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Supramolecular gas–solid reaction between formic acid vapours and solid [$Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)$]

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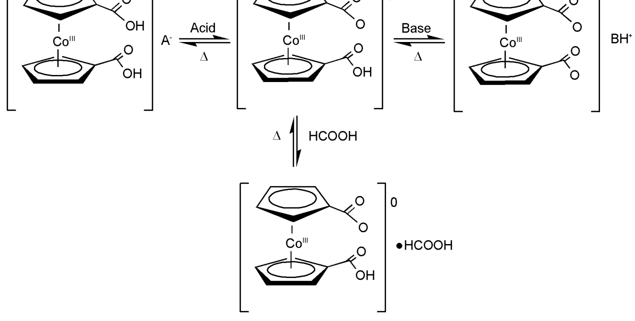
Exposure of the solid zwitterion [$Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)$] to vapours of formic acid quantitatively produces the co-crystal [$Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)$][HCOOH] without proton transfer from formic acid to the deprotonated –COO^- group on the zwitterion; formic acid can be quantitatively removed by mild thermal treatment, regenerating the starting material.

Detection and trapping of anthropogenic poisonous gases is one of the most pressing environmental issues of our time.[1] Formic acid, together with acetic acid, contributes to as much as 68% of the total un-neutralized acidity of rain in Southeast Asia[2] as well as in USA and represents one of the polluting agents from vehicular emissions in the atmosphere of Brazilian large cities.[3] It is also known that humid formic acid leads to copper corrosion, by formation of copper formiates.[4] On these premises, it is clear that trapping of formic acid is a relevant goal.

In this communication we report that the cheap and robust organometallic zwitterion [$Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)$] **1** reversibly absorbs formic acid from humid vapours forming selectively a 1 : 1 co-crystal, [$Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)$][HCOOH], **1**-[HCOOH], from which **1** can be fully recovered by mild thermal treatment. Complete conversion of crystalline **1** (50 mg) into **1**-[HCOOH] is attained in 4 h of exposure to hydrated vapours of HCOOH.† Single crystals of **1**-[HCOOH] can be obtained by crystallization from a water solution of HCOOH in which **1** is dissolved.‡

Compound **1** is a versatile reactant for gas–solid reactions towards acid (HCl, CF_3COOH, HBF_4) or base (NH_3, $(CH_3)_3N$, $(CH_3)NH_2$) vapours.[5] The amphoteric behaviour of **1** is due to the simultaneous presence of a deprotonated –COO^- and a protonated –COOH groups (Scheme 1), which can be protonated or deprotonated depending on the nature of reactant.

However, the behaviour of solid **1** towards formic acid vapours is intriguing since no proton transfer is observed. As shown in Fig. 1, crystalline **1**-[HCOOH] is composed of pairs of zwitterion molecules linked by O-H···O bonds between the protonated –COOH and the deprotonated –COO^- groups [O···O separation 2.526(4) Å]. The dimers of **1** interact with two formic acid molecules *via* O–H···O and C–H···O hydrogen bonds [O···O distance 2.541(4), (C)H···O distance 2.43(5) Å]. The intramolecular parameters are indicative of the presence of distinct –COOH and –COO^- groups over the zwitterionic complex **1** [C–O1 1.209(4), C–O2 1.306(4); C–O3 1.243(4), C–O4 1.247(4) Å]. On the other hand, the C–O distances within the HCOOH moiety [C–O5 1.305(5), C–O6 1.199(5) Å] indicate that the formic acid molecule retains its acidic hydrogen. This is also confirmed by ^{13}C CP-MAS NMR spectroscopy.§ Mootz and Wiechert have observed cocrystallisation of formic acid with pyridine.[6]



Scheme 1

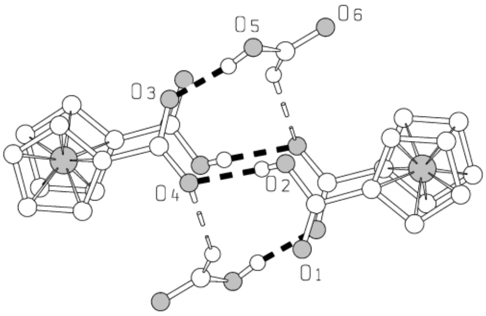


Fig. 1 The dimers of **1** interact with two formic acid molecules *via* O–H···O hydrogen bonds and C–H···O hydrogen bonds.

