Charge-assisted N–H$^{(+)}$···O$^{(-)}$ and O–H···O$^{(-)}$ hydrogen bonds control the supramolecular aggregation of ferrocenedicarboxylic acid and bis-amidines

Dario Braga,*[a] Lucia Maini,[a] Fabrizia Grepioni,*[b] André De Cian,[c] Olivier Félix,[c] Jean Fischer[c] and Mir Wais Hosseini*[c]

[a] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via F. Selmi 2, 40126 Bologna, Italy. E-mail: dbraga@ciam.unibo.it, http://catullo.ciam.unibo.it*
[b] *Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy. E-mail: grepioni@ssmain.uniss.it*
[c] *Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg, France. E-mail: hosseini@chimie.u-strasbg.fr*

Directional N–H···O and O–H···O hydrogen bonds reinforced by *charge assistance* in the presence of anion–cation interactions have been used to design and synthesise a whole family of new organic-organometallic supramolecular salts. The compounds $[C_5H_{16}N_4]^{2+}[(\eta^5-C_5H_4COO)_2Fe]^{2-} \cdot 2C_2H_5OH$, **1**, $[C_5H_{16}N_4]^{2+}\{[(\eta^5-C_5H_4COOH)(\eta^5-C_5H_4COO)Fe]_2\}^{2-}$, **2**, $[C_7H_{20}N_4]^{2+}[(\eta^5-C_5H_4COO)_2Fe]^{2-} \cdot 4H_2O$, **3**, $[C_7H_{20}N_4]^{2+}\{[(\eta^5-C_5H_4COOH)(\eta^5-C_5H_4COO)Fe]_2\}^{2-}$, **4**, and $[C_7H_{18}O_2N_4]^{2+}[(\eta^5-C_5H_4COO)_2Fe]^{2-} \cdot 4H_2O$, **5**, have been obtained by reacting $[(\eta^5-C_5H_4COOH)_2Fe]$ with the bis-amidines $[C_5H_{14}N_4]$, $[C_7H_{18}N_4]$ and $[C_7H_{16}O_2N_4]$. The self-assembly between singly and doubly deprotonated acids and the protonated cations is controlled by the stoichiometric ratio and by the choice of solvent. The effect of charge assistance on the N–H···O interactions is discussed on the basis of a CSD analysis.

The utilisation of non-covalent bonding is the paradigm of supramolecular chemistry,[1] while periodicity and symmetry are the paradigm of the crystalline state,[2] hence molecular crystal engineering can be regarded as the way to obtain *periodical supermolecules*. One of the promising areas of this booming field of research is represented by organometallic crystal engineering.[3] The interest in exploiting organometallic building blocks stems from the potential inherent in the use of crystal construction strategies[4] to prepare materials in which the variable valence, oxidation and spin state characteristics of transition metal atoms are brought to the crystals.[5] This objective can be achieved by controlling the non-covalent interactions established between the ligands, which are organic groups in most cases. Co-crystallisation of organic and organometallic systems has also proven to be a fruitful and reproducible method to obtain crystalline materials with interesting (and possibly useful) magnetic,[4b] conducting, super-conducting and non-linear optical properties.[5]

Charge-assisted hydrogen bonds,[6] *viz.* interactions of the X–H$^{(+)}$···Y$^{(-)}$ type with the X–H donor belonging to a cation and the Y acceptor belonging to an anion, represent one of the most widely employed devices in the construction of pre-defined crystalline architectures. The reason is essentially twofold: (*i*) charge-assisted X–H$^{(+)}$···Y$^{(-)}$ bonds combine the 'intrinsic' strength and directionality of the neutral hydrogen bond X–H···Y (X, Y = N, O) with a favourable location of the ionic charges (Coulombic forces between ions of opposite sign are strong but lack directionality and are, therefore, less useful as design tools) and (*ii*) they are easily obtained in crystal synthesis *via* acid–base reactions. Furthermore, the use of ions permits a great choice of components and hence may result in a wide range of *collective* properties. One may exploit the formation of charge-assisted hydrogen bonds to select and

'bring into the solid' anions and cations with different topology, bonding and electronic characteristics. The resulting materials can be seen as kinds of co-crystals in which the different molecular ions are linked *via* strong, selective, and, most importantly, reproducible interactions.

There are essentially two types of approaches to prepare charge-assisted hydrogen bonds *via* acid–base reactions.

Strategy 1: Building blocks are chosen so that the base cannot compete in the formation of strong charge-assisted interactions with the acid anion moiety.[7] This has been used by the Bologna group in reactions between organic or organometallic polycarboxylic acids, possessing from two to four –COOH groups, with organometallic bases such as $[(\eta^5-C_5H_5)_2Co][OH]$, $[(\eta^5-C_5Me_5)_2Co][OH]$, $[(\eta^6-C_6H_6)_2Cr][OH]$ and $[(\eta^6-C_6H_5Me)_2Cr][OH]$, which lack strong acceptor/donor hydrogen bond groups. With these pre-requisites the self-aggregation of the partially deprotonated acids leads to supramolecular structures with honeycomb, π-stack, and chiral features.[7] Instead of being connected by strong hydrogen bond interactions, anions and cations are linked *via* a profusion of charge-assisted C–H$^{\delta+}$···O$^{\delta-}$ bonds involving the C–H systems of the cyclopentadienyl and arene ligands and the available 'free' lone pairs of the carboxylic groups on the partially deprotonated acid moiety.

