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Statistically disordered short hydrogen bonds in (pipzH$_2$)(cdoH)$_2$ and a comparison with (pipzH$_2$)(cdo)·H$_2$O (pipz is piperazine and cdoH$_2$ is chelidonic acid)

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Two related proton-transfer compounds, namely piperazine-1,4-diium 4-oxo-4H-pyran-2,6-dicarboxylate monohydrate, $C_4H_{12}N_2^{2+}\cdot C_7H_2O_6^{2-}\cdot H_2O$ or (pipzH$_2$)(cdo)·H$_2$O, (I), and piperazine-1,4-diium bis(6-carboxy-4-oxo-4H-pyran-2-carboxylate), $C_4H_{12}N_2^{2+}\cdot 2C_7H_3O_6^{-}$ or (pipzH$_2$)(cdoH)$_2$, (II), were obtained by the reaction of 4-oxo-4H-pyran-2,6-dicarboxylic acid (chelidonic acid, cdoH$_2$) and piperazine (pipz). In (I), both carboxyl H atoms of chelidonic acid have been transferred to piperazine to form the piperazine-1,4-diium ion. The structure is a monohydrate. All potential N—H donors are involved in N—H···O hydrogen bonds. The water molecule spans two anions via the 4-oxo group of the pyranose ring and a carboxylate O atom. The hydrogen-bonding motif is essentially two-dimensional. The structure is a pseudomerohedral twin. In the asymmetric unit of (II), the anion consists of monodeprotonated chelidonic acid, while the piperazine-1,4-diium cation is located on an inversion centre. The single carboxyl H atom is disordered in two respects. Firstly, the disordered H atom is shared equally by both carboxylic acid groups. Secondly, the H atom is statistically disordered between two positions on either side of a centre of symmetry and is engaged in a very short hydrogen-bonding interaction; the relevant O···O distances are 2.4549 (11) and 2.4395 (11) Å, and the O—H···O angles are 177 (6) and 177 (5)°, respectively. Further hydrogen bonding of the type N—H···O places the (pipzH$_2$)$^{2+}$ cations in pockets formed by the chains of (cdoH)$^-$ anions. In contrast with (I), the (pipzH$_2$)$^{2+}$ cations form hydrogen-bonding arrays that are perpendicular to the anions, yielding a three-dimensional hydrogen-bonding motif. The structures of both (I) and (II) also feature π–π stacking interactions between aromatic rings.

Comment

4-Oxo-4H-pyran-2,6-dicarboxylic acid, also called chelidonic acid, is a weak acid extracted from the perennial herb celandine (*Chelidonium majus*) as a white crystalline substance (m.p. 538 K). The structures of several metal complexes containing the 4-oxo-4H-pyran-2,6-dicarboxylate dianion, (cdo)$^{2-}$, illustrate the versatile ability of this ligand to coordinate in a monodentate, bidentate or bridging fashion. Crystal structures include complexes of Ag$^+$, Be^{2+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, Sn^{2+}, Zn^{2+} and Tb^{3+} (Manojlovic-Muir *et al.*, 1999; Ng *et al.*, 2000; Olovsson *et al.*, 2001; Fainerman-Melnikova *et al.*, 2006; Yasodha, Govindarajan, Low & Glidewell, 2007; Chen, 2009; Zhang *et al.*, 2009; Zhou *et al.* 2009). A salt of [Ni(H$_2$O)$_6$](cdo) (Yasodha, Govindarajan, Manivannan & Büyükgüngör, 2007) has also been reported.

