

Driving crystal construction *via* stoichiometry: π - π stacks in squaric acid organometallic salts

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Depending on the stoichiometric ratio, squaric acid (H_2SQA) reacts with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2][\text{OH}]$ to form crystalline materials based on anion-cation π - π stacks and/or squarate ion ribbons held together by $\text{O-H}\cdots\text{O}$ hydrogen bonds between squarate anions and by charge-assisted $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ hydrogen bonds between organometallic and organic components.

Organometallic crystal engineering is an almost uncharted territory. Work in this field promises a great deal of new discoveries because of the possibility of combining physical and chemical features of organic and organometallic molecules and ions in the solid state.¹ This may lead to the isolation of materials with novel conducting, magnetic or optoelectronic properties.

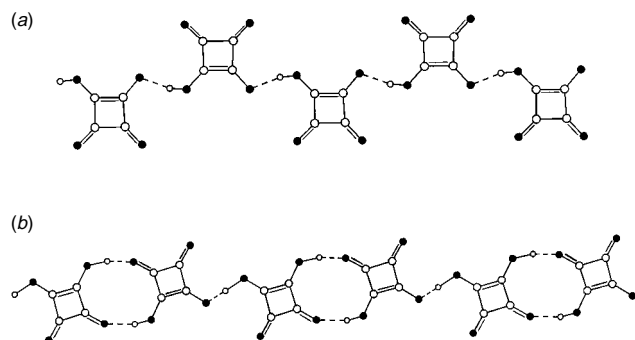
We have demonstrated that a great variety of new architectures can be obtained by combining organic moieties held together by strong $\text{O-H}\cdots\text{O}$ hydrogen bonds with non coordinating organometallic cations, such as $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ and $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$.² Chiral organic frameworks have also been obtained when enantiomerically pure chiral acids, such as L-tartaric and L-bisbenzoyltartaric acids have been used.³

We are now able to report that the reaction of the hydroxide $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2][\text{OH}]$ with squaric acid (3,4-dihydroxy cyclobut-3-ene-1,2-dione, H_2SQA) in water (or THF) yields two different crystalline materials, namely $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{HSQA})]^-$ **1** and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{HSQA})(\text{H}_2\text{SQA})]^-$ **2**, depending on the stoichiometric ratio between cobaltocenium hydroxide and squaric acid.[§] The different stoichiometry is associated with a dramatic change in crystal structure, which is also reflected in a different colour of the crystalline materials. Squaric acid has been widely investigated for its electronic and physical properties.⁴

When the stoichiometric ratio between cobaltocenium hydroxide and squaric acid is 1:1, crystalline **1** is obtained. Contrary to what is usually observed with cobaltocenium salts, which are yellow, crystals of **1** are orange. Indeed, the structure of **1** presents some unique features that may account for this physical difference. The crystal is constituted of ribbons of $[(\text{HSQA})]^-$ monoanions (Scheme 1) bonded *via* negatively charged $\text{O-H}\cdots\text{O}$ hydrogen bonds [$\text{O}\cdots\text{O}$ 2.446 Å] and of

ribbons of cobaltocenium cations, Fig. 1. The 1:1 stoichiometry, combined with a good matching in size and shape between the cyclopentadienyl ligands and the $[(\text{HSQA})]^-$ ions, leads to a superstructure in which the hydrogen bonded squarate ribbons intercalate between cobaltocenium cations (Fig. 1). The π - π distance is *ca.* 3.35 Å. The oxygen atoms form the outer rims of the $\{[(\text{HSQA})]^- \}_n$ ribbons and interact with the $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations on both sides *via* charge assisted $\text{C-H}^{\delta+}\cdots\text{O}^{\delta-}$ hydrogen bonds (five $\text{H}\cdots\text{O}$ distances in the range 2.272–2.500 Å). What is more, the packing arrangement is chiral in space group $P2_1$. The unusual orange colour suggests formation of a charge transfer complex and prompts for further investigations in due course.⁵

On changing the stoichiometry to 1:2, the yellow crystalline **2** is obtained. It is constituted of supramolecular monoanions $[(\text{HSQA})(\text{H}_2\text{SQA})]^-$ resulting from the loss of one proton every two squaric acid molecules and arranged in ribbons bonded *via* negatively charged $\text{O-H}\cdots\text{O}$ hydrogen bonds ($\text{O}\cdots\text{O}$ 2.440, 2.436 Å).⁶ The bonding within the superanions is provided by



Scheme 1 (a) The $\{[(\text{HSQA})]^- \}_n$ ribbon in crystalline **1** and (b) the $\{[(\text{HSQA})(\text{H}_2\text{SQA})]^- \}_n$ ribbon in crystalline **2**

