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Unexpected solid–solid reaction upon preparation of KBr pellets and its exploitation in supramolecular cation complexation

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Pressing solid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ with KBr to prepare samples for IR spectroscopy leads to a profound solid state rearrangement with formation of the supramolecular complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\cdot K^+Br^-$, which can also be obtained from solution crystallization. Similar solid–solid supramolecular complexation has been observed with $K[PF_6]$ and $[NH_4][PF_6]$.

Mechanically induced solid-state reactions are attracting the interest of scientists engaged in the quest for solvent free chemical processes,[1] which are important under both the environmental and topochemical viewpoints. Mechanochemical reactions have been exploited mainly with inorganic solids (alloying, milling of soft metals with ceramics, activation of minerals for catalysis, extraction, preparation of cements),[2] while they have seldom been employed as valuable alternative routes for the preparation of molecular materials.[3] Milling together of organic acids and amines has been investigated as a possible route to the preparation of amides.[4] More recently phosphonium salts have been prepared by milling triphenylphosphane with solid organic bromides,[5a] while supramolecular self-assembly[5b] and coordination polymers[5c] have been obtained by grinding transition metal inorganic salts with appropriate ligands.

We have exploited previously mechanochemical processes in the preparation of pseudo-polymorphic modifications of organometallic salts,[6a,b] as well as in the solid state synthesis of a series of novel hybrid organic–organometallic hydrogen bonded network compounds.[6c]

In this communication we report the (admittedly serendipitous) extension of this chemistry to the preparation of hybrid organometallic–inorganic salts by means of solid–solid reactions. In the course of our studies of solid–gas reactions exploiting the organometallic zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, **1**,[7] which carries a protonated –COOH and a deprotonated $\text{–COO}^{(-)}$ group, we were intrigued by the observation of large differences in the CO stretching frequency region between the IR spectra of **1** measured in Nujol and in KBr pellets (see Fig. 1).†

Alkaline halogenides, as KBr, used for IR pellets are known in some cases to interact physically or chemically with the embedded sample,[8] causing an alteration of the absorption frequencies with respect to those measured in solution or Nujol. For this reason we decided to investigate the possibility of a reaction between solid **1** and solid KBr. To this end we first attempted crystallization of **1** from a KBr solution.† Single-crystal structure determination‡ on the crystals thus obtained shows that the supramolecular complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\cdot K^+Br^-$, $\mathbf{1}_2\cdot K^+Br^-$, has formed (Fig. 2c). The complex results from the encapsulation of the K^+ cations within a cage formed by four zwitterionic molecules, dimerised *via* O–H···O hydrogen bonds, with the Br^- anions forming layers in between the cationic complexes. The structure is reminiscent of that of $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\cdot K^+[PF_6]^-$, $\mathbf{1}_2\cdot K^+[PF_6]^-$, previously obtained from the cationic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+[PF_6]^-$ by treatment with KOH.[9]

The experiment was then repeated in the solid state by manually grinding together solid **1** and solid KBr in stoichiometric 2 : 1 amount. The process is schematically represented in

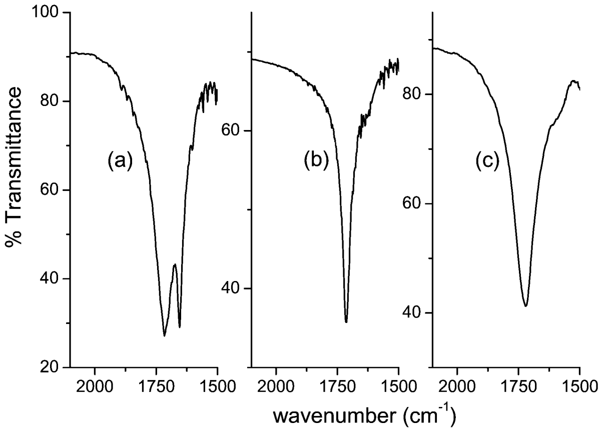

Fig. 1 Comparison of IR spectra of (a) **1** in Nujol, (b) **1** in KBr and (c) $\mathbf{1}_2\cdot K^+Br^-$ in Nujol.

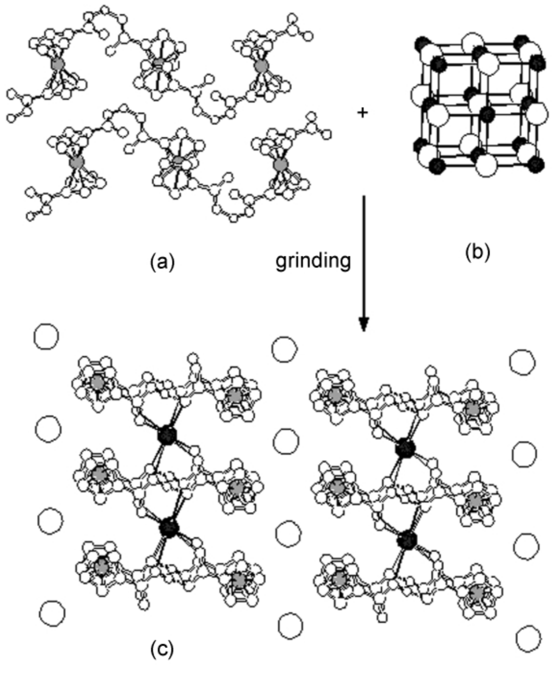

Fig. 2 The supramolecular rearrangement leading from crystalline **1** (a) and KBr (b) to crystalline $\mathbf{1}_2\cdot K^+Br^-$ (c). Note how the O–H···O hydrogen bonded chains need to be broken to allow formation of the complexating dimers. Empty and filled large spheres represent Br^- and K^+ ions, respectively. H_{CH} atoms omitted for clarity.