Strategy 2: Building blocks are chosen so that charge-assisted X–H$^{(+)}$···Y$^{(-)}$ bonds are formed directly between cations and anions. This is easily achieved, for instance, by using nitrogen-containing bases (amines, amides, amidines, *etc.*), which can accept a proton from polycarboxylic acid molecules, thus typically leading to formation of N–H$^{(+)}$···O$^{(-)}$ interactions. This strategy has been widely exploited by the Strasbourg group and by others.[8] Obviously, the utilisation of polycarboxylic acids, which contain more than one –COOH
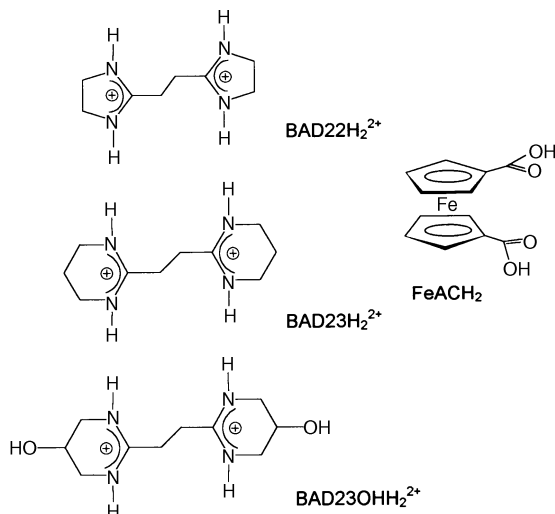
Scheme 1 The organic and organometallic building blocks utilised in the synthesis of **1–5**.

group, implies the possibility of competition between different types of hydrogen bonding interactions, such as $O–H\cdots O^{(-)}$ and $N–H^{(+)}\cdots O^{(-)}$, and also the possibility of interactions of the $O–H^{(-)}\cdots O^{(-)}$ type involving exclusively anions (this latter interaction is also present in crystals obtained with strategy 1. Whether the acidic moieties will show self-assembly into superanionic frameworks or a preference for interactions between ions of opposite sign usually depends on the acid : base stoichiometric ratio (see below).

In this study we combine the two strategies to prepare and structurally characterise a new family of materials obtained from the reaction of the dicarboxylic organometallic acid $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ (FeACH$_2$) and the tetradentate acceptor systems of the bis-amidine molecules $[C_5H_{14}N_4]$ (BAD22), $[C_7H_{18}N_4]$ (BAD23) and $[C_7H_{16}O_2N_4]$ (BAD23OH). The compounds $[C_5H_{16}N_4]^{2+}[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 2C_2H_5OH$, **1**, $[C_5H_{16}N_4]^{2+}\{[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]_2\}^{2-}$, **2**, $[C_7H_{20}N_4]^{2+}[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 4H_2O$, **3**, $[C_7H_{20}N_4]^{2+}\{[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]_2\}^{2-}$, **4**, and $[C_7H_{18}O_2N_4]^{2+}[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 4H_2O$, **5**, have been obtained. A schematic representation of the bis-amidine structures is shown in Scheme 1.

As precedence, $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ had been employed in reactions with the neutral organometallic molecules $[(\eta^6\text{-}C_6H_6)_2Cr]$ and $[(\eta^5\text{-}C_5H_5)_2Co]$, which are readily oxidised to the corresponding cations $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+$, producing organometallic supramolecular salts, which contain metal centres with different spin and oxidation states.[9] In these compounds the sandwich cations act as templating units around which the anions and neutral molecules self-aggregate by virtue of $O–H\cdots O$, $O–H\cdots O^{(-)}$, and $O–H^{(-)}\cdots O^{(-)}$ interactions. In the present case, however, the reaction of $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ with bis-amidines occurs *via* proton transfer from the organometallic acid to the organic base, leading to the formation of $N–H^{(+)}$ hydrogen bond 'donor' groups and hence to $N–H^{(+)}\cdots O^{(-)}$ interactions.

In order to put the analysis of $N–H^{(+)}\cdots O^{(-)}$ hydrogen bond formation into a broader perspective we have also searched the CSD[10] for neutral $N–H\cdots O$ and charge-assisted $N–H^{(+)}\cdots O^{(-)}$ interactions and the results will be compared in the following.

Experimental

The syntheses of the bis-amidine compounds were previously reported.[10] $[(\eta^5\text{-}C_5H_4COO)_2Fe]$ was purchased from Aldrich.

Growth of crystals

$[C_5H_{16}N_4]^{2+}[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 2C_2H_5OH$, 1.

