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Grinding of an organometallic crystalline material leads to quantitative formation of a hydrated polymorph

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The hydrated crystalline material $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)Fe]^-\cdot H_2O$ 3 is prepared by simply *grinding* either the crystalline powder 1 that precipitates from thf on reacting $[(\eta^5\text{-}C_5H_5)_2Co]$ with $[(\eta^5\text{-}C_5H_4CO_2H)_2Fe]$ or single crystals of $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)Fe]^-$ 2 obtained by recrystallization of 1 from nitromethane; on heating at 373K 3 loses water and reverts to the starting material 1.

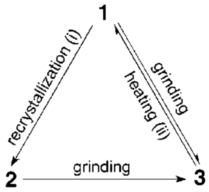
Crystal engineering is a bridge between supramolecular and molecular materials chemistry and constitutes one of the most attractive research fields in modern structural chemistry.[1] Crystal-to-crystal transformations are of obvious interest.

Recently, we have begun to utilize organometallic building blocks to prepare crystalline materials to exploit the variable valence, spin and charge states of coordination complexes.[2] Exciting new results are being obtained, in particular when the crystalline products are investigated by a combination of different solid state techniques.[3]

Here we report the unusual behaviour of the crystalline material[2b] $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)\text{-}Fe]^-$ **2**, previously synthesised together with the mixed-metal mixed-spin system $\{[(\eta^6\text{-}C_6H_6)_2Cr]^+\}_2\{[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)Fe]_2[(\eta^5\text{-}C_5H_4CO_2H)_2Fe]^{2-}\}$.[4]

We have discovered that the hydrated *pseudo*-polymorph $[(\eta^5\text{-}C_5H_5)_2Co]^+[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)Fe]^-\cdot H_2O$ **3** is obtained by *grinding* either the crystalline powder **1** that precipitates from thf on reacting $[(\eta^5\text{-}C_5H_5)_2Co]$ and $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ to prepare **2**,† or single crystals of **2** obtained by subsequent recrystallization of **1** from nitromethane or methanol.† Importantly, both **2** and **3** have been characterized by single crystal X-ray-diffraction, while powder diffractograms have been measured for **1** and **3** so that the relationship between reactant and product of this peculiar solid state transformation is known in detail.‡ The process is summarized in Scheme 1. The reverse process proceeds only from **3** → **1** as confirmed by thermal gravimetric analysis, which shows stoichiometric loss of water at *ca.* 373 K, and by powder X-ray diffraction, which shows the conversion into **1** of a sample of **3** heated for 2 h at 383 K under argon. Single crystals of **2** do not absorb water in the air, while crystalline **3**, once formed, behaves like any 'normal' crystalline salt, *i.e.* can be dissolved and recrystallized without further structural change.

The key structural features of **2** and **3** can be summarised as follows:



Scheme 1 *Reagents and conditions* i, from $MeNO_2$ or MeOH; ii, 383 K, 2 h, argon atmosphere.

(i) both **2** and **3** belong to the class of supramolecular salts (*supersalts*[2b]) in which the anions, obtained by deprotonation of the dicarboxylic acid $[(\eta^5\text{-}C_5H_4CO_2H)_2Fe]$, are self-assembled *via* O–H···O and/or $O\text{–}H\cdots O^-$ hydrogen bonding interactions and are linked to the cobaltocenium cations $[(\eta^5\text{-}C_5H_5)_2Co]^+$ *via* a profusion of *charge assisted* $C\text{–}H^{\delta+}\cdots O^{\delta-}$ interactions.[5] For sake of clarity only the anionic backbones are compared in Fig. 1. Relevant hydrogen bonding parameters are given in the caption.

(ii) In **2** the $[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)Fe]^-$ anions form chains with no cross-links, *viz.* a mono-dimensional network,[6] while in **3** the chains are *cross-linked* by water molecules inserted between $-CO_2$ groups, generating a two-dimensional network.

(iii) The ferrocene moieties in **2** and **3** not only show different ring conformations but have also different relative orientations along the chains.

