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Making and converting organometallic pseudo-polymorphs *via* non-solution methods†

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The organometallic pseudo-polymorphism that arises from cocrystallisation of organometallic molecules or ions with solvent molecules is discussed, together with the possibility of interconversion between polymorphs and pseudo-polymorphs. Three cases have been investigated: (i) the quantitative preparation of a monohydrated pseudo-polymorph of the supramolecular salt $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-$ **1** by *grinding* the powder material and subsequently *nucleating* and crystallising the hydrated form $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-\cdot H_2O$ **2**, (ii) the quantitative preparation, nucleation and crystallisation of the elusive anhydrous form of the neutral zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$ **4** by thermal dehydration of the hydrated species $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]\cdot 3H_2O$ **3**, and (iii) the formation of the salt $[Ru^{II}(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ **5** either by direct crystallisation from water or by desolvation of the pseudo-polymorph $[Ru^{II}(\eta^6\text{-}C_6H_6)_2][BF_4]_2\cdot MeNO_2$ **6** obtained from nitromethane. In order to investigate the processes, single crystal and powder X-ray diffraction measurements as well as thermogravimetry and differential scanning calorimetry have been carried out. These results show, *inter alia*, how elusive polymorphic or pseudo-polymorphic modifications of a given substance can be obtained by *non-solution* methods.

Introduction

Crystal polymorphism offers the intriguing possibility of isolating the same compound in different crystalline forms.[1,2] If we consider a crystal as a supramolecular entity, polymorphic modifications of molecular crystals can be seen as supramolecular isomers, which result from different distributions of the intermolecular interactions relevant to crystal packings. The utilisation of secondary (non-covalent) bonds to make molecular aggregates is of growing interest, and in this context the study of polymorphism falls into the mainstream of (molecular) crystal engineering.[3] Polymorphic modifications of of the same substance may differ markedly in chemical and physical properties such as diffraction pattern and solid state spectroscopy. Many drugs, for example, exist in polymorphic modifications characterised by a different solubility, hence efficiency of assimilation[4] and also mechanical properties relevant for comminution and tableting.[5] On the other hand, pseudo-polymorphism refers to the cases in which the same given substance includes solvent during crystallisation,[6] and this is the case of the compounds discussed in this paper. In spite of the enormous commercial and academic interest in the phenomenon of polymorphism, very little has been done so far in the field of organometallic chemistry.[7] Only in recent times, materials chemists have begun to appreciate the implications of having carbon-bound metal atoms and the foreseeable effects on the properties of solid state materials. The utilisation of metal-containing molecular building blocks to prepare solids with predefined physical and chemical properties is the paradigm of co-ordination[8] and organometallic crystal engineering.[9] The ultimate goal in the study of organometallic polymorphism is, in fact, that of attaining (and possibly controlling) different solid state properties by changing the arrangement of organometallic molecules in the solid state.[10]

We have found that pseudo-polymorphic modifications of organometallic systems, whether neutral or ionic, can be obtained and/or interconverted by mechanical grinding or thermal treatment, methods that, in this context, we define as *non-solution methods*. Once the desired powder material is produced, this can be used to *seed* the growth of crystals amenable to single-crystal X-ray diffraction.

In the following we will focus on three examples of preparation and interconversion of organometallic supramolecular salts and on the characterisation by X-ray diffraction of the crystalline materials. Preliminary reports concerning the preparation and interconversion of $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-$ **1** and its hydrated form $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-\cdot H_2O$ **2**,[11] as well as those of $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]\cdot 3H_2O$ **3** and its anhydrous form $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$ **4** have been published.[12] The formation of the salt $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ **5** either by direct crystallisation from water or by desolvation of the pseudo-polymorph $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2\cdot MeNO_2$ **6** obtained from nitromethane is discussed for the first time. This paper will show the importance of utilising a combination of diffraction and thermodynamic solid state techniques to prepare and characterise the new crystalline materials, and to investigate their phase transition behaviour and the loss or gain

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b003160g/

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of solvent molecules. Furthermore, it will be shown that the otherwise elusive polymorphic or pseudo-polymorphic modifications of the compounds listed above can be obtained not only by thermal dehydration in thermogravimetric experiments (TGA) but also by less conventional methods such as seeding and grinding or their combination.

Experimental

The syntheses of compounds **1**–**4** have been reported in preliminary communications[11,12] and will not be repeated here, whilst the synthesis and characterisation in the solid state of the ruthenium bis-benzene cationic complexes **5** and **6** have never been discussed before.

General

All reactions were carried out without any particular precaution. $RuCl_3·3H_2O$, 1,3-cyclohexadiene, CF_3CO_2H and $AgBF_4$ were purchased from Aldrich and used as provided.

