Organic−Organometallic Crystal Synthesis. 2. Organic Frameworks Constructed around $[(\eta^5\text{-}C_5H_5)_2Co]^+$ *via* Charge-Assisted O−H---O and C−H---O Hydrogen Bonds

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Received April 12, 1997[⊗]

The engineering of organic−organometallic crystals based on strong O−H---O and charge-assisted C−H---O hydrogen bonds is discussed. The organic acids D,L- and L-tartaric acid (D,L-H_2TA and L-H_2TA) can be utilized to generate honeycomb-type organic frameworks around the organometallic cation $[(\eta^5\text{-}C_5H_5)_2Co]^+$. The crystalline products of chemical formulae $[(\eta^5\text{-}C_5H_5)_2Co]^+$[(D,L-HTA)(D,L-$H_2$TA)]$^-$ (**1**) and $[(\eta^5\text{-}C_5H_5)_2Co]^+$[L-HTA]$^-$ (**3**) are, respectively, constituted of hexagonal and tetragonal superanions molded around the cobalticinium cations. On changing the stoichiometric ratio $[(\eta^5\text{-}C_5H_5)_2Co]$/(D,L-$H_2$TA) from 1:2 to 1:1, the crystalline material $[(\eta^5\text{-}C_5H_5)_2Co]^+$[D,L-HTA]$^-\cdot H_2O$ (**2**) is produced while the undecahydrate crystalline material $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2$[L-BTA]$^{2-}\cdot 11H_2O$ (**4**) is obtained when the organic partner is dibenzoyl-L-tartaric acid (L-H_2BTA). The use of chiral acids in the preparation of **2** and **4** provides a simple route to chiral crystals. The participation of water molecules in interactions of the C−H---O type is discussed. These results are used to put forward a practical design strategy for organometallic crystal engineering.

Introduction

As organometallic chemistry is a bridge between organic and inorganic chemistry, crystal engineering is a bridge between supramolecular chemistry and materials chemistry. The synthesis of crystals containing organic and organometallic molecules or ions is a means to *combine* physical, chemical, and structural features of the two types of systems. There is an enormous potential in this combinatory approach, as the number of possible synthetic strategies to obtain new solid products is limited only by the chemical imagination of the experimentalist. Organometallic chemistry is the perfect environment to develop supramolecular aggregate systems because organometallic molecules combine the intra- and intermolecular bonding features of organic fragments (the ligands) with the variable valence state and magnetic behavior of transition metal atoms.[1]

Crystal engineering has been traditionally concerned with the organic solid-state chemistry field. Research in this area have been carried out for the past three decades with remarkable results.[2] The logical connection with supramolecular chemistry[3] has given further impetus to the field. The basic idea is that of being able to rationally design solid materials with predefined arrangements of the component molecules or ions.[4]

We have recently reported the design, synthesis, and structural characterization of solid aggregates of the paramagnetic cations $[(\eta^6\text{-arene})_2Cr]^+$ (arene = benzene and toluene) obtained by utilizing superanions derived from 1,3-cyclohexanedione (CHD) as organic partners. In the crystals of $[(\eta^6\text{-}C_6H_6)_2Cr][(CHD)_2]\cdot(CHD)_2$ and $[(\eta^6\text{-}C_6H_5Me)_2Cr][(CHD)_2]$, the aggregation of the CHD systems in the superanions $[(CHD)_2]^-$ and $[(CHD)_2]^-\cdot(CHD)_2$ is based on the formation of a strong O−H---O hydrogen bond between two hydroxilic groups upon removal of an acidic proton.[5a,b] The inner hydrogen bond in $[(CHD)_2]^-\cdot(CHD)_2$ is markedly shorter than those with the two outer CHD molecules (O(H)---O 2.469(2) *versus* O(H)---O−C 2.544(2) and 2.570(2) Å) and comparable in length to that in the anion $[(CHD)_2]^-$ (2.437(5) Å). These bond lengths fall toward the lower values of O(H)---O hydrogen bonds and are associated with negatively charged hydrogen bonds.[6] In addition, the organic fragments and organometallic complexes establish C−H---O hydrogen bonds between the toluene or benzene ligands and the available "free" O-atom lone pairs of the embracing organic moieties. These bonds are strengthened by the opposite ionic charges carried by the organometallic complexes and the organic superanions, with several C−H---O bonds shorter than 2.32 Å and as short as 2.29 Å. Water oxygens can also

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) (a) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51. (b) Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* **1996**, 571.

(2) (a) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647. (b) Etter, M. C.; Urbonczyck-Lipkowska, Z.; Jahn, D. A.; Frye, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5871. (c) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*, Elsevier: Amsterdam, The Netherlands, 1989. (d) Sharma, C. V. K.; Desiraju, G. R. In *Perspective in Supramolecular Chemistry. The Crystal as a Supramolecular Entity*; Desiraju, G. D., Ed.; Wiley: New York, 1996.

(3) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.

(4) (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (b) Burrows, A. D.; Chan, C.-W.; Chowdry, M. M.; McGrady, J. E.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, 329. (c) Subramanian, S.; Zaworotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357. (d) Zaworotko, M. J. *Nature* **1997**, *386*, 220. (e) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1997**, 1475.

(5) (a) Braga, D.; Grepioni, F.; Byrne, J. J.; Wolf, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1023. (b) Part 1: Braga, D.; Costa, A. L.; Grepioni, F.; Scaccianoce, L.; Tagliavini, E. *Organometallics* **1997**, *16*, 2070.

(6) (a) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1984**, *106*, 1257. (b) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525. (c) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *Chem. Eur. J.* **1996**, *2*, 925.