Fig. 2 collects the evidence on the process depicted in Scheme 1 and compares the experimental (exp) X-ray powder diffractograms obtained for **1** and **3** with those calculated (calc) on the basis of the single-crystal structures for **2** and **3**. It can be seen that: (i) **1**(exp) ≠ **3** (exp) and **2** (calc), (ii) **3** (exp) ≠ **2** (calc), and (iii) **3** (exp) ≡ **3** (calc).

Although the effect of grinding samples for powder diffraction, as well as the possibility of monitoring solid state reactions

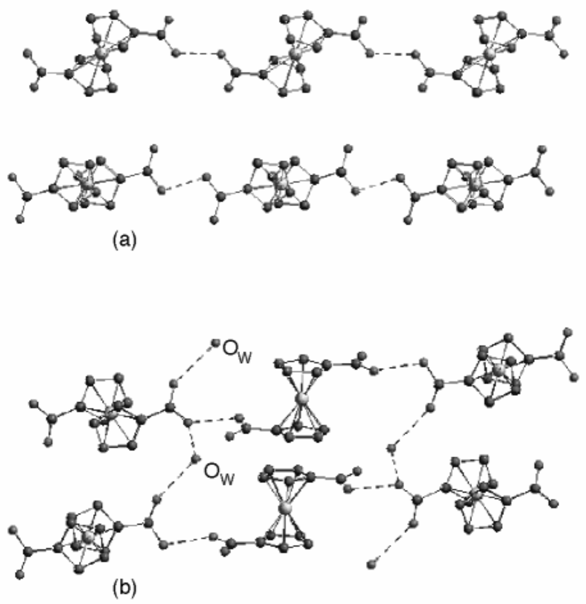


Fig. 1 Chains of O–H···O bonded $[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)Fe]^-$ anions in **2** (a) and **3** (b). Note how the water molecules in **3** act as *cross-links* between the anionic chains. Hydrogen atoms are omitted for clarity. Relevant O···O separations within the hydrogen bonded systems are: **2** anion–anion 2.45(2), **3** anion–anion 2.49(2) and 2.52(2), anion–water 2.81(2), 2.73(2), 2.83(2) Å.

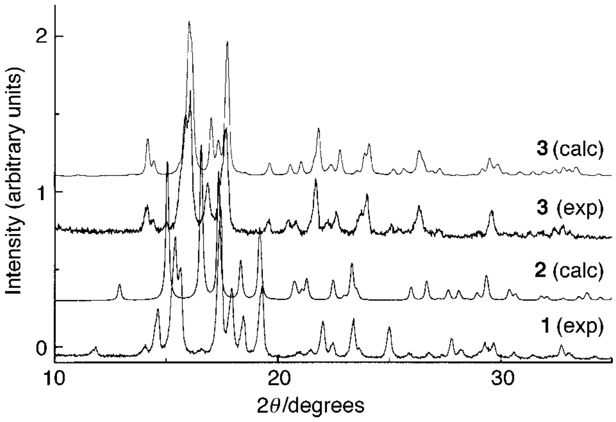


Fig. 2 Comparison between the experimental powder diffractograms of **1** (obtained from the reaction mixture in thf) and **3** (obtained by grinding crystalline **2**) and the diffractograms of **3** and **2** calculated on the basis of the experimental single-crystal structures. A colour version of this figure is shown in electronic form, see http://www.rsc.org/suppdata/cc/1999/937.

via powder diffraction, is well known,[7] what appears to be unprecedented in the case of the **1**, **2** → **3** transformations is the fact that water molecules can be inserted in stoichiometric ratio into a complex and highly organized crystal edifice without loss of crystallinity or (at least in the case of **2**) disruption of the anionic organization. The overall process is fully reproducible. The relationship between the structure of **1** and that of **2** remains unknown, though they are very likely two polymorphic modifications of the same anhydrous material.[8]

Although it is difficult (and somewhat 'unsafe') to model solid-to-solid transformations, *e.g.* between two thermodynamic free energy minima, it is still interesting to observe what is *preserved* and what is *changed* on passing from **2** to the *pseudo*-polymorph **3**. The anionic chain structure is maintained, together with the sequence of O–H···O interactions, while the distribution of cations, hence the distribution of weak C–H···O bonds, and the relative orientation of the ferrocene moieties along the chain change significantly. The former aspect reveals that the hydrogen bonded chain is a *structural determinant* which, together with inter-ion interactions, is responsible for crystal cohesion. Structural flexibility and the diffuse network of weak, less directional, interactions provide instead the necessary ion mobility and permeability to water molecules.

