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Mechanochemical assembly of hybrid organic–organometallic materials. Solid–solid reactions of 1,1′-di-pyridyl-ferrocene with organic acids†

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Manual kneading of the organometallic complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ with solid fumaric, succinic, tridecanedioic, terephthalic, trimesic and thiophene-2,5-dicarboxylic acids generated the corresponding adducts, whether salts or molecular complexes: $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(CH)_2COO]\cdot CH_3OH$, $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(CH_2)_2COO]\cdot[HOOC(CH_2)_2COOH]$, $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_{11}COOH]\cdot 2CH_3OH$, $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(C_6H_4)COOH]$, $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)_2][C_6H_3(COOH)_2(COO)]_2$ and $3\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(SC_4H_2)COO]\}\cdot[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot 2[HOOC(SC_4H_2)COOH]$. Direct reaction in solution yielded the same compounds, which were characterized by single crystal X-ray diffraction, thus allowing comparison of observed and calculated powder diffraction patterns. Kneading of the organometallic complex with maleic acid, on the other hand, yielded a different product from the one obtained *via* reaction in solution, which was characterized by single crystal X-ray diffraction as the salt $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)_2][HOOC(CH)_2COO]_2$. The solid–solid processes described herein imply molecular diffusion through the lattice and breaking and reassembling of hydrogen bonded networks with or without proton transfer from acid to base.

Introduction

It has long been known that solvent-free reactions between solid reactants often provide fast and quantitative routes to the preparation of novel compounds.[1] Thus far, reactions between solids have been mainly exploited for the preparation of organic molecules[2] or of inorganic materials such as alloys, cements, mixtures of soft metals with ceramics *etc*.[3] In recent years, under the impetus of crystal engineering,[4] *i.e.* the bottom-up construction of molecular materials starting from molecular or ionic building blocks, solid–solid reactions have begun to be investigated also as viable routes for the preparation of novel molecular and supramolecular aggregates.[5,6] The number of papers reporting mechanochemical preparation of molecular co-crystals, coordination networks, and salts is increasing rapidly.[7] The impact on the investigation of polymorphs and solvates is also noteworthy.[8] In particular, the current interest in molecular co-crystals, in view of their potential application as hybrid materials in various applications, is providing another strong motivation to the investigation of new ways to assemble molecules in the solid state.[9]

Besides being advantageous due to the absence of solvents, solid–solid reactions do often lead to very pure products and require very simple equipment to be carried out. The mixing of reactants can be achieved by simple manual grinding or by mechanical milling. The main disadvantage is inherent to the characterization of the (usually polycrystalline) reaction product, in particular when complex supramolecular systems are involved. In the absence of single crystals it is often difficult to determine, not only detailed structural features,[10] but often the very nature of the mechanochemical product.

There is also the intriguing possibility that crystallization from solution may not lead to the same product as obtained by mechanical mixing.[11] This is particularly important when crystallization from solution is under kinetic control, thus favouring formation of metastable phases.

We have been traditionally interested in the utilization of organometallic building blocks in solid-state supramolecular assembly. Our choice stems from the awareness that organometallic molecules afford a wealth of potentially important properties derived from the variable valence, spin and charge states of coordination complexes.[12]

In this paper we report the mechanochemical preparation of hybrid organic–organometallic supramolecular adducts obtained by reacting the ferrocenyl complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ with solid fumaric, succinic, tridecanedioic, terephthalic, trimesic and thiophene-2,5-dicarboxylic acid. In the presence of traces of solvent (kneading), the solid-state reaction rapidly yields the salts or co-crystals $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(CH)_2COO]\cdot CH_3OH$ (**1**), $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(CH_2)_2COO]\cdot[HOOC(CH_2)_2COOH]$ (**3**), $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_{11}COOH]\cdot 2CH_3OH$ (**4**), $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(C_6H_4)COOH]$ (**5**), $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)_2][C_6H_3(COOH)_2(COO)]_2$ (**6**) and $3\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(SC_4H_2)COO]\}\cdot[Fe(\eta^5\text{-}C_5H_4\text{-}$

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† Dedicated to Professor Jerry Atwood on the occasion of his 65th birthday.

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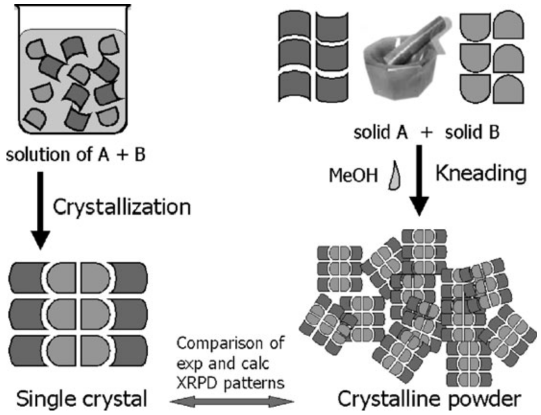

Scheme 1 The solid yielded by the mechanochemical process is compared *via* X-ray powder diffraction with the solids obtained by crystallization of A and B powders. The crystallization process allows preparation of single crystals that, after crystal structure determination, can be used to obtain calculated diffraction patterns.

