

Moulding a honeycomb framework around $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ via charge-assisted C–H \cdots O hydrogen bonds

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Strong O–H \cdots O hydrogen bonds between $[(\text{Hta})(\text{H}_2\text{ta})]^-$ anions derived from D,L-tartaric acid $[\text{H}_2\text{ta}]$ hold together a honeycomb superanion templated around the cation $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ via charge-assisted C–H \cdots O hydrogen bonds.

Organic–organometallic crystal engineering is a means to combine physical and chemical features of organic and organometallic molecules and ions in the solid state. Organic–organometallic crystals can be constructed by taking advantage of the complementary role of strong and directional O–H \cdots O hydrogen bonds to selectively and tightly link together organic molecules, and of diffuse networks of C–H \cdots O hydrogen bonds and anion–cation interactions to link the organic and organometallic fragments in the crystal.¹

Along this line, we have designed, synthesized and characterized supramolecular aggregates of the paramagnetic cations $[\text{Cr}(\eta^6\text{-arene})_2]^+$ (arene = benzene and toluene) with cyclohexane-1,3-dione (CHD). The aggregation of the CHD systems in superanions is based on strong hydrogen bonds, whereas the interaction between organic fragments and organometallic complexes is based on weak C–H \cdots O hydrogen bonds reinforced by the different polarity.² The participation of water oxygens in C–H \cdots O_{water} bonds has been evidenced by the structure of the hydrated $[\text{Cr}(\text{C}_6\text{H}_6)_2][\text{CHD}]\cdot 3\text{H}_2\text{O}$ and by the polar structure of the hydrated hydroxide $[\text{Cr}(\text{C}_6\text{H}_6)_2]\text{OH}\cdot 3\text{H}_2\text{O}$.³

Here we report that the reaction of the hydroxide $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]\text{OH}$ with D,L-tartaric acid $[\text{H}_2\text{ta}]$ in water (or THF) affords the novel supramolecular systems $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{Hta})(\text{H}_2\text{ta})]^-$ **1** and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Hta}]^-\cdot\text{H}_2\text{O}$ **2** depending on the stoichiometric ratio between cobaltocenium hydroxide and tartaric acid. The hydroxide is obtained *in situ* by bubbling oxygen through a water solution of cobaltocene.† Crystals suitable for X-ray diffraction‡ are obtained by evaporation of the solvent in the air at room temp.

The cobaltocenium cation in crystalline **1** is encapsulated within an anionic organic honeycomb framework (Fig. 1) of stoichiometry [tartrate-tartaric acid]_n generated by the aggregation of dimeric monoanions $[(\text{Hta})(\text{H}_2\text{ta})]^-$. The supramolecular monoanion $[(\text{Hta})(\text{H}_2\text{ta})]^-$ is formed as a consequence of the loss of one proton every two tartaric acid molecules, with the two units bonded *via* a strong –C(O)O–H \cdots O(O)C– hydrogen bond [2.434(1) Å]. The dimers are then linked in the honeycomb framework *via* O–H \cdots O bonds involving the two external carboxyl groups and the hydroxyl groups. The interaction between the supramolecular anionic network and the encapsulated $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations occurs *via* C–H \cdots O hydrogen bonds⁴ between the staggered cyclopentadienyl ligands of the cations and the –CO and the –OH groups of the anionic framework. Six independent C–H \cdots O interactions are observed in the range 2.10–2.35 Å.† These values fall towards the lower limit for interactions of this type clearly indicating that the electrostatic interaction C–H $\delta^+\cdots$ O δ^- is reinforced by the difference in charge between host and guest.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 participate in intramolecular –OH \cdots O

bonds) is likely to be the driving force towards aggregation around the $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations in **1**.

If the stoichiometry ratio between $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]\text{OH}$ and tartaric acid in the acid–base reaction is changed from 1 : 2 to 1 : 1, the hydrated crystalline salt $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Hta}]^-\cdot\text{H}_2\text{O}$ **2** is obtained. In contrast to **1**, the $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations are in eclipsed conformation. Crystalline **2** can be described as a layered structure in which a corrugated anionic network of $[\text{Hta}]^-$ ions and water molecules alternates with layers of cobaltocenium cations (Fig. 2). The water molecules form O–H \cdots O hydrogen-bond tetramers involving two hydroxyl groups of two neighbouring tartrate anions. As in **1**, the

