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Organometallic crystal engineering with multidentate building blocks and template guest size effect. Supra-anionic organic frameworks obtained from cyclobutane-1,2,3,4-tetracarboxylic and *trans*-acotinic acids †

Dario Braga,*[a] Oscar Benedi,[a] Lucia Maini[a] and Fabrizia Grepioni *[b]

[a] *Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy. E-mail: dbraga@ciam.unibo.it. URL: http://catullo.ciam.unibo.it*
[b] *Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 70100 Sassari, Italy. E-mail: grepioni@ssmain.uniss.it*

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The organic acids cyclobutane-1,2,3,4-tetracarboxylic $C_4H_4(CO_2H)_4$, and *trans*-acotinic acid $C_3H_3(CO_2H)_3$, have been treated in thf with the organometallic hydroxides $[Co(\eta^5\text{-}C_5H_5)_2]^+[OH]^-$, $[Co(\eta^5\text{-}C_5Me_5)_2]^+[OH]^-$, and $[Cr(\eta^6\text{-}C_6H_6)_2]^+[OH]^-$ prepared *in situ* from the oxidation of the corresponding neutral complexes, to yield the novel organic–organometallic crystalline materials $[Co(\eta^5\text{-}C_5H_5)_2]^+[C_4H_4(CO_2H)_3COO]^-$ **1**, $[Cr(\eta^6\text{-}C_6H_6)_2]^+[C_4H_4(CO_2H)_3CO_2]^-\cdot H_2O$ **2**, and $[Co(\eta^5\text{-}C_5Me_5)_2]^+[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-\cdot H_2O$ **3**. Self-assembly of the monodeprotonated organic acid $C_4H_4(CO_2H)_4$ generates supra-anionic framework structures held together by O–H···O and O–H···O$^-$ hydrogen bonds which accommodate the diamagnetic $[Co(\eta^5\text{-}C_5H_5)_2]^+$ and paramagnetic $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ cations, respectively. Crystalline **1** does not form single crystals with defined shapes but rather an "enamel" like material which grows parallel to the crystallographic *bc* plane. The same reaction between *trans*-acotinic acid and $[Co(\eta^5\text{-}C_5Me_5)_2]^+[OH]^-$generates a large honeycomb-type structure in $[Co(\eta^5\text{-}C_5Me_5)_2]^+[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-\cdot H_2O$ **3**. The effect of the size of the templating units $[Co(\eta^5\text{-}C_5H_5)_2]^+$ and $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ is discussed. The previously unknown structure of the starting material $[Co(\eta^5\text{-}C_5Me_5)_2]^+[PF_6]^-$ **4**, used for the preparation of $[Co(\eta^5\text{-}C_5Me_5)_2]^+[OH]^-$, has also been determined.

Introduction

Molecular crystal engineering is the modelling, synthesis and exploitation of crystalline materials with predefined aggregations of molecules or ions.[1] The utilisation of non-covalent bonding is the paradigm of supramolecular chemistry,[2] while periodicity and symmetry is the paradigm of the crystalline state,[3] hence molecular crystal engineering can be regarded as the way to obtain *periodical supermolecules*. The challenge is that of obtaining solids with desired arrangements of molecules and ions which can then express predefined chemical and physical properties.[4] The potentials of this research field are enormous and the interest in the development of expert synthetic strategies for the preparation of molecular solids is increasing rapidly.[5]

Cocrystallisation of organic and organometallic systems has proven to be a fruitful and reproducible method to bring within the crystal superstructure the electronic and topological features characteristic of transition metal complexes in order to obtain crystalline materials with interesting (and possibly useful) magnetic, conducting, superconducting and non-linear optical properties.[6] The leading idea is that of being able to combine the non-covalent intermolecular bonding capacity of organic molecules[7] with the co-ordination geometry, variable ionic charges, oxidation and spin states typical of organometallic complexes.[8]

The non-covalent interaction of choice is the hydrogen bond because it is directional, and its strength can easily be tuned by changing the nature of the donor/acceptor systems.[9] These attributes are of paramount importance if the (reproducible) preparation of robust materials is sought.

Our approach is based on the combination of redox and acid–base processes utilising organometallic bases and polyprotic (organic, inorganic, and organometallic) acids.[10] For instance, the oxidation by oxygen of the neutral complexes $[Co(\eta^5\text{-}C_5H_5)_2]$ and $[Cr(\eta^6\text{-}C_6H_6)_2]$ generates the strongly basic anion $O_2^{\cdot -}$ which is capable of fully or partially deprotonating, depending on the stoichiometric ratio, the polyprotic acid. Since the oxidation products, namely the cations $[Co(\eta^5\text{-}C_5H_5)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_6)_2]^+$, are not suitable for co-ordination by CO_2^- groups, self-assembly of the polycarboxylic acid is enforced with formation of one-, two- or three-dimensional superanionic framework structures around the organometallic cations. The interaction between the organic framework and organometallic cations is based on charge assisted C–H···O and O–H···O bonds. These interactions have extensively been studied and their role in controlling molecular self-assembly in the solid state is well established.[11]

