ORGANOMETALLICS
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Shape Takes the Lead: Templating Organic 3D-Frameworks around Organometallic Sandwich Compounds

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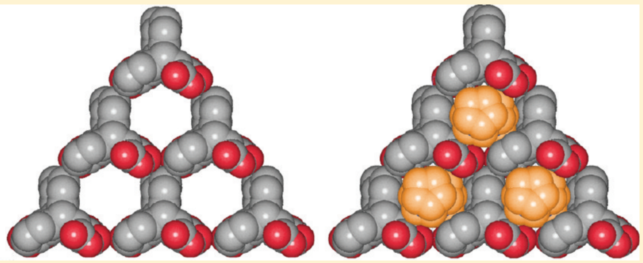
S *Supporting Information*

ABSTRACT: The novel organic−organometallic crystalline compounds $[(\eta^5\text{-}C_5H_5)_2Co][(\textit{cis}\text{-deccaH})(\textit{cis}\text{-deccaH}_2)]$ (**1**), $[(\eta^5\text{-}C_5H_5)_2Co][(\textit{cis}\text{-deccaH})(\textit{cis}\text{-deccaH}_2)]\cdot H_2O$ (**2**), $[(\eta^5\text{-}C_5H_5)_2Co][\textit{trans}\text{-deccaH}]$ (**3**), $[(\eta^5\text{-}C_5H_5)_2Co][(\textit{trans}\text{-deccaH})(\textit{trans}\text{-deccaH}_2)]$ (**4**), $[(\eta^5\text{-}C_5Me_5)_2Co][\textit{cis}\text{-deccaH}]$ (**5**), $[(\eta^5\text{-}C_5Me_5)_2Co][\textit{trans}\text{-deccaH}]\cdot 4H_2O$ (**6**), and $[(\eta^6\text{-}C_6H_6)_2Cr][\textit{trans}\text{-deccaH}]$ (**7**) have been prepared by direct reaction of neutral $[(\eta^5\text{-}C_5H_5)_2Co]$, $[(\eta^5\text{-}C_5Me_5)_2Co]$, and $[(\eta^6\text{-}C_6H_6)_2Cr]$ with the organic compounds *cis*-9,10-dihydroanthracene-9,10-*α*,*β*-succinic acid anhydride and *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (*cis*-decca and *trans*-deccaH$_2$, respectively). The organic building blocks have been chosen because of their three-stem star-like shape and the difference in hydrogen-bonding capacity. It is shown that the formation of a honeycomb-type anionic arrangement around the organometallic cations does not require the assistance of strong hydrogen-bonding interactions. Depending on the stoichiometric ratio and on the presence of water molecules, rectangular and layered crystal packings are also obtained.



■ INTRODUCTION

Making crystals by design is the paradigm of crystal engineering, an area of solid-state chemistry that encompasses molecular crystals and materials.[1] The assembly of building blocks into frameworks with predefined architectural (hence functional) features requires *control* over the interactions that are chosen to glue together the molecular or ionic components. It is unquestionable that, although the attention of researchers has been and is attracted by the whole range of possible supramolecular interactions, the hydrogen bond has taken the lion's share in crystal engineering studies.[2] The role of strong $\pi-\pi$ stacking interactions in the stabilization of homochiral, helical metal−organic frameworks has also been recently explored.[3] The number of papers dealing with hydrogen-bonded organic, inorganic, and organometallic building blocks is very large and still increasing. The reason for this interest stems from the potential applications of organometallic and metal−organic frameworks in diverse areas such as gas storage[4] and sensing,[5] but also catalysis[6] and separations,[7] among others.

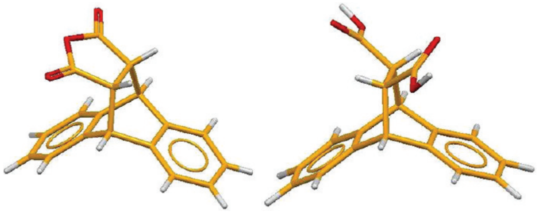
We have contributed with a number of studies dealing with hydrogen-bonded networks formed by organic or inorganic molecules and ions *templated* by organometallic sandwich cations such as $[Co(\eta^5\text{-}C_5H_5)_2]^+$, $[Cr(\eta^6\text{-}C_6H_6)_2]^+$, $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$, and $[Co(\eta^5\text{-}C_5Me_5)_2]^+$.[8−10] In all these cases the design criterion was based on the idea of *confining* all strong donor/acceptor hydrogen-bonding groups on the organic or inorganic (usually anionic) networks while *excluding* the organometallic fragments (usually cationic) from the direct participation in the hydrogen bonds. This strategy has led to hydrogen-bonded superstructures, whose topology depends on the size, shape, number, and geometry of the −OH/−COOH/COO$^-$ groups *around* the cationic sandwich. The regular cylindrical shape of these cations appeared to play a role in directing the assembly of the anionic frameworks, also with the participation of C−H···O interactions between the acceptor sites on the networks and the C−H groups protruding from the complex surface.[11] The relevance of interanionic hydrogen bonds sustained by the presence of nonparticipating cations (such as the organometallic sandwiches) has also been addressed by computational studies.[12] Early examples of this strategy are the compounds $[Co(\eta^5\text{-}C_5H_5)_2][(\text{D,L-taH})\cdot(\text{D,L-taH}_2)]$ and $[Co(\eta^5\text{-}C_5H_5)_2][\text{L-taH}]$, which were obtained with D,L- and L-tartaric acid (D,L-taH$_2$ and L-taH$_2$) respectively.[13] With oxalic acid (oxaH$_2$), compounds $[Fe(\eta^5\text{-}C_5Me_5)_2][(\text{oxaH})(\text{oxaH}_2)_{0.5}]$ and $[Cr(\eta^6\text{-}C_6H_6)_2][\text{oxaH}]\cdot H_2O$ were prepared,[14] while compounds $[Cr(\eta^6\text{-}C_6H_6)_2][\text{sqaH}]$ and $\{[Cr(\eta^6\text{-}C_6H_6)_2]\}_2[\text{sqa}]\cdot 6H_2O$ were prepared with squaric acid (sqaH$_2$).[15] With phthalic (paH$_2$) and terephthalic acids (tpaH$_2$) the compounds $\{[Co(\eta^5\text{-}C_5H_5)_2]\}_4[(\text{paH}_2)(\text{pa})]\cdot 4H_2O$, $[Cr(\eta^6\text{-}C_6H_6)_2][(\text{paH})(\text{paH}_2)]$, and $\{[Co(\eta^5\text{-}C_5H_5)_2]\}_2[\text{tpa}]\cdot 6H_2O$ were prepared,[16] while with trimesic acid (tmaH$_3$) $[Co(\eta^5\text{-}C_5H_5)_2][(\text{tmaH}_2)(\text{tmaH}_3)]\cdot 2H_2O$ was obtained,[17] and with R-binaphtol (R-bnH$_2$) were prepared $[Co(\eta^5\text{-}C_5H_5)_2][(\text{R-bnH})(\text{RbnH}_2)]$, and $[Co(\eta^5\text{-}C_5H_5)_2][(\text{R-bnH})(\text{R-bnH}_2)_{0.5}]$.[18,19]