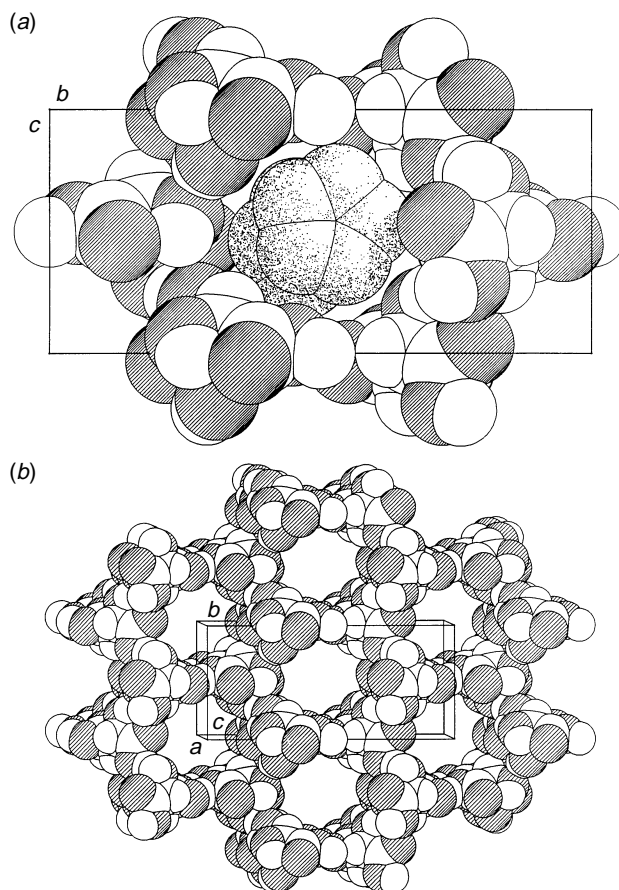


Fig. 1 (a) Space-filling representation of the tartaric acid template in crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{Hta})(\text{H}_2\text{ta})]^-$ **1**. (b) Space-filling representation of the anionic honeycomb framework formed by the $[(\text{Hta})(\text{H}_2\text{ta})]^-$ units, the cobaltocenium cations pile inside the channels extending along the *a*-axis. Relevant hydrogen-bonding parameters (in Å; O \cdots O < 2.8, C–H \cdots O < 2.5): intra, O_{OH} \cdots O_{(CO)OH} 2.711, 2.638; inter, O_{OH} \cdots O_{(CO)OH} 2.677; O_{OH} \cdots O_{OH} 2.776; O \cdots O_{OH} 2.434; C–H_{cp} \cdots O 2.396, 2.302, 2.333, 2.097, 2.354, 2.341, 2.253.† Relevant bonding parameters (in Å): mean Co–C 2.042(4); C=O 1.197(3), 1.222(3); C=O_{(CO)OH} 1.319(2), 1.280(3); C–O_{OH} 1.415(2), 1.417(2); mean C–C 1.521(6).

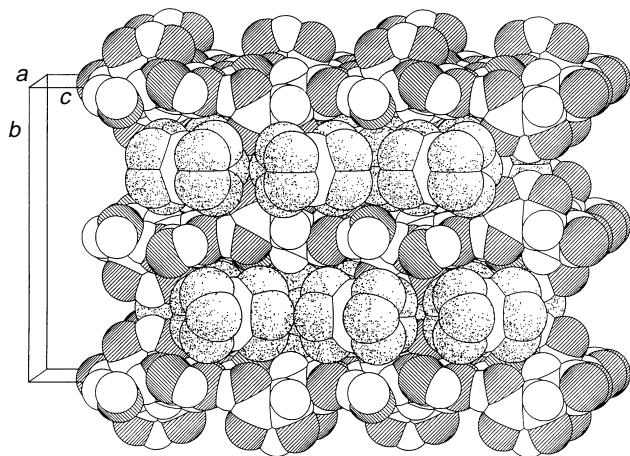


Fig. 2 Space-filling outline of the layered structure in crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Hta}]^-\cdot\text{H}_2\text{O}$ **2**. Relevant hydrogen bonding parameters (in Å, $\text{O}\cdots\text{O} < 2.8$, $\text{C}\cdots\text{O} < 2.5$ Å): intra $\text{O}_{\text{OH}}\cdots\text{O}_{\text{CO}_2\text{O}^-}$ 2.550, 2.640; inter $\text{O}_{(\text{CO})\text{OH}}\cdots\text{O}_{\text{W}}$ 2.725; $\text{O}_{\text{OH}}\cdots\text{O}_{\text{W}}$ 2.640, 2.784; $\text{O}^-\cdots\text{O}_{\text{OH}}$ 2.479; $\text{C}\cdots\text{H}_{\text{Cp}}\cdots\text{O}$ 2.222, 2.338, 2.238, 2.425, 2.445. Relevant bonding parameters (in Å): mean $\text{Co}\cdots\text{C}$ (over the two cations) 2.016(10); mean $\text{C}_{\text{Cp}}\cdots\text{C}_{\text{Cp}}$ 1.394(19); $\text{C}=\text{O}$ 1.225(8), 1.220(8); $\text{C}\cdots\text{O}_{(\text{CO})\text{OH}}$ 1.279(8), 1.251(8); $\text{C}\cdots\text{O}_{\text{OH}}$ 1.402(8), 1.410(8); mean $\text{C}\cdots\text{C}$ 1.528(14).