$C_5H_4N)_2]\cdot 2[HOOC(SC_4H_2)COOH]$ (**7**), respectively, while solid-state reactions with maleic acid yield a different compound from the one obtained from reaction in solution, this last being $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)_2][HOOC(CH)_2COO]_2$ (**2**). As will be apparent in the following, the formation of these mixed systems imply profound modifications of the hydrogen bonding motifs present in the starting materials, with breaking of O–H···O hydrogen bonds between the organic molecules and formation of $^{(-)}$O···H–N$^{(+)}$ and/or O–H···N interactions within the adducts.

All compounds have been characterized by means of powder and single crystal X-ray diffraction. Single crystals were obtained by mixing methanol solutions of the reagents and allowing slow evaporation of the solvent. Single crystal data, beside providing an exact knowledge of the structure of the products, permit comparison between the X-ray powder diffractograms measured on the reaction products and those calculated on the basis of the single crystal structures. The entire process is illustrated in Scheme 1.

Along the same line, we have previously shown that manual grinding of the solid organometallic complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ with the solid dicarboxylic acids of formula $HOOC(CH_2)_nCOOH$ [with n = 4 (adipic), 5 (pimelic), 6 (suberic), 7 (azelaic), 8 (sebacic)] in the presence of traces of MeOH (kneading) yields five novel compounds, as easily ascertained by comparing the powder diffraction patterns of the starting materials with those of the products.[13] All complexes, with the exception of the co-crystal with pimelic acid, share a common structural feature, namely the formation of supramolecular macrocycles constituted of two organometallic and two organic units linked in large tetramolecular units by O–H···N hydrogen bonds between the –COOH groups of the dicarboxylic acids and the N-atoms of the ferrocenyl complex.

The utilization of ferrocenyl units in solid-state processes and solvent-free reactions has been recently reviewed.[14]

Results and discussion

All compounds cited above have been obtained by direct reaction between the ferrocenyl complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ and the polyfunctional organic acids, which are available as polycrystalline solids at room temperature. In order to assist the reader, chemical formulae of both acids and resulting products are reported in Table 1, together with the acids' molecular schemes. It is worth recalling here that the organometallic starting reactant $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ can also be prepared in solvent free conditions.[15]

All preparations were carried out by grinding in an agate mortar equimolar quantities of the two solid materials, in the presence of a small amount of methanol ("kneading", see Experimental section). The resulting polycrystalline material was used as such for powder diffraction experiments. In the cases of succinic and fumaric acids the powder material obtained from the solid–solid reaction becomes more crystalline if the sample is left standing for a couple of days in the presence of methanol vapours (methanol vapour digestion). Vapour digestion has been proved to be a valuable method to obtain co-crystals of the adduct of $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ with anthranilic acid.[16]

In separate experiments equimolar quantities of acid and base were dissolved in methanol and the solvent was allowed to evaporate at room temperature. By comparison with the diffractograms measured on the raw reactants, it was possible to ascertain whether the starting materials had been converted into products. In the cases discussed in this paper, with the exception of the adduct with maleic acid, and partially with fumaric and trimesic acids, the compounds obtained mechanochemically are the same as those obtained from solution crystallization. Further details will be provided in the following.

We will first describe the solid state structures as obtained from single crystals and then proceed with the characterization of the mechanochemical products. Importantly, the structure determination by single-crystal X-ray diffraction allowed us also to establish unambiguously whether deprotonation had occurred. A word of caution is in order, the comparison of calculated and measured X-ray diffractograms does guarantee that the compounds obtained by the two routes (solid–solid and recrystallization from solvent) possess the same structural features but cannot be used confidently to state whether proton transfer has taken place. It is well known that O–H···N and $^{(-)}$O···H–N$^{(+)}$ interactions, associated with acid–base proton transfer, can be in competition and that proton transfer along the O···N hydrogen bond in the solid state depends on the temperature.[17]

Reaction with fumaric acid: the solid-state structure of $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(CH)_2COO]\cdot CH_3OH$, 1

The supramolecular organization observed in compound **1** is shown in Fig. 1. As observed for the compounds formed by $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ with longer chain dicarboxylic acids,[13] two monocations generated by protonation of the ferrocenyl complex form a supramolecular macrocycle with two hydrogen fumarate anions in between. The four units are held together by two O–H···N and two $^{(-)}$O···H–N$^{(+)}$ interactions [O···N distances 2.655(8) and 2.548(6)Å, respectively]. Two methanol molecules are attached to the tetramer *via* $O(H)_{MeOH}\cdots O^{(-)}$ interactions [O···O 2.88(1) Å]. The X-ray powder diffractograms measured on the ground polycrystalline product **1** and calculated on the basis of the structure determined by single crystal X-ray diffraction are compared in

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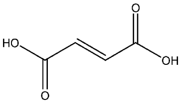
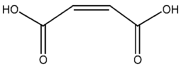
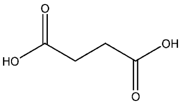
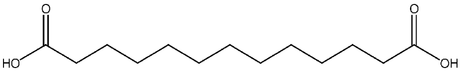
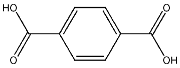
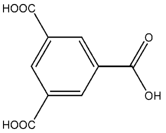
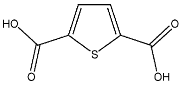
Table 1 Chemical names, formulae and schematic drawings of the starting acids, and formulae of the products

