Supramolecular assemblies in the crystals of carboxylate salts prepared from a ferrocene β-aminoalcohol

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ABSTRACT

(Ferrocenylmethyl)(2-hydroxyethyl)amine (**1**) reacts with mono- (CH_3CO_2H and $PhCO_2H$) and dicarboxylic acids ($HO_2C(CH_2)_nCO_2H$ ($n = 0$–2), (E)- and (Z)-$HO_2CCH=CHCO_2H$) to give the respective carboxylates, viz [**1**H](RCO_2) (**2**, R = CH_3; **3**, R = Ph), [**1**H]$_2$($O_2C(CH_2)_nCO_2$) (**4**, $n = 0$; **5**, $n = 1$; **6**, $n = 2$), [**1**H]$_2$((E)-$O_2CCH=CHCO_2$) (**7**) and [**1**H]$_2$((Z)-$HO_2CCH=CHCO_2$) (**8**), as defined crystalline solids. Crystal structures of **2**–**8** have been determined by single-crystal X-ray diffraction analysis, revealing extensive hydrogen bonding interactions based predominantly on charge-supported N^+–H···O^- and O–H···O^- hydrogen bonds, and on C–H···O contacts. Whereas the crystal assemblies of the monocarboxylate salts propagate preferentially in one dimension (**2**: cross-linked chains, **3**: columnar stacks), those of the salts prepared from the dicarboxylic acids (including hydrogenmaleate **8**) are best described as layered composite arrays resulting via alternation of polar, hydrogen-bonded layers and of non-polar sheets constituted by the ferrocenyl substituents.

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1. Introduction

The design of crystalline organometallic solids is nowadays receiving considerable attention owing to the possibility of preparing new materials with specific properties that result from cooperative superposition of properties of the individual molecules constituting the periodic crystal assembly [1]. Despite the recent effort, the field of organometallic crystal engineering still defies rational approach. This is mainly because of complicated and supportive nature of the solid-state interactions and due to a limited number of suitable organometallic building blocks, as well as the lack of knowledge regarding their self-assembly properties.

Ferrocenes appear to be suitable molecules for the preparation of crystalline metal-organic frameworks owing to their high chemical stability, defined stereochemistry and elaborate synthetic methodology [2,3]. Derivatives studied so far include ferrocene carboxylic acids, their salts with amines and carboxylic derivatives [4], ferrocene heterocycles [5], and ferrocenylated alcohols and their adducts [6]. These compounds typically form classical hydrogen bonds in the solid state (though frequently supported by additional intermolecular interactions) that seem to be better predictable than their softer counterparts (e.g, C–H···X) and interactions involving π-systems [1,7]. Furthermore, the acids and nitrogen derivatives are capable of proton transfer

reactions to give salts, the ionic nature of which typically provides additional electrostatic support to hydrogen bonding.

In our previous work, we have studied crystal assemblies of ferrocene alcohols bearing phosphorus substituents [8], phosphinocarboxylic acids [9] and ferrocene carboxamides bearing 2-hydroxyethyl groups at the amide nitrogens [10]. Later, we turned also to ferrocenylmethylated β-aminoalcohols, $FcCH_2NHCR_2CH_2OH$ ($R_2 = H_2$, Me_2, i-Pr/H), focusing on the crystal assemblies formed by the alcohols itself and, particularly, their salts with inorganic acids [11] and 2,4,6-trinitrophenol [12]. To conclude our studies on these polar molecules, we present here a comparison of the crystal structures of salts formed from $FcCH_2NHCH_2CH_2OH$ (**1**) and mono- and dicarboxylic acids (see Chart).
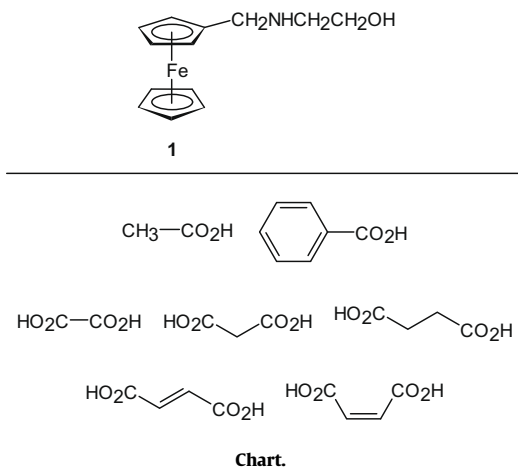
2. Results and discussion

2.1. Synthesis

Acid–base reaction between (ferrocenylmethyl)(2-hydroxyethyl)amine (**1**) and monocarboxylic acids CH_3CO_2H and $PhCO_2H$ in methanol afforded the respective ammonium salts [**1**H](RCO_2), where R = Me (**2**) and Ph (**3**). Similar reactions with dicarboxylic acids and two molar equivalents of **1** gave the corresponding salts [**1**H]$_2$(O_2CYCO_2), where Y = void (**4**), CH_2 (**5**), CH_2CH_2 (**6**), and (E)-CH=CH (**7**) whereas maleic acid gave the hydrogen salt [**1**H]{(Z)-$HO_2CCH=CHCO_2$} (**8**) under identical conditions. Compound **8** resulted also when the reaction of maleic acid and **1** was performed with equimolar amounts of the educts. Compounds

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Chart.

Fig. 2. A view of the molecular structure of **3** showing displacement ellipsoids at the 30% probability level. Selected structural data for the anion: C27–O2 1.248(2), C27–O3 1.274(2), C21–C27 1.508(2) Å; O2–C27–O3 124.6(1)°.

2–**8** were isolated as air stable, orange crystalline solids, whose composition was corroborated by elemental analysis. Their solid-state structures have been determined by single-crystal X-ray diffraction.
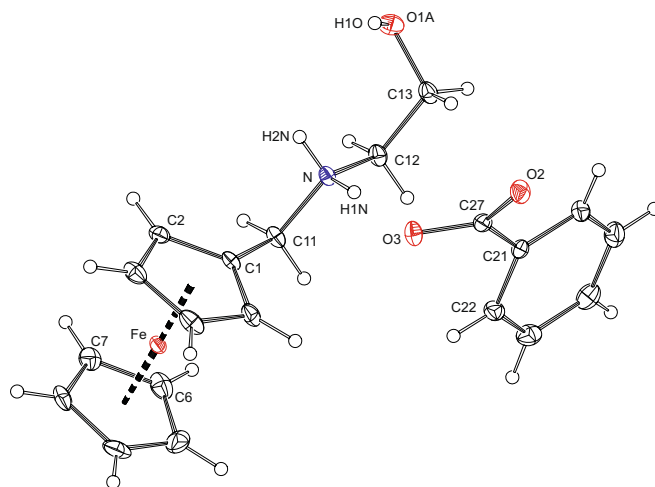
2.2. Molecular structures

Views of the molecular structures of the acetate (**2**) and benzoate (**3**) salts are depicted in Figs. 1 and 2 whilst Figs. 3–6 show the structures of salts **3–8** obtained from the dicarboxylic acids. Geometric data for the anions are presented in the figure captions.

The geometry of the cations in all the structures is very similar as far as interatomic distances and angles are concerned (Table 1). Ferrocene moieties exert alike Fe–Cg distances and negligible tilting of their cyclopentadienyl rings, the maximum being 4° for cation 1 in the structure of **4**. The distances and angles within the (2-hydroxyethyl)ammonium chain are also similar and compare favourably with those reported for salts involving the $(FcCH_2NH_2CR_2CH_2OH)^+$ cations [11,12]. However, notable differences can be found in the conformation of the ferrocene pendant
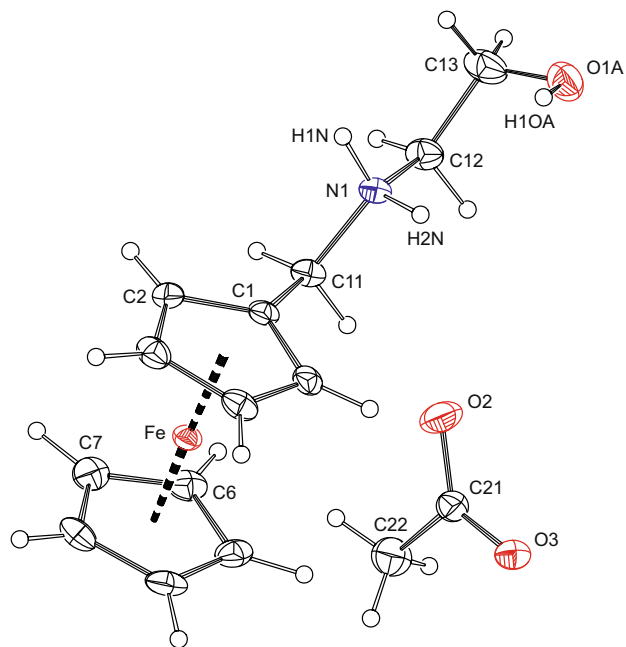
Fig. 1. A view of the molecular structure of **2** showing displacement ellipsoids at the 30% probability level. Structural data for the anion: C21–O2 1.252(3), C21–O3 1.247(3), C21–C22 1.512(3) Å; O2–C21–O3 123.4(2)°.

chain, which apparently reflects reorientation of the polar groups forced by intermolecular (inter-ion) interactions (see torsion angles in Table 1).

