A two-dimensional network in the molecular salt 2-methylimidazolium hydrogen glutarate, and three-dimensional networks in the salts 2-methylimidazolium hydrogen succinate and 2-methylimidazolium hydrogen adipate monohydrate

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All three title compounds, $C_4H_7N_2^+ \cdot C_4H_5O_4^-$, (I), $C_4H_7N_2^+ \cdot C_5H_7O_4^-$, (II), and $C_4H_7N_2^+ \cdot C_6H_9O_4^- \cdot H_2O$, (III), can be regarded as 1:1 organic salts. The dicarboxylic acids join through short acid bridges into infinite chains. Compound (I) crystallizes in the noncentrosymmetric $Cmc2_1$ space group and the asymmetric unit consists of a hydrogen succinate anion located on a mirror plane and a 2-methylimidazolium cation disordered across the same mirror. The other two compounds crystallize in the triclinic $P\bar{1}$ space group. The carboxylic acid H atom in (II) is disordered over both ends of the anion and sits on inversion centres between adjacent anions, forming symmetric short $O \cdots H \cdots O$ bridges. Two independent anions in (III) sit across inversion centres, again with the carboxylic acid H atom disordered in short $O \cdots H \cdots O$ bridges. The molecules in all three compounds are linked into two-dimensional networks by combinations of imidazolium–carboxylate $N^+ - H \cdots O$ and carboxylate–carboxylate $O - H \cdots O$ hydrogen bonds. The two-dimensional networks are further linked into three-dimensional networks by $C - H \cdots O$ hydrogen bonds in (I) and by $O_{water} - H \cdots O$ hydrogen bonds in (III). According to the ΔpK_a rule, such 1:1 types of organic salts can be expected unambiguously. However, a 2:1 type of organic salt may be more easily obtained in (II) and (III) than in (I).

Comment

In a continuation of our studies of organic salts formed by organic acids and imidazole derivatives (Meng, Xiao *et al.*,

2008; Meng, Lin & Li, 2008; Zhou *et al.*, 2009), we now report our findings on the three title compounds, (I)–(III), formed by aliphatic diacids and 2-methylimidazole (2-MeIm).

(I) m = 2, n = 0
(II) m = 3, n = 0
(III) m = 4, n = 1
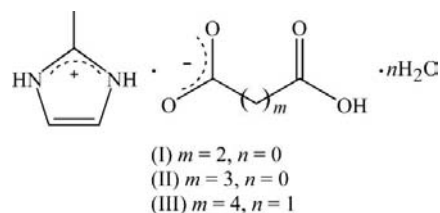
All three title compounds were obtained as 1:1 organic salts with one H atom transferred from a carboxyl group to an imidazole N atom. This can be corroborated by the distinct variations in the two carboxyl C—O bond lengths [C8—O3 = 1.231 (3) Å and C8—O4 = 1.278 (2) Å in (I); C5—O1 = 1.276 (2) Å, C5—O2 = 1.218 (2) Å, C9—O3 = 1.273 (2) Å and C9—O4 = 1.219 (2) Å in (II); C5—O1 = 1.244 (2) Å, C50—O2 = 1.264 (2) Å, C8—O4 = 1.232 (2) Å and C8—O3 = 1.294 (2) Å in (III)] and by the C—N—C bond angles in the 2-methylimidazolium (2-MeImH$^+$) cation [108.9 (3) and 109.7 (3)° in (I); 109.79 (17) and 109.72 (17)° in (II); 109.70 (16) and 109.24 (17)° in (III)]. These angles are 108.5 and 109.0° in an analogous compound in the Cambridge Structural Database [Allen (2002); refcode HILSOL (Qu, 2007)]. Besides the above-mentioned variations, some differences are also observed in the crystal structures of the three compounds.