In this paper we report an extension of these studies aimed at understanding the relationship between hydrogen-bonding capability and *shape* of the building blocks and how the shape

Received: September 6, 2011
Published: February 13, 2012

of the sandwich cation may act as a template for the aggregation of monoanions, all containing carboxylic and carboxylate groups, in 3-D networks. In the cases discussed herein the hydrogen-bonding interaction is confined either *within* the discrete units (0-D bricks) or between ions in the formation of 1-D stripes and channels, while the global architecture depends on *shape recognition* between building blocks. In other words, we attempt to address the question of whether the absence of extramolecular hydrogen-bonding capacity because of the formation exclusively of intramolecular bonds of no hydrogen-bonding capacity within organic dicarboxylic acids or anhydrates would lead, in the presence of the same sandwich cations as used in all cases referred to above, to different architectures. To this end we have selected and synthesized[20] two organic building blocks, namely, the dicarboxylic acid *trans*-9,10-dihydroethanoanthracene-11,12-dicarboxylic acid (*trans*-deccaH_2) and the anhydrate *cis*-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (*cis*-decca). Sketches are provided in Scheme 1. Upon hydrolysis, the latter generates the monoanion *cis*-9,10-dihydro-9,10- ethanoanthracene-11-carboxylate-12-carboxylic acid (*cis*-deccaH)$^-$.

Scheme 1. (Left) 9,10-Dihydroanthracene-9,10-α,β-succinic Acid Anhydride;[a] (Right) *trans*-9,10-Dihydroethanoanthracene-11,12-dicarboxylic Acid (*trans*-deccaH_2)



[a] We name the corresponding *cis*-acid as *cis*-deccaH_2.

In order to promote assembly around the organometallic cations, a combination of redox and acid−base processes are exploited. More specifically the spontaneous oxidation by oxygen of the neutral complexes cobaltocene, decamethyl cobaltocene, and bisbenzene chromium generates the strongly basic anion O_2^-, which is able to fully or partially deprotonate the polyprotic acids, depending on the stoichiometric ratio. Since the oxidation products, namely, the cations $[(\eta^5\text{-}C_5H_5)_2Co]^+$, $[Co(\eta^5\text{-}C_5Me_5)_2]^+$, and $[(\eta^5\text{-}C_6H_6)_2Cr]^+$, are not suitable for coordination by the $-COO^-$ groups, self-assembly of the neutral or deprotonated polycarboxylic acid moieties is promoted.

■ RESULTS AND DISCUSSION

Table 2 summarizes chemical information for the compounds part of this study. A brief description of the salient structural features will be provided in the following.

Table 1

formula	no.
$[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-}deccaH)(cis\text{-}deccaH_2)]$	1
$[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-}deccaH)(cis\text{-}deccaH_2)]\cdot H_2O$	2
$[(\eta^5\text{-}C_5H_5)_2Co][trans\text{-}deccaH]$	3
$[(\eta^5\text{-}C_5H_5)_2Co][(trans\text{-}deccaH)(trans\text{-}deccaH_2)]$	4
$[(\eta^5\text{-}C_5Me_5)_2Co][cis\text{-}deccaH]$	5
$[(\eta^5\text{-}C_5Me_5)_2Co][(trans\text{-}deccaH)]\cdot 4H_2O$	6
$[(\eta^6\text{-}C_6H_6)_2Cr][(trans\text{-}deccaH)]$	7

The anhydrous $[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-}deccaH)(cis\text{-}deccaH_2)]$ (**1**) and the monohydrate $[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-}deccaH)(cis\text{-}deccaH_2)]\cdot H_2O$ (**2**) crystalline salts share similar features and will be discussed together. In both crystalline **1** and **2** a neutral diacid molecule and a monodeprotonated unit interact via an $O(H)_{COOH}\cdots O_{COO^-}$ hydrogen bond [O···O distances 2.604(2) and 2.691(3) Å for **1** and **2**, respectively], thus forming the supramolecular anion $[(cis\text{-}deccaH)(cis\text{-}deccaH_2)]^-$ shown in Figure 1. These supramolecular anions are all connected via intermolecular hydrogen bonds of the kind $O(H)_{COOH}\cdots O_{COO^-}$ [O···O distances 2.595(2), 2.666(3), and 2.619(3) Å for **1** and **2**, respectively], originating tape motifs that extend along the crystallographic *a*-axis, as shown in Figure 2. The two moieties