Starting acid	Product of the solution reaction (solution *vs.* kneading products)
Fumaric $HOOC(CH)_2COOH$ 	$[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(CH)_2COO]\cdot CH_3OH$ (**1**) (Partly coincident)
Maleic $HOOC(CH)_2COOH$ 	$[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)_2][HOOC(CH)_2COO]_2$ (**2**) (Different)
Succinic $HOOC(CH_2)_2COOH$ 	$[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(CH_2)_2COO]\cdot[HOOC(CH_2)_2COOH]$ (**3**) (Coincident)[a]
Tridecanedioic $HOOC(CH_2)_{11}COOH$ 	$[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_{11}COOH]\cdot CH_3OH$ (**4**) (Coincident)
Terephthalic $HOOC(C_6H_4)COOH$ 	$[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(C_6H_4)COOH]$ (**5**) (Coincident)
Trimesic $C_6H_3(COOH)_3$ 	$[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)_2][C_6H_3(COOH)_2(COO)]_2$ (**6**) (Partly coincident)[a]
Thiophene-2,5-dicarboxylic $HOOC(SC_4H_2)COOH$ 	$3\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}C_5H_4NH)][HOOC(SC_4H_2)COO]\}\cdot$ $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot 2[HOOC(SC_4H_2)COOH]$ (**7**) (Coincident)

[a] The kneading process was followed by vapour digestion with MeOH.

Fig. 2. As can easily be appreciated, in this case the experimental pattern results from the superimposition of two patterns, one corresponding to solid **1**, the second to a still unidentified phase (peaks indicated by a star in Fig. 2). We tried to improve the yield of solid **1** by exposing the product of the solid state reaction to vapours of methanol (vapour digestion) for two days: this resulted in the enhancement of the sample crystallinity, but the powder profile remained essentially the same.

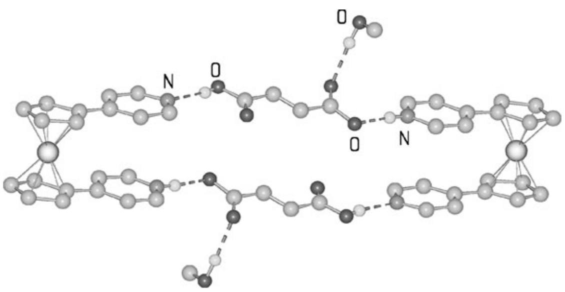


Fig. 1 The supramolecular macrocycle in crystalline **1**.

The structure of **1** is also reminiscent of the supramolecular adducts exploited by MacGillivray *et al.* in a series of elegant

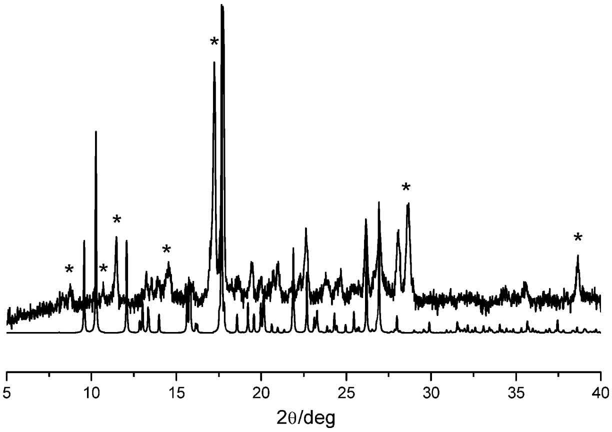


Fig. 2 Comparison between (top) the X-ray powder diffractogram measured on a sample of **1** obtained by kneading and (bottom) that calculated on the basis of single crystal data.

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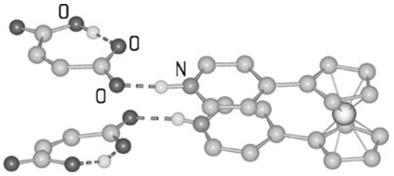

Fig. 3 The supramolecular arrangement in crystalline **2**.

studies on solid state photocyclization. Using a supramolecular templating strategy, MacGillivray *et al.* organize in space the unsaturations that, upon UV irradiation, yield cyclic systems.[18,19] We have attempted photoirradiation on the product of the solution crystallization, but failed to obtain the desired product.

Reaction with maleic acid: the solid-state structure of $[Fe(\eta^5-C_5H_4-C_5H_4NH)_2][HOOC(CH)_2COO]_2$, 2

The overall acid–base stoichiometry of compound **2** is 1 : 2 and not 1 : 1 as in the case discussed above. In compound **2** both pyridyl units are protonated, thus forming the dication $[Fe(\eta^5-C_5H_4-C_5H_4NH)_2]^{2+}$. As is commonly, though not always[20] observed, the maleate anions form intramolecular hydrogen bonds $[O\cdots O^{(-)}$ 2.64(1) and 2.67(1) Å] and links to the cations *via* charge-assisted $^{(-)}O\cdots H–N^{(+)}$ interactions $[^{(-)}O\cdots N^{(+)}$ 2.65(1) and 2.69(1) Å], as shown in Fig. 3. A comparison between the X-ray powder diffractograms measured on the ground polycrystalline product **2** and calculated on the basis of the structure determined by single crystal X-ray diffraction is shown in Fig. 4. As can be seen, the result of the solid-state process differs from the one obtained from solution. Also in this case, as for the unidentified phase in solid **1**, we were not able to further characterize the product. No peaks of the reagents are detectable. Vapour digestion with methanol did not appreciably change the reaction product.