Compound (I) crystallizes in the noncentrosymmetric space group $Cmc2_1$ and the asymmetric unit consists of a succinate monoanion located on a mirror plane and a 2-MeImH$^+$ cation. During the initial structure determination of (I), two sets of peaks were identified forming intertwined five-membered rings, related by a crystallographic mirror plane (Fig. 1). In the packing of (I), molecules are linked by six intermolecular hydrogen bonds (Table 1) into a three-dimensional network which can be easily analysed in terms of three substructures. Firstly, the succinate anion forms a one-dimensional anionic chain through an O1—H1A$\cdots$O4(x, 1 + y, z) hydrogen bond running parallel to the [010] direction. Secondly, the 2-MeImH$^+$ cation joins adjacent [010] chains together via an $R_6^5(28)$
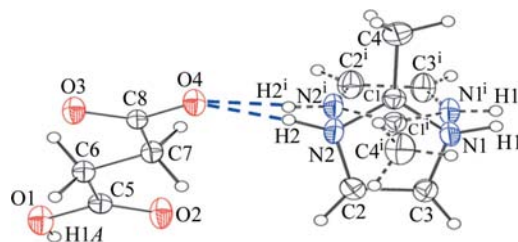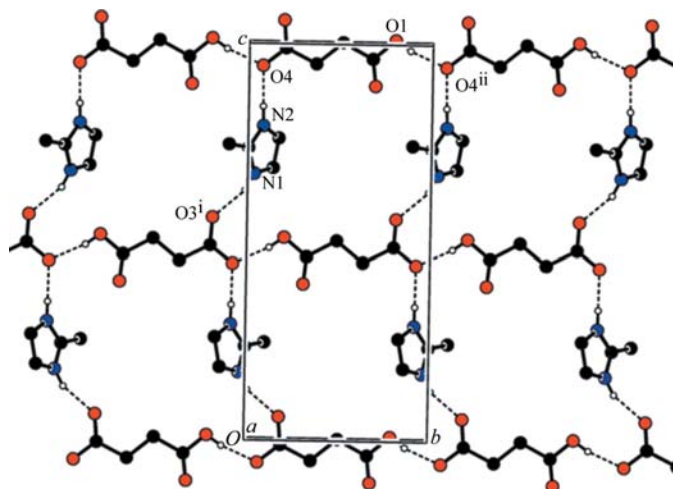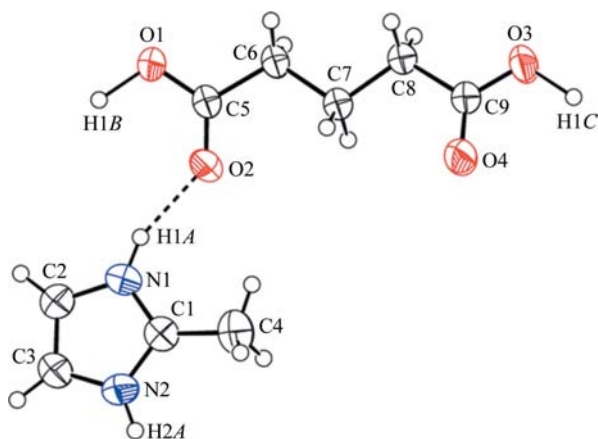

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. Both mirror-related components of the disordered 2-MeImH$^+$ cation are shown. [Symmetry code: (i) $-x + 1, y, z$.]
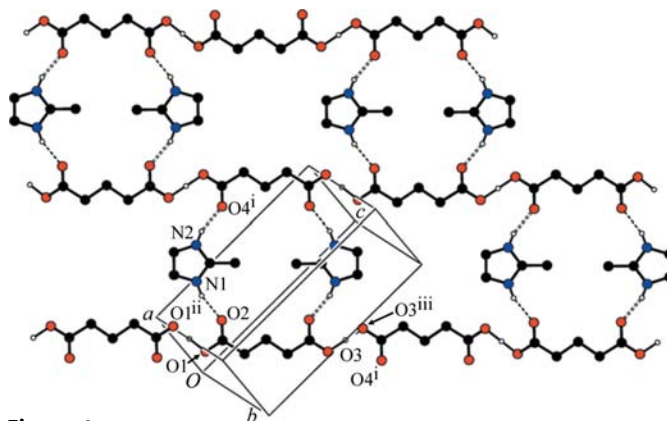
organic compounds

Figure 2
Part of the crystal structure of (I), showing the formation of the two-dimensional network built from $R_6^5(28)$ hydrogen-bonded rings. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. [Symmetry codes: (i) $-x + 1$, $-y$, $z - \frac{1}{2}$; (ii) x, $y + 1$, z.]