Table 2. Crystal Data and Details of Measurements for Compounds 1−7

	1	2	3	4	5	6	7
formula	$C_{46}H_{37}O_8Co$	$C_{46}H_{39}O_9Co$	$C_{28}H_{23}O_4Co$	$C_{46}H_{37}O_8Co$	$C_{76}H_{86}O_8\ Co_2$	$C_{38}H_{51}O_8Co$	$C_{30}H_{25}O_4Cr$
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pnma*	*Cc*	$P2_1/n$	$P\bar{1}$	$C2/c$	*Cc*
Z	2	4	4	4	2	4	4
a (Å)	6.9519(2)	12.948	15.9614(9)	9.446(2)	12.5536(6)	14.0376(7)	16.3726(9)
b (Å)	8.8643(4)	32.013	9.8616(5)	22.886(4)	14.6337(7)	19.4515(6)	9.9754(6)
c (Å)	30.6884(9)	9.058	14.7153(9)	17.238(3)	17.4280(8)	14.9838(7)	14.5407(8)
α (deg)	87.744(3)	90	90	90	88.839(4)	90	90
β (deg)	87.644(2)	90	105.083(7)	100.653(18)	89.410(4)	118.555(6)	104.215(6)
γ (deg)	77.553(3)	90	90	90	79.904(4)	90	90
fw	776.69	794.70	481.39	776.69	1245.31	693.72	501.50
V (Å^3)	1844.2(1)	3754.6	2236.5(2)	3662(1)	3151.32(1)	3593.7(3)	2302.1(2)
D_{calc} (Mg/m^3)	1.399	1.406	1.433	1.409	1.312	1.286	1.447
μ (mm^{-1})	0.523	0.517	0.801	0.527	0.584	0.528	0.534
no. of collected reflns	40 270	27 427	5109	13 743	25 385	10 720	17 557
no. of indep reflns	8892	3914	3042	7207	14 115	4063	7472
R1[on F_o^2, $I > 2\sigma(I)$]	0.0543	0.1415[a]	0.0412	0.0524	0.0909	0.0643	0.0487
wR2 (all data)	0.1091	0.4494	0.0833	0.1011	0.2633	0.1798	0.0941
T (K)	293	293	293	293	150	293	293

[a] Crystal data for this compound were not of high quality; part of the reason is probably the heavy disorder shown by the structure (see above).

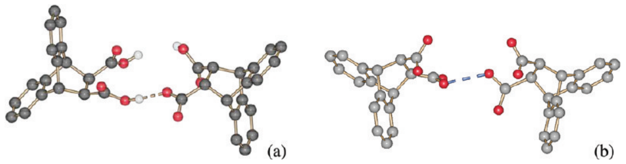


Figure 1. (a) Ball-and-stick representation of the supramolecular anion $[(cis\text{-deccaH})(cis\text{-deccaH}_2)]^-$ in crystalline **1** and **2** (only one of the possible images due to $COOH/COO^-$ disorder is shown here for **2**). H_{CH} is omitted for clarity.

are oriented differently with respect to each other within the two supramolecular anions (Figure 1); this is probably a consequence of the presence of one water molecule in **2**, which participates in the hydrogen bonds along the tape (Figure 2b).

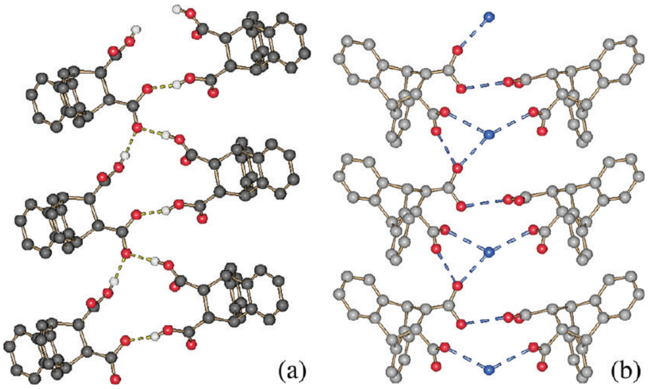


Figure 2. Ball-and-stick representation of the hydrogen-bonded tapes extending along the crystallographic *a*-axis in (a) anhydrous (**1**) and (b) monohydrated (**2**) $[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-deccaH})(cis\text{-deccaH}_2)]\cdot H_2O$ (only one of the possible images due to $COOH/COO^-$ groups disorder is shown here for **2**). Blue spheres in **2** represent water molecules. H_{CH} atoms are omitted for clarity.

One of the two COO(H) groups on the two moieties in **2** (which are related by symmetry) is affected by disorder over two positions; only one of the possible images of the supramolecular anion is shown in both Figures 1b and 2b.

The tapes are interlocked, taking advantage of the shape factor: the aromatic rings belonging to adjacent tapes are juxtaposed, so that geometrical complementarity is satisfied; no π-stacking interactions, though, are present, as in **1** and **2** the distance between the phenyl groups is 3.7 and 3.9 Å, respectively, therefore much larger than the one usually associated with π-stacking interactions[21] (see also Figure 3). This is not surprising, as the interacting dimers are both negatively charged; that is, their interaction has to be repulsive.