S0276-7333(97)00502-5 CCC: $14.00

participate in C−H---O$_{water}$ bonds, as evidenced by the structure of the hydrated $[(C_6H_6)_2Cr][CHD]{\cdot}3H_2O$ and by the polar structure of the hydrated hydroxide $[(C_6H_6)_2Cr][OH]{\cdot}3H_2O$.[5b]

C−H---O bonds have been extensively studied chiefly in the organic solid state chemistry field.[7] More recently, the importance of these interactions in organometallic crystal chemistry has been assessed.[8]

In this paper, we have taken our strategy to carboxylic acids. Since the reaction between $[(\eta^6\text{-arene})_2Cr]^+$ (arene = benzene and toluene) and 1,3-cyclohexanedione is essentially an acid−base reaction, the extension to carboxylic acids is quite natural.

We report that the reaction of the hydroxide $[(\eta^5\text{-}C_5H_5)_2Co][OH]$ produced *in situ* in THF or water, in the presence of bicarboxylic acids carrying a number of acceptor sites larger than that of acidic protons, affords novel organic−organometallic aggregates[9] whose structure can be varied by changing the stoichiometric ratios of cobalticinium hydroxide, organic acid, and solvent.

Moreover, the use of commercially available enantiomerically pure chiral acids permits the easy preparation of chiral crystals. This is one of the prerequisites for obtaining crystalline materials potentially useful for nonlinear optical applications.[10] The design of noncentrosymmetric crystals is one of the primary goals for the construction of molecule-based nonlinear optical materials and represents an important issue in materials chemistry.

Experimental Section

Crystal Synthesis. As in the case of the cyclohexanedione derivatives described in part 1 of this series,[5b] the synthetic aspect of this work is related to the synthesis and crystallization of the solid material. All reagents are commercially available organic and organometallic substances.

Synthesis of Crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\text{D,L-HTA})(\text{D,L-}H_2TA)]^-$ (1) and $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{D,L-HTA}]^-{\cdot}H_2O$ (2). Brown crystalline powder $(\eta^5\text{-}C_5H_5)_2Co$ (28 mg, 0.15 mmol) was suspended into 8 mL of doubly distilled water at room temperature. Oxygen was bubbled through the suspension until a bright yellow clear solution $[(C_5H_5)_2Co]^+[OH]^-$ was obtained (ca. 10 min). Alternatively, complete oxidation can be achieved by prolonged stirring (ca. 1 h) of the $(\eta^5\text{-}C_5H_5)_2Co$ suspension in water in the presence of air. The yellow solution was basic (pH > 10). White powder D,L-tartaric acid (45 mg, 0.3 mmol for **1**; 22.5 mg, 0.15 mmol for **2**) was then added with stirring. Crystals of **1** and **2** suitable for X-ray determination were obtained by evaporation at room temperature in the air. The same materials can be obtained by oxidizing a cobaltocene solution with O_2 in THF at room temperature in the presence of the appropriate stoichiometric amount of solid D,L-tartaric acid. The resulting insoluble materials separate out as yellow solids, which are then filtered and dissolved in a minimum quantity of water for recrystallization.

Synthesis of Crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\text{L-HTA})]^-$ (3). White powder L-tartaric acid (50 mg, 0.3 mmol) was placed in a flask with 8 mL of THF. Brown crystalline powder $(\eta^5\text{-}C_5H_5)_2Co$ (56 mg, 0.3 mmol) was added with stirring. Oxygen was bubbled through the solution at room temperature for 3 min, and a yellow precipitate was formed. The solid was filtered and crystallized from a mixture of water and methanol (1:1), and yellow crystals were obtained. Direct reaction between $[(\eta^5\text{-}C_5H_5)_2Co][OH]$ and the acid in water, as for **1** and **2**, failed to produce crystals suitable for the X-ray diffraction experiments.

Synthesis of Crystalline $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[(\text{L-BTA})]^{2-}{\cdot}11H_2O$ (4). Brown crystalline powder $(\eta^5\text{-}C_5H_5)_2Co$ (56 mg, 0.3 mmol) was put in a flask with 15 mL of water. This solution was left in the air with stirring (ca. 1h), and the cobaltocene was oxidized by the atmospheric oxygen to the hydroxide $[(\eta^5\text{-}C_5H_5)_2Co][OH]$. White powder 2,3-dibenzoyl-L-tartaric acid (54 mg, 0.15 mmol) was added directly to the hydroxide solution. Yellow crystals were obtained after complete evaporation of the water.

Tartaric acid, dibenzoyltartaric acid and cobaltocene were purchased from Aldrich. THF was distilled from Na benzophenone ketyl and was stored under Argon.

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[11a] and SHELXL92[11b] were used for structure solution and refinement based on F^2. Fractional atomic coordinates and anisotropic displacement parameters are available as Supporting Information. SCHAKAL92[11c] 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 the C atoms of the disordered cation in **3**, were refined anisotropically. The positions of the hydrogen atoms bound to the oxygens in **1** and **2** and of one of the carboxylic H atoms in **3** have been observed in the Fourier maps. H atoms bound to C atoms were added in calculated positions in the four crystals. The computer program PLATON[11d] was used to analyze the geometry of the hydrogen-bonding patterns. In order to evaluate the C−H---O bonds, C−H distances were normalized to the neutron-derived value of 1.08 Å.

Diffraction data for both crystals **1** and **2** have been measured at room temperature (*ca.* 293 K) and at 223(2) K on the same crystal specimen. In this paper, only the low-temperature data sets are discussed in detail. Diffraction data for crystals **3** and **4** were collected at 223 K. In **1**, the Cp ligands were found to be disordered over two sites of occupancy with a ratio of 3:2. The two measurements for crystal **1** allowed one to check the nature of the Cp ligand disorder: since site occupancy factors did not change on decreasing the temperature from 293 to 223 K, the disorder is likely to have a static origin. This is confirmed by the observation that the Cp ligands in the two orientations are involved in two alternative sets of C−H---O interactions with the host (see below). In **3** there are two “half” independent anions and two cations around the crystallographic 2-fold axes in the noncentrosymmetric space group $P222_1$. One of the two Cp_2Co^+ cations was found to be orientationally disordered (site occupation factors 3:2). As in **1**, the two orientations satisfy two alternative sets of C−H---O interactions.