Figure 3
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

Figure 4
Part of the crystal structure of (II), showing the formation of the two-dimensional network built from $R_4^4(24)$ and $R_8^8(40)$ hydrogen-bonded rings. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. [Symmetry codes: (i) $x - 1$, $y + 1$, z; (ii) $-x + 2$, $-y + 2$, $-z$; (iii) $-x + 1$, $-y + 2$, $-z$.]
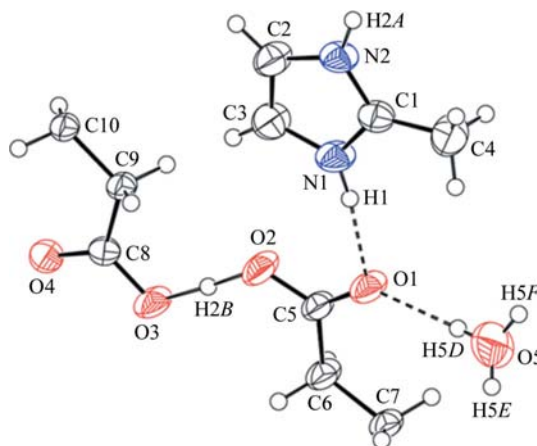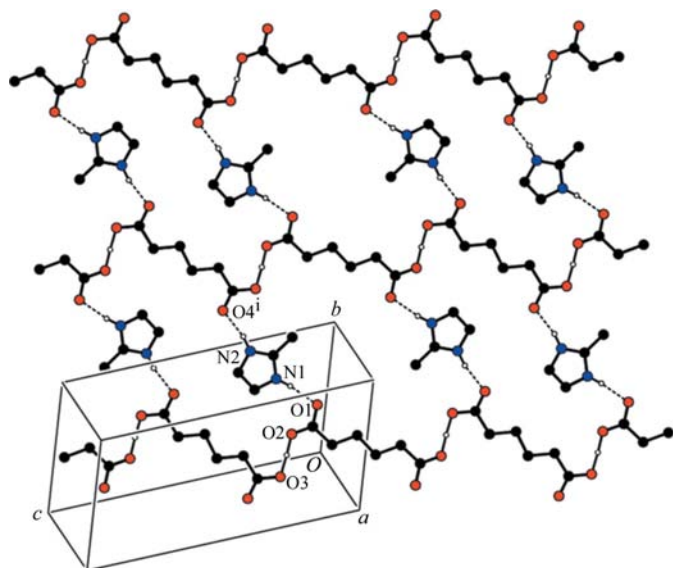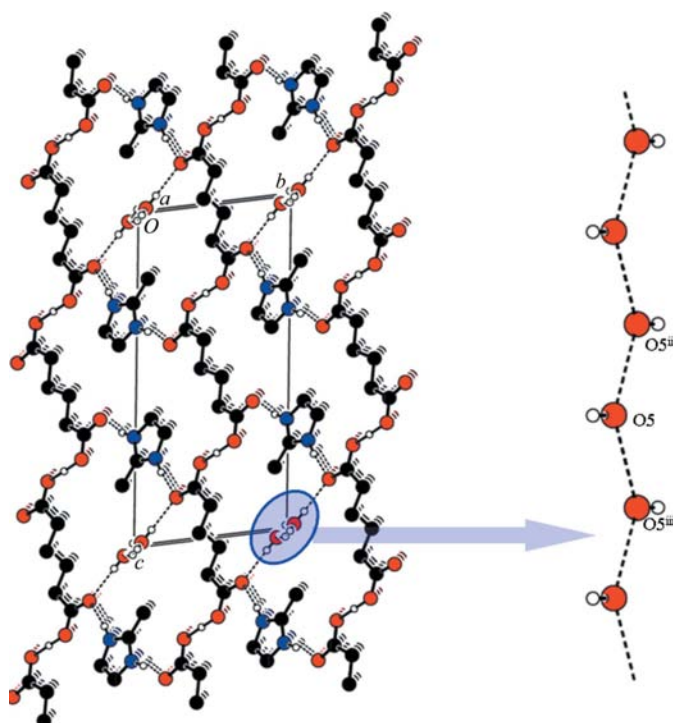