Reaction with succinic acid: the solid-state structure of $[Fe(\eta^5-C_5H_4-C_5H_4N)(\eta^5-C_5H_4-C_5H_4NH)][HOOC(CH_2)_2COO]\cdot[HOOC(CH_2)_2COOH]$, 3

The resulting base : acid stoichiometry of compound **3** is 1 : 2. Protonation of the ferrocenyl complex generates a monocation that forms an ion pair macrocycle with a second monocationic complex *via* $^{(+)}NH\cdots N$ interactions $[^{(+)}N\cdots N$ 2.734(2) Å], as shown in Fig. 5a. The monosuccinate anions form intramolecular hydrogen bonds $[O\cdots O$ 2.425(2) Å], and alternate with the succinic acids in the formation of hydrogen bonded chains $[O\cdots O$ 2.605(2) and 2.667(2) Å], as shown in Fig. 5b.

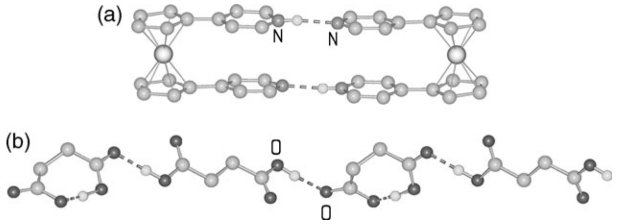

Fig. 5 The cationic dimer (a) and the chain formed by neutral and monodeprotonated acid units (b) in crystalline **3**.

It is worth noting that in this particular case the solution crystallization yielded single crystals of suitable size only if the base : acid ratio of 1 : 2 was employed. The same ratio allowed formation of solid **3** also in the kneading experiments, after the product was left standing for 3 days under methanol vapours (vapour digestion), as shown in Fig. 6. If the 1 : 1 ratio was used, no reaction could be detected, even after vapour digestion.

Reaction with tridecanedioic acid: the solid-state structure of $[Fe(\eta^5-C_5H_4-C_5H_4N)_2]\cdot[HOOC(CH_2)_{11}COOH]\cdot CH_3OH$, 4

Kneading of $[Fe(\eta^5-C_5H_4-C_5H_4N)_2]$ and tridecanedioic acid with MeOH leads to quantitative formation of the co-crystal $[Fe(\eta^5-C_5H_4-C_5H_4N)_2]\cdot[HOOC(CH_2)_{11}COOH]\cdot 2CH_3OH$, **4**.

The acid–base stoichiometry of compound **4** is 1 : 1, but no formation of acid : base macrocycles is observed; two different environments can be recognized for the ferrocenyl compound, with one complex interacting with two acid molecules *via* $N\cdots H–O$ hydrogen bonds $[N\cdots O$ 2.63(1) and 2.662(9) Å], while a second complex molecule is hydrogen bonded to one acid fragment $[N\cdots O$ 2.646(9) Å] and to one methanol molecule $[N\cdots O$ 2.67(1) Å], as shown in Fig. 7. The "supramolecular fragments" thus generated are connected *via* a second

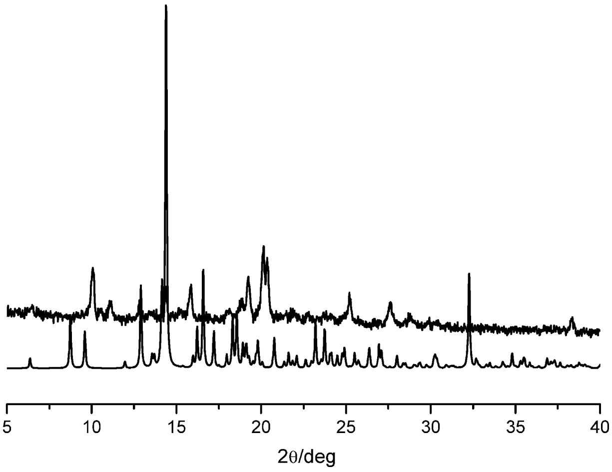

Fig. 4 Comparison between (top) the X-ray powder diffractogram measured on a sample of **2** obtained by kneading and (bottom) that calculated on the basis of single crystal data.

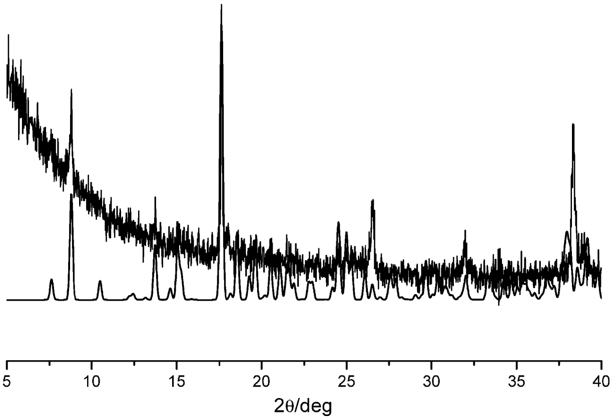

Fig. 6 Comparison between (top) the X-ray powder diffractogram measured on a sample of **3** obtained by kneading and subsequent vapour digestion in MeOH and (bottom) that calculated on the basis of single crystal data.