Two remarks to conclude this preliminary communication: (i) since the reaction products in crystal engineering are solids the utilization of powder diffraction is, sometimes, the only way to ascertain whether the whole solid material has the *same structure* as that characterized by single crystal X-ray diffraction.[9] Our findings are a *caveat* since a common method of sample preparation (powder grinding) may lead to dramatic solid state transformations.

(ii) Not less important is the notion that such crystal transformations may be quantitatively achieved by mechanical stress (and consequent thermal effect). Indeed this is something that may be exploited: work is in progress to ascertain whether other molecules with hydrogen bonding capacity similar to that of water may be used in solid state reactions with crystalline **2**.

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Notes and references

† $[(\eta^5\text{-}C_5H_5)_2Co]$ and $[(\eta^5\text{-}C_5H_4CO_2H)_2Fe]$ were purchased from Aldrich. For the preparation of crystalline **2** see ref. 4. Upon 1 : 1 reaction between $[(\eta^5\text{-}C_5H_4CO_2H)_2Fe]$ (84 mg, 0.30 mmol) and $[(\eta^5\text{-}C_5H_5)_2Co]$ (57 mg, 0.30 mmol) in 20 ml of anhydrous thf an orange powder precipitate **1** immediately formed. After 1 h, **1** was filtered and a portion was recrystallized overnight from nitromethane (or methanol), yielding air stable orange crystals of **2**. Grinding of the second portion of **1** to prepare a sample for powder diffraction led to formation of crystalline powder **3**, which on recrystallization from nitromethane gave single crystals of **3**. It is important to stress that, in the preparation of powder diffraction samples, we followed a conventional 'open-air' procedure. Grinding was performed manually for few minutes till a fine powder was obtained in order to avoid preferential orientation problems. If the grinding is done in a dry box, only partial hydration is observed and the powder spectrum is a mixture of those of **1** and **3**. This indicates that water for hydration comes both from ambient humidity and from surface wetting, this latter water is very difficult to remove.

‡ Powder X-ray diffraction measurements: Philips PW-1100 automated diffractometer, Cu-Kα radiation, monochromator graphite. Single crystal X-ray diffraction: CAD4 diffractometer, Oxford Cryostream liquid-N2 device, Mo-Kα radiation, monochromator graphite. Data were corrected for absorption by azimuthal scanning of high-χ reflections (min. and max. transmission 0.87 and 1.00). *Crystal data* for **3**: $C_{22}H_{21}CoFeO_5$, T = 223(2) K, M = 480.17, monoclinic, $P2_1/n$, a = 12.251(5), b = 17.276(6), c = 18.083(7) Å, β = 91.56(3), V = 3825.8(25) Å^3, Z = 8, F(000) = 1968, μ = 1.658 mm^{-1}, θ-range 3.0–25 °, 6933 reflections, 6710 independent, refinement on F^2 for 454 parameters, wR (F^2, all reflections) = 0.1495, R_1[I > $2\sigma(I)$] = 0.0455. SHELXS-97[10a] and SHELXL97[10a] were used for structure solution and refinement based on F^2. The asymmetric unit contains two cations, one anion, two 'half' anions located on inversion centres, and two water molecules unit. The hydrogen bond pattern in **3** is more complex than in **2** and will be discussed in a full report. SCHAKAL97[10b] was used for the graphical representation of the results.

CCDC 182/1223. See http://www.rsc.org/suppdata/cc/1999/937/ for crystallographic files in .cif format.

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