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Fig. 2. The powder diffraction pattern§ of the resulting ground material, $\mathbf{1}_2$·K$^+$Br$^-$, matches the one calculated on the basis of the single crystal structure (see Fig. 3), and the IR spectrum in Nujol shows nearly the same stretching frequencies as those observed in KBr pellets (see Fig. 1).

Thus, the routine method of IR sample preparation based on KBr pellets profoundly alters the solid state structure of the starting material via a complex supramolecular reaction. The structural rearrangement from **1** to $\mathbf{1}_2$·K$^+$Br$^-$ implies that the O–H···O hydrogen bonded chains present in crystalline **1** are disrupted with formation of hydrogen bonded dimeric units, which are able to encapsulate the alkali cation *via* O···K$^+$ interactions. It is noteworthy that the process also requires a change from *trans* to *cis* in the conformation of the C_5H_4-COO/COOH units (see Fig. 2).

In order to check the transferability of the solid state complexation process, the grinding experiment of **1** was also carried out with K[PF$_6$] and [NH$_4$][PF$_6$], which are known to yield the adducts $\mathbf{1}_2$·[NH$_4$/K]$^+$[PF$_6$]$^-$ from solution.[9] These two inorganic salts have been selected because crystalline $\mathbf{1}_2$·[NH$_4$/K]$^+$[PF$_6$$^-$] possess similar structural features[9] to $\mathbf{1}_2$·K$^+$Br$^-$, and the cages are almost isostructural. The comparison of the calculated and observed powder diffraction patterns confirms that the mechanochemical reaction leading to encapsulation of the inorganic cation is general.

We commented earlier on the topological analogy between the complexation of cations of appropriate size by [Co^{III}(η^5-C_5H_4COOH)(η^5-C_5H_4COO)] and the formation of supramolecular crown ethers.[9]

The discovery that a solvent-free solid-solid reaction can be used to obtain the same product as that obtained from solution opens new avenues to our crystal engineering endeavour, which is focused on the possibility of controlling breaking and formation of supramolecular bonding interactions between ions.[10] We are currently screening a number of inorganic salts and testing the selectivity of the solid–solid complexation with respect to a mixture of different salts.

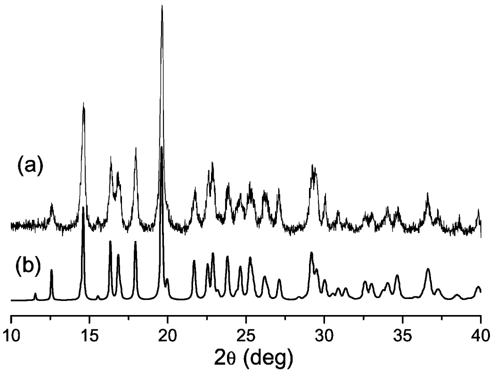

Fig. 3 Comparison between the observed (a, ground powder) and calculated (b, single crystal) X-ray diffraction patterns of $\mathbf{1}_2$·K$^+$Br$^-$.

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Notes and references

† **1** was obtained as previously reported.[7] KBr, K[PF$_6$] and [NH$_4$][PF$_6$] were purchased from Aldrich. Single crystals of $\mathbf{1}_2$K$^+$Br$^-$ were obtained by addition of a stoichiometric amount of KBr to a water solution of **1**. Crystallisation elemental analysis for $\mathbf{1}_2$K$^+$Br$^-$: Calcd: C, 42.94; O, 19.07; H, 2.70. Found: C, 43.01; O, 19.12; H, 2.65. IR spectra were registered on a FT-IR Nicolet spectrometer.

‡ *Crystal data* for $\mathbf{1}_2$·K$^+$[Br]: $C_{24}H_{18}BrCo_2KO_8$, triclinic, $P\bar{1}$, a = 5.985(1), b = 8.096(2), c = 12.614(2) Å, α = 78.28(2), β = 80.15(2), γ = 73.62(2)°, V = 570.0(2) Å^3, Z = 1, T = 293 K, 1983 independent reflections (2077 measured), 148 parameters, wR_2 = 0.0901, R_1 = 0.0316. All non-H atoms refined anisotropically. SHELX-97 used for structure solution and refinement on F^2 [G. M. Sheldrick, SHELX-97, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany (1997)]. CCDC 191071. See http://www.rsc.org/suppdata/cc/b2/b207493a/ for crystallographic data in CIF format.

§ Powder data were collected on a Philips X'Pert automated diffractometer with Cu-Kα radiation, graphite monochromator. The program PowderCell 2.2 was used for calculation of X-ray powder patterns [PowderCell programmed by W. Kraus and G. Nolze (BAM Berlin) © subgroups derived by Ulrich Müller (Gh Kassel)].

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