In this paper we report on two distinct, but related, developments of our crystal engineering strategy: (i) the synthesis and structural characterisation of the novel crystalline materials $[Co(\eta^5\text{-}C_5H_5)_2]^+[C_4H_4(CO_2H)_3CO_2]^-$ **1**, and $[Cr(\eta^6\text{-}C_6H_6)_2]^+[C_4H_4(CO_2H)_3CO_2]^-\cdot H_2O$ **2**, obtained by using $C_4H_4(CO_2H)_4$ as a tetradentate building block; and (ii) the study of the effect of the size of the templating organometallic unit on the supramolecular organisation of the polycarboxylic *trans*-acotinic acid $C_3H_3(CO_2H)_3$ when the larger decamethylcyclo-

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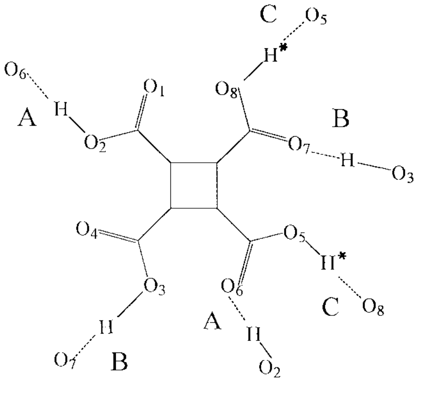
pentadienyl cobaltocenium complex $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ is used for the preparation of $[Co(\eta^5\text{-}C_5Me_5)_2]^+[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-\cdot H_2O$ **3**. The previously unknown solid state structure of the hexafluorophoshate salt of $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ **4** has also been characterised.

The paper also attempts a correlation between the structure of organometallic supersalt **1** and the macroscopic aspect of its crystalline material. The interest stems from the observation that **1** does not form crystals with well defined shapes but rather grows in the form of an enamel-like material (see below).

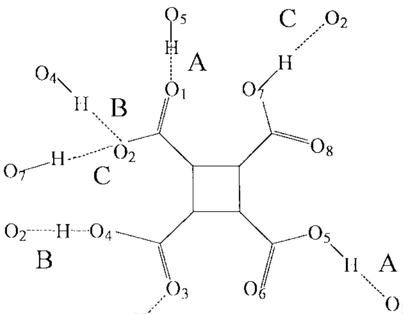
Results and discussion

Lists of bond distances and angles, as well as fully labelled pictures, have been deposited. For sake of clarity the following conventional description of hydrogen bonding structural parameters has been adopted: X(H) · · · Y (X = C or O; Y = O or F) indicates the distance between the donors C or O atoms and the acceptor O atom, (X)H · · · O indicates the distance between the donor H atom bound to X and the acceptor, while X–H · · · O indicates the angle; X–H distances have been normalised to the neutron diffraction values.

Both crystalline organometallic supersalt **1** and **2** are the product of monodeprotonation of the acid $C_4H_4(CO_2H)_4$. The most relevant hydrogen bonding parameters are schematically shown in Schemes 1 and 2. Full lists of intermolecular interactions of the O–H · · · O and C–H · · · O types have been deposited. It should be emphasised that, contrary to other crystal engineering strategies based on the formation of hydrogen bonds between anions and cations,[5] in our approach the organometallic counter ions cannot compete in hydrogen bond formation with the carboxylate anions. This has important consequences. The effect of deprotonation is twofold: not only does it deprive a potential donor (an OH group) of its proton, thus reducing the total number of donor atoms available, but also increases by one unit (the deprotonated oxygen atom) the number of acceptors. As a consequence, interanion hydrogen-bond-like $O\text{–}H^- \cdots O^-$ interactions ($O_{anion} \cdots O_{anion}$) are usually formed.[12] This is, in fact, observed in crystalline **1**, where there is a distinctly short O · · · O separation of 2.48(1) Å which well compares with other O · · · O separations in negatively charged systems, while the other hydrogen bonds in **1** are longer [2.67(1), 2.72(1) Å] and comparable to those formed by neutral carboxylic acids.[13] In **2**, on the contrary, all O · · · O separations [2.56(1), 2.57(1) Å] between carboxylate anions appear to be shorter than in neutral systems but longer than in **1**, with no specific localisation of the short interaction, the only 'long' O · · · O separation being that involving the water molecule [O9 in Scheme 2] of crystallisation. The difference between the $O_{anion} \cdots O_{anion}$ distances in **1** and **2** is intriguing. One may think, purely on the basis of the interaction metrics, that either the negative charge is more localised in **1** (on the O5/O6 system) than in **2** or that there is some static disorder of the distribution of the three remaining protons in **2** over the three CO_2H groups not involved in the bonding with water (*i.e.* excluding the O3/O4 system). A somewhat related distribution of $O_{water} \cdots O_{anion}$ and $O_{anion} \cdots O_{anion}$ bond distances has been discussed for the complexes formed by trimesic acid (1,3,5-benzenetricarboxylic acid).[14]



Scheme 1 The O–H · · · O hydrogen bond distribution around the anions in compound **1**. O · · · O distances (in Å): A 2.67(1), B 2.72(1) and C 2.48(1). The H atoms marked with * are disordered over two positions of equal occupancy.



Scheme 2 The O–H · · · O hydrogen bond distribution around the anions in compound **2**. O · · · O distances (in Å): A 2.56(1), B 2.57(1), C 2.56(1) and D 2.82(1).

