Università degli Studi di Bologna

FACOLTÀ DI SCIENZE MATEMATICHE, FISICHE E NATURALI

Dottorato di Ricerca in Scienze Chimiche e Chimica Industriale – XIX Ciclo - Progetto 1 – CHIM03

Dipartimento di Chimica "G. Ciamician"

PREPARAZIONE E CARATTERIZZAZIONE DI NUOVI MATERIALI MEDIANTE METODI "SOLVENT-FREE"

Tesi di Dottorato del:
Dr. Stefano Luca Giaffreda

Relatore:
Chiar.mo Prof.
DARIO BRAGA

Coordinatore:
Chiar.mo Prof.
Vincenzo Balzani

Anno Accademico 2006 - 2007

INDEX

Preface

Making crystals by design is the paradigm of crystal engineering, an area of solid-state chemistry that encompasses molecular crystals and materials [1]. The goal of this field of research is that of assembling "bottom-up" functionalized molecular and ionic components into a target network of supramolecular interactions [2]. The convolution of the physical and chemical properties of the individual building blocks with the periodicity and symmetry operators of the crystal generates *collective* supramolecular properties [3].

The Bolognese molecular crystal-engineering group has been active in the area of solid-state chemistry for more than a decade [4]. At the time of writing, several lines of research were being explored by this group. This review article will deal with one of the most productive of these lines, namely that focused on the design, synthesis, characterization and utilization of hydrogen bonded networks based on functionalized organometallic sandwich compounds. The reader interested to know more about the other research lines is addressed to recent review articles produced by the authors in the fields of the solvent-free preparation of crystalline materials [5], and of the investigation of polymorph preparation and interconversion [6].

Our interest in the use of organometallic molecules and ions as building blocks stems from the observation [4] that organometallic molecules combine the supramolecular bonding features of organic molecules (e.g. hydrogen bonding interactions) with the structural variability of coordination compounds (e.g. ligand–metal coordination, coordination geometry, structural flexibly, etc.). On the other hand, the utilization of interactions that are strong and, at the same time, directional is essential for the assembly of molecular components because such types of interactions guarantee transferability and reproducibility, beside strength. For such reasons the hydrogen bond [7] is the interaction of choice in many crystal-engineering experiments where neutral molecules or molecular ions are employed [8]. This is well demonstrated by the plethora of studies on hydrogen bonded molecular or ionic crystals [9].

In this review, we shall deal mainly with hydrogen bonding interactions between "classical" donor and acceptor groups, e.g. –COOH, –OH, –CONHR, etc. present on adequately chosen, or ad hoc prepared, organometallic moieties.

In previous studies, we have dealt with hydrogen-bonded networks formed by organic or inorganic molecules and ions *templated* by non-participating organometallic units (mainly sandwich compounds) [10] and [11]. The design criterion was based on the idea of *confining* all strong donor/acceptor hydrogen bonding groups on the organic or inorganic (usually anionic) networks while *excluding* the organometallic fragments (usually cationic) from the direct participation in the hydrogen bonds. This strategy led to product crystals characterized by selective self-assembling of the organic/inorganic fragments in hydrogen bonded superstructures, whose topology depended on the size, shape and number and geometry of the –OH/–COOH/COO$^{(-)}$ groups. To this end, cationic sandwich complexes such as $[Co(\eta^5\text{-}C_5H_5)_2]^+$, $[Cr(\eta^6\text{-}C_6H_6)_2]^+$, $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ were found particularly useful. The regular cylindrical shape of the organometallic moiety and the presence of C—H groups allows interactions with the surroundings by means of C—H...O interactions between the acceptor sites on the networks and the C—H groups protruding from the complex surface [12]. For instance, when D,L- and L-tartaric acids were used, the compounds $[Co(\eta^5\text{-}C_5H_5)_2]^+$(D,L-$HO_2CCH(OH)CH(OH)CO_2$) (D,L-$HO_2CCH(OH)CH(OH)CO_2H$)] and $[Co(\eta^5\text{-}C_5H_5)_2]^+$ [(L-$HO_2CCH(OH)CH(OH)CO_2$)]$^-$ were, respectively, obtained [13]. With oxalic acid, compounds $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$ and $[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]\cdot[H_2O]$ were prepared [14], while compounds $[Cr(\eta^6\text{-}C_6H_6)_2][HC_4O_4]$ and $\{[Cr(\eta^6\text{-}$

$C_6H_6)_2]\}_2[C_4O_4]\cdot 6H_2O$ were prepared with squaric acid [15]. With phthalic and terephthalic acids the compounds $\{[Co(\eta^5\text{-}C_5H_5)_2]^+\}_4\{[C_6H_4(COOH)(COO)]^-\}_2$ $[C_6H_4(COO)_2]^{2-}\cdot 4H_2O$, $[Cr(\eta^6\text{-}C_6H_6)_2]^+\{[C_6H_4(COOH)(COO)]^-[C_6H_4(COOH)_2]\}$, and $\{[Co(\eta^5\text{-}C_5H_5)_2]^+\}_2[C_6H_4(COO)_2]^{2-}\cdot 6H_2O$ were prepared [16], while with trimesic acid $[Co(\eta^5\text{-}C_5H_5)_2]^+\{[(C_6H_3(COOH)_3]\ [C_6H_3(COOH)_2(COO)]\}^-\cdot 2H_2O$ [17] was obtained, and with R-binaphtol were prepared $[Co(\eta^5\text{-}C_5H_5)_2][(R)\text{-}(+)\text{-}(HOC_{10}H_6C_{10}H_6O)]\cdot[(R)\text{-}(+)\text{-}(HOC_{10}H_6C_{10}H_6OH)]$, and $[Co(\eta^5\text{-}C_5H_5)_2]$ $[(R)\text{-}(+)\text{-}(HOC_{10}H_6C_{10}H_6O)]\cdot[(R)\text{-}(+)\text{-}(HOC_{10}H_6C_{10}H_6OH)]_{0.5}$ [18]. More recently, partially deprotonated inorganic oxoanions derived from sulphuric and phosphoric acids have been used to assemble organometallic cations in inorganic–organometallic hybrid systems by reacting the neutral sandwich compounds with acids such as H_2SO_4 and H_3PO_4 [19]. The anions HSO_4^- and $H_2PO_4^-$ resulting from partial deprotonation of the neutral acids were shown to assemble into hydrogen bonded mono- and bi-dimensional networks as in the case of organic anions. The structural features of these and several others hybrid organic/inorganic–organometallic superstructures were described before. The reader is addressed to Ref. [20] for further information.

When the donor/acceptor groups are *located on* the organometallic sandwich unit, the organometallic complexes are directly participating in the formation of hydrogen bonded supramolecular aggregates, such as dimers or higher complexity hydrogen bonded networks. This will be the main focus of this article. Besides, the possibility of alternative solutions to the problem of different spatial organization of the same molecular unit in the crystals, i.e. crystal polymorphism [21], will also be discussed whenever necessary [22]. In this respect, since different crystal forms imply the existence of different sets of supramolecular interactions between the same building blocks, polymorphs of the same molecular crystal can be seen as *crystal isomers*. It should also be pointed out that structural flexibility, a key characteristic of organometallic molecules [23], may favour formation of conformational crystal polymorphs, i.e. of different packings of the same molecule in different conformations. A classical example of organometallic conformational polymorphism is provided by ferrocene, for which one room temperature disordered and two low-temperature ordered crystalline forms are known [24].

Even though polymorphism is emerging as a fundamental structural and chemical aspect of organometallic solid-state chemistry, rather than devoting a specific section of this review to this phenomenon, the occurrence of polymorphic modifications will be described as we proceed.

References

[1] (a) G.R. Desiraju, Crystal Engineering: The Design of Organic Solids, Elsevier, Amsterdam (1989).
(b) D. Braga, F. Grepioni and G.R. Desiraju, *Chem. Rev.* 98 (1998), p. 1375.
(c) A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby and M. Schroder, *Coord. Chem. Rev.* 183 (1999), p. 117.
(d) Proceedings of the Dalton Discussion on Inorganic Crystal Engineering, the whole issue, J. Chem. Soc. Dalton Trans. (2000) 3705.
(e) B. Moulton and M.J. Zaworotko, *Chem. Rev.* 101 (2001), p. 1629.
(f) D. Braga, *Chem. Commun.* (2003), p. 2751.
(g) D. Braga, G.R. Desiraju, J. Miller, A.G. Orpen and S. Price, *Cryst. Eng. Commun.* 4 (2002), p. 500.
(h) M.D. Hollingsworth, *Science* 295 (2002), p. 2410.
(i) M.W. Hosseini, *Cryst. Eng. Commun.* 6 (2004), p. 318.
(j) L. Brammer, *Chem. Soc. Rev.* 33 (2004), p. 476.
(k) D. Braga, L. Brammer and N. Champness, *Cryst. Eng. Commun.* 7 (2005), p. 1.

[2] (a) G.R. Desiraju, *Angew. Chem. Int. Ed.* 34 (1995), p. 2311.
(b) D. Braga and F. Grepioni, *Acc. Chem. Res.* 33 (2000), p. 601.
(c) A.M. Beatty, *Cryst. Eng. Commun.* (2001), p. 51.

[3] In: D. Braga, F. Grepioni and A.G. Orpen, Editors, *Crystal Engineering: From Molecules and Crystals to Materials*, Kluwer Academic Publishers, Dordrecht (1999).

[4] (a) D. Braga and F. Grepioni, *Acc. Chem. Res.* 27 (1994), p. 51.
(b) D. Braga and F. Grepioni, *Chem. Commun.* (1996), p. 571.
(c) D. Braga and F. Grepioni, *Acc. Chem. Res.* 30 (1997), p. 81.

[5] (a) D. Braga and F. Grepioni, *Angew. Chem. Int. Ed.* 43 (2004), p. 4002.

(b) D. Braga and F. Grepioni In: F. Toda, Editor, *Topics Curr. Chem.* 254 (2005), p. 71.

[6] (a) D. Braga and F. Grepioni, Crystal design. In: G.R. Desiraju, Editor, *Structure and Function. Perspectives in Supramolecular Chemistry*, Whiley, Chichester, UK (2003), p. 7.
(b) D.F. Braga, *Grepioni Chem. Commun.* (2005), p. 3635. [7] (a) C.B. Aakeröy and K.R. Seddon, *Chem. Soc. Rev.* (1993), p. 397.
(b) M.S. Gordon and J.H. Jensen, *Acc. Chem. Res.* 29 (1996), p. 536.
(c) L.J. Prins, D.N. Reinhoudt and P. Timmerman, *Angew. Chem. Int. Ed. Engl.* 40 (2001), p. 2382.
(d) L. Brammer, D. Zhao, F.T. Ladipo and J. Braddock-Wilking, *Acta Cryst., Sec. B* 51 (1995), p. 632. (e) J.J. Novoa, I. Nobeli, F. Grepioni and D. Braga, *New J. Chem.* 24 (2000), p. 5.
(f) G.R. Desiraju, *Acc. Chem. Res.* 35 (2002), p. 565.
(g) K. Biradha, *Cryst. Eng. Commun.* 5 (2003), p. 374.

[8] (a) L.M. Epstein and E.S. Shubina, *Coord. Chem Rev.* 231 (2002), p. 165. (b) A.M. Beatty, *Coord. Chem. Rev.* 246 (2003), p. 131.
(c) A.M. Beatty, *Cryst. Eng. Commun.* (2001), p. 51.
(d) L. Brammer, J.C. Mareque Rivas, R. Atencio, S. Fang and F.C. Pigge, *J. Chem. Soc., Dalton Trans.* (2000), p. 3855. (e) C.M. Zakaria, G. Ferguson, A.J. Lough and C. Glidewell, *Acta Cryst., Sec. B* 58 (2002), p. 786.

(f) C. Elschenbroich, F. Lu and K. Harms, *Organometallics* 21 (2002), p. 5152.

(g) C. Elschenbroich, O. Schiemann, O. Burghaus and K. Harms, *J. Am. Chem. Soc.* 119 (1997), p. 7452.
(h) M.C. Tse, K.K. Cheung, M.C.W. Chan and C.M. Che, *Chem. Commun.* 21 (1998), p. 2295. (i) Y.J. Kim and J.G. Verkade, *Inorg. Chem.* 42 (2003), p. 4262.
(j) J.C.M. Rivas and L. Brammer, *Coord. Chem. Rev.* 183 (1999), p. 43.

(k) M. Oh, G.B. Carpenter and D.A. Sweigart, *Chem. Commun.* 18 (2002), p. 2168.
(l) M. Oh, G.B. Carpenter and D.A. Sweigart, *Acc. Chem. Res.* 37 (2004), p. 1. (m) C.M. Zakaria, G. Ferguson, A.J. Lough and C. Glidewell, *Acta Cryst., Sec. B* 58 (2002), p. 786.
(n) U. Geiger and J.A. Schlueter, *Chem. Rev.* 104 (2004), p. 5203.
(o) M. Oh, J.A. Reingold, G.B. Carpenter and D.A. Sweigart, *Coord. Chem. Rev.* 248 (2004), p. 561.
(p) C. Elschenbroich, M. Wolf, J. Pebler and K. Harms, *Organometallics* 23 (2004), p. 454.

[9] (a) M.J. Zaworotko, *Chem. Soc. Rev.* 23 (1994), p. 283.
(b) T. Steiner, *Angew. Chem. Int. Ed.* 41 (2002).
(c) M.J. Calhorda, *Chem. Commun.* (2000), p. 801.
(d) D. Braga, L. Maini, M. Polito and F. Grepioni, *Struct. Bond.* 111 (2004), p. 1.
(e) M. Nishio, *Cryst. Eng. Commun.* 6 (2004), p. 130. (g) A. Nangia, *Cryst. Eng. Commun.* (2002), p. 17.
(h) D. Braga, L. Maini, M. Polito and F. Grepioni, *Struct. Bond.* 111 (2004), p. 1.
(i) A.D. Burrows, *Struct. Bond.* 108 (2004), p. 55.

[10] D. Braga and F. Grepioni, *Coord. Chem. Rev.* 183 (1999), p. 19.

[11] (a) D. Braga, C. Bazzi, F. Grepioni and J.J. Novoa, *New J. Chem.* 23 (1999), p. 577.
(b) D. Braga, F. Grepioni, E. Tagliavini, J.J. Novoa and F. Mota, *New J. Chem.* (1998), p. 755.
(c) J.J. Novoa, I. Nobeli, F. Grepioni and D. Braga, *New J. Chem.* 24 (2000), p. 5.
(e) D. Braga, L. Maini, F. Grepioni, F. Mota, C. Rovira and J.J. Novoa, *Chem. Eur. J.* 6 (2000), p. 4536.
(f) D. Braga, E. D’Oria, F. Grepioni, F. Mota, J.J. Novoa and C. Rovira,

Chem. Eur. J. 8 (2002), p. 1173.

(g) D. Braga, F. Grepioni and J.J. Novoa, *Chem. Commun.* (1998), p. 1959.

[12] (a) In: G.R. Desiraju and T. Steiner, Editors, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford (1999).

(b) D. Braga, F. Grepioni, K. Biradha, V.R. Pedireddi and G.R. Desiraju, *J. Am. Chem. Soc.* 117 (1995), p. 3156.

(c) M.J. Calhorda, *Chem. Commun.* (2000), p. 801.

[13] (a) D. Braga, A. Angeloni, F. Grepioni and E. Tagliavini, *Chem. Commun.* (1997), p. 1447.

(b) D. Braga, A. Angeloni, F. Grepioni and E. Tagliavini, *Organometallics* 16 (1997), p. 5478.

[14] D. Braga, M. Eckert, M. Fraccastoro, L. Maini, F. Grepioni, A. Caneschi and R. Sessoli, *New J. Chem.* 26 (2002), p. 1280.

[15] D. Braga, L. Maini, L. Prodi, A. Caneschi, R. Sessoli and F. Grepioni, *Chem. Eur. J.* 6 (2000), p. 1310.

[16] D. Braga, A. Angeloni, L. Maini, A.W. Götz and F. Grepioni, *New J. Chem.* 23 (1999), p. 17.

[17] D. Braga, A. Angeloni, E. Tagliavini and F. Grepioni, *J. Chem. Soc. Dalton Trans.* (1998), p. 1961.

[18] F. Grepioni, S. Gladiali, L. Scaccianoce, P. Ribeiro and D. Braga, *New J. Chem.* 25 (2001), p. 690.

[19] D. Braga, M. Curzi, L. Maini, M. Polito and F. Grepioni, *Dalton Trans.* 16 (2004), p. 2432.

[20] (a) D. Braga and F. Grepioni, *J. Chem. Soc. Dalton Trans.* (1999), p. 1.

(b) D. Braga and F. Grepioni, *Acc. Chem. Res.* 33 (2000), p. 601.

(c) D. Braga, G. Coiazzi, L. Maini, M. Polito, L. Scaccianoce and F. Grepioni, *Coord. Chem. Rev.* 216 (2001), p. 225.

(d) D. Braga, L. Maini, M. Polito, E. Tagliavini and F. Grepioni, *Coord. Chem. Rev.* 246 (2003), p. 53.

[21] (a) S.R. Byrn, Solid State Chemistry of Drugs, Academic Press, New York (1982) p. 79. (b) J. Bernstein, R.J. Davey and J.-O. Henck, *Angew. Chem. Int. Ed. Eng.* 38 (1999), p. 3440. (c) N. Bladgen and R.J. Davey, *Chem. Brit.* 35 (1999). (d) J. Dunitz and J. Bernstein, *Acc. Chem. Res.* 28 (1995), p. 193.

[22] (a) D. Braga and F. Grepioni, *Chem. Soc. Rev.* 4 (2000), p. 229. (b) See also:D. Braga and F. Grepioni In: J.M. Brown and P. Hofmann, Editors, *Topics in Organometallic Chemistry* vol. 4, Springer-Verlag, Berlin (1999), p. 48.

[23] D. Braga, *Chem. Rev.* 92 (1992), p. 633.

[24] (a) P. Seiler and J.D. Dunitz, *Acta Cryst., Sec. B* 35 (1979), p. 2020. (b) F. Takusagawa and T.F. Koetzle, *Acta Cryst., Sec. B* 35 (1979), p. 1074. (c) P. Seiler and J.D. Dunitz, *Acta Cryst., Sec. B* 35 (1979), p. 1068. (d) D. Braga and F. Grepioni, *Organometallics* 11 (1992), p. 711. (e) J.D. Dunitz, *Acta Cryst., Sec. B* 51 (1995), p. 619. (f) J.D. Dunitz In: M.V. Kisakürek, Editor, *Organic Chemistry: Its Language and its State of the Art*, Verlag Basel, HCA (1993), p. 9.

1. Mechanochemical preparation of molecular and supramolecular organometallic materials and coordination networks

a. Introduction

The core paradigm of crystal engineering is the ability of assembling molecules or ions into *periodical* functional structures, the crystal, by controlling molecular recognition and aggregation *via* supramolecular interactions and coordination bonds.[1–7] Since the product of a crystal engineering experiment is *by definition* in the crystalline form, crystal engineers are *crystal makers* who constantly (and inevitably) face the problem of obtaining crystals for the characterization of their reaction products. Whether the products are obtained from solution, melt, vapour or from more forcing hydrothermal syntheses they will have to be investigated and characterized by solid-state techniques, in particular by X-ray diffraction. Amorphous materials are also extremely interesting,[8–16] but their investigation and use is still very limited mainly in view of the difficulty in their characterization.

In this *perspective* article we will demonstrate that novel crystalline materials can be obtained by reacting preformed crystalline materials with solid-state reactants in "solvent-free" conditions.[17] We will argue that " mechanochemical" reactions between solids represent alternative and, at times, unique ways to prepare a variety of crystalline materials from coordination networks to hydrogen bonded adducts *etc.*

It should be pointed out that part of the work discussed hereafter has been described previously in related review articles.[18–20] This *perspective*, however, is focused on the utilization of metal complexes as starting materials, which has been traditionally the field of interest of our Bolognese crystal engineering laboratory.[21–23]

Making crystalline materials by mechanochemical methods

The formation of crystals as products in solvent-free reactions between solid materials is controlled by the possibility of bringing reactants into contact. Therefore, intimate mixing of the reactants and large surface areas (*i.e.* small particle size) are, generally speaking, a prerequisite for successful reaction. Reactions between polycrystalline powders are usually carried out by mechanochemical methods such as manual co-grinding or milling (*vide infra*). Such methods generally produce materials also in the form of a polycrystalline powder and are, rather obviously, not suited for the growth of single crystals (for single-crystal diffractometers). Since mechanochemical mixing of reactants ultimately amounts to “making crystals by smashing crystals” the *single-crystal dogma*, on which the vast majority of crystal engineering studies is based, is seemingly contradicted. Unless one recurs to high intensity synchrotron radiation, microcrystals will allow only powder diffraction experiments, which only rarely can be used for *ab initio* structure determination in order to get those precise structural information that are so essential to the crystal engineer. Full structural characterization of the products, however, still replies on the possibility of obtaining single crystals, which might be often grown from solutions of the desired product by the *seeding* technique. Single-crystal X-ray diffraction experiments, in fact, will not only allow to know the structure of the products in fine details but also to carry out a useful comparison between the powder diffractograms measured on the bulk product and those calculated on the basis of the single-crystal structures. This is widely applied in the cases discussed herein.

Non-solution methods whether from solid–gas or solid–solid reactions (see Fig. 1) require the chemist, or crystal engineer, to explore/exploit methods that are not routinely used in chemical labs such as *grinding* and *milling*, which are less popular, when they are not dismissed as non-chemical, in academic research labs.[24–27]

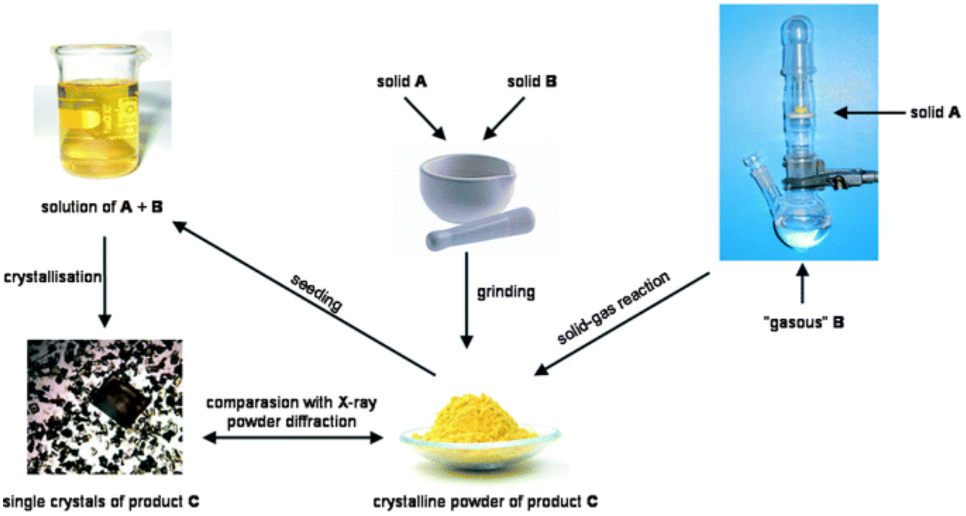


Fig. 1 *The solid–gas (right) and solid–solid (middle) processes and the strategy to obtain single crystals by recrystallisation of the solid reaction product in the presence of seeds (left) of the desired crystals.*

b. Grinding and milling

Typical mechanochemical reactions are those activated by co-grinding or milling of powder materials. These reactions are usually carried out either manually, in an agate mortar, or electro-mechanically, as in ball milling. In both cases the main difficulty is in controlling reaction conditions: grinding time, temperature, pressure exerted by the operator, *etc.* Furthermore, the heat generated in the course of the mechanochemical process can induce local melting of crystals or melting at the interface between the different crystals, so that the reaction might take place in the liquid phase even though solid products are ultimately recovered. One should also keep in mind that mechanical stress by fracturing the crystals increases surface area and facilitates interpenetration and reaction depending on the ability of molecules to diffuse through the crystal surfaces. Mechanochemical methods are commonly used at industrial level mainly with inorganic solids.[28–31]

In some cases the use of a small quantity of solvent can accelerate (when not make altogether possible) solid-state reactions carried out by grinding or milling.[32] The method based on the co-grinding of powdered reactants in the presence of a small amount of solvent, also known as kneading, has been described as a sort of "solvent catalysis" of the solid-state process, whereby the small amount of solvent provides a lubricant for molecular diffusion. The objection about whether a kneaded reaction between two solid phases can be regarded as a *bona fide* solid-state process is justified. However, in the context of this work, the interest lies more in the methods to make new crystalline materials rather than in the mechanisms. Industrial applications of kneading have been developed for pharmaceutical powders.[33,34] As an example of preparative lab scale one could mention the preparation by kneading of binary β-cyclodextrin bifonazole,[35] and of β-cyclodextrin inclusion compounds of ketoprofen,[36] ketoconazole[37] and carbaryl.[38]

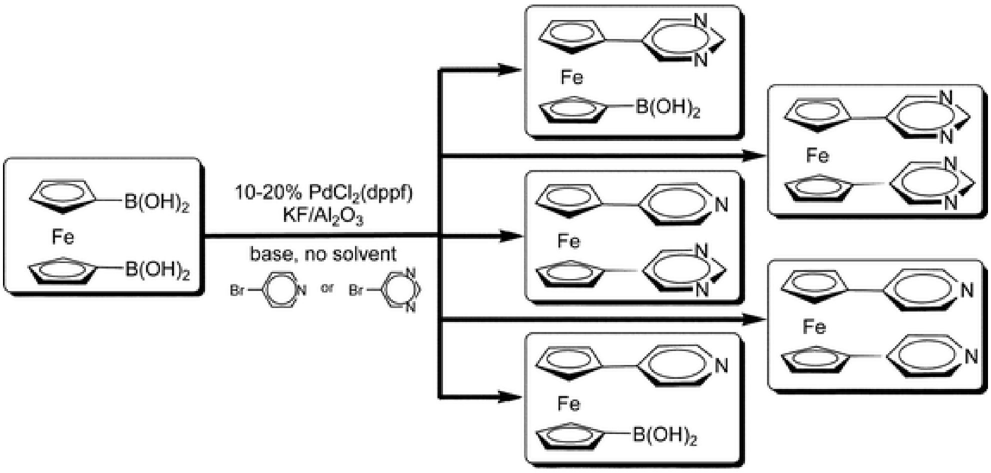
We have pointed out that, even though the product of a grinding, milling and kneading process is, in general, in the form of a powdered material, single crystals are still highly desirable (when not indispensable) for a thorough characterization of the reaction product. In such a case, *seeding* can provide a route to the growth of single crystals of the desired material.[17,39–41] The method, however, is not failure-proof, and other conditions, such as supersaturation, rate of solvent evaporation and temperature as well as the purity of the *seeding* powder obtained by grinding may still play a role in determining the crystallization outcome.

The use of *seeds* is also very important when there is the possibility of formation of different crystal forms, *i.e.* crystal polymorphism.[42,43] *Seeds* of isostructural or *quasi*-isostructural species that crystallise well can also been employed to induce crystallisation of unyielding materials (*heteromolecular seeding*).[44–46] For instance, chiral co-crystals of tryptamine and hydrocinnamic acid have also been prepared by crystallization in the presence of seeds of different chiral crystals.[47] Of course, unintentional *seeding* may also alter the crystallization process in an undesired manner.[48]

c. Mechanically-induced formation of covalent bonds

While mechanochemical methods have been widely used with organic[26] and inorganic[24] compounds, there are not many examples of the utilization of mechanochemical procedures in coordination chemistry. For instance, Balema *et al.* have shown that the *cis*-platinum complexes *cis*-$(Ph_3P)_2PtCl_2$ and *cis*-$(Ph_3P)_2PtCO_3$ can be prepared mechanochemically from solid reactants in the absence of solvent.[49] Orita *et al.* have reported that the reaction of (ethylenediamine)$Pt(NO_3)_2$ with 4,4′-bipyridine, which takes as long as 4 weeks at 100 °C to form metallamacrocyclic molecular squares,[50,51] is brought to completion within 10 min at room temperature by mixing reactants without solvents.[52] Similar reaction acceleration has been observed also with triazine based ligands.[53,54] Double helix formation under solvent free conditions has also been achieved by reacting chiral oligo(bipyridine) copper complexes with $[(CH_3CN)_4Cu]PF_6$. The progress of the reaction was monitored by measuring solid-state CD-spectra showing that after grinding for 5 min the desired helicate had been obtained.[52]

It has been reported that bis-substituted pyridine/pyrimidine ferrocenyl complexes can be prepared by mechanically-induced Sukuzi-coupling reaction[55–59] in the solid-state starting from ferrocene-1,1′-diboronic acid, $[Fe(\eta^5\text{-}C_5H_4\text{–}B(OH)_2)_2]$ (see Scheme 1).[60] The solvent-free reactions allow synthesis in the air and at room temperature of mono- and bis-substituted pyridine and pyrimidine ferrocenyl derivatives thus providing a valuable alternative to the preparation in solution. Actually, in the case of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$, the solvent-free process is much faster and more selective than the same reaction carried out in solution. Beside shorter reaction times, less workup, higher yield, and the absence of solvents the solid-state reaction affords the possibility of combining different synthetic steps in order to obtain homo- and hetero-ligands ferrocenyl complexes.

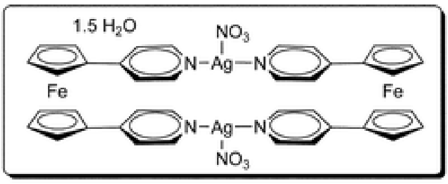


Scheme 1

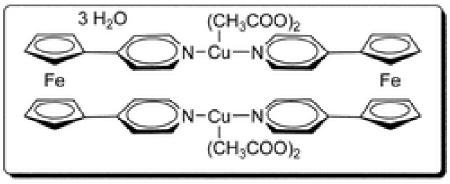
The solid-state synthesis of mono- and bis-substituted pyridine and pyrimidine ferrocenyl derivatives starting from ferrocene-1,1'-diboronic acid, $[Fe(\eta^5\text{-}C_5H_4\text{–}B(OH)_2)_2]$.

d. Preparation of "complexes-of-complexes": mixed metal superstructures derived from bispyridine

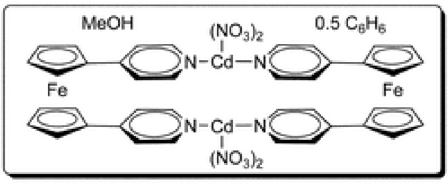
The bidentate compounds described in the previous section were employed for the preparation of supramolecular "complexes-of-complexes",[61] aiming to the construction of mixed-metal supramolecular materials with interesting electrochemical and spin properties. The bottom-up construction of supramolecular materials and coordination networks with desired properties is one of the main goals of crystal engineering.[62–91] Ferrocene-based pyridyl ligands have been studied for the possibility of exploiting their redox properties in various applications, such as amperometric sensors for metal ions. The focus, however, has been mainly on mono-substituted ferrocenes, while only few examples of bis-substituted ferrocene pyridyl complexes are known.[92–99] We have prepared a series of mixed-metal macrocyclic complexes by reacting mechanochemically prepared $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ with transition metal salts, such as $AgNO_3$, $Cd(NO_3)_2$, $Cu(CH_3COO)_2$, $Zn(CH_3COO)_2$ and $ZnCl_2$ (Scheme 2).[100] A similar approach has been used before by others by using aminocobaltocenes and aminoferrocenes to form complexes with Zn^{2+} and Co^{2+} metal ions.[95,101–117] while flexible bis-*p*-aminopyridine bidentate ligands have also been utilized to prepare metallamacrocycle complexes.[118–121] Analogously, neutral ligands (1,4-diazabicyclooctane, tetramethylpyrazine and pyrazine) have been used to link silver carboxylates in extended networks.[122]



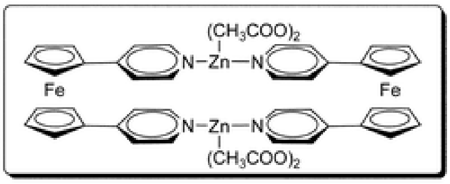
$[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Ag_2(NO_3)_2\cdot 1.5H_2O$



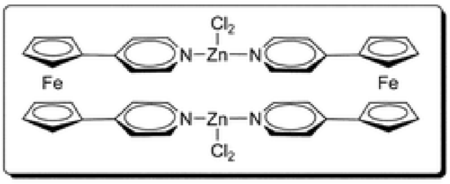
$[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cu_2(CH_3COO)_4\cdot 3H_2O$



$[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cd_2(NO_3)_4\cdot CH_3OH\cdot 0.5C_6H_6$



$[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2(CH_3COO)_4$



$[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2Cl_4$

Scheme 2.

In view of the conformational freedom of the two η^5-C_5H_4-1-C_5H_4N ligands in [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$] we were also intrigued by the question on whether the ligands would have adopted a *cisoid* or a *transoid* conformation upon coordination.[123] While the former conformation leads to the formation of finite coordination geometry, *i.e.* to a molecular complex, the latter might, in principle, lead to an infinite network. The two limiting situations are shown in Fig. 2.

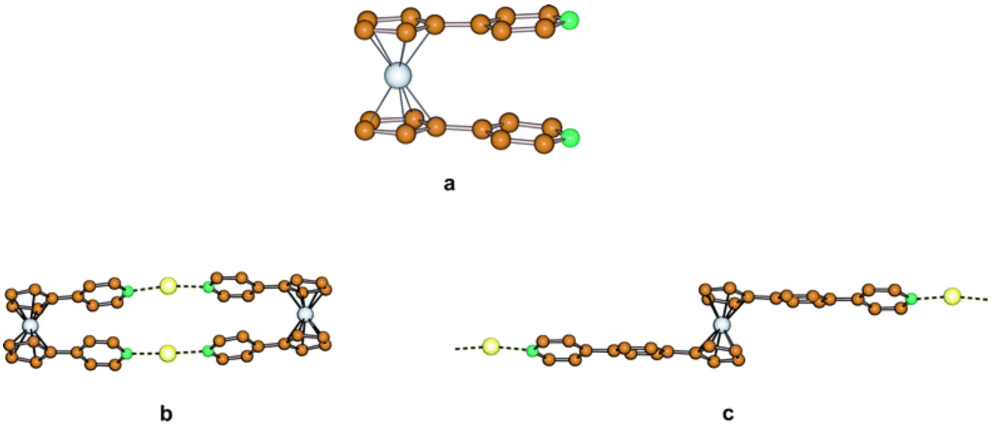
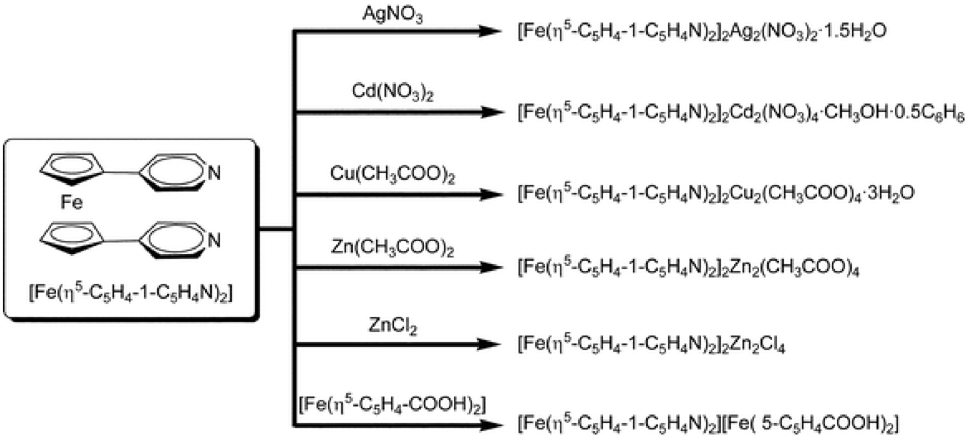


Fig. 2 *The cisoid and transoid conformation of two metallamacrocycle compounds (a) the [Fe(*η^5*-*C_5H_4*-4-*C_5H_4N*)*$_2$*. The [Fe(*η^5*-*C_5H_4*-4-*C_5H_4N*)*$_2$*] leads to a finite structure (as in (b)) but it could also, in principle, form a infinite network (as in (c)), even though the structure in (c) is a fictive one.*

However, all compounds in Scheme 3 do not form extended networks but metallamacrocycles. The solid-state structure of the heterobimetallic system complex [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$]$_2$$Ag_2(NO_3)_2\cdot 1.5H_2O$ is shown in Fig. 3. The two silver atoms interact directly with the pyridine ligands, with Ag···N distances between 2.123(8), and 2.145(8) Å. The Ag···Ag distance is 3.500(2) Å. This separation is comparable to that observed in other dimeric Ag-complexes.[124,125] The two nitrate anions play different roles in the crystal structure. While one is directly linked to the other nitrate anion *via* water molecules, the second anion acts as a bridge between dimeric units as shown in Fig. 4, with O···Ag distances of 2.752(9) and 2.870(1) Å, respectively. A similar ion-pairing link between neighbouring complexes has been observed in the complex with Ag^+ and bis-*p*-aminopyridine bidentate ligands.



Scheme 3

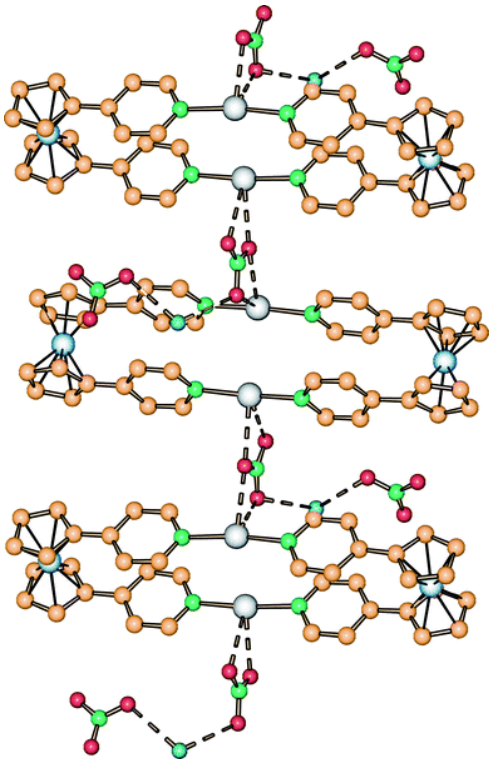


Fig. 3 *The heterometallic* $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Ag_2(NO_3)_2\cdot1.5H_2O$ *complex showing how the how the network is built up by bridging nitrate anions between the dimeric units.*

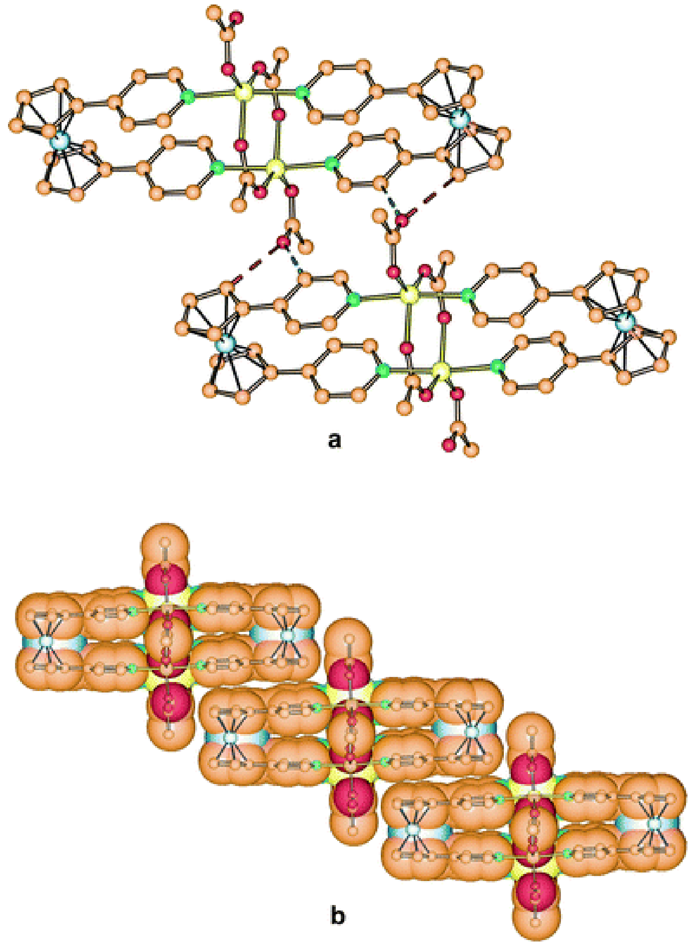


Fig. 4 *(a) The crystal structure of the* $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2(CH_3COO)_4$ *complex. (b) The space filling model of the* $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2(CH_3COO)_4$ *complex showing the packing.*

The complex $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2(CH_3COO)_4$ shows that the Cp-pyridine ligands are nearly eclipsed with a Zn⋯Zn separation of 3.875(1) Å. The two acetate ligands span the Zn⋯Zn system [Zn(1)–O(3) 2.018(3), Zn(1)–O(4) 2.018(2) Å] while two acetate ligands are dangling externally at a Zn⋯O separation of 2.042(3) Å(see Fig. 4). The Zn⋯Zn distance indicates that the interaction between the Zn centres is entirely repulsive, as would be expected from closed shell first row systems. The coordination around the Zn-centres can be described as a trigonal bipyramid. A space filling representation of the packing of [Fe(η^5-C_5H_4-1-$C_5H_4N)_2]_2Zn_2(CH_3COO)_4$ in the solid state is shown in Fig. 4(b).