Synthesis of $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ 5 and $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2·MeNO_2$ 6

The oligomeric compound $[Ru(\eta^6\text{-}C_6H_6)_2Cl_2]_2$ (250 mg, 0.5 mmol), prepared by literature methods,[13] was dissolved in acetone (30 ml); $AgBF_4$ (40 mg, 2.1 mmol) was then added and the mixture stirred for 2 h. The resulting mixture was filtered to give a clear orange solution, which was evaporated to dryness to give $[Ru(\eta^6\text{-}C_6H_6)(Me_2CO)_3][BF_4]_2$. This latter was dissolved in CF_3CO_2H (3 ml), an excess of benzene (0.5 ml) added and the resulting solution refluxed for 4 h. The solvent was removed under vacuum and the white precipitate of $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ (170 mg, 0.4 mmol, 40% yield) crystallised from $MeNO_2$ to form long needles which were characterised as $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2·MeNO_2$ **6**. Crystals of **6** are unstable in the air and convert into the crystalline powder **5**. Recrystallisation of **6** from water gives rise to the formation of colourless air stable crystals of $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ **5** suitable for single crystal X-ray analysis. The identity of **5** was confirmed by comparing experimental and calculated PXDPs. Rapid solvent loss prevented both the PXDP (in absence of solvent) and microanalysis from being recorded on **6**.

Crystal structure determination

Crystal data and details of measurements for crystalline compounds **1**–**6** are reported in Table 1. Diffraction intensities for **5** were collected on a Nonius CAD4 diffractometer equipped with an Oxford Cryosystem device for low temperature collection; for **6** the data were collected on a Bruker Smart CCD diffractometer. Both diffractometers were equipped with a graphite monochromator (Mo-Kα radiation, $\lambda = 0.71073$ Å). All refinements have been carried out on F^2 using all reflections. The computer program SHELX 97[14a] was used for structure solutions and refinements. In **5** and **6** all non-H atoms were refined anisotropically. For all compounds hydrogen atoms were added in calculated positions (C–H 0.95 Å). For all molecular representations the graphic program SCHAKAL 97[14b] was used. The program PLATON[14c] was used to calculate the hydrogen bonding interactions of the C–H···F, C–H···O, O–H···O types reported in Table 2. For these calculations all C–H distances were normalised to the neutron derived value (1.08 Å).

CCDC reference number 186/2007.

See http://www.rsc.org/suppdata/dt/b0/b003160g/ for crystallographic files in .cif format.

Other measurements

TGA for compound **3** was carried out on a Perkin-Elmer TGA-7 instrument in open aluminium pans under a N_2 atmosphere. The loss in weight at the two temperatures (see Fig. 4) corresponds to 1 and 2 water molecules per $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]·3H_2O$ molar unit, respectively. Powder X-ray diffractograms were collected on a Philips PW-1100 automated diffractometer [Cu-Kα, graphite monochromator].

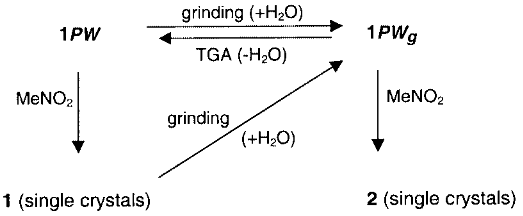
Results and discussion

The interconversion of compounds 1 and 2

The case of the salt $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-$ **1** will be discussed first. As a part of a wider project[15] centred on the utilisation of charge-assisted hydrogen bonds between organic and organometallic molecules and ions, **1** was initially obtained by treating cobaltocene $[Co^{III}(\eta^5\text{-}C_5H_5)_2]$ in THF and in the air with the organometallic acid $[Fe(\eta^5\text{-}C_5H_4CO_2H)_2]$.[16] Other supramolecular salts, including the mixed-metal mixed-valent species $[Cr(\eta^6\text{-}C_6H_6)_2]^+\{[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)][Fe(\eta^5\text{-}C_5H_4CO_2H)_2]_{0.5}\}^-$ which contains paramagnetic chromium(I) centres, have been obtained by varying the acid : base stoichiometric ratio and nature of the organometallic base.[17]

In this section we focus on the intriguing phenomenon observed when the crude powder of **1** (**1***PW*) that precipitates out from the THF original solution is mechanically ground for a few minutes using a pestle and mortar (**1***PW*$_g$). Serendipity played an important role in this initial and crucial step. Grinding, in fact, performed in order to prepare the sample for a powder diffraction experiment, is a procedure routinely used in crystal engineering laboratories to ascertain that the *whole* solid residue possesses the same structure as that determined by single crystal diffraction (if single crystals are available, of course).

The whole process is shown in Scheme 1. Our observations are the following: (i) recrystallisation of compound **1***PW* from nitromethane gives single crystals of the anhydrous salt $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-$ **1** whose structure was determined by single crystal X-ray diffraction (see Fig. 1); (ii) the powder X-ray diffraction pattern (PXDP) calculated from the single-crystal structure of **1** is different from that measured on a sample of **1***PW*, **1***PW*$_g$; (iii) recrystallisation from nitromethane of **1***PW*$_g$ yields single crystals of the hydrated form **2** (see Fig. 1); (iv) comparison of the calculated PXDP of **2** with that measured for **1***PW*$_g$ confirms that the two materials possess the same structure; (v) importantly, the measured PXDP on a crude sample of **1***PW* differs from that obtained from **1***PW*$_g$ *and* from that calculated on the basis of the single crystal structure of **1**, indicating that **1***PW* represents a different phase, *i.e.* one that does not correspond to either **1** or **2** for which single crystals can be obtained; (vi) once **1***PW*$_g$ is formed, single crystals of **2** can be grown from either water or nitromethane while formation of crystals of the anhydrous form **1** is no longer observed; (vii) however, on heating **1***PW*$_g$ at 373 K in a thermogravimetric (TGA) experiment water is lost and the PXDP shows that the material reverts to the starting **1***PW*; (vii) if the grinding is done in a dry-box only partial



Scheme 1 The crystallisation ⟶ grinding ⟶ dehydration ⟶ seeding that leads from the crude powder of $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+\text{-}[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-$ **1***PW* to the anhydrous and hydrated forms **1** and **2** and to their interconversion.