The tape interlocking generates walls and channels, in which the cations are accommodated in infinite piles that run along the *a*-axis (see Figure 4). In compound $[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-deccaH})(cis\text{-deccaH}_2)]\cdot H_2O$ (**2**), which is affected by orientational disorder of the cobalticinium moieties, the channels are wider and accommodate the disordered cations with their molecular axes perpendicular to the channel direction (see Figure 4b).

Crystallization in the presence of one equivalent or an excess (two equivalents) of anhydride invariably results in the formation of **2**, and it has not been possible, so far, to obtain a salt in which the neutral form of the acid is absent.

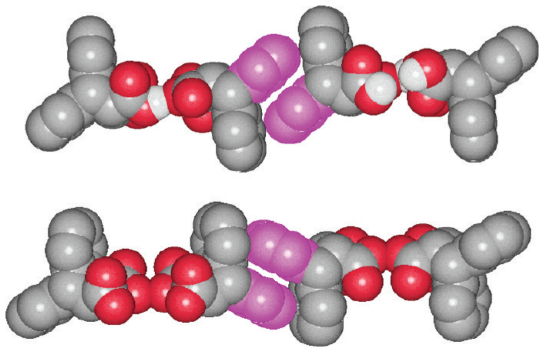


Figure 3. Space-filling representation of the juxtaposition of phenyl groups on adjacent tapes in **1** (top) and **2** (bottom). H_{CH} atoms are omitted for clarity.

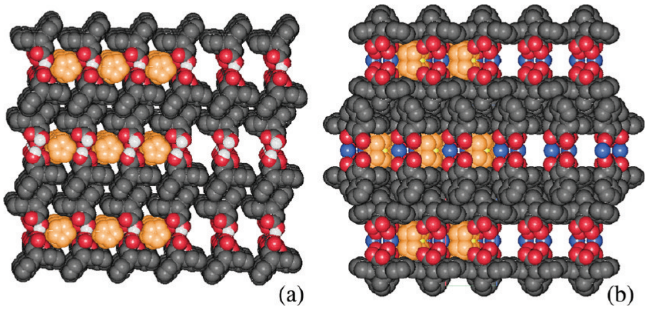


Figure 4. Projections along the crystallographic *a*-axis of the crystalline packing in **1** (a) and **2** (b); the walls and channels generated via tape interlocking are filled with the $[(\eta^5\text{-}C_5H_5)_2Co]$ cations. On the right side of each figure the cations (carbon atoms in orange) have been artificially removed, to show the anionic superstructures; H_{CH} atoms are omitted for clarity. The cations in **2** are disordered over two equivalent positions.

In the crystal architecture of $[(\eta^5\text{-}C_5H_5)_2Co][(trans\text{-deccaH})]$ (**3**) the organic superstructure recalls a honeycomb scaffold with large and almost hexagonal channels extending along the *c*-axis. The channels are occupied by columnar piles of organometallic cations, as represented in Figure 5.

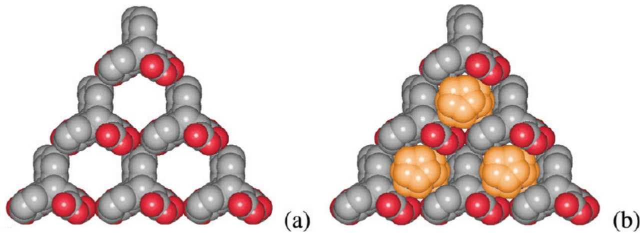


Figure 5. (a) Space-filling representation of the channels formed by the $[trans\text{-deccaH}]^-$ anions in crystalline **3**; (b) the channels are accommodating the cobalticinium piles extending along the *c*-axis. H_{CH} atoms are omitted for clarity.

The carboxylic and carboxylate groups do not participate in significant interactions between the anions, but are involved in a short intramolecular hydrogen bond ($O_{COO^-}\cdots O_{COOH}$ = 2.473(6) Å; see Figure 6); in this respect the system behaves quite differently from other geometrically related systems, i.e., tartaric, terephthalic, etc.,[13,16] in which intermolecular hydrogen bonds are responsible for the generation of the 3-D superanion networks. Contrary to what was observed earlier in the case of the adduct between cobalticinium and D,L-tartaric acid, for

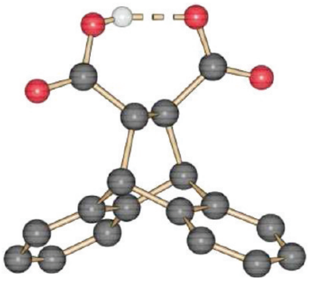


Figure 6. Intramolecular hydrogen bond observed in the (*trans*-deccaH)$^-$ anion. H_{CH} is omitted for clarity.

example, where the honeycomb superstructure is held together by interanionic hydrogen bonds, in the case of **3** it is only the combination of the shape of the cation (a cylinder) and of the anionic three-spike stars that yields the honeycomb structure. A comparison (see Figure 7) between the two packings shows the strong analogy between the two compounds.

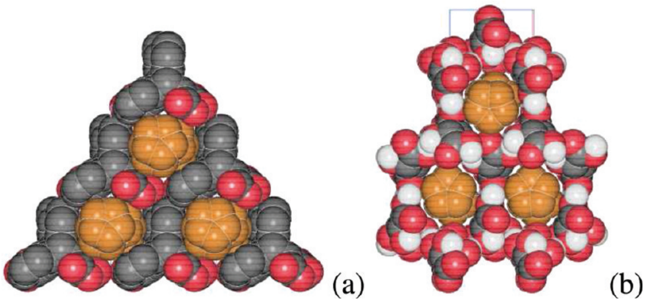


Figure 7. (a) Comparison of the packings for crystalline **3** (a) and $[Co(\eta^5\text{-}C_5H_5)_2][(\text{D,L-taH})\cdot(\text{D,L-taH}_2)]$ (b), showing how the same honeycomb motif is generated only by the matching shapes of cations and anions in **3**, while it is sustained by the presence of interanionic hydrogen bonds in $[Co(\eta^5\text{-}C_5H_5)_2][(\text{D,L-taH})\cdot(\text{D,L-taH}_2)]$. H_{CH} atoms are omitted for clarity.