The structure of the compound obtained by reacting the bispyridine with zinc chloride, [Fe(η^5-C_5H_4-1-$C_5H_4N)_2]_2Zn_2Cl_4$ is shown in Fig. 5. The constrain imposed by the tetrahedral coordination around the zinc centres [Zn–Cl distances 2.202(3), 2.224(3) Å] leads to the formation of a butterfly-type molecule, with the two $ZnCl_2$ units forming the hinge and the ferrocenyl units the wings of the butterfly Å(see Fig. 6(b) for a space filling representation). The distance between the two Zn centres is 6.125 Å.

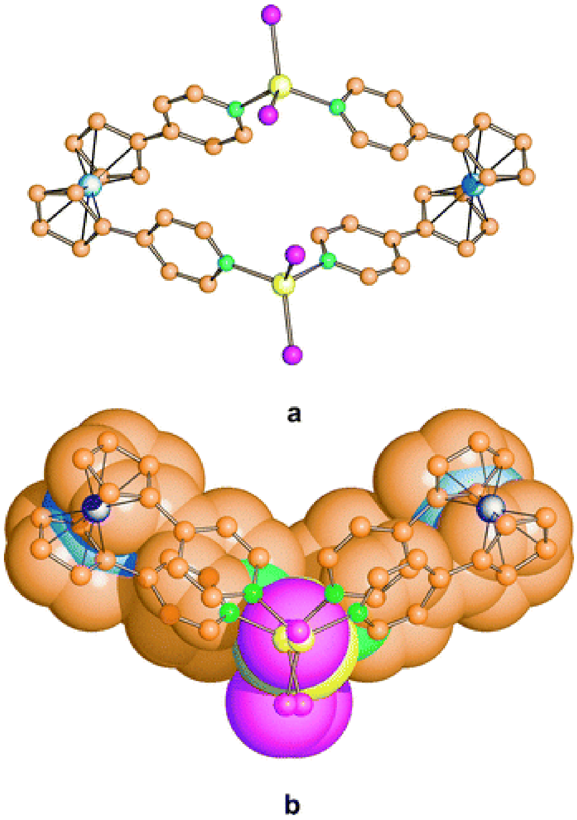


Fig. 5 *(a) The crystal structure of* $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Zn_2Cl_4$ *showing tetrahedral coordination geometry around the zinc centres. (b) This coordination geometry will lead to the formation of a butterfly-type molecule as shown by the space filling representation.*

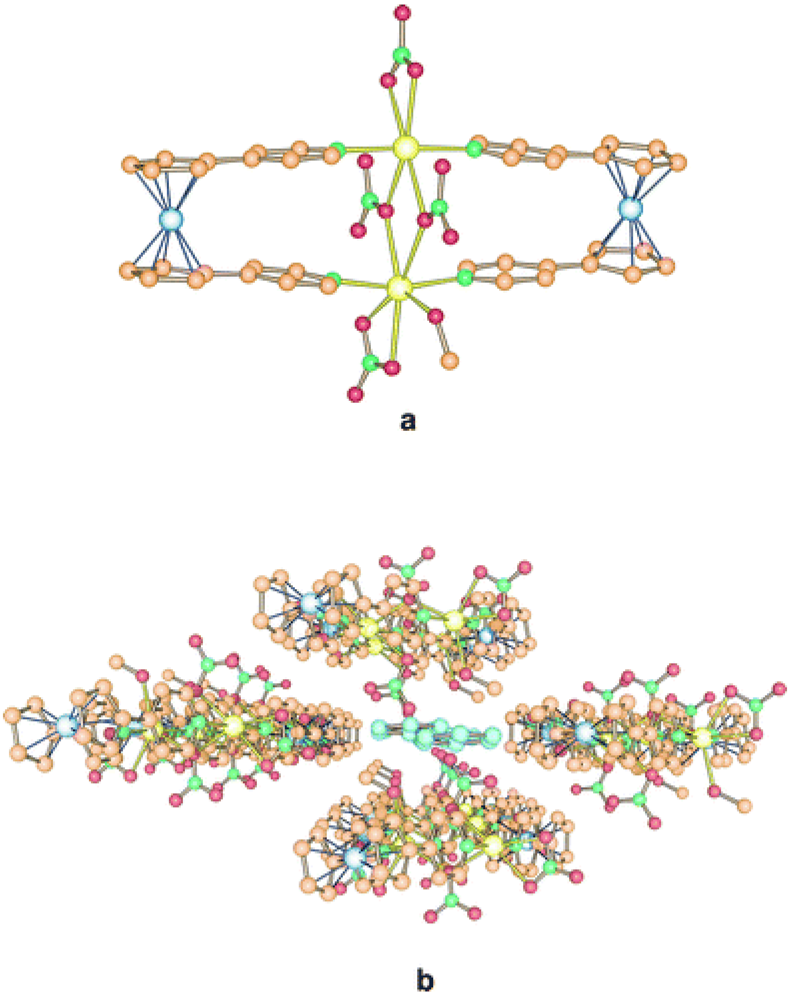


Fig. 6 *(a) The crystal structure of the* $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cd_2(NO_3)_4\cdot CH_3OH\cdot 0.5C_6H_6$ *complex showing the coordinated methanol molecule which leads to different coordination numbers around the two cadmium centres. (b) The complex form ample channels throughout the structure where solvent molecules (benzene) can be accommodated.*

The structure of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cd_2(NO_3)_4\cdot CH_3OH\cdot 0.5C_6H_6$ is reminiscent of that of the silver complex with the notable difference that the

Cd-centres are bridged by two asymmetric nitrate bridges [Cd(1)–O(9) 2.355(7), Cd(2)–O(9) 2.400(6), Cd(1)–O(1) 2.450(6), Cd(2)–O(1) 2.757(6) Å]. While the Cd(1) centre is six-coordinated, the Cd(2) centre is seven-coordinated because of additional presence of a coordinated methanol molecule (see Fig. 6). In summary, one Cd-centre is almost octahedral, while the other is seven-coordinated and the Cd···Cd distance is 4.225(3) Å. The ferrocenyl-pyridine systems stack at a distance of 3.47 Å, with the Cd-atoms completely screened from the surrounding by the N- and O-interactions. Fig. 6 shows how the supramolecular arrangement of the complexes leaves ample channels in the structure where the solvent molecules (light blue) can be accommodated.

The complex $[Fe(\eta^5-C_5H_4-1-C_5H_4N)_2]_2Cu_2(CH_3COO)_4·3H_2O$ possesses a structure that is reminiscent of that of $[Fe(\eta^5-C_5H_4-1-C_5H_4N)_2]_2Ag_2(NO_3)_2·1.5H_2O$, the Cp-pyridine ligands are in eclipsed conformation and bridge the two Cu-atoms (see Fig. 7). The Cu···Cu separations are 3.428(5) and 3.473(5) Å, respectively, for the two independent half molecules in the asymmetric unit. Similarly to what observed in $[Fe(\eta^5-C_5H_4-1-C_5H_4N)_2]_2Cd_2(NO_3)_4·CH_3OH·0.5C_6H_6$ the bimetallic Cu···Cu unit is spanned by two acetate anions [Cu(1)–O(2) 1.96(2), 2.49(2), Cu(2)–O(6) 2.06(2), 2.37(2) Å]. If one considers the additional acetate ions linked to each Cu atom, the coordination around copper can be described as distorted square pyramidal.

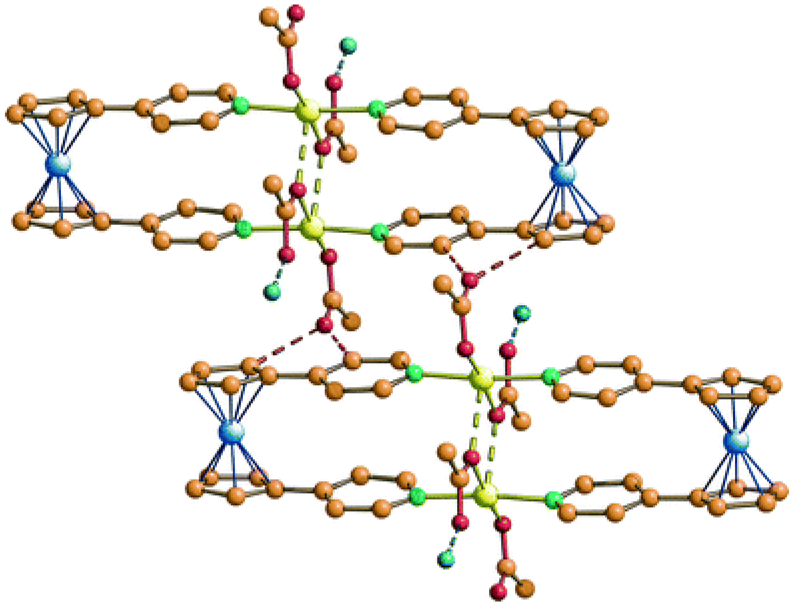


Fig. 7 *The heterometallic* $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]_2Cu_2(CH_3COO)_4\cdot 3H_2O$ *complex showing how the how the network is built up by bridging acetate anions between the dimeric units.*

Clearly the complex [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$] can also take part in hydrogen-bonding interactions with two N-acceptors on the pyridyl ligands. Hydrogen bonding is one of the core topics of molecular crystal engineering and has been investigated extensively because of its *tuneable* strength and directional features.[102–104,106,108–114] In order to compare the Lewis basicity of the pyridyl ligand in [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$] towards metal coordination and towards a protic acid, we have also reacted [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$] with the dicarboxylic organometallic acid [Fe(η^5-C_5H_4COOH)$_2$] obtaining the hydrogen bonded adduct [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$][Fe(η^5-C_5H_4COOH)$_2$], which will be described later in this *Perspective.*

e. Mechanochemical Preparation of Coordination Networks

In this section we will show that coordination polymers with bidentate nitrogen bases can be prepared mechanochemically.[126] Nichols, Steed and Raston have explored the use of mechanochemistry in the synthesis of extended supramolecular arrays.[127] Grinding of $Ni(NO_3)_2$ with 1,10-phenanthroline (phen) resulted in the facile preparation of $[Ni(phen)_3]^{2+}$ accompanied by a dramatic and rapid colour change. Addition of the solid sodium salt of tetrasulfonatocalix[4]arene (tsc) gives two porous π-stacked supramolecular arrays $[Ni(phen)_3]_2[tsc^{4-}]\cdot nH_2O$ and the related $[Na(H_2O)_4(phen)][Ni(phen)_3]_4$ $[tsc^{4-}][tsc^{5-}]\cdot nH_2O$ depending on stoichiometry. It has also been reported that the co-grinding of copper(II) acetate hydrate with 1,3-di(4-pyridyl)propane (dpp) gives a gradual colour change from blue to blue–green over *ca.* 15 min. The resulting material was shown by solid-state NMR spectroscopy to comprise a 1D coordination polymer with water-filled pores. The same host structure, $[\{Cu(OAc)_2\}_2(\mu$-

dpp)]$_n$, could be obtained from solution containing methanol, acetic acid or ethylene glycol guest species.[128]

We have reported preparation of the coordination polymer $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot5H_2O$ by co-grinding of silver acetate and $[N(CH_2CH_2)_3N]$ in 1:2 ratio (see Fig. 8). Single crystals suitable for X-ray diffraction were obtained from a water–methanol solution and used to compare calculated and experimental X-ray powder diffractograms. When $ZnCl_2$ is used instead of $AgCH_3COO$ in the equimolar reaction with $[N(CH_2CH_2)_3N]$, different products are obtained from solution and solid-state reactions, respectively. The preparation of single crystals of $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot5H_2O$ was obviously indispensable for the determination of the exact nature of the co-grinding product. In order to do so the powder diffraction pattern computed on the basis of the single-crystal structure was compared with the one measured on the product of the solid-state preparation. Fig. 9 shows that the structure of $Zn[N(CH_2CH_2)_3N]Cl_2$ is based on a one-dimensional coordination network constituted of alternating $[N(CH_2CH_2)_3N]$ and $ZnCl_2$ units, joined by Zn–N bonds. As mentioned above, upon co-grinding of the solid reactants a new Zn compound of unknown stoichiometry is obtained as a powder material. Even though attempts to obtain single crystals of this latter compound have failed, there is a relationship between the compound obtained initially by co-grinding and the one obtained from solution. In fact, the co-grind phase can be partially transformed by prolonged grinding into the known anhydrous phase $Zn[N(CH_2CH_2)_3N]Cl_2$ shown in Fig. 9.

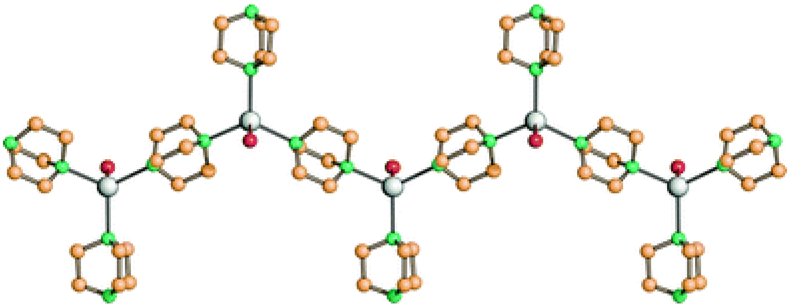


Fig. 8 *The coordination network in* $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot 5H_2O$ *is built up by chains of* $Ag\cdots[N(CH_2CH_2)_3N]\cdots Ag\cdots[N(CH_2CH_2)_3N]\cdots Ag$ *with each silver atom carrying an extra pendant* $[N(CH_2CH_2)_3N]$ *ligand. An extra coordinated water molecule leads to tetrahedral coordination geometry around the silver centres.*

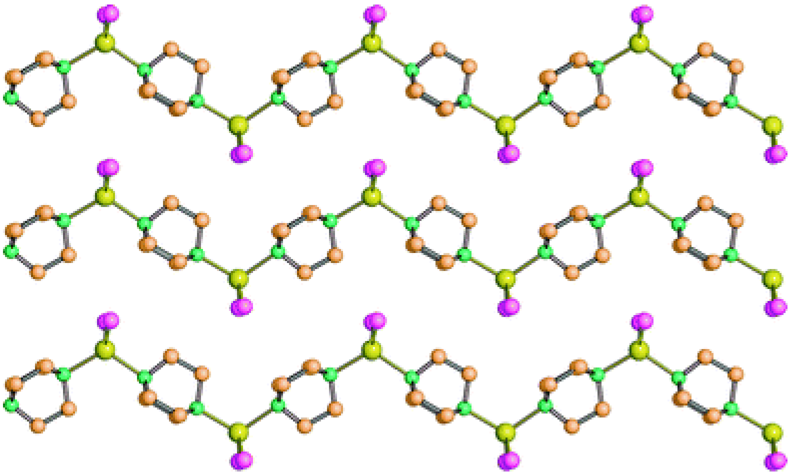
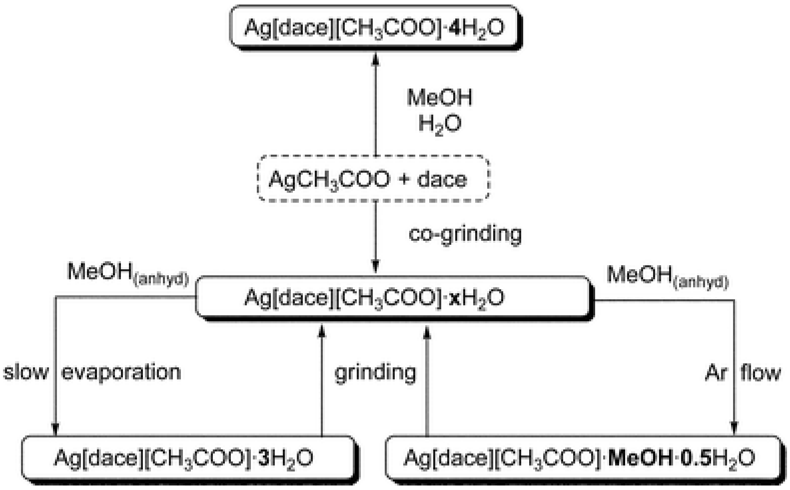


Fig. 9 *The one-dimensional coordination network present in crystals of* $Zn[N(CH_2CH_2)_3N]Cl_2$.

More recently we have applied the same procedure to the preparation of another class of compounds.[129] We have explored the solid-state and solution reactions between silver acetate and *trans*-1,4-diaminocyclohexane [$H_2NC_6H_{10}NH_2$], dace, a diamine having been little exploited as a divergent ligand in the construction of coordination networks.[130–137] The solid-state co-grinding of $AgCH_3COO$ and dace in 1 : 1 ratio results in a crystalline powder tentatively formulated as Ag[dace][CH_3COO]·$x$$H_2O$ (Scheme 4). Crystallisation of the same compounds from anhydrous MeOH yields two types of products depending on the solvent evaporation conditions: crystals of Ag[dace][CH_3COO][MeOH]·0.5H_2O, are obtained by crystallisation under argon flow, while slow evaporation in the air results in crystals of Ag[dace][CH_3COO]·3H_2O. Single-crystal X-ray diffraction experiments have shown that both of these compounds contain two isomeric forms of the coordination network $\{Ag[dace]^+\}_\infty$. If the same reaction between $AgCH_3COO$ and dace is carried out directly in MeOH–water solution, a third crystalline material is obtained, namely the tetrahydrate Ag[dace][CH_3COO]·4H_2O. In all cases, correspondence between bulk powder and single crystals was ascertained by comparing computed and observed powder diffractograms.



Scheme 4

In terms of chemical composition the three compounds differ only in the degree and nature of solvation. The differences in topology are, however, much more dramatic and the three compounds must be regarded as isomers of the same basic coordination network. The crystal structure of the $MeOH·0.5H_2O$ compound is constituted of a two-dimensional coordination network (Fig. 10(a)) formed by the divergent bidentate dace ligand and two silver atoms, which are joined together by an Ag···Ag bond of 3.323(1) Å and are asymmetrically bridged by two methanol molecules. There is a close structural relationship between the coordination networks in the $MeOH·0.5H_2O$ compound and in the trihydrated compound. This latter structure is built around a zigzag chain $Ag^{(+)}$···[dace]···$Ag^{(+)}$···[dace]···$Ag^{(+)}$ units as shown in Fig. 10(b). The Ag-atom is coordinated in a linear fashion. A projection perpendicular to the dace planes shows how the zigzag-chains extend in parallel fashion. The $Ag^{(+)}$···[dace]···$Ag^{(+)}$···[dace]···$Ag^{(+)}$ chains are bridged together *via* hydrogen bonds involving the N–H donors, the water molecules and the acetate anions. The tetrahydrated species

Ag[dace][CH_3COO]·$4H_2O$, contains an isomeric form of the coordination networks present in two former compounds. In the trihydrated compound two ligands are in *cisoid* relative orientation with respect to the silver atom, while in the tetrahydrated compound the two ligands adopt a *transoid* conformation. This is made possible by the different orientation of the N-atom lone pairs in dace ligand. The acetate anions form a hydrated network and interact with the base and the water molecules.

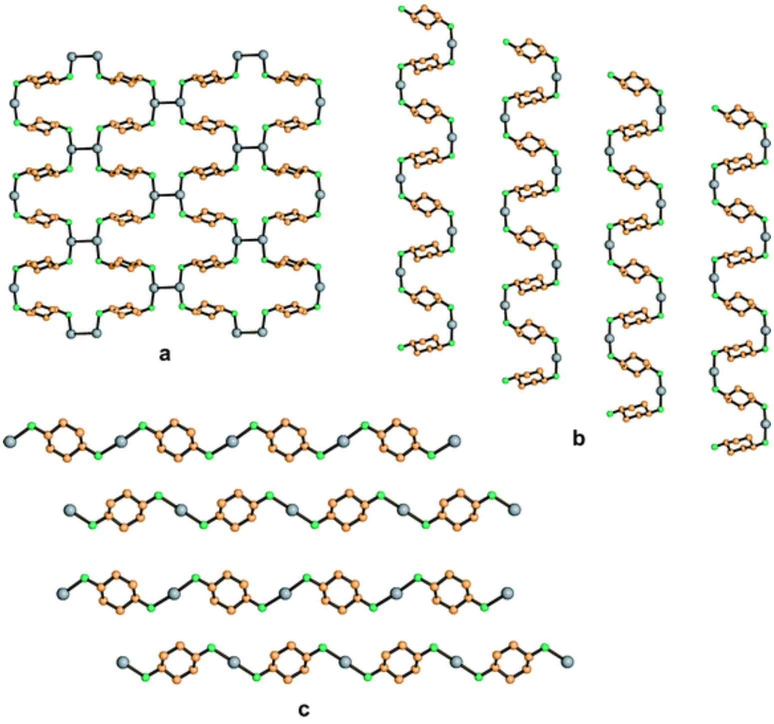
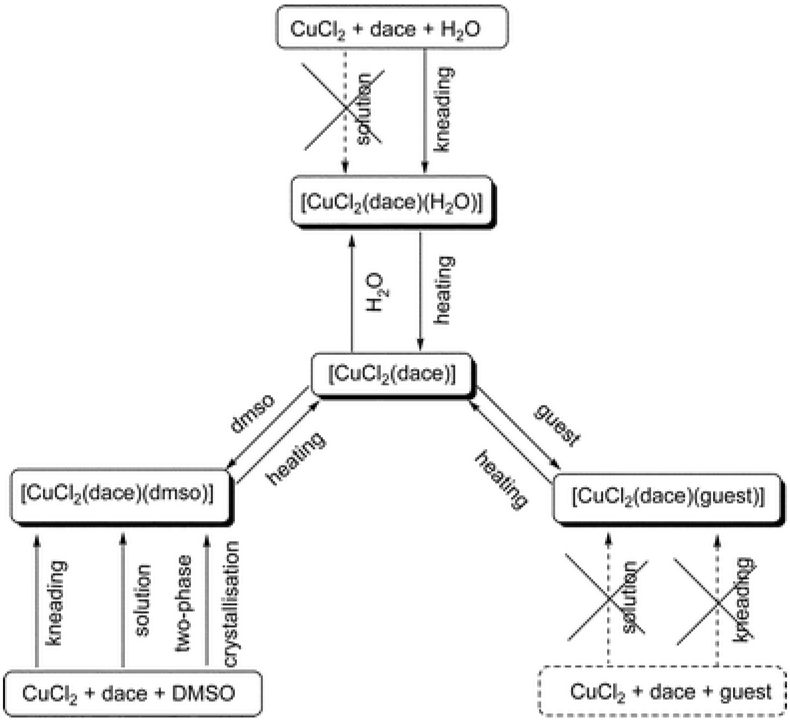


Fig. 10 *(a) Crystal structure of the* $Ag[dace][CH_3COO]\cdot 1.5H_2O$ *complex where the two-dimensional coordination network is formed by the divergent bidentate dace ligand with silver atoms. (b) Crystal structure of the* $Ag[dace][CH_3COO]\cdot 3H_2O$ *complex. (c) Crystal structure of the* $Ag[dace][CH_3COO]\cdot 4H_2O$ *complex where the ligands adopt a transoid relative orientation with respect to the silver atom.*

In summary, different isomers of the same coordination network have been obtained depending on the preparation and crystallisation conditions (Scheme 5). The relationship between supramolecular isomerism and network topology has been discussed.[66]



Scheme 5

In a further study of mechanochemical utilization of dace we have reported that compound $[CuCl_2(dace)]_\infty$ can be obtained by thermal treatment of the hydrated compound $[CuCl_2(dace)(H_2O)]_\infty$, which is prepared by *kneading* of solid $CuCl_2$ and dace in the presence of a small amount of water.[138] The structure of $[CuCl_2(dace)]_\infty$ is not known, since it is insoluble in most organic solvents, which does not permit the growth of single crystals of X-ray quality. However the DMSO adduct $[CuCl_2(dace)(DMSO)]_\infty$ has been fully characterised by single X-ray diffraction and therefore given some insight of the structure of $[CuCl_2(dace)]_\infty$. The DMSO adduct can also easily be obtained by kneading solid $CuCl_2$ and dace in the presence of a small amount of DMSO. This compound is formed of 1-D coordination networks, in which the $CuCl_2$ units are bridged by dace ligands in chains (see Fig. 11). Parallel 1-D $CuCl_2$–dace networks form layers and between the layers, the co-crystallised DMSO is intercalated.

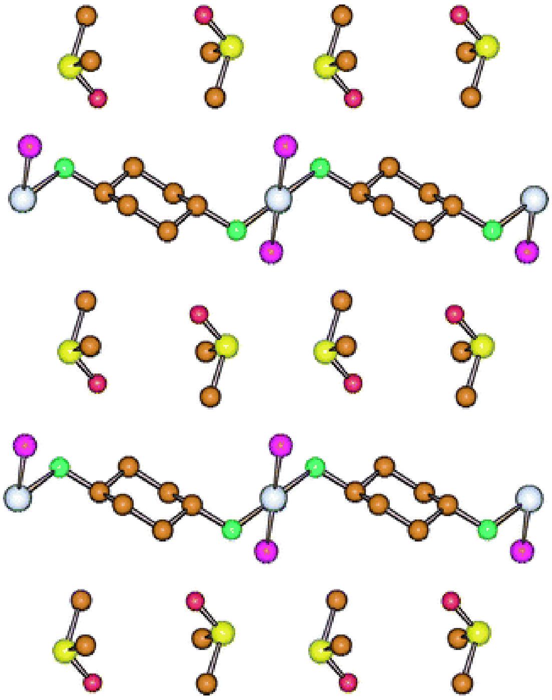


Fig. 11 *The* $[CuCl_2(dace)]_\infty$ *complex forming chains of* $CuCl_2$ *and dace ligands, where the chains form layers. Between the layers, co-crystallized DMSO is intercalated.*

Beside the interesting structural features, compound $[CuCl_2(dace)(DMSO)]_\infty$ is relevant because of its behaviour upon thermal treatment. When $[CuCl_2(dace)(DMSO)]_\infty$ is heated to 130 °C it converts to $[CuCl_2(dace)]_\infty$ as easily ascertained by comparing X-ray diffraction powder diffractograms. From the structure of $[CuCl_2(dace)(DMSO)]_\infty$ and from the knowledge of its thermal behaviour it is possible to infer that the structure of $[CuCl_2(dace)]_\infty$ is based on stacking sequence of layers as in $[CuCl_2(dace)(DMSO)]_\infty$, but "squeezed" at a shorter inter-layer separation as a consequence of DMSO removal. When a guest molecule enters between the layers, the spacing between the $CuCl_2$-dace chains is expanded and the layers are shifted back in position. A series of small molecules can be uptaken/released depending on the preparation method, *i.e.* kneading, suspension in the liquid guest or kneading followed by suspension. The latter approach is the most productive, when suspended in the desired liquid guest the $[CuCl_2(dace)]_\infty$ only takes up relatively small molecules (DMSO, acetone, water, methanol, *etc.*) while by kneading other guest molecules are also taken up. But if $[CuCl_2(dace)]_\infty$ is first kneaded with a small amount of the desired liquid and then left stirring in the same liquid for 12 h, partial or complete filling of the compound is observed, independently on the guest molecule.

Reversible gas–solid reactions and solid–solid reactions of the zwitterion sandwich complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$

As mentioned in the Introduction, solid–gas reactions provide another alternative (when not unique) solvent-free route to the preparation of novel materials. In this section we summarize the solvent-free chemistry of the zwitterion sandwich complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$.[139] The presence of one –COOH group, which can react with bases, and one –$COO^{(-)}$ group, which can react with acids confers an effective amphoteric behaviour to the complex. As a matter of fact, the molecule undergoes fully reversible gas–solid reactions with the hydrated vapours of a variety of acids (*e.g.* HCl, CF_3COOH, CCl_3COOH, CHF_2COOH, HBF_4, HCOOH and bases (*e.g.* NH_3, NMe_3, NH_2Me) as well as solid–solid reactions (see Fig. 12) with crystalline alkali salts MX (M = K^+, Rb^+, Cs^+, NH_4^+; X = Cl^-, Br^-, I^-, PF_6^-, though not in all permutations of cations and anions).[140–145] The zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ can be quantitatively prepared from the corresponding dicarboxylic cationic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$.

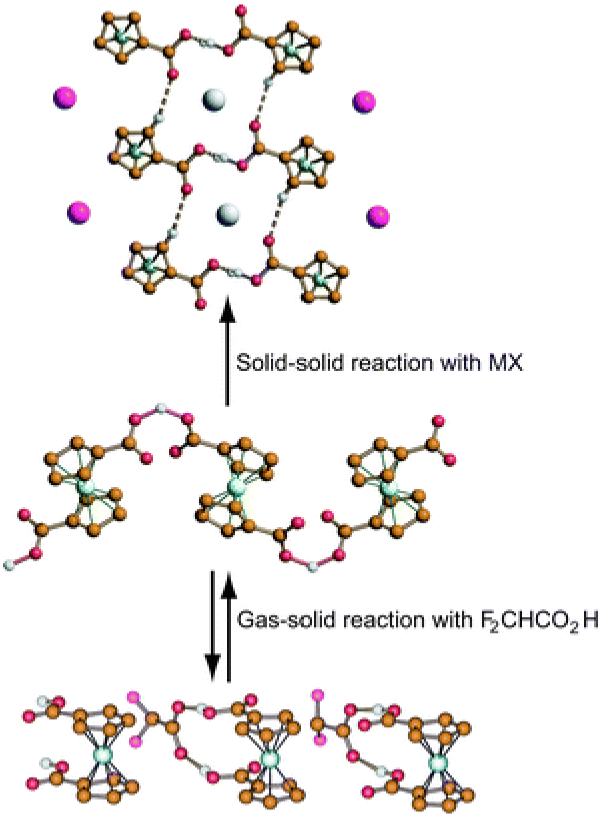


Fig. 12 *The solid–solid reaction and gas–solid reaction of the zwitterion sandwich* $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ *complex with crystalline MX and vapours of difluoroacetic acid, respectively.*

Manual grinding of the zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ with a number of alkali salts MX ($M = K^+, Rb^+, Cs^+, NH_4^+$; $X = Cl^-, Br^-, I^-, PF_6^-$ though not in all permutations of cations and anions, (see below) yields compounds of general formula $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}M^+X^-$.[140,141] Information on the hydrogen-bonding nature and on the relationship between structures in solution and those obtained in the solid state by mechanical grinding were obtained by a combination of solution and solid-state NMR methods. In some cases ($M = Rb^+, Cs^+$, $X = Cl^-, Br^-, I^-$) it was necessary to recur to *kneading* by adding a few drops of water to the solid mixture in order to obtain the desired product. All compounds of formula $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}M^+X^-$, ($M = K^+, Rb^+, Cs^+, NH_4^+$ $X = Br^-, I^-, PF_6^-$) are isostructural and are characterized by the presence of a supramolecular cage formed by four zwitterionic molecules encapsulating the alkali or ammonium cations. The cage is sustained by O–H···O hydrogen bonds between carboxylic –COOH and carboxylate $–COO^{(-)}$ groups, and by C–H···O bonds between $–CH_{Cp}$ and –CO groups, while the anions are layered in between the cationic complexes, as shown in Fig. 13 in the case of the CsI derivative. It is fascinating to think of the process leading to formation of the cages as a kind of sophisticated solvation based operated by the organometallic complex. The zwitterion is able of "extracting" *via* $O{\cdots}X^-$ interactions the alkali cations from their lattice while the anions are "extruded" and left to interact with the peripheral C–H groups *via* numerous C–H···X interactions. The solid–solid process can thus be seen as the dissolution of one solid (the alkali salt) into a *solid solvent.*

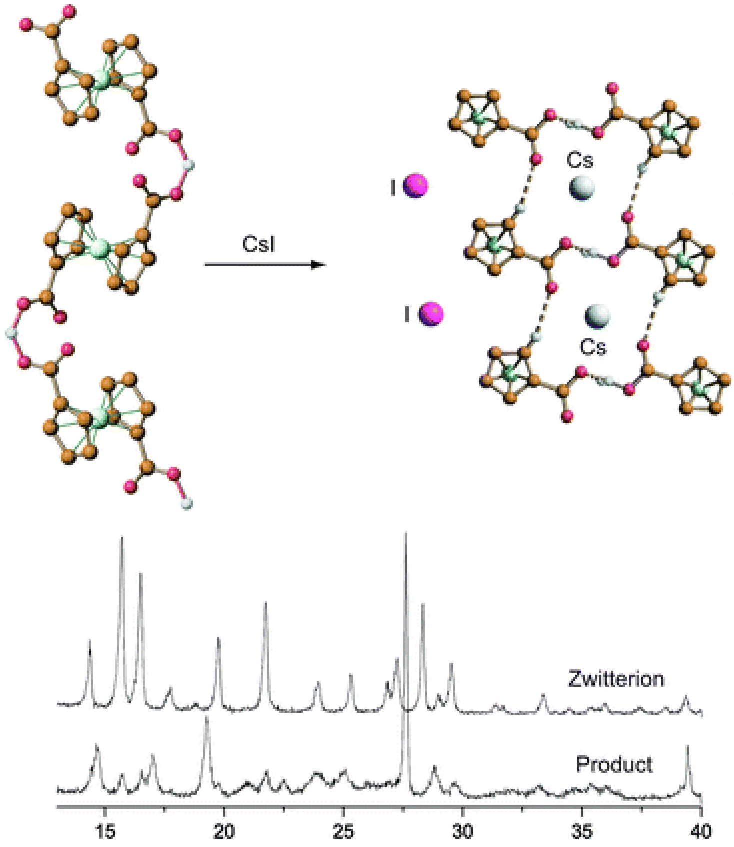


Fig. 13 A *pictorial representation of the process leading from* $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ *and* CsI *to* $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}Cs^+I^-$.

f. Mechanochemical preparation of hydrogen bonded adducts

Manual grinding of the ferrocenyl dicarboxylic acid complex $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ with nitrogen containing solid bases, namely 1,4-diazabicyclo[2.2.2]octane, 1,4-phenylenediamine, piperazine, *trans*-1,4-cyclohexanediamine and guanidinium carbonate, generates quantitatively the corresponding organic-organometallic adducts (see Fig. 14(a)).[146,147] The case of the adduct $[HC_6N_2H_{12}][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (see Fig. 14(b)) is particularly noteworthy because the same product can be obtained in three different ways: (i) by reaction of solid [Fe(η^5-$C_5H_4COOH)_2$] with vapours of 1,4-diazabicyclo[2.2.2]octane (which possesses a small but significant vapour pressure), (ii) by reaction of solid [Fe(η^5-$C_5H_4COOH)_2$] with solid 1,4-diazabicyclo[2.2.2]octane, *i.e.* by co-grinding of the two crystalline powders, and (iii) by reaction in MeOH solution of the two reactants. Clearly, the fastest process is the solid–solid reaction. It is also interesting to note that the base can be removed by mild treatment regenerating the structure of the starting dicarboxylic acid. The processes imply breaking and reassembling of hydrogen-bonded networks, conformational change from *cis* to *trans* of the –COO/–COOH groups on the ferrocene diacid, and proton transfer from acid to base. Crystals suitable for X-ray diffraction were grown *via seeding* from the solutions of the products originally prepared mechanochemically.

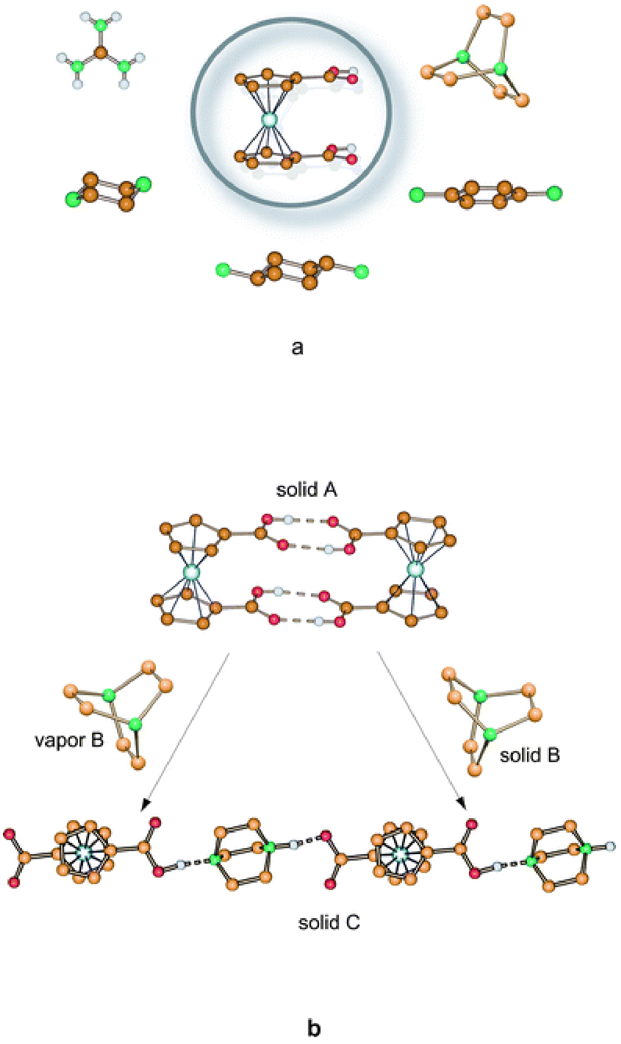


Fig. 14 *(a) Grinding of the organometallic complex* $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ *as a solid polycrystalline material with the solid bases 1,4-diazabicyclo[2.2.2]octane, guanidinium carbonate, 1,4-phenylenediamine, piperazine and trans-1,4-cyclohexanediamine generates quantitatively the corresponding adducts* $[HC_6H_{12}N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, $[C(NH_2)_3]_2[Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$, $[HC_6H_8N_2][Fe(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, $[H_2C_4H_{10}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]$, $[H_2C_6H_{14}N_2][Fe(\eta^5\text{-}C_5H_4COO)_2]\cdot 2H_2O$. *(b) The solid–gas and solid–solid reactions involving 1,4-diazabicyclo[2.2.2]octane with formation of the linear chain.*

In this context it is worth discussing the result of the mechanochemical reaction of the above mentioned complex [Fe(η^5–C_5H_4-1-C_5H_4N)$_2$] with the dicarboxylic ferrocenyl acid [Fe(η^5-C_5H_4COOH)$_2$]. The supramolecular structure of the hydrogen bond adduct [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$][Fe(η^5-C_5H_4COOH)$_2$] is shown in Fig. 15. It can be seen that [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$] and [Fe(η^5-C_5H_4COOH)$_2$] establishes a twin hydrogen-bonding interaction forming a sort of ferrocenyl dimer. The O···N separations [O(2)···N(1) 2.593(5), O(4)···N(2) 2.569(5) Å] are in agreement with the presence of conventional hydrogen bonds. It is interesting to observe that, judging from the diffraction data, no proton transfer from the –COOH groups to the N-sites takes place. Hence the two hydrogen-bonding interactions ought to be described as neutral O–H···N rather than as "charge assisted" $^{(-)}$O···H–N$^{(+)}$hydrogen bonds.[107,148–152] Both the two COOH groups in the diacid and the pyridine groups in [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$] are eclipsed. The arrangement is thus topologically related to that observed for the class of "complexes of complexes" discussed above with the exception of the $(Zn^{II}_{chloride})_2^{4+}$ derivative. It is interesting to note that the preference for an eclipsed conformation of the pyridyl ligands is maintained in the formation of the hydrogen bond adduct. In principle, [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$][Fe(η^5-C_5H_4COOH)$_2$] could possess an alternative network structure in the solid state based on 1-D chains of alternating pyridylcarboxylic ligands. This arrangement is fairly common when ferrocenyl dicarboxylic acid is used. It has been observed in hydrogen bonded adducts with bis-amidines[153] and with other bis-amines, such as 1,4-diazabicyclo[2.2.2]octane, $C_6H_{12}N_2$, DABCO.[146,154] In all these cases, however, the geometry of the base did not allow cyclization and *forced* the system to chain formation, while the conformational freedom of [Fe(η^5-C_5H_4-1-C_5H_4N)$_2$] permits, in principle, both linear chains and rings.

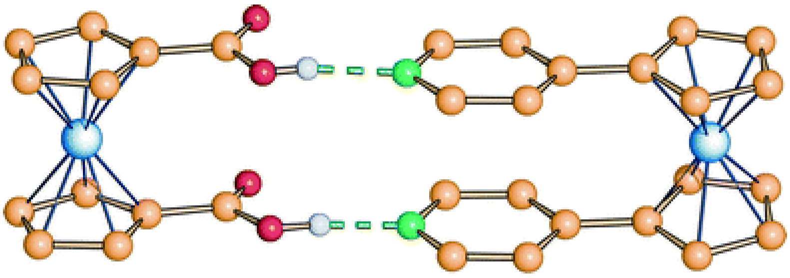


Fig. 15 *The solid-state structure of* $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]$ *showing the twin hydrogen-bonding interaction which form the ferrocenyl dimer.*

A similar situation is seen with the diacid $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ itself.[155–163] Contrary to most dicarboxylic acids that form chains linked by carboxylic rings, the ferrocenyl diacid forms cyclic dimers joined by a twin carboxylic ring in both its known polymorphic modifications (monoclinic and triclinic). It is noteworthy that the analogy between $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]$ and $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$ is not confined to the dimeric structure: the supramolecular arrangement in the solid state is also extremely similar. The effect of mechanical mixing of solid dicarboxylic acids $HOOC(CH_2)_nCOOH$ (n = 1–7) of variable chain length together with the solid base 1,4-diazabicyclo[2.2.2]octane, $C_6H_{12}N_2$, to generate the corresponding salts or cocrystals of formula $[N(CH_2CH_2)_3N]$–H–$[OOC(CH_2)_nCOOH]$ ($n = 1–7$) has also been investigated.[164]

g. Mechanochemical preparation of supramolecular crown ether adducts

In a further extension of the exploratory work in the use of mechanochemical methods to prepare hydrogen bonded supramolecular adducts we have used crown ethers to capture alkali metal cations and the ammonium cation in extended hydrogen bonded networks.[165] Crown ethers complexes have been the subject of an enormous number of studies because of the interest in ion recognition, complexation and in self-assembly processes.[166–170] In the study ammonium hydrate sulfate salts were used since the presence of hydrogen bonds between ions is a relevant supramolecular issue and hydrogen sulfate salts have found applications in a number of devises such as H_2 and H_2O sensors, fuel and steam cells and high energy density batteries.[171–174] Manual co-grinding of solid 18-crown[6] and solid $[NH_4][HSO_4]$ in the air leads to formation of the crown ether complex 18-crown[6]·$[NH_4][HSO_4]\cdot 2H_2O$ (Fig. 16), the water molecules being taken up from ambient humidity during grinding. The complex has been fully structurally characterised by single-crystal X-ray determination. In the complex the ammonium cation is trapped *via* $O_{crown}\cdots H–N$ hydrogen bonds by the crown ethers, while on the exposed side it interacts with the hydrogen sulfate anion. The sulfate anion and the water molecules also interacts *via* hydrogen bonding forming a ribbon that is sandwiched between 18-crown[6]·$[NH_4]^+$ units. Hydrogen bonds are also observed between water molecules and oxygen atoms in the crown ether.