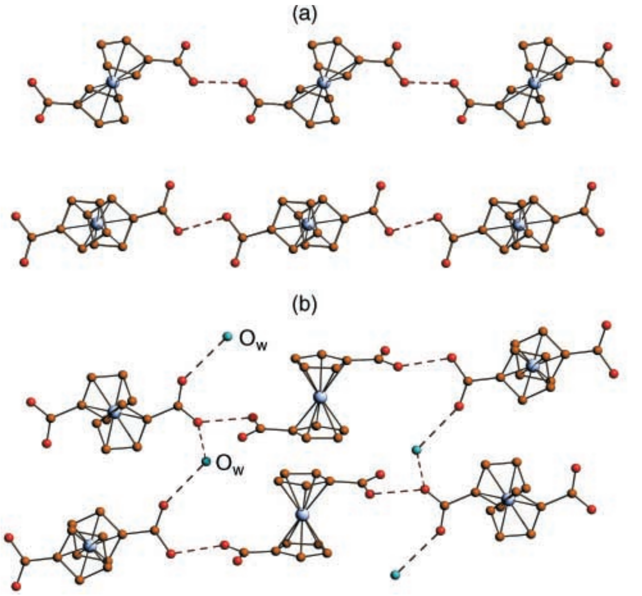


Fig. 1 A comparison of the ion organisation in the anhydrous form **1** and the hydrated form **2** of $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-$.

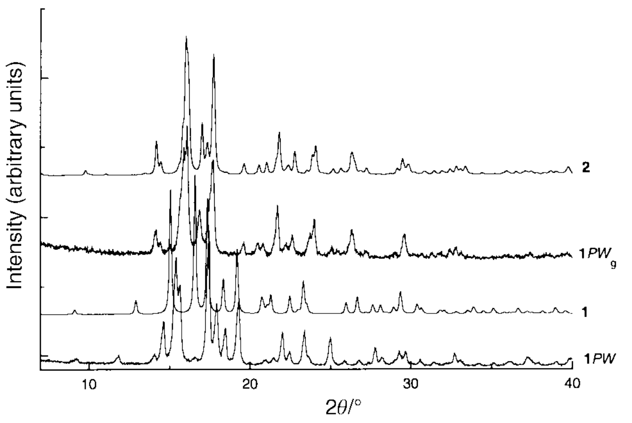


Fig. 2 Comparison of the PXDP for (a) compound **1***PW* (crude sample not ground), (b) **1***PW*$_g$ (observed), (c) **2** (calculated) and (d) **1** (calculated). Note how PXDP of **1***PW* ≠ **1** ≠ (**1***PW*$_g$ = **2**).

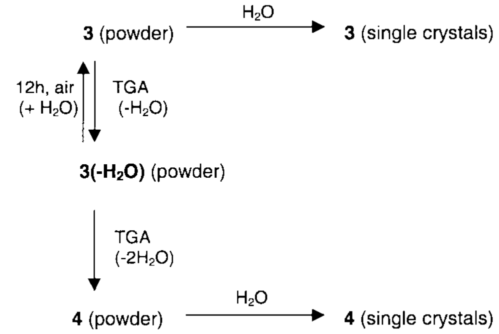
hydration is observed and the powder spectrum is a mixture of those of **1***PW* and **1***PW*$_g$.

A comparison of the PXDP of compound **1***PW* with those calculated for **1** and **2** on the basis of the observed single crystal determinations is reported in Fig. 2. In summary, the cases of **1** and **2** show that, as a consequence of mechanical grinding, water molecules are inserted in stoichiometric amount into a complex and highly organised crystal edifice without loss of crystallinity or disruption of the anionic organisation. An inspection of Fig. 1 shows how the hydrogen bonding network, based on O–H···O interactions between the anions, is not altered by the presence of water molecules, which are accommodated in between the chains and bridge the available oxygen atom acceptors.[18] The cobaltocenium cations are encapsulated between the anionic rows and interact *via* charge-assisted C–H···O hydrogen bonding interactions. A discussion of these structural features is, however, beyond the scopes of this report.[19]

The interconversion of compounds 3 and 4

In the quest for new organometallic building blocks for crystal engineering we have synthesized and structurally characterised a whole family of crystalline materials obtained from the cationic dicarboxylic acid $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)_2]^+$.[20] The cation was obtained together with the zwitterion form $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$ in the supramolecular salt $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)][Co^{III}(\eta^5\text{-}C_5H_4CO_2H)_2]^+[PF_6]^-$. The two components could only be separated by extraction with nitromethane of the salt $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)_2]^+[PF_6]^-$ (more soluble in nitromethane than in water) after treatment of the solution of $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)][Co^{III}(\eta^5\text{-}C_5H_4CO_2H)_2]^+[PF_6]^-$ with HCl. The remaining water solution gave, after complete removal of HCl in three to five cycles of heating to dryness and dissolution, crystals of the hydrated zwitterionic form $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]\cdot 3H_2O$ **3**. Since the previously described experiments on compound **2** had shown not only that water could be removed in a TGA experiment but also that this might be a way to prepare new crystalline systems, controlled thermal dehydration of **3** was attempted.