The acetate ion in the structure of **2** exerts perfectly balanced C–O distances (the absolute difference being only 0.005 Å) while the carboxyl group in **3** retains a partial dissymmetric character with $\Delta(C–O) = 0.026$ Å. This asymmetry can be attributed to hydrogen bonding as both benzoate oxygens act as donors in *different* bifurcated hydrogen bonds. Likewise, the formation of multicentered hydrogen bonds probably results in rotation of the carboxyl moiety {C27O2O3} by as much as 32.3(2)° from the plane of its bonding phenyl ring, which brings the oxygen atoms closer to their second H-bond partner and simultaneously facilitates the accommodation of the phenyl ring within the structure.

Whereas the compounds obtained from the monocarboxylic acids both behave as simple 1:1 salts, the products obtained from dicarboxylic acids exhibit a greater structural (and chemical) diversity. Oxalate **4** (Fig. 3) and malonate **5** (Fig. 4) crystallise, in accordance with their stoichiometry, with two cations and one anion per asymmetric unit. The oxalate anion is almost planar (dihedral angle of the carboxyl planes is 9.8(3)°) and quite symmetric, showing similar CO distances (1.244(2)–1.254(2) Å). The variation in the CO bond lengths (1.260(4)–1.271(4) Å) in the malonate anion is also statistically insignificant. However, the presence of methylene spacer makes the malonate ion more flexible, allowing for a mutual rotation of the carboxyl group into a near-to-perpendicular position (dihedral angle of the carboxyl planes being 84.6(5)°). Different disposition of the carboxyl oxygens is naturally reflected in the crystal packing.

Succinate **6** and fumarate **7** are isostructural (Fig. 5). The anions are planar, residing on the crystallographic inversion centres. This renders only one cation moiety and half of the anion symmetrically independent. In addition, the anions appear to be practically isosteric, both possessing an extended box shape with the fumarate ion being only slightly shorter (cf. the intramolecular distances in succinate/fumarate anions: O2···O2′ 5.015(2)/5.077(2) and O3···O3 6.031(2)/5.918(2) Å). Consequently, the anions can thus be interchanged with only negligible impact on the crystal packing.

As indicated above, the reaction of **1** with maleic acid proceeds differently than those with all other dicarboxylic acids studied, affording hydrogenmaleate **8** (Fig. 6) at both 1:1 and 2:1 **1**-maleic acid molar ratios. Such preferential formation of the hydrogen salt surely relates to stabilisation of the anion through intramolecular
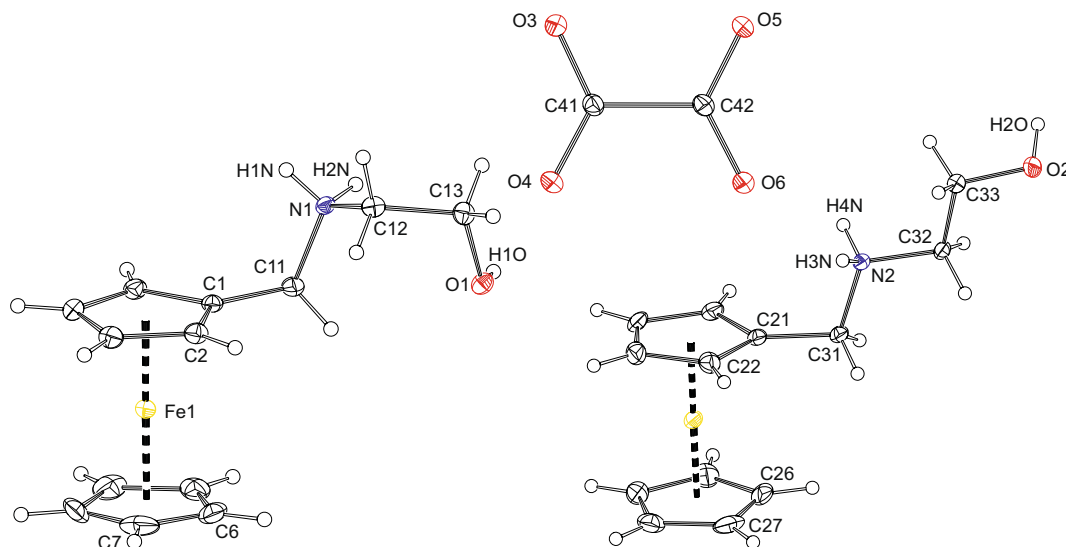
Fig. 3. Structures of the ions forming compound **4**. The displacement ellipsoids correspond to the 30% probability level. Mutual orientation of the ions does not correspond to that in the crystal. Structural data for the anion: C41—C42 1.569(3), C41—O3 1.253(2), C41—O4 1.250(2), C42—O5 1.254(2), C42—O6 1.244(2) Å; O3—C41—O4 126.8(2), O5—C42—O6 126.1(2)°.
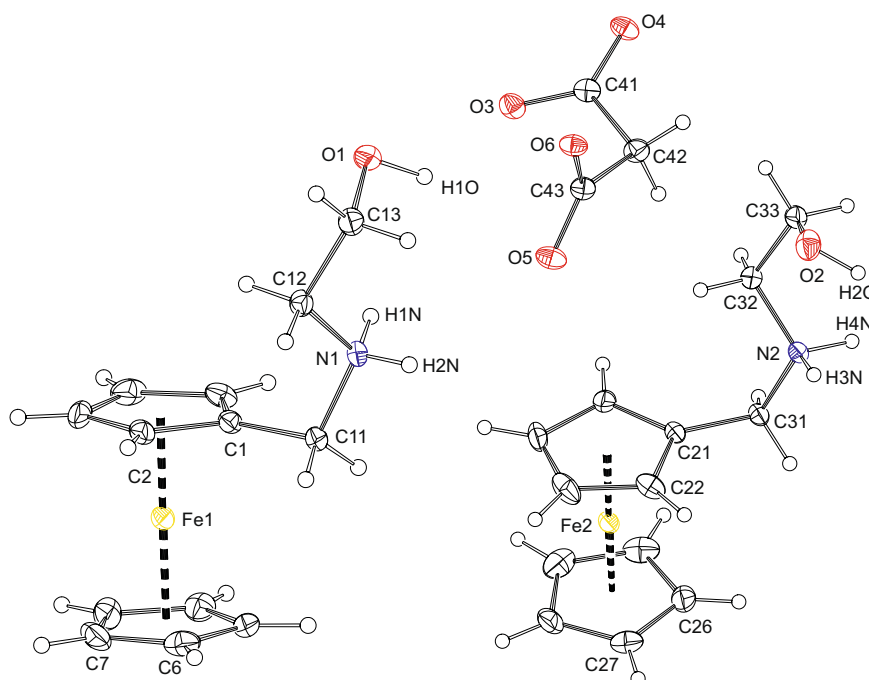
Fig. 4. Structures of the ions forming compound **5**. The displacement ellipsoids correspond to the 30% probability level. Mutual orientation of the ions does not correspond to that in the crystal. Structural data for the anion: C41—C42 1.525(5), C42—C43 1.526(4), C41—O3 1.260(4), C41—O4 1.263(4), C43—O5 1.255(4), C43—O6 1.271(4) Å; C41—C42—C43 110.7(3), O3—C41—O4 124.7(3), O5—C43—O6 124.9(3)°.

O–H···O hydrogen bond between appropriately pre-arranged carbonyl of one carboxyl group and the hydroxyl of the other [13]. Partial dissociation makes the hydrogenmaleate anion unsymmetric in bond lengths and angles (see Fig. 6). The CC=CC unit is almost planar (the dihedral angle C21—C22—C23—C24 being 5.2(4)°) but its peripheral carboxyl groups are mutually rotated by 13.7(3)° with the H-bonded oxygen atoms pointing in the same direction (a larger rotation is exerted by the dissociated carboxyl group; cf. the dihedral angles O3—C21—C22—C23 = 4.7(4)° and O4—C24—C23—C22 = 15.3(3)°). The maleate carboxyl groups retain partial localised character, which is more pronounced in the

protonated than in the dissociated carboxyl moiety (Δ(C–O): 0.075 Å vs. 0.05 Å).