A ball-and-stick representation of the anion packing in complex **1** is shown in Fig. 1(a) (projection along the *c* axis). The view allows one to appreciate that the supraanionic system presents 'niches' made of hydrogen bonded anions which surround the encapsulated cobaltocenium cations; a space filling representation of the whole system along the same direction is shown in Fig. 1(b). The interaction between the cation and the anionic organic cage is based on a large number of charge-assisted $C\text{–}H^{\delta+} \cdots O^{\delta-}$ interactions.[15]

The packing in organometallic salt **2** shows some similarity with that of **1**. The major difference is due to the presence of the water molecule. It would appear that the slight increase in size on passing from the cobaltocenium in **1** to the bis(benzene)chromium cation in **2** makes the 1 : 1 stoichiometry unfavourable. The role of the water molecule may be that of enlarging, without losing hydrogen bonding capacity, the size of the cavity made by the interlinked organic anions. A ball-and-stick projection along the *a* axis of the crystal structure of **2** is shown in Fig. 2(a), while a space filling representation along the same direction of the cations encapsulated by the organic cage is shown in Fig. 2(b). As in the case of **1**, there is a profusion of $C\text{–}H^{\delta+} \cdots O^{\delta-}$ hydrogen bonds involving the benzene ligands as donors (fourteen H · · · O separations <2.6 Å).

We were particularly intrigued by the macroscopic aspect of the crystalline material **1** because, upon crystallisation from water, it does not form well shaped single crystals but rather an 'enamel like' yellow material. We have obtained crystals suitable for the subsequent single crystal X-ray diffraction experiment (see Experimental section) by cutting out flakes of the material shown in Fig. 3(a). Fig. 3(b) shows crystalline **1** as viewed from a Leitz optical microscope with polarised light (magnification ×400). It can be appreciated how the polarised light is extinguished by the *entire* material, except for the fringes. This observation indicates that the whole layer is composed of a very large single crystal and is why *any* flake taken from the layer constitutes a well behaving (in terms of diffraction indexing and intensity) crystal. Fig. 3(c) shows the same material crystallised on a watch-glass; it can be appreciated how the tendency is to the formation of a layered structure, although on glass there are "empty islands" on the surface. Owing to the thinness of the enamel type layer, the flakes are very anisotropic in shape and can therefore easily

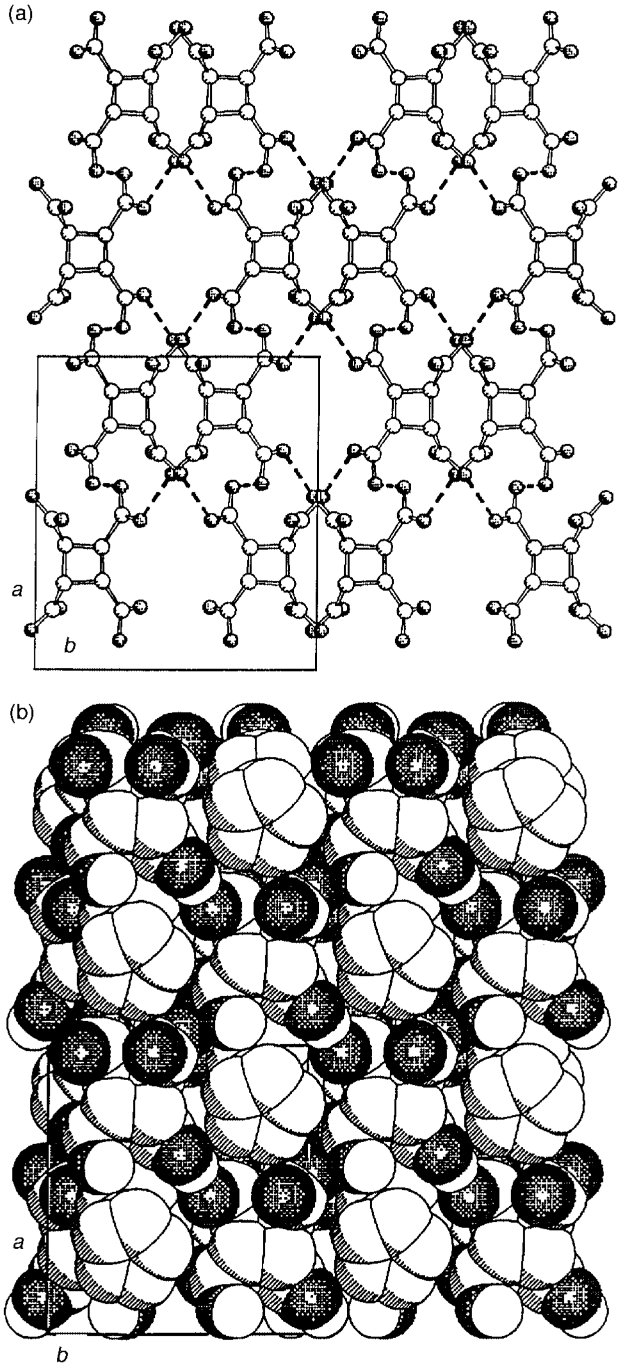


Fig. 1 (a) Ball-and-stick projection along the *c* axis of the supra-anionic network in crystalline complex **1** (filled atom spheres indicate the oxygen atoms). (b) A space filling representation of the packing around the encapsulated cobaltocenium cations; H atoms omitted for clarity.