The process is shown in Scheme 2. The results of the experiments can be summarised as follows. (i) PXDP shows that the bulk of the crystalline material obtained from crystallisation possesses the same structure as the one obtained from single crystals, *viz.* species **3** (see Fig. 3). **3** possesses a remarkable channelled superstructure in which water molecules create a sort of *pipeline* and are bound to the walls by O–H···O hydrogen bonds with the CO_2/CO_2H groups of the complex. The channelled structure accounts for the relatively facile removal of the water molecules, as observed in the TGA experiment. (ii) The TGA plot shows (Fig. 4) that the hydrated form **3** reversibly releases one water molecule at 378 K, while the loss of the two remaining water molecules occurs at *ca.* 506 K and is immediately followed by a phase transition. (iii) Powder diffraction shows that the first dehydration leaves the crystal structure almost unchanged. In fact the PXDP of the dehydrated powder is nearly coincident with that calculated on the basis of the single crystal structure of **3**, as shown in Fig. 5. (iv) The dehydrated powder material, on the other hand, has a PXDP that differs from that of **3** (calculated), as shown in Fig. 5. (v) Most remarkably, crystallisation *from the original water 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 anhydrous species **4**. On repeating the experiments several times the simultaneous presence of both **3** and **4** was observed. Crystallisation *in the absence of seeds* leads exclusively to the hydrated species **3**. (vi) Comparison of the calculated and measured powder spectra for **4** confirmed that the powder obtained at 506 K and the single crystals precipitated at room temperature after *seeding* possess the same structure. (vii) Prolonged grinding of the anhydrous form **4** leads to partial hydration and reconstruction of the channelled structure of **3**.



Scheme 2 The crystallisation ⟶ dehydration ⟶ seeding that leads from the hydrated to the anhydrous form of zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$.

It seems reasonable to conclude that the anhydrous form **4** is thermodynamically less stable than the hydrated one and can only be obtained by dehydration of $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]\cdot 3H_2O$ or *via seeding* of the solution, *i.e.* very likely under kinetic control.

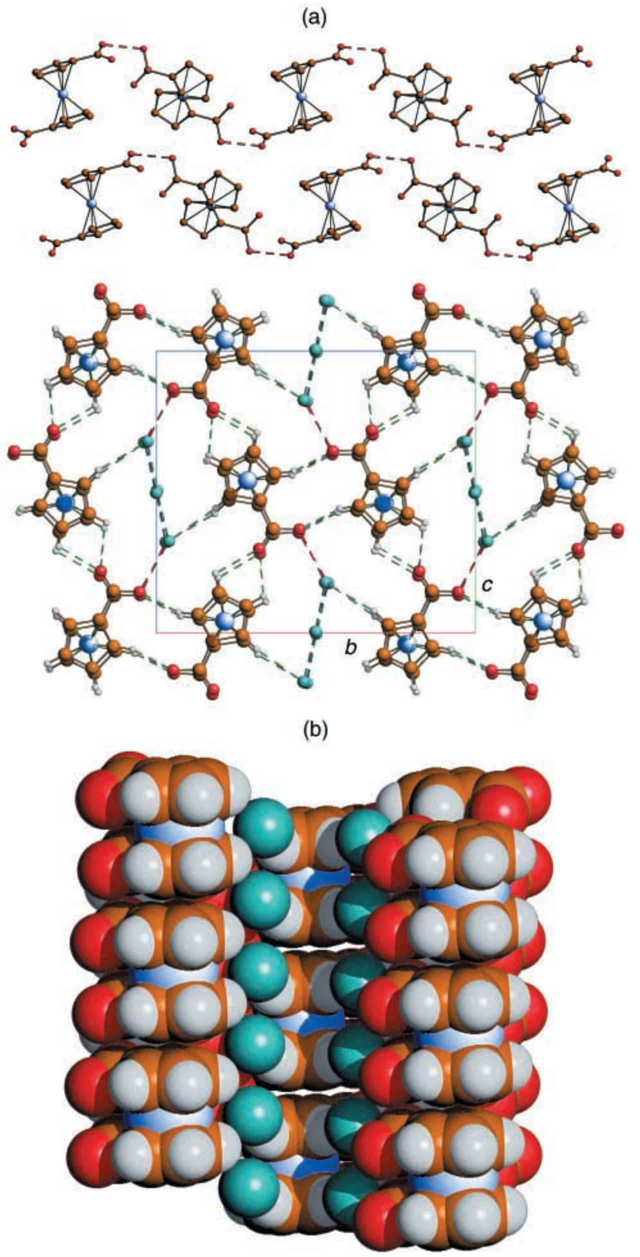


Fig. 3 (a) Comparison of the zwitterion arrangement in crystals of anhydrous $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$ **4** obtained by *seeding* of the initial water solution with 'seeds' prepared by stepwise dehydration and subsequent phase transition of the hydrated species **3**, $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]\cdot 3H_2O$, (b) The "pipeline" in crystalline **3** showing the channel after removal of the central water molecule.

