

# Mechanochemical assembly of hydrogen bonded organic-organometallic solid compounds

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Received (in Cambridge, UK) 9th October 2002, Accepted 5th November 2002

First published as an Advance Article on the web 18th November 2002

Solvent-free reactions with molecular systems have been exploited to prepare hybrid organic-organometallic solids: grinding of the complex  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]$  with solid bases **B** generates quantitatively the corresponding hydrogen bonded salts  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})][\text{HB}]$  (**B** = 1,4-diazabicyclo[2.2.2]octane, 1,4-phenylenediamine); gas-solid reactions are also possible with volatile bases.

The continuing expansion of the supramolecular perception of chemical reactivity brings about the possibility of exploring less conventional synthetic procedures for the preparation of molecular aggregates.<sup>1</sup> This applies also to the fields of molecular crystal engineering<sup>2</sup> and solid state chemistry.<sup>3</sup>

Mechanochemistry is an established branch of chemical sciences whereby reactants are mixed together in the solid state without the intermediacy of solvents.<sup>4</sup> However, mechanically activated reactions have been exploited mainly with inorganic solids, while less has been done with molecular (and mainly organic) systems.<sup>5</sup> Solvent free molecular reactions are attractive under both the environmental and topochemical viewpoints,<sup>6</sup> often offering alternative preparative routes to novel chemicals and materials.<sup>7,8</sup>

We have begun to utilize organometallic building blocks to prepare novel molecular crystalline materials. Interesting results are being obtained, in particular in the cases of solid-gas reactions.<sup>9</sup>

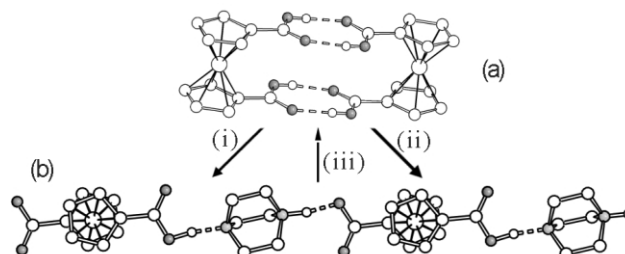
In this communication we describe the preparation of novel mixed organic-organometallic compounds by *co-grinding* of solid reactants and the full structural characterization of the products from single crystals obtained *via seeding*.

Moderate manual grinding of solid  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]$ , **1**, monoclinic form,<sup>10</sup> together with solid 1,4-diazabicyclo[2.2.2]octane ( $\text{C}_6\text{H}_{12}\text{N}_2$ , DABCO), **2**, and 1,4-phenylenediamine, **4**, in 1:1 ratio, leads to quantitative formation of the corresponding compounds  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})][\text{HC}_6\text{H}_{12}\text{N}_2]$ , **3**, and  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})][\text{C}_6\text{H}_4(\text{NH}_2)(\text{NH}_3)]$ , **5**, respectively.† No formation of intermediate liquid phases<sup>7</sup> has been observed.

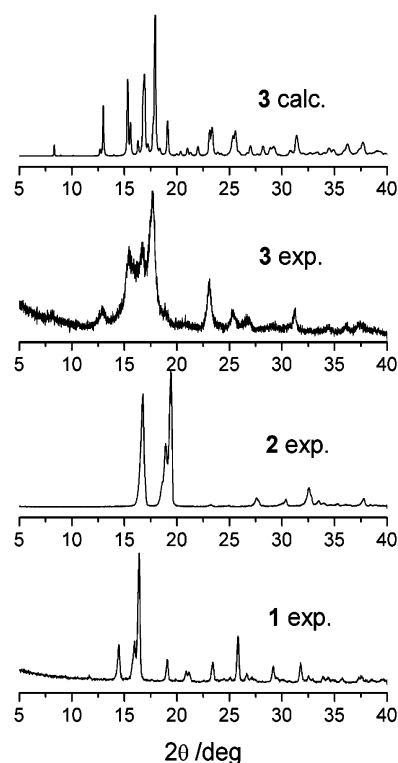
Interestingly, **3** can also be obtained from the (hetero-phase) uptake of vapour of **2** by solid **1**, although the kinetics is expectedly much slower than in the case of the co-grinding.‡ The reaction is reversible since **1** can be fully regenerated if **2** is sublimed off solid **3** by thermal treatment at *ca.* 235 °C. The overall process is depicted in Fig. 1.