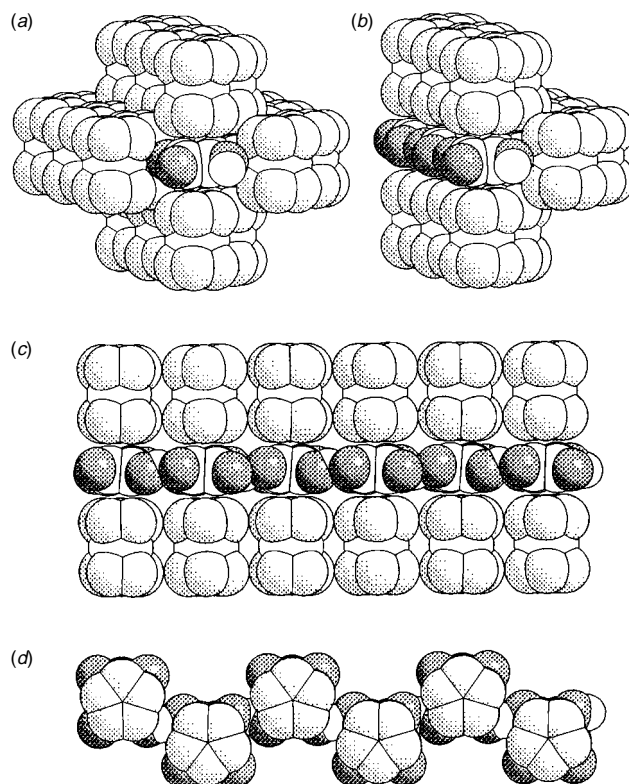


Fig. 1 'Dissection' of the packing arrangement in crystalline **1**: space filling representation of the $\{[(\text{HSQA})]^- \}_n$ ribbon encapsulated within four (a), three (b) and two (c) rows of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ cations. Note the good match in size and shape of the squaric acid moieties and of the cyclopentadienyl ligands (d). H atoms of the cations omitted for clarity. Relevant hydrogen bonding parameters (in Å, $\text{C-H}\cdots\text{O} < 2.5$ Å): $\text{O}\cdots\text{O}_{\text{OH}}$ 2.446; $\text{C-H}_{\text{CP}}\cdots\text{O}$ 2.272, 2.339, 2.455, 2.455, 2.467.¶

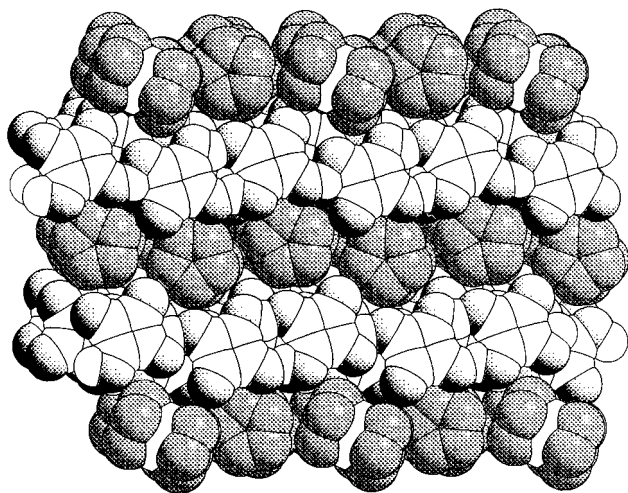


Fig. 2 Space filling representation of the stacking sequence of $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\}_n/\{[(\text{HSQA})(\text{H}_2\text{SQA})]^{-}\}_n$ in crystalline **2**. H atoms of the cations omitted for clarity. Relevant hydrogen bonding parameters (in Å, C–H...O < 2.5 Å): O_H...O_{CO} 2.550, 2.550, 2.574, 2.539; O...O_H 2.436, 2.440; C–H_{Cp}...O 2.192, 2.213, 2.314, 2.328, 2.343, 2.401, 2.407, 2.408, 2.414, 2.437, 2.453, 2.465, 2.499, 2.500.†

O–H...O hydrogen bonds, with formation of ten-membered ring systems (O...O distances in the range 2.539–2.574 Å) reminiscent of the carboxylic rings (Scheme 1). The ribbons are stacked in such a way that squarate moieties overlap hydrogen bonded rings, resulting in layers with oxygen atoms protruding above and below the layer surface. The cobaltocenium cations lie side-on the layer and interact *via* charge-assisted C–H^{δ+}...O^{δ-} hydrogen bonds (14 distances in the range 2.191–2.500 Å). Hence crystalline **2** can be described as a stacking sequence $\{[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\}_n/\{[(\text{HSQA})(\text{H}_2\text{SQA})]^{-}\}_n$ along the *c*-axis in the *P1* crystal (Fig. 2).