Interconversion of compounds 5 and 6

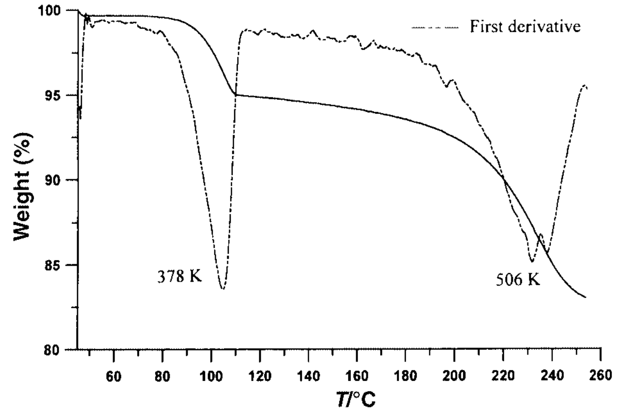


Fig. 4 The TGA plot obtained for the interconversion of the hydrated species **3**, $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]\cdot 3H_2O$ in the anhydrous form **4**, $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$.

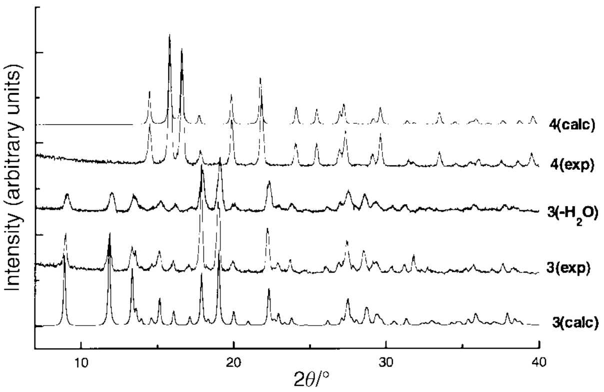


Fig. 5 Comparison of the PXDP obtained for compounds **3** and **4**. Note how PXDP of $\mathbf{3}_{obs} = \mathbf{3}_{calc} \neq \mathbf{4}_{obs} = \mathbf{4}_{calc}$.

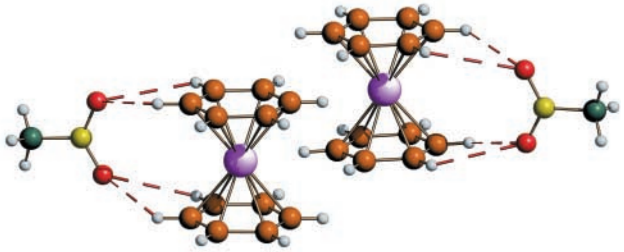
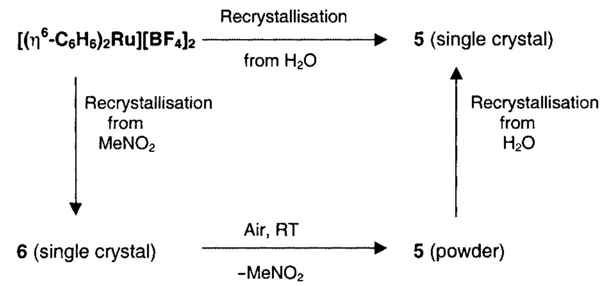


Fig. 6 The nitromethane solvate system **6** showing the interactions of the C–H · · · O type with the nitromethane molecule.



Scheme 3 The interconversion between $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ **5** and $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2\cdot MeNO_2$ **6**.

Crystallisation of $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ from nitromethane affords crystals of $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2\cdot MeNO_2$ **6**, unstable in the absence of (nitromethane) mother liquor. On the basis of a PXDP comparison, it can be shown that **6** rapidly converts into a different crystalline material. Crystals of the unsolvated form $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$ **5** suitable for single crystal X-ray analysis were initially obtained after recrystallisation from water of the powder derived from **6**. However, the same form **6** could not be obtained by *seeding* the initial nitromethane solution, as previously described for **4**. The process is described in Scheme 3. The solvent molecules assist the formation of a hydrogen bond network constituted by interactions of the type $C\text{–}H^{(\delta+)}\cdots O$ [(C)H · · · O distances in the range 2.56–2.60 Å] between the oxygens of nitromethane and the hydrogens of the benzene rings forming clamps, as shown in Fig. 6. An example of a similar clamping effect can be observed in crystalline $[Ru(\eta^6\text{-}C_6H_6)_2][O_3SC_6H_4Me\text{-}p]_2$ where charge assisted $C\text{–}H^{(\delta+)}\cdots O^{(\delta-)}$ interactions are shorter [(C)H · · · O distances in the range 2.15–2.40 Å] and more numerous.[21] In **6** there are also bifurcated $C\text{–}H\cdots F^{(\delta-)}$ interactions between the methyl group of nitromethane and the BF_4^- anions with $(C)H\cdots F^{(\delta-)}$ distances in the range 2.29–2.48 Å. This arrangement, however, is not stable at room temperature and in the air. The molecules

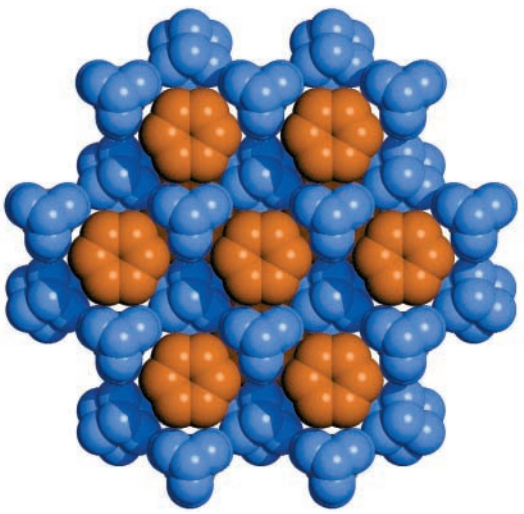


Fig. 7 Space filling representation of the hexagonal ion arrangement in crystalline compound **5**.