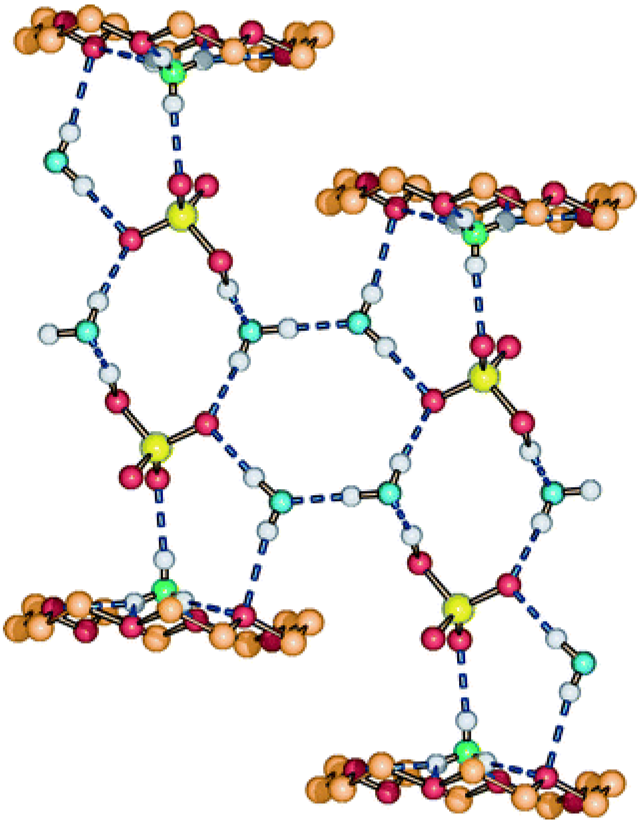


Fig. 16 *The solid-state structure of the crown ether complex 18-crown[6]·[NH₄][HSO₄]·2H₂O.*

The crown ether 15-crown[5] is a liquid in room temperature, so when it is kneaded instead of grinded, with the ammonium hydrate sulfate, a similar reaction as for the 18-crown[6] takes place. The product, (15-crown[5])$_3$·[NH$_4$]$_2$[HSO$_4$]$_3$·H$_2$O, also fully structurally determined by single-crystal X-ray determination, is also obtained when the reaction takes place in solution. The (15-crown[5])$_3$·[NH$_4$]$_2$[HSO$_4$]$_3$·H$_2$O is reminiscent of that of the 18-crown[6] because of the formation of hydrogen bonded ribbons intercalated between the crown ether layers. The difference between the two adducts are, however, the two different types of interactions between the ammonium cation and the crown ether that is presence in the 15-crown[5] adduct. One ammonium cation is sandwiched between two crown ether units, while the other is linked to the hydrogen sulfate anion by N–H···O hydrogen bonds. In the 15-crown[5] adduct also a hydrogen bonded $[H_3O]^+$ ion is needed to neutralise the overall charge.

h. Conclusions

Crystal engineering amounts to the deliberate construction of a molecular solid[1] (whether a molecular complex, an adduct or a co-crystal)[175,176] that can perform desired functions, hence it is conceptually related to the construction of a supermolecule.[166,177] In both molecular crystals and supermolecules the collective properties depend on the aggregation *via* intermolecular bonds of two or more component units. These supramolecular interactions can be coordination bonds between ligands and metal centres and non-covalent bonds between neutral molecules or ions or, of course, any of their combinations. Processes that lead to such non-covalent bonds from reactants to products, either *via* breaking or forming of intermolecular bonds, are therefore supramolecular reactions. In this *Perspective* article we have shown that non-covalent bonds can be broken and formed in a controlled way by reactions that do not imply the use of solvent but that can be carried out directly between two crystalline solids or between a crystalline solid and a vapour. Reactions of this type have been the subject of investigation for decades in the fields of organic and of inorganic chemistry. Although solid–gas and solid–solid reactions are at the basis of a number of industrial processes that range from preparation of pharmaceutical compounds[178,179] to inorganic alloying,[24] they still enjoy little popularity in the field or organometallic and coordination chemistry.[180,181] This is probably due, on the one hand, to the fact that crystals are depicted (even at the level of crystallography courses) as rigid, stiff, fragile materials that are good for little else beside structural analysis, and, on the other hand, to the belief that molecular crystals, being held together by non-covalent interactions, cannot compete with covalent or ionic inorganic solids in terms of cohesion and stability and are not the best materials for gas uptake and/or mechanical treatment.

Our experience is that adequately chosen crystalline materials can withstand reversible gas–solid reactions with vapours of both acidic and basic substances as well as mechanically activated reactions with other molecular crystals and inorganic salts. Primarily, the interest in solvent-free conditions stems from the possibility of obtaining the same product as that from solution *without solvent* because the process is cheaper, less time consuming and often more environmentally friendly. On the other hand one may be interested in solvent-free conditions for the possibility of obtaining products not otherwise accessible from solvents. In this latter case, however, one is often faced with the problem of characterization, because the lack of single crystals complicates the matter significantly and *ab initio* structural determination from powder diffraction data alone is not yet a valid alternative with complex structures such as those described above.

In this *Perspective*, we have confined ourselves to essentially four classes of reactions involving organometallic molecular crystals or coordination compounds as reactants: (i) reactions between a hydrogen bonded molecular crystal and a vapour with formation of hydrogen bonded supramolecular adducts, (ii) reactions leading to formation of covalent bonds for the preparation of building blocks, (iii) reactions between hydrogen bonded molecular crystals to produce new molecular crystals based on hydrogen bonds, and (iv) reactions between a molecular crystals and ionic crystals leading to "solid-state solvation". Clearly, all these reactions (perhaps with the exception of those of type (ii) are diffusion controlled and are not necessarily reactions in the solid state as mechanical stress may cause local melting, co-grinding may form an intermediate eutectic phase, and *kneading* probably generates locally *hyper*saturated solutions wherefrom crystals of the new phase nucleate. In all these cases the crystal lattice is destroyed and reformed through recrystallization. In such processes hydrogen bonds, π-stacking, van der Waals, ion pairing interactions *etc.* in are broken and formed through the reaction process leading to formation of supramolecular compounds or hybrid molecular crystals.

On closing, it may be useful to stress that reactions involving solid coordination and organometallic compounds represent "green chemistry" ways to the preparation of metal containing materials since recovery, storage and disposal of solvents are not required.[182] Furthermore solvent-free reactions often lead to very pure products and reduce the formation of solvate species and may thus be exploited in the quest for elusive crystal polymorphs.[183–189] These might be useful notions for crystal engineers and solid-state chemists.

References

1 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989.

2 D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, 98, 1375–1405 _.

3 *J. Chem. Soc., Dalton Trans.*, 2000, 3705–3998, Proceedings of the Dalton Discussion on Inorganic Crystal Engineering.

4 M. D. Hollingsworth, *Science*, 2002, 295, 2410–2413 _.

5 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, 2311–2327 _.

6 D. Braga, F. Grepioni and A. G. Orpen, *Crystal Engineering: from molecules and crystals to materials*, Kluwer Academic Publishers, Dordrecht, 1999.

7 D. Braga, *Chem. Commun.*, 2003, 2751–2754 _.

8 L. Addadi and M. Geva, *CrystEngComm*, 2003, 5, 140–146 _.

9 J. Aizenberg, G. Lambert, S. Weiner and L. Addadi, *J. Am. Chem. Soc.*, 2002, 124, 32–39 _.

10 E. Beniash, J. Aizenberg, L. Addadi and S. Weiner, *Proc. R. Soc. London, Ser. B*, 1997, 264, 461–465 _.

11 L. Addadi, S. Raz and S. Weiner, *Adv. Mater.*, 2003, 15, 959–970 _.

12 J. Johnston, H. E. Merwin and E. D. Williamson, *Am. J. Sci.*, 1916, 41, 473–512.

13 S. Raz, S. Weiner and L. Addadi, *Adv. Mater.*, 2000, 12, 38–42 _.

14 E. Loste and F. C. Meldrum, *Chem. Commun.*, 2001, 901–902 _.

15 J. Aizenberg, G. Lambert, L. Addadi and S. Weiner, *Adv. Mater.*, 1996, 8, 222–226 _.

16 D. Braga, *Angew. Chem., Int. Ed.*, 2003, 42, 5544–5546 _.

17 D. Braga and F. Grepioni, *Chem. Soc. Rev.*, 2000, 29, 229–238 _.

18 D. Braga and F. Grepioni, *Angew. Chem., Int. Ed.*, 2004, 43, 4002–4011 _.

19 D. Braga, D. D'Addario, L. Giaffreda Stefano, L. Maini, M. Polito and F. Grepioni, *Top. Curr. Chem.*, 2005, 254, 71–94 _.

20 D. Braga and F. Grepioni, *Chem. Commun.*, 2005, 3635–3645 _.

21 D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 1999, 1–8 _.

22 D. Braga and F. Grepioni, *Coord. Chem. Rev.*, 1999, 183, 19–41 _.

23 D. Braga, L. Maini, M. Polito, L. Scaccianoce, G. Cojazzi and F. Grepioni, *Coord. Chem. Rev.*, 2001, 216–217, 225–248 _.

24 V. V. Boldyrev and K. Tkacova, *J. Mater. Synth. Process.*, 2000, 8, 121–132 _.

25 J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, 71, 581–586 _.

26 G. Kaupp, *Compr. Supramol. Chem.*, 1996, 8, 381–423.

27 G. Kaupp, *CrystEngComm*, 2003, 5, 117–133 _.

28 J. M. Cairney, S. G. Harris, L. W. Ma, P. R. Munroe and E. D. Doyle, *J. Mater. Sci.*, 2004, 39, 3569–3575 _.

29 G. Bettinetti, M. R. Caira, A. Callegari, M. Merli, M. Sorrenti and C. Tadini, *J. Pharm. Sci.*, 2000, 89, 478–489 _.

30 Y. A. Kim, T. Hayashi, Y. Fukai, M. Endo, T. Yanagisawa and M. S. Dresselhaus, *Chem. Phys. Lett.*, 2002, 355, 279–284 _.

31 K. Wieczorek-Ciurowa, K. Gamrat and K. Fela, *Solid State Ionics*, 2003, 164, 193–198 _.

32 N. Shan, F. Toda and W. Jones, *Chem. Commun.*, 2002, 2372–

2373 _.

33 S. Watano, T. Okamoto, M. Tsuhari, I. Koizumi and Y. Osako, *Chem. Pharm. Bull.*, 2002, 50, 341–345 _.

34 S. Watano, J. Furukawa, K. Miyanami and Y. Osako, *Adv. Powder Technol.*, 2001, 12, 427–441.

35 N. Morin, A. Chilouet, J. Millet and J. C. Rouland, *J. Therm. Anal. Calorim.*, 2000, 62, 187–201 _.

36 G. Bruni, A. Marini, V. Berbenni, R. Riccardi and M. Villa, *J. Inclusion Phenom. Macrocyclic Chem.*, 1999, 35, 517–530.

37 F. Taneri, T. Gueneri, Z. Aigner and M. Kata, *J. Inclusion Phenom. Macrocyclic Chem.*, 2002, 44, 257–260.

38 R. Saikosin, T. Limpaseni and P. Pongsawasdi, *J. Inclusion Phenom. Macrocyclic Chem.*, 2002, 44, 191–196.

39 T. L. Threlfall, *Analyst*, 1995, 120, 2435–2460 _.

40 N. Kubota, N. Doki, M. Yokota and D. Jagadesh, *J. Chem. Eng. Jpn.*, 2002, 35, 1063–1071.

41 D. Braga and F. Grepioni, in *Crystal Design*, ed. G. R. Desiraju, John Wiley & Sons, Weinheim, 2003.

42 W. C. McCrone, in *Polymorphism in Physics and Chemistry of the Organic Solid State*, ed. D. Fox, M. M. Labes and A. Weissemberg, Interscience, New York, 1965, vol. 2, p. 726.

43 J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press, Oxford, 2002.

44 P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1982, 38, 1741–1745 _.

45 D. Braga, G. Cojazzi, D. Paolucci and F. Grepioni, *CrystEngComm*, 2001, 3, 159–161 _.

46 R. J. Davey, N. Blagden, G. D. Potts and R. Docherty, *J. Am. Chem. Soc.*, 1997, 119, 1767–1772 _.

47 H. Koshima and M. Miyauchi, *Cryst. Growth Des.*, 2001, 1, 355–357 _.

48 J. D. Dunitz and J. Bernstein, *Acc. Chem. Res.*, 1995, 28, 193–200 _.

49 V. P. Balema, J. W. Wiench, M. Pruski and V. K. Pecharsky, *Chem. Commun.*, 2002, 1606–1607 _.

50 M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, 112, 5645–5647 _.

51 M. Fujita, J. Yazaki and K. Ogura, *Chem. Lett.*, 1991, 1031–1032 _.

52 A. Orita, L. Jiang, T. Nakano, N. Ma and J. Otera, *Chem. Commun.*, 2002, 1362–1363 _.

53 C. R. Woods, M. Benaglia, F. Cozzi and J. S. Siegel, *Angew. Chem., Int. Ed. Engl.*, 1996, 35, 1830–1833 _.

54 R. Annunziata, M. Benaglia, M. Cinquini, F. Cozzi, C. R. Woods and J. S. Siegel, *Eur. J. Org. Chem.*, 2001, 173–180 _.

55 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, 95, 2457–2483 _.

56 T. Ishiyama, H. Kizaki, T. Hayashi, A. Suzuki and N. Miyaura, *J. Org. Chem.*, 1998, 63, 4726–4731 _.

57 D. Villemin and F. Caillot, *Tetrahedron Lett.*, 2001, 42, 639–642 _.

58 G. W. Kabalka, R. M. Pagni and C. M. Hair, *Org. Lett.*, 1999, 1, 1423–1425 _.

59 M. Melucci, G. Barbarella and G. Sotgiu, *J. Org. Chem.*, 2002, 67, 8877–8884 _.

60 D. Braga, D. D'Addario, M. Polito and F. Grepioni, *Organometallics*, 2004, 23, 2810–2812 _.

61 D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, L. Sturba and F. Grepioni, *Organometallics*, 2003, 22, 2142–2150 _.

62 D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, 33, 601–608 _.

63 A. M. Garcia, D. M. Bassani, J.-M. Lehn, G. Baum and D. Fenske, *Chem.–Eur. J.*, 1999, 5, 1234–1238 _.

64 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, 34, 319–330 _.

65 S. R. Batten, *CrystEngComm*, 2001, 18, 1–17 _.

66 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, 101, 1629–1658 _.

67 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schroder, *Coord. Chem. Rev.*, 1999, 183, 117–138 _.

68 S. R. Batten, B. F. Hoskins and R. Robson, *Chem.–Eur. J.*, 2000, 6, 156–161 _.

69 J. Lu, B. Moulton, M. J. Zaworotko and S. A. Bourne, *Chem. Commun.*, 2001, 861–862 _.

70 B. Rather and M. J. Zaworotko, *Chem. Commun.*, 2003, 830–831 _.

71 B. Moulton, H. Abourahma, M. W. Bradner, J. Lu, G. J. McManus and M. J. Zaworotko, *Chem. Commun.*, 2003, 1342–1343 _.

72 M. Fujita, *Chem. Soc. Rev.*, 1998, 27, 417–425 _.

73 B. Olenyuk, A. Fechtenkotter and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1998, 1707–1728 _.

74 M. D. Ward, *Science*, 2003, 300, 1104–1105 _.

75 D. Braga, G. R. Desiraju, J. S. Miller, A. G. Orpen and S. L. Price, *CrystEngComm*, 2002, 4, 500–509 _.

76 G. Ferey, M. Latroche, C. Serre, F. Millange, T. Loiseau and A. Percheron-Guegan, *Chem. Commun.*, 2003, 2976–2977 _.

77 F. A. Cotton, C. Lin and C. A. Murillo, *J. Chem. Soc., Dalton Trans.*, 2001, 499–501 _.

78 F. A. Cotton, C. Lin and C. A. Murillo, *Chem. Commun.*, 2001, 11–12 _.

79 W. Mori and S. Takamizawa, *J. Solid State Chem.*, 2000, 152, 120–129 _.

80 L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2002, 4, 121–129 _.

81 *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992.

82 S. R. Marder, *Inorg. Mater.*, 1992, 115–164 _.

83 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, 21–38 _.

84 T. J. Marks and M. A. Ratner, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, 155–173 _.

85 D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev. (Washington, DC)*, 1994, 94, 195–242.

86 O. Khan, *Molecular Magnetism*, VCH, New York, 1993.

87 D. Gatteschi, *Adv. Mater.*, 1994, 6, 635–645 _.

88 J. S. Miller and A. J. Epstein, *Chem. Eng. News*, 1995, 73, 30–41 _.

89 J. S. Miller, *Angew. Chem., Int. Ed.*, 2003, 42, 27–29 _.

90 L. Pan, M. B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B.

Bockrath and J. K. Johnson, *J. Am. Chem. Soc.*, 2004, 126, 1308–1309 _.

91 D. Braga, L. Brammer and N. R. Champness, *CrystEngComm*, 2005, 7, 1–19 _.

92 H. Plenio and D. Burth, *Organometallics*, 1996, 15, 4054–4062 _.

93 E. C. Constable, A. J. Edwards, M. D. Marcos, P. R. Raithby, R. Martinez-Manez and M. J. L. Tendero, *Inorg. Chim. Acta*, 1994, 224, 11–14 _.

94 C. D. Hall, T. K. U. Truong and J. H. R. Tucker, *Chem. Commun.*, 1997, 2195–2196 _.

95 C. B. Aakeroy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 22, 397–407 _.

96 K. Biradha, *CrystEngComm*, 2003, 5, 374–384 _.

97 H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, 236, 91–119 _.

98 A. M. Beatty, *Coord. Chem. Rev.*, 2003, 246, 131–143 _.

99 E. A. Bruton, L. Brammer, F. C. Pigge, C. B. Aakeroey and D. S. Leinen, *New J. Chem.*, 2003, 27, 1084–1094 _.

100 D. Braga, M. Polito, D. D'Addario, E. Tagliavini, D. M. Proserpio, F. Grepioni and J. W. Steed, *Organometallics*, 2003, 22, 4532–4538 _.

101 R. Schneider, M. W. Hosseini, J.-M. Planeix, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 1625–1626 _.

102 G. Desiraju and T. Steiner, *The Weak Hydrogen Bond: Applications to Structural Chemistry and Biology*, Oxford Univ. Press, New York, 1999.

103 D. Braga, F. Grepioni, K. Biradha, V. R. Pedireddi and G. R.

Desiraju, *J. Am. Chem. Soc.*, 1995, 117, 3156–3166 _.

104 M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, 23, 283–288 _.

105 T. Steiner, *Angew. Chem., Int. Ed.*, 2002, 41, 48–76 _.

106 M. J. Calhorda, *Chem. Commun.*, 2000, 801–809 _.

107 D. Braga, L. Maini, M. Polito and F. Grepioni, *Struct. Bonding (Berlin)*, 2004, 111, 1–32 _.

108 C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, 36, 1431–1434 _.

109 S. George, A. Nangia, M. Bagieu-Beucher, R. Masse and J.-F. Nicoud, *New J. Chem.*, 2003, 27, 568–576 _.

110 M. Nishio, *CrystEngComm*, 2004, 6, 130–158 _.

111 J. Hulliger, *Chem.–Eur. J.*, 2002, 8, 4578–4586 _.

112 L. Brammer, M. D. Burgard, M. D. Eddleston, C. S. Rodger, N. P. Rath and H. Adams, *CrystEngComm*, 2002, 4, 239–248 _.

113 L. Brammer, *Dalton Trans.*, 2003, 3145–3157 _.

114 A. D. Burrows, *Struct. Bonding (Berlin)*, 2004, 108, 55–96 _.

115 *J. Organomet. Chem.*, 2001, 637–639, 1–875 (whole issue).

116 M. W. Hosseini and A. De Cian, *Chem. Commun.*, 1998, 727–733 _.

117 D. Braga and F. Grepioni, *Chem. Commun.*, 1996, 571–578 _.

118 T.-Y. Liu, Y. J. Chen, C.-C. Tai and K. S. Kwan, *Inorg. Chem.*, 1999, 38, 674–679 _.

119 K. Hutchison, J. C. Morris, T. A. Nile, J. L. Walsh, D. W. Thompson, J. D. Petersen and J. R. Schoonover, *Inorg. Chem.*, 1999, 38, 2516–2523 _.

120 E. M. Barranco, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna and M. D. Villacampa, *J. Organomet. Chem.*, 1999, 592, 258–264 _.

121 E. C. Constable, A. J. Edwards, R. Martinez-Manez, P. R. Raithby and A. M. W. C. Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 645–650 _.

122 L. Brammer, M. D. Burgard, C. S. Rodger, J. K. Swearingen and N. P. Rath, *Chem. Commun.*, 2001, 2468–2469 _.

123 D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, D. M. Proserpio and F. Grepioni, *Chem. Commun.*, 2002, 1080–1081 _.

124 C.-Y. Su, B.-S. Kang, Q.-G. Wang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 2000, 1831–1833 _.

125 G. W. Eastland, M. A. Mazid, D. R. Russell and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1980, 1682–1687 _.

126 D. Braga, S. L. Giaffreda, F. Grepioni and M. Polito, *CrystEngComm*, 2004, 6, 458–462.

127 P. J. Nichols, C. L. Raston and J. W. Steed, *Chem. Commun.*, 2001, 1062–1063 _.

128 W. J. Belcher, C. A. Longstaff, M. R. Neckenig and J. W. Steed, *Chem. Commun.*, 2002, 1602–1603 _.

129 D. Braga, M. Curzi, F. Grepioni and M. Polito, *Chem. Commun.*, 2005, 2915–2917 _.

130 J. L. Stark, A. L. Rheingold and E. A. Maatta, *J. Chem. Soc., Chem. Commun.*, 1995, 1165–1166 _.

131 N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2002, 41, 284–287 _.

132 O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, 31, 474–484 _.

133 H. Li, M. Eddaoudi, M. O'Keeffe and M. Yaghi, *Nature*, 1999,

402, 276–279 _.

134 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and M. Yaghi Omar, *Science*, 2002, 295, 469–472 _.

135 N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, 4, 401–404 _.

136 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, 300, 1127–1130 _.

137 M. E. Braun, C. D. Steffek, J. Kim, P. G. Rasmussen and O. M. Yaghi, *Chem. Commun.*, 2001, 2532–2533 _.

138 D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini and F. Grepioni, *Angew. Chem., Int. Ed.*, 2006, 45, 142–146 _.

139 D. Braga, L. Maini, M. Polito and F. Grepioni, *Organometallics*, 1999, 18, 2577–2579 _.

140 D. Braga, G. Cojazzi, D. Emiliani, L. Maini and F. Grepioni, *Chem. Commun.*, 2001, 2272–2273 _.

141 D. Braga, G. Cojazzi, D. Emiliani, L. Maini and F. Grepioni, *Organometallics*, 2002, 21, 1315–1318 _.

142 D. Braga, L. Maini, M. Mazzotti, K. Rubini and F. Grepioni, *CrystEngComm*, 2003, 5, 154–158 _.

143 D. Braga, L. Maini, M. Mazzotti, K. Rubini, A. Masic, R. Gobetto and F. Grepioni, *Chem. Commun.*, 2002, 2296–2297 _.

144 G. Kaupp, M. R. Naimi-Jamal, L. Maini, F. Grepioni and D. Braga, *CrystEngComm*, 2003, 5, 474–479 _.

145 D. Braga, G. Cojazzi, D. Emiliani, L. Maini, M. Polito, R. Gobetto and F. Grepioni, *CrystEngComm*, 2002, 4, 277–281 _.

146 D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Commun.*, 2002, 2960–2961 _.

147 D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem.–Eur. J.*, 2003, 9, 4362–4370 _.

148 C. C. Wilson, *Acta Crystallogr., Sect. B*, 2001, 57, 435–439 _.

149 T. Steiner, I. Majerz and C. C. Wilson, *Angew. Chem., Int. Ed.*, 2001, 40, 2651–2654 _.

150 D. Wiechert and D. Mootz, *Angew. Chem., Int. Ed.*, 1999, 38, 1974–1976 _.

151 D. Braga, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem.–Eur. J.*, 2004, 10, 3261–3269 _.

152 D. Braga, K. Rubini and L. Maini, *CrystEngComm*, 2004, 6, 236–238 _.

153 D. Braga, L. Maini, F. Grepioni, A. De Cian, O. Felix, J. Fischer and M. Wais Hosseini, *New J. Chem.*, 2000, 24, 547–553 _.

154 C. M. Zakaria, G. Ferguson, A. J. Lough and C. Glidewell, *Acta Crystallogr., Sect. B*, 2002, 58, 786–802 _.

155 F. Takusagawa and T. F. Koetzle, *Acta Crystallogr., Sect. B*, 1979, 35, 2888–2896 _.

156 G. J. Palenik, *Inorg. Chem.*, 1969, 8, 2744–2749 _.

157 S. Takamizawa, E.-i. Nakata, T. Saito, T. Akatsuka and K. Kojima, *CrystEngComm*, 2004, 6, 197–199 _.

158 S. Takamizawa, E.-i. Nakata and T. Saito, *Angew. Chem., Int. Ed.*, 2004, 43, 1368–1371 _.

159 S. Takamizawa, E.-i. Nakata and T. Saito, *CrystEngComm*, 2004, 6, 39–41 _.

160 S. Takamizawa, E.-i. Nakata, H. Yokoyama, K. Mochizuki and W. Mori, *Angew. Chem., Int. Ed.*, 2003, 42, 4331–4334 _.

161 E. Le Fur, E. Demers, T. Maris and J. D. Wuest, *Chem. Commun.*,

2003, 2966–2967 _.

162 D. Laliberte, T. Maris and J. D. Wuest, *J. Org. Chem.*, 2004, 69, 1776–1787 _.

163 O. Saied, T. Maris and J. D. Wuest, *J. Am. Chem. Soc.*, 2003, 125, 14956–14957 _.

164 D. Braga, L. Maini, G. de Sanctis, K. Rubini, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem.–Eur. J.*, 2003, 9, 5538–5548 _.

165 D. Braga, M. Curzi, M. Lusi and F. Grepioni, *CrystEngComm*, 2005, 7, 276–278 _.

166 J. W. Steed and J. L. Atwood, *Supramolecular Chemistry: A Concise Introduction*, John Wiley & Sons, Ltd., London, 2000.

167 M. Calleja, S. A. Mason, P. D. Prince, J. W. Steed and C. Wilkinson, *New J. Chem.*, 2003, 27, 28–31 _.

168 P. C. Junk, B. J. McCool, B. Moubaraki, K. S. Murray, L. Spiccia, J. D. Cashion and J. W. Steed, *J. Chem. Soc., Dalton Trans.*, 2002, 1024–1029 _.

169 J. L. Atwood, K. T. Holman and J. W. Steed, *Chem. Commun.*, 1996, 1401–1407 _.

170 J. W. Steed, *Coord. Chem. Rev.*, 2001, 215, 171–221 _.

171 J. Lipkowski, B. Baranowski and A. Lunden, *Pol. J. Chem.*, 1993, 67, 1867–1876 _.

172 S. M. Haile, *Mater. Res. Soc. Symp. Proc.*, 1999, 547, 315–326 _.

173 S. M. Haile, D. A. Boysen, C. R. I. Chisholm and R. B. Merle, *Nature*, 2001, 410, 910–913 _.

174 C. R. I. Chisholm and S. M. Haile, *Solid State Ionics*, 2000, 136–137, 229–241 _.

175 G. R. Desiraju, *CrystEngComm*, 2003, 5, 466–467 _.

176 J. D. Dunitz, *CrystEngComm*, 2003, 5, 506 _.

177 J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.

178 A. Burger, in *Topics in Pharmaceutical Science*, ed. D. Breimer and P. Speiser, Elsevier, Amsterdam, 1983, p. 347.

179 S. R. Byrn, *Solid-State Chemistry of Drugs*, Academic Press, New York, 1982.

180 M. Albrecht, M. Lutz, A. L. Spek and G. van Koten, *Nature*, 2000, 406, 970–974 _.

181 M. Albrecht, R. A. Gossage, M. Lutz, A. L. Spek and G. van Koten, *Chem.–Eur. J.*, 2000, 6, 1431–1445 _.

182 P. Anastas and J. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.

183 K. Tanaka and F. Toda, *Chem. Rev.*, 2000, 100, 1025–1074 _.

184 K. Tanaka and F. Toda, *Solvent-Free Organic Synthesis*, Wiley-VCH, London, 2003.

185 D. Bradley, *Chem. Br.*, 2002, 38, 42–45.

186 G. W. V. Cave, C. L. Raston and J. L. Scott, *Chem. Commun.*, 2001, 2159–2169 _.

187 G. Rothenberg, A. P. Downie, C. L. Raston and J. L. Scott, *J. Am. Chem. Soc.*, 2001, 123, 8701–8708 _.

188 F. Toda, *CrystEngComm*, 2002, 4, 215–222 _.

189 L. R. Nassimbeni, *Acc. Chem. Res.*, 2003, 36, 631–637 _.

2. Novel organometallic building blocks for molecular crystal engineering.

Part 4. Synthesis and characterization of mono- and bis-amido derivatives of $[Co^{III}(\eta^5-C_5H_4COOH)_2]^+$ and their utilization as ligands

a. Introduction

We are contributing,[1] together with others,[2] to expanding the library of organometallic building blocks that can be used in the engineering of organometallic supramolecular complexes[3] and networks.[4] Our interest is focused on systems that could both coordinate to metal centres in the formation of supramolecular complexes and take part in intermolecular/interionic hydrogen bonding interactions. The intent is to widen the field of organometallic solid-state chemistry towards crystal engineering,[5] the emerging discipline that aims to the design, bottom-up constructions and evaluation of molecular materials.[6]

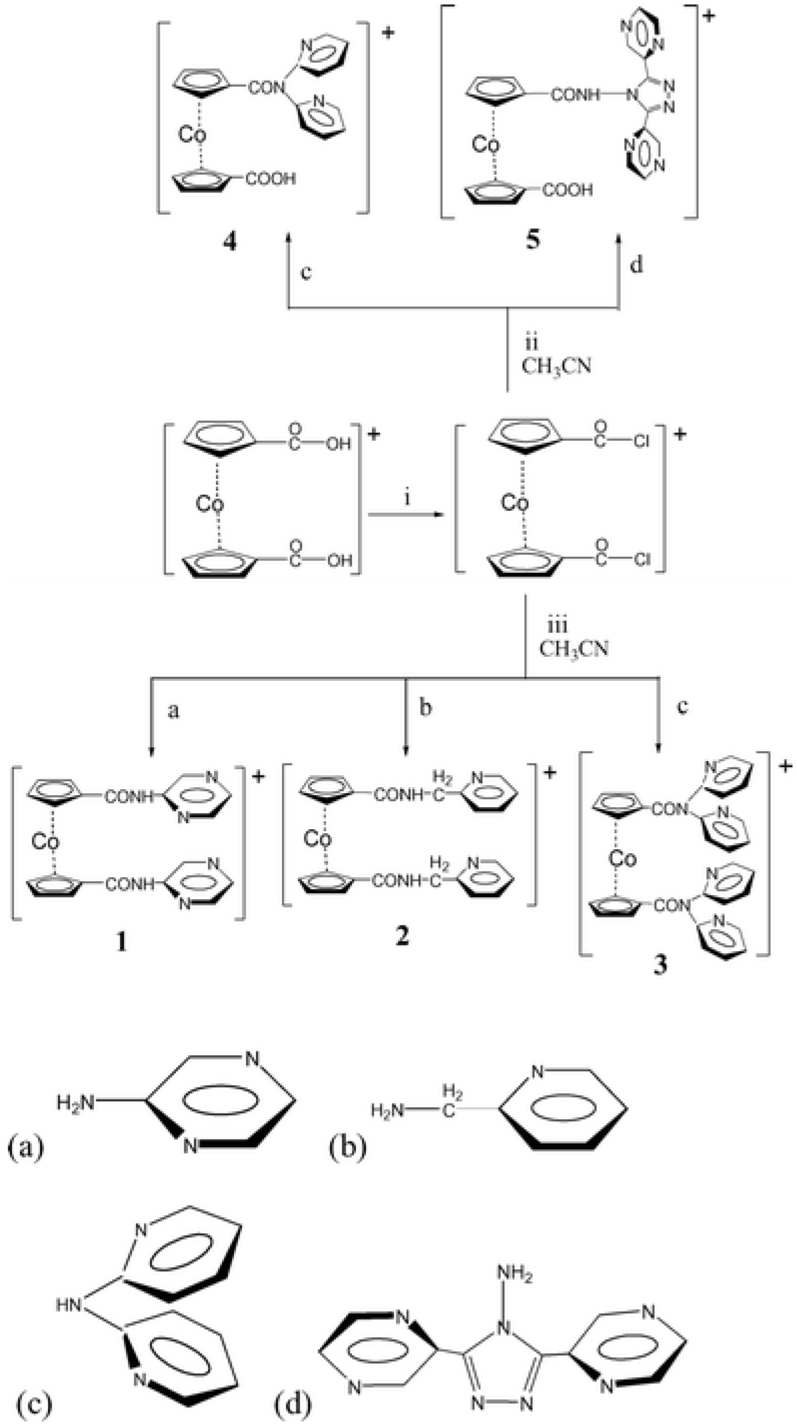
In previous studies,[7] we have investigated the participation in intermolecular interactions between organometallic and coordination complexes carrying –COOH and –OH groups showing that they form essentially the same type of hydrogen bonding interactions whether as part of organic molecules or as metal coordinated ligands. This is not surprising, as hydrogen bonds formed by such strong donor and acceptor groups are at least one order of magnitude stronger than most non-covalent interactions.[8]

In terms of crystal engineering *via* hydrogen bonds,[9] dicarboxylic acid molecules are often favoured because they can generate hydrogen bonding networks thanks to the twin hydrogen bonding function.[7–10] We have extensively exploited this feature in the utilization of the sandwich acids $[Fe(\eta^5-C_5H_4COOH)_2]$,[11] $[Co(\eta^5-C_5H_4COOH)_2]^+$,[12] and $[Cr(\eta^6-C_6H_5COOH)_2]$.[13] The cobaltocenium cationic complex $[Co(\eta^5-$

$C_5H_4COOH)_2]^+$, in particular, has proved to be extremely versatile for the selective trapping of alkali ions and for use in solid–solid and solid–gas reactions.[14]

The aim of this paper is essentially twofold. First, we expand our chemistry and crystal engineering efforts from the carboxylic groups towards a different supramolecular bonding functionality, namely the amido group, and second we explore the possibility of using the substituted amido group as a coordinating ligand in the preparation of *complexes of complexes*.

In the following we will report the synthesis, characterization and the analysis of the hydrogen bonding in the solid state of a series of complexes obtained from the carbonyl chloride $[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+$ prepared from the parent acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ (*vide infra*). Depending on the stoichiometric ratios and reaction conditions, the carbonyl chloride $[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+$ has been used (see Scheme 1) to prepare the substituted bis-amide cationic sandwich compounds 1,1′-bis(4-pyrazinaminocarbonyl)cobaltocenium, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_4H_3N_2)_2]^+$ (1), 1,1′-bis(2-aminomethylpyridylcarbonyl)cobaltocenium, $[Co^{III}(\eta^5\text{-}C_5H_4CONHCH_2C_5H_4N)_2]^+$ (2) and 1,1′-bis(di(2-pyridyl)aminocarbonyl)cobaltocenium, $[Co^{III}(\eta^5\text{-}C_5H_4CON(C_5H_4N)_2)_2]^+$ (3), as well as the mono-amido carboxyl complexes 1-di(2-pyridyl)aminocarbonyl)-1′-(carboxylic acid)cobaltocenium, $[Co^{III}(\eta^5\text{-}C_5H_4CON(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^+$ (4) and 1-(4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazylcarbonyl)-1′-(carboxylic acid) cobaltocenium, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^+$ (5), all isolated and crystallized in the form of hexafluorophosphate $[PF_6]^-$ salts.



Scheme 1 *Reagents and conditions: (i) $SOCl_2$;(ii) 1 :1 stoichiometric ratio; (iii) 2 :1 stoichiometric ratio.*

The potential of these cationic sandwiches as ligands in the formation of supramolecular adducts, whether coordination networks or complexes of complexes, has been demonstrated with the preparation of a supramolecular adduct of the mono-amido carboxyl complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^+$ (5). The reaction between 5 and $Cd(NO_3)_2$ has yielded the hexa-cationic mixed-metal complex $[Cd(NO_3)_2\{Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)(C_5H_4NH))(\eta^5\text{-}C_5H_4COOH)\}_2]^{6+}$ (6). We have analysed both ligand–Cd coordination and supramolecular bonding arising from the presence of the hydrogen bonding donor/acceptor –COOH group.

Finally, we have also taken the opportunity of this report to describe the structure of the carbonyl chloride cation $[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+$ (7) crystallized as its tetrachloro cobaltate salt. To the best of the author's knowledge there is only one example of a structurally characterized organometallic carbonyl chloride, namely the sandwich complex 4-ferrocenylcarbonyl-4′-chlorocarbonylbiphenyl,[15] while several organic compounds are known.

b. Experimental

Synthesis of 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate[16]

1.5 g of 1,1'-di(carboxylic acid)cobaltocenium hexafluorophosphate were dissolved in an excess of $SOCl_2$, the solution was stirring for 24 h under argon atmosphere. The product was separated by filtration (1.25 g, yield 75%) and stored under argon atmosphere.

Synthesis of 1,1'-bis(4-pyrazinaminocarbonyl)cobaltocenium hexafluorophosphate, 1[PF_6]

To a solution of 4-aminopyrazine (0.5 g, 5.2 mmol) and triethylamine (0.53 g, 5.3 mmol) in dry CH_3CN (60 mL) a solution of 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate (1.2 g, 2.6 mmol) in CH_3CN (60 mL) was added dropwise under nitrogen at room temperature. On addition, the colour of the solution changed from colourless to green and a yellow precipitate formed. The mixture was allowed to stir for 12 h. The crude product, a yellow solid, was filtered off (1.1 g, 1.9 mmol; yield 50%) and subsequently dissolved in hot water; an excess of NH_4PF_6 was then added. After cooling, a fine bright yellow powder was recovered by filtration and dried. Calc.: H, 2.80; C, 41.68; N, 14,58. Found: H, 2.80; C, 41.56; N, 14,58%)

Synthesis of 1,1'-bis(2-aminomethylpyridylcarbonyl)cobaltocenium hexafluorophosphate, 2[PF_6]

To a solution of 2-aminomethylpyridine (0.56 g, 5.2 mmol) and triethylamine (0.53 g, 5.3 mmol) in dry CH_3CN (60 mL) a solution of 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate (1.2 g, 2.6 mmol) in CH_3CN (60 mL) was added dropwise under nitrogen at room temperature. On addition, the colour of the solution changed from colourless to green and a yellow precipitate formed. The mixture was allowed to stir for 12 h, and the yellow solid was isolated by filtration as the crude product (1.1 g, 1.9 mmol; yield 80%). The crude product was dissolved in hot water and an excess of NH_4PF_6 was added. On cooling, the pure product formed as a fine bright yellow powder that was isolated by filtration and dried. Calc: H, 3.68; C, 47.85; N, 9.30. Found: H, 3.67; C, 47.70; N: 9.29%.

Synthesis of 1,1'-bis(di(2-pyridyl)aminocarbonyl)cobaltocenium, 3[PF_6]

To a solution of di(2-pyridyl)amine (0.9 g, 5.2 mmol) and triethylamine (0.53 g, 5.3 mmol) in dry CH_3CN (60 mL) a solution of 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate (1.2 g, 2.6 mmol) in CH_3CN (60 mL) was added dropwise under nitrogen. On addition, the colour of the solution changed from colourless to green and a yellow precipitate formed. The mixture was allowed to stir for 12 h, and the yellow solid was isolated by filtration as the crude product (1.1 g, 1.5 mmol; yield. 74%). The crude product was dissolved in hot water and an excess of NH_4PF_6 was added. On cooling, the pure product formed as a fine bright yellow powder that was isolated by filtration and dried. Calc: H, 3.32; C, 52.76; N, 11.54. Found: H, 3.32; C, 52.90; N, 11.51%.