### 2.3. Description of the crystal assemblies

2.3.1. Salts with the monocarboxylic acids

Interpretation of the crystal packing of acetate **2** is somewhat complicated by the disorder of the OH group terminating the aminoalcohol side chain. The hydroxyl group seems to randomly occupy two different positions originating from the rotation along the C12–C13 bond with overall 70:30 relative populations. Both OH
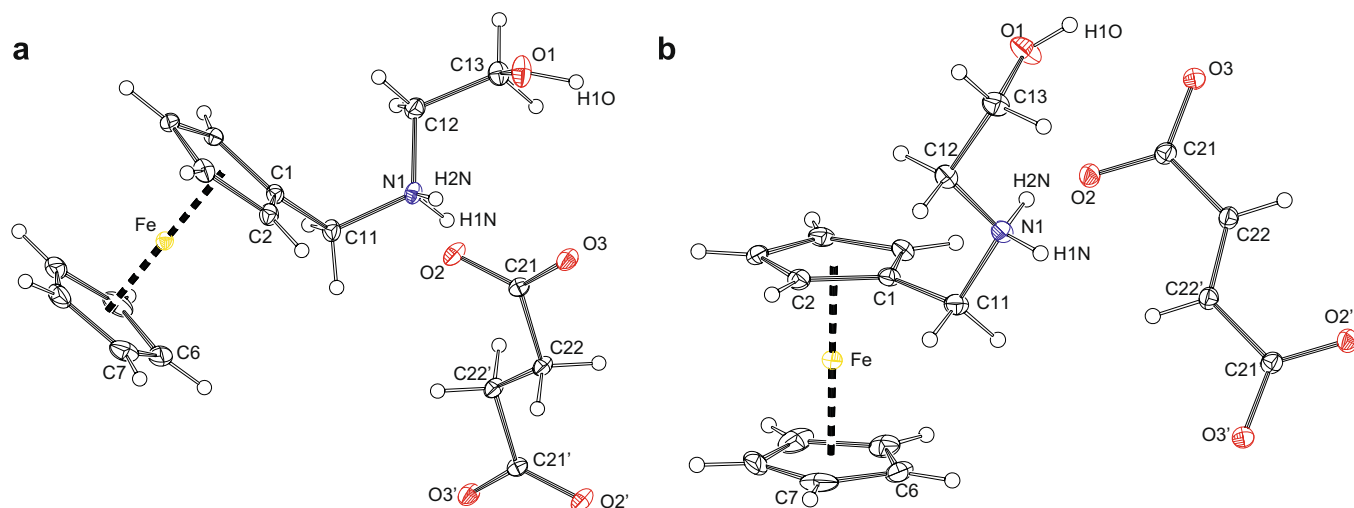
Fig. 5. A view of the molecular structures of **6** (a) and **7** (b). Displacement ellipsoids enclose 30% probability level. Structural data for the succinate anion in **6**: C21—C22 1.522(2), C22—C22′ 1.520(2), C21—O2 1.248(2), C21—O3 1.273(2) Å; C22′—C22—C21 114.6(1), O2—C21—O3 123.4(1)°. Structural data for the fumarate anion in **7**: C21–C22 1.505(2), C22—C22′ 1.322(2), C21—O2 1.250(2), C21—O3 1.269(2) Å; C22′—C22—C21 123.4(1), O2—C21—O3 124.5(2)°.
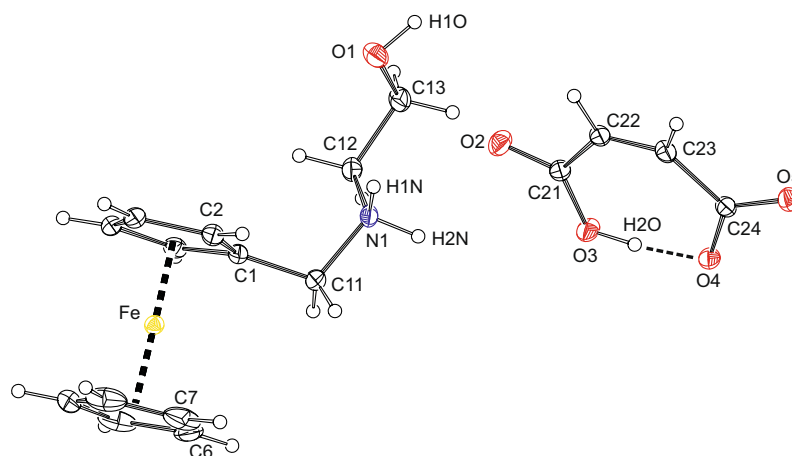
Fig. 6. A view of the molecular structure of **8** showing displacement ellipsoids at the 30% probability level. Structural data for the anion: C21—C22 1.488(3), C22—C23 1.331(3), C23—C24 1.506(3), C21—O2 1.229(2), C21—O3 1.304(2), C24—O4 1.288(2), C24—O5 1.237(2) Å; C21—C22—C23 131.3(2), C22—C23—C24 130.6(2), O2—C21—O3 121.5(2), O4—C24—O5 123.8(2)°.

Table 1
Comparison of the structural parameters for the (ferrocenylmethyl)(2-hydroxyethyl)ammonium cations in the structure of **2–8**[a]

Parameter	**2**	**3**	**4** (cation 1/2)[c]	**5** (cation 1/2)[c]	**6**	**7**	**8**
Fe–Cg1	1.642(1)	1.6452(6)	1.6525(9)/1.644(1)	1.652(2)/1.646(2)	1.6420(7)	1.6394(7)	1.6400(9)
Fe–Cg2	1.646(1)	1.6490(7)	1.655(1)/1.646(1)	1.653(2)/1.651(2)	1.6531(8)	1.6492(9)	1.657(1)
∠Cp1,Cp2	2.7(1)	2.67(9)	4.0(1)/1.7(1)	1.9(2)/1.8(2)	0.9(1)	0.5(1)	1.3(1)
C1–C11	1.492(3)	1.493(2)	1.494(3)/1.495(3)	1.496(4)/1.493(4)	1.500(2)	1.501(2)	1.498(3)
C11–N1	1.500(3)	1.499(2)	1.506(2)/1.489(3)	1.503(4)/1.507(4)	1.502(2)	1.500(2)	1.503(2)
N1–C12	1.493(3)	1.494(2)	1.486(2)/1.489(2)	1.483(4)/1.486(4)	1.481(2)	1.484(2)	1.492(2)
C12–C13	1.507(3)	1.514(2)	1.518(3)/1.513(3)	1.519(4)/1.519(4)	1.515(2)	1.511(2)	1.509(3)
C13–O1	1.315(3)/1.418(6)[b]	1.413(2)	1.425(2)/1.417(3)	1.421(4)/1.418(5)	1.412(2)	1.412(2)	1.414(2)
C1–C11–N1	112.1(2)	111.2(1)	111.0(2)/108.6(2)	111.9(2)/113.1(2)	113.2(1)	113.7(1)	112.7(1)
C11–N1–C12	112.3(2)	112.6(1)	115.2(2)/115.0(2)	115.4(2)/114.2(2)	114.1(1)	114.0(1)	115.2(2)
N1–C12–C13	112.1(2)	111.9(1)	115.5(2)/108.9(2)	110.9(2)/111.2(3)	111.4(1)	111.6(1)	110.2(2)
C12–C13–O1	116.3(2)/114.8(3)[b]	112.6(1)	111.8(2)/110.6(2)	112.1(3)/111.7(3)	108.5(1)	108.1(1)	106.8(2)
C1–C11–N1–C12	176.7(2)	174.7(1)	87.5(2)/−179.8(2)	59.8(3)/−51.8(3)	−66.5(2)	63.1(2)	−66.5(2)
C11–N1–C12–C13	175.7(2)	178.9(1)	95.0(2)/167.1(2)	176.8(2)/−178.6(3)	177.8(1)	−179.7(1)	169.5(2)
N1–C12–C13–O1	71.1(3)/150.9(3)[b]	−72.0(1)	−56.9(2)/−175.0(2)	65.7(3)/−63.0(3)	−64.7(2)	64.8(2)	−66.9(2)

[a] The ring planes are defined as follows: Cp(1) = C(1–5), Cp2 = C(6–10). Cg(1) and Cg(2) are the respective ring centroids.

[b] Two values due to disordered OH group.

[c] Labelling scheme used for the second cation in the structure is strictly analogous. Atomic labels of the carbon atoms take the value C(n + 20), with Cn being the atomic label in cation one, while the labels of all other heavy atoms (Fe, O, N) have the numerical part changed from 1 to 2.

groups are involved in hydrogen bonding but play different roles in the propagation of the crystal assembly.

The hydroxy group residing at the more populated site interacts with a proximal acetate anion via O–H⋯O hydrogen bond, complementing two N–H⋯O hydrogen bonds formed between one of the NH protons and both carboxylic oxygens (Fig. 7a, Table 2). The formed, highly organised ion pairs (three X–H⋯O hydrogen bonds per the ion pair) further associate into infinite chains via N–H⋯O hydrogen bonds between the other NH proton and acetate oxygen in adjacent entities related by crystallographic glide plane operation (x, $1-y$, $\pm 1/2 + z$). On the other hand, the OH group located on the less populated position (three of every ten molecules on average) is directed outside the H-bonded chain, forming O–H⋯O hydrogen bonds to acetate ions in *neighbouring* linear assemblies (Fig. 7b). The individual chains are thus cross-linked into a complex three-dimensional array. Additional support to the formed assembly comes from inter-ion C11–H11A⋯O2 and C11–H11A⋯O2 contacts (Table 2) and C–H⋯π-ring interac-

tions between near-to-perpendicular cyclopentadienyl rings (C7–H7⋯Cg2^i: C7⋯Cg2 3.922(3) Å, H7⋯Cg2 2.95 Å, angle at H7 159°; *i*. x, −y, −1/2 + z).