BAD22 (15 mg, 0.09 mmol) along with 25 mg (0.09 mmol) of ferrocenedicarboxylic acid were dissolved in 15 ml of ethanol. The solution was heated up to 50 °C and was allowed to cool slowly to 4 °C. Crystals suitable for X-ray diffraction were obtained in a sealed tube. Crystals of **1** are unstable and lose solvent if the mother liquid is removed.

$[C_5H_{16}N_4]^{2+}\{[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]_2\}^{2-}$, 2.

BAD22 (7 mg, 0.045 mmol) along with 25 mg (0.09 mmol) of ferrocenedicarboxylic acid were dissolved in 15 ml of ethanol. The solution was heated up to 50 °C and was allowed to cool slowly to 4 °C. Crystals suitable for X-ray diffraction were obtained in a sealed tube.

$[C_7H_{20}N_4]^{2+}[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 4H_2O$, 3.

BAD23 (15 mg, 0.077 mmol) along with 21 mg (0.077 mmol) of ferrocenedicarboxylic acid were dissolved in 5 ml of ethanol. The solution was heated up to 50 °C and water was added dropwise until the solution became clear; the solution was then allowed to cool slowly to 4 °C. If no crystals appeared isopropyl ether was added until saturation and the solution then cooled. Crystals of **3** are unstable out of the mother liquid.

$[C_7H_{20}N_4]^{2+}\{[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Fe]_2\}^{2-}$, 4.

BAD23 (15 mg, 0.077 mmol) along with 41 mg (0.15 mmol) of ferrocenedicarboxylic acid were dissolved in 5 ml of ethanol. The solution was heated up to 50 °C and water was added dropwise until the solution became clear, which was followed by slow cooling to 4 °C. If no crystals appeared isopropyl ether was added until saturation and the solution then cooled.

$[C_7H_{18}O_2N_4]^{2+}[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}\cdot 4H_2O$, 5.

BAD23OH (10 mg, 0.044 mmol) along with 12.12 mg (0.044 mmol) of ferrocenedicarboxylic acid were dissolved in 3 ml of ethanol. The solution was heated up to 50 °C and water was added dropwise until the solution became clear; it was then allowed to cool slowly to 4 °C. If no crystals appeared isopropyl ether was added until saturation and the solution then cooled. The crystals are unstable out of the mother liquid. All crystals obtained were orange in colour.

Crystal structure characterisation

For crystals of **3** and **4** X-ray diffraction data collection was carried out on a Nonius CAD-4 diffractometer equipped with an Oxford Cryostream liquid N_2 device using graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å. Diffraction data were corrected for absorption by azimuthal scanning of high-χ reflections. SHELXL97[11a] was used for structure solution and refinement based on F^2. For crystals of **1**, **2** and **5** X-ray diffraction data collection wase carried out on a Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å) and analysed using the Nonius OpenMoleN package.[11b] Crystal data and details of measurements are reported in Table 1. SCHAKAL97[11c] was used for the graphical representation of the results. All non-H atoms were refined anisotropically. The H atoms bound to C and N atoms were added in calculated positions in all compounds. The H atoms bound to the carboxylic O atoms could not be located. The computer program PLATON[11d] was used to analyse the geometry of the hydrogen bonding patterns.

CCDC reference number 440/188. See http://www.rsc.org/suppdata/nj/b0/b002061n/ for crystallographic files in .cif format.

Table 1 Crystal data and details of data collection for **1–5**

	1	2	3	4	5
Formula	$C_{24}H_{36}FeN_4O_6$	$C_{32}H_{34}Fe_2N_4O_8$	$C_{22}H_{30}FeN_4O_7$	$C_{34}H_{38}Fe_2N_4O_8$	$C_{22}H_{36}FeN_4O_{10}$
Formula weight	532.42	714.34	518.34	742.38	572.4
T/K	294(2)	294(2)	203(2)	293(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$Pbcn$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
$a/\text{Å}$	17.3450(4)	7.6960(1)	5.799(8)	11.91(1)	5.7680(6)
$b/\text{Å}$	13.8160(3)	7.7810(4)	9.962(7)	10.623(5)	10.553(1)
$c/\text{Å}$	10.5130(3)	25.554(1)	11.54(2)	13.516(9)	11.536(1)
α/deg	90	90	102.12(8)	90	109.374(1)
β/deg	90	90.23(6)	104.0(1)	107.96(8)	94.184(1)
γ/deg	90	90	103.66(8)	90	90.998(1)
$U/\text{Å}^3$	2519.3(2)	1530.2(2)	603(1)	1627(2)	660.0(2)
Z	4	2	1	2	1
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.654	1.007	0.675	0.951	0.632
Measd./unique reflns	18 527/3199	7860/4249	2347/2026	2972/2845	5265/4093
$R(\text{int})$	0.024	0.026	0.111	0.032	0.039
R_1 [on F, $I > 2\sigma(I)$]	0.048	0.046	0.090	0.038	0.046
wR_2 (on F^2, all data)	0.067	0.106	0.271	0.113	0.074

CSD searches

The search for intermolecular and inter-ionic distances was carried out on the October 1999 version of the CSD[12] with the limitation that donor and acceptor atoms be separated by a distance <3.1 Å and that the N–H⋯O angles be >90°. All structures were individually examined and duplicate hits manually removed. Histograms were obtained with the package VISTA.