of nitromethane are arranged in rows perpendicular to the crystallographic 101 plane and can easily come out from the network leaving the ions to collapse and rearrange into the new unsolvated crystalline form **5**. The ion packing in **5** is seemingly more efficient (see Fig. 7). While in form **6** the honeycomb-type arrangement formed by the anions and the solvent reflects the existence of channels in the structure (Fig. 8), in form **5** there is always a BF_4^- anion on top of a benzene ligand. In both compounds there is a network of charge-assisted interactions of the type $C–H^{(\delta+)}\cdots F^{(\delta-)}$ between the benzene ligands and the anions [(C)H···F distances in the range 2.39–2.54 and 2.20 Å in form **6** and **5**, respectively]. The presence of the double charge is probably the explanation for the very short H···F distance in **5**. Charge-assisted interactions of this type have been found to be almost ubiquitous in crystalline salts containing BF_4^- or PF_6^- anions.[22] Contrary to the cases discussed in the previous sections, the loss of nitromethane from **6** is much easier and occurs at room temperature making measurement of the powder diffractogram without loss of solvent relatively difficult. Since the powder diffraction experiment must be carried out in the presence of the solvent ($MeNO_2$), the diffraction power is very much reduced resulting in a poor pattern. A comparison between measured and calculated PXDP for **5** and that calculated for **6** is shown in Fig. 9.

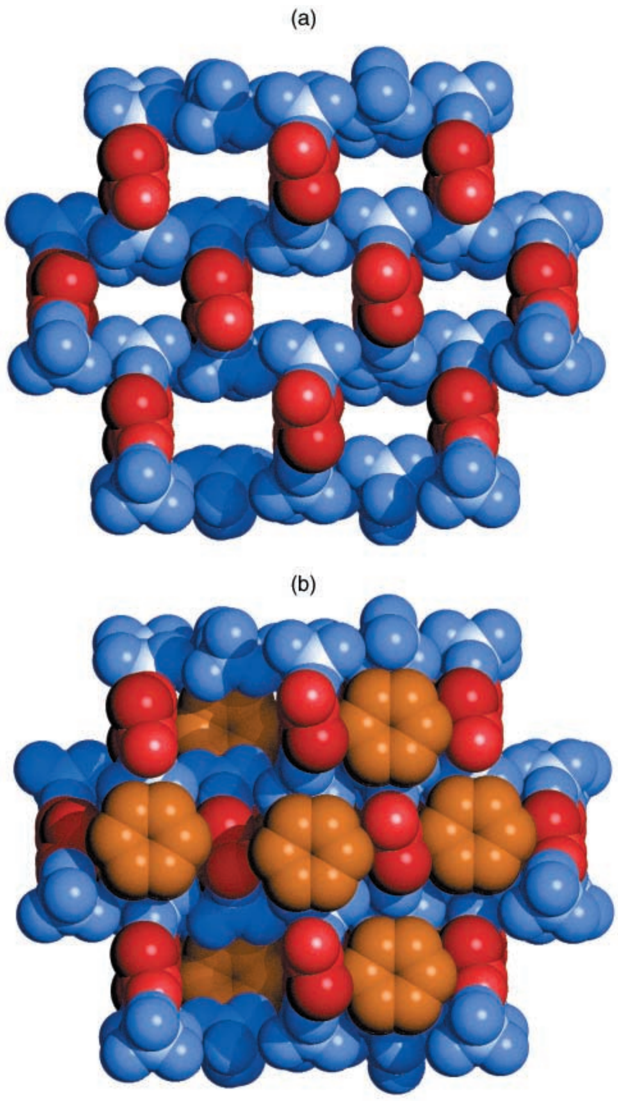


Fig. 8 (a) Space filling representation of the ion packing in crystalline compound **6**. (b) The honeycomb-type packing of the BF_4^- anions and solvent molecules in **6**; note how the nitromethane molecules group in rows in the crystal structure.

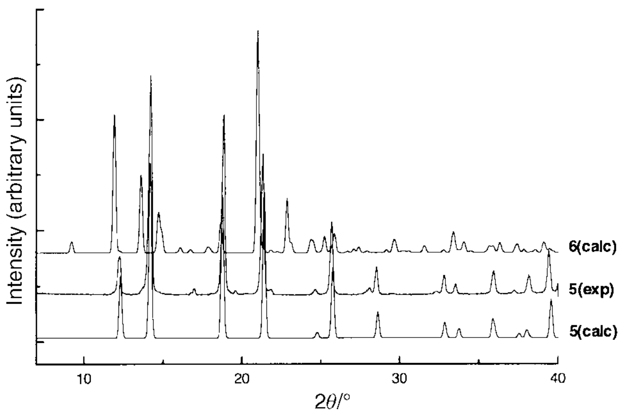


Fig. 9 Comparison between the observed PXDP for compounds $\mathbf{5}_{obs}$, $\mathbf{5}_{calc}$ and $\mathbf{6}_{calc}$.

