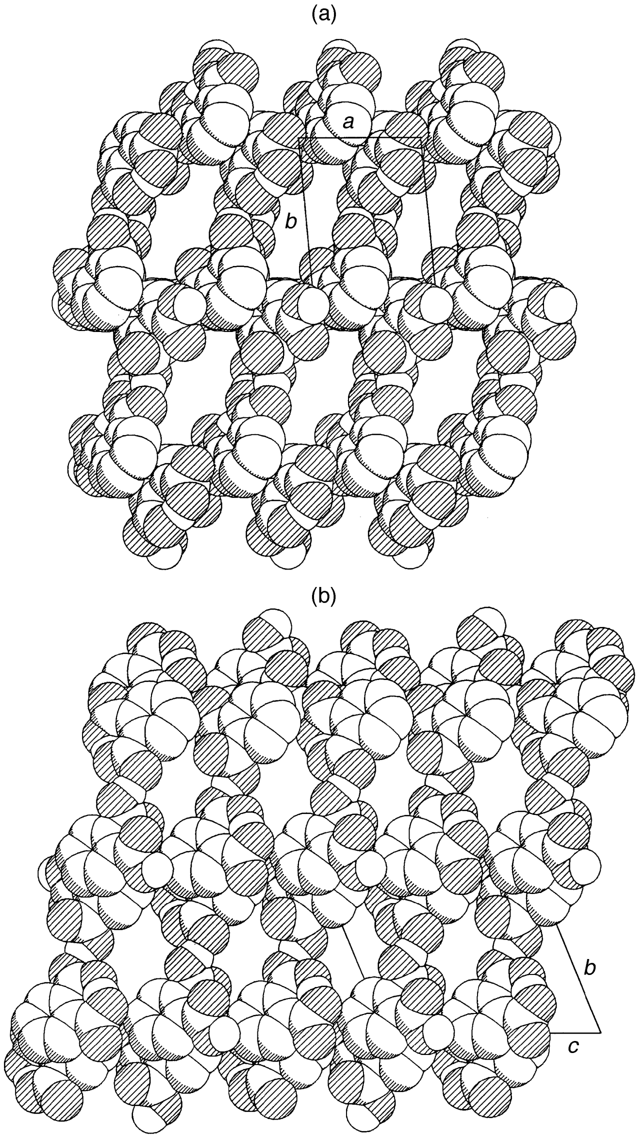


Fig. 5 Space-filling representation of the packing motif in crystalline **2**. Projections in the (*a*) *ab* and (*b*) *bc* planes.

structure accommodates the $\{[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations [see Fig. 7(*b*)]. A view of the TPA^{2-} layers is shown in Fig. 7(*c*). It can be appreciated how the TPA^{2-} anions are linked by two different bridging systems formed by water molecules.

The crystalline edifice of $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+\}_2[TPA]^{2-} \cdot 6H_2O$ (4)

Crystalline **4** bears some resemblance with the structure of **3**. As in the case of **3** the acid is completely deprotonated and the hydrogen bond scaffolding is provided by water molecules joining the TPA^{2-} anions. Moreover, the channels have a shape similar to those in **3** with the organic anions forming the floor and the ceiling [see Fig. 8(*a*)]. The $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations occupy two different sites, one along the channel and one in between the water bridges. One way to look at the relationship between the crystals **3** and **4** is that of ideally expanding with another row of TPA^{2-} anions the width of the channels. The conjunction between TPA^{2-} anions is provided by hexamers of water molecules [Fig. 8(b)], which form the steps of a kind of staircase.

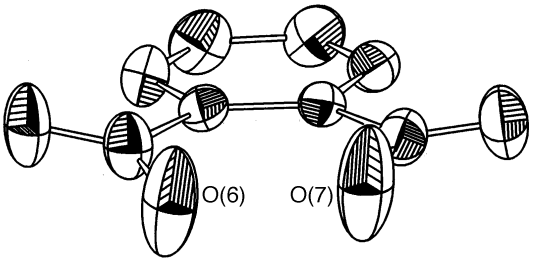


Fig. 6 ORTEP representation of the anisotropic displacement parameters of the monoanion in crystalline **2**. Note how the O(6) and O(7) atoms show extensive displacement perpendicular to the ring plane.