Fig. 2 shows a comparison of the X-ray powder diffraction pattern measured on the polycrystalline product with that calculated on the basis of the single-crystal structure.‡ It is evident that crystalline **1**-[HCOOH], whether obtained from the hetero-phase reaction or from solution, possesses the same solid-state structure and that no other solid product or unreacted **1** is present. It should be stressed that these results could not be

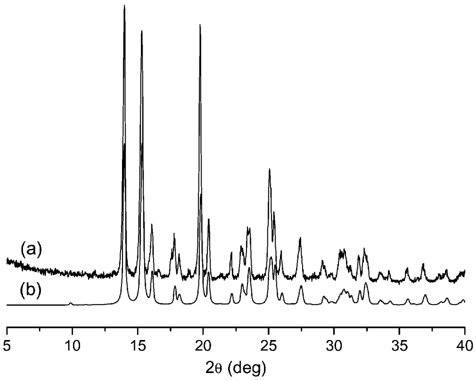


Fig. 2 Comparison between (a) the powder diffraction pattern measured on a sample of **1**-[HCOOH] obtained from the heterogeneous reaction and (b) that calculated on the basis of the single crystal structure of **1**-[HCOOH].

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predicted *a priori*, since the crystallization from solution might lead to solvated species or to a different stoichiometric ratio. Based on our observations, the intermediacy of a liquid phase in the solid-to-solid transformation of **1** into **1**-[HCOOH] cannot be ruled out.[7]

Crystalline **1**-[HCOOH] can be converted back to **1** by leaving the sample at room temperature in the air for few days or by mild heating in a thermogravimetric experiment¶ (stoichiometric loss of formic acid at 417 K). The powder diffractogram of the degassed product corresponds precisely to that of **1**, which can be cycled through several absorption and release processes without decomposition or detectable formation of amorphous material.

The process was also investigated by ^{13}C CP-MAS NMR spectroscopy.§ Fig. 3 shows the comparison between the NMR spectra of solid **1** and **1**-[HCOOH]. The resonance at 164.4 ppm is attributed to the formic acid molecules consistent to the data available in the literature for HCOOH in solution (166.3 ppm), while the chemical shift reported for the $HCOO^-$ in solution is 171.4 ppm.[8] As observed previously,[9a] the presence of only one resonance for the carboxylic carbon atoms of **1** at 167.9 ppm is indicative of proton exchange, on the NMR time scale, between the donor and acceptor atoms along the O–H–O bond. These groups are 'frozen out' as distinct $-COO^-$ and –COOH units in the X-ray diffraction experiment.[9b]

Pioneering studies of gas–solid reactions between organic acids and bases were carried out by Paul and Curtin,[10] More recently hetero-phase gas–solid reactions have been extensively explored by Kaupp[11] and Toda *et al.*[12] Coordination compounds have begun to be used in the quest for new solid state sensors and traps. Van Koten and coworkers have shown, for instance, that organo-platinum(II) complexes containing N,C,N tridentate coordinating anion 'pincers' reversibly bind gaseous SO_2 in the solid state, leading to quantitative adduct formation.[13]