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[7] (a) Berkovitch-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr.* **1984**, *B40*, 159. (b) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063. (c) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (d) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (e) Steiner, T. *Cryst. Rev.* **1996**, *6*, 1.

[8] Braga, D.; Biradha, K.; Grepioni, F.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156. Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1997**, *30*, 81.

[9] For a preliminary report on the structures of the D,L-H_2TA derivatives, see: Braga, D.; Angeloni, A.; Grepioni, F.; Tagliavini, E. *J. Chem. Soc., Chem. Commun.* **1997**, 1447.

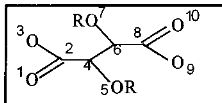
[10] Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155. Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. Long, N. J. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 21.

[11] (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. *SHELXL92, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1993. (c) Keller, E. *SCHAKAL92, Graphical Representation of Molecular Models*; University of Freiburg: Germany, 1993. (d) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C31.

Table 1. Crystal Data and Details of Measurements for Crystals 1, 2, 3, and 4

	1	2	3	4
formula	$C_{18}H_{21}Co_1O_{12}$	$C_{14}H_{17}Co_1O_7$	$C_{14}H_{15}Co_1O_6$	$C_{38}H_{54}Co_2O_{19}$
mol wt	488.28	356.21	338.19	466.34
temp (K)	223(2)	223(2)	223(2)	223(2)
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pnma$	$P222_1$	$P2_1$
a (Å)	6.589(2)	12.048(9)	9.823(9)	11.936(5)
b (Å)	18.210(4)	16.683(5)	10.244(5)	11.402(9)
c (Å)	8.208(2)	14.458(5)	14.250(10)	15.969(7)
β (deg)	92.19(2)			98.18(3)
V (Å^3)	984.1(4)	2906(2)	1434(2)	2151(2)
Z	2	2	4	2
F(000)	504	1472	696	976
transmission coeff (min−max)	0.90−1.0	0.85−1.0	0.82−1.0	0.92−1.0
μ(Mo Kα) (mm^{-1})	0.939	1.214	1.221	0.847
θ-range (deg)	3.0−28.0	3.0−28.0	3.0−30.0	3.0−23.0
octants explored ($h_{\min}$, $h_{\max}$; $k_{\min}$, $k_{\max}$; $l_{\min}$ $l_{\max}$)	−8, 8; 0, 24; 0, 10	0, 14; 0,22; 0, 17	0, 13; 0, 14;0, 19	−13, 12; 0, 12; 0, 16
no. of measd reflns	2606	3353	2377	3260
no. of unique reflns	2362	3050	2359	3127
no.of refined params	169	209	159	421
GOF on F^2	1.024	0.919	0.926	1.009
R1(on F, $I > 2\sigma(I)$)	0.0333	0.0526	0.0983	0.0684
wR2(on F^2, all data)	0.0920	0.1778	0.3671	0.2188

Table 2. Comparison of Relevant Geometric Parameters in 1, 2, 3, and 4[a]

	1-2 2-3 8-9 8-10	1-2-3 9-8-10	4-5 6-7	2-4	4-6	6-8
1 R=H	1.197(3) 1.319(2) 1.280(3) 1.222(3)	125.0(2) 124.0(2)	1.415(2) 1.417(2)	1.513(3)	1.524(3)	1.527(3)
2 R=H	1.220(8) 1.251(8) 1.225(8) 1.279(9)	128.3(7) 125.4(6)	1.410(8) 1.402(8)	1.547(9)	1.515(9)	1.523(8)
3 R=H (b)	1.24(2) 1.26(2) 1.24(2) 1.22(2)	125(2) 124(2)	1.42(2) 1.36(2)	1.52(2) 1.52(2)	1.47(2) 1.58(2)	
4 R=C(O)C_6H_5	1.21(2) 1.28(2) 1.24(2) 1.21(2)	129(2) 125(2)	1.37(2) 1.42(2)	1.54(2)	1.55(2)	1.50(2)

[a] Distances in Å, angles in deg. [b] Two "half" independent anions (see text).

Results and Discussion

As shown above, the synthesis of crystals **1**−**4** essentially requires three steps: (i) oxidation of cobaltocene to the cobalticinium cation which is formed as a hydroxide in solution (see below), (ii) acid−base reaction between $[(\eta^5\text{-}C_5H_5)_2Co][OH]$ and the organic acid, and (iii) precipitation of the crystalline aggregate. The preparation can be carried out in water or THF: in water, the hydroxide $[(\eta^5\text{-}C_5H_5)_2Co][OH]$ can be prepared first and then reacted 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 solutions.[12]

Though it may appear simple, the formation of the desired crystalline 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 the first and second deprotonations of the diprotic acid. The reason why several other diprotic organic acids have, in the same conditions, failed to give crystalline materials suitable for X-ray diffraction is under investigation.

Structural Characterization. Relevant intra- and intermolecular bonding parameters are reported in Tables 2 and 3, respectively. A full listing of the bond distances and angles, as well as fully labeled ORTEP pictures, are reported as Supporting Information. The following discussion will be necessarily based on the graphical representation of the crystalline products.