C–H^{δ+}...O^{δ-} distances in both **1** and **2** fall towards the lower limit for interactions of this type, clearly indicating that the electrostatic interaction is reinforced by the difference in charge between organic anionic ribbons and organometallic cations.⁷

We have previously shown that self-aggregation of organic molecules into robust supramolecular frameworks can be controlled by reacting common organic acids with metallocene or metallocene hydroxides. Since the organometallic cations possess only C–H donors they do not compete in the formation of strong hydrogen bonds. We have now shown that the same strategy can be used to obtain different structures starting from the same acid by changing the stoichiometry ratio. Though simple it may appear, this allows us to control the number of strong hydrogen bonding donor and acceptor sites, therefore the resulting crystal architectures. Analogous reactions involving the bis-benzene chromium cation are under investigation.

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Notes and References

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§ Brown powder of $[\text{Co}(\text{C}_5\text{H}_5)_2]$ (4.73 mg, 0.025 mmol) was added to 10 ml of bidistilled water at room temperature. Oxygen was bubbled to completely

oxidize cobaltocene to bright yellow $[\text{Co}(\text{C}_5\text{H}_5)_2]^+$. The resulting solution of $[\text{Co}(\text{C}_5\text{H}_5)_2][\text{OH}]$ is strongly basic (pH > 10). White powder of squaric acid (2.8 mg, 0.025 mmol for **1**, 5.6 mg, 0.050 mmol for **2**) was then added. **1** and **2** were crystallized by evaporation at room temperature in the air. The same materials can be obtained by oxidizing cobaltocene in THF at room temperature in the presence of the appropriate stoichiometric amount of solid squaric acid. The reaction in THF very likely proceeds *via* formation of the peroxide anion ($\text{CoCp}_2 + \text{O}_2 \rightarrow \text{CoCp}_2^+ + \text{O}_2^-$) which deprotonates the acid as in the case of the reaction between $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ and cyclohexane-1,3-dione.² Compounds **1** and **2** separate out as orange and yellow solids, respectively, which are filtered and dissolved in a minimum quantity of water for recrystallization.

¶ *Crystal data*: $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{HSQA})]^-$ **1**: $\text{C}_{14}\text{H}_{11}\text{CoO}_4$, $T = 150(2)$ K, $M = 302.16$, monoclinic, space group $P2_1$, $a = 7.368(3)$, $b = 11.017(6)$, $c = 7.368(2)$ Å, $\beta = 94.66(2)$, $U = 596.1(4)$ Å³, $Z = 2$, $D_c = 1.683$ g cm⁻³, $F(000) = 308$, $\mu = 1.445$ mm⁻¹, θ -range 3.0–28°, 1626 reflections measured, 1512 of which independent, refinement on F^2 for 154 parameters, wR (F^2 , all reflections) = 0.1624, R_1 [1196 reflections with $I > 2\sigma(I)$] = 0.0402. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+[(\text{HSQA})(\text{H}_2\text{SQA})]^-$ **2**: $\text{C}_{18}\text{H}_{13}\text{CoO}_8$, $T = 223(2)$ K, $M = 416.21$, triclinic, space group $P\bar{1}$, $a = 6.732(3)$, $b = 11.582(11)$, $c = 21.033(7)$ Å, $\alpha = 92.99(6)$, $\beta = 92.43(3)$, $\gamma = 96.34(6)^\circ$, $U = 1626(2)$ Å³, $Z = 4$, $D_c = 1.700$ g cm⁻³, $F(000) = 848$, $\mu = 1.103$ mm⁻¹, θ -range 3.0–25°, 6315 reflections measured, 4984 of which independent, refinement on F^2 for 454 parameters, wR (F^2 , all reflections) = 0.2092, R_1 [3229 reflections with $I > 2\sigma(I)$] = 0.0662. Three cobaltocenium cations were found, one in general position and two lying on two independent inversion centres, while two squaric acid and two squarate moieties were found in general positions. Common to both compounds: Mo-K α radiation, $\lambda = 0.71069$ Å, monochromator graphite, ψ -scan absorption correction. 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^{8a} and SHELXL92^{8b} were used for structure solution and refinement. The computer program SCHAKAL92 was used for all graphical representations.^{8c} In order to evaluate the C–H...O bonds the C–H distances were normalized to the neutron derived value of 1.08 Å and the program PLATON was used.^{8d} CCDC 182/808.

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