Results and discussion

Since the focus of this paper is on the supramolecular features of the crystalline materials, details of the structures of the ions will not be described, while some attention will be given to the conformational geometry of the anions derived from the ferrocenedicarboxylic acid molecule. As will become apparent through the following discussion, the $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ acid is structurally very versatile not only because it can participate in hydrogen-bonded networks as singly and doubly protonated species, but also because of the conformational freedom of the two cyclopentadienyl ligands about the co-ordination axis. Scheme 2 shows the rotameric conformations of the $C_5H_4COO^-$ and C_5H_4COOH ligands in the five crystal structures.

Table 2 collects all the relevant hydrogen bonding distances. In general $N\text{-}H^{(+)}\cdots O^{(-)}$ and $O\text{-}H\cdots O^{(-)}$ hydrogen bonding distances and angles are comparable to those

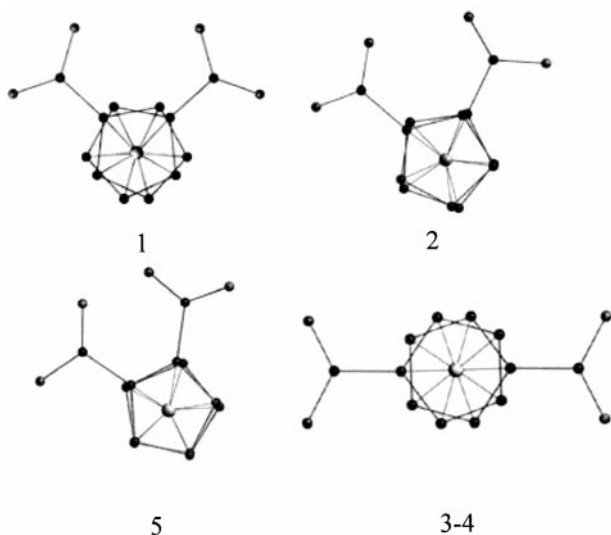**Scheme 2** Conformations of the anions derived from $[(\eta^5\text{-}C_5H_4COOH)_2Fe]$ in the crystals of **1–5**.

observed in other crystalline *polycarboxylic acid anions* discussed previously.[9,10] The following observations are made. (*i*) The $N\text{-}H^{(+)}$ donors belonging to the bis-amidine cations form hydrogen bonds exclusively with oxygen atoms belonging to the anions. $N\cdots O$ distances are shorter than in neutral hydrogen bonds (2.88–2.93 Å). (*ii*) Water–water hydrogen bonds are, in general, shorter than $O\text{-}H\cdots O$ bonds in neutral systems (2.71–2.80 Å), very likely because of the electrostatic compression due to the presence of ions.[13] (*iii*) The two shortest $O\cdots O$ distances [2.546(2) and 2.542(3) Å in **2** and **4**, respectively] correspond to inter-anionic hydrogen bonding interactions.

Ion organisation in 1, 3 and 5

Crystalline **1**, **3** and **5** were obtained by reacting acid and base in a 1 : 1 stoichiometric ratio, hence leading to complete deprotonation of the acid and formation of the dianion $[(\eta^5\text{-}C_5H_4COO)_2Fe]^{2-}$ ($FeAC^{2-}$). Because of this similarity, the three compounds will be discussed together.

In crystalline **1** the $FeAC^{2-}$ anions act as bridges between two bis-amidines, which, in turn, link together two $FeAC^{2-}$ anions in a chevron-like fashion, as shown in Fig. 1 [N(H)⋯O distances of 2.716(2) and 2.673(2) Å]. The carboxylic oxygen not involved in N–H⋯O bonding links the solvate ethanol molecules *via* an O–H⋯O hydrogen bond. This interaction, however, does not prevent the solvent molecules from being affected by disorder.

The ion organisation in crystalline **3** is similar to that in **1** with alternating $FeAC^{2-}$ anions and bis-amidine dications

Table 2 Relevant donor–acceptor distances (Å, esds in parentheses) in crystalline **1–5**