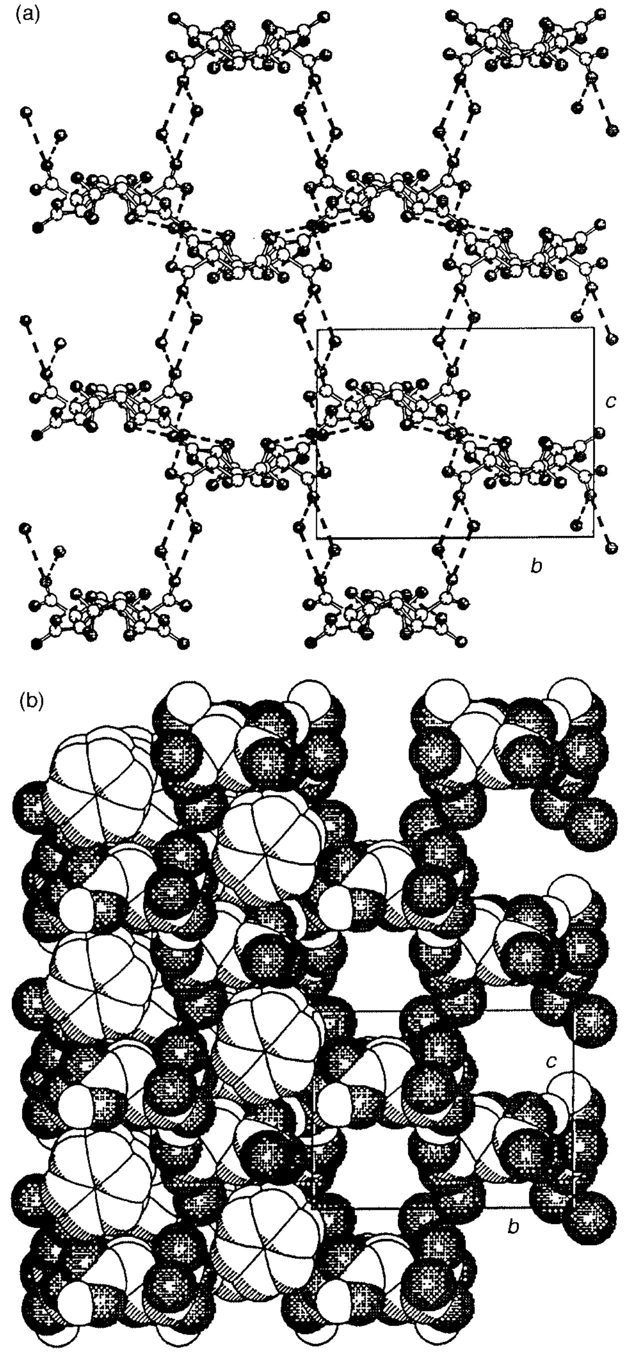


Fig. 2 (a) Projection along the *a* axis of the supra-anionic network in crystalline complex **2**. (b) Space filling representation showing how the channels in the organic cage (right-hand side) are filled by the cations (left-hand side) encapsulated within the organic cage; H atoms omitted for clarity.

be oriented on a flat camera (see Experimental section) in order to ascertain the axis of crystal growth. The growth occurs parallel to the *bc* plane.

The crystal structures of $[Co(\eta^5\text{-}C_5Me_5)_2]^+[C_3H_3(CO_2H)_2\text{-}CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-\cdot H_2O$ **3**, and that of the precursor of $[Co(\eta^5\text{-}C_5Me_5)_2]^+[PF_6]^-$ **4**, will now be discussed. All organic–organometallic supramolecular salts, synthesized so far, contain either the cobaltocenium or the bis(benzene) chromium cation, which are comparable in size. The reason for the choice of these two sandwich complexes has been discussed briefly in the Introduction: the oxidation from neutral to cationic complexes is spontaneous in both water and organic solvents and in the presence of oxygen.[16] Since the same redox behaviour as for $[Co(\eta^5\text{-}C_5H_5)_2]$ is shown by the decamethylated complex $[Co(\eta^5\text{-}C_5Me_5)_2]$,[16] we have attempted preparation of organic–organometallic crystals by following the same sequence of redox/acid–base/solubility processes by which **1** and **2** have been obtained, with the aim of *forcing* self-assembly of the deprotonated acid around the much larger templating unit provided by cation $[Co(\eta^5\text{-}C_5Me_5)_2]^+$. Unfortunately, cyclobutane-1,2,3,4-tetracarboxylic acid $C_4H_4(CO_2H)_4$, successfully employed to obtain **1** and **2**, failed to give well diffracting material when precipitated in the presence of $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ (see Experimental section), irrespective of the acid:base stoichiometric ratio. We attributed this failure to the low flexibility of the framework of $C_4H_4(CO_2H)_4$.

