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# *Seeds* obtained from a hydrated polymorph permit crystallisation of an elusive anhydrous organometallic zwitterion

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**Single crystals of the anhydrous polymorphic modification of the organometallic zwitterion [$Co^{III}(\eta^5$-$C_5H_4CO_2H)(\eta^5$-$C_5H_4CO_2)$] can only be obtained by seeding the solution with *seeds* prepared after stepwise dehydration and consequent phase transition at 506 K of the hydrated material [$Co^{III}(\eta^5$-$C_5H_4CO_2H)(\eta^5$-$C_5H_4CO_2)]\cdot3H_2O$.**

The control of crystallisation processes is of great interest both in crystal engineering,[1] where molecular materials with predefined organisation of the component molecules or ions are sought, and in the study of polymorphism,[2] where different polymorphs of the same substance may show different physical properties.

Here we report that single crystals of the elusive anhydrous polymorphic modification of the neutral zwitterion [$Co^{III}(\eta^5$-$C_5H_4CO_2H)(\eta^5$-$C_5H_4CO_2)$], **ZW**, can be obtained by *seeding* the starting solution† with 'seeds' prepared by stepwise dehydration and subsequent phase transition of the hydrated species [$Co^{III}(\eta^5$-$C_5H_4CO_2H)(\eta^5$-$C_5H_4CO_2)]\cdot3H_2O$, **ZW**$\cdot3H_2O$. This hydrate is the only product of the crystallisation from a aqueous solution of [$Co^{III}(\eta^5$-$C_5H_4CO_2H)(\eta^5$-$C_5H_4CO_2)$] obtained from the organometallic cationic diacid [$Co^{III}(\eta^5$-$C_5H_4CO_2H)_2]^+$.[3] Both **ZW** and **ZW**$\cdot3H_2O$ have been structurally characterised by single crystal‡ and powder diffraction while the conversion of the initial product **ZW**$\cdot3H_2O$ into anhydrous **ZW** has been monitored by thermogravimetry.

The most relevant features of **ZW**$\cdot3H_2O$ and **ZW** can be summarised as follows.

(i) In contrast to the related dicarboxylic acid [$Fe^{II}(\eta^5$-$C_5H_4CO_2H)_2$] and the parent cation [$Co^{III}(\eta^5$-$C_5CO_2H)_2]^+$,[4] in crystalline **ZW**$\cdot3H_2O$ there are no O–H···O hydrogen bonds between the –$CO_2H$/–COO groups, while C–H···$O_{(CO_2/CO_2H)}$ hydrogen bonded 'dimers' (D) are formed as shown in Fig. 1(a).

(ii) The dimeric units are linked in chains *via* a further, almost symmetric, bifurcated C–H···$O_{(CO_2/CO_2H)}$ hydrogen bond (C) between two adjacent C–H groups of a cyclopentadienyl ring and one O-atom lone-pair resulting in the formation of 'pipelines' through the crystal.

(iii) The pipelines are occupied by three water molecules per formula unit [Fig. 1(b)]. Two molecules are linked *via* O–H···O hydrogen bonds to the –$CO_2$/–$CO_2H$ groups on the walls of the channels and provide links between zwitterion stacks, whilst the central molecule interacts solely with the neighbouring water molecules.

(iv) Thermogravimetric analysis (TGA)§ shows that **ZW**$\cdot3H_2O$ releases one water molecule at 378 K (Fig. 2). Powder diffraction‡ shows that the crystal structure remains almost unchanged. This first dehydration is reversible and the crystal is rehydrated in *ca.* 24 h at room temperature in the air. The remaining two water molecules are lost together at *ca.* 506 K. The second loss of water is immediately followed by a phase transition to a different crystalline form as revealed by powder diffraction.