Figure 5
The molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

hydrogen-bond motif (Bernstein *et al.*, 1995), generating a two-dimensional network parallel to the (100) plane (Fig. 2). Finally, neighbouring (100) networks are linked by C2—H6···O2($x - \frac{1}{2}$, $y - \frac{1}{2}$, z) and C3—H7···O3($-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$) hydrogen bonds into a three-dimensional network.

The asymmetric unit of (II) contains one 2-MeImH$^+$ cation and one hydrogen glutarate anion (Fig. 3). The single carboxylic acid H atom is statistically distributed over the two ends of the carboxylate forming short O···H···O bridges with adjacent anions. They link the glutarate anions into a one-dimensional chain parallel to the [2$\overline{1}\overline{1}$] direction. The 2-MeImH$^+$ cations then connect adjacent chains *via* N1—H1A···O2 and N2—H2A···O4($2 - x$, $1 - y$, $1 - z$) hydrogen bonds, resulting in a two-dimensional network parallel to the (120) plane (Fig. 4). In contrast with (I), all methyl groups on one side of the [2$\overline{1}\overline{1}$] chain in (II) adopt a head-to-head

arrangement, *i.e.* methyl pointing to methyl (Fig. 4). In the two-dimensional network, $R_4^4(24)$ and $R_8^8(40)$ hydrogen-bond motifs are shaped by a combination of O1···H1B···O1($2 - x$, $1 - y$, $-z$) and O3···H1C···O3($-x$, $2 - y$, $1 - z$) hydrogen bonds. No hydrogen-bond interactions are present between adjacent two-dimensional networks, as reported by *PLATON* (Spek, 2009).

Similar to (II), compound (III) crystallizes in the $P\overline{1}$ space group, but its asymmetric unit is composed of one cation, two independent adipate anions where each anion sits across a centre of inversion and one water molecule (Fig. 5). The two half-molecules are linked into a one-dimensional chain parallel to the [10$\overline{1}$] direction *via* the short, nearly symmetrical, O2—H2B···O3 hydrogen bond. The 2-MeImH$^+$ cation links neighbouring chains together, forming a two-dimensional network parallel to the (111) plane. If atom H2B is regarded as a discrete atom, two types of $R_6^6(34)$ hydrogen-bond motifs are formed (Fig. 6), one narrow and the other wide. It is worth mentioning that the methyl groups on both

Figure 6
Part of the crystal structure of (III), showing the formation of the (111) two-dimensional network built from two different sized edge-fused $R_6^6(34)$ hydrogen-bonded rings. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. [Symmetry code: (i) $x - 1$, $y + 1$, z.]

Figure 7
Part of the crystal structure of (III), showing the formation of the three-dimensional network (left) built from N1···O1, N2···O4($x - 1$, $y + 1$, z) and O2···O3 hydrogen bonds, and the one-dimensional water chain (right). Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms bonded to C atoms and the disordered water H atoms have been omitted. [Symmetry codes: (ii) $-x + 2$, $-y + 2$, $-z$; (iii) $-x + 1$, $-y + 2$, $-z$.]

sides of the [10$\bar{1}$] chain in (III) adopt an inclined side-by-side arrangement, which is very different from those in (I) and (II). Unlike the anhydrous compounds, (I) and (II), one solvent water molecule is incorporated into the crystal structure of (III) and plays a pivotal role in forming the three-dimensional network. These water molecules assemble into a one-dimensional water chain *via* two water–water O···O hydrogen bonds [2.715 (4) Å for symmetry code ($1 - x$, $2 - y$, $-z$) and 2.770 (4) Å for symmetry code ($2 - x$, $2 - y$, $-z$)] parallel to the [100] direction (Fig. 7). The water chain is hydrogen bonded to the two-dimensional (111) network *via* O5···O1 [2.843 (2) Å], resulting in a three-dimensional network in (III).