If the cobalticinium cation $[(\eta^5\text{-}C_5H_5)_2Co]^+$ is crystallized in the presence of two equivalents of *trans*-deccaH$_2$, the cocrystalline derivative $[(\eta^5\text{-}C_5H_5)_2Co][(trans\text{-deccaH})(trans\text{-deccaH}_2)]$ (**4**) is obtained, analogously to what is observed in the case of the *cis*-decca derivative (**2**). In crystalline $[(\eta^5\text{-}C_5H_5)_2Co][(trans\text{-deccaH})(trans\text{-deccaH}_2)]$ (**4**) we observe the presence of supramolecular anions held together by intermolecular hydrogen bonds ($O_{COO^-}\cdots O_{COOH}$ = 2.603(6) Å). The superanions, in turn, participate in a hydrogen-bonded network ($O_{COO^-}\cdots O_{COOH}$ = 2.557(6)−2.759(7) Å) that yields connected cavities along the *a*-axis, as shown in Figure 8. Two cobalticinium cations fit within each cavity with their axes perpendicular to the *a*-axis direction.

In the case of compound $[(\eta^5\text{-}C_5Me_5)_2Co][cis\text{-deccaH}]$ (**5**) there are two independent cations and two anions of (*cis*-deccaH)$^-$ in the asymmetric unit. The decamethylcobalticinium cations are much more demanding in terms of space with respect to the smaller cobalticinium ones. This results in a different superstructure consisting of adjacent cationic $[(\eta^5\text{-}C_5Me_5)_2Co]^+$ piles forming an almost layered packing alternated by organic anionic planes. In addition to this, the carboxylic/carboxylate functions, localized on the anion, form very short intramolecular hydrogen bonds [$O_{COOH}\cdots O_{COO^-}$ = 2.395(8) and 2.384(10) Å]. See Figure 9.

In the crystal structure of compound $[(\eta^5\text{-}C_5Me_5)_2Co][(trans\text{-deccaH})]\cdot 4H_2O$ (**6**) we observe the presence of an R4 cyclic water tetramer (shown in blue in Figure 10)[22] held together by hydrogen bonds [$O_w\cdots O_w$ distances in the range 2.882(10)−2.992(8) Å, $O_w\cdots O_w\cdots O_w$ angles in the range 101.7(4)−103.9(7)° and 71.1(5)−74.0(6)°], in a sort of "butterfly" conformation (dihedral angle ca. 151°). To the best of our knowledge this conformation is unusual because (i) it strongly deviates from planarity and (ii) two angles are much smaller than those usually observed for these kinds of clusters. The majority of water tetramers either predicted[23] or observed[24] are planar or quasi-planar, with angles ranging from ca. 90° to ca. 125°. In crystalline **6** H-atoms could not be directly located from a Fourier difference map, but a possible distribution is presented in Figure 10: as it can be seen, the small $O_w\cdots O_w\cdots O_w$ angles are possible because the tetramer is also hydrogen bonded to the anion [$O_w\cdots O_{COO^-/COOH}$ distances 3.025(4) and 2.788(6) Å], and no acute H−O−H angles are actually present.

This tetramer, in turn, interacts through a net of hydrogen bonds, with the [*trans*-deccaH]$^-$ monoanion. The small water clusters act as "reinforcement" units along the anionic chain [$O_{COOH}\cdots O_{COO}{}^-$ = 2.471(2) Å; $O_w\cdots O_{COOH}$ = 2.987(5) Å], as it is shown in Figure 10.

Yellow spheres represent H_{water} and H_{COOH} atoms. Blue solid lines represent intermolecular H-bonds involving water molecules; red solid lines represent anion···anion H-bonds: here the H-atom has been arbitrarily assigned to one of the COO groups.

As it can be seen in Figure 11, these infinite chains are arranged to form almost hexagonal channels that run along the [1 0 1] direction, which are filled by stacks of $[(\eta^5\text{-}C_5Me_5)_2Co]^+$ cations. In projection the overall structure is closely reminiscent of that of compound **3**.

The role of the water molecules may be that of enlarging, via hydrogen bonds formation, the size of the channels formed by

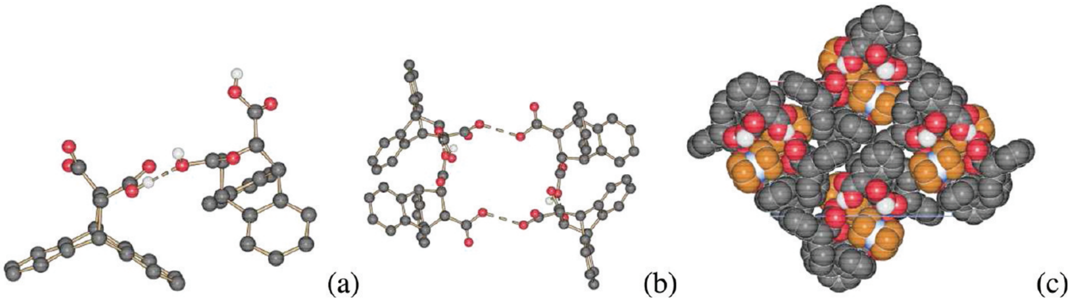


Figure 8. (a) Ball-and-stick representation of the supramolecular anion $[(cis\text{-deccaH})(cis\text{-deccaH}_2)]^-$ in crystalline **4**; (b) hydrogen-bonding interaction network and (c) how the cations fit inside the niches, both viewed along the *a*-axis. H_{CH} atoms are omitted for clarity.