(v) Most remarkably, crystallisation from an *aqueous* solution of the powder obtained from TGA at 506 K in the presence of *seeds* (a small portion of the *same* powder) leads to formation of single crystals of the species **ZW**. The structure of **ZW** is based on a one-dimensional network of O–H···O bonded zwitterion molecules (Fig. 3). Comparison of the calculated and

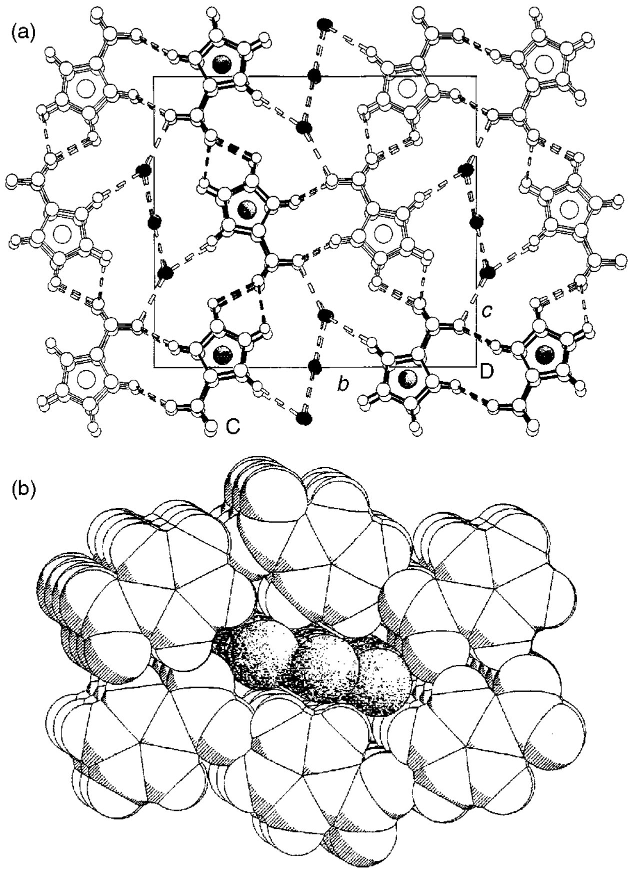

**Fig. 1** (a) The zwitterions [$Co^{III}(\eta^5$-$C_5H_4CO_2H)(\eta^5$-$C_5H_4CO_2)$] pile up along the *a*-axis with the –$CO_2$(H) groups pointing inward along the channels and forming O–H···O hydrogen bonds with two rows of water molecules. The organometallic units interact solely by means of C–H···O hydrogen bonds. Note how the 'dimers' (motif D) are linked in chains *via* bifurcated C–H···O hydrogen bonds; filled atom spheres represent the water oxygens. (*b*) Space filling representation of the channel in [$Co^{III}(\eta^5$-$C_5H_4CO_2H)(\eta^5$-$C_5H_4CO_2)]\cdot3H_2O$, **ZW**$\cdot3H_2O$, showing the three water molecules (dotted shading) occupying the channel. Relevant O···O distances (Å) are $O_{CO_2/CO_2H}\cdots O_{water}$ 2.758, 2780; $O_{water}\cdots O_{water}$ 2.823, 2838(2) Å.

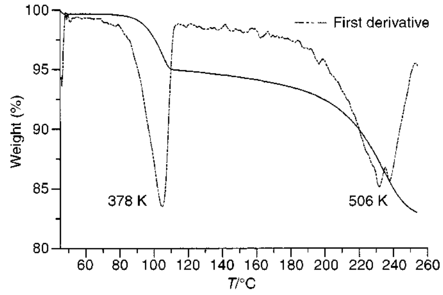

**Fig. 2** TGA plot of the dehydration process. Note how the first water molecule is lost at 378 K, while the other two water molecules are released at 506 K. This second loss of water is followed by a phase transition.

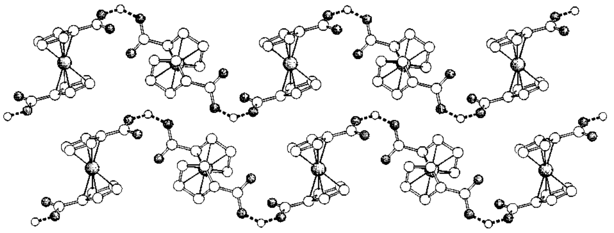

**Fig. 3** Chains of O–H···O bonded zwitterions $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$ in the anhydrous crystalline phase **ZW** crystallised *via* seeding of the solution obtained from the dehydrated powder; O···O 2.456(2) Å.

measured powder spectra of **ZW** confirms that the powder obtained at 506 K and the single crystals precipitated at room temperature after seeding possess the same structure. Importantly, crystallisation of the original solution mentioned in point (i), in the presence of seeds of **ZW**, also leads to isolation of the anhydrous crystalline material **ZW**, while, in the *absence* of seeds, the hydrated species **ZW**·$3H_2O$ is obtained.