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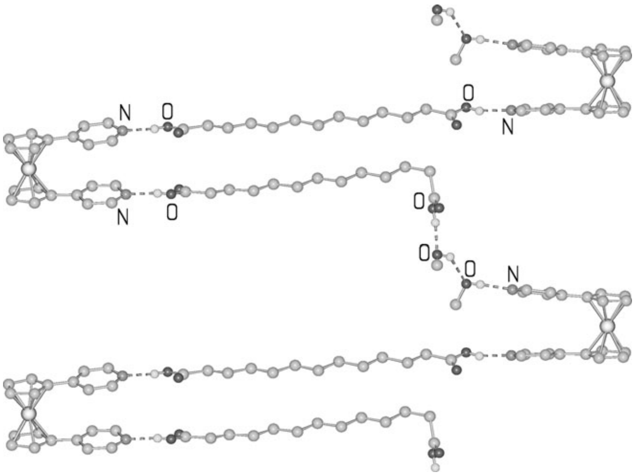

Fig. 7 The infinite hydrogen bonded zig-zag chain constituted of neutral acid and base moieties, plus water molecules, in crystalline **4**.

methanol molecule [O···O 2.62(1) and 2.62(1) Å] to form infinite zig-zag chains.

Direct reaction of the reagents in solution allowed the growth of single crystals of the same species, with the same composition as obtained *via* the solid–solid process.

A comparison between the X-ray powder diffractogram measured on the ground polycrystalline product **4** and that calculated on the basis of the structure determined by single crystal X-ray diffraction is shown in Fig. 8.

Reaction with terephthalic acid: the solid-state structure of [Fe(η^5-C_5H_4-C_5H_4N)$_2$]·[HOOC(C_6H_4)COOH], 5

Kneading of [Fe(η^5-C_5H_4-C_5H_4N)$_2$] with terephthalic acid leads to quantitative formation of the co-crystal [Fe(η^5-C_5H_4-C_5H_4N)$_2$]·[HOOC(C_6H_4)COOH] **5**.

The supramolecular arrangement in crystalline **5** is shown in Fig. 9. Two ferrocenyl complexes form a supramolecular macrocycle with two terephthalatic acids in between. The four units are held together *via* hydrogen bonds of the N···H–O type [N···O 2.604(5) and 2.579(5) Å].

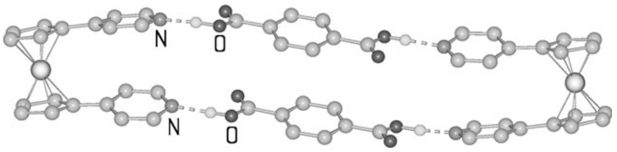

Fig. 9 The supramolecular macrocycle, constituted of neutral acid and base molecules, in crystalline **5**.

Direct reaction of the reagents in solution allowed the growth of single crystals of the same species, with the same composition as obtained *via* the solid–solid process.

A comparison between the X-ray powder diffractogram measured on the ground polycrystalline product **5** and that calculated on the basis of the structure determined by single crystal X-ray diffraction is shown in Fig. 10.

Reaction with trimesic acid: the solid-state structure of [Fe(η^5-C_5H_4-C_5H_4NH)$_2$][C_6H_3(COOH)(COO)$_2$]$_2$, 6

Direct reaction of [Fe(η^5-C_5H_4-C_5H_4N)$_2$] and trimesic acid in a methanol solution leads to formation of the salt [Fe(η^5-C_5H_4-C_5H_4NH)$_2$][C_6H_3(COOH)$_2$(COO)]$_2$, **6**. The supramolecular arrangement in crystalline **6** is shown in Fig. 11. The [C_6H_3(COOH)$_2$(COO)]$^-$ anions are bound to each other *via* $^{(-)}$O···H–O$^{(+)}$ hydrogen bonds [O···O 2.574(3) and 2.630(3) Å], thus forming an anionic ribbon (Fig. 11a), while the dications [Fe(η^5-C_5H_4-C_5H_4NH)$_2$]$^{2+}$ are laterally dangling along the ribbons and bridging adjacent chains *via* $^{(-)}$O···H–N$^{(+)}$ hydrogen bonds [O···N 2.630(3) Å] (Fig. 11b). Kneading of the reagents in stoichiometric quantities was not successful, and an X-ray powder diffraction measurement showed that, apart from the presence of two extra peaks, common with the calculated pattern, the pattern was simply a superimposition of the patterns of the reagents. Exposure of the mixture to vapours of methanol for 3 days (vapour digestion) resulted in the formation of compound **6**, plus a second, unidentified phase (indicated by stars in Fig. 12).

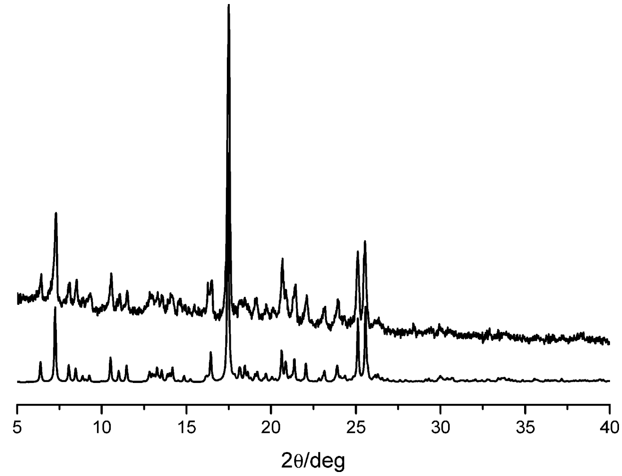

Fig. 8 Comparison between (top) the X-ray powder diffractogram measured on a sample of **4** obtained by kneading and (bottom) that calculated on the basis of single crystal data.