	$N(H)^{(+)}\cdots O^{(-)}$	$O\cdots O$
1	2.716(2)	2.769(2) $O_{anion}\cdots O_{ethanol}$
	2.673(2)	
2	2.832(2)	2.546(2) $O_{anion}\cdots O_{anion}$
	2.799(2)	
3	2.761(2)	2.796(2) $O_{anion}\cdots O_{water}$
	2.762(2)	2.750(2) $O_{water}\cdots O_{water}$
		2.861(2) $O_{anion}\cdots O_{water}$
4	2.724(3)	2.542(3) $O_{anion}\cdots O_{anion}$
	2.764(3)	
5	2.774(3)	2.684(3) $O_{cation}\cdots O_{water}$
	2.774(3)	2.712(3) $O_{anion}\cdots O_{water}$
	2.776(3)	2.729(3) $O_{anion}\cdots O_{water}$
	2.776(3)	2.789(3) $O_{anion}\cdots O_{water}$
		2.803(3) $O_{water}\cdots O_{water}$
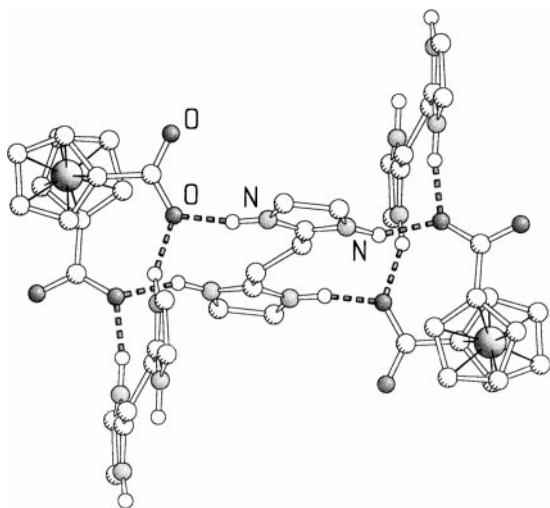
Fig. 1 Charge-assisted $N–H^{(+)}\cdots O^{(-)}$ hydrogen bonds between BAD22H^{2+} cations and FeAC^{2-} dianions [2.716(2), 2.673(2) Å] in **1**. Only H$_{(NH)}$ atoms are shown for clarity.

that form a one-dimensional network. In **3**, however, all carboxylate oxygens are involved in interactions with the diprotonated bis-amidines (see Fig. 2), as previously observed in crystals obtained from bis-amidines and organic acids.[10] The two water molecules present in the crystal structure of **3** act as a bridge between the chains, forming a two-dimensional layer structure [O$_{anion}\cdots$O$_{water}$ distances of 2.861(2) and 2.796(2) Å] and also forming an O$_{water}\cdots$O$_{water}$ hydrogen bond [2.750(2) Å]. As shown in Fig. 2(b) the water molecules are located in channels formed by the chains of alternating BAD23H$_2^{2+}$ and FeAC^{2-} ions.

The preference for O–H$\cdots$O bonds when a sufficient number of donors and acceptors is available is clearly demonstrated by the structure of the tetrahydrate **5**, which is obtained *via* reaction with the bis-amidine diol BAD23OH to form the dication [C$_7$H$_{18}$O$_2$N$_4$]$^{2+}$ (BAD23OHH$_2^{2+}$) by diprotonation. As in the case of **1** and **3** the FeAC^{2-} dianions in
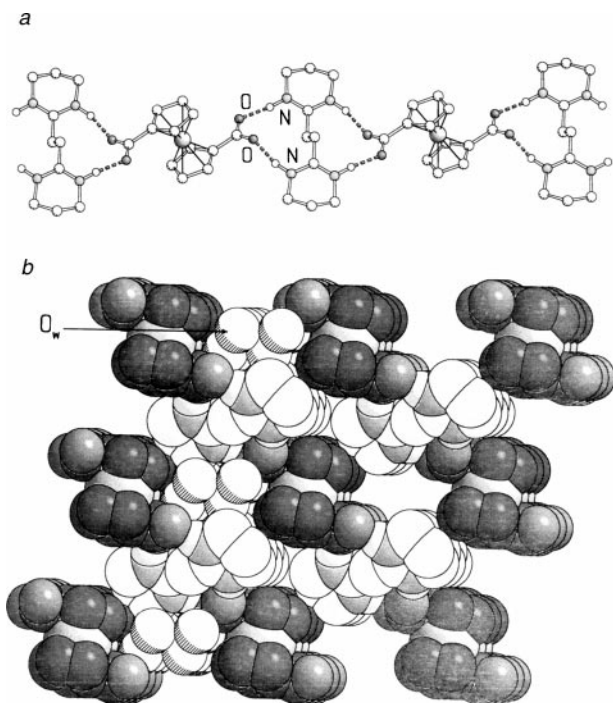
5 form one-dimensional networks with the dications, as described above [see Fig. 3(a)]. The four water molecules form hydrogen-bonded tetrameric units of the type commonly observed with alcohols and water hydrates. Two of these water molecules interact with the hydroxyl group of the bis-amidine cations *via* O–H$\cdots$O bonds [O$\cdots$O 2.684(2) Å] as shown in Fig. 3(b).

Therefore, the role of the solvent molecules in **1**, **3** and **5** is essentially to compensate for the fewer number of hydrogen bond donors with respect to acceptor groups by providing additional –OH donor groups. There is, however, an undesired 'secondary' effect. Solvent molecules are loosely accommodated in channels and cavities from which they are easily lost (as in the case of **3** and **5**). This can severely affect the robustness of the crystalline materials. In fact, all of these crystals are unstable out of the mother liquid and readily lose solvent at room temperature. It is likely that the solvent molecules are *carried into the solid* because the strong water–ion (or ethanol–ion in the case of **1**) solvation interactions cannot be efficiently replaced by inter-ionic ones during crystal nucleation. In other words, when the acid is fully deprotonated the dianion can be expected to be strongly solvated by hydrogen bonding donor solvents such that the actual building block is, very likely, a solvated one. Solvent–ion interactions are, of course, stronger than hydrogen bonds between solvent molecules. We have recently shown, in the case of the hydrated zwitterionic species [(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)Co], that water can be removed thermally and the dehydrated powder may then be used to nucleate the otherwise elusive anhydrous form of the zwitterion.[14] Attempts to apply the same strategy to species **1**–**5** have been frustrated by the tendency of the materials to decompose.