The cobalticinium cation in crystalline **1** is encapsulated within an organic honeycomb framework (see Figure 1) of stoichiometry $\{[(\text{D,L-HTA})(\text{D,L-}H_2\text{TA})]^-\}_n$, generated by the aggregation of supramolecular mono-

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[12] The oxidation reaction in water may proceed *via* the following hypothetical steps:

$$\begin{array}{lll}
(1) & Cp_2Co + O_2 & \longrightarrow Cp_2Co^+ + O_2^{-\bullet} \\
(2) & O_2^{-\bullet} + H_2O & \longrightarrow HO_2^{\bullet} + OH^- \\
(3) & Cp_2Co + HO_2^{\bullet} & \longrightarrow Cp_2Co^+ + HO_2^- \\
(4) & HO_2^- + H_2O & \longrightarrow H_2O_2 + OH^- \\
(5) & 2Cp_2Co + H_2O_2 & \longrightarrow 2\,Cp_2Co^+ + 2\,OH^- \\
\hline
 & 4Cp_2Co + O_2 + 2H_2O & \longrightarrow 4Cp_2Co^+ + 4OH^-
\end{array}$$

On the basis of this stoichiometry, 1 mol of oxygen oxidizes 4 mol of cobaltocene. The insoluble aggregate precipitates immediately. In THF, the peroxide anion directly deprotonates the acid, as in the case of the reaction between $(C_6H_6)_2Cr$ and 1,3-cyclohexanedione;[5b] two water molecules are generated *in situ*.

Table 3. Relevant Hydrogen-Bonding Parameters in Crystalline 1, 2, 3, and 4[a]

hydrogen-bond type	1	2	3	4
O_{COO}---O_{COOH}	2.434(2)	2.479(8)	2.440(10), 2.413(10)	
O_{COOH}---O_{OH}	(intra) 2.711(2), 2.638(2), 2.677(2)	2.550(8), 2.640(8)	2.847(10), 2.925(10)	
O_{OH}---O_{OH}	2.776(2)			
O_{COOH}---O_{W}		2.725(8)		
O_{COO}---O_{W}				2.828(12), 2.772(12), 2.802(12), 2.743(12), 2.822(12), 2.757(13), 2.800(12)
O_{OH}---O_{W}		2.640(10), 2.784(10)		
O_{W}---O_{W}				2.736(13), 2.825(13), 2.728(13), 2.779(13), 2.827(13), 2.762(13), 2.701(13), 2.719(13), 2.670(13), 2.936(13)
C−H_{Cp}---O	2.396(2), 2.302(2), 2.333(2), 2.097(2), 2.354(2), 2.341(2), 2.253(2)	2.222(8), 2.338(8), 2.238(8), 2.425(8), 2.445(8)	2.454(12), 2.136(12), 2.157(12), 2.069(12), 2.450(12), 2.151(12), 2.398(12), 2.562(12), 2.427(12)	2.40(2), 2.51(2), 2.51(2)
C−H_{Cp}---O_{W}				2.45(2), 2.27(2), 2.52(2), 2.56(2), 2.44(2), 2.49(2), 2.57(2), 2.47(2), 2.49(2), 2.43(2)

[a] Distances are given in Angstroms (Å).

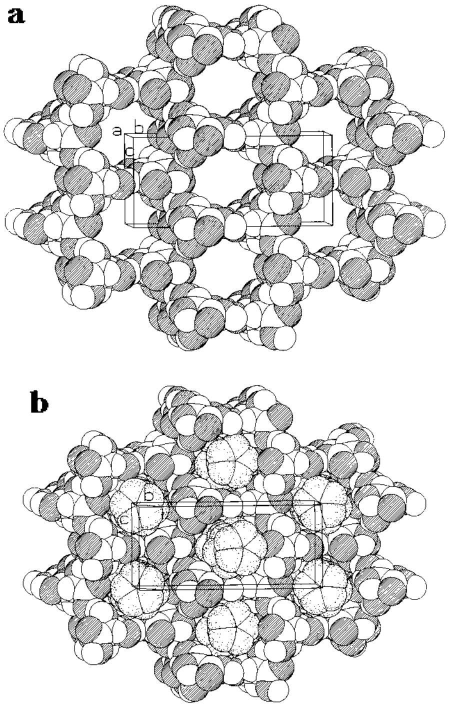

Figure 1. (a) Space-filling representation of the anionic honeycomb framework formed by the [(D,L-HTA)(D,L-H_2TA)]$^-$ units in crystalline [(η^5-C_5H_5)$_2$Co]$^+$[(D,L-HTA)(D,L-H_2TA)]$^-$ (**1**). (b) The cobalticinium cations pile inside the channels extending along the *a*-axis; cation H atoms are omitted for clarity. The oxygen atoms are represented as shaded spheres.

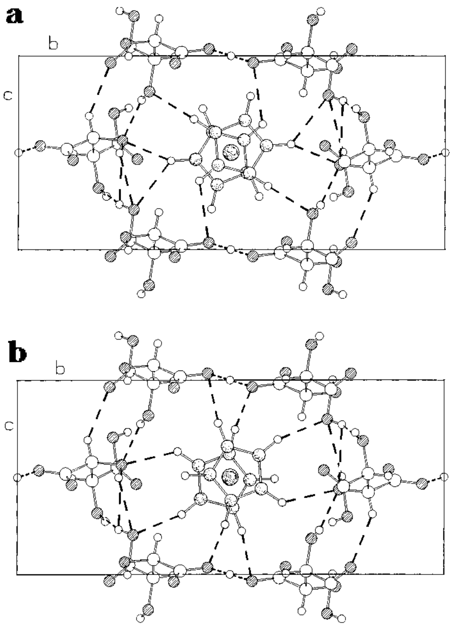

Figure 2. Ball and stick representations of the anionic cage in crystalline [(η^5-C_5H_5)$_2$Co]$^+$[(D,L-HTA)(D,L-H_2TA)]$^-$ (**1**), showing the O−H---O and C−H---O hydrogen bond networks established by [(η^5-C_5H_5)$_2$Co]$^+$ in its two disordered orientations (see text).