The problem of the structural characterization of powder materials yielded by mechanochemical methods<sup>11a</sup> can be circumvented by using a portion of the polycrystalline material to *seed*<sup>11b</sup> from suitable solvents the growth of single crystals for X-ray diffraction.‡ Comparison of the powder diffraction patterns calculated on the basis of the single crystal structure with that obtained from the ground polycrystalline material allows us to determine whether the products have the same chemical and structural composition.§ Fig. 2 shows that this is the case for the reaction between monoclinic **1**<sup>10</sup> and **2**. Even though the crystallinity of **3** obtained *via grinding* is not high, all significant peaks can be easily recognised, while peaks attributable to the starting materials **1** and **2** are absent.

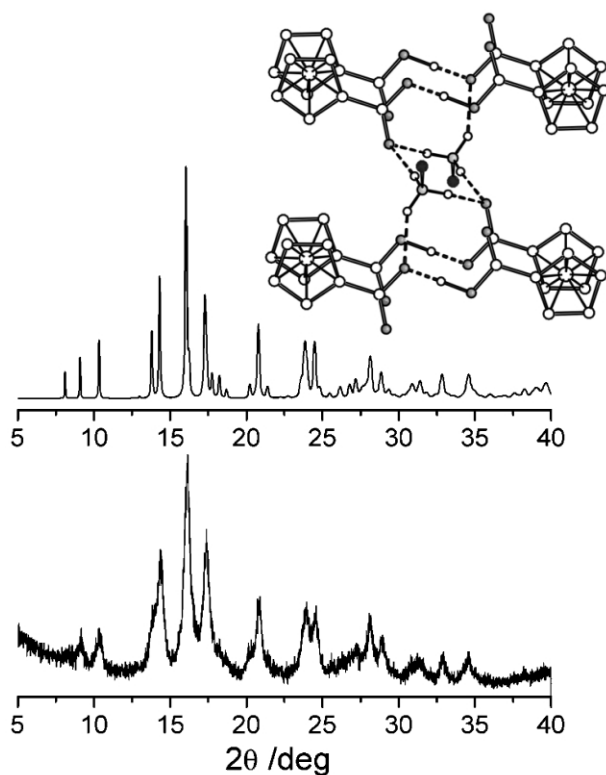
As for the reverse process, thermogravimetric measurements indicate that, on heating at *ca.* 235 °C, solid **3** loses 1 mole of **2**. No decomposition is observed and the nature of the final product, *i.e.* **1**, has again been confirmed by powder diffraction. Co-grinding of the two solids in stoichiometric ratios other than 1:1 (*e.g.* 1:2 and 2:1) leads to formation of solid mixtures with diffraction peaks corresponding to the unreacted excess reagent in addition to the peaks of **3**. It is also worth noting that



**Fig. 1** Reactivity scheme. (i) Mechanochemical treatment of solid **1** and **2** to give **3**; (ii) uptake of **2** vapour by finely ground **1**; (iii) removal of **2** from solid **3** by thermal treatment. (a) The hydrogen bonded dimer in monoclinic **1**; (b) the hydrogen bonded chain in solid **3**. H<sub>CH</sub> atoms omitted for clarity.



**Fig. 2** From top to bottom: comparison of X-ray powder diffractograms for **3** (calculated and experimental), **2** (experimental) and **1** (experimental).