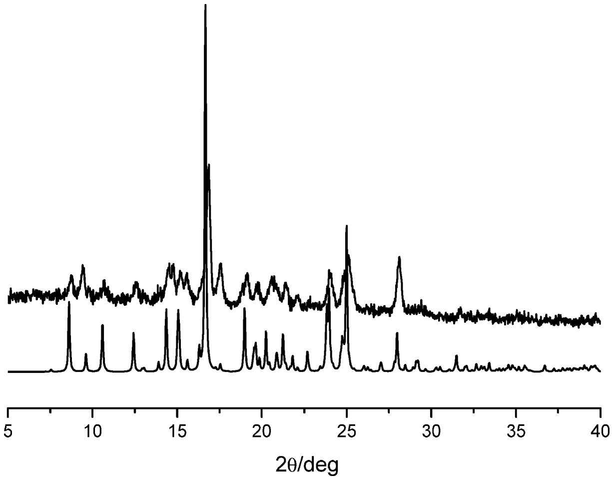

Fig. 10 Comparison between (top) the X-ray powder diffractogram measured on a sample of **5** obtained by kneading and (bottom) that calculated on the basis of single crystal data.

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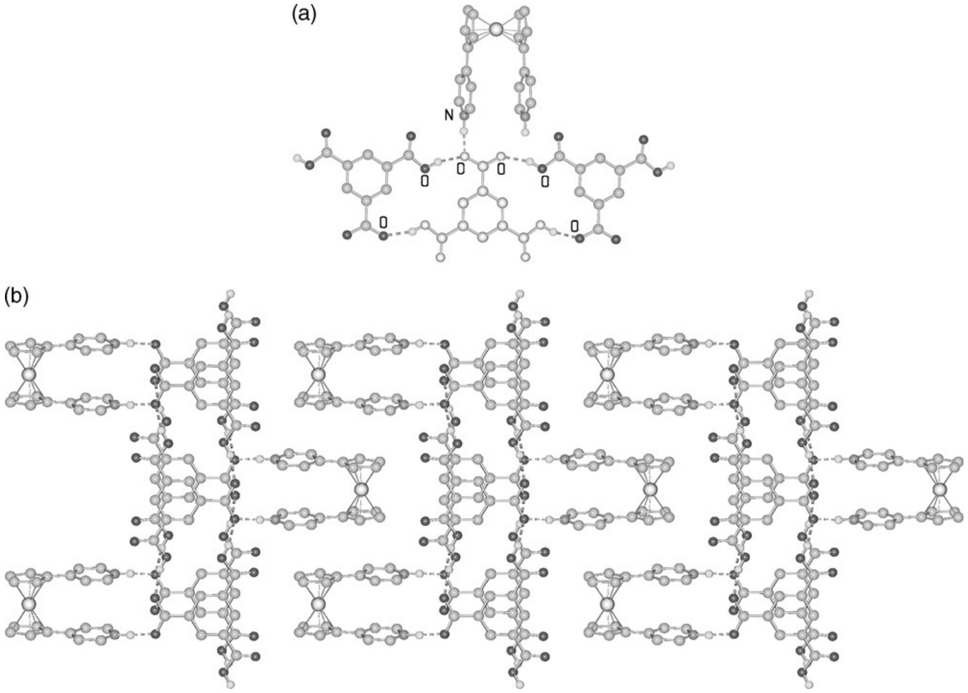

Fig. 11 The supramolecular packing in crystalline **6**, showing the anionic ribbon (a) and the lateral hydrogen bonding connection of the organic moieties with the anionic ribbons (b).

A comparison between the X-ray powder diffractogram measured after vapour digestion and that calculated on the basis of the structure determined by single crystal X-ray diffraction is shown in Fig. 12.

Reaction with thiophene-2,5-dicarboxylic acid: the solid-state structure of 3{[Fe(η^5-C_5H_4-C_5H_4N)(η^5-C_5H_4-C_5H_4NH)]-[HOOC(SC_4H_2)COO]}·[Fe(η^5-C_5H_4-C_5H_4N)$_2$]·2[HOOC(SC_4H_2)COOH], 7

Kneading of [Fe(η^5-C_5H_4-C_5H_4N)$_2$] with thiophene-2,5-dicarboxylic acid leads to formation of the compound 3{[Fe(η^5-C_5H_4-C_5H_4N)(η^5-C_5H_4-C_5H_4NH)][HOOC(SC_4H_2)COO]}·[Fe(η^5-C_5H_4-C_5H_4N)$_2$]·2[HOOC(SC_4H_2)COOH], **7**. The main packing feature (see Fig. 13a) is represented by an infinite zig–zag chain, formed by monoprotonated and neutral organometallic units and acid moieties, all linked together and to acid moieties *via* $^{(+)}$N–H···N, N–H···O and O–H···O hydrogen bonds [N···N 2.684(6), N···O 2.580(5), O···O 2.541(4) and 2.534(4) Å]. A dimer of monoprotonated ferrocenyl units (Fig. 13b) is also present in the crystal [N···N 2.706(4) Å], while the monodeprotonated acid units are linked together *via*