Synthesis of 1-di(2-pyridyl)aminocarbonyl)-1'-(carboxylic acid)cobaltocenium hexafluorophosphate, 4[PF_6]

A solution of 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate (1.2 g, 2.6 mmol) in dry CH_3CN (60 mL) was prepared in a bottom flask with two necks and stirred under nitrogen at room temperature. To this a solution of di(2-pyridyl)amine (0.22 g, 1.3 mmol) and triethylamine (0.13 g, 1.3 mmol) in CH_3CN (60 mL) was added dropwise under nitrogen. On addition a precipitate formed. The mixture was allowed to stir for 24 h and was then filtered. Removal of solvent from the solution yielded a yellow powder, which was dissolved in hot water; an excess of NH_4PF_6 was added. On cooling, the pure product was recovered as a fine bright yellow powder that was filtered and dried. Elemental analysis calc: H, 2.98; C, 45.93; N, 7.30%. Found: H, 2.98; C, 45.80; N, 7.29%.

Synthesis of 1-(4-amino-3,5-di-2-pyridyl-4H-1,2,4-triazylcarbonyl)-1'-(carboxylic acid)cobaltocenium hexafluorophosphate, 5[PF$_6$]

A solution of 1,1'-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate (1.2 g, 2.6 mmol) in dry CH_3CN (60 cm^3) was made up in bottom flask with two necks and stirred under nitrogen at room temperature. To this was added a solution of 4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole (0.31 g, 1.3 mmol) and triethylamine (0.13 g, 1.3 mmol) in CH_3CN (60 cm^3) dropwise and under nitrogen. On addition a precipitate formed. The mixture was allowed to stir for 24 h and was then filtered. Removal of solvent from the solution yielded a yellow powder, which was dissolved in hot water; an excess of NH_4PF_6 was added. On cooling, the pure product was recovered as a fine bright yellow powder that was filtered off and dried. Calc: H, 2.82; C, 44.88; N, 13.08. Found: H, 2.82; C, 44.99; N, 13.12%.

Synthesis of $[Cd(NO_3)_2\{Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)(C_5H_4NH))(\eta^5\text{-}C_5H_4COOH)\}_2]^{6+}2[PF_6]^{-}2[CO_3]^{2-}\cdot H_2O$, $6[PF_6]_2[CO_3]_2\cdot 2H_2O$

0.22 mmol of $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^{+}[PF_6]^{-}$ and 0.11 mmol of $Cd(NO_3)_2$ were dissolved in 5 mL of water. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of the solvent. Calc: H, 2.10; C, 29.64; N, 9.37. Found: H, 2.10; C, 29.74; N, 9.39%.

Synthesis of 2$[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+[CoCl_4]^{2-}$, $7_2[CoCl_4]$

$7_2[CoCl_4]$ was obtained as well shaped large green crystals from the mother-solution of the $[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+[PF_6]^-$ reaction, left on standing after filtration. The $[CoCl_4]^{2-}$ counterion is likely formed by decomposition of the sandwich complex. Calc: H, 0.82; C: 14.78. Found: H, 0.82; C: 14.74%.

c. Crystal structure determination

Crystal data for all compounds were collected on a Bruker ApexII CCD diffractometer. Crystal data and details of measurements are summarized in Table 1. Common to all compounds: Mo-Kα radiation, λ= 0.71073 Å, monochromator graphite. The computer program SHELX97[17a] was used for structure solution and refinement based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were added in calculated positions. The $[PF_6]^-$ anion in $1[PF_6]$ is disordered around one of the anion four-fold axes; the occupancy ratio was refined to 70 :30. One of the chlorocarbonyl C–O–Cl ligands in 7 is disordered over two positions, which were refined with an occupancy ratio of 80 :20. SCHAKAL99[17b] was used for the graphical representation of the results. Hydrogen-bonding interactions were evaluated by the program PLATON.[17c]

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

	1[PF$_6$]	2[PF$_6$]	3[PF$_6$]	4[PF$_6$]	5[PF$_6$]
Formula	$C_{20}H_{16}Co_1F_6N_6O_2P$	$C_{24}H_{22}CoF_6N_4O_2P$	$C_{32}H_{24}CoF_6N_6O_2P$	$C_{22}H_{17}CoF_6N_3O_3P$	$C_{24}H_{20}CoF_6N_6O_4P$
M	576.29	602.36	728.48	575.29	660.36
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	8.2145(2)	7.232(2)	11.186(3)	10.034(2)	7.735(2)
b/Å	10.0998(3)	12.581(3)	12.622(3)	24.647(5)	13.136(4)
c/Å	25.6180(7)	13.607(7)	13.089(4)	9.579(4)	13.535(4)
α/°	90	88.91(3)	64.82(2)	90	105.762(1)
β/°	98.322(1)	79.74(3)	67.27(3)	108.70(3)	90.15(1)
γ/°	90	89.46(2)	80.85(2)	90	101.52(10)
V/Å^3	2103.0(1)	1218.0(8)	1542.5(7)	2244(1)	1294.61(6)
Z	4	2	2	4	2
T/K	293	293	293	293	293
F(000)	1160	612	740	1160	668
μ(Mo-Kα)/mm^{-1}	0.980	0.848	0.686	0.918	0.813
Measd. reflns.	17330	5788	5668	4859	10464
Unique reflns.	5058	5567	5410	2513	4557
Parameters	351	352	433	344	366
GOF on F^2	0.996	0.985	0.983	0.725	0.985
$R1$ (on F [$I > 2\sigma(I)$])	0.0650	0.0670	0.0676	0.0367	0.0498
$wR2$ (on F^2, all data)	0.1940	0.2134	0.1650	0.1159	0.1454

	$6[PF_6]_2[CO_3]_2\cdot2H_2O$	$7_2[CoCl_4]$
Formula	$C_{50}H_{42}CdCo_2F_{12}N_{14}O_{20}P_2$	$C_{24}H_{16}Cl_8Co_3O_4$
M	1679.18	828.76
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$I4_1/a$
a/Å	8.715(3)	13.855(1)
b/Å	12.051(6)	13.855(1)
c/Å	15.228(6)	29.570(9)
α/°	81.61(4)	90
β/°	73.61(3)	90
γ/°	88.83(4)	90
V/Å^3	1517.5(11)	5676(2)
Z	1	8
T/K	293	293
$F(000)$	840	3272
μ(Mo-Kα)/mm^{-1}	1.065	2.519
Measd. reflns.	5543	2702
Unique reflns.	5326	2482
Parameters	447	172
GOF on F^2	1.010	1.043
$R1$ (on F $[I > 2\sigma(I)]$)	0.0470	0.0442
$wR2$ (on F^2, all data)	0.1386	0.1273

d. Results and discussion

With reference to Scheme 1, we shall first describe the solid-state structures of the bis-amido complexes $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_4H_3N_2)_2]^+$ (1), $[Co^{III}(\eta^5\text{-}C_5H_4CONHCH_2C_5H_4N)_2]^+$ (2) and $[Co^{III}(\eta^5\text{-}C_5H_4CON(C_5H_4N)_2)_2]^+[PF_6]^-$ (3[PF_6]). All complexes have been crystallized as their hexafluorophosphate salts and characterized by single-crystal X-ray diffraction.

In crystals of the salt $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_4H_3N_2)_2]^+[PF_6]^-$, 1[$PF_6$], the pyrazinaminocarbonyl groups are eclipsed with superimposition of both rings and (C=O)–NH groups (Fig. 1(a)). The eclipsed conformation might appear unfavored in view of the steric requirements of the ligands. However, the same eclipsed conformation has been observed in the crystal of the congener $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$,[1] and also in the corresponding ferrocenyl derivatives $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$.[11]

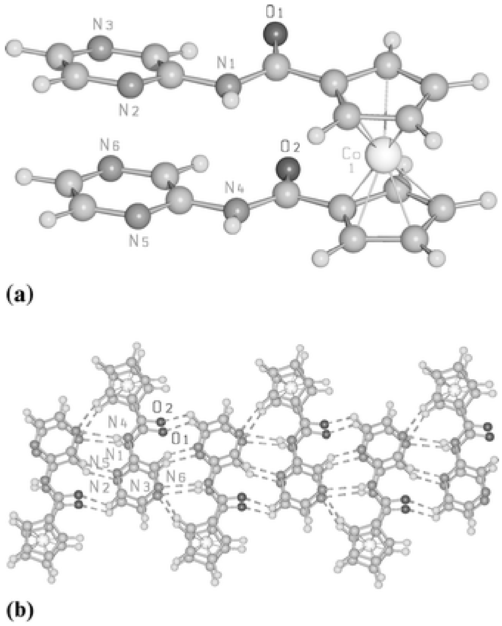


Fig. 1 *The structure of the complex cation* $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_4H_3N_2)_2]^+$*(1). (a) A view of the molecular structure of 1 together with the labelling scheme; note how the pyrazinamino-carbonyl groups are slightly tilted with respect to the cyclopentadienyl ligands. (b) The packing arrangement showing the overlap of the pyrazinamino-carbonyl groups and the network of N–H···N, C–H···N and C–H···O interactions between neighbouring organometallic cations.*

Fig. 1(a) shows the molecular conformation and the atomic labelling scheme. The packing arrangement of complex 1 is shown in Fig. 1(b). It is noteworthy that the pyrazinamino-carbonyl groups are interdigitated, allowing for the formation of a network of long N–H···N, C–H···N and C–H···O contacts between neighbouring organometallic cations.

In compound $[Co^{III}(\eta^5\text{-}C_5H_4CONHCH_2C_5H_4N)_2]^+$ (2) the aminomethylpyridyl groups linked to the cyclopentadienyl ligands have an additional degree of conformational freedom, as well as additional steric requirements, with respect to the pyrazino and pyridino substituents. This is reflected in the structure of the cation (see Fig. 2(a)), with the pyridyl moieties tilted with respect to the amido C(O)–NH unit. Fig. 2(b) shows how the packing arrangement of cations and $[PF_6]^-$ anions in the crystal.

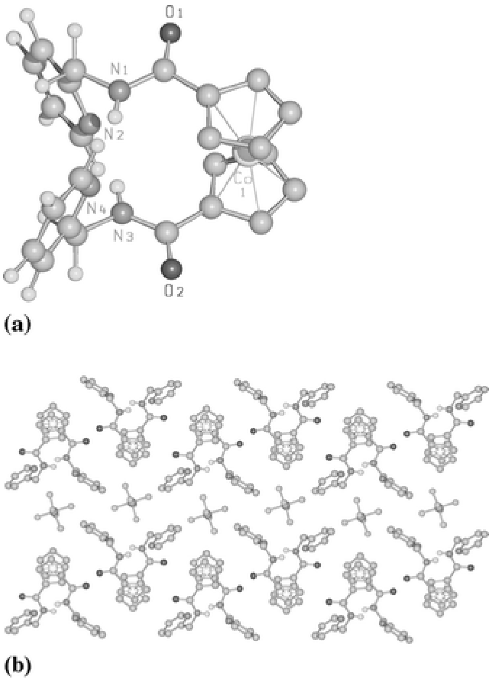


Fig. 2 *The structure of the complex cation* $[Co^{III}(\eta^5\text{-}C_5H_4CONHCH_2C_5H_4N)_2]^+$*(2). (a) A view of the molecular structure together with the labelling scheme; note how the pyridyl moieties are tilted with respect to the amido C(O)–NH unit and to the cyclopentadienyl ligands. (b) A view of the packing down the a-axis* (H_{CH} *atoms not shown for clarity).*

In compound $[Co^{III}(\eta^5-C_5H_4CON(C_5H_4N)_2)_2]^+$ (3), the bulk of the dipyridylamino moieties forces the two ligands in *transoid* conformation. This arrangement is not generally favoured in the crystals of substituted cobaltocenium complexes. In view of the pyridyl nitrogen atoms, this molecular cation is a good candidate for *divergent* coordination, *i.e.* for the formation of extended coordination networks. The structure of the cation, together with the atomic labelling, is shown in Fig. 3(a), while Fig. 3(b) shows a view of the packing arrangement of the cations. It is worth noting that there is a number of C–H···N/O interactions involving the cyclopentadienyl C–H groups, the dipyridylamino N atoms and the amido O atoms of neighbouring organometallic cations [C(1)···N(1) 3.24(1), C(11)··· N(3) 3.25(1), C(17)···O(2) 3.19(1) Å].

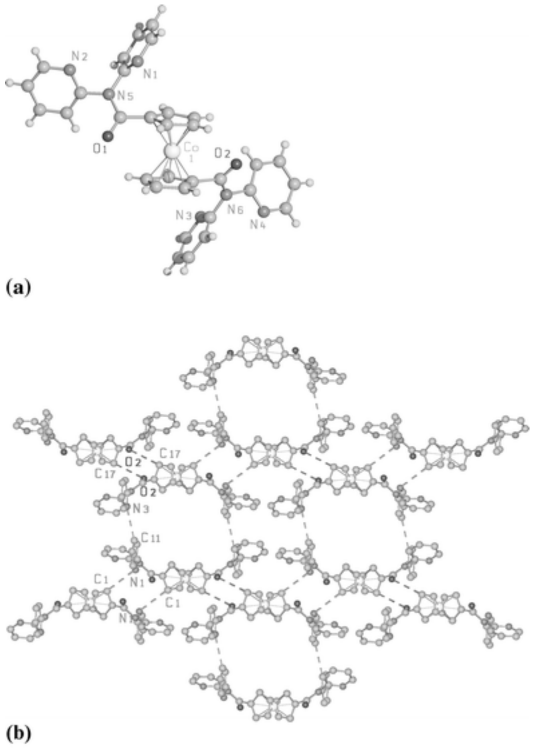


Fig. 3 *(a) The structure of the complex cation* $[Co^{III}(\eta^5\text{-}C_5H_4CON(C_5H_4N)_2)_2]^+$*(3), together with the labelling scheme; note how the dipyridylamino moieties forces the two ligands in transoid conformation with respect to the cyclopentadienyl ligands. (b) A view of the packing arrangement in crystalline* $3[PF_6]$*, showing the C–H···N/O interactions between neighbouring organometallic cations [C(1)···N(1) 3.24(1), C(11)··· N(3) 3.25(1), C(17)···O(2) 3.19(1) Å](*H_{CH} *atoms not shown for clarity).*

With reference to Scheme 1, we shall now describe the structures and packings of the amido-carboxyl complexes $[Co^{III}(\eta^5\text{-}C_5H_4CON(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^+$ (4) and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^+$ (5), which "retain" one carboxylic unit from the parent molecule $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$.

In the complex cation [$Co^{III}(\eta^5$-$C_5H_4CON(C_5H_4N)_2)(\eta^5$-$C_5H_4COOH)]^+$ (4) the di(2-pyridyl)aminocarbonyl ligand is tilted with respect to the cyclopentadienyl plane (see Fig. 4(a)), thus adopting a conformation that closely resembles the one discussed above for 3. Far more interesting is the behaviour of the carboxylic group. As shown in Fig. 4(b), the –COOH unit links to a pyridyl nitrogen atom of a neighbouring cation, forming an hydrogen bonded dimer with an O···N distance of 2.780(7) Å. It is interesting to speculate on the possible existence of a supramolecular isomer of this crystal, as it is conceivable that the dimer formation is replaced by an extended one-dimensional network based on O–H···N interactions between consecutive cations in a row. As a matter of fact, the extended hydrogen bonded network is the motif present in the hydrated $[PF_6]^-$ salt of cation [$Co^{III}(\eta^5$-$C_5H_4CONHC_2N_3(C_5H_4N)_2)(\eta^5$-$C_5H_4COOH)]^+$ (5). The molecular structure of compound 5 is shown in Fig. 5(a) together with the labelling scheme. The bulky 1-(4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazylcarbonyl ligand is placed in a *transoid* conformation with respect to the –COOH group, which is then able to form an inter-cationic O–H···N hydrogen bond (see Fig. 5(b)), which is appreciably shorter [O(2)···N(5) 2.650(4) Å] than the analogous interaction in 4 [2.780(7) Å]. Besides, the presence of water molecules provides hydrogen bonds between cationic rows by bridging together the amido hydrogen atom [N(1)···O(100) 2.803(4) Å] and the triazyl nitrogen [N(3)···O(100) 2.874(4) Å].

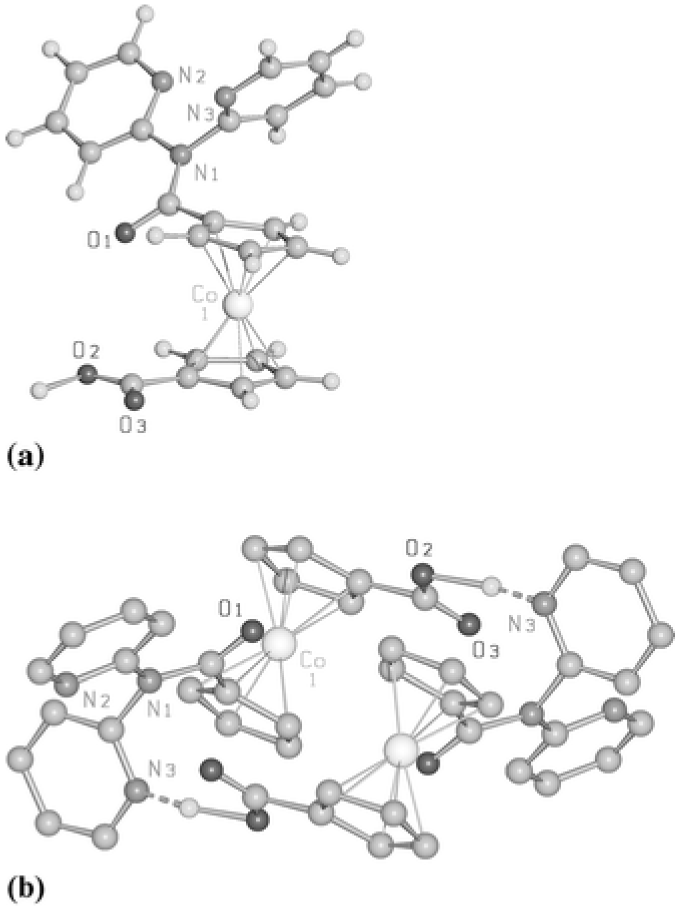


Fig. 4 *The structure of the complex cation* $[Co^{III}(\eta^5\text{-}C_5H_4CON(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^+$*(4). (a) A view of the complex together with the labelling scheme; note how the dipyridylaminocarbonyl group is slightly tilted with respect to the cyclopentadienyl ligand, similarly to what is observed in complex 3. (b) The –COOH unit links to a pyridyl nitrogen atom of another cation, forming a hydrogen bonded dimer [O(2)··· N(3) 2.780(7) Å](*H_{CH} *atoms not shown for clarity).*

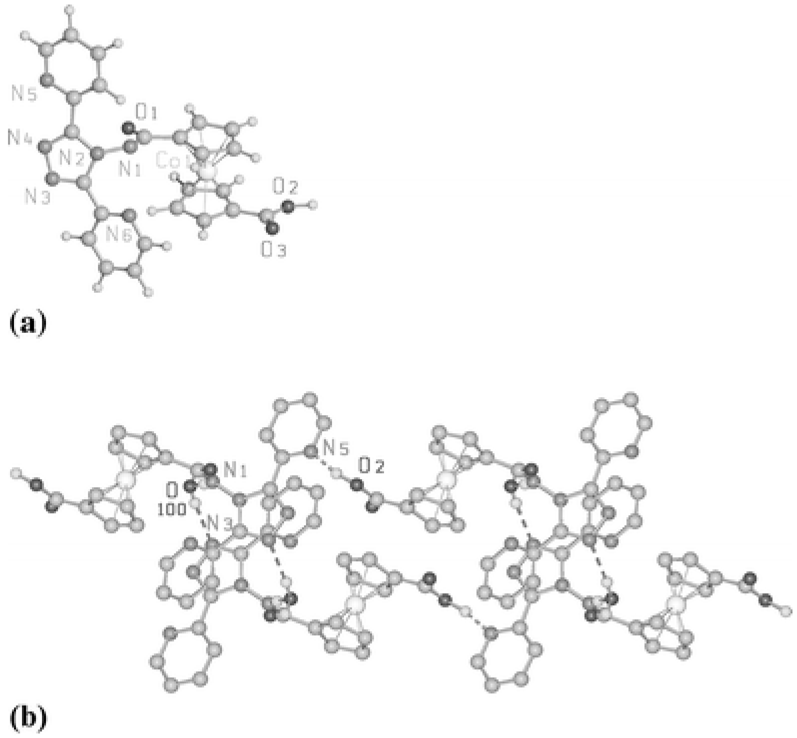


Fig. 5 *The structure of the complex cation* $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)_2)(\eta^5\text{-}C_5H_4COOH)]^+$*(5). (a) A view of the complex together with the labelling scheme; note how the 1-(4-amino-3,5-di-2-pyridyl-4H-1,2,4-triazylcarbonyl ligand is transoid with respect to the –COOH group. (b) The inter-cationic O–H···N hydrogen bond [O(2)···N(5) 2.650(4) Å] links the cations in one-dimensional hydrogen bonded networks. The water molecules provide hydrogen bonds between the cationic rows [N(1)···O(100) 2.803(4), N(3)···O(100) 2.874(4), O(1)···O(100) 3.116(3) Å]*(H_{CH} *atoms not shown for clarity).*

This latter amido-carboxyl cation has been used as a ligand for the preparation of a *complex of complexes*. The reaction between 5 and $Cd(NO_3)_2$ has yielded the supramolecular cation $[Cd(NO_3)_2\{Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)(C_5H_4NH)(\eta^5\text{-}C_5H_4COOH)\}_2]^{6+}$ (6). The structure of the cation is shown in Fig. 6(a). It can be seen that two complexes 5 coordinate the cadmium atom as bidentate ligands, while the two nitrate anions fill in the octahedral coordination above and below the square plane defined by the four N···Cd interactions. Chelation takes place by means of one triazyl nitrogen and one of the pyridyl nitrogen atoms. Interestingly, rather than "turning around" and adopting a transoid conformation with respect to the sterically crowded Cd-centres, the –COOH groups adopt an eclipsed conformation with respect to the C(O)–NH amido group. Stabilization to what may appear an unfavourable stereogeometry seems to derive from the complex network of hydrogen bonding interactions that involve the –COOH groups and the water molecules, as well as the nitrate and carbonate anions [O(3)···O(100) 2.599(8), N(1)···O(9) 2.773(8), N(3)···O(7) 2.752(7), O(100)···O(9) 2.848(8), O(100)···O(4) 3.017(8), O(100)···O(5) 3.006(10) Å]. It is noteworthy that the shortest of such bonds is between the carboxylic oxygen and the water molecule.

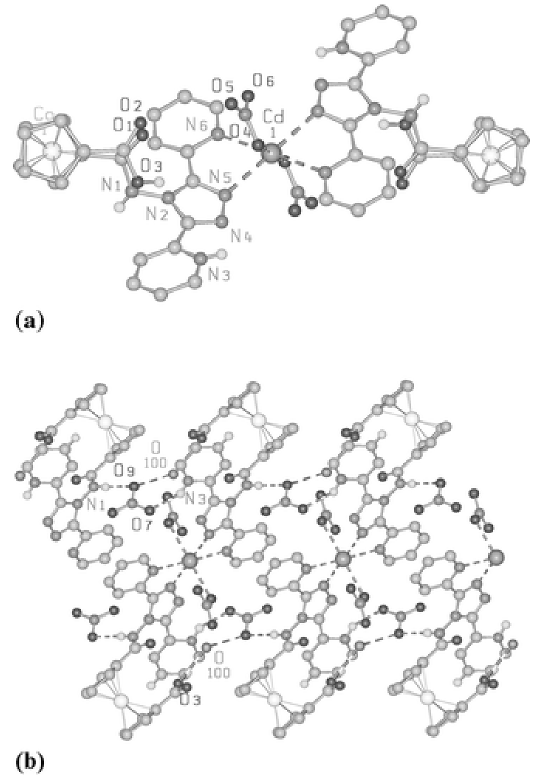


Fig. 6 *(a) The structure of the supramolecular cation* $[Cd(NO_3)_2\{Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)(C_5H_4NH)(\eta^5\text{-}C_5H_4COOH)\}_2]^{6+}$*(6), together with the labelling scheme. (b) A view of the packing arrangement showing the complex pattern of hydrogen bonding interactions involving the –COOH groups and the water molecules as well as the nitrate and carbonate anions. Relevant hydrogen bonding interactions (Å) are O(3)⋯O(100) 2.599(8), N(1)⋯O(9) 2.773(8), N(3)⋯O(7) 2.752(7), O(100)⋯O(9) 2.848(8), O(100)⋯O(4) 3.017(8), O(100)⋯O(5) 3.006(10)* (H_{CH} *atoms not shown for clarity).*

There are not many examples of structurally characterized carbonyl chlorides, and only one, to the best of the author's knowledge, of an organometallic sandwich, namely the ferrocenyl complex 4-ferrocenylcarbonyl-4′-chlorocarbonylbiphenyl, where the C(=O)Cl group, however, is linked to a biphenyl "spacer" bound to the cyclopentadienyl ligand.[15] Furthermore, compound $[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+$, 7, is the only example available of a cationic carbonyl chloride. Crystals of 7 have been obtained, rather serendipitously, from the mother-solution wherefrom the hexafluorophosphate salt used as precursor in all subsequent reactions had been precipitated (see Scheme 1 and the Experimental section). While single crystals of the $[PF_6]^-$ salt of 7 could not be obtained, the salt $\{[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+\}_2[CoCl_4]^{2-}$ crystallized easily in the form of deep green large crystals, the counterion $[CoCl_4]^{2-}$ being very likely formed from decomposition of the sandwich compound. Fig. 7(a) shows the structure of the cationic complex; it can be seen that the two carbonyl chloride substituents are in eclipsed conformation. Fig. 7(b) shows the packing arrangement of the cations in the crystal; it is worth noting that the cations are arranged in rows parallel to the *a*-axis, in such a way that the Cl atoms of the chlorocarbonyl ligands are grouped in "clusters", with Cl···Cl interactions below 3.800 Å. The preferential Cl···Cl clustering might be a reason for the eclipsed conformation of the chlorocarbonyl groups in the complex; steric considerations alone would suggest a transoid arrangement.

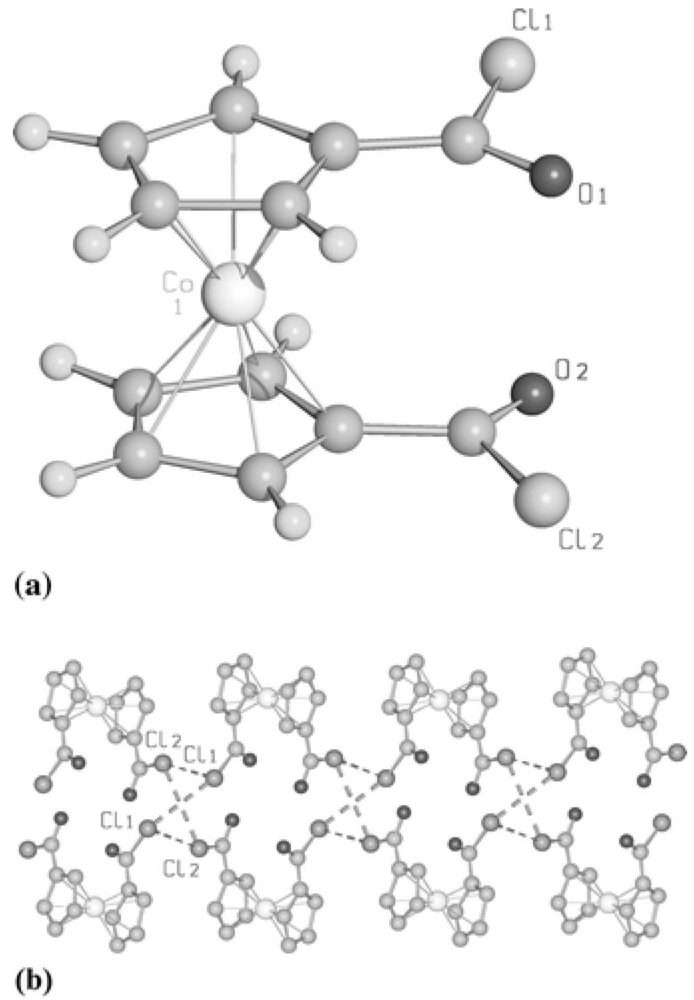
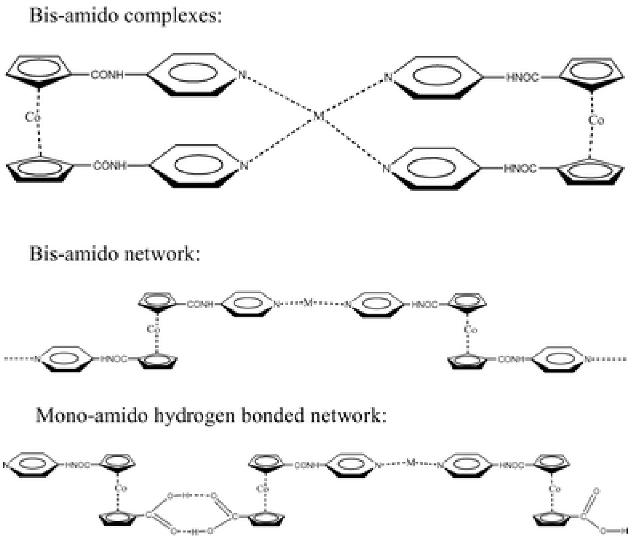


Fig. 7 *(a) The structure of the complex cation* $[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+$*(7)(only the major image of disorder is shown (see experimental). (b) In the crystal the cations are arranged in rows parallel to the a-axis; the Cl atoms of the chlorocarbonyl ligands are grouped in " clusters", with Cl···Cl interactions below 3.800 Å(*H_{CH} *atoms not shown for clarity).*

e. Conclusions

In this paper we have reported the synthesis and crystallographic characterization of a series of novel bis-amido and mono-amido-carboxyl complexes based on the cationic cobaltocenium sandwich core $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+$. The substituents on the amido groups have been chosen so as to contain basic N-atoms potentially available for coordination towards metal centers[4] and for hydrogen bonding with suitable donors. All compounds have been obtained *via* the bis-carbonyl-chloride $[Co^{III}(\eta^5\text{-}C_5H_4COCl)_2]^+$ 7, which is a unique example of structurally characterized organometallic cationic carbonyl chloride. The basic idea is to use the bis-amido complexes either as *spacers* in the construction of mixed-metal organometallic coordination networks or to prepare mixed-metal complexes of complexes as schematised in Scheme 2. In this latter case the formation of metalla-macrocycles of the type obtained with substituted ferrocenyl bipyridine complexes ought also to be considered.[1c,d]



Scheme 2.

In the case of the mono-amide $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)(C_5H_4NH)(\eta^5\text{-}C_5H_4COOH)]^+$ we have indeed shown that formation of a *complex of complexes* is possible, even though the cationic nature of the ligand generates ionic charge "build up". In fact the resulting complex is hexacationic, $[Cd(NO_3)_2\{Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)(C_5H_4NH)(\eta^5\text{-}C_5H_4COOH)\}_2]^{6+}$. However, the presence of two carboxylic groups on the complex might allow partial charge compensation if two carboxylic protons can be removed from the carboxylic groups, with formation of the hypothetical tetra-cationic zwitterionic species $[Cd(NO_3)_2\{Co^{III}(\eta^5\text{-}C_5H_4CONHC_2N_3(C_5H_4N)(C_5H_4NH)(\eta^5\text{-}C_5H_4COO)\}_2]^{4+}$.

Work is in progress to fully explore the potentials of these ligands as supramolecular building blocks for coordination chemistry applications and crystal engineering.

References

1 (*a*) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, L. Sturba and F. Grepioni, *Organometallics*, 2003, 22, 2142 _; (*b*) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, D. M. Proserpio and F. Grepioni, *Chem. Commun.*, 2002, 1080 _; (*c*) D. Braga, M. Polito, D. D'Addario, E. Tagliavini, D. M. Proserpio, F. Grepioni and J. W. Steed, *Organometallics*, 2003, 22, 453; (*d*) D. Braga, M. Polito and F. Grepioni, *Cryst. Growth Des.*, 2004, 4, 769 _; (*e*) D. Braga, S. L. Giaffreda, M. Polito and F. Grepioni, *Eur. J. Inorg. Chem.*, 2005, 2737 _.

2 L. Brammer, J. C. Mareque Rivas, R. Atencio, S. Fang and F. C. Pigge, *J. Chem. Soc., Dalton Trans.*, 2000, 3855 _; C. M. Zakaria, G. Ferguson, A. J. Lough and C. Glidewell, *Acta Crystallogr., Sect. B*, 2002, 58, 786 _; C. Elschenbroich, F. Lu and K. Harms, *Organometallics*, 2002, 21, 5152 _; C. Elschenbroich, O. Schiemann, O. Burghaus and K. Harms, *J. Am. Chem. Soc.*, 1997, 119, 7452 _; M. C. Tse, K. K. Cheung, M. C. W. Chan and C. M. Che, *Chem. Commun.*, 1998, 21, 2295; Y. J. Kim and J. G. Verkade, *Inorg. Chem.*, 2003, 42, 4262 _; J. C. M. Rivas and L. Brammer, *Coord. Chem. Rev.*, 1999, 183, 43 _; M. Oh, G. B. Carpenter and D. A. Sweigart, *Organometallics*, 2003, 22, 2364 _; M. Oh, G. B. Carpenter and D. A. Sweigart, *Angew. Chem., Int. Ed. Engl.*, 2002, 41, 3650 _; M. Oh, G. B. Carpenter and D. A. Sweigart, *Chem. Commun.*, 2002, 18, 2168; M. W. Hosseini, *Acc. Chem. Res.*, 2005, 38, 313 _.

3 I. Haiduc and F. T. Edelmann, *Supramolecular Organometallic Chemistry*, Wiley-VCH, New York, 1999; J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley & Sons, New York, 2000.

4 M. Eddaouddi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, 34, 319 _; S. R. Batten, *CrystEngComm*, 2001, 3, 67 _; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schroder, *Coord. Chem. Rev.*, 1999, 183, 117 _; L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, 246, 247 _; L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2003, 5, 269 _; M. Oh, G. B. Carpenter and D. A. Sweigart, *Acc. Chem. Res.*, 2004, 37, 1 _; K. T. Holman, A. M. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, 34, 107 _; O. M. Yaghi, G. Li and H. Li, *Nature*, 2000, 37, 703; S.-I. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, 39, 2082 _; M. Fujita, *Acc. Chem. Res*, 1999, 32, 53 _; O. R. Evans, R. G. Xiong, Z. Y. Wang, G. K. Wong and W. B. Lin, *Angew. Chem., Int. Ed.*, 1999, 38, 536 _; O. R. Evans and W. B. Lin, *Acc. Chem. Res.*, 2002, 35, 511 _; P. J. Steel, *Acc. Chem. Res.*, 2005, 38, 243 _.

5 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; *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 _; C. B. Aakeröy and A. S. Borovik, *Coord. Chem. Rev.*, 1999, 183, 1 _; D. Braga, *Chem. Commun.*, 2003, 1258 _; M. W. Hosseini, *CrystEngComm*, 2004, 6, 318 _.

6 *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry*, ed. G. R. Desiraju, Wiley, Chichester, UK, 1996, vol. 2. See, for a general entry in the area of inorganic crystal engineering, *J. Chem. Soc., Dalton Trans.*, 2000, 3705 _ (the whole issue).

7 D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, 33, 601 _; D. Braga and F. Grepioni, *Coord. Chem. Rev.*, 1999, 183, 19 _; D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, 98, 1375 _.

8 G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991; L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem., Int. Ed.*, 2001, 40, 2382 _; G. Gilli and P. Gilli, *J. Mol. Struct.*, 2000, 552, 1 _; T. Steiner, *Angew. Chem., Int. Ed.*, 2002, 41, 48 _; G. R. Desiraju, *Acc. Chem. Res.*, 2000, 35.

9 See, for example: C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397 _; A. M. Beatty, *CrystEngComm*, 2001, 3, 243 _; K. Biradha, *CrystEngComm.*, 2003, 5, 374 _; H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, 236, 91 _; A. M. Beatty, *Coord. Chem. Rev.*, 2003, 246, 131 _; A. D. Burrows, *Struct. Bonding (Berlin)*, 2004, 108, 1; D. Braga, L. Maini, M. Polito and F. Grepioni, *Struct. Bonding (Berlin)*, 2004, 111, 1 _; P. Hubberstey and U. Suksangpanya, *Struct. Bonding (Berlin)*, 2004, 111, 33; R. Vilar, *Struct. Bonding (Berlin)*, 2004, 111, 85 _; M. J. Hardie, *Struct. Bonding (Berlin)*, 2004, 111, 139 _; L. Brammer, *Dalton Trans.*, 2003, 16, 3145.

10 D. Braga, L. Maini, M. Polito, M. Rossini and F. Grepioni, *Chem. Eur. J.*, 2000, 6, 4227 _; D. Braga and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 1999, 1 _; D. Braga, L. Maini, L. Prodi, A. Caneschi, R. Sessoli and F. Grepioni, *Chem. Eur. J.*, 2000, 6, 1310 _; D. Braga, L. Maini, M. Polito and F. Grepioni, *Organometallics*, 1999, 18, 2577 _.

11 D. Braga, L. Maini, F. Grepioni, A. DeCian, O. Felix, J. Fisher and M. W. Hosseini, *New. J. Chem.*, 2000, 24, 547 _; D. Braga, M. Polito,

D. D'Addario, E. Tagliavini, D. M. Proserpio, F. Grepioni and J. W. Steed, *Organometallics*, 2003, 22, 4532 _.

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

13 D. Braga, L. Maini, F. Grepioni, C. Elschenbroich, F. Paganelli and O. Schiemann, *Organometallics*, 2001, 20, 1875 _.

14 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 _; D. Braga, L. Maini, M. Mazzotti, K. Rubini, A. Masic, R. Gobetto and F. Grepioni, *Chem. Commun.*, 2002, 2296 _; D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Eur. J.*, 2003, 9, 4362 _; D. Braga and F. Grepioni, *Angew. Chem., Int. Ed.*, 2004, 43, 4002 _.

15 A. Z. Ahmed, G. Ferguson and C. Glidewell, *J. Organomet. Chem.*, 1999, 585, 331 _.

16 P. Beer and S. E. Stokes, *Polyhedron*, 1995, 14, 873 _.

17 (*a*) G. M. Sheldrick, *SHELX97, Program for Crystal Structure Determination*, 1997, University of Göttingen, Göttingen, Germany; (*b*) E. Keller, *SCHAKAL99, Graphical Representation of Molecular Models*, University of Freiburg, Germany, 1999; (*c*) A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, 46, C31.

3. Design, Preparation and Characterization of the Adducts of the Bis-Amido Cobalticinium Complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][PF_6]$ with Fumaric and Maleic Acids

a. Introduction

In the context of crystal engineering[1] organometallic molecules and ions are beginning to attract an increasing interest because organometallic molecules and molecular ions combine the supramolecular bonding capacity of organic molecules with the presence of metal atoms. The number of possible combinations of the valence, spin and charge states of the metals atoms with the coordination geometries and supramolecular bonding capacity of functionalised organometallic complexes is virtually unlimited.[2] One of the important issues in this area of chemistry is that of being able to design, synthesize and ultimately exploit the topological properties of solid state materials based on coordination compounds, whether linked together to form supramolecular complexes or joined in extended coordination networks through space.[3] The goal is that of reaching an intelligent control of the recognition and assembly processes that lead from molecular or ionic components to superstructures,[4] hence from individual to collective chemical and physical properties.[5]

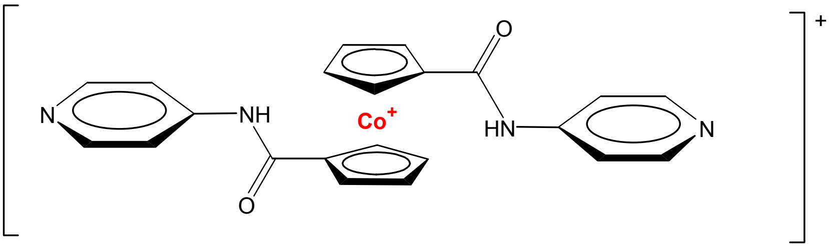
In recent years, we have been directing our efforts,[6] together with others,[7] to the exploration of the area of organometallic supramolecular solid state chemistry and crystal engineering. While many organic compounds often utilized by the crystal engineer are commercially available and can be used directly in the supramolecular assembly experiment, this is not so with organometallic species, which need, most often, to be synthesized on purpose.

With this idea in mind we have begun to prepare, also in collaboration with others, novel organometallic building blocks with adequate supramolecular bonding functionalities for the construction of target architectures.[8] We have focused our strategy on the possibility of adding hydrogen bonding donor/acceptor groups to robust sandwich complexes. The rationale for this choice is that the hydrogen bond is the strongest of the non-covalent interactions and the one that best combines strength and directionality.[9] Strength is synonym of cohesion and stability, while directionality implies topological control and selectivity, which are fundamental prerequisites for a successful control of the aggregation processes.[10]

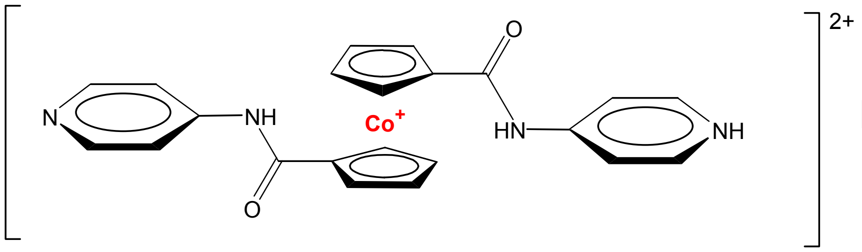
It is now well demonstrated that coordination ligands functionalised with -COOH and -OH groups form essentially the same type of hydrogen bonding interactions whether as part of organic molecules or as part of metal complexes.[2,7,11] This is not surprising, as hydrogen bonds formed by such strong donor and acceptor groups are at least one order of magnitude stronger than most non-covalent interactions. In terms of topology, dicarboxylic acid molecules allow construction of supramolecular networks because of the twin hydrogen bonding function. We have extensively exploited this feature by using sandwich organometallic dicarboxylic acids such as $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_5COOH)_2]$.[12] The cobalt cationic complex, in particular, has proved to be extremely versatile for applications in solid-solid and solid-gas reactions.[13]

Recently, we have expanded this chemistry towards organometallic bis-amido complexes. We have reported the solid-state investigation of the bis-amido cobalticinium complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][PF_6]$, $[\mathbf{1}]^+[PF_6]^-$, together with its utilization in the formation of a hydrogen bonded adduct with ferrocene dicarboxylic acid, namely $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$.[14] It is worth stressing that $[\mathbf{1}]^+$ possesses, at least in principle, both the capacity of acting as a cationic *di-base* for protonation and hydrogen bond formation as well as that of acting as a coordination ligand. In this study we explore the first such characteristics. The downside of this is that the counterion (in all cases discussed herein the $[PF_6]^-$ anion) is also "carried through" the acid base reaction and the subsequent crystallization, which decreases the level of predictability of the supramolecular architectures resulting from acid-base aggregation. As it will be seen in the following, our compounds can be described as hetero-anionic salts, e.g. containing both $[PF_6]^-$ and the anions obtained from deprotonation of fumaric and maleic acids, of the protonated bis-amide $[\mathbf{1}]^+$.