anions [(D,L-HTA)(D,L-H_2TA)]$^-$ formed as a consequence of the loss of one proton for every two tartaric acid molecules. The tartaric acid dimers are characterized by the presence of a strong−C(O)O−H---O(O)C−hydrogen bond (2.434(1) Å) between the two units and are linked in the honeycomb framework *via* O−H---O bonds involving the two *external* carboxyl groups and the hydroxyl groups, as shown in Figure 2. The interaction between the supramolecular anionic network and the encapsulated [(η^5-C_5H_5)$_2$Co]$^+$ cations occurs via C−H---O hydrogen bonds between the *staggered* cyclopentadienyl ligands of the cations and the −CO and the −OH groups of the anionic framework (see Figure 2). The cobalticinium cations are present in two different orientations within the cavity. The occupancy ratio (3:2) for the two sites does not change on decreasing the temperature from 293 to 223 K, thus indicating the static nature of the disorder. Both orientations allow the formation of C−H---O bonds, though between different donor/acceptor pairs, as shown in Figure 2. Six independent C−H---O interactions are observed in the (C)H---O distance range 2.10−2.35(1) Å (see Table 3). These values fall toward the lower limit for interactions of this type,[7] clearly indicating that the electrostatic interaction C−H$^{\delta+}$---O$^{\delta-}$ is reinforced by the difference

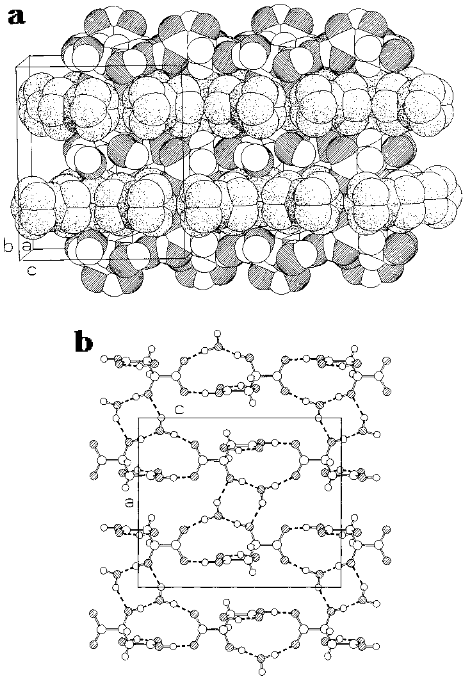

Figure 3. (a) Space-filling outline of the layered structure in crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{D,L-HTA}]^-\cdot H_2O$ (**2**); cation H atoms are omitted for clarity. (b) The $(-OH)_4$ tetramer formed by two hydroxyl groups belonging to two tartrate ions and by two water molecules, note how the water molecules effectively bridge parallel chains of tartrate ions.

in charge between the host and guest. A similar relationship between disorder and the presence of alternative C−H---O interaction patterns has been observed in crystalline $[(\eta^6\text{-}C_6H_5Me)_2Cr][(CHD)_2]$, where the two arene fragments occupy two sites (in the ratio 1:1) that allow equivalent participation in C−H---O bonding with the $[(CHD)_2]^-$ superanion.[5]

The imbalance between the number of −OH and C=O acceptor sites and the number of "conventional" donors (four −OH groups out of five participates in intramolecular −O−H---O bonds) is likely to be the driving force toward aggregation around the $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations in **1**.

If the stoichiometric ratio between $[(\eta^5\text{-}C_5H_5)_2Co][OH]$ and tartaric acid in the acid−base reaction is changed from 1:2 to 1:1, the hydrated crystalline salt $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{D,L-HTA}]^-\cdot{}_2O$ (**2**) is obtained. Contrary to **1**, the $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations are in an *eclipsed* conformation. Crystalline **2** can be described as a layered structure in which a corrugated anionic network of $[\text{D,L-HTA}]^-$ ions and water molecules alternate with layers of cobalticinium cations (see Figure 3a). The shortest O−H---O bond (2.479(8) Å) links tartrate monoanions in chains throughout the crystal structure. The acidic proton is selectively removed from O(2), as confirmed by the observation in the Fourier map of the hydrogen atom bound to O(6).

While both −OH groups in **1** form intramolecular interactions, the same is not true in **2**. The water molecules form O−H---O hydrogen bonds involving two hydroxyl groups of two neighboring tartrate anions. Figure 3b shows the tetramer-like $(-OH)_4$ hydrogen-bonded unit formed by two hydroxyl groups belonging to two tartrate ions and by two water molecules (the hydrogen atoms involved in these bonds were also observed). Hence, the water molecules bridge parallel chains of tartrate ions, forming the hydrated anionic organic sheets shown in Figure 3a. The hydroxyl tetramer is one of the most common hydrogen-bonding patterns observed in crystalline organic alcohols as well as in organometallic complexes.[13]

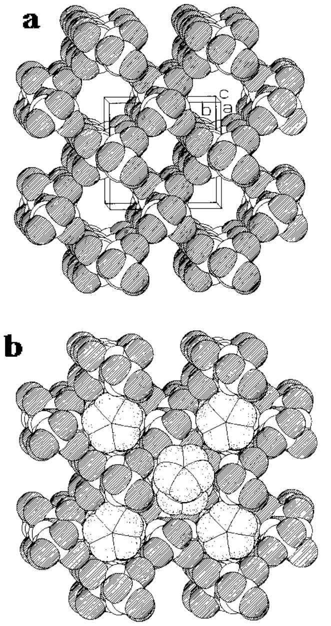

Figure 4. (a) Space-filling representation of the L-tartaric acid framework in crystalline $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{L-HTA}]^-$ (**3**). (b) The cobalticinium cations pile inside the channels extending along the *c*-axis; cation H atoms are omitted for clarity.

As in **1**, the interaction between the anion and cation is based on C−H---O hydrogen bonds (of which three are in the range 2.222−2.338(8) Å, Table 3) between the Cp hydrogens and the −OH and −COOH groups. Interestingly, the two sets of C−H---O bonds in **1** and **2** stabilize, respectively, the staggered and eclipsed conformations of the organometallic cation.