interaction between anion and cation is based on $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds (of which three in the range 2.20–2.35 Å) between the cyclopentadienyl hydrogens and the $-\text{OH}$ and $-\text{CO}_2\text{H}$ groups. Interestingly, the two sets of $\text{C}\cdots\text{H}\cdots\text{O}$ bonds in **1** and **2** stabilize, respectively, the staggered and eclipsed conformations of the organometallic cation.

With this study we have provided evidence that charge-assisted $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds can be used to mould $\text{O}\cdots\text{H}\cdots\text{O}$ 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 reaction with organometallic hydroxides produced *in situ*. This simple strategy opens a simple route to the preparation of a number of organic–organometallic crystalline aggregates.

Work is in progress to isolate and characterize other crystalline salts based on the utilization of chiral acids,⁷ including natural amino acids, to obtain chiral organometallic crystals potentially useful for non-linear optical studies.⁸

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Footnotes

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† Powdered $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$ (28 mg, 1.5 mmol) was added to 8 ml of bidistilled water at room temp. Oxygen was bubbled to completely oxidize

cobaltocene into bright yellow $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$. Powdered D,L-tartaric acid (45 mg, 3 mmol for **1**, 22.5 mg, 1.5 mmol for **2**) was then added and **1** and **2** were crystallized by evaporation at room temp. in air. The same materials can be obtained by oxidizing cobaltocene in THF at room temp. in the presence of the appropriate stoichiometric amount of solid D,L-tartaric acid. The resulting insoluble materials separate out as yellow solids, which were filtered off and dissolved in a minimum quantity of water for recrystallization. The reaction in THF very likely proceeds *via* formation of the peroxide anion $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2] + \text{O}_2 \rightarrow [\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+ + \text{O}_2^-\}$ which deprotonates the acid as in the reaction between $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ and cyclohexane-1,3-dione.^{2b}

‡ *Crystal data*: $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Hta}](\text{H}_2\text{ta})^-$ **1**: $\text{C}_{18}\text{H}_{21}\text{CoO}_{12}$, $M = 488.28$, monoclinic, space group $P2_1/n$, $a = 6.589(2)$, $b = 18.210(4)$, $c = 8.208(2)$ Å, $\beta = 92.19(2)^\circ$, $U = 984.1(4)$ Å³, $Z = 2$, $D_c = 1.648$ g cm⁻³, $F(000) = 504$, $\mu = 0.939$ mm⁻¹, θ range 3.0–28°, 2606 reflections measured, 2362 of which were independent, refinement on F^2 for 169 parameters, R_w (F^2 , all reflections) = 0.0920, R_1 [1839 reflections with $I > 2\sigma(I)$] = 0.0333. Two disordered positions were found for the cyclopentadienyl rings with site occupancy of 0.60 and 0.40, respectively that did not change with temperature indicating a static disorder. The two orientations correspond to two alternative sets of $\text{C}\cdots\text{H}\cdots\text{O}$ interactions.

$[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[\text{Hta}]^-\cdot\text{H}_2\text{O}$ **2**: $\text{C}_{14}\text{H}_{17}\text{CoO}_7$, $M = 356.21$, orthorhombic, space group $Pnma$, $a = 12.048(9)$, $b = 16.683(5)$, $c = 14.458(5)$ Å, $U = 2906(2)$ Å³, $Z = 8$, $D_c = 1.628$ g cm⁻³, $F(000) = 1472$, $\mu = 1.214$ mm⁻¹, θ range 3.0–28°, 3353 reflections measured, 3050 of which were independent, refinement on F^2 for 209 parameters, R_w (F^2 , all reflections) = 0.1778, R_1 [1153 reflections with $I > 2\theta(I)$] = 0.0526. Common to both compounds: graphite monochromated Mo-K α radiation, $\lambda = 0.71069$ Å, $T = 223(2)$ K. All non-H atoms were refined anisotropically. (O)H atoms directly located from Fourier maps and not refined. H atoms bound to C atoms were added in calculated positions. The computer programs SHELX86^{6a} and SHELXL92^{6b} were used for structure solution and refinement. The computer program SCHAKAL92 was used for all graphical representations.^{6c} In order to evaluate the $\text{C}\cdots\text{H}\cdots\text{O}$ bonds the $\text{C}\cdots\text{H}$ distances were normalized to the neutron derived value of 1.08 Å. CCDC 182/492.

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