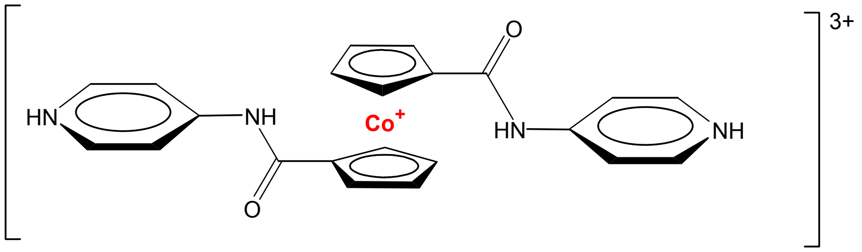
In this paper we describe our results in the reactions between $[\mathbf{1}]^+[PF_6]^-$ and the dicarboxylic fumaric and maleic acids. Our interest stems from the observation that the cationic starting material can, at least in principle, behave both as a mono- and as a di-protonic acceptor on the two N-termini (thus leading to the formation of di- and tri-cationic complexes, see Chart 1). These protonated forms can form hydrogen bridges with suitable hydrogen bond acceptors. Furthermore, the presence of the two -(CO)NH amido groups confers to the molecule additional hydrogen bonding capacity.



$[\mathbf{1}]^+$



[**1**H]$^{2+}$



[**1**H$_2$]$^{3+}$

Chart 1

b. Results and Discussion

As pointed out above, the organometallic amide [**1**]$^+$ can exist in solution in three different forms depending on the degree of protonation, i.e. $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$, [**1**]$^+$, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$, [**1**H]$^{2+}$ and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}$, [**1**H$_2$]$^{3+}$. In the reaction with acids the degree of protonation can be generally "tuned" by varying the base:acid molar ratio. Of the three cations only the structure of [**1**]$^+$ has been reported before and we address the reader to the previous publication,[14] while the structure of the mono protonated and di-protonated compounds have not been reported before. Since the supramolecular structure of [**1**H]$^{2+}$ bears on the following discussion we shall first describe the packing of the dication $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$, [**1**H]$^{2+}$, while the tri-cation [**1**H$_2$]$^{3+}$ will be seen in the structure of the adducts discussed below. Selected hydrogen bonding parameters for [**1**H]$^{2+}$ as well as for all the other species described herein are reported in Table 1.

The mono-protonation product $[\mathbf{1}H]^{2+}$ has been crystallized as its $[PF_6]^-$ salt in the form $2[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$ $4[PF_6]^- \cdot H_2O$, $2[\mathbf{1}H]^{2+}$ $4[PF_6]^- \cdot H_2O$. The most interesting feature, which bears on the following discussion, is that the dication forms hydrogen bonded dimers in the solid state via N-H···N interactions, as shown in Figure 1. The resulting supramolecular aggregate is thus a tetra-cation "kept together" by two N-H···N hydrogen bonds [N(4)···N(3) 2.715(4), N(8) ···N(6) 2.738(4) Å, for the two crystallographically independent units shown in Figure 1].

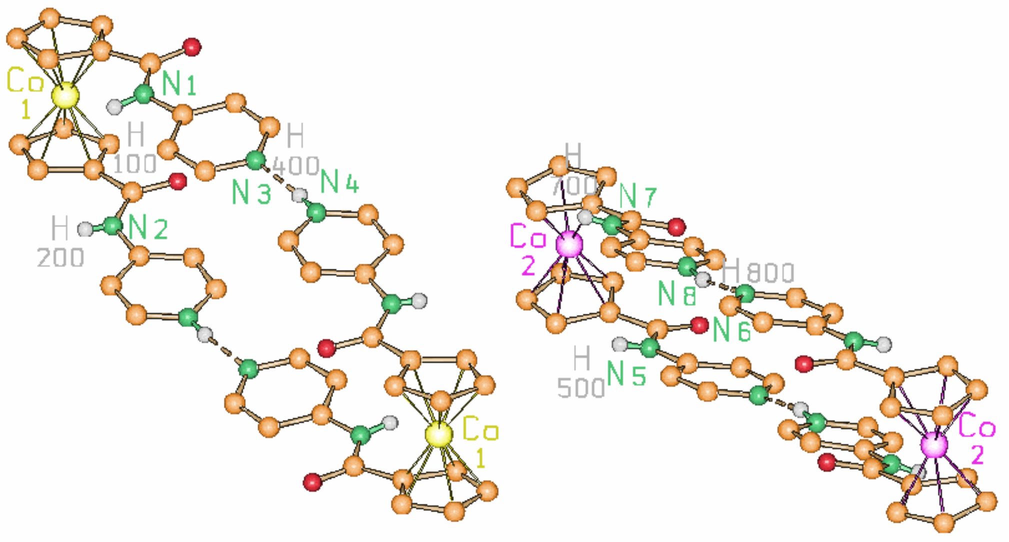


Figure 1.

It is worth noting that one of the tetra-cations is hydrogen bridged with two water molecules [N···O 2.943(5)Å] and both cations also interact with the $[PF_6]^-$ anions, establishing N-H···F hydrogen bonding interactions with the amidic N-H units [N···F distances in the range 3.025(4) – 3.072(5) Å], as shown in Figure 2.

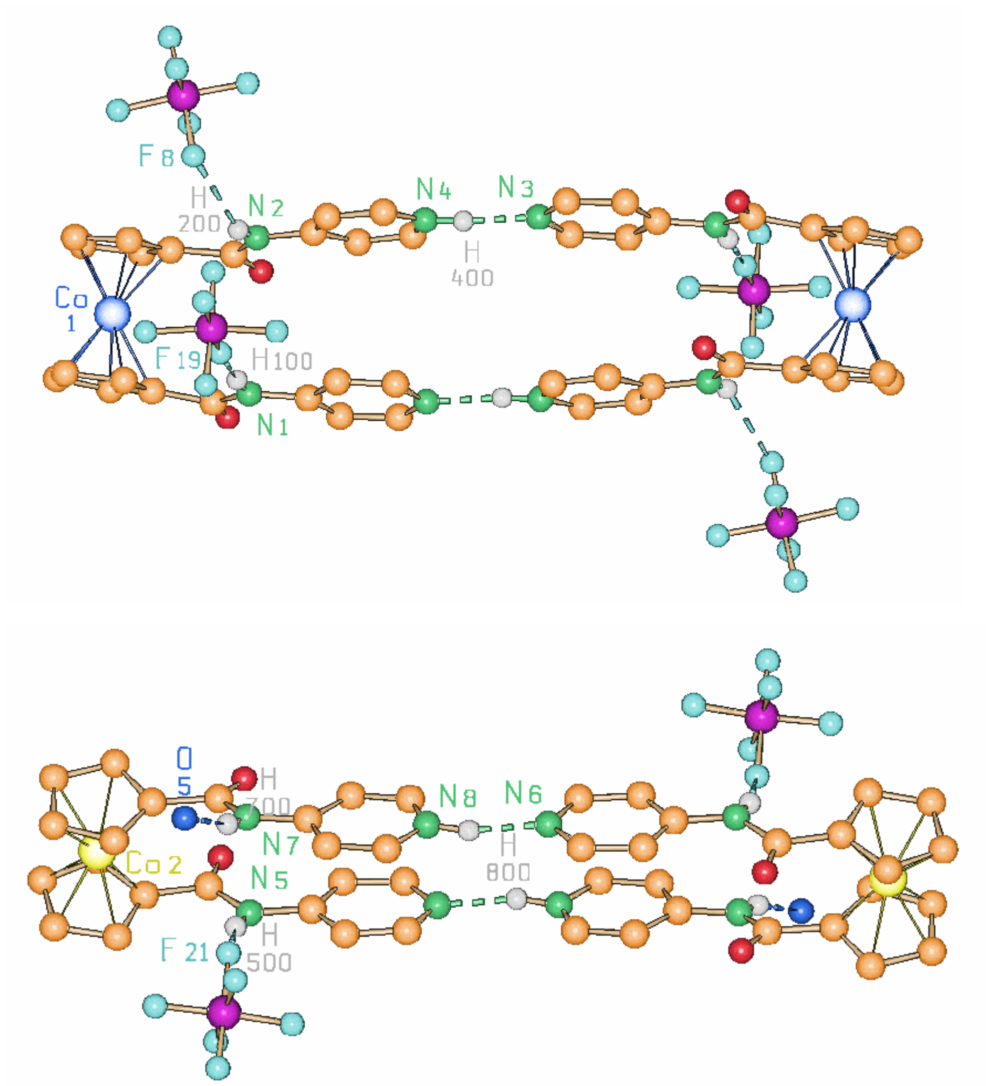


Figure 2

c. Reactions with fumaric acid

Even though it is possible to envisage several stoichiometric molar ratios between base and acid in the reaction of $[\mathbf{1}]^+$ with acids (see Table 1), our experiments show that only two stoichiometries yield crystalline aggregates, namely $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot$ $[PF_6]^-$ $\cdot 1/2[\text{fumarate}]^{2-}$, $[\mathbf{1}H]^{2+}\cdot PF_6^-\cdot 1/2[\text{fumarate}]^{2-}$, and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+\cdot H_2O$, $[\mathbf{1}H_2]^{3+}$ $\cdot[PF_6]^-$

$\cdot$[H(fumarate)$_2$]$^{3-}$$\cdot$$H_3O^+$$\cdot$$H_2O$, obtained from the 2:1 and the reverse 1:2 amide:acid ratios, respectively. Amide:acid ratios 2:1, 1:1 and 1:1.5 all yielded the fumarate derivative [**1**H]$^{2+}$•[PF$_6$]$^-$$\cdot$1/2[fumarate]$^{2-}$, while ratios 1:2 and 1:3 both yielded the hydrogen fumarate derivative [**1**H$_2$]$^{3+}$$\cdot$[PF$_6$]$^-$ $\cdot$[H(fumarate)$_2$]$^{3-}$$\cdot$$H_3O^+$$\cdot$$H_2O$. Why other stoichiometries, in particular the 1:1, are not obtained, is difficult to say. One should keep in mind, however, that the acid:base protonation equilibrium in solution is not the only aspect that may influence the final solid-state product stoichiometry. Solubility equilibria, for example, may favour one species over another, while kinetic aspects may have their role in the formation of long living crystal nuclei in solution.

In the cases yielding [Co^{III}(η^5-$C_5H_4CONHC_5H_4N$)(η^5-$C_5H_4CONHC_5H_4NH$)]$^{2+}$$\cdot$ [PF$_6$]$^-$$\cdot$1/2[fumarate]$^{2-}$, [**1**H]$^{2+}$$\cdot$PF$_6^-$$\cdot$1/2[fumarate]$^{2-}$, the diprotic acid is able to protonate two molecules of the amide, raising the charge of the organometallic moiety from +1 to +2. This product is formed with stoichiometric ratios up to 1:1.5 (which, incidentally, implies that there is unreacted fumaric acid that precipitates out together with the crystals of the adduct). Above 1:1.5 the protonation equilibrium changes: the excess of fumaric acid leads to complete protonation of the bis-amido complex, to a total cationic charge of +3 and formation of the complex [**1**H$_2$]$^{3+}$. The resulting material [**1**H$_2$]$^{3+}$$\cdot$[PF$_6$]$^-$$\cdot$[H(fumarate)$_2$]$^{3-}$$\cdot$$H_3O^+$$\cdot$$H_2O$ is crystallized together with a protonated water molecule (see below). The expected product [**1**H$_2$]$^{3+}$$\cdot$[PF$_6$]$^-$$\cdot$ [fumarate]$^{2-}$ corresponding to the stoichiometric ratio 1:1 has not been isolated.

Thus, the two crystals $[\mathbf{1}\mathrm{H}]^{2+}\bullet[\mathrm{PF}_6]^{-}\cdot 1/2[\mathrm{fumarate}]^{2-}$ and $[\mathbf{1}\mathrm{H}_2]^{3+}\cdot[\mathrm{PF}_6]^{-}\cdot[\mathrm{H(fumarate)}_2]^{3-}\cdot\mathrm{H}_3\mathrm{O}^{+}$ contain the di-protonated and the three-protonated organometallic complexes, respectively. In spite of this difference, the two complexes show interesting structural relationships in the solid state:

i) The organometallic complexes in both crystals $[\mathbf{1}\mathrm{H}]^{2+}\bullet[\mathrm{PF}_6]^{-}\cdot 1/2[\mathrm{fumarate}]^{2-}$ and $[\mathbf{1}\mathrm{H}_2]^{3+}\cdot[\mathrm{PF}_6]^{-}\cdot[\mathrm{H(fumarate)}_2]^{3-}\cdot\mathrm{H}_3\mathrm{O}^{+}\cdot\mathrm{H}_2\mathrm{O}$ adopt a cisoid (eclipsed) conformation of the Cp-pyridyl ligands.

ii) In $[\mathbf{1}\mathrm{H}]^{2+}\bullet[\mathrm{PF}_6]^{-}\cdot 1/2[\mathrm{fumarate}]^{2-}$ the monoprotonated amide forms a cyclic dimer with another complex via N-H···N hydrogen bonds [N(3)···N(4) 2.669(7) Å], as shown in Figure 3.

iii) Such dimers are linked together in a zigzag fashion via the interaction of the deprotonated fumarate dianions and the outer amido N-H groups (see Figure 3) [N(1)···O(3) 2.809(6), N(2)···O(4) 2.703(6)Å]. Each carboxylate unit "pinches" both N-H groups of one complex, in such a way the organometallic cation and the fumarate dianion interact via four N-H···O bonds.

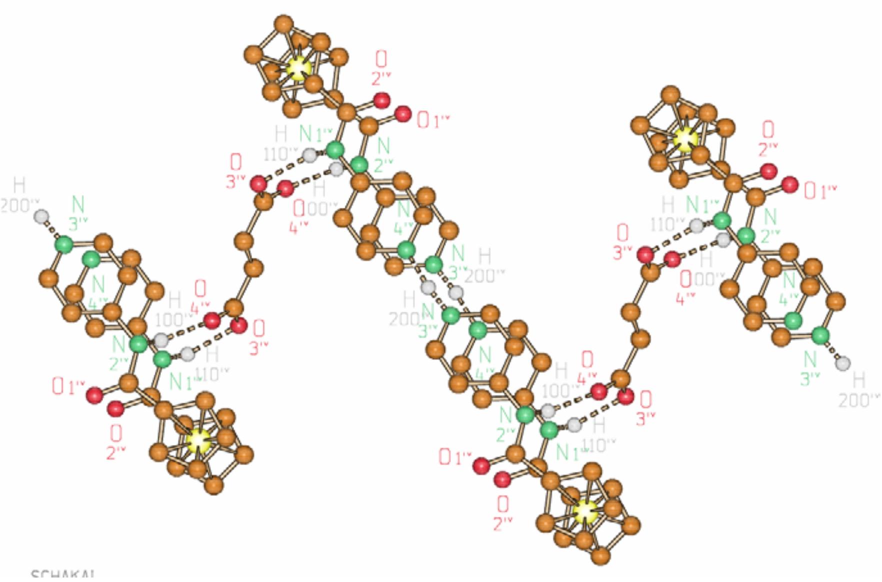
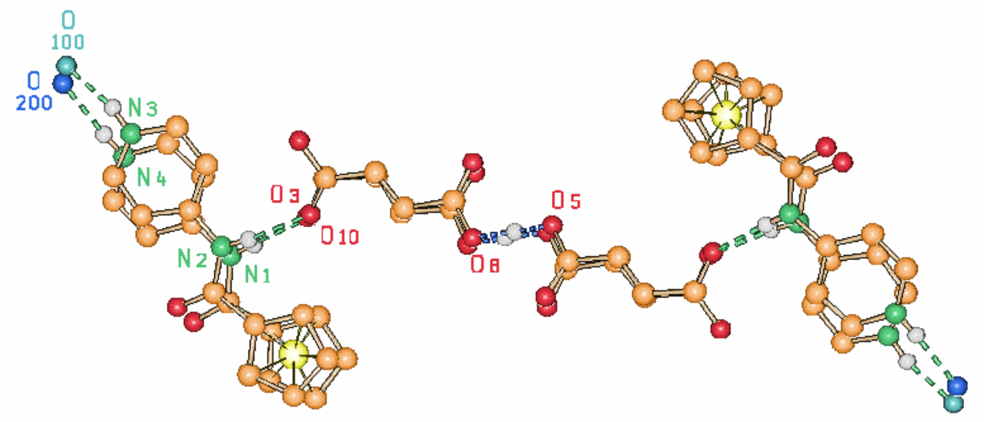


Figure 3.

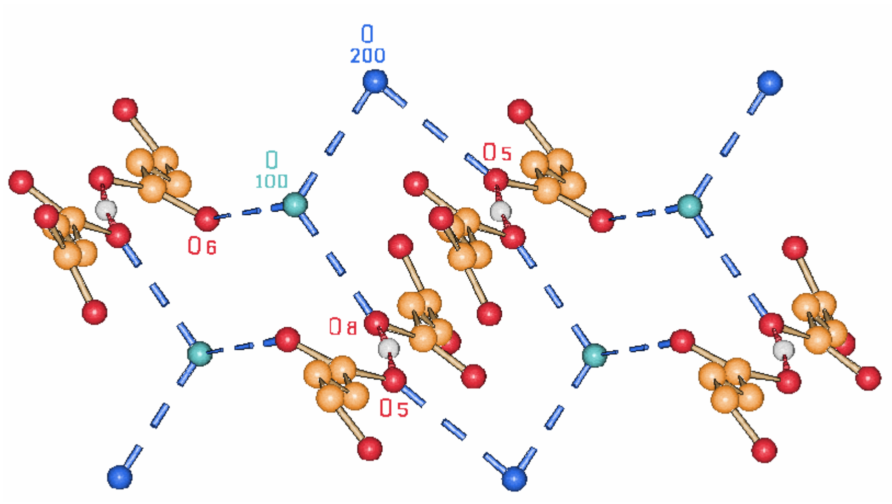
iv) In the case of $[\mathbf{1}H_2]^{3+}$, on the other hand, a dimer cannot form because both N-termini are protonated, nonetheless the complex retains the eclipsed geometry of the ligands and substituents (see Figure 4a). The pyridyl NH groups interact via hydrogen bonding with the $[H_3O]^+$ cation and the water molecule [N(3)···O(100) 2.690(4) and N(4)···O(200) 2.743(4) Å, respectively], which in turn interact with each other [O(100)···O(200) 2.829(4) Å]. The $[H_3O]^+$ cation and the water molecule are also hydrogen bonded to the $[H(\text{fumarate})_2]^{3-}$ anions (see Figure 4b) [O(100) ···O(6) 2.703(4), O(100) ···O(8) 2.739(4), O(200) ···O(5) 2.976(5) Å].

v) The trications $[\mathbf{1}H_2]^{3+}$ are linked together by a supramolecular anion formed by a hydrogen fumarate unit and a fumarate dianion. Since the proton is mid-way along the O···O bond [O(5)···O(8) 2.466(4) Å], it is more appropriate to describe the system as a superanion of formula $[H(\text{fumarate})_2]^{3-}$.

vi) On both sides the supramolecular trianion $[H(\text{fumarate})_2]^{3-}$ interacts with the amido N-H groups as observed in $[\mathbf{1}H]^{2+}$ with N(1)···O(3) and N(2)···O(10) separations of 2.763(4) and 2.965(5)Å, respectively.



(a)



(b)

Figure 4.

d. Reactions with maleic acid

In terms of supramolecular bonding capacity and hydrogen bond formation, maleic acid differs from fumaric acid mainly in the fact that mono-deprotonation leads in general to formation of an intra-molecular hydrogen bond. As a consequence of the intramolecular hydrogen bonding formation the carboxylate groups are available only for hydrogen bonding acceptance.

The structure of $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$•$5/2[PF_6]^-$• $3/2[Hmaleate]^-$, $2[\mathbf{1}H]^{2+}$•$5/2[PF_6]^-$• $3/2[Hmaleate]^-$**,** is reminiscent of those of the mono-protonated amide salt $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$ $\cdot 4[PF_6]^- \cdot H_2O$ and of the hydrogen fumarate salt $[\mathbf{1}H]^{2+}$•$[PF_6]^- \cdot 1/2[maleate]^{2-}$. These systems have in common the presence of hydrogen bond dimers in the solid state (see Figure 5). The N-H···N separations are comparable in length [N(4)···N(8) 2.688(6); N(6)···N(2) 2.686(6) Å]. Note, however, that the amido groups are eclipsed in one of the two dications and staggered in the other. This difference seems to suggest that in solution the complex is present with both, possibly dynamically interconverting conformations, which are frozen out at the stage of crystallization. It is also noteworthy that compound $2[\mathbf{1}H]^{2+}$•$5/2[PF_6]^-$• $3/2[$Hmaleate$]^-$ is the only case, in this study, where the Cp-amido ligands show *both* the staggered and eclipsed relative orientations of the C(=O)NH units. The arrangement of the hydrogen maleate anions provides a possible rationale for the difference. As shown in Figure 6, the hydrogen maleate anions provide two types of bridges between next neighbouring dimers.

Because of the mentioned scarcity of hydrogen bonding donor sites, the interaction links have to utilize the amido N-H groups. The structure can be described as formed of “dimers of dimers” held together by two ordered hydrogen maleate anions, for a total of six N-H···O interactions [N(3)···O(5) 2.923(5), N(5)···O(7) 2.916(6), N(7)···O(8) 2.836(6) Å]. The N(1)-H(100) donor group, which is not involved in the “dimer of dimer” formation, can thus be used to link together the “dimers of dimers” via the disordered hydrogen maleate [N(1)···O(100) 2.832(6) Å] (see Figure 6). This picture also provides a rationale for the disorder observed in this latter hydrogen maleate anion, which is oriented randomly in two positions around the crystallographic inversion centre.

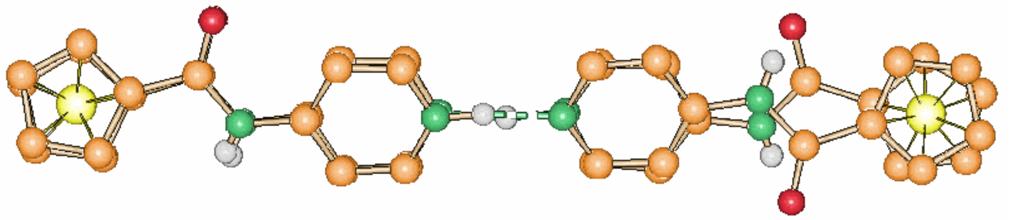


Figure 5.

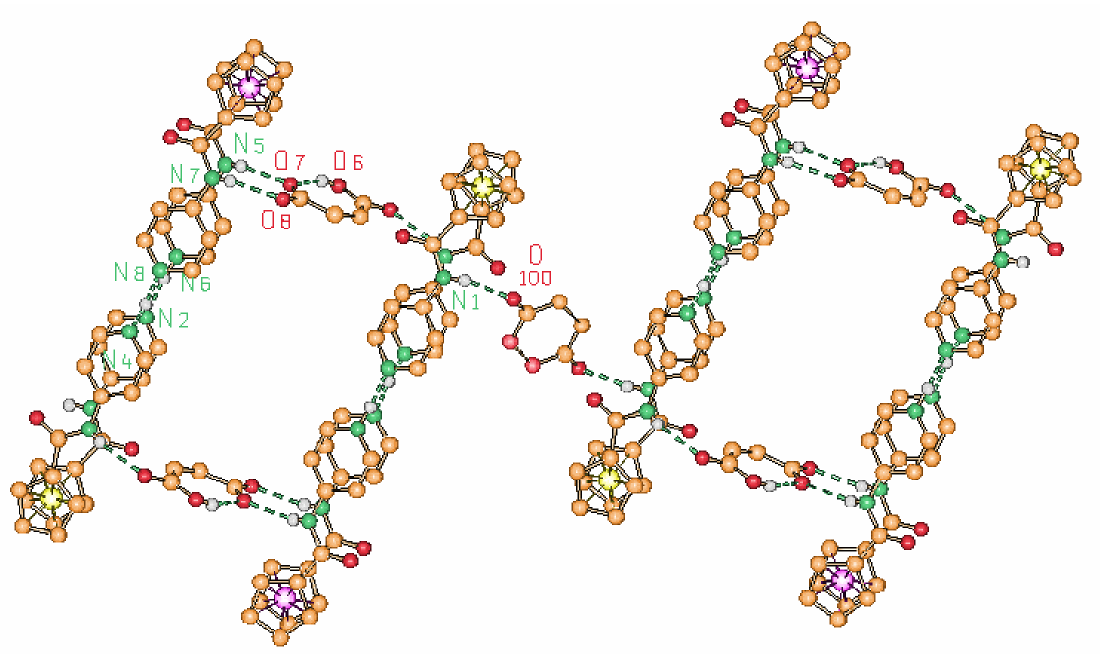
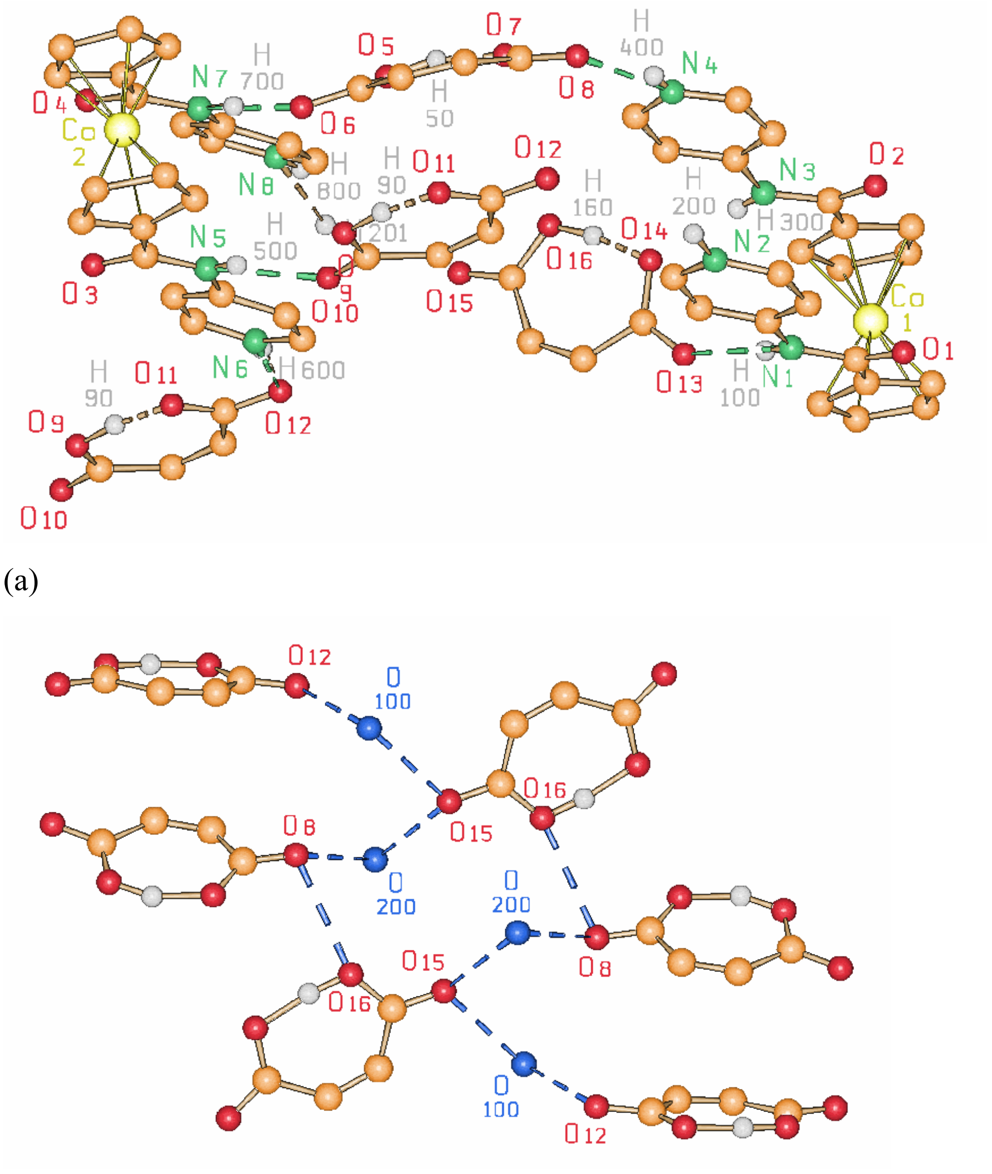


Figure 6.

Let us now consider the cases of compounds $2[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}{\cdot}3[PF_6]^-{\cdot}\ 3[Hmaleate]^-\ {\cdot}2H_2O$, $2[\mathbf{1}H_2]^{3+}{\cdot}3[PF_6]^-{\cdot}\ 3[Hmaleate]^-\ {\cdot}2H_2O$ and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}{\cdot}2[PF_6]^-\ {\cdot}[Hmaleate]^-{\cdot}H_2O$, $[\mathbf{1}H_2]^{3+}{\cdot}2[PF_6]^-{\cdot}[Hmaleate]^-\ {\cdot}\ H_2O$. These tow crystalline materials, in spite of the different stoichiometry, bear some close structural relationship. In both systems the intramolecular hydrogen maleate anion acts as a bridge between two tri-cations (compare Figures 7 and 8) by accepting hydrogen bond donation from the protonated pyridine N-terminus [N(7)···O(6) 2.794(4) and N(1)···O(3) 2.884(7) Å for the two compounds, respectively] and from the amido N-H system of two distinct cations [N(4)···O(8) 2.789(5), and N(2)···O(5) 2.923(7) and N(2)···O(6) 2.873(8) Å for the two compounds, respectively]. The hydrogen maleate bridges thus generate an extended network of alternating cations and anions, thanks also to the rotational freedom about the Cp-Co-Cp axis. In addition to this, in compound $2[\mathbf{1}H_2]^{3+}{\cdot}3[PF_6]^-{\cdot}\ 3[Hmaleate]^-\ {\cdot}2H_2O$ the two hydrogen maleates that do not act as bridges still interact each with an organometallic cation via NH···O hydrogen bonds [N(5)···O(10), N(8)···O(9), N(1)···O(13) Å] (Figure 8) and establish hydrogen bonding interactions with the water molecules [O···O distances in the range 2.771(5)-2.936(5)Å].



(a)

(b)

Figure 7.

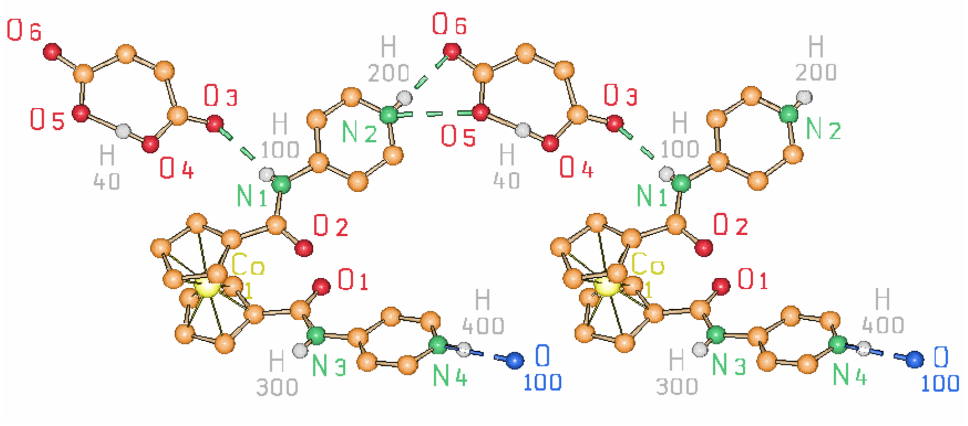


Figure 8.

e. Conclusions

The aim of this study has been that of exploring the supramolecular bonding capacity of the cationic bis-amide complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][PF_6]$, $[\mathbf{1}]^+[PF_6]^-$, towards the dicarboxylic fumaric and maleic acids. The idea was that of using the -COOH groups as a probe of the hydrogen bonding capacity of the organometallic complex. In previous studies we have extensively investigated the behaviour of organometallic dicarboxylic acids such as $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_5COOH)_2]$[12] towards a variety of organic and inorganic acids or bases.

The results of these studies have led us to the successful exploitation of the acid:base behaviour of one such species, namely the zwitterionic form $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ obtained by deprotonation of the cobalticinium cationic acid, in heterogeneous reactions with vapours of acids and bases.[15] In a parallel investigation we have investigated the reactivity of neutral di-substituted pyridyl and pyrimidyl ferrocenyl species towards acids and metal complexes.[16] With the present work we intended to extend these findings to a new class of supramolecular synthons, namely that of *cationic* bis-amido complexes, of which $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$ is the prototype.[17]

In the course of this investigation we have shown that both fumaric and maleic acids are sufficiently strong as to protonate the pyridine moiety. The protonation yields a series of aggregates based on hydrogen bonds. Interestingly the complexes seem to violate a rule-of-thumb of hydrogen bonding interactions. Most, but not all, contain the dimer formed by the monoprotonated dication $[\mathbf{1}H]^{2+}$ which are held together by inter-cation N-H···N hydrogen bonds between a protonated and a free pyridyl N-atom, while the O-atoms acceptors on the fumarate and hydrogen maleate anions appear to be involved exclusively in interactions with the amido -(CO)N-H hydrogen bond donors. Only in the case of $[\mathbf{1}H_2]^{3+}\cdot 2[PF_6]^-\cdot[\text{Hmaleate}]^-\cdot H_2O$ interaction between the N-atom and the acid is observed.

The difference between fumaric and maleic acid is as expected: in the latter case formation of the intramolecular hydrogen bond which is particularly stable yields compounds that contain only this monoanion, while in the case of fumaric acid, both the completely deprotonated fumarate dianion and the supramolecular tri-anion formed by one hydrogen fumarate monoanion and one fumarate dianion is possible.

Similar dimer has been obtained previously in the case of the mixed metal supramolecular complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$, which also bears some resemblance with the dimer formed in the solid state by the cationic complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]^{(+)}$. This similarity of behaviour seems to suggest that these sandwich complexes act as supramolecular synthons and that the eclipsed conformation is rather favoured. Hence, whether formed via N-H···N or N-H···O or O-H···O these organometallic complex tend to behave as supramolecular dimmers.

In terms of crystal engineering there are two major drawbacks. If crystal engineering is obtaining the desired architecture by exploiting the predictable arrangement of molecules and ions by exploiting supramolecular bonding capacity, the presence of two types of counterions, one innocent (the $[PF_6]^-$) and one responsible of the packing (the mono- and di-acid anions), complicates the matter enormously. Furthermore these crystals often co-crystallize with hydrogen bonded water molecules. In total, many of the complexes described in this paper contain up to four independent chemical units, the organometallic cations, the hexafluorophosphate anions and the anions derived from the organic acids and the water molecules. Clearly the possibility of predicting the outcome of the aggregation would be easier if the “dimensionality” of the problem related to the efficient packing of all particles, is reduced.

Further studies are in progress to utilize the bis-amido complexes in the formation of complexes of complexes, for applications in coordination chemistry and crystal engineering.

f. Experimental Section

All reactants were purchased from Aldrich and used without further purification. Reagent grade solvents and bidistilled water were used.

Synthesis of $[\mathbf{1H}]^{2+}\cdot 2[\mathbf{PF_6}]^-$: $[1H]^{2+}$ was synthesized following a procedure, slightly modified, reported by Beer et Stokes.[18]

Synthesis of $[1]^{+}\cdot[PF_6]^{-}$: $[1H]^{2+}$ was treated with a solution of NH_3 0.1M, in order to obtain deprotonation of the two pyridine moieties.

Synthesis of $[1H]^{2+}\cdot[PF_6]^{-}\cdot1/2[\text{fumarate}]^{2-}$: 0.11 mmol of $[1]^{+}\cdot[PF_6]^{-}$ and 0.11 mmol of fumaric acid, $C_4O_4H_2$, were dissolved in 5 ml of water. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of water. The same compound was obtained after reaction of 0.11 mmol of $[1]^{+}\cdot[PF_6]^{-}$ with 0.5 and 1.5 mmol of $C_4O_4H_2$ (2:1 and 1:1.5 reagents ratio, respectively).

Synthesis of $[1H_2]^{3+}\cdot[PF_6]^{-}\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^{+}\cdot H_2O$: 0.11 mmol of $[1]^{+}\cdot[PF_6]^{-}$ and 0.22 mmol of fumaric acid, $C_4O_4H_2$, were dissolved in 5 ml of water. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of water. The same compound was obtained after reaction of 0.11 mmol of $[1]^{+}\cdot[PF_6]^{-}$ with 0.33 mmol of $C_4O_4H_2$ (1:3 reagents ratio).

Synthesis of $2[1H]^{2+}\cdot5/2[PF_6]^{-}\cdot3/2[\text{maleate}]^{2-}$: 0.22 mmol of $[1]^{+}\cdot[PF_6]^{-}$ and 0.11 of maleic acid, $C_4O_4H_2$, were dissolved in 5 ml of water. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of water.

Synthesis of $2[1H_2]^{3+}\cdot3[PF_6]^{-}\cdot3[\text{Hmaleate}]^{-}\cdot2H_2O$: 0.11 mmol of $[1]^{+}\cdot[PF_6]^{-}$ and 0.22 of maleic acid, $C_4O_4H_2$, were dissolved in 5 ml of water. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of water.

Synthesis of $[1H_2]^{3+}\ 2[PF_6]^{-}\cdot[\text{Hmaleate}]^{-}\cdot H_2O$: 0.11 mmol of $[1]^{+}\cdot[PF_6]^{-}$ and an excess of maleic acid, $C_4O_4H_2$, were dissolved in 5 ml of water. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of water.

Crystal structure determination: Crystal data for all compounds were collected on a Bruker ApexII CCD diffractometer. Crystal data and details of measurements are summarised in Table 2. Common to all compounds: Mo-Kα radiation, $\lambda = 0.71073$ Å, monochromator graphite. Data for

2[**1**H]$^{2+}$·5/2[PF$_6$]$^-$ ·3/2[Hmaleate]$^-$ were collected at 293K, all other data were collected at 273K. SHELX97[19a] was used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. The [PF$_6$]$^-$ anion in [**1**H]$^{2+}$·[PF$_6$]$^-$·1/2[fumarate]$^{2-}$ is disordered over two positions (refined with an occupancy ratio of 80:20) around the F1-F5 axis. One of the two [Hmaleate]$^-$ ions in [**1**H]$^{2+}$·5/2[PF$_6$]$^-$ ·3/2[Hmaleate]$^-$ is disordered over two equivalent positions around an inversion centre, and was difficult to model; the position of the independent carbon atom and of the oxygen atom involved in the intra-molecular hydrogen bond could not be well separated from those of the second, inverted image; the refinement was then done by attributing to the two atoms an average C/O scattering factor. All Hydrogen atoms bound to nitrogen and oxygen atoms were located via difference Fourier syntheses. Only the hydrogen atoms bound to the water molecule in 2[**1**H]$^{2+}$·4[PF$_6$]$^-$·H$_2$O and [**1**H$_2$]$^{3+}$·2[PF$_6$]$^-$·[Hmaleate]$^-$ ·H$_2$O, and the H_{COOH} hydrogen in the disordered maleate monoanion in 2[**1**H]$^{2+}$·5/2[PF$_6$]$^-$ ·3/2[Hmaleate]$^-$ could not be located. Hydrogen atoms bound to carbon atoms were added in calculated positions. SCHAKAL99[19b] was used for the graphical representation of the results. The program PLATON[19c] was used to calculate the hydrogen bonding interactions reported in Table 1. CCDC 260092 - 260097 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

References

[1] a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, **1989**; b) D. Braga, F. Grepioni, A. G. Orpen, (Eds.), *Crystal Engineering: from Molecules and Crystals to Materials*, Kluwer Academic Publishers, Dordrecht, **1999**; c) C. B. Aakeröy, A. S. Borovik, *Coord. Chem. Rev.* **1999**, *183*, 1; d) M. D. Hollingsworth, *Science* **2002**, *295*, 2410; e) D. Braga, *Chem. Commun.* **2003**, 1258; e) D. Braga, J. Miller, G. R. Desiraju, A. G. Orpen, S. L. Price, *CrystEngComm*, **2002**, *4*, 500; f) L. Brammer, *Chem. Soc. Rev.*, **2004**, *33*, 476; g) M. W. Hosseini, *CrystEngComm,* **2004**, *6*, 318.

[2] D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375.