Ion organisation in 2 and 4

An acid : base stoichiometric ratio of 2 : 1 allows partial deprotonation of the acid, thus affording species that show the simultaneous presence of inter-anion O–H$^{(-)}\cdots$O$^{(-)}$ and

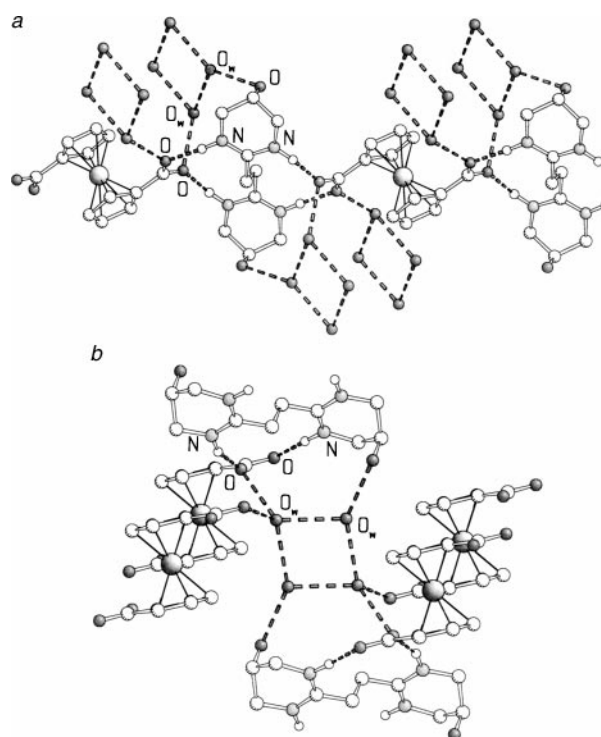**Fig. 2** A one-dimensional network formed by the alternation of BAD23H^{2+} and FeAC^{2-} ions in **3**. The carboxylate group interacts with the bis-amidines in *dihapto* mode with charge-assisted N–H$^{(+)}\cdots$O$^{(-)}$ hydrogen bonds [2.761(2) and 2.762(2) Å].

Fig. 3 (a) One-dimensional network in crystalline **5**. (b) Hydrogen bonds involving the water molecules; note also how the water molecules interact with the carboxylate groups of the anions and with the hydroxyl group of the cations. Only H$_{(NH)}$ atoms are shown for clarity.

cation–anion N–H$^{(+)}$···O$^{(-)}$ interactions but that do not contain solvent molecules. This is an important (*albeit* simple) stoichiometric control on the superstructure of the crystalline materials. If –COOH groups are 'left' on the anion there is competition in hydrogen bond formation between the –NH$^{(+)}$ donor (favoured by the positive ionic charge carried by the bis-amidine cations) and the –OH donor, which generally forms O–H···O bonds that are stronger than neutral N–H···O ones.

While all attempts to obtain suitable crystals of a 2 : 1 product with the bis-amidine diol BAD23OH were unsuccessful, the bis-amidines BAD22 and BAD23 yielded crystalline materials **2** and **4** that contain the organometallic mono-anion [(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)Fe]$^-$ (FeAcH$^-$) in place of the fully deprotonated dianion FeAc^{2-}. The absence of solvent molecules indicates that in both **2** and **4** the number of donor –OH and –NH groups resulting from partial deprotonation of the diacid and protonation of the base is sufficient to 'satisfy' all acceptor sites with strong interactions.

Crystalline **2** can be described as formed by chains of carboxylic acid mono-anions interacting with the bis-amidines in dihapto mode. Fig. 4 shows a two-dimensional network in **2**: the ionic arrangement can be described either as composed of chains of O–H$^{(-)}$···O$^{(-)}$ interacting [(η^5-C$_5$H$_4$COOH)(η^5-C$_5$H$_4$COO)Fe]$^-$ anions joined by bis-amidine bridges, or as trimeric units each formed by a bis-amidine dication hooking together two ferrocene carboxylate acid mono-anions. The hydrogen bonds between the bis-amidine and the carboxylate groups [N(H)···O of 2.832(2) and 2.799(2) Å] are longer than those discussed previously. This lengthening may be attributed either to the decreased ionic charge on the acceptor (hence to some weakening of the charge-assistance effect) or to the stereogeometry of the bis-amidine since the cyclopentane ring separates the two nitrogen atoms by a distance that does not allow optimum interaction with the O atoms on the carboxylate groups. The O–H···O interaction along the carboxylate acid anion chain is short [2.546(2) Å] and comparable in length to that present in crystalline **4**. Indeed, crystalline **4** can also be described as formed of chains of singly deprotonated FeAcH$^-$ anions interacting with the protonated bis-amidine BAD23H$_2^{2+}$ in dihapto mode. The N···O distances of the charged-assisted hydrogen bonds [N–H···O of 2.724(3) and 2.764(3) Å] are comparable to the values discussed before. As in **2** the organometallic anions form a sort of helical arrangement *via* an O–H···O interaction [2.542(2) Å] between the organometallic anions (see Fig. 5).