**Fig. 3** Comparison of calculated (top) and measured (bottom) X-ray powder diffractograms for **5**, together with a representation of the crystal packing; black spheres represent the  $C_5H_4(NH_2)$  moiety bound to the  $-NH_3^+$  unit.  $H_{CH}$  atoms omitted for clarity.

mechanical grinding, vapour uptake and crystallization from solution all lead to formation of the same product.

Analogously to **3**, grinding of **1** with 1,4-phenylenediamine, **4**, in 1:1 ratio leads to quantitative formation of  $[Fe(\eta^5-C_5H_4COOH)(\eta^5-C_5H_4COO)] [C_6H_4(NH_2)(NH_3)]$ , **5**.<sup>†</sup> As in the case of **3**, recrystallization from solution of the ground sample allowed us to grow single crystals<sup>‡</sup> of the same species obtained *via* the solid–solid process (Fig. 3).

In summary we have shown that solvent-free mechanochemical reactions with molecular systems can be exploited to prepare new hybrid organic–organometallic materials. Solid–solid reactions between molecular solids can be regarded as *supramolecular reactions* between periodical (solid) supermolecules.<sup>12</sup> In the reaction between molecular solid reactants to form a new molecular solid product the covalent bonding is not affected while *non-covalent* van der Waals or hydrogen bonding interactions are broken and formed.

The mechanochemical reaction generating **3** and **5** is quite general. Reaction products have also been observed, for instance, by co-grinding **1** with solid guanidine carbonate and piperazine. These compounds will be described in a future report together with the optimisation of the experimental conditions for all processes described herein.

We thank MIUR (projects *Supramolecular Devices* and *Solid Supermolecules*), the Universities of Bologna (project *Innovative Materials*) and Sassari for financial support.

## Notes and references

<sup>†</sup> 1,4-Diazabicyclo[2.2.2]octane, **2**, 1,4-phenylenediamine, **4**, and  $[Fe(\eta^5-C_5H_4COOH)_2]$  were purchased from Aldrich. Mechanical preparation of **3**:

20 mg (72 mmol) of **1** and 8.1 mg (72 mmol) of **2** were manually ground in an agate mortar for 5 min. Mechanical preparation of **5**: 20 mg (72 mmol) of **1** and 7.8 mg (72 mmol) of **4** were manually ground in an agate mortar for 5 min. More prolonged grinding did not result in any appreciable change in the diffraction patterns. For the reaction in hetero-phase 20 mg of **1** were exposed at room temperature to vapours of **2** obtained by producing a mild vacuum (water pump, *ca.* 30–40 mmHg) in the reaction apparatus; after 30 days the diffraction pattern showed peaks of the adduct together with residual peaks due to the starting diacid.

<sup>‡</sup> Single crystals of **3** and **5** were obtained by recrystallization in methanol of the powders resulting from the grinding processes. X-Ray data collected at 293 K on a Nonius-CAD4 diffractometer; MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). *Crystal data* for **3**: triclinic,  $P\bar{1}$ ,  $a = 7.452(2)$ ,  $b = 10.804(2)$ ,  $c = 11.319(2)$  Å,  $\alpha = 104.83(2)$ ,  $\beta = 98.96(2)$ ,  $\gamma = 105.33(2)^\circ$ ,  $V = 824.9(3)$  Å<sup>3</sup>,  $Z = 2$ , 2894 independent reflections (3052 measured),  $wR_2 = 0.1084$ ,  $R_1 = 0.0476$ . For **5**: triclinic,  $P\bar{1}$ ,  $a = 7.228(7)$ ,  $b = 10.216(4)$ ,  $c = 11.803(2)$  Å,  $\alpha = 103.74(3)$ ,  $\beta = 105.57(2)$ ,  $\gamma = 96.88(2)^\circ$ ,  $V = 799.7(9)$  Å<sup>3</sup>,  $Z = 2$ , 4646 independent reflections (4852 measured),  $wR_2 = 0.1794$ ,  $R_1 = 0.0593$ . SHELX97<sup>13a</sup> and SCHAKAL99<sup>13b</sup> were used for structure solution and graphical representations. CCDC 191507 and 191508. See <http://www.rsc.org/suppdata/cc/b2/b209861j/> for crystallographic data in CIF format.