[3] a) C. B. Aakeröy, *Acta Crystallogr.*, Sect. B, **1997**, *53*, 569; b) D. Braga, F. Grepioni, *Coord. Chem. Rev.* **1999**, *183* , 19; c) L. *J.* Brammer, *Chem. Soc. Dalton Trans.* **2001**, *16*, 3145; d) L. Brammer, *Dalton Trans.* **2003**, *16*, 3145; e) M. W. Hosseini, *Coord. Chem. Rev.* **2003**, *240*, 157; f) M. Eddaouddi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34,* 319; g) S. R. Batten, *CrystEngComm* **2001**, 28; h) K. T. Holman, A. M. Pivovar, J. A. Swift, M. D. Ward, *Acc. Chem. Res.* **2001**, *34*, 107; i) O. M. Yaghi, G. Li, H. Li, *Nature* **2000**, *37,* 703; j) S.-I. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed.* **2000**, *39*, 2082; l) S. B. Batten, R. Robson, *Angew. Chem. Int. Ed. Engl.* **1998**, *37,* 1460; g) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53; m) O. R. Evans, R. G. Xiong, Z.Y. Wang, G. K. Wong, W. B. Lin, *Angew. Chem. Int. Ed.* **1999**, *38*, 536; n) O. R. Evans, W. B. Lin, *Acc. Chem. Res.* **2002**, *35*, 511; o) C. Janiak, *Dalton Trans.* **2003**, *14*, 2781; p) L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngComm* **2003**, *5*, 269; q) H. W. Roesky, M. Andruh, *Coord. Chem. Rev.* **2003**, *236*, 91; r) O. M. Yaghi, M.

O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; s) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; t) M. D. Ward and M. J. Horner, *CrystEngComm*, **2004**, *6*, 401; u) S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, **2003**, *246*, 145; v) C. Janiak, *Dalton Trans*. 2003, 2781.

[4] a) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**. b) I. Haiduc, F. T. Edelmann, *Supramolecular Organometallic Chemistry*, Wiley-VCH, **1999**; c) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley & Sons, **2000**.

[5] a) G. R. Desiraju, *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry*, vol. 2, (Ed.) Wiley, Chichester, UK, **1996**; b) *J. Chem. Soc. Dalton Trans*, **2000**, 3705 the whole issue; c) *Perspectives in Supramolecular Chemistry*, Vol. 7 – Crystal Design: *Structure and Function*, ed. G. R. Desiraju, Wiley, Chichester, **2003**.

[6] D. Braga, F. Grepioni, *Acc. Chem. Res.* **2000**, *33*, 601; b) D. Braga, L. Maini, F. Grepioni, C. Elschenbroich, F. Paganelli, O. Schiemann, *Organometallics* **2001**, *20*, 1875.

[7] a) A. M. Beatty, *CrystEngComm* **2001**, 51; b) L. Brammer, J. C. Mareque Rivas, R. Atencio, S. Fang, F. C. Pigge, *J. Chem. Soc., Dalton Trans*. **2000**, 3855; c) C. M. Zakaria, G. Ferguson, A. J. Lough, C. Glidewell, *Acta Cryst. Sect B*, **2002**, *58*, 786; d) C. Elschenbroich, F. Lu, K. Harms, *Organometallics*, **2002**, *21*, 5152; e) C. Elschenbroich, O. Schiemann, O. Burghaus, K. Harms, *J. Am. Chem. Soc*, **1997**, *119*, 7452; f) M. C. Tse, K. K. Cheung, M. C. W. Chan, C. M. Che, *Chem. Commun.* **1998**, *21*, 2295; g) Y. J. Kim, J. G. Verkade, *Inorg. Chem.* **2003**, *42*, 4262; h) J. C. M. Rivas, L. Brammer, *Coord. Chem. Rev.* **1999**, *183*, 43; i) M. Oh, G. B. Carpenter, D. A. Sweigart, *Organometallics* **2003**, *22*, 2364; j) M. Oh,

G. B. Carpenter, D. A. Sweigart, *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 3650; k) M. Oh, G. B. Carpenter, D. A. Sweigart, *Chem. Commun.* **2002**, *18*, 2168; l) M. Oh, G. B. Carpenter, D. A. Sweigart, *Acc. Chem. Res.* **2004,** 37, 1; m) C. M. Zakaria, G. Ferguson, A. J. Lough, C. Glidewell *Acta Cryst. Sec. B* **2002**, *58*, 786; n) U. Geiger, J. A. Schlueter *Chem. Rev.* **2004**, *104,* 5203; o) M. Oh, J. A. Reingold, G. B. Carpenter, D. A. Sweigart, *Coord. Chem. Rev.* **2004**, *248*, 561; p) C. Elschenbroich, M. Wolf, J. Pebler, K. Harms, *Organometallics* **2004**, *23*, 454.

[8] a) D. Braga, L. Maini, M. Polito, M. Rossini, F. Grepioni, *Chem. Eur. J.* **2000**, *6*, 4227; b) D. Braga, L. Maini, F. Grepioni, A. DeCian, O. Felix, J. Fisher, M. W. Hosseini, *New. J. Chem*. **2000**, *24*, 547; c) D. Braga, F. Grepioni, *J. Chem. Soc. Dalton Trans.* **1999**, 1; d) D. Braga, L. Maini, L. Prodi, A. Caneschi, R. Sessoli, F. Grepioni, *Chem. Eur. J.* **2000**, *6*, 1310, e) D. Braga, L. Maini, M. Polito, F. Grepioni, *Organometallics* **1999**, *18*, 2577.

[9] a) L. J. Prins, D. N. Reinhoudt, P. Timmerman, *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2382; b) C. B. Aakeröy, K. R. Seddon, *Chem. Soc. Rev.* **1993**, 397; c) M. S. Gordon, J. H. Jensen, *Acc. Chem. Res.* **1996**, *29*, 536; d) D. Braga, F. Grepioni, *Acc. Chem. Res*. **1997**, *30*, 81; e) L. Brammer, D. Zhao, F. T. Ladipo, Braddock-Wilking, J. *Acta Crystallogr. Sect. B* **1995**, *B51*, 632;

f) J. J. Novoa, I. Nobeli, F. Grepioni, D. Braga, *New J. Chem.* **2000**, *24***,** 5;

[10] a) G. R. Desiraju, *Acc. Chem. Res.* **2002**, *35*, 565; b) D. Braga, L. Maini, M. Polito, and F. Grepioni, *Structure and Bonding*, **2004**, *111*, 1; c) K. Biradha, *CrystEngComm* **2003**, *5*, 374.

[11] See for example, a) A. D. Burrows, **2004**, *108*, 55; b) L. M. Epstein, E. S. Shubina, *Coord. Chem Rev.* **2002**, *231*, 165; c) A. M. Beatty *Coord. Chem. Rev.* **2003,** *246*, 131.

[12] D. Braga, L. Maini, M. Polito, E. Tagliavini, and F. Grepioni, *Coord. Chem. Rev.* **2003**, *246*, 53.

[13] a) D. Braga, G. Cojazzi, D. Emiliani, L. Maini, F. Grepioni, *Chem. Commun.* **2001**, 2272; b) D. Braga, G. Cojazzi, D. Emiliani, L. Maini, F. Grepioni, *Organometallics* **2002**, *21,* 1315; c) D. Braga, L. Maini, M. Mazzotti, K. Rubini, A. Masic, R. Gobetto, F. Grepioni, *Chem. Commun.* **2002**, 2296.

[14] D. Braga, M. Polito, F. Grepioni, *Cryst. Growth & Des* **2004**, *4*, 769.

[15] a) D. Braga, L. Maini, M. Polito and F. Grepioni, *Organometallics* **1999**, *18*, 2577; b) D. Braga, G. Cojazzi, D. Emiliani, L. Maini, and F. Grepioni, *Chem. Commun.* **2001**, *21*, 2272; c) D. Braga, G. Cojazzi, D. Emiliani, L. Maini, and F. Grepioni, *Organometallics* **2002**, *21*, 1315; d) D. Braga, L. Maini, M. Mazzotti, K. Rubini and F. Grepioni, *CrystEngComm* **2003**, *29*, 154; e) D. Braga, L. Maini, M. Mazzotti, K. Rubini, A. Masic, R. Gobetto, and F. Grepioni, *Chem. Commun.* **2002**, *20*, 2296.

[16] a) D. Braga, D. D'Addario, F.Grepioni, M. Polito, D. M. Proserpio, J.W. Steed and E. Tagliavini, *Organometallics* **2003**, *22*, 4532.

[17] D. Braga, F. Grepioni, S. Giaffreda unpublished results

[18] P. Beer and S. E. Stokes, *Polyhedron* **1995**, *14*, 873.

[19] a) G. M. Sheldrick, **SHELXL97**, Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997; b) E. Keller, **SCHAKAL99** Graphical Representation of Molecular Models; University of Freiburg, Germany, 1999; c) A. L. Speck**,** *Acta Crystallogr. Sect. A* **1990**, *46*, 9574.

Captions to Scheme and Figures

Chart 1. The cationic bis-amide complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]$, $[\mathbf{1}]^+$, together with the di- and tri-cationic species $[\mathbf{1}H]^{2+}$ and $[\mathbf{1}H_2]^{3+}$ obtained via mono- and di-protonation of the two N-termini.

Figure 1. The supramolecular aggregates present in $2[\mathbf{1}H]^{2+}\,4[PF_6]^-\cdot H_2O$. The tetra-cation is "kept together" by two N-H···N hydrogen bonds [N(4) ···N(3) 2.715(4), N(8) ···N(6) 2.738(4) Å for the two crystallographically independent units]. [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Figure 2. N-H···O and N-H···F hydrogen bonding interactions between the bis-amide $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$ and the hexafluorophosphate anions and the water molecules. [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Figure 3. Crystalline $[\mathbf{1}H]^{2+}\bullet[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$. The hydrogen bridged amide dimers [N(3)···N(4) 2.669(7) Å] are linked together in a zigzag fashion via the interaction of the deprotonated fumarate dianions and the outer amido N-H groups, [N(1)···O(3) 2.809(6), N(2)···O(4) 2.703(6)Å]. Each carboxylate unit "pinches" both the amido N-H groups of one complex, in such a way each fumarate dianion interacts with the

organometallic cations via four N-H···O bonds. [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Figure 4. (a) In crystalline $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^{-}\cdot[H(fumarate)_2]^{3-}\cdot H_3O^{+}\cdot H_2O$ the trications are linked together by a supramolecular anion formed by a hydrogen fumarate unit and a fumarate dianion. Since the proton is mid-way along the O···O bond in this unit, it is more appropriate to describe the systems as a superanion $[H(fumarate)_2]^{3-}$, with a O(5)···O(8) separation of 2.466(4) Å. (b) The $[H_3O]^+$ cation and the water molecule interact via hydrogen bonding with each other [O(100)···O(200) 2.829(4) Å] and with the $[H(fumarate)_2]^{3-}$ anion [O(100)···O(6) 2.703(4), O(100) ···O(8) 2.739(4), O(200) ···O(5) 2.976(5) Å]. [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Figure 5. The hydrogen bonded dimer in crystalline $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\bullet 5/2[PF_6]^{-}\bullet\ 3/2[Hmaleate]^{-}$, $2[\mathbf{1}H]^{2+}\bullet 5/2[PF_6]^{-}\bullet\ 3/2[Hmaleate]^{-}$. Note how the amido groups are eclipsed in one of the two di-cations and staggered in the other. [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Figure 6. The structure of $2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^{-}\cdot\ 3/2[Hmaleate]^{-}$ shows the presence of hydrogen bond dimers in the solid state of the type observed for $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\ \cdot[PF_6^{-}]_4\cdot H_2O$ as well as the hydrogen fumarate salts $[\mathbf{1}H]^{2+}\bullet[PF_6]^{-}\cdot 1/2[fumarate]^{2-}$. Note, however, that the amido groups are eclipsed in one of the two di-cations and staggered in the other (see Figure 5). The "dimers of dimers" are held together by a hydrogen oxalate anion, which is disordered over two

orientations (only one of the two images is shown here for clarity). [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Figure 7. (a) The extended hydrogen bonded network in crystalline $2[\mathbf{1}H_2]^{3+}$•$3[PF_6]^-$• $3[\text{Hmaleate}]^-$ • $2H_2O$. Note how one hydrogen maleate anion acts as a bridge between trications while another one establishes hydrogen at the intra-cation level. (b) The hydrogen bonding interactions between the water molecules and the hydrogen maleates that are not involved in the cation bridging (water hydrogen atoms not shown for clarity). [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Figure 8. (a) The extended hydrogen bonded network in crystalline $[\mathbf{1}H_2]^{3+}$•$2[PF_6]^-$•$[\text{Hmaleate}]^-$ • H_2O. Note how the hydrogen maleate anion acts as a bridge between trications forming an extended network. [H_{CH}, H_{water} and H $_{[H_3O]^+}$ atoms not shown for clarity].

Table 1. Relevant hydrogen bonding parameters for all species discussed herein

Compound	Donor···Acceptor	D···A (Å)
$2[\mathbf{1}H]^{2+}\cdot 4[PF_6]^{-}\cdot H_2O$	N(1)···F(19)	3.037(5)
	N(2)···F(8)	3.025(4)
	N(4)···N(3)	2.715(4)
	N(5)···F(21)	3.072(5)
	N(7) ···O(5)	2.943(5)
	N(8) ···N(6)	2.738(4)
$[\mathbf{1}H]^{2+}\cdot [PF_6]^{-}\cdot 1/2[\text{fumarate}]^{2-}$	N(2) ···O(4)	2.703(6)
	N(1) ···O(3)	2.809(6)
	N(3) ···N(4)	2.669(7)
$[\mathbf{1}H_2]^{3+}\cdot [PF_6]^{-}\cdot [H(\text{fumarate})_2]^{3-}\cdot H_3O^{+}\cdot H_2O$	N(1) ···O(3)	2.763(4)
	N(2) ···O(10)	2.965(5)
	N(3) ···O(100)	2.690(4)
	N(4) ···O(200)	2.743(4)
	O(100) ···O(8)	2.739(4)
	O(100) ···O(200)	2.829(4)
	O(100) ···O(6)	2.703(4)
	O(200) ···O(100)	2.829(4)
	O(200) ···O(5)	2.976(5)
	O(5) ···O(8)	2.466(4)
$2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^{-}\cdot 3/2[\text{Hmaleate}]^{-}$	N(4) ···N(8)	2.688(6)
	N(6) ···N(2)	2.686(6)
	N(1) ···O(100)	2.832(6)
	N(3) ···O(5)	2.923(5)
	N(5) ···O(7)	2.916(6)
	N(7) ···O(8)	2.836(6)
	O(6) ···O(7)	2.460(5)
$2[\mathbf{1}H_2]^{3+}\cdot 3[PF_6]^{-}\cdot 3[\text{Hmaleate}]^{-}\cdot 2H_2O$	N1···O13	2.757(5)
	O100···O15	2.798(7)
	O100···O12	2.771(5)
	N2···O100	2.689(5)
	O200···O8	2.936(5)
	O200'···O8	2.838(5)
	N3···O14	3.016(5)
	N4···O8	2.789(5)
	N5···O10	2.822(5)
	N6···O12	2.791(6)
	N7···O6	2.794(4)
	N8···O200	2.702(6)

$[\mathbf{1}H_2]^{3+}\cdot 2[PF_6]^{-}\cdot[\text{Hmaleate}]^{-}\cdot H_2O$	O5···O7	2.407(4)
	O9···O11	2.416(4)
	O16···O14	2.477(5)
	O(4)···O(5)	2.411(5)
	N(1)···O(3)	2.884(7)
	N(2)···O(5)	2.923(7)
	N(2)···O(6)	2.873(8)
	N(4)···O(100)	2.787(8)
	O(100)···F(7)	3.1750(8)
	N(3)···F(12)	3.179(7)

Table 2. Crystal data and details of measurements for $2[1H]^{2+}\cdot4[PF_6]^-\cdot H_2O$, $[1H]^{2+}\cdot[PF_6]^-\cdot1/2[fumarate]^{2-}$, $[1H_2]^{3+}\cdot[PF_6]^-\cdot[H(fumarate)_2]^{3-}\cdot H_3O^+\cdot H_2O$, $2[1H]^{2+}\cdot5/2[PF_6]^-\cdot3/2[Hmaleate]^-$, $2[1H_2]^{3+}\cdot3[PF_6]^-\cdot3[Hmaleate]^-\cdot2H_2O$ and $[1H_2]^{3+}\cdot2[PF_6]^-\cdot[Hmaleate]^-\cdot H_2O$

compound	$2[1H]^{2+}\cdot4[PF_6]^-\cdot H_2O$	$[1H]^{2+}\cdot[PF_6]^-\cdot1/2[fumarate]^{2-}$	$[1H_2]^{3+}\cdot[PF_6]^-\cdot[H(fumarate)_2]^{3-}\cdot H_3O^+\cdot H_2O$	$2[1H]^{2+}\cdot5/2[PF_6]^-\cdot3/2[Hmaleate]^-$	$2[1H_2]^{3+}\cdot3[PF_6]^-\cdot3[Hmaleate]^-\cdot2H_2O$	$[1H_2]^{3+}\cdot2[PF_6]^-\cdot[Hmaleate]^-\cdot H_2O$
formula	$C_{44}H_{40}Co_2F_{24}N_8O_5P_4$	$C_{24}H_{20}CoF_6N_4O_4P$	$C_{30}H_{30}CoF_6N_4O_{12}P$	$C_{50}H_{41.50}Co_2F_{15}N_8O_{10}P_{2.5}$	$C_{56}H_{53}Co_2F_{18}N_8O_{18}P_3$	$C_{26}H_{25}CoF_{12}N_4O_7P_2$
M_r	1458.58	632.34	482.48	1394.70	1678.83	854.37
system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
space group	$P2_1/c$	$P2_1/n$	P-1	P-1	P-1	$P2_1/a$
a [Å]	23.468(2)	7.9833(3)	7.583(7)	10.6826(5)	12.7015(8)	13.1655(4)
b [Å]	15.373(1)	29.284(1)	13.552(5)	14.2849(7)	14.6608(9)	12.7040(4)
c [Å]	15.304(1)	10.5411(4)	16.526(4)	19.6711(9)	19.758(1)	19.7122(6)
α [°]	90	90	89.38(2)	95.080(1)	70.667(1)	90
β [°]	92.714(3)	90.836(1)	84.90(4)	104.807(1)	86.814(1)	97.7600(10)
γ [°]	90	90	80.66(5)	107.763(1)	70.147(1)	90
V [Å³]	5515.1(7)	2464.1(2)	1669(2)	2718.2(2)	3258.7(3)	3266.8(2)
Z	4	4	2	2	2	4
T [K]	293	293	293	273	293	293
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.852	0.848	1.676	0.802	0.712	1.737
measured reflns	63612	23263	13537	26312	38487	25629
unique reflns	16083	5369	5844	9654	15238	5745
refined parameters	823	372	471	782	970	463
GOF on F²	1.018	0.885	1.010	1.074	0.823	1.024
R1 [on F, $I > 2\sigma(I)$]	0.0641	0.0611	0.0648	0.0550	0.0543	0.0656
$wR2$ (on F^2,all data)	0.2342	0.1832	0.1392	0.1758	0.1576	0.2010

4. Mechanochemical and solution preparation of the coordination polymers $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot5H_2O$ and $Zn[N(CH_2CH_2)_3N]Cl_2$

a. Introduction

Mechanochemical methods based on co-grinding or milling of reactants have been shown to provide viable routes for the synthesis of novel molecular compounds.[1] Recently, mechanochemical methods have also been utilized in the field of crystal engineering.[2] The basic idea is that of breaking and forming supramolecular interactions with no need for the intermediacy of a solvent. Under this point of view solvent-free reactions between or within molecular crystals can be regarded as a *green way* to crystal engineering.[3] Even though mechanochemical reactions have often been used in the preparation of molecular materials,[4,5] they have mainly been exploited for the alloying of metals with ceramics, the activation of minerals for catalysis, and other inorganic materials applications.[6,7] It is worth mentioning that, in general, the powdered products obtained by co-grinding do not permit a straightforward determination of the structural features, of the type obtainable from single crystals. The problem can often be circumvented by growing crystals of the desired phase *via seeding*, *i.e.* by using pre-formed micro-crystals, in the form of crystalline powder, obtained by grinding.[8] Seeding procedures are commonly employed in pharmaceutical industries to guarantee formation of the desired crystal form.[9] If single crystals are obtained *via seeding*, it is possible to verify *a posteriori* whether the material obtained from solution crystallization and that yielded by solid–solid processes possess the same structure, by comparing the observed powder diffraction pattern with that computed on the basis of the single crystal structure. This approach has previously been used by us and by others to determine the structure of polycrystalline products obtained by "non-solution" methods (grinding, dehydration, thermal treatment).[10] It is important to stress that crystallization from solution does not always yield the same product as is obtained by mechanical treatment. This is particularly relevant in those cases where crystallization from solution is under kinetic control, and leads to crystallization of those species that nucleate first and form less soluble nuclei, or to formation of solvate species that are not obtained by solid-state methods.

In Bologna, we have exploited mechanochemical processes in the preparation of a series of organic and hybrid organic–organometallic hydrogen bonded network compounds.[11] We have also reported recently the solid–solid preparation of hybrid organometallic–inorganic salts, obtained by reacting the organometallic zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ with a number of alkali salts MX ($M = K^+, Rb^+, Cs^+, NH_4^+$; $X = Cl^-, Br^-, I^-, PF_6^-$).[12]

Herein we report our preliminary results of the solid state co-grinding of the transition metal salts $AgCH_3COO$ and $ZnCl_2$ with the bidentate *divergent* ligand 1,4-diazabicyclooctane, $[N(CH_2CH_2)_3N]$. This base has been widely exploited in crystal engineering both in the formation of hydrogen bonded adducts and in the formation of coordination networks.[13] We report that the coordination polymer $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot 5H_2O$ has been obtained by solid-state co-grinding in the air of silver acetate and $[N(CH_2CH_2)_3N]$ (1:2). When $ZnCl_2$ is used instead, rather than $AgCH_3COO$ in a 1:1 reaction with $[N(CH_2CH_2)_3N]$, the solution and solid-state products are different. The former product has been identified on the basis of single crystal X-ray diffraction as the Zn-based coordination polymer $Zn[N(CH_2CH_2)_3N]Cl_2$. The product of the grinding process, characterized only by X-ray powder diffraction, converts, on prolonged grinding, into the same phase as obtained *via* reaction in solution, *i.e.* $Zn[N(CH_2CH_2)_3N]Cl_2$.

b. Results and discussion

The two preparations, both as solid–solid and as solution reactions, have been studied together and will be discussed below. When silver acetate and $[N(CH_2CH_2)_3N]$, in a 1:2 ratio, are manually ground together in an agate mortar, the compound $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot 5H_2O$, 1, is obtained quantitatively. However, the chemical formula could only be defined after collecting single-crystal X-ray data on crystals obtained by slow evaporation of a water–methanol (1:1) solution. We shall first describe the coordination network identified from the single-crystal data. Fig. 1 shows that the basic network in $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot 5H_2O$ is built around a chain of $Ag^{(+)}$–$[N(CH_2CH_2)_3N]$–$Ag^{(+)}$–$[N(CH_2CH_2)_3N]$–$Ag^{(+)}$ units, with each silver cation carrying an extra pendant $[N(CH_2CH_2)_3N]$ ligand and a metal-coordinated water molecule. In this way the coordination geometry around the Ag^+ cation can be described as tetrahedral. The acetate anions participate in the hydrogen bonding network, involving the bound metal as well as the remaining four water molecules of crystallization, with formation of a layered structure, as depicted in Fig. 2a. The pendant base unit also accepts hydrogen bond formation from a water molecule [$O(5)\cdots N(2)^{IV}$ 2.805(5) Å], as shown in Fig. 2b. The role of the water molecules is quite clear: the structure of compound 1 contains a large number of potential hydrogen bonding acceptor atoms (the "free" N terminus on the base and the two oxygen atoms of the acetate anion) and no hydrogen bonding donor. It is thus not surprising that this material takes up water from air during grinding and crystallizes with water molecules from solution.

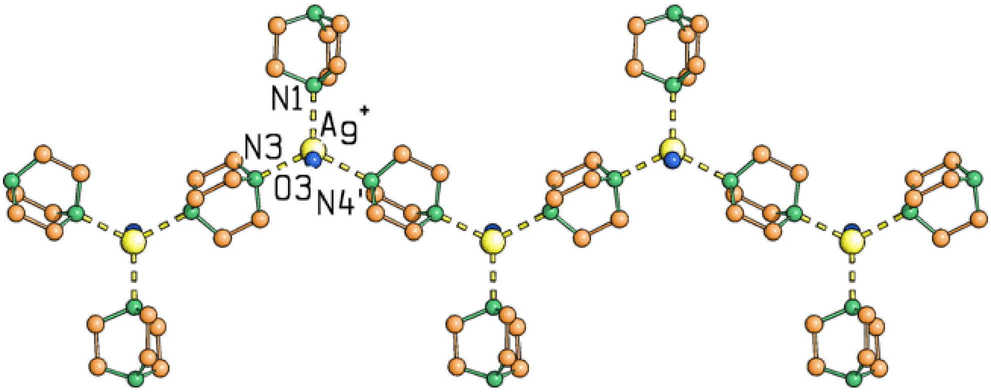


Fig. 1 *The coordination network in* $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot 5H_2O$. *Note the chain of* $Ag^{(+)}$–$[N(CH_2CH_2)_3N]$–$Ag^{(+)}$–$[N(CH_2CH_2)_3N]$–$Ag^{(+)}$ *with each silver cation carrying an extra pendant* $[N(CH_2CH_2)_3N]$ *ligand and a coordinated water molecule in tetrahedral coordination geometry. H atoms not shown for clarity. [Symmetry operator for N(4)': –x, y– 1/2, 1/2 +z]. Click here to access a 3D image of Fig. 1.*

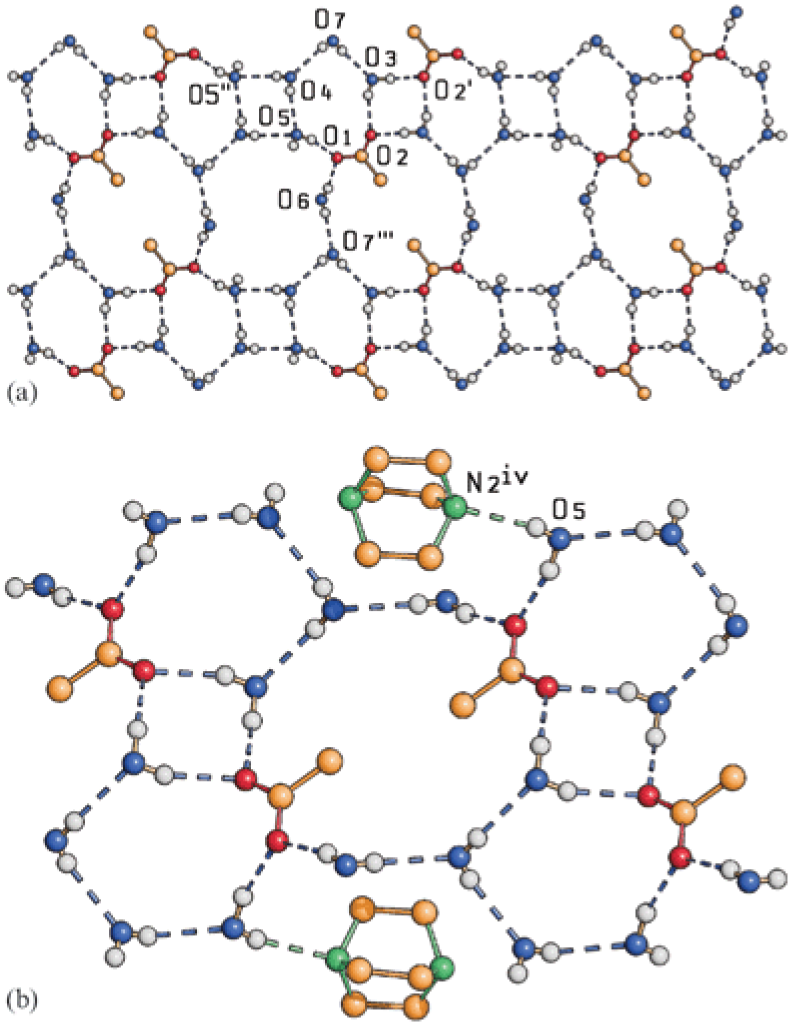


Fig. 2 *(a) The acetate anions in* $Ag[N(CH_2CH_2)_3N]_2[CH_3COO]\cdot 5H_2O$ *participate in the hydrogen bonding network together with the metal bound water molecule and the four water molecules of crystallization. (b) The* $[N(CH_2CH_2)_3N]$ *moiety is involved in a hydrogen bonding interaction with a water molecule* $[O(5)\cdots N(2)^{IV}\ 2.805(5)\text{Å}]$. H_{CH} *atoms not shown for clarity.*

The Ag–N distances in 1 are of comparable length [Ag(1)–N(3) 2.322(3), Ag(1)–N(4)′ 2.334(3), Ag(1)–N(1) 2.345(4) Å], while the silver–water Ag(1)–O(3) bond is longer, 2.630(3) Å. In terms of hydrogen bonds one can see from Fig. 2 that the four "independent" water molecules form a classic tetrameric ring with O···O separations of 2.808(5) (O4–O5) and 2.886(5) (O4–O5″) Å. Another tetrameric hydrogen bonded ring is formed between two acetate anions and two water molecules [O(2)···O(3) 2.792(6), O(2)′···O(3) 2.701(5) Å]. In Table 1 are listed all relevant hydrogen bonding interactions involving acetate and water oxygen atoms. As mentioned above, the preparation of single crystals of 1 was instrumental to the determination of the nature of the product. It was in fact possible, once the structure of 1 had been established, to compare the powder diffraction pattern computed on the basis of the single-crystal structure with the one measured on the product of solid-state preparation. Fig. 3 shows the close correspondence of the two diffractograms.

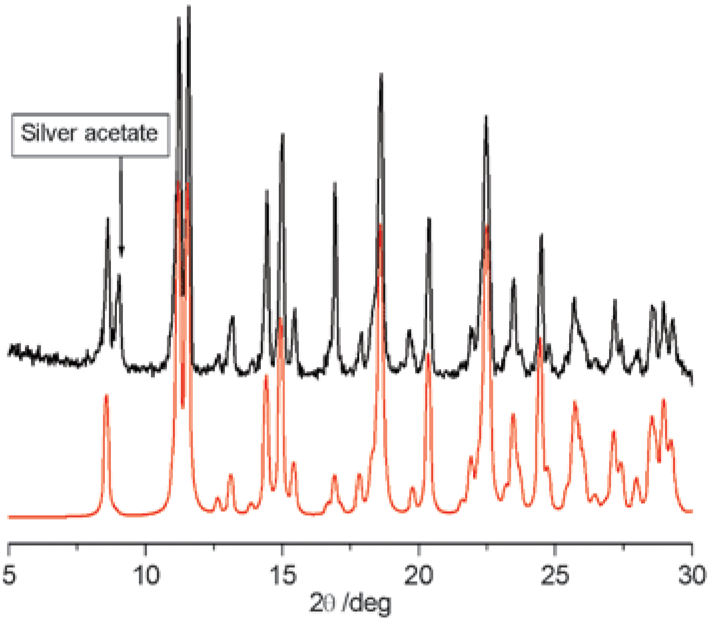


Fig. 3 *Comparison between the powder diffractograms calculated (bottom) on the basis of the single-crystal structure and that measured (top) on the ground sample of 1. A trace of unreacted silver acetate (marked with an arrow) can be detected.* *j*

Table 1 Relevant hydrogen bonding parameters for 1

Interaction	O–H (Å)	H···O (Å)	O···O (Å)	O–H···O (deg)	Operators for generating equivalent atoms
O(3)–H(301)···O(2)^{i}	0.91	1.81	2.701(5)	167	$x, 1/2 - y, -1/2 + z$
O(3)–H(302)···O(2)	0.81	2.01	2.792(6)	162	
O(4)–H(401)···O(5)^{ii}	0.74	2.15	2.886(5)	174	$-x, -1/2 + y, 1/2 - z$
O(4)–H(402)···O(5)	0.65	2.18	2.808(5)	162	
O(5)–H(501)···O(1)	0.87	1.90	2.749(5)	164	
O(6)–H(601)···O(7)^{iii}	0.74	2.10	2.818(7)	164	$1 - x, 1/2 + y, 1/2 - z$
O(6)–H(602)···O(1)	0.74	2.05	2.774(6)	165	
O(7)–H(701)···O(3)	0.74	2.11	2.827(7)	165	
O(7)–H(702)···O(4)	0.61	2.18	2.770(7)	166	
O(5)–H(502)···N(2)^{iv}	0.74	2.11	2.805(5)	158	$1 - x, 1 - y, 1 - z$

The same solid-state and solution experiments used to obtain 1 have been carried out with a number of other salts. The only other successful experiment, thus far, has been with $ZnCl_2$. Single crystals of $Zn[N(CH_2CH_2)_3N]Cl_2$, 2sc, (see below) have been obtained by layering a solution of $ZnCl_2$ in methanol over a solution of $[N(CH_2CH_2)_3N]$ in CH_2Cl_2. The structure of 2sc is based on a one-dimensional coordination network constituted of alternating $[N(CH_2CH_2)_3N]$ and $ZnCl_2$ units, joined by Zn–N bonds.

The Zn^+ cation, as in 1, possesses a tetrahedral coordination geometry (see Fig. 4). The metal–ligand distances are Zn(1)–Cl(1) 2.219(1), Zn(1)–N(1) 2.076(5), Zn(1)–N(2)^{ii} 2.086(5) Å. The coordination polymer in 2sc bears some resemblance to the coordination polymer in 1, both being based on an alternating sequence of metal and di-nitrogen base, the main difference arising from the necessary presence of a counterion in 1, which brings about the network of hydrogen bonds involving water molecules, as described above.

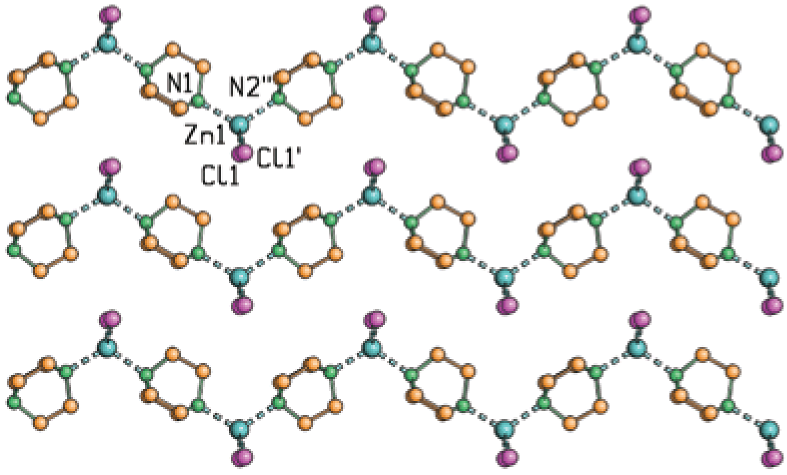


Fig. 4 *The one-dimensional coordination network present in crystals of* $Zn[N(CH_2CH_2)_3N]Cl_2$*2sc as obtained from solution crystallization. H atoms not shown for clarity. [Symmetry operators for Cl(1)' and N(2)'': x, y, 1/2 –z and –x– 1/2, y– 1/2, 1/2 –z, respectively.]*

Upon co-grinding of the solid reactants a new compound 2pw is obtained as a powder material. Powder diffraction clearly indicates that 2pw does not bear any relationship with the starting solid materials $ZnCl_2$ and $[N(CH_2CH_2)_3N]$, except for the presence of traces of the two reactants. However, all attempts to obtain single crystals of compound 2pw have failed, due to either hydrolysis of the compound, once dissolved, or to precipitation of compound 2sc even if *seeds* of 2pw are used. However, a relationship can be found between the compound obtained initially by co-grinding and the one obtained from solution. The phase 2pw can be transformed into phase 2sc by vigorous and prolonged‡ (at least 10 min) manual grinding. See Fig. 5 for a comparison of powder diffraction patterns.

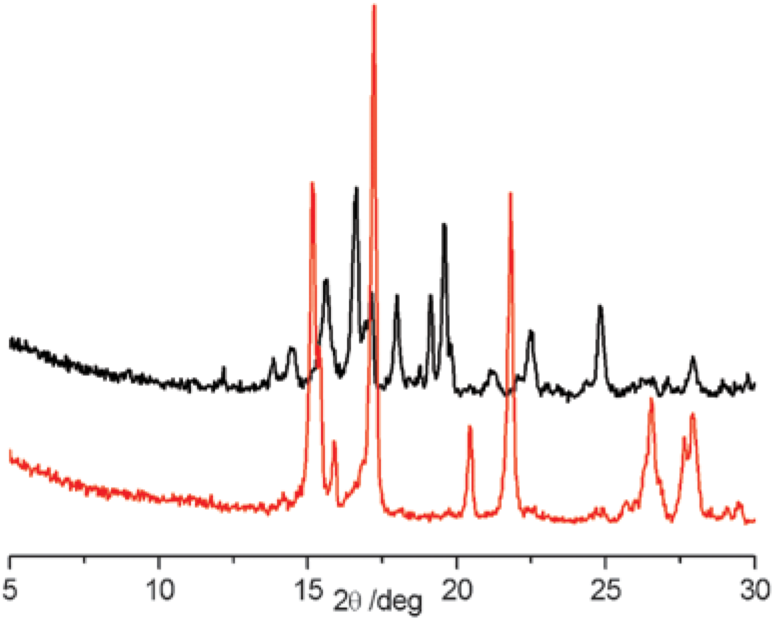


Fig. 5 *The powder diffraction patterns measured on 2pw as obtained by initial co-grinding (top) and the diffraction pattern measured after 10 min of vigorous grinding of 2pw(bottom).*

Table 2 Crystal data and details of measurements for 1 and 2sc

	1	*2sc*
Formula	$C_{14}H_{37}AgN_4O_7$	$C_6H_{12}Cl_2N_2Zn$
M_w	*481.34*	*248.45*
Crystal system	*Monoclinic*	*Orthorhombic*
Space group	$P2_1/c$	*Pbnm*
a/Å	*10.561(2)*	*6.606(2)*
b/Å	*12.782(3)*	*11.502(2)*
c/Å	*16.147(3)*	*11.680(2)*
α/°	*90*	*90*
β/°	*101.72(3)*	*90*
γ/°	*90*	*90*
$V/Å^3$	*2134.1(7)*	*887.5(3)*
Z	*4*	*4*
F(000)	*1008*	*504*
$\mu(\text{Mo K}\alpha)/mm^{-1}$	*0.984*	*3.304*
Measured reflns	*3192*	*935*
Unique reflns	*3031*	*807*
Parameters	*251*	*59*
GOF on F^2	*0.895*	*1.036*
R1 (on F $[I > 2\sigma(I)]$*)*	*0.0317*	*0.0320*
wR2 (on F^2*, all data)*	*0.0953*	*0.0819*

This latter powder diffractogram is compared in Fig. 6 with that calculated on the basis of the single-crystal structure of Zn[N(CH_2CH_2)$_3$N]Cl_2 2sc. Even though there are few peaks that can still be attributed to 2pw, the formation of phase 2sc is very clear.

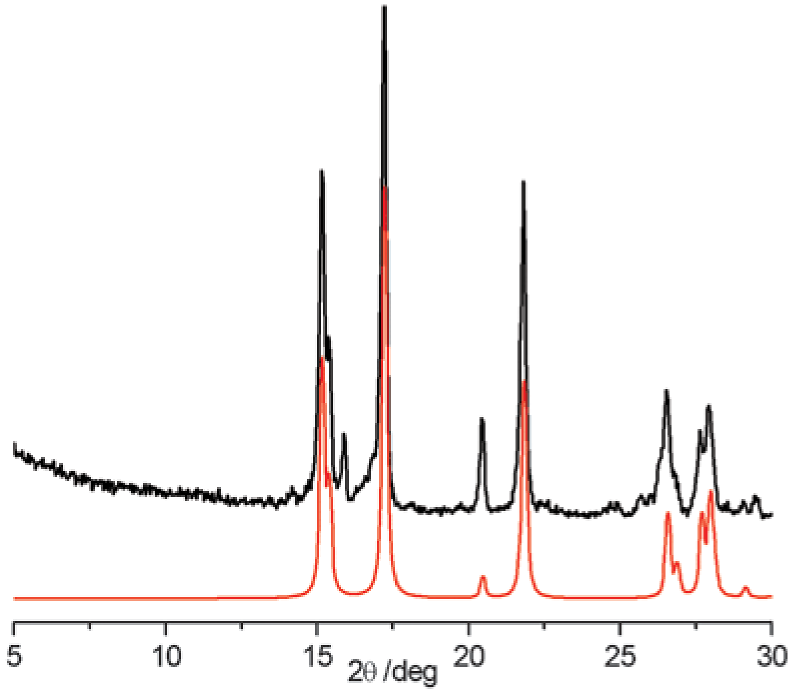


Fig. 6 *Comparison between the powder diffraction pattern measured on the co-grinding sample 2pw as obtained after vigorous manual grinding (10 min) and the diffraction pattern calculated on the basis of the single-crystal structure of Zn[N(CH_2CH_2)$_3$N]$Cl_2$2sc obtained from solution crystallization.*

At this stage, we can only speculate on the relationship between 2pw and 2sc. Since 2pw is obtained by grinding $N(CH_2CH_2)_3N$, which is always wet and difficult to dry because the base easily sublimes, we could envisage formation of a hydrated phase analogous to 1. Manual grinding of this phase would then extrude part of the water leading to formation of the anhydrous crystalline phase 2sc. We have confirmed this aspect by carrying out a thermogravimetric analysis (TGA) of compound 2pw. The experiment indicates that *ca*. 4 equivalents of water are retained in the crystal structure of the initial mechanochemical product (*e.g.*, 2pw). Furthermore, the powder recovered after TGA gives a diffractogram that corresponds precisely to that of 2sc, confirming that the dehydration product is the same as that obtained from reaction in solution (CH_3OH/CH_2Cl_2) or from extensive grinding of 2pw. Phase 2sc can also be obtained directly from the reactants $ZnCl_2$ and $N(CH_2CH_2)_3N$ if they are dried carefully prior to use and ground together in a glove bag.

c. Conclusions

In this paper, we have reported some initial successes in the solvent-free *mechanochemical* synthesis of coordination polymers. The method is based on the manual co-grinding of solid reactants. The reaction product is recovered in the form of a polycrystalline powder while single crystals, suitable for X-ray diffraction are obtained by conventional crystallization from solution assisted by *seeding*. Comparison between calculated and measured powder diffractograms allows identification of the products. In the case of the silver compound, the solution and solid-state treatments yield the same compound, while, in the case of zinc compound, the solution and solid-state treatment initially yield different products. The product of grinding undergoes a further transformation upon further mechanical treatment to yield, eventually, the unsolvated phase obtained from solution.