Charge-assisted N–H$^{(+)}$···O$^{(-)}$ interactions

Charge assistance is a practical way to reinforce the hydrogen bond.[13] Since the interaction is essentially electrostatic in
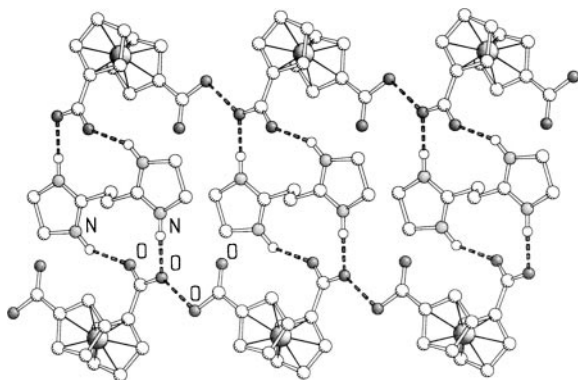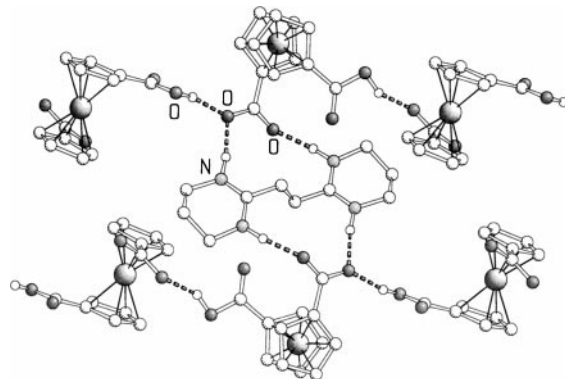
Fig. 5 Portion of the three-dimensional network formed by the mono-anion FeACH$^-$ chains interacting with the dication BAD23H$_2^{2+}$ in **4**. Only H$_{(NH)}$ and H$_{(COOH)}$ atoms are shown for clarity.

nature, the polarity of the donor and acceptor groups is enhanced if the donor belongs to a cation and the acceptor belongs to an anion. This type of charge assistance becomes particularly relevant with weak and very weak hydrogen bonds, such as C–H···O,[15a] C–H···F,[15b] C–H···Cl,[15c] and C–H···π interactions.[15d] The very possibility of molding superanionic frameworks around organometallic sandwich cations as described in strategy 1 arises from the profusion of C–H donors on the cationic sandwich complexes.[9] Of course the shape of the cation also plays a relevant role. The effect of the ionic charge on hydrogen bonds has also been investigated spectroscopically[16] and theoretically.[17]

In the present study use has been made of N–H$^{(+)}$···O$^{(-)}$ hydrogen bonds between the bis-amidine dications and mono- and dianions obtained by deprotonation of the organometallic diacid. In order to compare charge-assisted N–H$^{(+)}$···O$^{(-)}$ bonds with neutral N–H···O interactions as supramolecular organisers in crystals a CSD search has been undertaken (see Experimental). Neutral N–H···O bonds have been studied before.[18] The search was confined to nitrogen atoms belonging to amine, bis-amidine and imine groups as donors and to oxygen acceptors belonging to either carboxylic or carboxylate groups. Zwitterionic compounds and amides[19] were excluded from the search. Fig. 6 shows a comparison between the N–H···O and N–H$^{(+)}$···O$^{(-)}$ populations as a function of the N···O distances between donor and acceptor groups.

The comparison of the average structural parameters reported in Table 3 and the histograms in Fig. 6 afford a rather consistent picture: the N···O distances, in both average and lowest decile (10%) values, show a marked difference between neutral N–H···O and charged N–H$^{(+)}$···O$^{(-)}$ interactions. The donor–acceptor distances associated with the latter interaction appear to be definitely shorter than those involving neutral molecules. Whether this shortening reflects an effective *increase* in the strength of the N–H···O interactions *per se* or the fact that the appropriate location of the charges contributes with ion-pairing cation–anion attractive forces to bring the interacting atoms closer together is difficult to establish on the basis of structural parameters alone. We

Fig. 4 The ribbons formed by two chains of FeACH$^-$ interacting with the dication BAD22H$_2^{2+}$ *via* charge-assisted hydrogen bonds in **2**. Only H$_{(NH)}$ atoms are shown for clarity.