Benzoate 3 crystallises with the symmetry of the monoclinic space group $P2_1/c$. Unlike the acetate 2, ions in the structure 3 associate into closed centrosymmetric dimers that are decorated with ferrocenyl groups at their exterior (Fig. 8). In the dimeric unit, each protonated aminoalcohol chain is connected to the benzoate counter ion via a pair of N–H⋯O and O–H⋯O hydrogen bonds whilst another N–H⋯O hydrogen bond involving the second NH proton is responsible for assembly of two [**1**H](PhCO$_2$) units into the dimer (Table 2). The individual dimer moieties associate into tilted columnar stacks by means of C–H⋯O contacts (Fig. 9).

2.3.2. Salts with dicarboxylic acids

Compounds **4–8** all form rather complicated H-bonding patterns in the crystals, often involving bifurcated hydrogen bonds. A salient feature of all the molecular assemblies is the formation
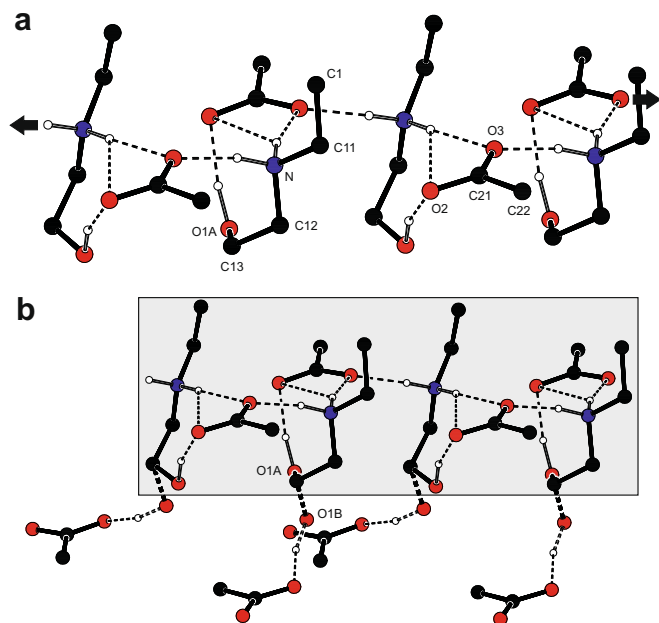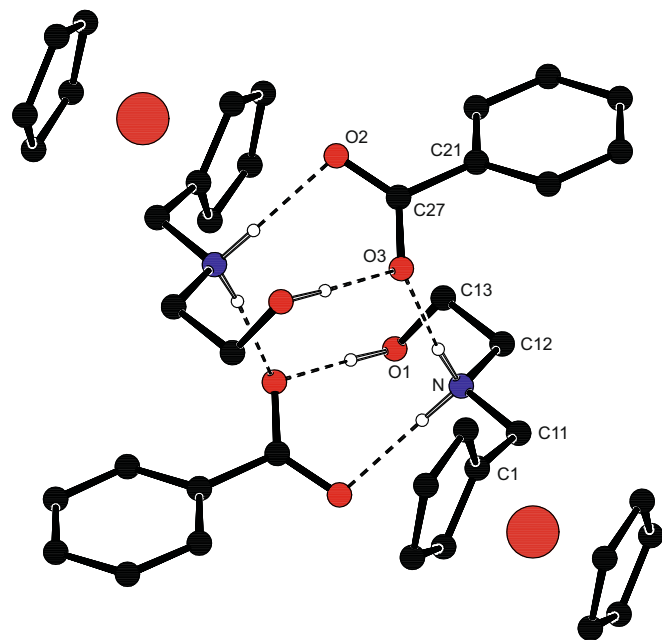

Fig. 7. Crystal assembly of **2** showing only one (the more populated) (a) and both (b) positions of the disordered OH group. To avoid complicating the Figure, only the pivotal carbon atom of the ferrocenyl group (C1) and the acetate ions from proximal chains serving as hydrogen bond acceptors to OH groups are shown. The grey box in part (b) encloses the single hydrogen-bonded chain depicted in part (a).

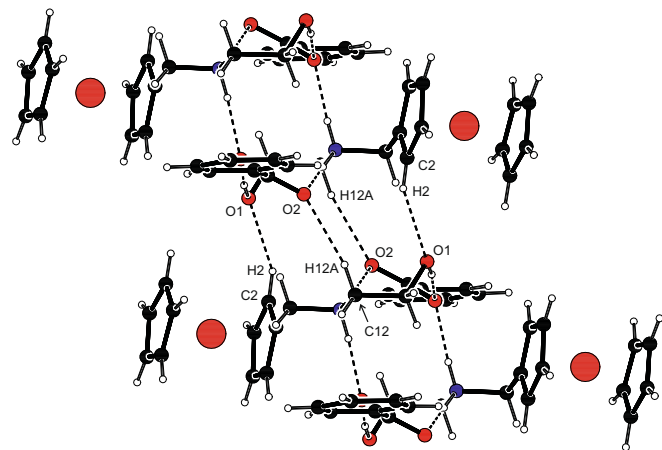**Fig. 8.** View of the dimeric unit in the crystal of **3**. Only hydrogen bonded H-atoms are shown.

Table 2
Hydrogen bond parameters for compounds **2** and **3** (in Å and °)

D–H⋯A	D⋯A	Angle at H
Compound 2		
O1A–H1OA⋯O2^i	2.779(3)	165
N1–H1N⋯O3^{ii}	2.748(2)	167
N1–H2N⋯O2^i	3.326(3)	136
N1–H2N⋯O3^i	2.787(2)	164
C11–H11A⋯O2	3.247(3)	168
C13–H13A⋯O2^{iii}	3.381(3)	160
Compound 3		
N1–H1N⋯O3	2.773(1)	174
O1–H1O⋯O3^{iv}	2.699(1)	175
N1–H2N⋯O2^{iv}	2.777(2)	169
C2–H2⋯O1^v	3.344(2)	138
C12–H12A⋯O2^{vi}	3.367(2)	165

D = donor, A = acceptor. Symmetry operations: (*i*) x, 1 − y, −½ + z; (*ii*) x, y, −1 + z; (*iii*) ½ − x, ½ − y, 1 − z; (*iv*) −1 − x, −y, 2 − z, (*v*) −1 − x, −1 − y, 2 − z; (*vi*) x, −1 + y, z.
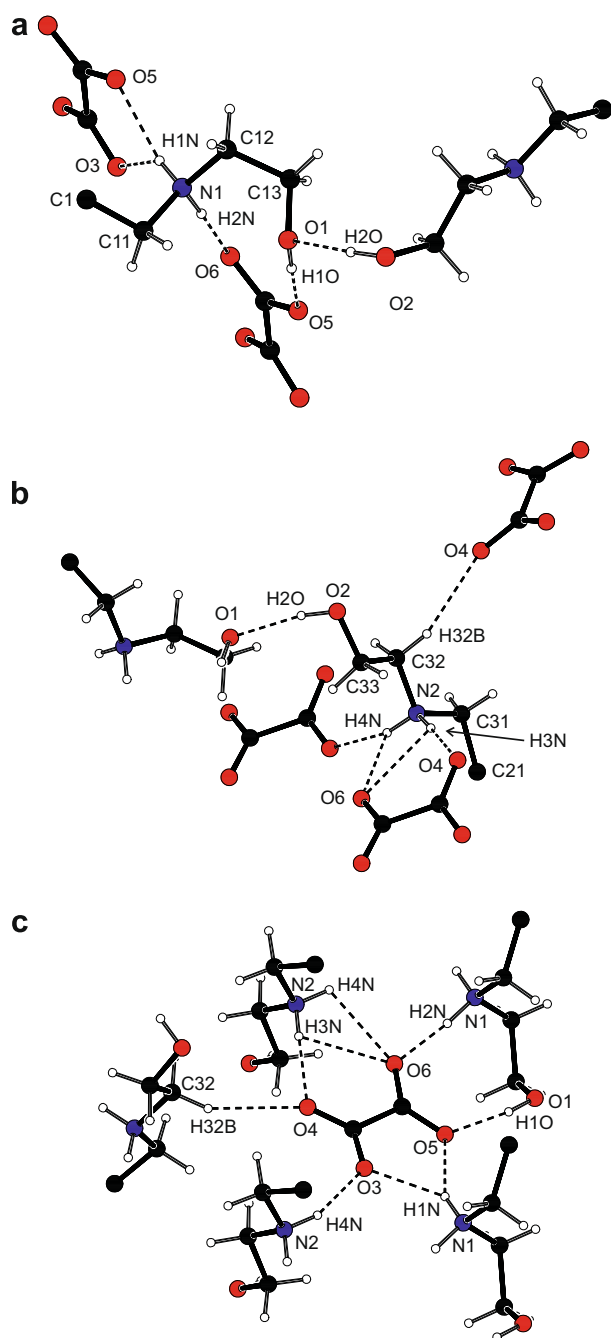

Fig. 9. Section of the columnar assembly in the structure of **3**.

of periodic arrays via alternation of non-polar layers (accommodating the bulky hydrophobic ferrocenyl units) and polar sheets (constructed from hydrogen-bonded carboxylate ions and the (2-hydroxyethyl)ammonium moieties).