Besides those reported herein, there are not yet many examples of the utilization of mechanochemical procedures in coordination chemistry.[14,15] Balema *et al.* have shown that the *cis*-platinum complexes *cis*-$(Ph_3P)_2PtCl_2$ and *cis*-$(Ph_3P)_2PtCO_3$ can be prepared mechanochemically from solid reactants in the absence of solvent.[14*a,b*] Steed and Raston *et al.* have explored the use of mechanochemistry in the synthesis of extended supramolecular arrays.[15] Grinding of $Ni(NO_3)_2$ with 1,10-phenanthroline (phen) resulted in the facile preparation of $[Ni(phen)_3]^{2+}$ accompanied by a dramatic and rapid colour change. Addition of the solid sodium salt of tetrasulfonatocalix[4]arene (tsc) gives two porous π-stacked supramolecular arrays $[Ni(phen)_3]_2[tsc^{4-}]\cdot nH_2O$ and the related $[Na(H_2O)_4(phen)][Ni(phen)_3]_4[tsc^{4-}][tsc^{5-}]\cdot nH_2O$, depending on stoichiometry.[15*a*] Grinding copper(II) acetate hydrate with 1,3-di(4-pyridyl)propane gives a 1D coordination polymer with water-filled pores.[15*b*] In a recent study, Orita *et al.* have reported the supramolecular self-assembly of a number of two- or three-dimensional helicates.[16]

The approach developed in this paper shows promising results. Clearly, the interest in solid–solid processes, beside those related to green-chemistry aspects, is also in the possibility of obtaining products that cannot be obtained from conventional solution methods.

References

1 (*a*) G. W. V. Cave, C. L. Raston and J. L. Scott, *Chem. Commun.*, 2001, 2159; (*b*) G. Rothenberg, A. P. Downie, C. L. Raston and J. L. Scott, *J. Am. Chem. Soc.*, 2001, 123, 8701; (*c*) F. Toda, *CrystEngComm*, 2002, 4, 215; (*d*) G. Kaupp, *CrystEngComm*, 2003, 5, 117; (*e*) G. Kaupp, in *Comprehensive Supramolecular Chemistry*, vol. 8, ed. J. E. D. Davies, Elsevier, Oxford, 1996, pp. 381–423; (*f*) K. Tanaka and F. Toda, *Chem. Rev.*, 2000, 100, 1025 and references therein.

2 D. Braga, *Chem. Commun.*, 2003, 2751.

3 D. Braga and F. Grepioni, *Angew. Chem. Int. Ed.*, 2004, 43, 2.

4 See, for instance, (*a*) V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*, 1996, 987; (*b*) R. Kuroda, Y. Imai and N. Tajima, *Chem. Commun.*, 2002, 2848; (*c*) Y. Imai, N. Tajima, T. Sato and R. Kuroda, *Chirality*, 2002, 14, 604; (*d*) M. R. Caira, L. R. Nassimbeni and A. F. Wildervanck, *J. Chem. Soc., Perkin Trans.*, 1995, 2, 2213; (*e*) R. Kuroda, Y. Imai and N. Tajima, *Chem. Commun.*, 2002, 2848; (*f*) M. R. Caira, L. R. Nassimbeni and A. F. Wildervanck, *J. Chem. Soc., Perkin Trans.*, 1995, 2, 2213; (*g*) J. Schmeyers, F. Toda, J. Boy and G. Kaupp, *J. Chem. Soc., Perkin Trans.*, 1998, 2, 989.

5 (*a*) M. C. Etter, *J. Phys Chem.*, 1991, 95, 4601; (*b*) M. C. Etter, S. M. Reutzel and C. G. Choo, *J. Am. Chem. Soc.*, 1993, 115, 4411; (*c*) W. H. Ojala and M. C. Etter, *J. Am. Chem. Soc.*, 1992, 114, 10228; (*d*) a classical example of the "mortar and pestle" technique is the preparation of unsymmetrical substituted quinhydrones by co-grinding of quinone and hydroquinone, see A. O. Patil, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, 1984, 106, 348.

6 V. V. Boldyrev and K. Tkacova, *J. Mater. Synth. Proc.*, 2000, 8, 121 _.

7 (*a*) J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, 71, 581 _; (*b*) J. Fernandez-Bertran, J. Blanco Pascual, M. Hernandez and R. Rodriguez, *React. Solids*, 1988, 5, 95 _.

8 D. Braga and F. Grepioni, *Chem. Soc. Rev.*, 2000, 29, 229 _.

9 T. L. Threlfall, *Analyst*, 1995, 120, 2435 _.

10 (*a*) D. Braga, G. Cojazzi, A. Abati, L. Maini, M. Polito, L. Scaccianoce and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 2000, 3969 _; (*b*) N. Kubota, N. Doki, M. Yokota and D. Jagadesh, *J. Chem. Eng. Jpn.*, 2002, 35, 1063; (*c*) D. Braga, G. Cojazzi, D. Paolucci and F. Grepioni, *CrystEngComm*, 2001, 1 _; (*d*) D. Braga, L. Maini and F. Grepioni, *Chem. Commun.*, 1999, 937 _; (*e*) D. Braga, G. Cojazzi, L. Maini, M. Polito and F. Grepioni, *Chem. Commun.*, 1999, 1949 _.

11 (*a*) D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Commun.*, 2002, 24, 2960; (*b*) D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Eur. J.*, 2003, 9, 4362 _; (*c*) D. Braga, L. Maini, G. de Sanctis, K. Rubini, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem. Eur. J.*, 2003, 9, 5538 _.

12 (*a*) D. Braga, L. Maini, M. Polito and F. Grepioni, *Chem. Commun.*, 2002, 2302 _; (*b*) D. Braga, L. Maini, G. de Sanctis, K. Rubini, F. Grepioni, S. Giaffreda, M. R. Chierotti and R. Gobetto, *Chem. Eur. J.*, 2004, 13, 326.

13 (*a*) L. Brammer, M. D. Burgard, C. S. Rodger, J. K. Swearingen and N. P. Rath, *Chem. Commun.*, 2001, 2468 _; (*b*) L. Brammer, M. D. Burgard, M. D. Eddleston, C. S. Rodger, N. P. Rath and H. Adams, *CrystEngComm*, 2002, 4, 239 _; (*c*) L. Brammer, J. K.

Swearingen, E. A. Bruton and P. Sherwood, *Proc. Nat. Acad. Sci., U. S. A.*, 2002, 99, 4956 _; (*d*) L. Brammer, J. C. Mareque Rivas and D. Zhao, *Inorg. Chem.*, 1998, 37, 5512 _; (*e*) J. C. Mareque Rivas and L. Brammer, *Inorg. Chem.*, 1998, 37, 4756 _; (*f*) Dong Zhao, F. T. Ladipo, J. Braddock-Wilking, L. Brammer and P. Sherwood, *Organometallics*, 1996, 15, 1441 _.

14 (*a*) V. P. Balema, J. W. Wiench, M. Pruski and V. K. Pecharsky, *Chem. Commun.*, 2002, 1606 _; (*b*) V. P. Balema, J. W. Wiench, M. Pruski and V. K. Pecharsky, *Chem. Commun.*, 2002, 724 _; (*c*) A. Orita, L. Jiang, T. Nakano, N. Ma and J. Otera, *Chem. Commun.*, 2002, 1362 _; (*d*) W. J. Becker, C. A. Longstaff, M. R. Neckenig and J. W. Steed, *Chem. Commun.*, 2002, 1602 _.

15 (*a*) P. J. Nichols, C. L. Raston and J. W. Steed, *Chem. Commun.*, 2001, 1062 _; (*b*) W. J. Belcher, C. A. Longstaff, M. R. Neckenig and J. W. Steed, *Chem. Commun.*, 2002, 1602 _.

16 A. Orita, L. S. Jiang, T. Nakano, N. C. Ma and J. Otera, *Chem. Commun.*, 2002, 1362 _.

17 PowderCell programmed by W. Kraus and G. Nolze (BAM Berlin) © subgroups derived by Ulrich Müller (Gh Kassel).

18 (*a*) G. M. Sheldrick, SHELXL97, *Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, 1997; (*b*) E. Keller, SCHAKAL99, *Graphical Representation of Molecular Models*; University of Freiburg, Germany, 1999; (*c*) A. L. Speck, *Acta Crystallogr., Sect. A*, 1990, 46, C34; (*d*) A. L. Speck, PLATON – *A multipurpose crystallographic tool*, Utrecht University, Utrecht, The Netherlands, 2002

5. Making crystals from crystals: three solvent-free routes to the hydrogen bonded co-crystal between 1,1'-di-Pyridil-Ferrocene and Anthranilic Acid

a. Introduction

Solvent-free reactions, such as the mechanical mixing of solid reactants, often provide fast and quantitative routes to the preparation of novel organic and inorganic compounds.[1-3] In recent years, under the impetus of crystal engineering,[4] solvent-free processes have begun to be investigated for the preparation of crystalline materials.[5,6] The number of papers reporting preparation of molecular co-crystals,[7] coordination networks,[8] salts,[9] as well as the investigation of polymorphs[10] is increasing rapidly. Beside inter-crystal reactions, those occurring in the solid state, such as cycloadditions,[11] and many other organic reactions[12] have been the subject of successful investigations. Undoubtedly, the number of reactions and processes that can be carried out in the solid state is enormous and the statement that "all (organic) reactions can be conducted in solvent free conditions" is largely justified.[13]

We have reported a large number of cases where preparation of hydrogen-bonded co-crystals has been achieved by simple grinding of the solid reactants.[14] However, the nature of the processes leading from reagents to products is not fully understood because the experimental conditions are not completely under control. For instance, it is difficult to estimate the extent of thermal effects associated with sheering and pressuring during manual or mechanical co-grinding. Furthermore, ambient humidity or intentional *kneading*, viz. the use of a micro quantity of solvent, can play a crucial role for the occurrence of the reaction.

In order to gain insight into these aspects we have chosen as a benchmark case the preparation of the 1:1 hydrogen bonded co-crystal $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[(C_6H_4)NH_2COOH]\}_2$. The compound has been obtained from the solid-state reaction of crystalline $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ and anthranilic acid. It is worth recalling that the starting reactant $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ can also be prepared in solvent-free conditions.[15]

Anthranilic acid was chosen also because it is known to exist in three polymorphic modifications,[16] with the so called form I and form II thermally interconverting at ca. 90 °C. Importantly, the mechanically induced conversion of form I into II by grinding had been investigated by Etter,[17] while Shan and co-workers have found several new kneading ways for the interconversion among the three known forms.[16d]

We have made use of a multi-technique approach for the investigation of the solid state reactions products, which have been characterized via a complementary use of both single-crystal and powder X-ray diffraction, solid-state NMR spectroscopy and DSC analysis.

b. Results and Discussion

The initial solid-state preparation was carried out by manual grinding in an agate mortar of equimolar quantities of the two solid materials. In order for the reaction to take place, *kneading* was required, i.e. a drop of MeOH was added during workup. For anthranilic acid the most stable form I was used. After grinding, the polycrystalline material was used as such for powder diffraction experiments. In a separate experiment, equimolar quantities of acid and base were dissolved in methanol and the solvent was allowed to evaporate at a temperature of 5°C. By comparison with the diffractograms measured on the raw reactants, it was possible to ascertain that in both cases the starting material had been fully converted into the product. Methanol (99.8%) was used to grow single-crystals of the co-crystal for the X-ray diffraction experiment. The structure determined from the single crystal experiment (see below) was in turn used to calculate the reference powder diffraction pattern. In the crystal structure the hydrogen bond interactions (Figure 1) show that anthranilic acid molecules act as bridges between the organometallic molecules, which are in a *cisoid* (eclipsed) conformation.

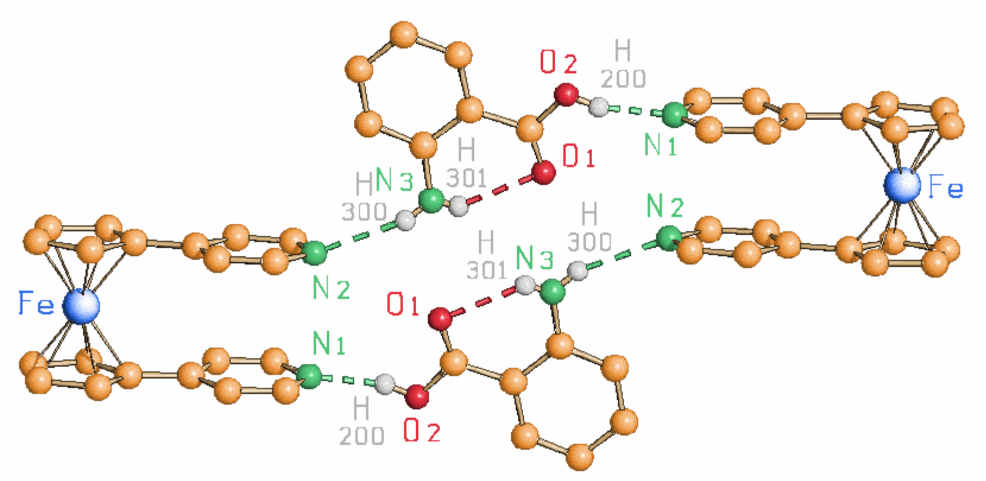


Figure 1. *The anthranilic acid molecules bridge together two organometallic sandwich molecules [H_{CH} atoms not shown for clarity].*

The complex can be described as a supramolecular macrocycle whereby two $(C_6H_4)NH_2COOH$ molecules and two $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ complexes are joined by alternate O-H···N and N-H···N hydrogen bonding interactions. This is the most common arrangement for co-crystals involving two $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ molecules and polyprotic acid units, although the alternative geometry based on an infinite acid-base hydrogen bonded network has been observed in at least one case.[18] On the basis of the single crystal X-ray structure, it appears that the hydrogen atoms are ordered along the hydrogen bonds with the formation of three hydrogen bonding interactions, e.g. an intermolecular O-H···N [N(1)···O(2) 2.609(7) Å], an intramolecular O-H···N

[N(3)···O(1) 2.718(9) Å] and an N···H-N interaction [N(2)···N(3) 3.079(10) Å]. This description of the hydrogen bonds, together with the structural information on the C-O and C=O distances, indicate that proton transfer from the acid to the base does not take place (see below) and that the compound is better described as a neutral hydrogen bonded adduct than a salt. Figure 2 shows a comparison between the X-ray powder diffractogram of the ground polycrystalline product (top) and that calculated on the basis of the structure determined by single crystal X-ray diffraction (bottom). Even though the crystallinity of the sample of $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2][(C_6H_4)NH_2COOH]\}_2$ obtained *via* grinding is not high, all significant peaks can be easily recognized.

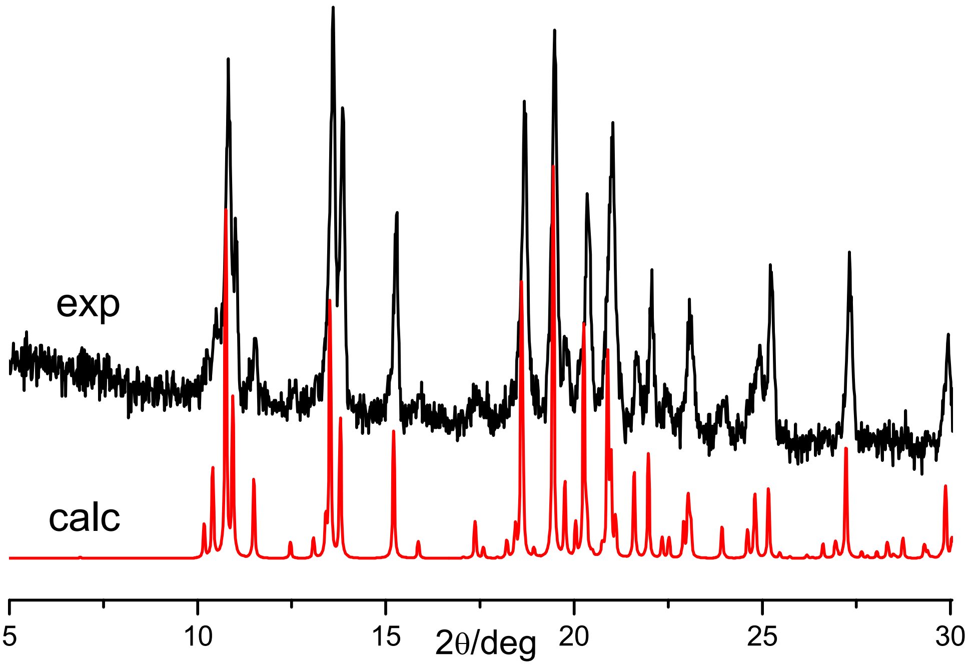


Figure 2. *{[Fe(η^5-C_5H_4-$C_5H_4N)_2$] [(C_6H_4)NH_2COOH]}$_2$ .Comparison between the X-ray powder diffractogram of the ground polycrystalline product (top) and that calculated on the basis of the structure determined by single crystal X-ray diffraction (bottom).*

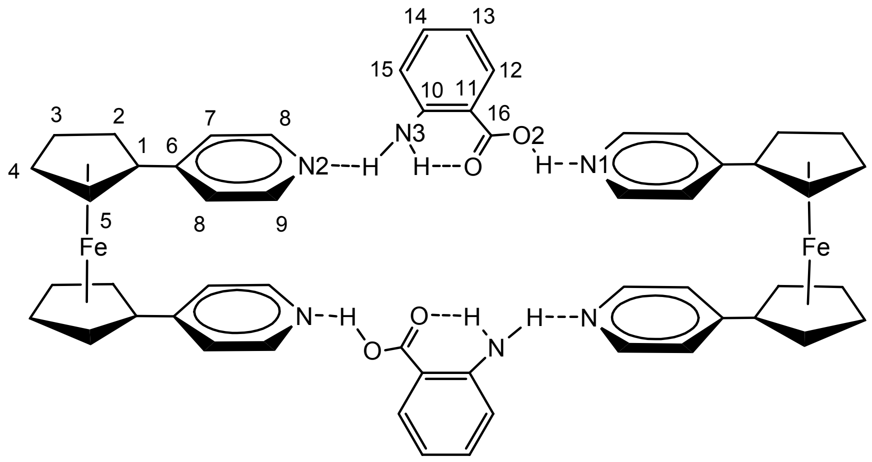
c. Solid state NMR characterization of the $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[(C_6H_4)NH_2COOH]\}_2$ co-crystal

All the NMR data are listed in Table 1 and the number of carbon atoms follows the numeration proposed in Scheme 1. The ^{13}C CPMAS spectrum of $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[(C_6H_4)NH_2COOH]\}_2$ (Figure 3) is characterized by the presence of a signal at 172.3 ppm attributed to the anthranilic COOH group (C16). The chemical shift value is typical of a carboxylic group, in agreement with the formation of an O-H···N interaction [N(1)···O(2) 2.609(7) Å] with no proton transfer from the acid to the nitrogen base. A similar chemical shift for this group (171.5 ppm) has been previously observed by Harris and Jackson for the neutral molecule present in the form I of the free acid, confirming the presence of a COOH instead of a COO^- group.[19]

The pyridine and the anthranilic aromatic carbon resonances fall in the range between 154 and 113 ppm. The complete assignment is reported in Table 1. It is worth noting that it was possible to detect by ^{13}C NQS experiment two quaternary carbons (C6 and C6’) for the pyridine moiety at 147.0 ppm and at 144.2 ppm. This is due to the presence of two different hydrogen bonds formed between pyridine and anthranilic acid, i.e. the O-H···N [N(1)···O(2) 2.609(7) Å], and the N···H-N interaction [N(2)···N(3) 3.079(10) Å]. The difference in hydrogen bonding induces differences in the pyridine rings of the same $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ moiety. This is confirmed also by the ^{15}N CPMAS spectrum (Figure 4), which shows two signals for the nitrogen pyridine atoms at 276.9 and at 243.1 ppm assigned to the nuclei involved in the N(2)···N(3) and N(1)···O(2) interactions, respectively. Considering the chemical shift value of the nitrogen atom in the pure pyridine (293.8 ppm) and the influence of the hydrogen bond, the observed shifts of 16.9 and 50.7 ppm are in agreement with a weak N···N interaction and with a stronger N···O hydrogen bond interaction, respectively.

This difference affects also the Cp rings, which, in fact, show two signals for the C1 and C1' carbons (82.4 and 81.3 ppm) and two resonances for the other Cp atoms at 71.7 and 67.2 ppm attributed to C2, C2', C5, C5' and to C3, C3', C4, C4', respectively.

By comparing our results with the chemical shifts reported by Harris et al. for the free known forms, we can argue that in the $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[(C_6H_4)NH_2COOH]\}_2$ adduct the acidic moiety is in a neutral form similar to that of polymorph I. The only remarkable difference is observed for the C10 carbon atom, whose peak shifts from 148 ppm (free acid) to 153.3 ppm (adduct). This is probably due to the different hydrogen bonding environment around the amine moiety in the adduct with respect to the free acid. In the former two hydrogen bonds are present (N(2)-N(3)$_{inter}$ (3.079 Å) and N(3)-O(1)$_{intra}$ (2.718 Å,)), while in the latter three hydrogen bonds are involved (O-N$_{intra}$ (2.688 Å,), N-N$_{inter}$ (2.872 Å) and O-N$_{inter}$ (2.894 Å)). The different HB network greatly influences the ^{15}N chemical shift of the amine nitrogen N(3), with a ^{15}N resonance at 45.3 ppm for the NH_2 group (Figure 4) shifted to higher frequencies by about 23.7 ppm with respect to that of the pure anthranilic acid (form I, neutral molecule).



Scheme 1

Table 1. ^{13}C and ^{15}N NMR data for $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2][(C_6H_4)NH_2COOH]\}_2$. For the assignment we followed the carbon numeration shown in Scheme 1.

δ ^{13}C / ppm	Note	δ ^{15}N / ppm	Note
172.3	C16	276.9	**N2**-H···N3
153.9	C10	243.1	**N1**···H-O2
151.0	C8	45.3	**N3**H_2
148.8	C8’		
147.0	C6, C9, C9’		
144.2	C6’		
132.5	C12, C14		
122.1	C7, C8		
119.7	C13, C7’		
116.8	C15, C8’		
113.8	C11		
82.4	C1		
81.3	C1’		
71.7	C2, C5, C2’, C5’		
67.2	C3, C4, C3’, C4’		

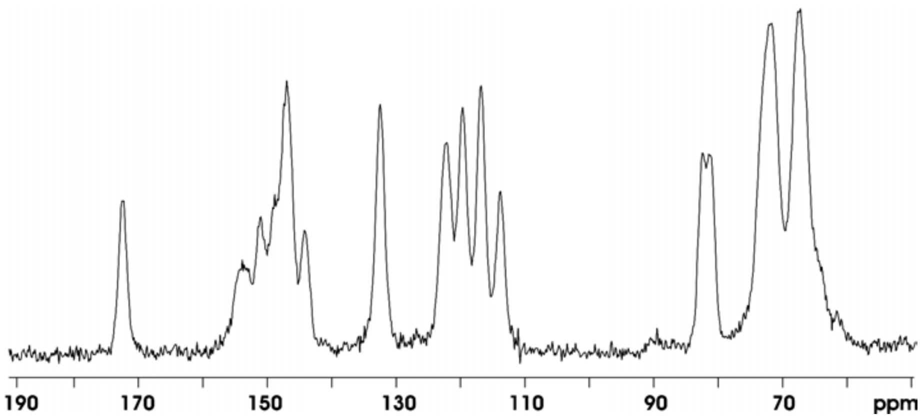


Figure 3. *^{13}C CPMAS NMR spectrum of the co-crystal {[Fe(η^5-C_5H_4 $C_5H_4N)_2$]· [(C_6H_4)NH_2COOH]}$_2$ recorded at 5.5 kHz.*

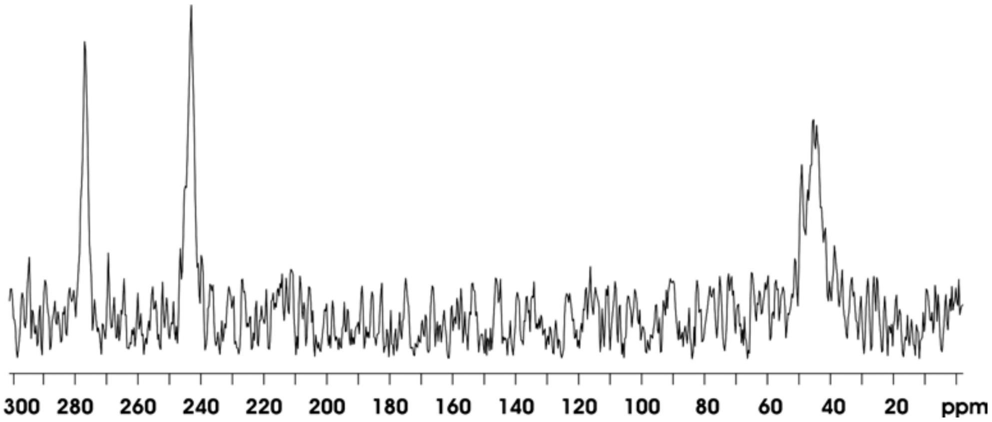


Figure 4. ^{15}N CPMAS NMR spectrum of the co-crystal {[Fe(η^5-C_5H_4-$C_5H_4N)_2$]· [(C_6H_4)NH_2COOH]}$_2$ recorded at 5.0 kHz.

d. Alternative solvent-free preparations of the co-crystal $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[(C_6H_4)NH_2COOH]\}_2$

In order to gain insight on the factors controlling the process leading to formation of the supramolecular macrocycle $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[(C_6H_4)NH_2COOH]\}_2$, we attempted its preparation in different ways, as detailed in the following:

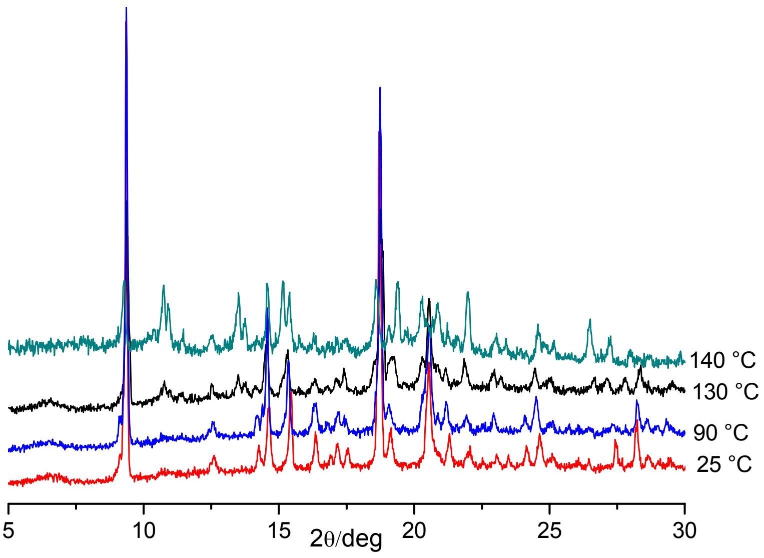
(i) *Dry compression.* Carefully dried powdered samples of anthranilic acid, form I, and of $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ were gently mixed together at room temperature. An X-ray powder diffractogram showed that no reaction had taken place. The sample was then pressed in an IR pellet maker. The resulting pellet was then ground and subjected to an X-ray measurement. The resulting superimposition of the two reactants powder patterns showed that no reaction had taken place.

(ii) *Wet compression, viz. solvent drop and compression.* The same experiment was repeated with the addition of a drop of MeOH to the mixture before compression. The XRPD pattern showed formation of the compound $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\ [(C_6H_4)NH_2COOH]\}_2$, thus indicating that the tiny amount of solvent was necessary for the reaction to take place.

(iii) *"Digestion" in the presence of solvent vapour.* The same reaction was carried out by placing an equimolar mixture of anthranilic acid and ferrocenyl complex in a closed beaker containing MeOH vapour and leaving the reactants in the MeOH atmosphere. After 5 days, the change of colour, from orange-red to purple indicated formation of the compound $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\ [(C_6H_4)NH_2COOH]\}_2$, which was then ascertained by powder diffraction. The important role of solvent vapours in increasing the efficiency of a solid state reaction was also reported by Toda et al.[1h]

(iv) *Thermally induced reaction*. Finally, the reaction between anthranilic acid and $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ was carried out by heating the mixture of reactants directly under X-ray diffraction conditions. The process was also analysed by differential scanning calorimetry, which shows that the polymorphism of anthranilic acid does not play any significant role, because transition from form I to form II takes places in the heating process at 90°C.

The thermally induced reaction experiment requires a more detailed description of the results. Figure 5a shows the variation with temperature of the powder diffraction patterns collected on a static mixture of the reactants from 25°C to 140°C. It can be seen that, on increasing the temperature to ca. 130 °C, peaks of the product start to appear, and they are evident at 140°C (which corresponds to the melting point of anthranilic acid), viz. the reaction occurs between a crystalline solid and a melt. Figure 5b shows a comparison between the room temperature pattern after reaction and the calculated pattern.



(a)

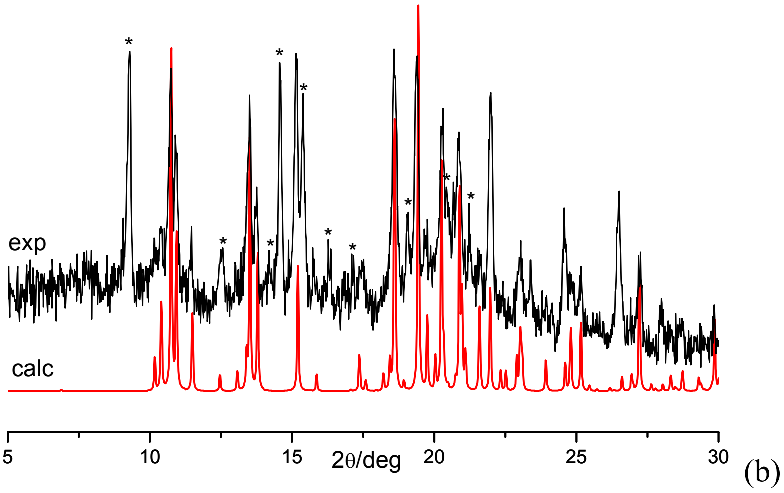


Figure 5. *Thermally induced reaction of a mixture of solid [Fe(η^5-C_5H_4-$C_5H_4N)_2$] and [(C_6H_4)NH_2COOH]. X-ray diffraction patterns were collected on a static mixture of the reactants from 25 to 140°C. (a) The variation with temperature of the XRPD pattern. (b) Comparison between (top) the experimental pattern measured at room temperature after the reaction and (bottom) the calculated one. Partial sublimation of the anthranilic acid prevents completeness of the reaction, as indicated by the presence of unreacted [Fe(η^5-C_5H_4-$C_5H_4N)_2$] (starred peaks).*

The previous reaction was also conducted in a glass vial immersed in an oil bath, in order to show that the reaction can be visually detected. Solid [Fe(η^5-C_5H_4-$C_5H_4N)_2$] and [(C_6H_4)NH_2COOH] are orange and white, respectively, at room temperature, while the colour of the product is purple. Figure 6 shows the glass vial at room temperature and after the bath temperature has reached 143°C.

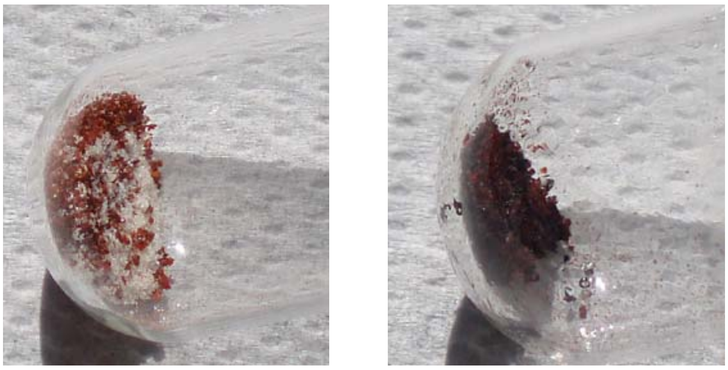


Figure 6. *The orange-white mixture of solid reagents (left) and the purple solid product (right) can be visually appreciated if the thermally induced reaction is carried out in a glass vial.*

In summary, *kneading* (i.e. manual grinding of a wet mixture), *wet compression* and *vapour digestion* achieve the same result as the static heating of the reactants and lead to formation of the product $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\,[(C_6H_4)NH_2COOH]\}_2$, while *dry compression* and *dry grinding* do not. Altogether, these experiments indicate that the process leading from solid anthranilic acid and solid $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ to the co-crystal can be more appropriately described as a solvent-free, rather than a solid-state reaction because, in order to occur, it requires either the intervention of a solvent, albeit in *catalytic* amount, or that one of the reactants is in the liquid state.

e. Conclusions

In this paper we have reported that solid $[Fe(\eta^5-C_5H_4-C_5H_4N)_2]$ reacts with the anthranilic acid $(C_6H_4)NH_2COOH$ to generate the hydrogen bonded supramolecular macrocycle $\{[Fe(\eta^5-C_5H_4-C_5H_4N)_2][(C_6H_4)NH_2COOH]\}_2$. The product has been characterized by means of X-ray powder diffraction, ^{13}C and ^{15}N solid-state NMR and of single crystal X-ray diffraction. Both spectroscopic and diffraction experiments concurs to indicate that no protonation of the organometallic molecule takes place so that the overall structure can be described as formed of a supramolecular macrocycle where two neutral anthranilic acid molecules link together two ferrocenyl units via O-H···N hydrogen bonds. This compound belongs to a family of supramolecular adducts of $[Fe(\eta^5-C_5H_4-C_5H_4N)_2]$ with organic acids, all obtained by mechanical mixing of the reactants.[18]

The focus of this study is, however, on the preparation conditions. Different mixing conditions of the solid reactants $[Fe(\eta^5-C_5H_4-C_5H_4N)_2]$ and $(C_6H_4)NH_2COOH$ have been tested with the aim of understanding the factors controlling product formation.

The results of the five experiments described above indicate that product formation is controlled by molecular diffusion. Molecular diffusion can be attained by grinding in the presence of "catalytic" amounts of solvent (*kneading* or *wet compression*), by exposing the dry mixture of reactants to vapours of the solvent (*solvent digestion*) or by thermal treatment. In this latter case, we have shown that one of the components, namely anthranilic acid, melts before reaction.

We would thus argue in favour of experimental conditions (grinding, kneading etc.) that can *assist* diffusion of the molecules of anthranilic acid in the lattice of the ferrocenyl complex. Clearly, once the reaction has occurred and the new supramolecular bonds between the organic and the organometallic molecules established, the new crystal phase needs to nucleate and grow as the remaining crystalline phase is destroyed. The driving force appears to be the formation of the hydrogen bonds between the anthranilic acid and the ferrocenyl complex, a highly favourable process because there are no strong hydrogen bonds in the crystals of the organometallic molecules while those in the organic crystals have been demolished by thermal treatment and/or by the intervention of methanol in a process of "local solvation". It can be correctly argued that these processes cannot be regarded as *bona fide* solid state reactions. Several authors in a number of relevant papers have shown that many reactions between solid reactants are not ultimately taking place in the solid state.[2] Such is the case of the process discussed in this report and very likely also that of many other reactions between solids described by us and by others. We would, however, tend to favour a liberal view of these processes because, even though they are not solid-state reactions, the reactants and the products are crystalline phases and the solvent, if present, is used in minimal quantity and acts only as a catalyst. These notions should help, *inter alia*, to develop a better understanding of solvent-free reactions (or *quasi* solvent-free) for the development of cheaper processes and for the benefit of the environment.

f. Experimental Section

Anthranilic acid was purchased from Sigma-Aldrich and used without further purification. Reagent grade solvents were used. *Synthesis of* $Fe[\eta^5\text{-}C_5H_4\text{-}1\text{-}(4\text{-}C_5H_4N)]_2$

The ferrocenyl derivative was prepared as previously reported. A solution of 4-bromopyridine hydrochloride (0.177 g, 0.91 mmol) in dioxane (6.5 mL) was stirred under nitrogen atmosphere with a solution of Na_2CO_3 (1M, 4.3 mL) to obtain the 4-bromo-pyridine. The solution was heated at 50°C for 30 min. $PdCl_2$[1,1'-bis(diphenilfosphino)ferrocene] (0.006 g, 0.007 mmol) was then added followed by ferrocene diboronic acid (0.100 g, 0.37 mmol) and NaOH (3M, 0.24 mL) in DME (3 mL). The solution was refluxed for 2 days, quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with NH_4Cl and water, dehydrated with Na_2SO_4 and concentrated. The crude product was purified by column chromatography CH_2Cl_2/MeOH (95:5) (yield 53%).

Solid-state preparation of $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\ [(C_6H_4)NH_2COOH]\}_2$. A stoichiometric 1:1 mixture of $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ and $(C_6H_4)NH_2COOH$ was manually ground in an agate mortar for 5 min and subjected to X-ray powder diffraction measurement (see below). A change in colour from orange-red to purple was also diagnostic of product formation. It is noteworthy that the same solid-state reaction carried out with an excess of either reactant invariably led to formation of a mixture of the same product and of the reactant in excess. Single crystals of $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2][(C_6H_4)NH_2COOH]\}_2$ suitable for X-ray diffraction were obtained by slow evaporation of a solution obtained dissolving $[Fe(\eta^5\text{-}Cp\text{-}C_5H_4N)_2]_2$ and $(C_6H_4)NH_2COOH$ in 5 mL of methanol 99.8%.

Solution synthesis of $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\ [(C_6H_4)NH_2COOH]\}_2$. $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ and $(C_6H_4)NH_2COOH$ were dissolved in stoichiometric amount in methanol 99.8% and stirred for 5 min. The solution colour changed from orange-red to purple. A polycrystalline product was then recovered after evaporation of the solvent to dryness. The nature of the product was confirmed by X-ray powder diffraction.

Digestion of $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\ [(C_6H_4)NH_2COOH]\}_2$ *in the presence of methanol vapour*. The compounds obtained from grinding reactions were exposed at room temperature to vapours of methanol (99,8%). After 7 days the diffraction pattern showed that crystallinity of all samples had improved.

Crystal structure determination. Crystal data were collected at room temperature on a Nonius CAD4 diffractometer. Crystal data and details of measurements are summarised in Table 2. Mo-Kα radiation, $\lambda = 0.71073$ Å, monochromator graphite. SHELX97[20a] was used for structure solution and refinement based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to N and O atoms were directly located from a Fourier difference map and refined, while the H_{CH} atoms were added in calculated positions. Data were corrected for absorption by azimuthal scanning of high-χ reflections. SCHAKAL99[20b] was used for the graphical representation of the results. The program PLATON[20c] was used to calculate the hydrogen bonding interactions. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Powder diffraction measurements: Powder diffraction for all samples was measured on a Philips PW-1100 automated diffractometer, CuKα, monochromator graphite, using quartz sample holders; for the pure reagents 30 mg of substance were employed. The program PowderCell 2.2[20d] was used for calculation of X-ray powder patterns on the basis of the single crystal structure determinations. Prolonged grinding of the compounds did not alter the diffraction patterns significantly.

Solid state NMR measurements: All ^{13}C and ^{15}N spectra were recorded on a JEOL GSE 270 equipped with a Doty probe operating at 67.8 MHz for ^{13}C and at 27.25 MHz for ^{15}N. A standard cross-polarization pulse sequence has been used with a contact time of 3.5 ms for ^{13}C and of 5 ms for ^{15}N, a 90° pulse of 4.5 ms, recycle delay of 10-15 s and a number of 600-4000 transients. Powdered samples were spun at 4-5 kHz at room temperature in a cylindrical 5 mm o.d. zirconia rotors with sample volume of 120 mL. The ^{13}C results are reported with respect to TMS assuming the hexamethylbenzene methyl peak is at 17.4 ppm. ^{15}N chemical shifts were referenced via the resonance of solid $(NH_4)_2SO_4$ (–355.8 ppm with respect to CH_3NO_2). For all samples the magic angle was carefully adjusted from the ^{79}Br spectrum of KBr by minimising the linewidth of the spinning sideband satellite transitions.

References

1. a) R. P. Rastogi, P. S. Bassi and S. L. Chadha, *J. Phys. Chem.*, 1963, **67**, 2569; b) R. P. Rastogi and N. B. Singh, *J. Phys. Chem.*, 1966, **70**, 3315; c) R. P. Rastogi and N. B. Singh, *J. Phys. Chem.*, 1968, **72**, 4446; d) A.O. Patil, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, 1984, **106**, 348; e) J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, **71**, 581; f) J. Fernandez-Bertran, J. C. Alvarez and E. Reguera, *Solid State Ionics*, 1998, **106**, 129; g) N. Shan, F. Toda and W. Jones, *Chem. Commun.* 2002, 2372; h) S. Nakamatsu, S. Toyota, W. Jones, F. Toda, *Chem. Commun*. 2005, 3808.