In summary, compounds (I)–(III) are all 1:1 organic salts in which two- or three-dimensional networks are formed. One remaining question is whether a 1:2 salt of an aliphatic diacid with 2-MeIm can be formed. According to the ΔpK_a rule [$\Delta pK_a = pK_a$(base H$^+$) $- pK_a$(acid)], an organic salt is formed when ΔpK_a is greater than 3 and a cocrystal is obtained when ΔpK_a is less than 0 (Childs & Hardcastle, 2007; Childs *et al.*, 2007). For a system with $0 < \Delta pK_a < 3$, the outcome will be easily affected by the crystallization conditions, such as solvent polarity, temperature, concentration, rate of cooling, *etc.* In order to identify whether a 1:2 salt of an aliphatic diacid with 2-MeIm exists theoretically, the pK_a and ΔpK_a values of these diacids and bases in an aqueous medium at 300 K have been calculated using the program *SOLARIS* (Advanced Chemistry Development, 2005). It can be seen from Table 4 that 1:1 organic salts can be easily formed when they are mixed in aqueous solution. In addition, 2:1 salts may be more likely to be formed in (II) and (III) than in (I). Further work on this is in progress.

Experimental

1:2 Molar quantities of succinic acid (0.2 mmol, 23.6 mg) and 2-methylimidazole (0.4 mmol, 32.8 mg) for (I), glutaric acid (0.2 mmol, 26.4 mg) and 2-methylimidazole (0.4 mmol, 32.8 mg) for (II), and adipic acid (0.2 mmol, 29.2 mg) and 2-methylimidazole (0.4 mmol, 32.8 mg) for (III) were dissolved in water (15 ml). Each mixture was stirred for 10 min at ambient temperature and then filtered. The resulting colourless solutions were kept in air for several days. Crystals of (I), (II) and (III) were grown by slow evaporation.

Salt (I)

Crystal data

$C_4H_7N_2{}^+ \cdot C_4H_5O_4{}^-$	$V = 967.6$ (2) Å^3
$M_r = 200.20$	$Z = 4$
Orthorhombic, $Cmc2_1$	Mo $K\alpha$ radiation
$a = 6.8017$ (10) Å	$\mu = 0.11$ mm^{-1}
$b = 8.1580$ (11) Å	$T = 296$ K
$c = 17.438$ (2) Å	$0.25 \times 0.12 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	5389 measured reflections
	654 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	573 reflections with $I > 2\sigma(I)$
$T_{min} = 0.963$, $T_{max} = 0.991$	$R_{int} = 0.024$

organic compounds

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O3^i	0.86 (2)	1.87 (2)	2.691 (4)	158 (4)
N2—H2···O4	0.87 (2)	1.81 (2)	2.680 (4)	175 (6)
O1—H1A···O4^{ii}	0.81 (2)	1.76 (2)	2.558 (3)	169 (5)
C2—H6···O2^{iii}	0.93	2.40	3.113 (5)	134
C3—H7···O3^{iv}	0.93	2.38	3.311 (5)	175
C4—H4C···O2^v	0.96	2.58	3.455 (5)	152

Symmetry codes: (i) $-x + 1, -y, z - \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x, y - 1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.092$
$S = 1.10$
654 reflections
112 parameters
4 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

Salt (II)

Crystal data

$C_4H_7N_2^+\cdot C_5H_7O_4^-$
$M_r = 214.22$
Triclinic, $P\bar{1}$
$a = 5.4433$ (10) Å
$b = 8.3842$ (16) Å
$c = 12.598$ (2) Å
$\alpha = 77.910$ (3)°
$\beta = 82.342$ (3)°

$\gamma = 82.971$ (3)°
$V = 554.51$ (18) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 295$ K
$0.40 \times 0.15 \times 0.04$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.951$, $T_{max} = 0.996$

5770 measured reflections
2151 independent reflections
1720 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.158$
$S = 1.09$
2151 reflections
144 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Salt (III)