As mentioned above, oxalate **4** crystallises with two independent cations and one anion in the asymmetric unit. The cations differ predominantly by the conformation of the β-hydroxyammonium moieties, which apparently reflects rotational reorientation of their polar chains required for effective formation of hydrogen bonds. Indeed, the role of the two cations in the crystal assembly (H-bonding patterns) differs. Each cation 1 forms four hydrogen bonds as the donor towards two oxalate ions and one H-bond as the acceptor from the OH group of a neighbouring

Table 3
Hydrogen bond parameters for compounds **4** and **5** (in Å and °)

D—H···A	D···A	angle at H
Compound 4		
N1–H1N···O3^{i}	2.772(2)	131
N1–H1N···O5^{i}	2.795(2)	148
N1–H2N···O6^{ii}	2.697(2)	174
O1–H1O···O5^{ii}	2.645(2)	166
N2–H3N···O4	2.792(2)	177
N2–H3N···O6	2.832(2)	103
N2–H4N···O3^{iii}	2.728(2)	159
N2–H4N···O6	2.832(2)	106
O2–H2O···O1^{iv}	2.746(2)	169
C32–H32B···O4^{iv}	3.368(2)	153
Compound 5		
N1–H1N···O4^{v}	2.656(3)	152
N1–H2N···O6^{vi}	2.784(3)	174
O1–H1O···O3^{v}	2.711(3)	177
N2–H3N···O5^{vii}	2.798(3)	168
N2–H4N···O6^{viii}	2.751(3)	160
O2–H2O···O3^{vii}	2.811(3)	152
C11–H11A···O2	3.515(4)	169
C11–H11B···O4^{vi}	3.196(4)	148
C31–H31A···O5^{viii}	3.195(4)	139
C31–H31B···O1^{ix}	3.407(4)	179

D = donor, A = acceptor. Symmetry operations: (i) $-1 + x, -1 + y, z$; (i) $-1 + x, y, z$; (iii) $x, -1 + y, z$; (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; ($v$) $x, 1 + y, z$; (vi) $-1 + x, 1 + y, z$; (vii) $1-x, \frac{1}{2} + y, \frac{1}{2} - z$; ($viii$) $2-x, \frac{1}{2} + y, \frac{1}{2} - z$, ($ix$) $x, -1 + y, z$.

Fig. 10. Survey of hydrogen bonds formed by the individual ions in the crystal of oxalate **4**: (a) cation 1, (b) cation 2, (c) the anion. To avoid complication of the figure, only the pivotal carbon atoms (C1 and C21) are shown from the ferrocenyl units.

cation 2 (Fig. 10a, Table 3). On the other hand, cation 2 behaves exclusively as hydrogen bond donor, being involved in five 'classical' hydrogen bonds with two oxalate ions and one cation (OH from cation 1) and, additionally, one C–H···O(oxalate) contact (Fig. 10b). As a consequence, each oxalate ion forms nine hydrogen bonds (Fig. 10c) either with the adjacent OH/NH protons or with the C32–H32B bond, possibly polarised by the neighbouring NH$_2^+$ unit.

When taken together, the hydrogen bonds (both N/O–H···O and C–H···O in cooperation) in the structure of **4** result in the formation of infinite polar layers parallel to the crystallographic *ab* plane. The bulky ferrocenyl substituents are directed outside these layers and separate the polar domains (Fig. 11). The non-polar regions are packed at the van der Waals distances; no significant interactions involving the aromatic ring (π···π and C–H···π) are detected in the structure.

Similarly to the oxalate salt, malonate **5** crystallises with two cations and one anion in the asymmetric unit. Contrary to **4**, however, the geometry of the independent cations including conformation of their side chains, as well as the role of the cations in the hydrogen bonded assembly, do not differ significantly (Figs. 12a and 12b). Each cation in the structure of **5** forms N–H···O hydrogen bonds to two malonate ions that are mutually related by translation along the crystallographic *a* axis (Table 3). In addition, the cations form two C–H···O contacts from the ferrocenyl-linking methylene group (C11/C31); one to the H-bonded malonate ion and one to OH group of a neighbouring cation (cation 1 → cation 2 and vice versa). The malonate ion is embedded in a cavity bordered by four cations (2× cation 1 and 2× cation 2) so that each of its four oxygen atoms forms two hydrogen bonds towards OH/NH or CH protons (Fig. 12c).

Although differing in details, the overall mode of H-bond interactions in the crystal assemblies of **4** and **5** is rather similar (compare Figs. 10 and 12). Consequently, compound **5** also forms hydrogen-bonded layers parallel to the *ab* plane that are regularly spaced by the non-polar sheets accommodating the ferrocene moieties. Yet, the crystal packing of **5** seems to be "more neat", likely reflecting an enhanced mobility of the anion imparted by the presence of the flexible methylene spacer. Furthermore, as the carboxyl groups are moved apart (and bent) in the malonate anion
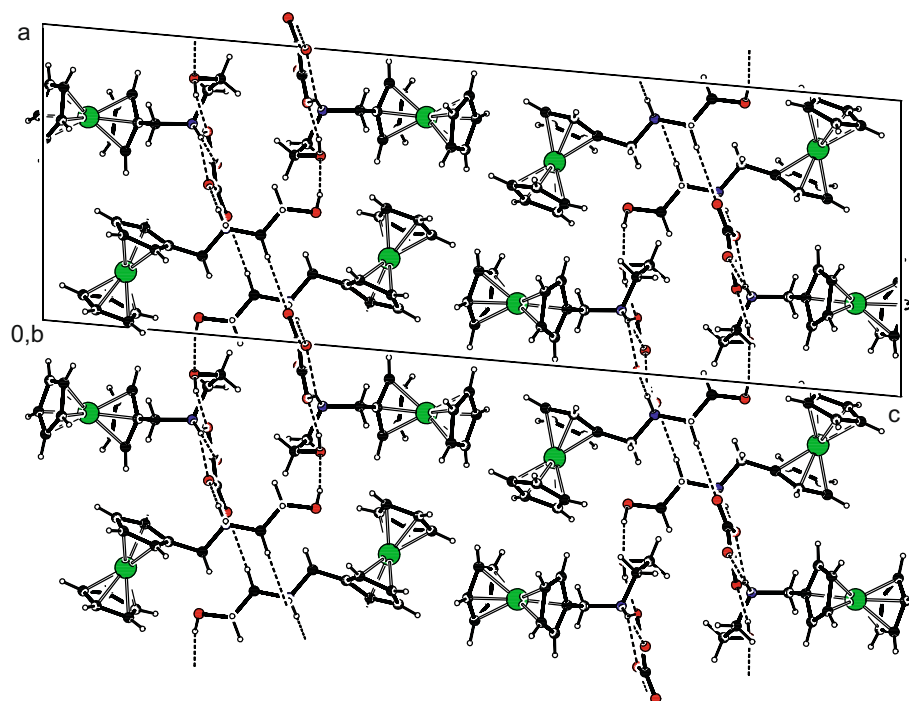
Fig. 11. Projection of the crystal assembly of **4** along the crystallographic *b* axis.

(compared to the oxalate), the structure of **5** totally lacks *donor* bifurcated hydrogen bonds resulting from enforced spatial contacts (N.B. *acceptor* bifurcated bonds are still present; see Fig. 12c).

Compounds **6** and **7** are essentially isostructural, generating virtually identical principal interactions. Hence, their crystal assemblies will be discussed jointly (Fig. 13, Table 4). Each cation in the structure of **6** and **7** behaves as an H-bond donor towards three proximal anions, forming a bifurcated bond with one of them. Conformation of the side chain allows for formation of additional intramolecular N1–H2N···O1 hydrogen bonds though with rather acute angles at the hydrogen (around 100°). Due to the imposed crystal symmetry (see above), the anion (succinate or maleinate) can be regarded as consisting of two independent parts. Each carboxyl group of the anions acts as H-bond acceptor for the H1N and H1O protons of the aminoalcohol chain and also for the C11–H11B bond, which is located in a proximal anion moiety. The latter soft interactions are supported with additional C11–H11A···O2 contacts. Both compounds also show intramolecular C–H···O2 contacts involving one of the cyclopentadienyl CH groups adjacent to the pivotal atom (these interactions are not indicated in Fig. 13: C···O2 = 3.162(2)/3.226(2) Å, angle at H = 123/125° for **6/7**).

As indicated above, the influence of the anions is minimised by their similar geometry, the most notable difference reflecting the nature of the anion backbone (tetrahedral sp^3–CH$_2$ vs. trigonal sp^2–CH=). Whereas one of the succinate CH$_2$ protons (activated by the attached carboxyl group) is properly positioned for the C22–H22B···O3 interaction, the fumarate ion does not interact similarly because the =CH hydrogen is not directed towards the adjacent oxygen atom (Table 4). In analogy to compounds **4** and **6**, intermolecular interactions in the crystal of succinate and fumarate salts result into the formation of layers oriented parallel to the crystallographic *bc* plane, running at *a* = 0 and 1 in the cell. Again, these layers are separated by the non-polar ferrocenyl groups that fill the remaining space in a zig–zag fashion because of crystallographic symmetry.