Conclusion

The cases of the anhydrous and hydrated forms of the mixed metal organometallic salts $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+[Fe(\eta^5\text{-}C_5H_4\text{-}CO_2H)(\eta^5\text{-}C_5H_4CO_2)]^-$, **1** and **2**, and of the cobaltocenium zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)]$, **3** and **4**, demonstrate the possibility of controlling the formation of polymorphic or pseudo-polymorphic forms if microcrystals, *seeds*, can be obtained by methods alternative to crystallisation from solvents. The case of $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2\cdot MeNO_2$ **6** shows, on the other hand, that an unstable material can also be crystallised from a solvent like nitromethane *via* formation of weak hydrogen bonds between the cations and the oxygen atoms of the solvent. Loss of solvent from **6** at room temperature is accompanied by a phase transition with formation of the unsolvated phase **5**, $[Ru(\eta^6\text{-}C_6H_6)_2][BF_4]_2$. Indeed, the hydrogen bonds between solvent and host systems seem to play an important role in the formation of the pseudo-polymorphic forms. In the cases of **2** and **4** the water oxygens form strong O–H···O interactions with the carboxylic groups, so that phase transitions to the hydrated and anhydrous phases imply hydrogen bond forming and breaking, respectively. The "history" of the two systems suggests that the hydrated forms are those more stable thermodynamically (most probably because of the entropic contribution from the solvent to the crystal free energy) while the anhydrous species are less stable. However, while in the cases of **1** and **2** the anhydrous species is the first to precipitate out of the solution and conversion into the hydrated species requires mechanical activation, with **3** and **4** the situation is reversed. The hydrated **3** is the first form to

Table 1 Crystal data for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{22}H_{19}CoFeO_4$	$C_{44}H_{42}Co_2Fe_3O_{10}$	$C_{12}H_9CoO_4$	$C_{12}H_{15}CoO_7$	$C_{12}H_{12}B_2F_8Ru$	$C_{13}H_{15}B_2F_8NO_2Ru$
M	462.15	1016.19	276.12	330.17	430.91	491.95
T/K	213(2)	223(2)	293(2)	223(2)	223(2)	293(2)
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Hexagonal	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/n$	$P6_3/mmc$	$P2_1/n$
Z	2	4	4	4	2	8
a/Å	9.792(6)	12.251(5)	7.403(2)	6.0707(3)	8.2920(10)	18.184(4)
b/Å	9.249(4)	17.276(6)	10.964(8)	14.997(4)	8.2920(10)	11.865(3)
c/Å	10.338(8)	18.083(7)	12.293(3)	13.453(4)	12.5370(10)	18.251(4)
β/°	98.70(6)	91.56(3)	94.30(3)	99.84(2)	90	117.118(5)
V/Å^3	925.5(10)	3825.8(25)	995.0 (8)	1333.3	746.5(1)	35058(1)
μ(Mo-Kα)/mm^{-1}	1.706	2.023	1.722	1.316	1.128	0.983
Measured reflections	1726	6933	903	2230	2781	48694
Unique reflections	1629	6710	863	2230	308	13045
$R1$ [on F, $I > 2\sigma(I)$]	0.0449	0.0456	0.0362	0.0851	0.0227	0.0540
$wR2$ (F^2, all data)	0.1386	0.1457	0.1020	0.2467	0.0618	0.1546

precipitate and can be transformed into the anhydrous systems only upon thermal treatment suggesting that **3** is both the kinetic and thermodynamic product. In both **1/2** and **3/4** the formation of *seeds* is then exploited to control the crystallisation process. Although the nitromethane solvate **6** differs from the water solvates in that the association with the solvent is much less tight, the relationship between polymorph and pseudo-polymorph is of the same type. Upon desolvation the solvate system undergoes a phase transition to the binary salt **5**. This salt can be obtained directly only in the absence of nitromethane.

These examples suggest that controlled desolvation of solvate species may represent a useful "non-solution" method to obtain formation of otherwise elusive phases. Once a new crystalline powder has been obtained, it is possible to "drive" the crystallisation process towards the desired phase. In order to do so, however, one should make sure that not all crystal nuclei are destroyed. The suggested strategy is that of dissolving the powders obtained after thermal or mechanical treatment in the minimum amount of solvent and let crystallisation proceed by slow evaporation. In such a way, crystal growth preferably occurs on the microcrystals acting as templates.

Quantitative hydration upon grinding (cases **1/2**) is admittedly a less predictable phenomenon. The notion that powder grinding may lead to solid state transformations and to formation of new polymorphic modifications is, however, crucial for the success of crystal engineering strategies. While scientists in pharmaceutical industries are well aware of the possible consequences of tableting and other mechanical processing of solid drugs on the polymorphic modification of choice,[4,5] this awareness is not diffuse in the field of crystal engineering.