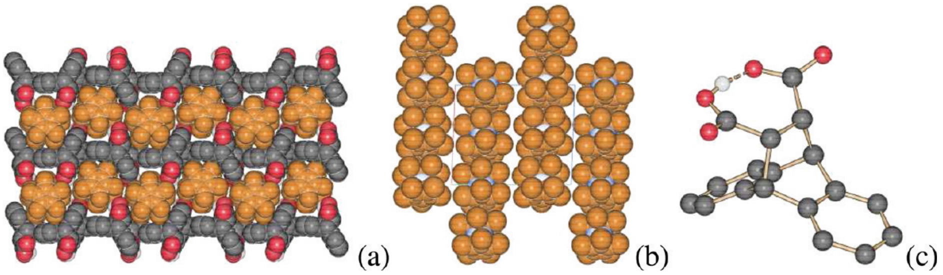


Figure 9. (a) Space-filling representation of the layered structure of compound $[(\eta^5\text{-}C_5Me_5)_2Co][\textit{cis}\text{-deccaH}]$ (**5**) viewed along the *b*-axis; (b) projection along the *a*-axis of the cationic piles formed by the decamethylcobalticinium cations; and (c) the intramolecular hydrogen bond observed in the $(\textit{cis}\text{-deccaH})^-$ anion. H_{CH} atoms are omitted for clarity.

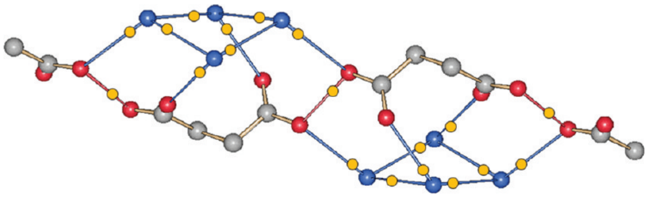


Figure 10. Ribbon formed by water tetramers and $(\textit{trans}\text{-deccaH})^-$ anions in crystalline **6**. For the sake of clarity only the HOOC−C−C-COO^- fragments are shown for the anions. H_{CH} atoms are omitted for clarity.

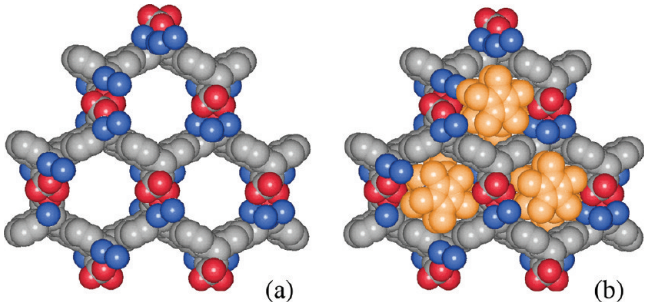


Figure 11. (a) Projection along the [1 0 1] direction of the channels formed by the anions $(\textit{trans}\text{-deccaH})^-$ and the water tetramers in solid **6**; (b) view along the same direction filled by cationic stacks. H atoms omitted for clarity.

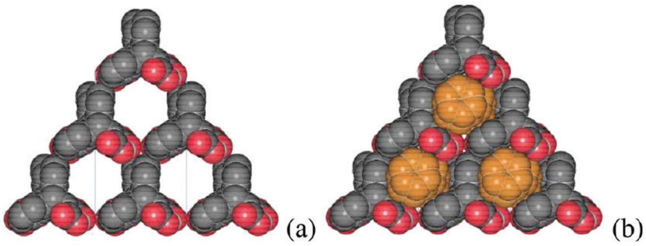


Figure 12. (a) Space-filling representation of the honeycomb framework formed by the $[\textit{trans}\text{-deccaH}]^-$ anions; (b) space-filling representation of how the cationic piles fit inside the channels extending along the *c*-axis. H_{CH} atoms are omitted for clarity.

the organic anions, thus allowing the bulky cations to fit inside. In the absence of water molecules the $[\textit{trans}\text{-deccaH}]^-$ anions could not fold around the $[(\eta^5\text{-}C_5Me_5)_2Co]^+$ cations, as observed in compound **3**.

Crystalline $[(\eta^6\text{-}C_6H_6)_2Cr][(\textit{trans}\text{-deccaH})]$ (**7**), the only derivative of bis-benzene chromium reported in this paper, provides a further example of how a hexagonal honeycomb-type arrangement of the organic moieties *unsustained* by strong hydrogen bonds can be organized around the organometallic cations. The packing is shown in Figure 12 and ought to be compared with those shown above in Figures 7 and 11. The intramolecular hydrogen bond within the $[\textit{trans}\text{-deccaH}]^-$ monoanion is comparable to those observed in the other compounds of this series ($O_{COOH}\cdots O_{COO^-}$ 2.457(3) Å).