The structure of compound **8** differs from the structures of other salts with dicarboxylic anions in that the hydrogenmaleate anion forms relatively strong intramolecular O–H···O hydrogen bond. By contrast, the geometry of the cation is unexceptional and its conformation is similar to that in **5**–**7**. Each (2-hydroxyethyl)ammonium chain in the structure of **8** interacts with three different anions via three N/O–H···O hydrogen bonds and, additionally, is involved in a bent intramolecular N1–H1N···O1 contact (angle at H = 103°; Fig. 14a, Table 5). The hydrogenmaleate ions bind three [**1**H]$^+$ cations via conventional H-bond donors and are also linked to one anion via a soft C22–H22···O3 interaction (Fig. 14b).

Despite the mentioned differences, hydrogenmaleate **8** also forms a bedded crystal structure (Fig. 15). The crystal assembly resembles a layered composite, consisting, in perfect alternation, of double layers made up by the ferrocene units (A) and triple layers in which the inner sheet of hydrogenmaleate anions (C) is sandwiched by two layers generated by the H-bonded (2-hydroxyethyl)ammonium chains (B). The centre layer (C) coincides with the middle of the unit cell (i.e., it is located at *a* = ½ as the mean).

3. Conclusions

Simple mono- and dicarboxylic acids react with **1** under proton transfer to afford well-defined air-stable crystalline (ferrocenylmethyl)(2-hydroxyethyl)ammonium ([**1**H]$^+$) carboxylates. In the solid state, these ammonium salts generate complex hydrogen bonded arrays via charge supported N$^+$–H···O$^-$ and O–H···O$^-$ hydrogen bonds, and C–H···O contacts. Bifurcated bonds are relatively common in the formed assemblies owing to proximity of the hydrogen-bonded groups. The crystal assemblies of salts with monocarboxylic acids propagate preferentially in one dimension (**2**: cross-linked chains, **3**: columnar stacks). By contrast, all salts prepared from the dicarboxylic acids (including the hydrogenmaleate) form layered composite structures where polar layers formed from hydrogen bonded hydroxyammonium and
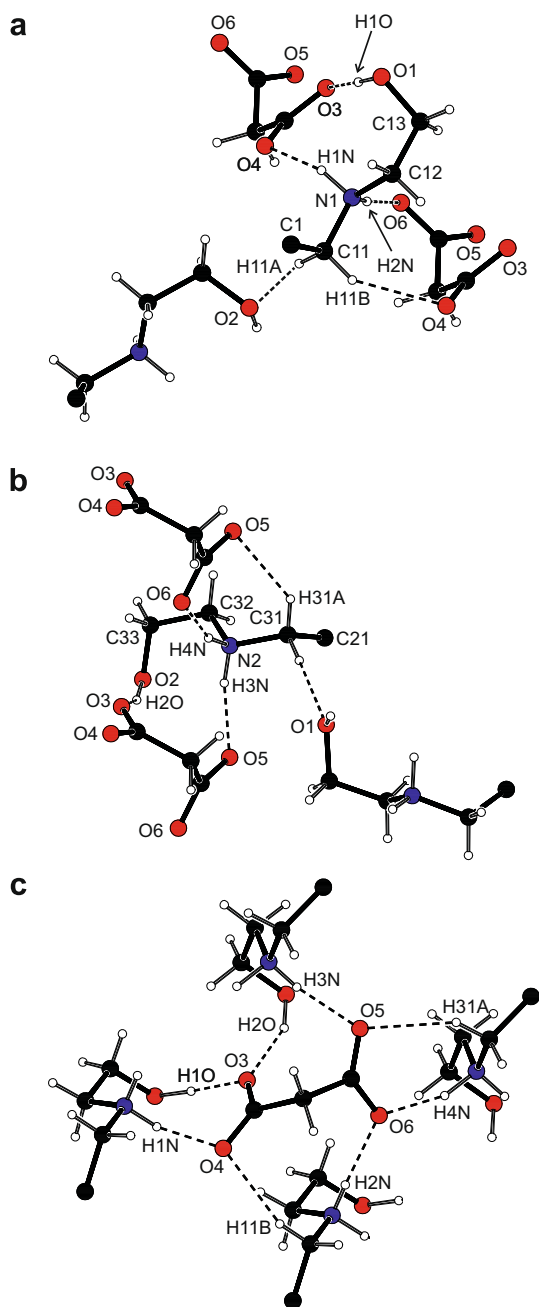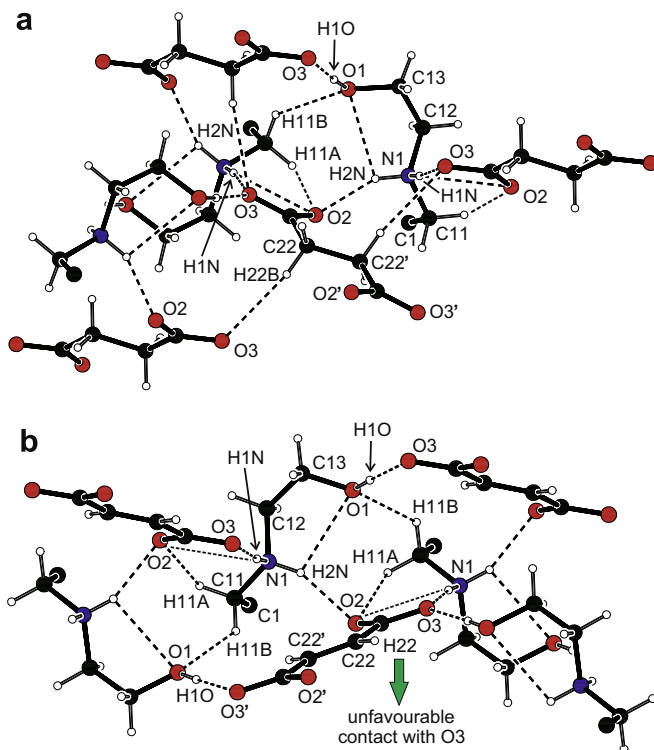
Fig. 12. Hydrogen bonds formed by individual ions in the crystals of malonate **5**: (a) cation 1, (b) cation 2, (c) the anion. For clarity, only the pivotal carbon atoms (C1 and C21) are shown from the ferrocenyl units.

Fig. 13. Comparison of the hydrogen bonded arrays in the structures of succinate **6** (a) and fumarate **7** (b). The sections are virtual mirror images because of the selection of the independent molecules. Compared to **6**, the diagram for **7** contains one more aminoalcohol chain to illustrate an additional C11–H11A···O2 contact and lacks one anion which does not form favourable C22–H22···O3 contact for steric reasons. For clarity, interactions generated by the anions are shown in full only for the crystallographically independent halves and the ferrocene units are omitted except for their pivotal C1 carbon atom.

Table 4
Hydrogen bond parameters for compounds **6** and **7** (in Å and °)

Compound **6**			Compound **7**		
D—H···A	D···A	Angle at H	D—H···A	D···A	Angle at H
N1–H1N···O2^{i}	3.143(2)	120	N1–H1N···O2^{iv}	3.180(2)	121
N1–H1N···O3^{i}	2.715(2)	170	N1–H1N···O3^{iv}	2.714(2)	172
N1–H2N···O1	2.894(2)	101	N1–H2N···O1	2.891(2)	103
N1–H2N···O2	2.789(2)	154	N1–H2N···O2	2.806(2)	156
O1–H1O···O3^{ii}	2.689(2)	177	O1–H1O···O3^{v}	2.706(2)	178
C11–H11A···O2^{i}	3.211(2)	118	C11–H11A···O2^{iv}	3.224(2)	125
C11–H11B···O1^{i}	3.356(2)	138	C11–H11B···O1^{iv}	3.256(2)	132
C22–H22B···O3^{iii}	3.512(2)	168	–^{a}		

D = donor, A = acceptor. Symmetry operations: (i) x, ½ − y, −½ + z; (ii) 1−x, ½ + y, 3/2 − z; (iii) 1 − x, −½ + y, 3/2 − z; (iv) x, −½ − y, ½ + z; (v) −x, −½ + y, −½ − z.
 ^{a} An interaction similar to the C22–H22B···O3 contact observed in the structure of **6** has, in the case of **7**, somewhat longer C···O separation (ca. 3.61 Å) and unfavourable angle at H22 (ca. 89°).

carboxylate moieties alternate with non-polar ones accommodating the ferrocene units.

4. Experimental

4.1. Materials and methods

Aminoalcohol **1** was prepared from ferrocenecarboxaldehyde and 2-aminoethanol as described in the literature [14]. Methanol was distilled prior to use. All other chemicals (the carboxylic acids, diethyl ether) were used as received. Combustion analyses were performed by the analytical laboratory of the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic. Details on crystal structure determination are given in Section 4.4.