The *trans*-acotinic acid $C_3H_3(CO_2H)_3$ is more flexible because the C–C skeleton is not closed in a tense ring and could be a good candidate for self-assembly around a larger cation. Indeed, a (somewhat poor) crystalline material could be

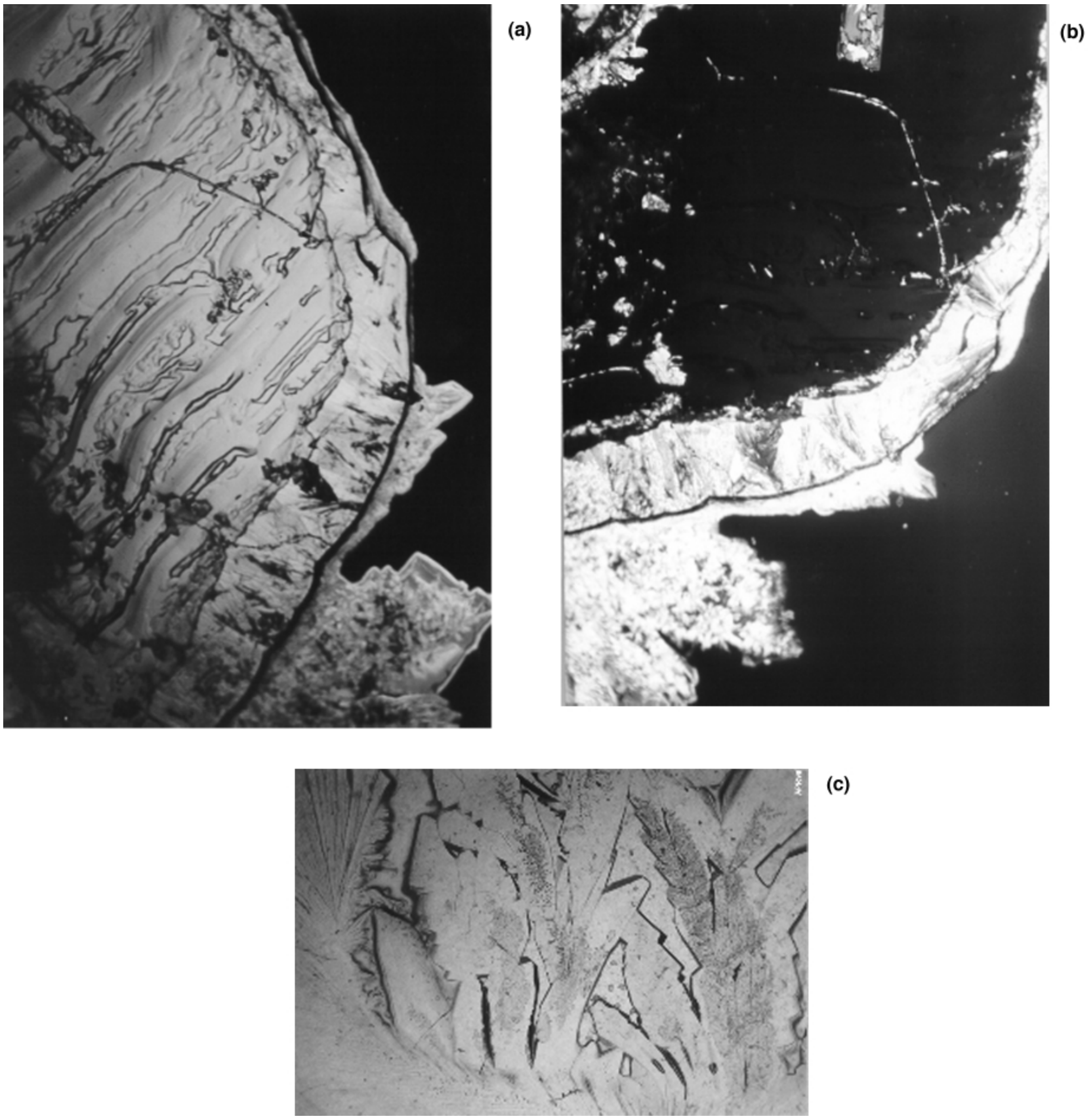


Fig. 3 Enamel like crystalline complex **1** as viewed from a Leitz optical microscope (×400) with (a) and without a polarising filter (b); (c) 'leaves' of crystalline **1** obtained over a watch-glass.

obtained with the cation $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ only by using a 2:1 acid:sandwich ratio. The supramolecular salt $[Co(\eta^5\text{-}C_5Me_5)_2]^+[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-\cdot H_2O$, **3**, has been isolated and structurally characterised. The fundamental building block of the organic framework in **3** is based on pairs of *trans*-acotinic acid moieties, *e.g.* $[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-$ [see Fig. 4(a)], from which one H^+ has been removed. The resulting superanion retains four CO_2H groups available for 'neutral' $O\text{–}H\cdots O$ hydrogen bonding, while the deprotonated CO_2^- forms a 'charge enhanced' type hydrogen bond within the superanion. The $O\cdots O$ separation of 2.432(2) Å well compares with those separations in negatively charged systems as well as in **1** and **2**.[12]

Self-assembly of the hydrated $[Co(\eta^5\text{-}C_5Me_5)_2]^+[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-$ units results in a large honeycomb superstructure, a space-filling representation of which is shown in Fig. 4(b). The overall arrangement is reminiscent of the hexagonal and squared honeycomb superanion frameworks obtained by using D,L- and L-tartaric acids, respectively.[17] The channels extend along the *a* axis and are *filled* by the decamethylcobaltocenium cations [see Fig. 4(b)]. It is unfortunate that, so far, we have not succeeded in isolating crystals of the cobaltocenium and decamethylcobaltocenium cations with the *same* acid systems (although this will probably never be possible because our experiments are showing that there is an important and definite matching requirement between templating unit and self-assembling building blocks, see below).