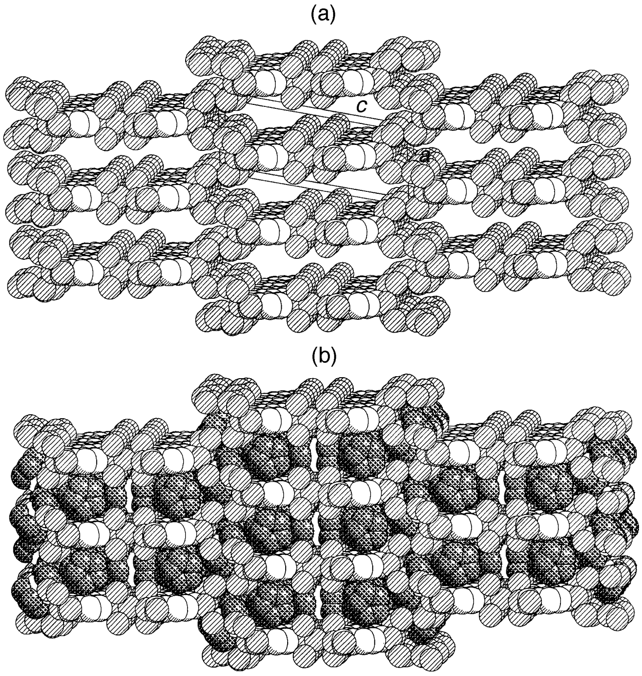


Fig. 7 The anionic superstructure in crystalline **3**. (*a*) The channels are delimited on both sides by water molecules only and above and below by the terephthalate anions. (b) The large channeled structure accommodates the $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations. H atoms are omitted for clarity. Line-shaded spheres are the oxygen atoms. (*c*) A view of the TPA^{2-} layers showing how the anions are linked *via* water bridges.

Quite surprisingly, the packing organization of crystalline **4** very strongly resembles that observed in the crystal structure of a chemically very different system, namely the hydrated hydroxide $[(\eta^5\text{-}C_5H_5)_2Co]^+[OH]^- \cdot 4H_2O$.[7b] As a matter of fact, the two crystals are *almost* isomorphous [compare the unit cell of the hydroxide: $a = 22.28(2)$, $b = 8.805(2)$, $c = 13.81(1)$ Å, $\beta = 101.55(9)°$, $U = 2654$ Å^3, space group $C2/c$, with the data for **4** in Table 1].[7b] In crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[OH]^- \cdot 4H_2O$ the OH^- groups are obviously indistinguishable from the water molecules. The phthalate anions in **4** take the place of the oxygen hexagonal rings in the hydroxide species [compare Fig. 8(*a*) with Fig. 9]. It is reasonable to attribute this very peculiar case of *pseudo*-polymorphism to the analogy in shape between the flat elongated TPA^{2-} anions with its four protruding O atoms and a hydrogen-bonded water hexamer. In other words, the two hydrogen bond networks, though chemically different, are, topologically, extremely similar. While in **4**, as in all other crystals, the interaction between hydrated organic networks and the cations is provided by a profusion of weak, charge-assisted, $C{-}H\cdots O$ interactions, in the crystalline hydroxide these are replaced by $C{-}H\cdots O_{water}$ interactions with the water/hydroxyl network. This analogy, together with those discussed previously for **1** and **3**, and for **3** and **4**, provides evidence of the interplay, at the stage of crystal formation and growth of these peculiar salts, between the need to optimize hydrogen bonding, which has precise geometrical requirements, and the templating effect of the cylindrical cations.

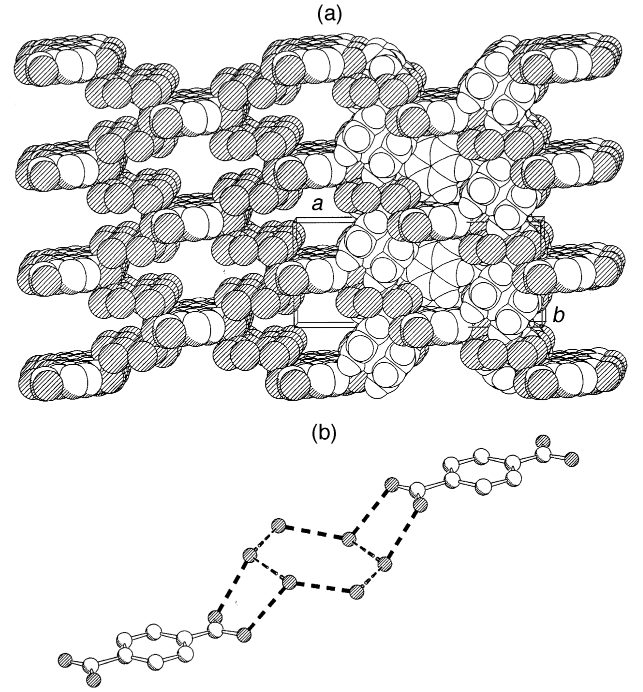


Fig. 8 (a) Space-filling representation of the terephthalate/water network in crystalline **4**. Line-shaded spheres are the oxygenatoms. The hydrogen-bonded superstructure hosts the bis(benzene)chromium cations. (*b*) The conjunction between TPA^{2-} anions is provided by hexamers of water molecules, which form the steps of a kind of staircase.