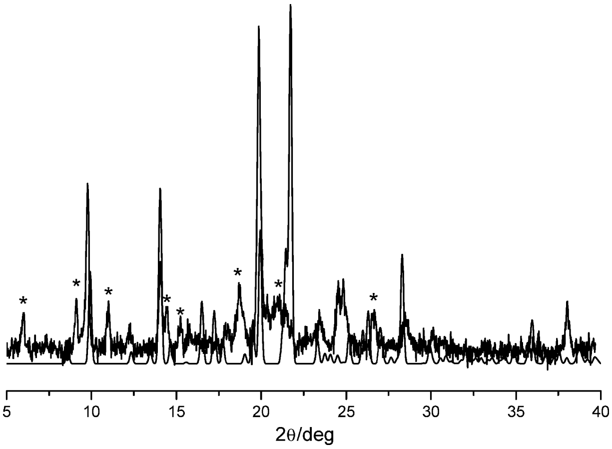

Fig. 12 Comparison between (top) the X-ray powder diffractogram measured on a sample of **6** obtained by kneading and subsequent vapour digestion in MeOH and (bottom) that calculated on the basis of single crystal data. Stars indicate the presence of an additional, unidentified phase.

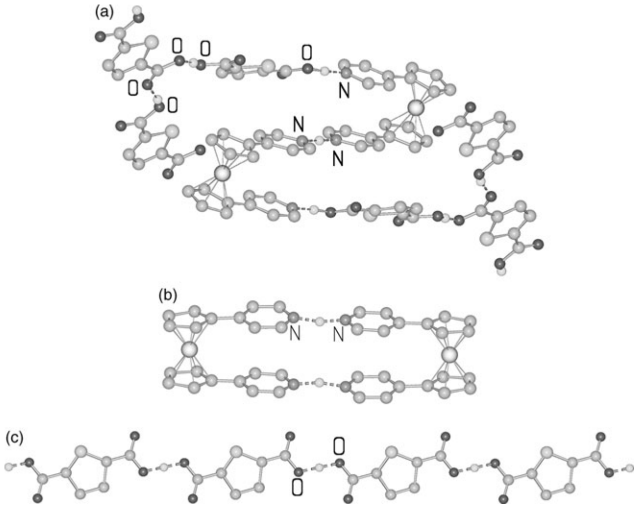

Fig. 13 Packing patterns in crystalline **7**: (a) the infinite zig-zag chain, formed by monoprotonated and neutral organometallic units and acid moieties, (b) the dimer of monoprotonated ferrocenyl units and (c) the anionic chain formed by the monodeprotonated acid units (only one of the two images of disorder is shown, see the Experimental section).

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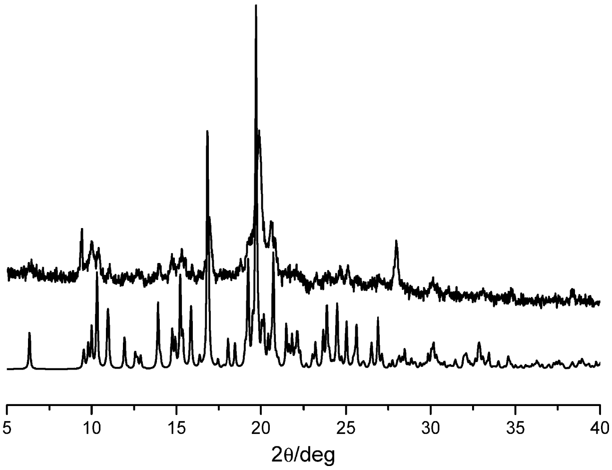

Fig. 14 Comparison between (top) the X-ray powder diffractogram measured on a sample of **7** obtained by kneading and (bottom) that calculated on the basis of single crystal data.

O–H···O$^{(-)}$ hydrogen bonds to form an infinite chain (Fig. 13c) [O···O 2.503(4) Å].

Direct reaction of the reagents in solution allowed the growth of single crystals of the same species as obtained *via* the solid–solid process.

A comparison between the X-ray powder diffractogram measured on the ground polycrystalline product **7** and that calculated on the basis of the structure determined by single crystal X-ray diffraction is shown in Fig. 14.

Conclusions

This study extends our previous experience with direct solid–solid reactions between organic and organometallic crystalline materials to a new class of acid–base adducts, where the base is the ferrocenyl complex [Fe(η^5-C_5H_4-C_5H_4N)$_2$], also obtained by mechanochemical solvent-free synthesis, and the organic moiety is constituted of a series of organic acids.

The main outcomes of this study can be summarized as follows:

(i) In most cases the solid state reaction leads to complete conversion of the starting solid reactants into the products, as shown by X-ray powder diffraction.

(ii) Reaction in a methanol solution leads to single crystals suitable for X-ray diffraction.

(iii) In compounds **3**, **4**, **5**, **7** and, at least partially, in **1** and **6**, there is exact correspondence between the calculated and measured powder diffractograms, hence the mechanochemical products possess the same structural features as those determined by single-crystal X-ray diffraction, while direct reaction in solution for compound **2** yields a different solid product.

In conclusion, we have provided further examples of the use of direct solid–solid mixing as a valid alternative route to solution preparation of hydrogen bonded hybrid materials. The number of applications that can be envisaged in the organometallic and coordination chemistry fields, as well as across all traditional subdivisions of chemistry, is considerable.