Sodium *meso*-tartaric acid salts of stoichiometry $Na_2[TA]$[14a] and $Na[(HTA)(H_2TA)]$[14b] have been structurally characterized. The latter salt, similar to what is observed in **1,** contains a dimeric unit with an O---O separation of 2.448 Å. A hydrogen atom is situated on the inversion center relating the two moieties (O−H 1.224(2) Å), although the aggregation of tartaric acid and tartrate units does not constitute an infinite three-dimensional network.

When the chiral acid L-H_2TA is employed, the chiral crystal $[(\eta^5\text{-}C_5H_5)_2Co]^+[\text{L-HTA}]^-$ (**3**) is obtained. As in the case of **1**, the chemical formula is misleading. The crystal is in fact constituted of a three-dimensional organic superanion similar to that described above for **1**. The honeycomb-type structure (see Figure 4a) is no longer based on hexagonal channels but on square ones extending along the *c*-axis in the chiral space group $P222_1$. The two types of square channels differ in size and accommodate two crystallographically independent cobalticinium cations (see Figure 4b). In terms of

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(13) Brock, C. P.; Duncan, L. L. *Chem. Mater.* **1994**, *6*, 1307. Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju, G. R. *Organometallics* **1994**, *13*, 3532. Walther, D.; Klettke, T.; Schmidt, A.; Görls, H.; Imhof, W. *Organometallics* **1966**, *15*, 2314. Braga, D.; Grepioni, F.; Walther, D.; Klettke, T.; Schmidt, A.; Görls, H.; Imhof, W. *Organometallics*, in press.

(14) (a) Blankensteyn, A. J. A. R.; Kroon, J. *Acta Crystallogr.* **1985**, *C41*, 182. (b) Blankensteyn, A. J. A. R.; Kroon, J. *Acta Crystallogr.* **1986**, *C42*, 291.

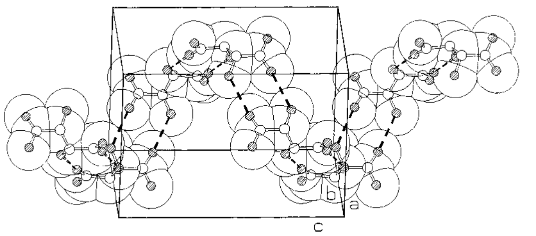

Figure 5. A spiral of hydrogen-bonded L-tartaric acid ions in crystalline **3**. The spirals are interwoven to form the channels shown in Figure 4.

hydrogen bonds, the following observations can be made: (i) The two independent L-HTA^- ions form strong negatively charge-assisted O−H---O^- hydrogen bonds of the type discussed above for **1** and **2** (see Table 3), generating parallel chains extending along the *c*-axis. These chains are, therefore, similar to those present in **2**, and the interion O−H---O hydrogen bonds are comparable in length (O(H)---O 2.440(10), 2.413(10) Å in **3**). Each chain is formed by only one crystallographically independent acid anion.

(ii) The interchain link is guaranteed here by −OH---O=C hydrogen bonds with the carbonyl groups that do not participate in the chain construction (O(H)---O 2.847(10) and 2.925(10) Å). These are the bonds that interlink the one-dimensional chain pattern in a three-dimensional network and that generate the channels shown in Figure 4a.

(iii) An alternative way to look at the crystal architecture is to observe how the interchain links generate spirals (one of them is shown in Figure 5) formed by an alternation of the two independent L-HTA^- ions. The spirals are interwoven to form the channels depicted in Figure 4a and wrap around the cobalticinium cations.

(iv) The interaction between the anionic superstructure and the encapsulated organometallic complex is again provided by C−H---O hydrogen bonds.

Finally, the crystalline material $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[\text{L-BTA}]^{2-}\cdot 11H_2O$ (**4**) needs to be described. The presence of 11 molecules of water of crystallization *per* L-BTA^{2-} dianion is noteworthy. The reader may object that a crystalline material with such an unusual formula can only be the result of serendipity rather than of *intelligent desk modeling*. Indeed this is so. Nonetheless, **4** provides some insight into the relationship between molecular shape and crystal architecture.

In contrast to D,L-H_2TA and L-H_2TA, the acid in **4** is deprotonated on both carboxylic groups, *viz.* there is no hydrogen-bonding donor group available versus the presence of 12 potentially hydrogen-bonding acceptor sites over the organic moiety. Hydrogen-bonding distance analysis shows that the four carboxylic O atoms interact directly with seven crystallographically independent water molecules (see Table 3). O---O separations are in the range 2.743−2.828(12) Å. The other oxygen atoms belonging to the benzoyl groups take part in fewer interactions with the water molecules. Four of the 11 water oxygens (O(10), O(12), O(13), and O(18)) only interact with other water molecules. The O---O separations between the molecules are shorter, falling in the range 2.670−2.827(13) Å, and are comparable to those observed in ice and other hydrated systems.[15] The network of O---O interactions form a layer as shown in Figure 6a. Hexagonal patterns, similar to those observed in the structure of ice and constituted only of water oxygens, can be detected within the network.

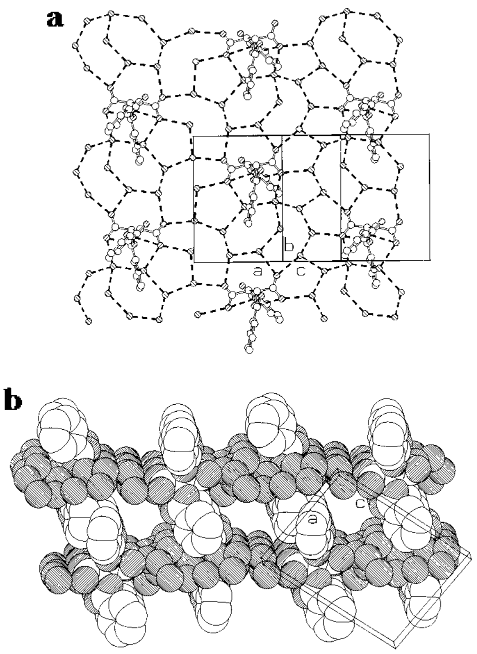

Figure 6. (a) A projection perpendicular to the network of O---O_{water} hydrogen bond interactions in crystalline $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[\text{L-BTA}]^{2-}\cdot 11H_2O$ (**4**). (b) Space-filling representation of the cage in crystalline $\{[(\eta^5\text{-}C_5H_5)_2Co]^+\}_2[\text{L-BTA}]^{2-}\cdot 11H_2O$ (**4**). Note how the channels extending along the *b*-axis are delimited on two sides by the water layers and on the other two by phenyl groups. H atoms are omitted for clarity.