2. a) K. Tanaka and F. Toda, *Chem. Rev*., 2000, **100**, 1025; b) D. Braga and F. Grepioni, *Angew. Chem. Int Ed.*, 2004, **43**, 2; (c) D. Braga and F. Grepioni, in *Topics Curr. Chem.*, ed. F. Toda, 2005, **254**, 71; (d) A. V. Trask and W. Jones, in *Topics Curr. Chem.*, ed. F. Toda, 2005, **254**, 41; (e) G. Kaupp in *Topics Curr. Chem.*, ed. F. Toda, 2005, **254**, 95; (f) G. W. V. Cave, C. L. Raston and J. L. Scott, *Chem. Commun.* 2001, 2159; (g) G. Rothenberg, A. P. Downie, C. L. Raston and J. L. Scott, *J. Am. Chem. Soc*. 2001, **123**, 8701.

3. a) D. W. Brice and D. O'Hare, *Inorganic Materials*, Wiley & Sons, 1992; b) M. Gielen, R. Willen and B. Wrackmeyer, *Solid State Organometallic Chemistry, Methods and Applications*, Wiley & Sons, 1999. c) V. V. Boldyrev, *Solid State Ionics*, 1995, **63-65**, 537.

4. a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, **1989**; b) D. Braga, F. Grepioni and A. G. Orpen (Eds.), *Crystal Engineering: from Molecules and Crystals to Materials*, Kluwer Academic Publishers, Dordrecht, 1999; c) M. D. Hollingsworth, *Science*, 2002, **295**, 2410; d) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; e) D. Braga, G. R. Desiraju, J. Miller, A. G.

Orpen and S. Price, *CrystEngComm*, 2002**, 4**, 500; f) G. R. Desiraju in *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry, Vol. 2*, (Eds.: Wiley: Chichester) 1996, p. 107. g) D. Braga, G. R. Desiraju, J. Miller, A. G. Orpen and S. Price, *CrystEngComm*, 2002, **4**, 500; h) G. R. Desiraju Ed., *Crystal Design, Structure and Function. Perspectives in Supramolecular Chemistry*, Whiley & Sons, Chichester, UK, 2003, Vol. 7. i) D. Braga, L. Brammer and N. Champness, *CrystEngComm*, 2005, **7**, 1. j) E. R. T. Tiekink, J. J. Vittal Eds., *Frontiers in Crystal Engineering*, Wiley & Sons, Chichester, 2006.

5. see for instance: a) M. Ogawa, T. Hashizume, K. Kuroda and C. Kato, *Inorg. Chem.,* 1991, **30**, 584; b) D. Braga, L. Maini and F. Grepioni, *Chem. Commun.,* 1999, 937; c) J. M. Thomas, R. Raja, G. Sankar, B. F. G. Johnson and D. W. Lewis, *Chem. Eur. J.,* 2001, **7**, 2973; d) P. J. Nichols, C. L. Raston and J. W. Steed, *Chem. Commun.,* 2001, 1062; e) R. Kuroda and Y. Imal, T. Sato, *Chirality,* 2001, **13**, 588.

6. a) M. R. Caira, L. R. Nassimbeni and A. F. Wildervanck, *J. Chem. Soc. Perkin Trans.,* 1995, 2213; b) L. R. Nassimbeni and H. Su, *New J. Chem.,* 2002, **26**, 989; c) M. R. Caira, L. R. Nassimbeni, F. Toda and D. Vujovic, *J. Am. Chem. Soc.,* 2000, **122**, 9367; d) S. Apel, M. Lennartz, L. R. Nassimbeni, E. Weber, *Chem. Eur. J.*, **2002** , **83**, 67849; e) L. R. Nassimbeni, *Acc. Chem. Res.*, 2003, **36**, 631; f) L. R. Nassimbeni, *CrystEngComm,* 2002, **5**, 200.

7. a) M. C. Etter, *J. Phys Chem.,* 1991, **95**, 4601; b) M. C. Etter, S. M. Reutzel and C. G. Choo, *J. Am. Chem. Soc.,* 1993, **115**, 4411; c) W. H. Ojala and M. C. Etter, *J. Am. Chem. Soc.*, 1992, **114**, 10228; d) V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*,

1996, 987; e) A. V. Trask, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, 2004, 890

8. a) D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini and F. Grepioni, *Angew. Chem. Int. Ed.*, 2006, **45**, 142; b) A. Pichon, A. Lazuen-Garay and S. L. James, *CrystEngComm*, 2006, **8**, 211; c) D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi and M. Polito, *Dalton Trans.*, 2006, 1249.

9. a) D. Braga, M. Curzi, M. Lusi and F. Grepioni, *CrystEngComm*, 2005, **7**, 276; b) A. V. Trask, D. A. Haynes, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, 2006, 51.

10. a) J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press, Oxford, 2002; b) D. Braga and F. Grepioni, in *Crystal Design*, ed. G. R. Desiraju, John Wiley & Sons, Weinheim, Editor edn., 2003. c) D. Braga, J. Bernstein in *Making Crystals by Design. Methods, Techniques, Applications*, ed. D. Braga, F. Grepioni, John Wiley & Sons, Weinheim, Editor edn., 2006. d) J. Bernstein, R.J. Davey, and J.-O. Henck, *Angew. Chem. Int. Ed. Eng*. 1999, **38**, 3440.

11. a) L. R. MacGillivray, J. L. Reid and J. A. Ripmeester, *J. Am. Chem. Soc.,* 2000, **122**, 7817; b) G. S. Papaefstathiou, A. J. Kipp and L. R. MacGillivray, *Chem. Commun.,* 2001, 2462; c) D. B. Varshney, G. S. Papaefstathiou and L. R. MacGillivray, *Chem. Commun.,* 2002, 1964; d) T. Friščić and L. R. MacGillivray, *Chem. Commun.,* 2003, 1306; e) X. Gao, T. Friščić and L. MacGillivray, *Angew. Chem. Int. Ed.,* 2004, **43**, 232; f) L. R. MacGillivray, *CrystEngComm,* 2002, **4**, 37.

12. a) *Organic Solid-State Reactions* (Ed.: F. Toda), Kluwer Acad. Pub., 2002. b) K. Tanaka and F. Toda, *Solvent-Free Organic Synthesis*, Wiley-VCH, London, 2003; c) F. Toda, *CrystEngComm*, 2002, **4**, 215-222; d) G. Kaupp *Angew. Chem. Int. Ed.,* 1992, **31**, 592; e) G. Kaupp, *Angew. Chem. Int. Ed.,* 1992, **31**, 595; f) K. Tanaka, F. Toda, E. Mochizuki, N. Yasui, Y. Kai, I. Miyahara and K. Hirotsu, *Angew. Chem. Int. Ed.,* 1999, **38**, 3523; g) V. P. Balema, J. W. Wiench, M. Pruski and V. K. Pecharsky, *Chem. Commun.,* 2002, 1606; h) V. P. Balema, J. W. Wiench, M. Pruski and V. K. Pecharsky, *Chem. Commun.,* 2002, 724; i) V. P. Balema, J. W. Wiench, M. Pruski and V. K. Pecharsky, *J. Am. Chem. Soc.,* 2002, **124**, 6244.

13. G. Kaupp, *CrystEngComm,* 2003, **5**, 117.

14. (a) D. Braga, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem. Eur. J.,* 2004, **10**, 3261; (b) D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Eur. J.,* 2003, **9**, 4362; (c) D. Braga, M. Curzi, F. Grepioni and M. Polito, *Chem. Commun.*, 2005, 2915.

15. D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini and L. Sturba, Organometallics, 2003, **22**, 2142.

16. a) H. Takazawa, S. Ohba and Y. Saito, *Acta Cryst.*, 1986, **C42**, 1880; b) T. H. Lu, P. Chattopadhyay, F. L. Liao and J. M. Lo, *Analytical Science*, 2001, **17**, 905; c) C. J. Brown and M. Ehrenberg, *Acta Cryst.*, 1985, **C41**, 441; d) A. T. Trask, N. Shan, W. D. S. Motherwell, W. Jones, S. Feng, R. B. H. Tan and K. J. Carpenter, *Chem. Commun.*, 2005, 880.

17. H. O. William and M.C. Etter, *J. Am. Chem. Soc.*, 1995, **114**, 10288.

18. D. Braga, S. L. Giaffreda and F. Grepioni, *Chem. Commun.*, 2006, DOI: 10.1039/b608691h

19. R. K. Harris and P. Jackson, *J. Phys. Chem. Solids,* 1987, **48**, 813.

20. a) G. M. Sheldrick, **SHELXL97**, Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997; b) E. Keller, **SCHAKAL99**, Graphical Representation of Molecular Models; University of Freiburg, Germany, 1999; c) A. L. Spek, *Acta Crystallogr. Sect. A,* 1990, **46**, C31; d) PowderCell programmed by W. Kraus and G. Nolze (BAM Berlin) © subgroups derived by Ulrich Müller (Gh Kassel).

Table 2. Crystal Data

Compound	$\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2][(C_6H_4)NH_2COOH]\}_2$
Formula	$C_{27}H_{23}FeN_3O_2$
M	477.33
System	Triclinic
Space group	P -1
a /Å	9.565(9)
b /Å	9.897(4)
c /Å	13.201(4)
α /°	99.77(3)
β /°	94.17(4)
γ /°	115.74(7)
U /Å³	1094(1)
Z	2
Density /g cm^{-3}	1.449
μ (Mo-Kα) /mm^{-1}	0.720
Reflections collected	4010
Indep refls, *R*(int)	3829
Observed [$F_o > 4\sigma(F_o)$]	2740
*R*1 [$F_o > 4\sigma(F_o)$]	0.0843
*wR*2 (all data)	0.2491

6. Mechanochemical Preparation of Hybrid Organometallic-Organic Macrocyclic Adducts with Long Chain Dicarboxylic Acids

Mechanochemistry is an established branch of the chemical sciences whereby solid reactants are ground together in the solid state to obtain polycrystalline products.[1] In recent years there has been an expansion of this chemistry in the areas of supramolecular chemistry[2] and crystal engineering,[3] fuelled by the interest in exploring *solvent free* synthetic procedures for the preparation of molecular aggregates as alternate to conventional solution chemistry.[4]

The number of papers reporting solid-state preparation of molecular co-crystals,[5] coordination networks[6] and salts[7] is increasing rapidly. The impact on the investigation of crystal polymorphs and solvates is also noteworthy.[8]

Besides being advantageous for the absence of solvents, reactions between solids do often lead to very pure products and require very simple equipments to be carried out. The mixing of reactant can be achieved by simple manual grinding or by mechanical milling. Sometimes the reaction is accelerated, or made altogether possible, by *kneading* (also called "solvent drop grinding"), i.e. by carrying out the grinding process in the presence of a "catalytic" amount of solvent.[5,7]

The main drawback of inter-solid reactions arises from the characterization of the polycrystalline reaction products. In the case of complex supramolecular systems, such as those described herein, the lack of single crystals can forsake a detailed knowledge of the structure, when not of the very nature of the reaction product. This problem can be circumvented if single crystals of the target material can be grown from solution, often by *seeding*.[9]

We have already used solid-state methods in the preparation of molecular co-crystals, mainly with organometallic building blocks, and coordination networks.[10]

In this communication we report the solid-state preparation of a series of novel hybrid organic-organometallic macrocycles of general formula $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot [HOOC(CH_2)_nCOOH]\}_2$ (n = 4, 6, 7), while the adducts with n = 5 and n = 8 have been obtained from solution crystallization. In all cases the organic and organometallic moieties are held together by hydrogen bonds between the carboxylic –OH groups and the pyridine nitrogen atoms. More specifically, manual grinding of the solid organometallic complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$[†] (1) 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. No formation of intermediate liquid phases has been observed. The reactions are easily followed by a change in colour, which is diagnostic: while all organic acids are white, and the organometallic complex 1 is orange, the colour of the solid macrocycle varies from orange-red to purple-red. It is worth recalling that the starting organometallic complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ (1) can also be prepared by Suzuki-coupling in solvent-free conditions.[11]

Single crystals[§] of 1·adipic(4), 1·pimelic(5), 1·suberic(6), 1·azelaic(7) and 1·sebacic(8) (numbers in parenthesis indicate the number of CH_2 groups in the acid chain) were grown from MeOH solutions where direct reaction between complex 1 and the acid had occurred. In the cases of 1·adipic(4), 1·suberic(6), and 1·azelaic(7) comparison between the X-ray diffraction patterns measured on the *kneaded* samples and those calculated on the basis of the single crystal structures confirmed that the same compound had been prepared from solution and mechanochemically, whereas in the cases of 1·pimelic(5) and 1·sebacic(8) the observed and calculated patterns were different (*vide infra*).

All complexes, with the exception of 1·pimelic(5), 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-atom of the ferrocenyl complex. Figure 1 shows the structures of 1·adipic(4), 1·suberic(6), 1·azelaic(7) and 1·sebacic(8). It can be appreciated how the even/odd alternation of carbon atoms in the organic spacers is accommodated by the twist of the cyclopentadienyl-pyridyl groups and by the eclipsed or staggered juxtaposition of the organic moieties.

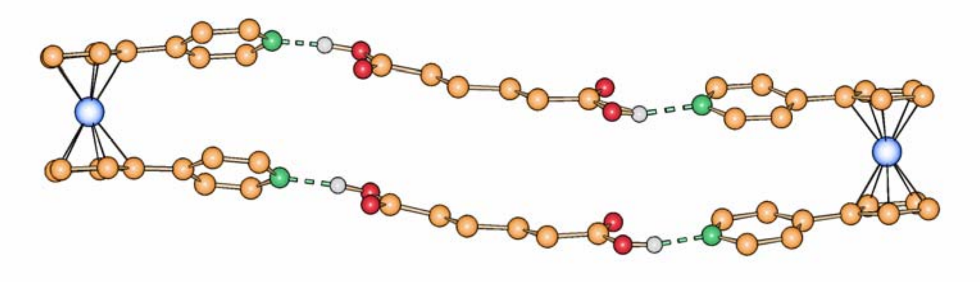


Fig. 1a

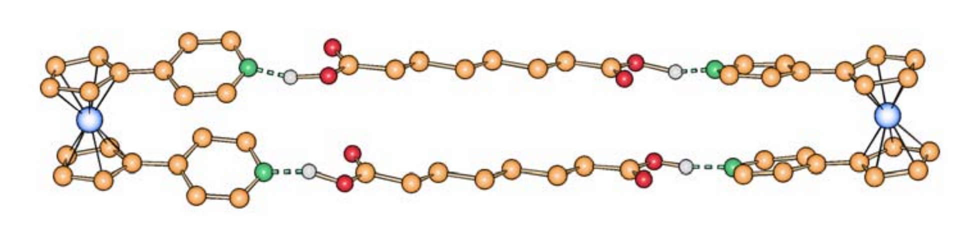


Fig. 1b

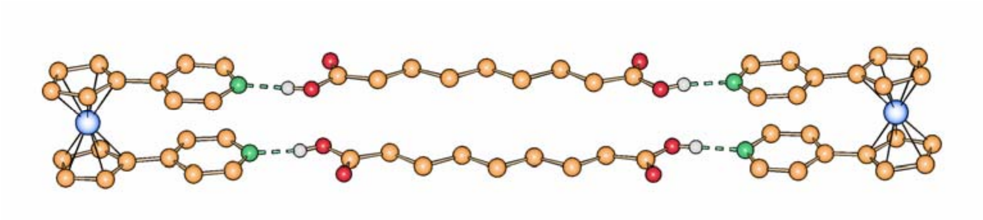


Fig. 1c

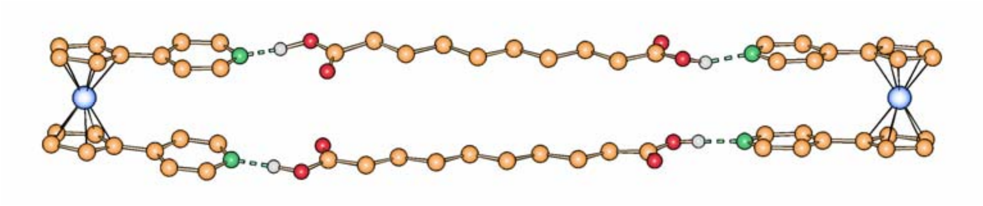


Fig. 1d

Fig. 1. The supramolecular structures of the macrocycles 1·adipic(4) (a), 1·suberic(6) (b), 1·azelaic(7) (c) and 1·sebacic(8) (d) showing the hydrogen bond links between the two outer organometallic molecules and the inner organic spacers.

The comparison between observed and calculated X-ray powder diffraction patterns in the case of 1·suberic(6), taken as example, is shown in Figure 2.

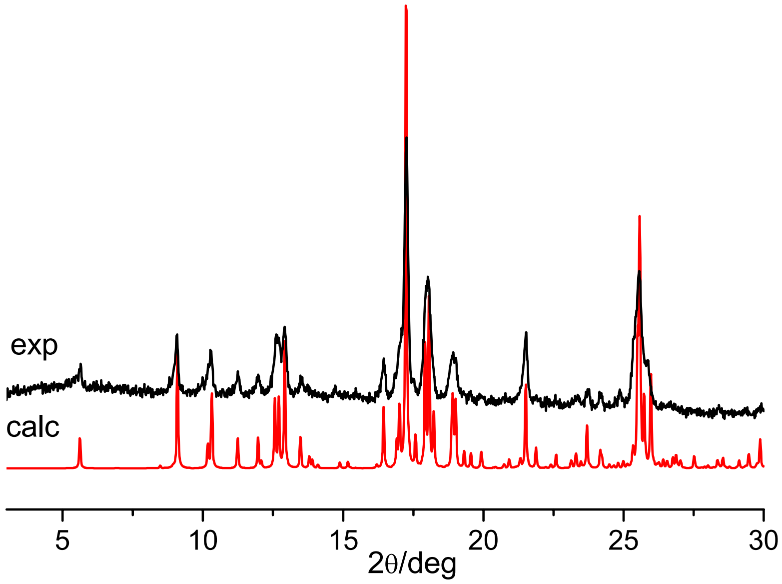


Fig. 2. Comparison between experimental (top) and calculated (bottom) X-ray powder patterns for 1·suberic(6).

As mentioned above, in the case of 1·pimelic(5) crystallization from solution yields an adduct with the same stoichiometric composition as the macrocycles 1·adipic(4), 1·suberic(6), 1·azelaic(7), but with acid and base moieties organized in a zig-zag chain instead than in a macrocycle, and linked via O-H$_{COOH}$···N hydrogen bonds, as shown in Figure 3. This structure does not yield the same powder diffraction pattern as that obtained by grinding. It is therefore interesting to speculate on the possibility of structural isomerism between closed (macrocycles) and open (zig-zag or other chains structures) arrangements and also on the possible interconversion, which may also depend on the choice of solvent.[12] A similar, though inverse, situation is observed in the case of 1·sebacic(8): crystallization from solution yields the macrocycle, while the grinding experiments produces a different substance, which has not yet been characterized. Further studies are needed to address the problem of supramolecular isomerism in this class of compounds.

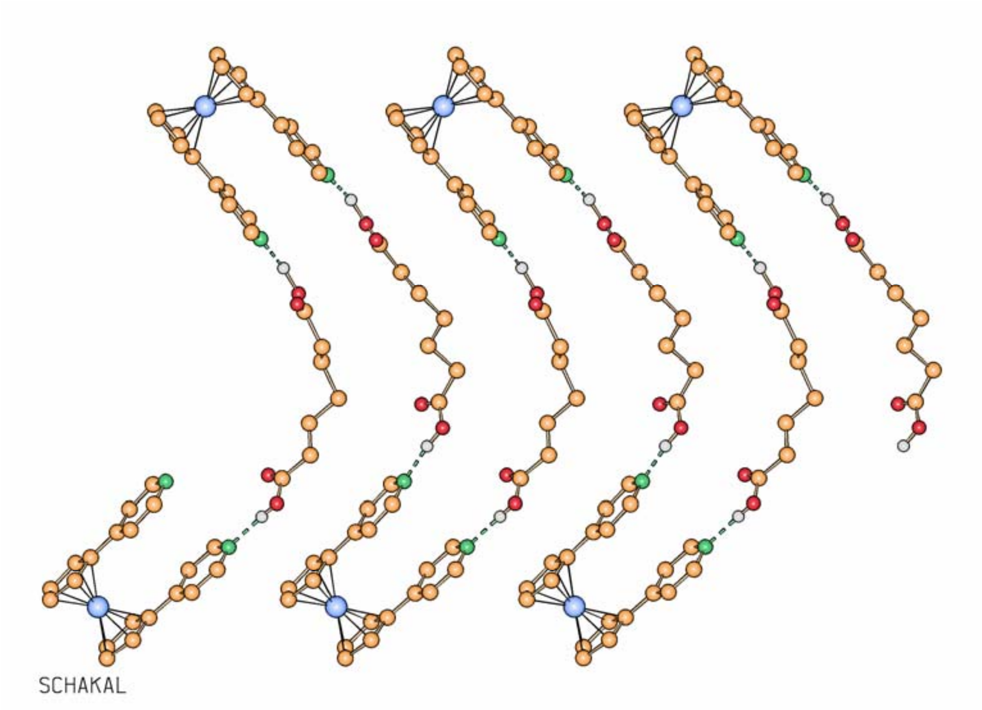


Fig. 3. The zigzag chain found in 1·pimelic(5). This structure is suggestive of the existence of supramolecular isomers of the macrocyclic structures shown in Fig. 1.

It is worth noting that, even though the quality of the X-ray data does not allow to draw confident conclusions, no proton transfer from acid to base appears to take place, therefore all adducts are made of neutral components. A solid state NMR investigation,[10a] however, is under way. The supramolecular metalla-macrocycles share also some remarkable packing features in the solid state with all compounds forming layered structures as shown in Figure 4. The macrocycles are very anisotropic in shape, being characterized by two smaller dimensions (those corresponding approximately to the size of the ferrocenyl moiety, which are constant) and one long dimension, which varies with the dicarboxylic acid length, and form a "LEGO"® type of construct. These macrocycles are then placed next to each other in layers that can be wavy (1·adipic(4) and 1·suberic(6)) or planar (1·azelaic(7) and 1·sebacic(8)).

It is interesting to speculate on the fact that the formation of these complex packings implies molecular diffusion and significant molecular motion and bond breaking/forming in agreement with Kaupp's model of molecular motion and phase reconstruction and extrusion as the solid-state reaction proceeds.[13]

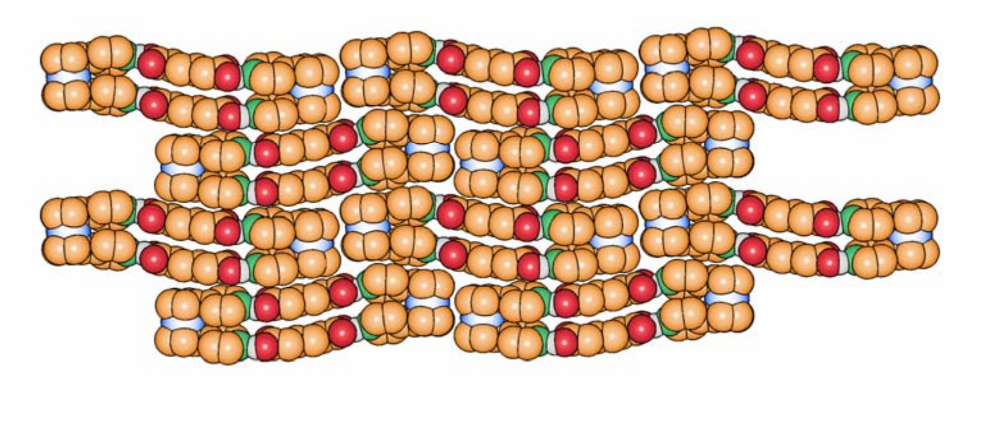


Fig. 4a

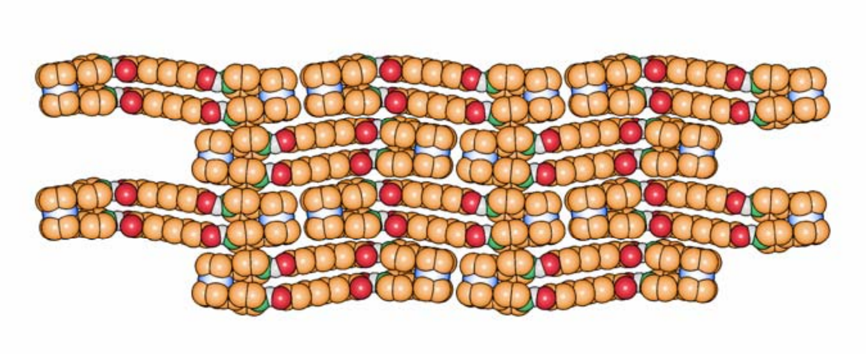


Fig. 4b

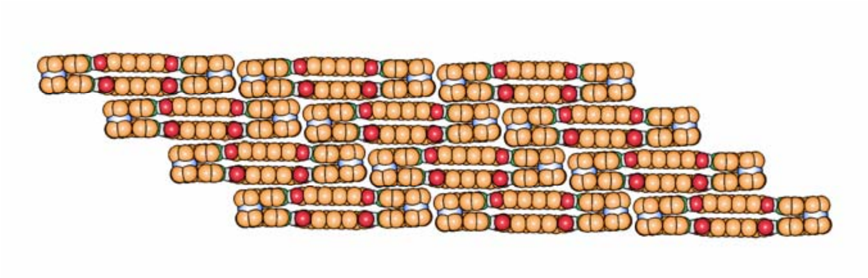


Fig. 4c

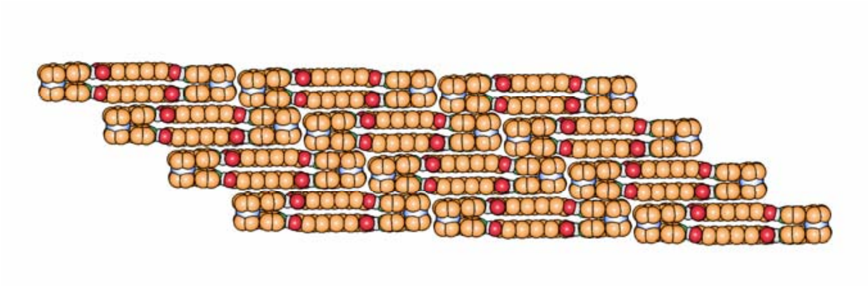


Fig. 4d

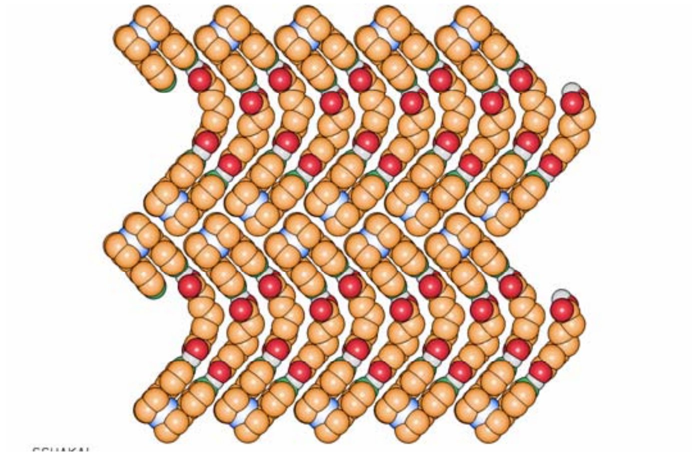


Fig. 4e

Fig. 4. The strong structural analogy in supramolecular organization ion of the layers in 1·adipic(4) (a), 1·suberic(6) (b), 1·azelaic(7) (c) and 1·sebacic(8) (d). Note also the structural relationship with the ribbons in 1·pimelic(5) (e).

Reactions between crystalline solids of the type used to prepare the macrocycles can be regarded as *supramolecular reactions* between solid, periodical supermolecules. 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. In summary, we have provided further evidence that *kneading* of organometallic and organic crystals can be exploited to prepare new supramolecular hybrid organic-organometallic macrocycles and networks.

Notes and references

† All reagents were purchased from Sigma-Aldrich and used without further purification. Reagent grade solvents were used. $Fe[\eta^5\text{-}C_5H_4\text{-}1\text{-}(4\text{-}C_5H_4N)]_2$ was synthesized as previously reported.[11]All crystallization solutions and mixtures for grinding reactions were initially prepared with an excess of the acid with respect to $[Fe(\eta^5\text{-}Cp\text{-}C_5H_4N)_2]_2$. After characterization, preparations were repeated with the 1:1 stoichiometric ratio. The mixtures of $[Fe(\eta^5\text{-}Cp\text{-}C_5H_4N)_2]_2$ and of $COOH(CH_2)_nCOOH$ (n = 4, 5, 6, 7 and 8) were manually ground in an agate mortar for 5 min; single crystals of **1·adipic(4)**, **1·pimelic(5)**, **1·suberic(6)**, **1·azelaic(7)** and **1·sebacic(8)** suitable for single crystal X-ray diffraction were obtained by slow evaporation of a solution obtained by dissolving equimolar quantities of $[Fe(\eta^5\text{-}Cp\text{-}C_5H_4N)_2]_2$ (50 mg, 0.147 mmol) and $COOH(CH_2)_nCOOH$ (0.147 mmol, 21, 23, 25, 27 and 30 mg for n = 4, 5, 6, 7 and 8, respectively) in 5 mL of MeOH 99.8%. Co-grinding of the solids in stoichiometric ratios other than 1:1 (e.g. 1:2 and 2:1) led to formation of solid mixtures with

diffraction peaks corresponding to the unreacted excess reagent in addition to the peaks of the 1:1 compounds.

§ Crystal data for all adducts were collected either at 293 K (**1·adipic(4)**, **1·pimelic(5)**, **1·suberic(6)**, **1·sebacic(8)**) or at 273 K (**1·azelaic(7)**) on a Brucker APEX II diffractometer [monochromator graphite, MoKα radiation (λ = 0.71073 Å)]. Crystals suitable for diffraction experiments were difficult to grow, in most cases polycrystalline powders were obtained with only few poorly formed single crystals. For all compounds, Z is referred to the number of macrocycles in the unit cell. **1·adipic(4)**: $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_4COOH]\}_2$, M = 972.68, triclinic, P-1, a = 11.276 (2), b = 14.816(3), c = 28.600(6) Å, α = 89.201(4), β = 87.275(4), γ = 68.551(3) °, V = 4442(2) Å^3, Z = 4, μ = 0.716, 15394 independent reflections (31703 measured), wR_2 (all data) = 0.3563, R_1 (I >2σ(I)) = 0.1189. **1·pimelic(5)**: $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_5COOH]\}_2$, M = 2001.46, P-1, a = 9.396 (2), b = 10.667(3), c = 24.172(2) Å, α = 78.03(5), β = 88.93(2), γ = 81.25(4) °, V = 2342.2(8) Å^3, Z = 1, μ = 0.681, 8019 independent reflections (16818 measured), wR_2 (all data) = 0.1990, R_1 (I >2σ(I)) = 0.0645. **1·suberic(6)**: $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_6COOH]\}_2$, M = 1028.78, monoclinic, $P2_1$/c, a = 11.107(9), b = 31.467(18), c = 14.846(12) Å, β = 110.33(8) °, V = 4866(6) Å^3, Z = 4, μ = 0.658, 7134 independent reflections (15533 measured), wR_2 (all data) = 0.4224, R_1 (I >2σ(I)) = 0.1271 (Only 83% of data collection completed, because of crystal decay). **1·azelaic(7)**: $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_7COOH]\}_2$, M = 1056.83, triclinic, P-1, a = 9.8845(5), b = 10.7413(6), c = 13.4321(7) Å, α = 76.177(1), β = 78.844(1), γ = 68.146(1)°, V = 1276.6(1) Å^3, Z = 1, μ = 0.629, 5782 independent reflections (11137 measured), wR_2 (all data) = 0.1046, R_1 (I >2σ(I)) = 0.0390. **1·sebacic(8)**: $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_8COOH]\}_2$, M =

1084.88, triclinic, *P*-1, $a = 11.028(2)$, $b = 13.747(3)$, $c = 18.765(4)$ Å, $\alpha = 96.076(3)$, $\beta = 102.689(3)$, $\gamma = 105.048(3)°$, $V = 2639.6(9)$ Å^3, $Z = 2$, $\mu = 0.610$, 5277 independent reflections (12282 measured), wR_2 (all data) = 0.2152, R_1 ($I > 2\sigma(I)$) = 0.0694. SHELX97[14a] and SCHAKAL99[14b] were used for structure solution and graphical representations. CCDC xxxxxx-xxxxxx. See http://www.rsc.org/suppdata/cc/xx/xxxxxxxx/ for crystallographic data in CIF format.

‡ Powder data for all samples were collected on a Philips PW-1100 automated diffractometer with Cu-Kα radiation, graphite monochromator, using quartz sample holders. For the pure reagents 25 mg of substance were employed. The program PowderCell[14c] was used for calculation of X-ray powder patterns.

References

1 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. Letters*, 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.*, 1995, 2213;

2 M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley & Sons, Chichester, 2000.

3 D. Braga, G. R. Desiraju, J. Miller, A. G. Orpen and S. Price, *CrystEngComm*, 2002, **4**, 500; G. R. Desiraju Ed., *Crystal Design,*

Structure and Function. Perspectives in Supramolecular Chemistry, Whiley & Sons, Chichester, UK, 2003, Vol. 7; D. Braga, L. Brammer and N. Champness, *CrystEngComm*, 2005, **7**, 1; E. R. T. Tiekink, J. J. Vittal Eds., *Frontiers in Crystal Engineering*, Wiley & Sons, Chichester, 2006.

4 D. Braga and F. Grepioni, *Angew Chem. Int Ed.*, 2004, **43**, 2; D. Braga and F. Grepioni, in *Topics Curr. Chem.*, ed. F. Toda, 2005, **254**, 71; A. V. Trask and W. Jones, in *Topics Curr. Chem.*, ed. F. Toda, 2005, **254**, 41; G. W. V. Cave, C. L. Raston, and J. L. Scott, *Chem. Commun.* 2001, 2159; G. Rothenberg, A. P. Downie, C. L. Raston, and J. L. Scott, *J. Am. Chem. Soc*. 2001, **123**, 8701.

5 M. C. Etter, *J. Phys Chem.,* 1991, **95**, 4601; M. C. Etter, S. M. Reutzel and C. G. Choo, *J. Am. Chem. Soc.,* 1993, **115**, 4411; W. H. Ojala and M. C. Etter, *J. Am. Chem. Soc.*, 1992, **114**, 10228; V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*, 1996, 987; A. V. Trask, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, 2004, 890; A. V. Trask, N. Shan, W. D. S. Motherwell, W. Jones, S. Feng, R. B. H. Tan and K. J. Carpenter, *Chem. Commun.*, 2005, 880.

6 D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini and F. Grepioni, *Angew. Chem. Int. Ed.*, 2006, **45**, 142; A. Pichon, A. Lazuen-Garay and S. L. James, *CrystEngComm*, 2006, **8**, 211; D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi and M. Polito, *Dalton Trans.*, 2006, 1249.

7 D. Braga, M. Curzi, M. Lusi and F. Grepioni, *CrystEngComm*, 2005, 7, 276; A. V. Trask, D. A. Haynes, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, 2006, 51.

8 (a) J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press, Oxford, 2002; (b) J. D. Dunitz, *CrystEngComm*, 2003, **5**, 506; (c) G. R. Desiraju, *CrystEngComm*, 2003, 466.

9 J. Dunitz and J. Bernstein, *Acc. Chem. Res.*, 1995, **28**, 193.

10 (a) D. Braga, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem. Eur. J.,* 2004, **10**, 3261; (b) D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem. Eur. J.,* 2003, **9**, 4362; (c) D. Braga, M. Curzi, F. Grepioni and M. Polito, *Chem. Commun.*, 2005, 2915.

11 D. Braga, D. D'Addario, M. Polito and F. Grepioni, *Organometallics*, 2004, **23**, 2810.

12 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schroder, *Coord. Chem. Rev.*, 2001, **222**, 155.

13 G. Kaupp, *CrystEngComm,* 2003, **5**, 117; G. Kaupp in *Topics Curr. Chem.*, ed. F. Toda, 2005, **254**, 95.

14 (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)].

7. Conclusions

We have shown that organometallic building blocks functionalized with classical hydrogen bonding donor/acceptor groups (e.g. –COOH, $-B(OH)_2$, pyridine, amides, etc.) can be successfully utilized in a broad range of crystal engineering exercises for the formation of supramolecular adducts and hydrogen bonded networks. The building block of choice in this report is a sandwich compound (whether bis-arene of bis-cyclopentadienyl sandwich) carrying hydrogen bonding functional groups. We have shown in the first section that most dicarbocylic acids utilize the twin intermolecular hydrogen bonding to form cyclic dimers, which are then *maintained* in the crystal structures as supramolecular units of packing. The packing of such dimeric units is then that of supramolecular van der Waals objects capable, to the most, of weak C—H…O interactions. The existence of three polymorphs of such dimers in the case of $\{[Fe(\eta^5\text{-}C_5H_4COOH)_2]\}_2$ is noteworthy. Interestingly, compounds such as the dicarboxylic acids $\{[Fe(\eta^5\text{-}C_5H_4COOH)_2]\}_2$, $\{[Co(\eta^5\text{-}C_5H_4COOH)_2]\}_2$ and $\{[Cr(\eta^6\text{-}C_6H_5COOH)_2]\}_2$ or, just as well, the dication $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4NH)(\eta^5\text{-}C_5H_4COO)]^+\}_2$ and the supramolecular adduct $\{[Co(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2]\}^+$, which forms dimers, show an important topological difference from the relative "organic-only" compounds (i.e. organic dicarboxylic acids, bis-amides, etc.) because these latter compounds are, in general not "allowed" the conformational freedom of sandwich compounds and, therefore, cannot dimerize. In fact, dicarboxylic organic acids tend to form chains in the solid state, rather than self-assemble in dimeric units. The chain formation, on the other hand is not precluded to the organometallic sandwich acids. Not only the chain motif is also possible for a same species, as in the case of form II of $[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]$, but it is also the motif of choice in all cases of cationic acids, e.g. the two polymorphs of $[Cr(\eta^6\text{-}C_6H_5COOH)_2][PF_6]$ and $[Co(\eta^5\text{-}C_5H_4COOH)_2]X$ ($X = PF_6^-$, BF_4^-). In these cases, the chain structure might be favoured because of the need to optimize simultaneously the Coulombic interactions between ions of opposite charge as well as the hydrogen bonds in between anions.

We have put the emphasis on the structural and supramolecular features of the sandwich compounds, but it should made clear that, *before* these building blocks can be used in supramolecular bonding they *have to be made*. In many instances, it was necessary to synthesize ab initio, the building block of choice because only few of the starting materials are commercially available. Details of the solution chemistry that precedes the crystal engineering steps are available in the original papers quoted through the review.

We have also shown that the preparation of molecular crystals of the type described in this contribution is not confined to traditional crystallization from solution. Solvent-free methods, such as solid–solid reactions, vapour uptake from a solid, *kneading* of crystalline solids with small amount of solvent or liquid reactant can be exploited to prepare novel compounds, some of which cannot be otherwise obtained by traditional solution methods. These methods, widely used in the organic solid-state chemistry field [45], can be predicted to have an important future also in the neighbouring field of solid-state organometallic chemistry [46].

Beside the preparation of crystalline materials based on hydrogen bonds, we are currently investigating the use of some of the building blocks described above, such as pyridine and amido ferrocenyl and cobalticinium complexes, in the preparation of complexes of complexes [47], the exploitation of mechanochemical methods to prepare coordination networks [48], and the preparation of supramolecular adducts based on acid salts [49]. These results will constitute the subject matter of future reports.

References

[45] (a) G. Kaupp In: F. Toda, Editor, *Topics Curr. Chem.* 254 (2005), p. 95. (b) G.W.V. Cave, C.L. Raston and J.L. Scott, *Chem. Commun.* (2001), p. 2159.
(c) G. Rothenberg, A.P. Downie, C.L. Raston and J.L. Scott, *J. Am. Chem. Soc.* 123 (2001), p. 8701.
(d) A.V. Trask and W. Jones, *Topics Curr. Chem.* 254 (2005), p. 41.

[46] In: M. Gielen, R. Willem and B. Wrackmeyer, Editors, *Solid State Organometallic Chemistry*, Wiley (1999).

[47] (a) D. Braga, M. Polito, D. D'Addario, E. Tagliavini, D.M. Proserpio, F. Grepioni and J.W. Steed, *Organometallics* 22 (2003), p. 4532.
(b) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, D.M. Proserpio and F. Grepioni, *Chem. Commun.* 10 (2002), p. 1080. D. Braga, M. Polito, S.L. Giaffreda and F. Grepioni, *Dalton Trans.* 16 (2005), p. 2766.

[48] (a) D. Braga, M. Curzi, M. Lusi and F. Grepioni, *Cryst. Eng. Commun.* 7 (2005), p. 276. (b) D. Braga, M. Curzi, F. Grepioni and M. Polito, *Chem. Commun.* 23 (2005), p. 2915.

[49] (a) D. Braga, M. Curzi, L. Maini, M. Polito and F. Grepioni, *Dalton Trans.* 16 (2004), p. 2432.
(b) D. Braga, M. Curzi, M. Lusi and F. Grepioni, *Cryst. Eng. Commun.* 7 (2005), p. 276.