Polymorphism has many facets. Another relationship between polymorphic modifications is that shown by bis-formylferrocene [Fe(η^5-$C_5H_4CHO)_2$].[23] The room temperature phase undergoes an order ⟶ disorder phase transition on heating (at *ca.* 311 K) to yield a plastic phase which transforms on cooling to a thermodynamically more stable form. Once the new room-temperature phase is formed, the initial crystalline form cannot be obtained any longer, unless the compound is redissolved and recrystallised.[24] In this case, however, all attempts to nucleate the supposedly thermodynamic phase have failed because, upon grinding, the material undergoes a chemical reaction with formation of a ferrocene-based polymer. The intriguing possibility of observing *concomitant polymorphs* crystallised from the same crystallisation process has also recently been reviewed.[24]

All these examples should demonstrate (were it at all necessary) how the investigation of polymorphism and pseudo-polymorphism represents a way to acquire fundamental information on the factors responsible for crystal stability, on the nucleation processes, and on the interconversion of crystalline materials. For historical and utilitarian reasons, however, polymorphism has traditionally been a subject of research in the organic chemistry field.[24–26] It can easily be predicted that, as the interest in using metal-containing molecular materials increases in the quest for new properties and new functional solids, the subject of inorganic polymorphism and pseudo-polymorphism will soon become an area of systematic research.[7]

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References

1 W. C. McCrone, in *Polymorphism in Physics and Chemistry of the Organic Solid State*, eds. D. Fox, M. M. Labes and A. Weissemberg, Interscience, New York, 1965, vol. II, p. 726.

2 J. Bernstein and A. T. Hagler, *J. Am. Chem. Soc.*, 1978, **100**, 673; J. Bernstein, in *Organic Solid State Chemistry*, ed. G. R. Desiraju, Elsevier, Amsterdam, 1987, p. 471; in *Structure and Properties of Molecular Crystals*, ed. M. Pierrot, Elsevier, Amsterdam, 1990.

3 See, for a general entry: *Crystal Engineering: from Molecules and Crystals to Materials*, eds. D. Braga, F. Grepioni and A. G. Orpen, Kluwer Academic Publishers, Dordrecht, 1999.

4 A. Burger, in *Topics in Pharmaceutical Sciences*, eds. D. D. Breimer and P. Speiser, Elsevier, Amsterdam, 1983, p. 347; I. J. Lin and S. Nadiv, *Mater. Sci. Eng.*, 1979, **39**, 193.

5 S. R. Byrn, in *Solid State Chemistry of Drugs*, Academic Press, New York, 1982, p. 79.

6 T. L. Threlfall, *Analyst* (*London*), 1995, **120**, 2435. See also C. Bilton, J. A. K. Howard, N. N. L. Madhavi, A. Nangia, G. R. Desiraju, F. H. Allen and C. C. Wilson, *Chem. Commun.*, 1999, 1675.

7 D. Braga and F. Grepioni, *Chem. Soc. Rev.*, 2000, in the press.

8 S. R. Batten and R. Robson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1461; K. A. Hisch, D. Venkataraman, S. R. Wilson, J. S. Moore and S. Lee, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2199; L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem. Eur. J.*, 1999, **5**, 237; D. Whang and K. Kim, *J. Am. Chem. Soc.*, 1997, **119**, 451; A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schroder, *Coord. Chem. Rev.*, 1999, **183**, 117.

9 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; D. Braga and F. Grepioni, *Coord. Chem. Rev.*, 1999, **183**, 19.

10 See for example: J. S. Miller and A. J. Epstein, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 385; D. Braga, F. Grepioni, L. Maini, L. Prodi and R. Sessoli, *Chem. Eur. J.*, 2000, **6**, 1310; E. Coronado, J. Galan-Mascaros, C. Gomez-Garcia, J. Ensling and P. Guetlich, *Chem. Eur. J.*, 2000, **6**, 552.

11 D. Braga, L. Maini, M. Polito and F. Grepioni, *Chem. Commun.*, 1999, 1949.

12 D. Braga, F. Grepioni and L. Maini, *Chem. Commun.*, 1999, 937.

13 M. A. Bennett and A. K. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 233.

14 (*a*) SHELX 97, G. M. Sheldrick, Program for Crystal Structure Determination, University of Göttingen, 1997; (*b*) SCHAKAL 97, E. Keller, Graphical Representation of Molecular Models, University of Freiburg, 1997; (*c*) PLATON, A. L. Spek, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, C31.

15 D. Braga and F. Grepioni, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1.

16 F. Takusagawa and T. F. Koetzle, *Acta Crystallogr.*, *Sect. B*, 1979, **35**, 2888.

17 D. Braga, L. Maini and F. Grepioni, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2240.

18 D. Braga, L. Maini and F. Grepioni, *J. Organomet. Chem.*, 2000, **593**, 101.

19 D. Braga and F. Grepioni, *Acc. Chem. Res.*, in press.

20 D. Braga, L. Maini, M. Polito and F. Grepioni, *Organometallics*, 1999, **18**, 2577.

21 U. Beck, W. Hummel, H.-B. Burgi and A. Ludi, *Organometallics*, 1987, **6**, 20.

22 F. Grepioni, G. Cojazzi, S. M. Draper, N. Scully and D. Braga, *Organometallics*, 1998, **17**, 296.

23 J. Bernstein, R. J. Davey and J.-O. Henck, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 3440.

24 D. Braga, F. Paganelli, E. Tagliavini, S. Casolari, G. Cojazzi and F. Grepioni, *Organometallics*, 1999, **18**, 4191 and references therein.

25 A number of extremely useful examples, beside an entertaining reading, on elusive polymorphic forms are discussed in J. Dunitz and J. Bernstein, *Acc. Chem. Res.*, 1995, **28**, 193. See also J. Dunitz, *Acta Crystallogr.*, *Sect. B*, 1995, **51**, 619.

26 N. Bladgen and R. J. Davey, *Chem. Br.*, 1999, **35**, 44.