Figure 6b shows a space-filling side view of the $[\text{L-TBA}]^{2-}\cdot 11H_2O$ superstructure. It can be appreciated how the phenyl groups define two sides of the square-channels in which the cobalticinium cations are accommodated. The crystalline edifice is, therefore, constituted of "isolated" $[\text{L-BTA}]^{2-}$ dianions bridged by hydrogen-bonded water molecules, which form the other two sides of the channels.

The interactions of the C−H---O type involve mainly the benzylic C=O groups (see Table 3), although the water molecules also provide acceptor sites for C−H---O hydrogen bonds. Similar behavior has been previously observed in the crystal structures of the hydrated species $[(C_6H_6)_2Cr][CHD]\cdot 3H_2O$[5] and $[(C_6H_6)_2Cr][OH]\cdot 3H_2O$[5] and in other classes of compounds.[16]

The solid-state structure of the ferricinium trichloroacetate salt $[(\eta^5\text{-}C_5H_5)_2Fe]^+[(CCl_3COO)(CCl_3COOH)]^-$ (**5**) was reported by Boeyens.[17] In view of the results discussed above, we felt that the ion organization in this seemingly related material had to be examined. As a matter of fact, the crystal presents a close structural analogy with system **1**, as easily observed in Figure 7a, where a space-filling representation of the crystal structure of **5** is shown. The supramolecular $\{[(CCl_3COO)(CCl_3COOH)]^-\}_n$ framework is formally constituted of one CCl_3COO^- ion and of one neutral

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[15] Bouquiere, J. P.; Finney, J. L.; Savage, H. J. F. *Acta Crystallogr., Sect. B* **1994**, *B50*, 566. Savage, H. F.; Finney, J. L. *Nature* **1986**, *322*, 717. Falk, M.; Knop, O. *Water. A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press, New York, **1973**; Vol. 2, p 55

[16] Steiner, T.; Saenger, W. J. *Am. Chem. Soc.* **1993**, *115*, 4540. Steiner, T.; Saenger, W. *Acta Crystallogr., Sect. B* **1992**, *B48*, 819.

[17] Allen, C. C.; Boeyens, J. C. A.; Neuse, E. W. *S. Afr. J. Chem.* **1987**, *40*, 17.

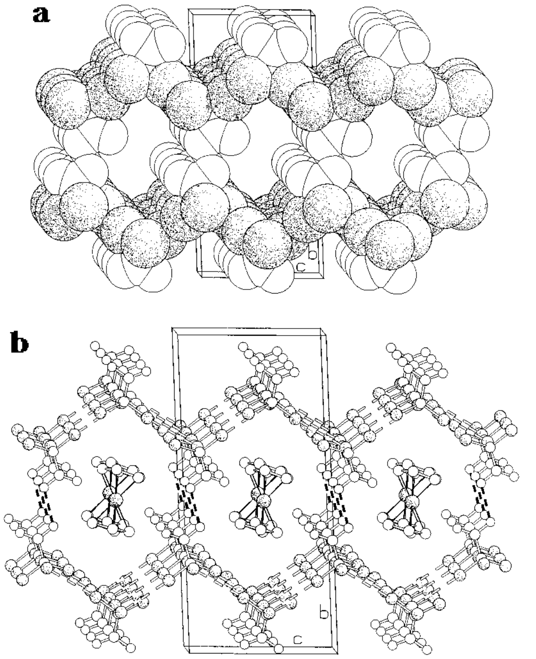

Figure 7. (a) Space-filling representation of the honeycomb-type framework in the crystal structure of the ferricinium trichloroacetate salt $[(\eta^5\text{-}C_5H_5)_2Fe]^+[(TCA)_2]^-$ (**5**, coordinates are from the original structural report[17]). Note the close similarity with the structure of **1** (Figure 1). Shaded atoms represent the chlorine atoms. (b) The sheets of chlorine atoms are linked by the O−H---O hydrogen bonds. Broken empty lines indicate the shortest Cl---Cl distances (3.518 Å).

CCl_3COOH molecule organized in a honeycomb-type structure encapsulating the ferricinium cations, *viz.* the stoichiometry is the same as for crystalline **1**. There are some remarkable features that deserve a close examination.

(i) The interaction between the CCl_3COO^- ion and the neutral CCl_3COOH molecule is of the same type as that discussed in **1**, **2**, and **3**, *i.e.*, arising as a consequence of the loss of one acid proton for every two trichloroacetate acid molecules. The bond linking the two moieties of the $[(CCl_3COO)(CCl_3COOH)]^-$ unit is, therefore, a negatively charge-assisted O−H---O$^-$ hydrogen bond of the type discussed above. The O---O separation of 2.463 Å is comparable to the values in Table 3.

(ii) These hydrogen bonds define two opposite edges of the distorted hexagonal frame as shown in Figure 7a, while the other four edges are generated *via* interlocking and stacking of the CCl_3 moieties. The shortest Cl---Cl distance is 3.518 Å.