4.2. Preparation of the salts with monocarboxylic acids

(Ferrocenylmethyl)(2-hydroxyethyl)amine (**1**; 26 mg, 0.10 mmol) was dissolved in a minimum amount of methanol and the resulting solution was introduced to a solution of the respective monocarboxylic acid in methanol (0.10 mmol). The mixture was carefully layered with diethyl ether and allowed to crystallise in the dark by diffusion of diethyl ether vapours at 4 °C. Crystalline products formed during several days were filtered off, washed with diethyl ether and dried under vacuum.
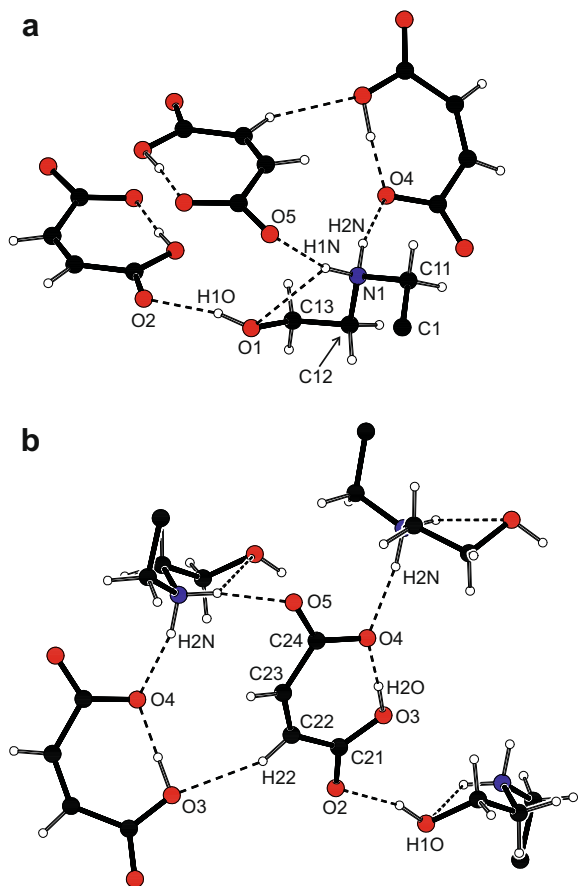
Fig. 14. Hydrogen bonds formed by the cation (a) and anion (b) in the crystal of **8**. For clarity, only the pivotal carbon atom (C1) is shown from each ferrocenyl group.

Table 5
Hydrogen bond parameters for compound **8** (in Å and °)

D—H···A	D···A	Angle at H
N1–H1N···O1	2.867(2)	103
N1–H1N···O5^i	2.899(2)	164
N1–H2N···O4	2.769(2)	163
O1–H1O···O2	2.724(2)	163
O3–H2O···O4	2.448(2)	171
C22–H22···O3	3.235(2)	154

D = donor, A = acceptor. Symmetry operations: (*i*) $1 - x$, ½ + *y*, ½ − *z*; (*ii*) $1 - x$, $1 - y$, $1 - z$; (*iii*) *x*, ½ − *y*, −½ + *z*.

Fig. 15. Projection of the crystal assembly of maleate **8** along the crystallographic *b* axis. Alternation of the layer is highlighted (A = layers accommodating the ferrocene units; B = layer generated by the (2-hydroxyethyl)ammonium chains, and C = the layer built up from hydrogenmaleate ions).

*(Ferrocenylmethyl)(2-hydroxyethyl)ammonium acetate (**2**)* was prepared from **1** (26 mg, 0.10 mmol) and acetic acid (6 mg, 0.10 mmol). Anal. Calc. for $C_{15}H_{21}FeNO_3$: C, 56.44; H, 6.63; N, 4.39%. Found: C, 56.03; H, 6.58; N, 4.31%.

*(Ferrocenylmethyl)(2-hydroxyethyl)ammonium benzoate (**3**)* was prepared from **1** (26 mg, 0.10 mmol) and benzoic acid (12 mg, 0.10 mmol). Anal. Calc. for $C_{20}H_{23}FeNO_3$: C, 63.00; H, 6.08; N, 3.67%. Found: C, 62.74; H, 6.10; N, 3.60%.

4.3. Preparation of the salts with dicarboxylic acids

Salts with dicarboxylic acids were prepared and isolated as described above starting with **1** (26 mg, 0.10 mmol) and the corresponding dicarboxylic acid (0.05 mmol). The mixture was allowed to crystallise in the dark by diffusion of diethyl ether vapours at room temperature.

*Bis{(ferrocenylmethyl)(2-hydroxyethyl)ammonium} oxalate (**4**)* was synthesised from **1** (26 mg, 0.10 mmol) and oxalic acid (4.5 mg, 0.05 mmol). Anal. Calc. for $C_{28}H_{36}Fe_2N_2O_6$: C, 55.28; H, 5.97; N, 4.61%. Found: C, 55.14; H, 5.80; N, 4.51%.

*Bis{(ferrocenylmethyl)(2-hydroxyethyl)ammonium} malonate (**5**)* was prepared from **1** (26 mg, 0.10 mmol) and malonic acid (5 mg, 0.05 mmol). Anal. Calc. for $C_{29}H_{38}Fe_2N_2O_6$: C, 55.97; H, 6.16; N, 4.50%. Found: C, 55.92; H, 6.17; N, 4.38%.

*Bis{(ferrocenylmethyl)(2-hydroxyethyl)ammonium} succinate (**6**)* was prepared from **1** (26 mg, 0.10 mmol) and succinic acid (6 mg, 0.05 mmol). Anal. Calc. for $C_{30}H_{40}Fe_2N_2O_6$: C, 56.62; H, 6.34; N, 4.40%. Found: C, 56.45; H, 6.34; N, 4.34%.

*Bis{(ferrocenylmethyl)(2-hydroxyethyl)ammonium} fumarate (**7**)* was obtained from **1** (26 mg, 0.10 mmol) and fumaric acid (6 mg, 0.05 mmol). Anal. Calc. for $C_{30}H_{38}Fe_2N_2O_6$: C, 56.80; H, 6.04; N, 4.42%. Found: C, 56.45; H, 6.00; N, 4.27%.

*(Ferrocenylmethyl)(2-hydroxyethyl)ammonium hydrogenmaleate (**8**)* was obtained by reaction **1** (26 mg, 0.10 mmol) with maleic acid (6 mg, 0.05 mmol). The same compound resulted also at 1:1 molar ratio. Anal. Calc. for $C_{17}H_{21}FeNO_5$: C, 54.42; H, 5.64; N, 3.73%. Found: C, 54.32; H, 5.49; N, 3.66%.

Table 6
Crystallographic data, data collection and structure refinement parameters for **2–8**[a]

Compound	2	3	4	5	6	7	8
Formula	$C_{15}H_{21}FeNO_3$	$C_{20}H_{23}FeNO_3$	$C_{28}H_{36}Fe_2N_2O_6$	$C_{29}H_{38}Fe_2N_2O_6$	$C_{15}H_{20}FeNO_3$[f]	$C_{15}H_{19}FeNO_3$[f]	$C_{17}H_{21}FeNO_5$
M (g mol^{-1})	319.18	381.24	608.29	622.31	318.17	317.16	375.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	36.344(1)	10.5286(2)	11.9424(2)	5.9776(2)	17.1760(2)	17.4587(4)	20.6531(2)
b(Å)	9.8347(3)	8.1048(1)	6.3957(1)	13.3234(4)	8.1212(2)	7.7622(3)	7.3379(2)
c (Å)	8.3374(2)	21.4866(5)	34.7603(6)	34.948(1)	10.0907(5)	10.2314(5)	11.0787(6)
β (°)	98.517(2)	102.545(1)	95.1160(9)	94.006(1)	93.942(2)	91.487(2)	102.958(2)
V (Å^3)	2947.2(1)	1789.73(6)	2644.42(8)	2776.5(2)	1404.22(8)	1386.07(9)	1636.2(1)
Z	8	4	4	4	4	4	4
D_{calc} (g mL^{-1})	1.439	1.415	1.528	1.489	1.505	1.520	1.523
μ (Mo Kα) (mm^{-1})	1.030[e]	0.861	1.143	1.091	1.080	1.094	0.949
$2\theta_{max}$ (°)	27.5	28.3	27.5	27.4	27.5	27.5	27.5
Diffractions total, R_{int} (%)[b]	19734, 4.18	19081, 4.0	22682, 4.6	29263, 2.4	20046, 3.3	16814, 3.4	20570, 3.5
Unique/observed[d] diffractions	3391/2684	4384/3994	5995/5113	6272/4993	3231/2710	3158/2785	3739/3241
R (observed data) (%)[c]	3.58	2.75	3.69	5.15	2.83	2.90	3.30
R, wR (all data) (%)[d]	5.23, 9.08	3.12, 6.78	4.63, 10.2	6.76, 14.2	3.70, 7.11	3.49, 7.68	4.04, 8.49
$\Delta\rho$ (e Å^{-3})	0.52, −0.37	0.35, −0.41	0.42, −0.61	0.90, −0.81	0.32, −0.33	0.43, −0.41	0.66, −0.41

[a] Common details: $T = 150(2)$ K.
[b] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where F_o^2 (mean) is the average intensity of symmetry-equivalent diffractions.
[c] Diffractions with $I_o > 2\sigma(I_o)$.
[d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\, w(F_o^2)^2]^{1/2}$.
[e] Corrected for absorption. The range of transmission coefficients = 0.873–0.930.
[f] Only half of the "molecule" (i.e., **[1**H](anion)$_{0.5}$) is structurally independent.