§ Powder data for all samples were collected on a Philips PW-1100 automated diffractometer with Cu-K $\alpha$  radiation, graphite monochromator, using quartz sample holders. For the pure reagents 25 mg of substance were employed. The program PowderCell<sup>13c</sup> was used for calculation of X-ray powder patterns.

- M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley & Sons, Chichester, 2000.
- Crystal Engineering: from Molecules and Crystals to Materials*, ed. D. Braga, F. Grepioni and A. G. Orpen, Kluwer Academic Publishers, Dordrecht, 1999; M. D. Hollingsworth, *Science*, 2002, **295**, 2410.
- Inorganic Materials*, ed. D. W. Brice and D. O'Hare, Wiley & Sons, 1992.
- J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, **71**, 581; V. V. Boldyrev, *Solid State Ionics*, 1995, **63–65**, 537; R. P. Rastogi, N. B. Singh and R. P. Singh, *J. Solid State Chem.*, 1977, **20**, 191; F. Toda and H. Miyamoto, *Chem. Lett.*, 1995, 861; V. D. Makhaev, A. P. Borisov and L. A. Petrova, *J. Organomet. Chem.*, 1999, **590**, 222.
- M. C. Etter, S. M. Reutzel and C. G. Choo, *J. Am. Chem. Soc.*, 1993, **115**, 4411; R. Rastogi and N. B. Singh, *J. Phys. Chem.*, 1968, **72**, 4446; M. R. Caira, L. R. Nassimbeni and A. F. Wildervanck, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2213; V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*, 1996, 987; P. J. Nichols, C. L. Raston and J. W. Steed, *Chem. Commun.*, 2001, 1062.
- K. Tanaka and F. Toda, *Chem. Rev.*, 2000, **100**, 1025; F. Toda, *CrystEngComm*, 2002, **4**, 1; R. Kuroda, Y. Imai and T. Sato, *Chirality*, 2001, **13**, 588.
- G. Rothenberg, A. P. Downie, C. L. Raston and J. L. Scott, *J. Am. Chem. Soc.*, 2001, **123**, 8701; G. W. V. Cave, C. L. Raston and J. L. Scott, *Chem. Commun.*, 2001, 2159.
- J. Fernandez-Bertran, J. C. Alvarez and E. Reguera, *Solid State Ionics*, 1998, **106**, 129.
- D. Braga, G. Cojazzi, D. Emiliani, L. Maini and F. Grepioni, *Chem. Commun.*, 2001, 2272; D. Braga, G. Cojazzi, D. Emiliani, L. Maini and F. Grepioni, *Organometallics*, 2002, **21**, 1315.
- F. Takusagawa and T. F. Koetzle, *Acta Crystallogr., Sect. B*, 1979, **35**, 2888.
- (a) D. Braga, L. Maini and F. Grepioni, *Chem. Commun.*, 1999, 937; (b) D. Braga, G. Cojazzi, L. Maini, M. Polito and F. Grepioni, *Chem. Commun.*, 1999, 1949.
- The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry*, ed. G. R. Desiraju, Wiley, Chichester, 1996, vol. 2, p. 107.
- (a) G. M. Sheldrick, SHELXL97: Program for Crystal Structure Determination, University of Göttingen, Germany, 1997; (b) E. Keller, SCHAKAL99: Graphical Representation of Molecular Models, University of Freiburg, Germany, 1999; (c) W. Kraus and G. Nolze, PowderCell 2.2 (BAM Berlin) © subgroups derived by Ulrich Müller (Gh Kassel).