(iii) The encapsulated ferricinium cation adopts a different orientation inside the channels with respect to the orientation observed in **1**. This choice may be related to the possibility of optimizing C−H---O hydrogen bonds between the cyclopentadienyl ligands and the O atoms of the acid which are only present on the sides of the channel.

The main structural difference between crystalline **1** and **5** is that in **1** the whole *hexagon* is held together by hydrogen bonds (Figure 1a) while hydrogen bonds form only two edges in **5**, the remaining four being defined by the Cl---Cl interlocking (Figure 7a). The CCl_3 groups form zigzag sheets in the crystal structure, as shown in Figure 7b.

The problem of whether the Cl---Cl separations (which are shorter than the sum of the van der Waals radii[18]) represent attractive interactions or are the result of anisotropy of the chlorine atomic shape is still being debated.[19] Many organic molecular crystals have Cl---Cl distances in the range 3.2−3.4 Å, and a very short distance of 3.27 Å is also present in solid chlorine.[19] It is hard to add anything to this debate, which is well-documented and falls beyond the scope of this article. It is only worth stressing that the analogies and differences between the crystal structures of **1** and **5** may represent an important manifestation of a supramolecular analogy between hydrogen bonds and Cl---Cl interactions.

Conclusions and Perspectives

With this study we have provided evidence that charge-assisted C−H---O hydrogen bonds can be used to mold O−H---O hydrogen bond networks around organometallic cations.

We have also demonstrated that it is possible to promote supramolecular aggregation of common organic acids *via* acid−base reactions with organometallic hydroxides produced *in situ*. The deprotonation reaction, which is such a simple chemical process, generates negatively charged O−H---O hydrogen bonds that constitute a robust backbone for the three-dimensional aggregation of the organic fragments. These bonds have been shown to possess dissociation energies in the range from 14 to 29 kcal/mol.[6a,b] The O---O distances involving the negative charge-assisted hydrogen bonds present in crystalline **1**, **2**, **3**, and **5** are comparable to the values observed in other partially protonated salts, such as sodium hydrogen maleate trihydrate,[20a] $NaH[C_4H_2O_4]\cdot 3H_2O$ (2.445(1) Å), and potassium hydrogen dicrotonate[20b] $KH[C_4H_5O_2]_2$ (2.488(2) Å).

It has been stated that "crystal engineering is not an esoteric type of crystallography but rather addresses the problem of intermolecular interactions."[19b] Our strategy opens a simple route to the preparation of a number of organic−organometallic crystalline aggregates, starting from a knowledge of the cooperative effect of strong and weak noncovalent bonds. Our design criteria can be summarized as follows: (1) Requisites of the organic partners: (a) presence of strong donor/acceptor hydrogen-bonding groups and (b) a larger number of acceptor than donor sites. The dione in $[(\eta^6\text{-}C_6H_6)_2Cr][(CHD)_2]\cdot(CHD)_2$,[5] for instance, possesses three acceptor sites but only one OH donor, while tartaric acid possesses eight potential acceptor sites against four O−H donor groups. Feature (a) will lead to self-assembling of the organic fragments, while feature (b) will allow other weaker interactions to become important.

(2) Requisites of the organometallic partners: (c) absence of strong hydrogen-bonding donor/acceptor systems that may compete with the organic fragments

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[18] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985**, *B41*, 274. Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 7384.

[19] (a) Mirsky, K.; Cohen, M. D. *Chem. Phys.* **1978**, *28*, 193. (b) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222. (c) Price, S. L.; Stone, A. J.; Lucas, J.; Rowland, R. S.; Thornley, A. E. *J. Am. Chem. Soc.* **1994**, *116*, 4910.

[20] (a) McGregor, D. R.; Speakman, J. C.; Lehmann, M. S. *J. Chem. Soc., Perkin II* **1977**, 1740. (b) Olovsson, G.; Olovsson, I.; Lehmann, M. S. *Acta Crystallogr.* **1984**, *C40*, 152.

and (d) a large number of acidic C−H groups, typically containing sp- or sp^2-hybridized C atoms, which will not be able to self-aggregate but will rather interact with the acceptor sites on the organic partner.

(3) The electrostatic nature of the hydrogen-bonding interactions is reinforced by charge assistance. The formation of charge-assisted O−H---O$^-$ between the organic components, as well as of C−H$^{\delta+}$---O$^{\delta-}$ bonds between organic and organometallic components, is the result of the acid−base reaction which leads to organic anions *via* deprotonation and consequent stabilization of the organic−organometallic interactions.

The latter point is somewhat related to the "electrostatic templating" method put forward by Fagan and Ward[21] to prepare crystalline materials for charge-transfer applications. Electrostatic templating introduces constraints to the crystal build-up sequence since anions and cations need to organize in a way that maintains electroneutrality. The topology of the template depends on the shape and geometry of the cations and anions as well as on the spatial arrangements of the positive and negative charges which can be utilized to form one-, two- and three-dimensional aggregates.

The availability of different rotameric conformations for the cobalticinium cation in crystals **1** and **2**, in agreement with the low barrier to internal rotation in metallocene complexes,[22] is advantageous because the templating unit can adopt the conformation that optimizes interactions with the surrounding organic framework.

Work is in progress to isolate and characterize other crystalline aggregates based on the utilization of other chiral acids, including natural amino acids, and of different organometallic molecules and ions.

Acknowledgment. Financial support by MURST and by the University of Bologna (Project: Intelligent Molecules and Molecular Aggregates) is acknowledged.

Supporting Information Available: Tables of anisotropic thermal parameters, fractional atomic coordinates, and complete bond lengths and angles and ORTEP drawings for **1**−**4** (36 pages). Ordering information is given on any current masthead page.

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(21) Fagan, P. J.; Ward, M. D. *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry*; Desiraju, G. R., Ed.; John Wiley and Sons, Chichester, 1996; Vol. 2, p 107.

(22) Braga, D. *Chem. Rev.* **1992**, *92*, 369 and references therein.