Crystalline **ZW**·$3H_2O$ can be seen as a pseudo-polymorphic modification of **ZW**. The anhydrous form appears to be thermodynamically less stable and can only be obtained by dehydration of **ZW**·$3H_2O$ or *via* seeding of the solution, *i.e.* very likely under kinetic control.

It is worth stressing that the C–H···O bonds between zwitterions and the O–H···O bonds between zwitterion and water molecules along the walls of the channels are sufficient to keep the crystal together up to *ca.* 500 K. To the best of our knowledge, **ZW**·$3H_2O$ is the first case of an organometallic nanoporous material[5] with channels formed *via* C–H···O hydrogen bonds, with two structural water molecules acting as O–H···O bridges along the channels. Potential applications of nanoporous compounds are in catalysis, molecular sieves, molecule storage, ion exchange and solid sensors.[6]

The characterisation of **ZW** shows, *inter alia*, that single crystals of elusive polymorphic modifications can be obtained by controlling the crystallisation process *via* seeding, a crystallisation technique exploited also in organometallic solid state chemistry.[7] Clearly, the possibility of obtaining microcrystalline seeds by *non-solution* techniques (*dehydration* but also *grinding*[8]) is fascinating and opens up potentially useful alternative routes for the engineering of molecular materials.

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## Notes and references

† The starting material, **ZW**·$3H_2O$, is obtained from an aqueous solution of the salt $\{[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]\cdot[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)_2]\}^+\text{-}[PF_6]^-$ (0.3 mmol, 0.209 g, 20 ml water) after extraction of $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)_2]^+[PF_6]^-$ with nitromethane (70 ml in total).[3] Evaporation of the aqueous solution yielded yellow, sword-like, crystals of **ZW**·$3H_2O$ (0.099 g). Correspondence between the structure determined by single-crystal X-ray diffraction (see below) and the bulk material was confirmed by powder diffraction measurements.

‡ *Crystal data*: **ZW**·$3H_2O$: monoclinic, space group $P2_1/n$, $a$ = 6.707(3), $b$ = 14.997(4), $c$ = 13.453(4) Å, $\beta$ = 99.84(1)°, $Z$ = 4, $V$ = 1333(8) Å$^3$, $\mu$ = 1.316 mm$^{-1}$, $\theta$ range 3–25°, $T$ = 223(2) K, 2230 independent reflections, $R1$ [$I > 2\sigma(I)$] 0.0851, $wR^2$ (all data, $F^2$) 0.2467.

**ZW**: monoclinic, space group $C2/c$, $a$ = 7.403(2), $b$ = 10.964(8), $c$ = 12.293(3) Å, $\beta$ = 94.30(3)°, $Z$ = 4, $V$ = 995.0(8) Å$^3$, $\mu$ = 1.722 mm$^{-1}$, $\theta$ range 3–25°, $T$ = 273(2) K, 863 independent reflections, $R1$ [$I > 2\sigma(I)$] 0.0362, $wR^2$ (all data, $F^2$) 0.0996. The SHELXL97[9a] package was used for structure solution and refinement based on $F^2$. SCHAKAL97[9b] was used for all graphical representations. Diffraction data on **ZW**·$3H_2O$ have been collected on three different crystal specimens to investigate the small disorder affecting the inner O-atom occupying the centre of the channel (site occupancies between 0.80 and 1.00). CCDC 182/1386. See http://www.rsc.org/suppdata/cc/1999/1949/ for crystallographic files in .cif format. Powder diffractograms of **ZW**·$3H_2O$ calculated on the basis of the single crystal structure, measured at room temperature, measured after the first dehydration at 378 K, and measured after phase transition upon complete removal of the three water molecules, and a comparison between this latter diffractogram and the calculated spectrum of **ZW** are available as supplementary material upon request to the authors.

§ TGA was carried out on a Perkin-Elmer TGA-7 instrument in open Al pans under $N_2$ atmosphere. The loss in weight at the two temperatures (see Fig. 2) corresponds to one and two water molecules per **ZW** molar unit, respectively.

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