A final comment concerns the $C\text{–}H^{\delta+}\cdots O^{\delta-}$ hydrogen bonds between the organic superanion and the encapsulated cations. Although the positions of the methyl hydrogens in complex **3** are not available from the Fourier maps and model hydrogens had to be used, it is worth noting that the shortest $C\text{–}H\cdots O$ distances are longer than in **1** and **2** (calculated H atom positions; only one distance of 2.38 Å and three distances in the range 2.70–2.80 Å). This is easy to explain because the same ionic charge is 'distributed' on a much larger number of peripheral hydrogen atoms in decamethylcobaltocenium with respect to cobaltocenium, which implies that the polarisation enhancement is much reduced.

Finally, the structure of the precursor $[Co(\eta^5\text{-}C_5Me_5)_2]^+[PF_6]^-$ **4** is worth a brief description. A space filling projection of the packing is shown in Fig. 5. It can be appreciated how the small $[PF_6]^-$ anions fill in the interstices between the large $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ cations which are almost in contact. An observation analogous to that on the length of $C\text{–}H\cdots O$

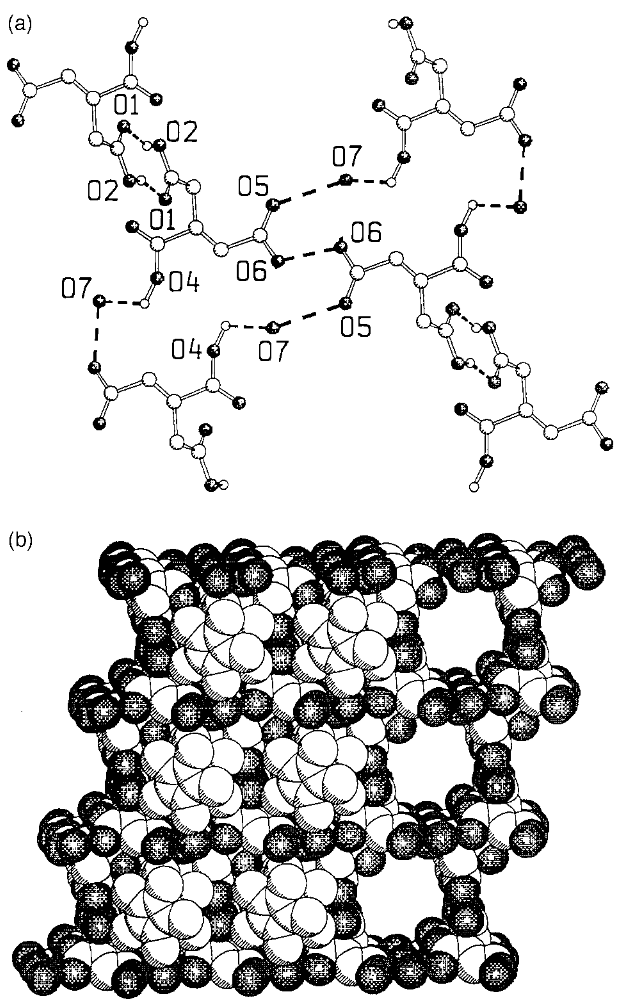


Fig. 4 (a) The O–H···O hydrogen bond distribution around the *trans*-acotinate anions in complex **3**. O(H)···O distances (in Å): O(1)···O(2) 2.610(2), O(4)···O(7)$_{water}$ 2.615(2), O(5)···O(7)$_{water}$ 2.838(2), O(6)···O(6) 2.432(2). (b) The honeycomb superstructure formed by self-assembly of the hydrated $[Co(\eta^5\text{-}C_5Me_5)_2]^+$-$[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2CO_2]^-$ units; space filling representation along the *a* axis showing how the channels in the organic cage (right-hand side) are filled by the decamethylcobaltocenium cations (left-hand side); H atoms omitted for clarity.

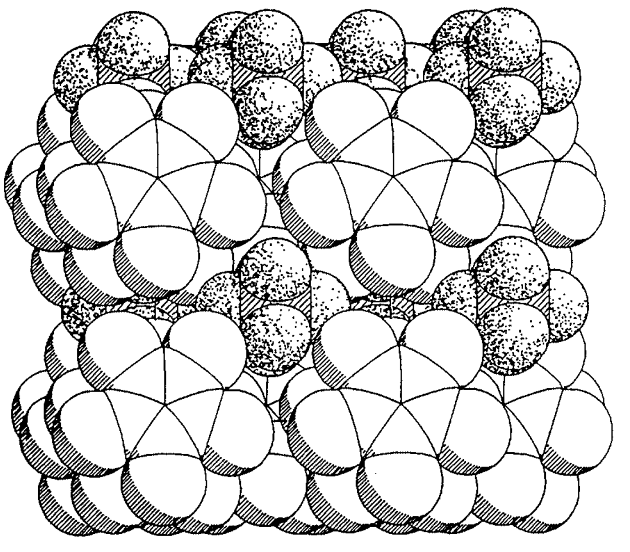


Fig. 5 A space filling projection of the packing in $[Co(\eta^5\text{-}C_5Me_5)_2]^+[PF_6]^-$ **4**; note how the small $[PF_6]^-$anions fill in the interstices between the large $[Co(\eta^5\text{-}C_5Me_5)_2]^+$cations; H atoms omitted for clarity.