In the course of parallel investigations, for example, we have shown that mechanochemical processes can be used to form porous coordination compounds.[21,22] Other examples are beginning to appear in the literature and one can foresee an increasing number of applications. Other contributions in the field of coordination chemistry are beginning to appear.[23]

Experimental section

All acids were purchased from Sigma-Aldrich and used without further purification. Reagent grade solvents were used.

The ferrocenyl compound has been prepared as previously reported.[13,15]

Solid-state and solution syntheses of compounds 1–7

Mixtures of [Fe(η^5-C_5H_4-C_5H_4N)$_2$] and the carboxylic acids were manually ground in an agate mortar for 5 min in the presence of a catalytic amount of methanol (kneading). The stoichiometric base : acid ratio range was 1 : 1. An excess of

Table 2 Crystal data and details of measurements for compounds **1–7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{25}H_{24}FeN_2O_5$	$C_{28}H_{24}FeN_2O_8$	$C_{28}H_{28}FeN_2O_8$	$C_{34}H_{44}FeN_2O_5$	$C_{28}H_{22}FeN_2O_4$	$C_{38}H_{28}FeN_2O_{12}$	$C_{112}H_{82}Fe_4N_8O_{20}S_5$
M_r	488.31	572.34	576.37	616.56	506.33	760.47	2243.61
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2(1)/a$	$P2(1)/n$	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$
a/Å	8.705(2)	12.544(3)	12.2785(8)	10.929(2)	27.40(2)	14.775(1)	9.2235(6)
b/Å	11.432(3)	14.785(5)	9.0344(6)	14.972(5)	8.934(7)	17.803(1)	9.5841(6)
c/Å	11.615(3)	15.723(7)	23.580(2)	21.338(4)	21.51(2)	14.148(2)	28.326(2)
α/°	72.904(4)	90.00	90.00	80.54(2)	90.00	90.00	92.599(1)
β/°	81.691(4)	117.89(2)	99.799(1)	80.66(1)	121.29(4)	121.425(3)	98.530(1)
γ/°	89.650(4)	90.00	90.00	68.66(2)	90.00	90.00	104.326(1)
V/Å^3	1092.4(5)	2577(2)	2577.5(3)	3188(1)	4498(6)	3175.6(6)	2390.5(3)
Z	2	4	4	4	8	4	1
μ(Mo-Kα)/mm^{-1}	0.731	0.640	0.641	0.516	0.711	0.551	0.785
$2\theta_{max}$/°	59	50	56	50	52	55	57
Measured reflns	7314	12607	27936	9189	22330	17689	20854
Unique reflns	3479	2783	5888	8868	4283	3648	10819
Ref. parameters	289	350	364	723	338	254	649
GOF on F^2	1.020	1.004	1.047	1.012	0.990	0.960	0.992
$R1$ [on F, $I > 2\sigma(I)$]	0.0590	0.0763	0.0371	0.0768	0.0425	0.0448	0.0524
w$R2$ (on F^2, all data)	0.1515	0.2399	0.1061	0.2731	0.1101	0.1162	0.1523

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acid also resulted in the formation of the same compounds. In the case of succinic acid, though, only a stoichiometric ratio of 1 : 2, followed by vapour digestion in MeOH, ensured the formation of the desired product **2**. Vapour digestion in MeOH was also necessary for the formation of **6**.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solutions obtained on dissolving $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ (50 mg, 0.147 mmol) in 5 mL of methanol 99.8% together with the following acids: fumaric (17.06 mg, 0.147 mmol), maleic (17.06 mg, 0.147 mmol), succinic (34.72 mg, 0.294 mmol), tridecanedioic (31.51 mg, 0.147 mmol), terephthalic (24.42 mg, 0.147 mmol), trimesic (30.90 mg, 0.147 mmol) and thiophene-2,5-dicarboxylic (25.30 mg, 0.147 mmol).

Crystal structure determination

Crystal data of compounds **1**, **2**, **3**, **5**, **6** and **7** were collected at RT on a Bruker Smart ApexII CCD diffractometer; crystal data of compound **4** were collected on a Nonius CAD4 diffractometer. Crystal data and details of measurements are summarized in Table 2. Common to all compounds: Mo-Kα radiation, λ = 0.71073 Å, monochromator graphite, T = 293(2) K. The program SHELX97[24a] was used for structure solution and refinement based on F^2. All non-hydrogen atoms were refined anisotropically. One of the three acid moieties in **7** is 50 : 50 disordered, as it lies on a crystallographic inversion centre. All H_{CH} atoms were added in calculated positions and refined riding on their respective carbon atoms. All H_{COOH} and H_{NH} atoms were located from difference Fourier maps. Only data with $2\theta < 25$ were used for compounds **2** and **4**, as diffraction was extremely poor at higher angles. SCHAKAL99[24b] was used for the graphical representation of the results. The program PLATON[24c] was used to calculate the hydrogen bonding interactions. CCDC reference numbers 670778–670781. For crystallographic data in CIF format see DOI: 10.1039/b714923a

X-Ray powder diffraction measurements

X-Ray powder diffractograms were collected on a PANalytical X'Pert PRO automated diffractometer with Cu-Kα radiation and X'Celerator detector without monochromator. The program PowderCell 2.2[24d] was used for calculation of X-ray powder patterns on the basis of the single crystal structure determinations.

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