Crystal data

$C_4H_7N_2^+\cdot C_6H_9O_4^-\cdot H_2O$
$M_r = 246.26$
Triclinic, $P\bar{1}$
$a = 4.9383$ (4) Å
$b = 8.0682$ (6) Å
$c = 16.6840$ (13) Å
$\alpha = 96.880$ (1)°
$\beta = 92.794$ (1)°

$\gamma = 106.611$ (1)°
$V = 630.00$ (8) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 297$ K
$0.20 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.970$, $T_{max} = 0.990$

6477 measured reflections
2421 independent reflections
1905 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A···O4^i	0.863 (15)	1.865 (17)	2.695 (2)	161 (2)
O1—H1B···O1^{ii}	1.23	1.23	2.462 (3)	180
O3—H1C···O3^{iii}	1.23	1.23	2.458 (3)	180
N1—H1A···O2	0.879 (16)	1.881 (17)	2.720 (2)	159 (2)

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z$; (iii) $-x, -y + 2, -z + 1$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O1	0.889 (15)	1.867 (16)	2.751 (2)	172 (2)
N2—H2A···O4^i	0.913 (15)	1.846 (16)	2.7464 (19)	168.4 (19)
O2—H2B···O3	1.22 (2)	1.25 (2)	2.4747 (19)	177 (2)
O5—H5D···O1	0.80 (4)	2.04 (4)	2.843 (2)	178 (4)
O5—H5F···O5^{ii}	0.785 (19)	2.01 (3)	2.770 (4)	162 (7)
O5—H5E···O5^{iii}	0.825 (19)	1.93 (3)	2.715 (4)	157 (7)

Symmetry codes: (i) $x - 1, y + 1, z$; (ii) $-x + 2, -y + 2, -z$; (iii) $-x + 1, -y + 2, -z$.

Table 4
ΔpK_a [= pK_a(base H$^+$) − pK_a(acid)] for the three title compounds in water.

Compound	Molecular components†	ΔpK_{a1}	ΔpK_{a2}
(I)	2-MeIm and Succ	3.91	2.63
(II)	2-MeIm and Glut	3.82	2.88
(III)	2-MeIm and Adip	3.76	3.02

† 2-MeIm = 2-methylimidazole (pK_a = 8.15 for its conjugated cation), Succ = succinic acid (pK_{a1} = 4.24, pK_{a2} = 5.52), Glut = glutaric acid (pK_{a1} = 4.33, pK_{a2} = 5.27) and Adip = adipic acid (pK_{a1} = 4.39, pK_{a2} = 5.13). All pK_a values were calculated using *SOLARIS* (Advanced Chemistry Development, 2005).

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.159$
$S = 1.10$
2421 reflections
173 parameters
7 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

For all three compounds, H atoms bonded to C atoms were positioned geometrically, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene), and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}$(aromatic and methylene C) or $1.5U_{eq}$(methyl C). In (I), H atoms bonded to N and O atoms were found in a difference map and the N—H and O—H distances were refined with restraints of N—H = 0.86 (2) Å and O—H = 0.82 (2) Å, and with $U_{iso}(H) = 1.2U_{eq}$(N) and $1.5U_{eq}$(O). The cation is disordered over a mirror plane. Friedel pairs were averaged. H atoms bonded to N atoms in (II) were also found in a difference map and refined with the restraint N—H = 0.86 (2) Å, and with $U_{iso}(H) = 1.2U_{eq}$(N). The acid H atom is statistically disordered over two locations, both of which lie on inversion centres, and was refined with U_{iso}(H1B) = $1.5U_{eq}$(O1) and U_{iso}(H1C) = $1.5U_{eq}$(O3). In (III), H atoms bonded to N atoms were similarly found in a difference map and refined with the restraint N—H = 0.86 (2) Å, and with $U_{iso}(H) = 1.2U_{eq}$(N). Atom H2B was found 1.22 Å from atom O2 and placed on a general position. The O2—

H2*B* distance was refined freely and the final outcome gave an indication of hydrogen-bridging in the adipate monoanion. Two water H atoms were also found in a difference map, one of which was disordered over two sites with occupancies of 0.5; these H atoms were refined with restraints of O—H = 0.82 (2) Å and H⋯H = 1.35 (2) Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3296). Services for accessing these data are described at the back of the journal.

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