In this communication we have reported a novel behaviour of the zwitterion **1** in heterogeneous gas–solid processes. At variance with the behaviour of **1** towards vapours of HCl or other strong acids, trapping of the formic acid molecules in **1**-[HCOOH] takes place *without proton transfer* from HCOOH to the zwitterion **1** (see Scheme 1). Since HCOOH is a weaker Brønsted acid than HCl, HBF_4 and CF_3COOH, one may tentatively attribute the different behaviour to the difference in relative acidity of the absorbed acid with respect to the zwitterion. Even though the weaker HCOOH acid does not protonate **1**, it is still capable of association with the zwitterion *via* strong O–H···O hydrogen bonding interactions. On this premise, the reaction between **1** (solid) and HCOOH (vapour) would be more appropriately described as a special kind of solvation rather than as a heterogeneous acid–base reaction. In a sense, gas–solid reaction and gas–solid solvation differ only in the energetic ranking of the interactions (whether covalent or non-covalent) that are broken or formed through the processes. In the reversible *supramolecular reaction* of solid **1** with gaseous HCOOH, O–H···O and C–H···O bonds are disrupted and/or rearranged, while covalent bonds are not affected.

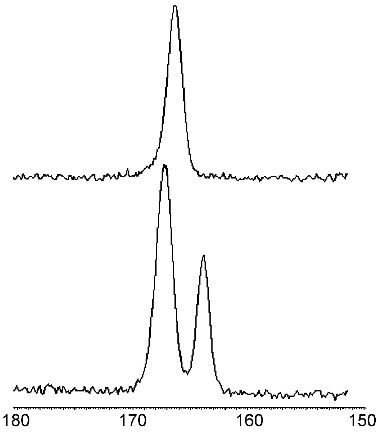

Fig. 3 Comparison between the ^{13}C CP-MAS NMR spectra of solid **1** (top) and **1**-[HCOOH] (bottom).

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Notes and references

† HCOOH was purchased from Aldrich and used without any further purification. **1** is quantitatively prepared from the corresponding dicarboxylic cationic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$. Exposure to the acid vapours was attained by filling the bottom of a Duran desiccator with 200 ml of a 30% solution of HCOOH and allowing the vapour to diffuse over a glass holder containing 50 mg of powdered **1**. In this way the powder and the solution were not in contact; the reaction took place in a closed system. Full conversion to **1**-HCOOH was achieved after 4 h.

‡ Single crystals were obtained by crystallization of **1** from a solution of 30% HCOOH. Diffraction data were measured on a Bruker SMART diffractometer at 223 K. *Crystal data* for **1**: $C_{13}H_{11}CoO_6$, monoclinic, $P2_1/c$, M = 322.15, a = 7.555(3), b = 8.937(3), c = 17.822(6) Å, β = 90.842(10)°, V = 1203.2(7) Å^3, Z = 4, μ = 1.450, 3511 independent reflections, R_{int} = 0.1029, wR (on F^2, all data) = 0.1551, R (on F, $I > 2\sigma I$) = 0.0591. CCDC reference number 191329. See http://www.rsc.org/suppdata/cc/b2/b207581d/ for crystallographic files in CIF or other electronic format. Powder data were collected on a Philips PW-1710 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)].

§ The high resolution ^{13}C CP-MAS NMR spectra were recorded on a Jeol GSE 270 (6.34 T) operating at 67.8 MHz under conditions of $^1H \rightarrow ^{13}C$ cross-polarization, high power proton decoupling and magic angle spinning. The 90° pulse was 5.50 μs and the contact pulse was 5 ms. Spectra were collected after 400 scans using a recycle delay of 40 s. The line broadening was set to be 5 Hz. External TMS was used as a reference (δ = 0). Cylindrical 6 mm o.d. zirconia rotors with sample volume of 120 μL were employed with spinning speed in the range from 4.5–5.5 kHz. For all samples the magic angle was carefully adjusted from the ^{79}Br MAS spectrum of KBr by minimizing the line width of the spinning side band satellite transitions.

¶ The TGA experiments were carried out on a Perkin-Elmer TGA-7 instrument in open Al pans under N_2 atmosphere.

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