interactions above, can be made on comparing the shortest C–H···-F separations in **4** with those observed in the crystal structure of $[Co(\eta^5\text{-}C_5H_5)_2]^+[PF_6]^-$ at the same temperature:[18] there are only four contact distances in the range 2.64–2.81 in **4** while seven distances are observed in the range 2.42–2.58 Å in the room temperature form of the cobaltocenium salt. This difference is small but it is of some interest because it goes, within a completely different crystal structure, in the same direction as that of the $C\text{–}H^{\delta+}\cdots O^{\delta-}$ distances, *viz.* the reduced polarisation of the C–H(sp^3) with respect to the C–H(sp^2) is manifested also in the length of the weak C–H···F interactions.[19]

Conclusion

With this paper we have shown that the two polycarboxylic acids are useful building blocks for the preparation of novel mixed organic–organometallic aggregates. In complex **1** the monodeprotonated acidate $C_4H_4(CO_2H)_3(CO_2)^-$ is capable of forming a microporous anionic superstructure held together by neutral and charged O–H···O interactions, whereas a ‘spacer’ (a water molecule) is required to host the slightly larger bis(benzene) chromium cation in **2**. On moving to the much larger decamethylcobaltocenium cation, the structural rigidity of $C_4H_4(CO_2H)_4$ and of its deprotonation product $C_4H_4(CO_2H)_3(CO_2)^-$ does not permit efficient hydrogen bonding interlocking, while the smaller, but more flexible, acid $C_3H_3(CO_2H)_3$ is capable of forming a sophisticated honeycomb structure with large channels that can host the large cation $[Co(\eta^5\text{-}C_5Me_5)_2]^+$.

Materials **1**–**3** are new members in the rich family of *organometallic supersalts*[10] which owe their cohesion and stability mainly to electrostatic forces, while the architecture depends on the directionality, predictability and reproducibility of the strong and weak hydrogen bonds. The discovery that larger supra-anionic honeycomb type structures can be obtained by varying the size of the cationic unit not only demonstrates experimentally that it is the organometallic cation that *templates* the organic superstructure and controls the self-assembly process, but also it opens an interesting way to manipulation of the content of the channels. It should be stressed, in fact, that, contrary to microporous systems based on co-ordination[20] or covalent networks,[21] the organic superstructures of the species discussed in this paper exist only thanks to the electrostatic field generated by the interaction between the superanions and the organometallic cations. Were the cations (ideally) removed, the whole superstructure would explode because of anion–anion repulsions.[22] It is, however, conceivable to envisage experiments to attempt substitution of the cations, ionic exchange, or self-assembly of the organic acids in the presence of a mixture of large and small cations.

Experimental

Crystal synthesis

As in the cases discussed in Part 5 and preceding, the synthetic aspect of this work is related to the synthesis and crystallisation of solid materials. It should be stressed that all usual spectroscopic tools for the characterisation of chemical products in solution can not be used in the context of a crystal synthesis. The products of the synthesis exist only in the condensed phase for which diffraction techniques are essential. Cobaltocene, $C_4H_4(CO_2H)_4$ as well as $[Co(\eta^5\text{-}C_5Me_5)_2]^+[PF_6]^-$ used as starting material in the preparation of organometallic supersalt **3** (see below) were purchased from Aldrich, bis(benzene) chromium from Strem. Crystals of $[Co(\eta^5\text{-}C_5Me_5)_2]^+[PF_6]^-$ **4** were obtained by crystallisation from water of the commercial materials, whereas those of $C_3H_3(CO_2H)_3$ suitable for X-ray diffraction could not be obtained.

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

	2	3	4	5
Formula	$C_{18}H_{17}CoO_8$	$C_{20}H_{21}CrO_9$	$C_{32}H_{45}CoO_{14}$	$C_{20}H_{30}CoF_6P$
M	420.25	457.37	712.61	474.34
T/K	223(2)	223(2)	223(2)	273(2)
System	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	Cc	$P2_1/a$	$P\bar{1}$	$C2/m$
a/Å	13.990(4)	13.240(10)	7.707(9)	14.130(9)
b/Å	11.623(4)	13.79(2)	10.233(7)	8.892(3)
c/Å	11.960(4)	11.200(10)	11.420(8)	9.250(9)
α/°			99.77(5)	
β/°	114.35(3)	112.63(7)	99.79(8)	113.57(6)
γ/°			97.63(8)	
V/Å^3	1771.8(10)	1888(4)	862.5(13)	1065.2(13)
Z	4	4	1	2
D_c/mg m^{-3}	1.575	1.610	1.372	1.479
Minimum, maximum transmission	0.79–1.00	0.84–1.00	0.81–1.00	0.75–1.00
μ(Mo-Kα)/mm^{-1}	1.013	0.660	0.564	0.935
Measured reflections	1592	4762	2947	991
Unique reflections	1516	4537	2906	987
Refined parameters	206	247	206	75
$R1$ (F, $I > 2\sigma(I)$)	0.0658	0.0860	0.1089	0.0592
$wR2$ (F^2, all data)	0.1770	0.2616	0.3171	0.1656