Table 3 Comparison of structural parameters for neutral intermolecular N–H···O and charge-assisted inter-ionic N–H$^{(+)}$···O$^{(-)}$ interactions in the 2.0 < N···O < 3.1 Å range

Interaction	No. observations	N···O distance/Å	
		Mean (esds)	Lowest 10% decile
N–H···O	47	2.89(0.01)	2.760
N–H$^{(+)}$···O$^{(-)}$	306	2.748(0.006)	2.635
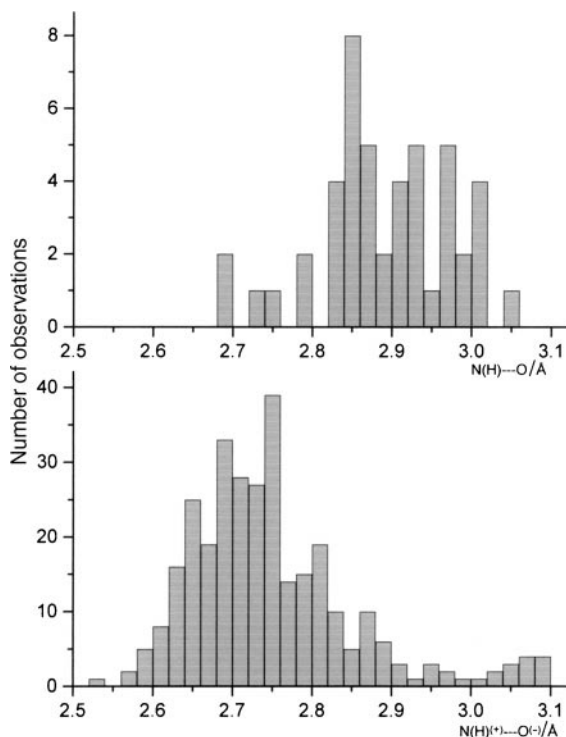
Fig. 6 Histograms showing the distributions of N···O distances for neutral intermolecular N–(H)···O and charge-assisted inter-ionic N–(H)$^{(+)}$···O$^{(-)}$ interactions. See Table 3 for mean values and lowest deciles.

have pointed out that there is no rule-of-thumb to follow when dealing with weak non-covalent interactions immersed in the electrostatic field generated by ions of opposite sign.[20] However, in the case of the interaction between bis-amidine cations and organometallic anions it is reasonable to assume that the positive charge carried by the cation decreases the shielding of the proton on the donor N–H groups and makes them 'more acidic'; simultaneously, the presence of a negative charge on the acceptor increases its nucleophilicity. This is, therefore, one way to make weak interactions stronger.[13]

Conclusions

In this study we have combined the strategies of the Bologna and Strasbourg groups to prepare a number of novel mixed organic–organometallic crystalline materials based on two distinct building blocks. The organic building blocks (the bis-amidines shown in Scheme 1) had been successfully employed in the construction of one-, two- and three-dimensional organic networks.[8a] The organometallic component is the dicarboxylic acid [(η^5-C$_5$H$_4$COOH)$_2$Fe], previously employed to prepared mixed-metal organometallic crystals.[7] While in the Bologna compounds *self-aggregation* of the partially deprotonated acid into anionic chains was the primary result because the sandwich cations [(η^5-C$_5$H$_5$)$_2$Co]$^+$ and [(η^6-C$_6$H$_6$)$_2$Cr]$^+$ could not compete in the formation of strong hydrogen bonding interactions, this is not so when bis-amidines are used. As in the case of the organic systems synthesised in Strasbourg, direct association between anions and cations *via* N–H$^{(+)}$···O$^{(-)}$ interactions could be attained. Depending upon the type of bis-amidine and the stoichiometric ratio it was possible to prepare and structurally characterise two categories of compounds. In the first category the acid is fully deprotonated (hence the carboxylate groups can only act as hydrogen bond acceptors from the protonated bis-amidine cations and/or from crystallisation solvent molecules) and we observe formation of one-dimensional networks in which the organic cation and the organometallic anion alter-

nate. In the second category the presence of singly deprotonated organometallic carboxylic acid anions, obtained by using a higher acid : base molar ratio, allows the formation of $^{(-)}$O–H···O$^{(-)}$ interactions between the anions in addition to the formation of N–H$^{(+)}$···O$^{(-)}$ interactions between anions and cations. We have observed that when the acid is fully deprotonated (compounds **1**, **3**, **5**) the *need* for extra hydrogen bond donors is manifested in the co-crystallisation of water or ethanol solvent molecules, whilst when the acid is singly deprotonated, there is no need for solvent mediation since the O–H groups left on the acid engage the carboxylate groups directly. Finally, the effect of charge assistance on the N–H$^{(+)}$···O$^{(-)}$ interactions between organic cations and organometallic anions has been discussed in the light of the results of a CSD-based comparison between neutral N–H···O and N–H$^{(+)}$···O$^{(-)}$ interactions. It has been shown that the presence of the ionic charge enhances the hydrogen bonding effect by bringing donor and acceptor closer together. This is a useful concept because it allows, in devising crystal engineering strategies, to take advantage simultaneously of the directionality (hence predictability and reproducibility) of strong hydrogen bonds and of the cohesive effect of Coulombic attractions in the ions pairs forming the repeating units.

Acknowledgements

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