4.4. X-ray crystallography

Crystals used for single-crystal X-ray diffraction analysis were selected from the synthesis mixtures; **2**: orange bar (0.08 × 0.08 × 0.30 mm^3), **3**: orange prism (0.25 × 0.42 × 0.50 mm^3), **4**: orange needle (0.15 × 0.20 × 0.60 mm^3), **5**: orange needle (0.10 × 0.13 × 0.63 mm^3), **6**: orange plate (0.12 × 0.28 × 0.55 mm^3), **7**: orange plate (0.12 × 0.40 × 0.50 mm^3), and **8**: orange plate (0.05 × 0.30 × 0.60 mm^3).

Full-set diffraction data (±h±k±l, $2\theta \leqslant 54.8$–56.6°) were collected with a Nonius KappaCCD diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) using graphite monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å). The data were analysed with the HKL program package [15]. The data for **2** have been corrected for absorption by a numerical method incorporated in the diffractometer software. The range of the transmission factors is given in Table 6.

The structures were solved by direct methods (SIR97) [16] and refined by weighted full-matrix least-squares procedure on F^2 (SHELXL97) [17]. All non-hydrogen atoms were refined with anisotropic displacement parameters with the exception of disordered OH oxygens in the structure of **2**. The disordered OH group in **2** was modelled over two positions (70:30) and the oxygen atoms were refined isotropically. The NH and OH hydrogens were identified on the difference electron density maps and refined isotropically as riding atoms. All other hydrogen atoms were included in their calculated positions and refined as riding atoms with U_{iso}(H) assigned to a multiple of U_{eq}(C) of their bonding carbon atom.

Relevant crystallographic data are summarised in Table 6. Geometric parameters and structural drawings were obtained by using a recent version of the PLATON program [18].

5. Supplementary material

CCDC 696704, 696705, 696706, 696707, 696708, 696709 and 696710 contain the supplementary crystallographic data for compounds **2–8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] G.R. Desiraju, Crystal Engineering: Design of Organic Solids, Elsevier, Amsterdam, 1989.
[2] (a) D. Braga, M. Curzi, S.L. Giaffreda, F. Grepioni, L. Maini, A. Petersen, M. Polito, Crystal Engineering with Ferrocene Compounds, in: P. Štěpnička (Ed.), Ferrocenes: Ligands, Materials and Biomolecules, Wiley, Chichester, 2008, pp. 465–498 (Chapter 12);
(b) D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375;
(c) D. Braga, Chem. Commun. (2003) 2751;
(d) D. Braga, L. Maini, M. Polito, E. Tagliavini, F. Grepioni, Coord. Chem. Rev. 246 (2003) 53.
[3] For an overview of ferrocene chemistry, see: P. Štěpnička (Ed.), Ferrocenes: Ligands, Materials and Biomolecules, Wiley, Chichester, 2008.
[4] (a) C.M. Zakaria, G. Ferguson, A.J. Lough, C. Glidewell, Acta Crystallogr., Sect. C, Cryst. Struct. Commun. 57 (2001) 687;
(b) D. Braga, L. Maini, F. Paganelli, E. Tagliavini, S. Casolari, F. Grepioni, J. Organomet. Chem. 637–639 (2001) 609;
(c) C.M. Zakaria, G. Ferguson, A.J. Lough, C. Glidewell, Acta Crystallogr., Sect. B, Struct. Sci. 58 (2002) 786;
(d) C.M. Zakaria, G. Ferguson, A.J. Lough, C. Glidewell, Acta Crystallogr., Sect. C, Cryst. Struct. Commun. 59 (2003) m271;
(e) D. Braga, L. Maini, M. Polito, L. Mirolo, F. Grepioni, Chem. Eur. J. 9 (2003) 4362;
(f) H. Miyaji, M. Dudic, G. Gasser, S.J. Green, N. Moran, I. Prokeš, G. Labat, H. Stoeckli-Evans, S.M. Strawbridge, J.H.R. Tucker, Dalton Trans. (2004) 2831.
[5] (a) Selected examples: D.M. Shin, Y.K. Chung, I.S. Lee, Cryst. Growth Des. 2 (2002) 493;
(b) I.S. Lee, D.M. Shin, Y.K. Chung, Cryst. Growth Des. 2 (2002) 493;
(c) D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, L. Sturba, Organometallics 22 (2003) 2142;
(d) D. Braga, M. Polito, D. D'Addario, E. Tagliavini, D.M. Proserpio, F. Grepioni, J.W. Steed, Organometallics 22 (2003) 4532;
(e) R. Horikoshi, C. Nambu, T. Mochida, New J. Chem. 28 (2004) 26;
(f) Y. Gao, B. Twamley, J.M. Shreeve, Organometallics 25 (2006) 3364;
(g) D. Braga, S.L. Giaffreda, F. Grepioni, Chem. Commun. (2006) 3877;;
(h) T. Mochida, F. Shimizu, H. Shimizu, K. Okazawa, F. Sato, D. Kuwahara, J. Organomet. Chem. 692 (2007) 1834;
(i) D. Braga, S.L. Giaffreda, K. Rubini, F. Grepioni, M.R. Chierotti, R. Gobetto, CrystEngComm 9 (2007) 39;
(j) D. Braga, S.L. Giaffreda, F. Grepioni, G. Palladino, M. Polito, New J. Chem. 32 (2008) 820.
[6] (a) Representative examples: C. Glidewell, G. Ferguson, A.J. Lough, C.M. Zakaria, J. Chem. Soc. Dalton Trans. (1994) 1971;
(b) J.F. Gallagher, G. Ferguson, C. Glidewell, C.M. Zakaria, Acta Cryst. Sect. C 50 (1994) 18;
(c) C. Glidewell, C.M. Zakaria, G. Ferguson, C. Glidewell, C.M. Zakaria, Acta Cryst. Sect. C 50 (1994) 678;
(d) G. Ferguson, C. Glidewell, A. Lewis, C.M. Zakaria, J. Organomet. Chem. 492 (1995) 229;
(e) C. Glidewell, R.B. Klar, P. Lightfoot, C.M. Zakaria, G. Ferguson, Acta Cryst. Sect. B 52 (1996) 110;

(f) W. Bell, G. Ferguson, C. Glidewell, Acta Cryst. Sect. C 52 (1996) 3009;
(g) C. Glidewell, S.Z. Ahmed, J.F. Gallagher, G. Ferguson, Acta Cryst. Sect. C 53 (1997) 1775;
(h) C.M. Zakaria, G. Ferguson, A.J. Lough, C. Glidewell, Acta Crystallogr. Sect. C, Cryst. Struct. Commun. 57 (2001) 914;
(i) C.M. Zakaria, G. Ferguson, A.J. Lough, C. Glidewell, Acta Crystallogr. Sect. C, Cryst. Struct. Commun. 58 (2002) m1;
(j) C.M. Zakaria, G. Ferguson, A.J. Lough, C. Glidewell, Acta Crystallogr. Sect. C, Cryst. Struct. Commun. 58 (2002) m5.
[7] (a) G.R. Desiraju, Angew. Chem. Int. Ed. Engl. 34 (1995) 2311;
(b) C.A. Hunter, K.R. Lawson, J. Perkins, C.J. Urch, J. Chem. Soc. Perkin Trans. 2 (2001) 651. and references therein;
(c) G.R. Desiraju, Acc. Chem. Res. 35 (2002) 565;
(d) T. Steiner, Angew. Chem. Int. Ed. 41 (2002) 48;
(e) A.D. Burrows, Struct. Bond. 108 (2004) 55;
(f) G.R. Desiraju, Chem. Commun. (2005) 2995;
(g) C. Garau, A. Frontera, D. Quiñonero, P. Ballester, A. Costa, P.M. Deyà, Chem. Phys. Lett. 382 (2003) 534.
[8] P. Štěpnička, I. Císařová, New J. Chem. 26 (2002) 1389.
[9] P. Štěpnička, Eur. J. Inorg. Chem. (2005) 3787.
[10] P. Štěpnička, I. Císařová, CrystEngComm. 7 (2005) 37.

[11] P. Štěpnička, I. Císařová, J. Ludvík, J. Organomet. Chem. 689 (2004) 631.
[12] P. Štěpnička, M. Zábranský, M. Lamač, I. Císařová, P. Němec, J. Organomet. Chem. 693 (2008) 1779.
[13] A search in Cambridge Structural Database (version 5.29 of November 2007 with updates of January 2008) revealed that such geometry is rather common among structures featuring both ionic ("free") and coordinated hydrogenmaleate ions (around 140 hits with this arrangement).
[14] (a) A. Hess, O. Brosch, T. Weyhermueller, N. Metzler-Nolte, J. Organomet. Chem. 589 (1999) 75;
(b) See also: J.L. Kerr, J.S. Landells, D.S. Larsen, B.H. Robinson, J. Simpson, J. Chem. Soc. Dalton Trans. (2000) 1411.
[15] Z. Otwinowski, W. Minor, HKL DENZO AND SCALEPACK program package by Nonius BV, Delft, 1997. For a reference, see: Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
[16] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[17] G.M. Sheldrick, SHELXL97. Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, Germany, 1997.
[18] (a) A. L. Spek, Platon, a multipurpose crystallographic tool, Utrecht University, Utrecht, The Netherlands, 2007, <http://www.cryst.chem.uu.nl/platon/>.;
(b) For a reference, see A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.