Syntheses

$[Co(\eta^5\text{-}C_5H_5)_2]^+[C_4H_4(CO_2H)_3CO_2]^-$ 1. A brown powder of $[Co(C_5H_5)_2]$ (100 mg, 0.53 mmol) was suspended in 20 ml of bidistilled water with stirring at room temperature in air, until a clear solution of bright yellow $[Co(C_5H_5)_2]^+[OH]^-$ (pH > 10) was obtained. When a white powder of $C_4H_4(CO_2H)_4$ (122 mg, 0.53 mmol) was added to the solution of cobaltocenium hydroxide in stoichiometric 1(acid) : 1(hydroxide) amount slow evaporation of the water solution at room temperature on a watch-glass yielded crystalline material **1**. Correspondence between the structure determined by the single crystal experiment and the structure of the bulk solid material was verified by comparing calculated and measured powder spectra. Other stoichiometric ratios failed to give crystalline material suitable for single-crystal X-ray diffraction.

$[Cr(\eta^6\text{-}C_6H_6)_2]^+[C_4H_4(CO_2H)_3CO_2]^-\cdot H_2O$ 2. A brown powder of $[Cr(\eta^6\text{-}C_6H_6)_2]$ (69 mg, 0.33 mmol) was added to a suspension of $C_4H_4(CO_2H)_4$ (77 mg, 0.33 mmol) in anhydrous THF (20 ml). A yellowish precipitate immediately formed which turned into bright yellow in 30 min. The powder was filtered off and dissolved in water and crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature on a watch-glass. Other stoichiometric ratios failed to give crystalline material suitable for single-crystal X-ray diffraction.

$[Co(\eta^5\text{-}C_5Me_5)_2]^+[C_3H_3(CO_2H)_2CO_2(H)\cdot C_3H_3(CO_2H)_2\text{-}CO_2]^-\cdot H_2O$ 3. Since neutral $[Co(\eta^5\text{-}C_5Me_5)_2]$ is not commercially available, commercial $[Co(\eta^5\text{-}C_5Me_5)_2]^+[PF_6]^-$ was used first to reduce the cation by means of Na/Hg amalgam to $[Co(\eta^5\text{-}C_5Me_5)_2]$. The solution of decamethylcyclopentadienyl cobaltocene obtained was then used in a sequence of redox/deprotonation/precipitation as described above for **1** and **2**. As mentioned above, reaction with $C_4H_4(CO_2H)_4$ failed to give diffracting material. Crystals of acceptable quality could be obtained only by using the *trans*-acotinic acid $C_3H_3(CO_2H)_3$ in a stoichiometric amount 2(acid) : 1(hydroxide). Other stoichiometric ratios, as when $C_4H_4(CO_2H)_4$ was employed, failed to give crystalline material suitable for single-crystal X-ray diffraction although it should be pointed out that the control of the stoichiometry could only be approximate because of the imprecise yield of the intermediate oxidation–reduction step required to produce neutral $[Co(\eta^5\text{-}C_5Me_5)_2]$. The preparation of complex **3** was reproduced by using an excess of the acid, stoichiometric amount >2(acid) : 1(hydroxide).

Crystal structure characterisation

All X-ray diffraction data collections were carried out on a Nonius CAD-4 diffractometer equipped with an Oxford Cryostream liquid-N_2 device. Crystal data and details of measurements are reported in Table 1. Diffraction data were corrected for absorption by azimuthal scanning of high-χ reflections. The SHELXL 97[23a] package was used for structure solution and refinement based on F^2, SCHAKAL 97[23b] for the graphical representation of the results. Common to all compounds: Mo-Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator. All non-H atoms in **1**, were refined anisotropically. The positions of two out of three $H(CO_2H)$ hydrogen atoms in, respectively, **1** and **2** were observed in the Fourier maps but not refined. In the case of **1** two positions (marked by * in Scheme 1) were observed for the H atom involved in the $CO_2^- \cdots HO_2C$ link; both positions were added with site occupancy factor (s.o.f) = 0.5 and not refined. The quality of the data obtained for **3** was not high. Several attempts to obtain better diffracting material failed. This reflects, in our experience, the 'difficulty' to attain efficient self-assembly, which, given the complexity of the systems under investigation, is not surprising and should be taken at face value. The information is still sufficiently relevant with respect to the crystal engineering strategy to deserve consideration. The H atoms bound to C atoms were added in calculated positions in all compounds. The computer program PLATON[23c] was used to analyse the geometry of the hydrogen bonding patterns. In order to evaluate $C\text{–}H\cdots O$ bonds the C–H distances (when H atom positions were available experimentally) were normalised to the neutron derived value of 1.08 Å. In **3** and **4** hydrogen atoms were put in geometrically calculated positions. Morphological investigations were carried out with a flat camera by using Cu-Kα radiation.

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See http://www.rsc.org/suppdata/dt/1999/2611/ for crystallographic files in .cif format.

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