CONCLUSIONS

In previous studies we have reported several examples of organic−organometallic superstructures obtained with the idea that *confinement* of all strong donor/acceptor hydrogen-bonding groups on the organic or inorganic networks would lead to spontaneous self-assembly of the anions in the honeycomb or other porous structures that could accommodate the organometallic cations $[Co(\eta^5\text{-}C_5H_5)_2]^+$, $[Cr(\eta^6\text{-}C_6H_6)_2]^+$, $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$, and $[Co(\eta^5\text{-}C_5Me_5)_2]^+$. The regular cylindrical shape of these cations appeared to play a role in directing the assembly of the anionic frameworks, also with the participation of C−H···O interactions between the acceptor −COOH/COO^- sites on the networks and the C−H groups protruding from the complex surface.[11]

In this paper we have shown that, although the "hydrogen-bonding confinement" strategy is essentially correct and can be extended to more complex dicarboxylic acids, such as *cis*-9,10-dihydroanthracene-9,10-*α*,*β*-succinic acid anhydride (*cis*-decca) and *trans*-9,10-dihydro-9,10- ethanoanthracene-11,12-dicarboxylic acid (*trans*-deccaH_2), leading to novel architectures, the hydrogen bond *is not* the key structure-directing interaction. In compounds **1**, **2**, and **4**, in which the organometallic/organic stoichiometric ratio is 1:2, the hydrogen-bonding donor/acceptor ratio is larger compared to that in compounds **3**, **5**, **6**, and **7**, formation of interanionic hydrogen bonds is possible, and the resulting structures show extended network patterns and self-assembly around the cations of the type observed before. In compounds **3**, **5**, **6**, and **7**, where deprotonation leads to intramolecular hydrogen bonds, hence forbids interanionic hydrogen bonding, alternative solutions are adopted. In compounds **3** and **7** the three-stem star-like shape of the anions *takes the lead* and generates the observed close-packing arrangement thanks to a perfect match in terms of size and shape with the small sandwich organometallic cations $[Co(\eta^5\text{-}C_5H_5)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_6)_2]^+$. Compounds **5** and **6**, on the other hand, provide a sort of proof of concept because the larger shape of the cations does not allow an equivalent efficient arrangement; hence the crystal structure of **5** adopts a columnar organization, while **6** drags in four water molecules as space fillers to generate a honeycomb arrangement similar to that in **3** and **7**.

The use of organometallic building blocks in the preparation of two-dimensional (2-D) and three-dimensional (3-D) framework materials has obvious potential; yet, in spite of the large efforts in crystal engineering, it remains an area that is relatively underdeveloped. The observation that the same topology can be attained by selecting molecular/ionic components on the basis of their shape, rather than their supramolecular bonding capacity, might affect the way we look at the engineering of metal−organic frameworks. All in all, the series of compounds examined in this study shows how difficult it still is to "make crystals by design", because of the complex interplay of different and not always converging factors/interactions such as hydrogen bonding, shape, charge balance, and space filler solvent molecules in the formation of stable crystalline aggregates. However, the analysis of differences between crystal structures obtained with structurally similar molecules may indicate ways to obtain polymorphs of the same compound or ways to interconvert crystal forms by adding/removing solvent molecules. A study of this type is under way.

EXPERIMENTAL SECTION

The neutral compound $[(\eta^5\text{-}C_5H_5)_2Co]$, bought from Alfa-Aesar, and all reactants and reagents, purchased from Sigma-Aldrich, were used without further purification. Reagent-grade solvents and bidistilled water were used. ^{1}H NMR spectra were recorded on a Varian Mercury400, and chemical shifts of ^{1}H NMR signals were expressed in parts per million (δ_H) using internal standard TMS ($\delta_H = 0.00$).

Synthesis of *trans*-deccaH$_2$. Dioxane (25 mL) was added to a mixture of fumaric acid (0.645 g, 5.6 mmol) and anthracene (3.0 g, 17 mmol). After refluxing for 3 days at 104 °C the solvent was removed by rotary evaporation under reduced pressure. A saturated solution (100 mL) of Na_2CO_3 was added, and the mixture was stirred for half a day. The mixture was filtered (in order to remove the unreacted anthracene), and concentrated HCl was added to the clear solution to pH = 1. The solid product was recovered by filtration of the hot solution. Yield = 90%. Mp = 251−252 °C (lit. mp = 252.5 °C). Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.12; H, 4.34. ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ_H: 12.52 (s, 2H, COOH), 7.065−7.371 (m, 8H, aromatic CH), 4.707 (s, 2H, methine CH) and 3.549 (s, 2H, methine CH).

Synthesis of *cis*-decca. *p*-Xylene (30 mL) was added to a mixture of maleic anhydride (0.346 g; 5.3 mmol) and anthracene (0.62 g; 3.56 mmol). The mixture was refluxed at 135 °C for 1 h. The resulting solution was allowed to cool to room temperature, yielding a white powder, which was removed by filtration and washed with a few milliliters of ethyl acetate. Solid *cis*-decca was recrystallized from hot ethyl acetate. Colorless prismatic crystals formed upon cooling the ethyl acetate solution. Yield = 80%. Mp = 262 °C (lit. mp = 262−263 °C). Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.36; H, 4.54. ^{1}H NMR (400 MHz, CDCl$_3$-d_1, TMS) δ_H: 7.41 (m, 8H, aromatic CH), 4.87 (s, 2H, methine CH) and 3.55 (s, 2H, methine CH).

Synthesis of $[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-}deccaH)(cis\text{-}deccaH_2)]$ (1). A 30 mg (0.16 mmol) amount of $[(\eta^5\text{-}C_5H_5)_2Co]$ was suspended in ca. 15 mL of nitromethane. Oxygen was bubbled into the suspension until a dark yellow solution was obtained. Then 44 mg (0.16 mmol) of *trans*-deccaH$_2$ was added to the solution, which was kept under stirring for two hours. The solution was then filtered, to remove unreacted material, and kept in the dark. Pale brown crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at RT. Anal. Calcd for $C_{46}H_{37}O_8Co$: C, 71.13; H, 4.80. Found: C, 71.33; H, 4.92.