Conclusions

With this paper we have shown that phthalic acid is a very versatile building block for the construction of hydrogen-bonded anionic organic frameworks. Contrary to previously used tartaric acid, which is flexible,[7a] phthalic acid adds some degree of rigidity to the crystal construction process. Whether neutral, mono- or diprotonated the phthalic acid structure is substantially flat and, thanks to its anchoring points, can be used to *pave* channeled structures. While phthalic acid tends to give mono-deprotonation products, both compounds obtained from terephthalic acid are the result of complete deprotonation. This behavior matches the p*K*s of the two acids (H_2PA: $pK_1 = 2.3$, $pK_2 = 5.5$: H_2TPA: $pK_1 = 3.9$, $pK_2 = 4.3$). Terephthalic acid is less acidic than H_2PA with respect to first deprotonation, but the loss of its second proton is easier. It is thus not surprising that, when reacting with organometallic bases, H_2TPA behaves as a strong diprotic acid.

Complete deprotonation is not inconsequential for our crystal engineering strategy. The strongly basic TPA^{2-} dianions bring into the crystal a large number of water molecules (6 water molecules *per* cation unit in **3** and **4**). These water molecules have a twofold role. They provide the "missing" hydrogens for stabilization *via* hydrogen bonding and act as "space fillers" between the anions, thus reducing inter-anion electrostatic repulsions, which are certainly more relevant in the case of the dianions in **3** and **4**. A similar relationship between full deprotonation and high hydration had been observed previously in the crystalline material $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[\text{L-BTA}]^{2-}\cdot 11H_2O$ (L-**BTA** = L-bisbenzoyltartaric acid)[7a] as well as in the case of the mixed-metal crystalline system $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}$ $7.75H_2O$.[7d] The formation of highly hydrated species is an intriguing aspect of crystal engineering, which may have interesting consequences in the development of new design strategies. We have observed previously that the polar crystal of the hydroxide $[(\eta^6\text{-}C_6H_6)_2Cr]^+[OH]^-\cdot 3H_2O$ possesses a layered architecture in which the $[OH]^-\cdot 3H_2O$ layers have the structure of hexagonal ice.[16] More recently, the role of a water decamer $(H_2O)_{10}$, which possesses an ice-like molecular arrangement within a large supramolecular complex in the solid state, has been discussed.[16] We are learning that water itself can be used, in a somewhat predictable way (*i.e.*, within the design strategy), to generate intermolecular scaffolding and to link strongly nucleophilic building blocks. This also points to the role of ionic charges. The effect of the Coulombic field generated by the ionic charges on the strength of the various types of hydrogen-bonding interactions is difficult to evaluate. It is worth mentioning, in this respect, that theoretical *ab initio* calculations have demonstrated that the shortest $C{-}H\cdots O$ interaction in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ $[CrO_3(OCH_3)]^-$ cannot hold together anions because of strong inter-anion Coulombic repulsions.[17] In general, however, a positive charge carried by the cation decreases the shielding of the proton on the donor $C{-}H$ groups and makes it more acidic, while the presence of a negative charge on the acceptor increases its nucleophilicity resulting in a strengthening of the weak bonds. This is the situation commonly observed when the organometallic cations interact with supramolecular anions as in crystalline **1**–**4**.

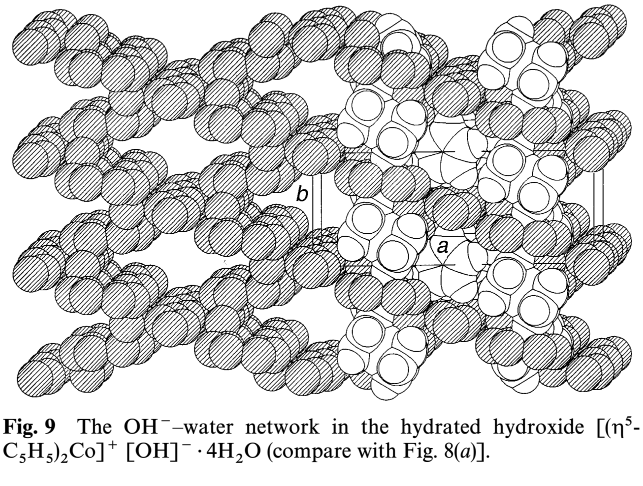


Fig. 9 The OH^-–water network in the hydrated hydroxide $[(\eta^5\text{-}C_5H_5)_2Co]^+$ $[OH]^-\cdot 4H_2O$ (compare with Fig. 8(*a*)].

Work is in progress to isolate and characterize other crystalline aggregates and to investigate the hydrogen bonding by means of spectroscopic, diffraction, and theoretical tools.

Acknowledgements

Financial support by M.U.R.S.T. (*Supramolecular Devices* project) and by the University of Bologna (*Innovative Materials* project) is acknowledged.

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