Synthesis of $[(\eta^5\text{-}C_5H_5)_2Co][(cis\text{-}deccaH)(cis\text{-}deccaH_2)]\cdot H_2O$ (2). A 30 mg (0.16 mmol) sample of $[(\eta^5\text{-}C_5H_5)_2Co]$ was suspended in ca. 10 mL of water. Oxygen was bubbled into the suspension until a bright yellow solution was obtained. Then 44 mg (0.16 mmol) of *trans*-deccaH$_2$ was added to the solution, which was kept under stirring for two hours. The solution was then filtered, to remove unreacted material, and kept in the dark. Recrystallization of the bright yellow powder from water yielded single crystals suitable for X-ray diffraction. Anal. Calcd for $C_{46}H_{39}O_9Co$: C, 69.52; H, 4.95. Found: C, 69.82; H, 4.67.

Synthesis of $[(\eta^5\text{-}C_5H_5)_2Co][trans\text{-}deccaH]$ (3). A 30 mg (0.16 mmol) portion of $[(\eta^5\text{-}C_5H_5)_2Co]$ was suspended in ca. 15 mL of nitromethane and oxidized by bubbling oxygen into the suspension until a dark yellow solution was obtained. Then 47 mg (0.16 mmol) of *trans*-deccaH$_2$ were added to the solution, which was kept under stirring for two hours, and the solution was filtered, to remove unreacted material, and kept in the dark. Pale brown crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at RT. Anal. Calcd for $C_{28}H_{23}O_4Co$: C, 69.71; H, 4.81. Found: C, 69.54; H, 4.43.

Synthesis of $[(\eta^5\text{-}C_5H_5)_2Co][(trans\text{-}deccaH)(trans\text{-}deccaH_2)]$ (4). The same procedure used for the synthesis of **1** was repeated here, but using two equivalents of *trans*-deccaH$_2$ (94 mg; 0.31 mmol). Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at RT. Solid **4** can also be obtained directly in the solid state by manually grinding solid **3** for 10 min with one equivalent of *trans*-deccaH$_2$. Anal. Calcd for $C_{46}H_{37}O_8Co$: C, 71.13; H, 4.80. Found: C, 71.45; H, 4.96.

Synthesis of $[(\eta^5\text{-}C_5Me_5)_2Co][cis\text{-}deccaH]$ (5). A 36.5 mg (0.11 mmol) amount of $[(\eta^5\text{-}C_5Me_5)_2Co]$ was suspended in ca. 20 mL of nitromethane. Oxygen was bubbled into the suspension until a dark yellow solution was obtained. Then 26.1 mg (0.11 mmol) of *cis*-decca was added to the solution, which was kept under stirring for two hours; the solution was then filtered, to remove unreacted material, and kept in the dark. Pale brown crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at RT. Anal. Calcd for $C_{38}H_{43}O_4Co$: C, 73.30; H, 6.96. Found: C, 73.11; H, 6.74.

Synthesis of $[(\eta^5\text{-}C_5Me_5)_2Co][trans\text{-}deccaH]\cdot 4H_2O$ (6). A 40.7 mg (0.12 mmol) sample of $[(\eta^5\text{-}C_5Me_5)_2Co]$ was suspended in ca. 15 mL of bidistilled water. The suspension was stirred until a bright yellow solution was obtained. Then 37 mg (0.13 mmol) of *trans*-deccaH2 was added to the solution, which was kept under stirring for two hours; the solution was then filtered, to remove unreacted material, and placed in the dark. Pale brown crystals suitable for X-ray diffraction were obtained by slow evaporation of water at RT. Anal. Calcd for $C_{38}H_{51}O_8Co$: C, 65.69; H, 7.40. Found: C, 65.37; H, 7.31.

Synthesis of $[(\eta^6\text{-}C_6H_6)_2Cr][(trans\text{-}deccaH)]$ (7). A 20 mg (0.10 mmol) amount of $[(\eta^6\text{-}C_6H_6)_2Cr]$ was suspended in ca. 15 mL of nitromethane and oxidized by bubbling oxygen into the suspension until a dark yellow solution was obtained. Then 28 mg (0.10 mmol) of *trans*-deccaH$_2$ was added to the solution, which was kept under stirring for two hours; the solution was filtered, to remove unreacted material, and placed in the dark. Pale brown crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at RT. Anal. Calcd for $C_{30}H_{25}O_4Cr$: C, 71.85; H, 5.02. Found: C, 71.59; H, 5.35.

X-ray Diffraction. Single-crystal data for compounds **1**−**7** were collected on an Oxford X'Calibur S CCD diffractometer equipped with a graphite monochromator (Mo Kα radiation, $\lambda = 0.71073$ Å) and operating at room temperature except for compound **5**, which was collected at 150 K. Crystal data and details of measurement for all compounds are listed in Table 2. All non-hydrogen atoms were refined anisotropically; H_{OH} atoms were either directly located or added in calculated positions; H_{CH} atoms for all compounds were added in calculated positions and refined riding on their respective carbon atoms. SHELX97[25a] was used for structure solution and refinement on F^2; PLATON[25b] and SCHAKAL99[25c] were used for hydrogen bonding analysis and molecular graphics, respectively.

X-ray powder data were collected on a Philips X'Pert automated diffractometer with Cu Kα radiation. The program PowderCell[25d] was used for calculation of X-ray powder patterns on the basis of single-crystal data. The identity between bulk materials and single crystals was always verified by comparing calculated and experimental powder diffraction patterns.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Ortep drawings and CIF files for compounds **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

We thank University of Bologna and MiUR for financial support.

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