As a continuation of our research on the synthesis of proton-transfer compounds by the use of different dicarboxylic acids and numerous amines [for a similar proton-transfer compound of pyridine-2,6-dicarboxylic acid with piperazine, see Aghabozorg, Ghadermazi *et al.* (2006), and for a proton-transfer compound of piperazine with oxalate, see Aghabozorg, Ghadermazi & Sheshmani (2006)], we report here the synthesis and structure determination of two proton-transfer compounds, (I) and (II), obtained from 4-oxo-4H-pyran-2,6-dicarboxylic acid (cdoH$_2$) and piperazine (pipz).
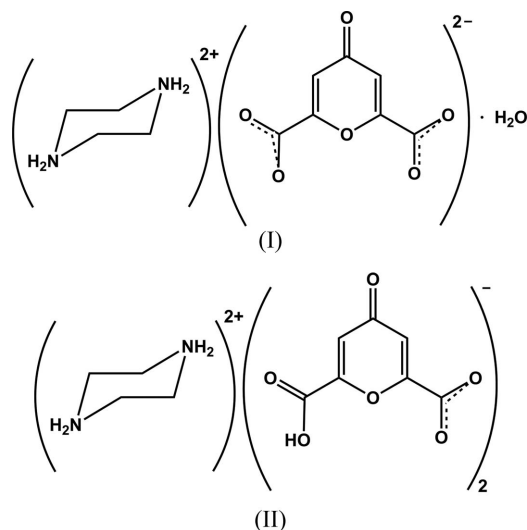
In (pipzH$_2$)(cdo)·H$_2$O, (I) (Fig. 1), both H atoms of cdoH$_2$ are transferred to pipz, and the negative charge of (cdo)$^{2-}$ is balanced by the doubly protonated piperazine-1,4-diium ion. All possible N—H donors are engaged in hydrogen bonds to O atoms (see Table 1). The water molecule spans two different anions via the 4-oxo group of the pyranose ring (O4) and a carboxylate O atom (O2). Atom O2 is also hydrogen bonded to an N—H donor. These hydrogen-bonding interactions form a motif that is two-dimensional and lies parallel to the (101) plane (Fig. 2).

In (pipzH$_2$)(cdoH)$_2$, (II) (Fig. 3), the H atom of the (cdoH)$^-$ anion is disordered with respect to exchange between the two

Figure 1
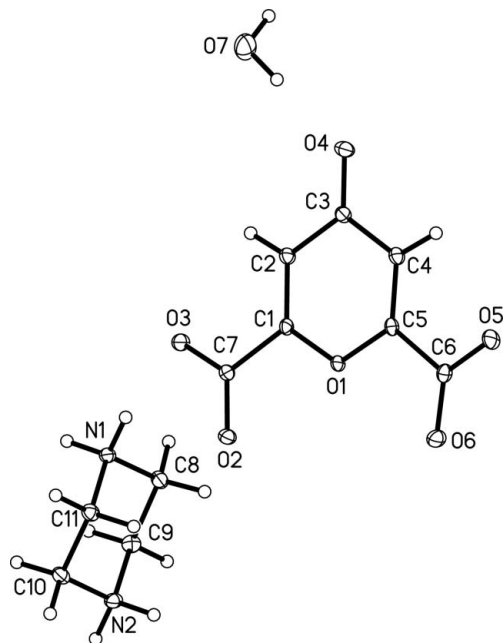A view of (I), with displacement ellipsoids drawn at the 50% probability level.

Figure 3
A view, approximately down the *a* axis, of the packing of (I). Hydrogen-bonding interactions are shown as dashed lines.
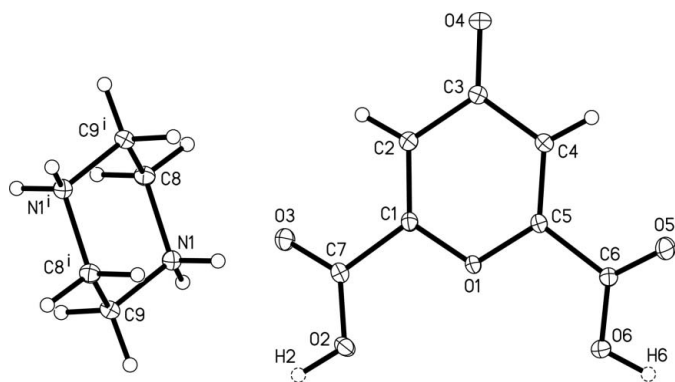

Figure 2
A view of (II), with displacement ellipsoids drawn at the 50% probability level. Atoms H2 and H6 are at half-occupancy. [Symmetry code: (i) $-x + 2$, $-y + 2$, $-z - 1$.]

Figure 4
A portion of the structure of (II), depicting the short hydrogen bonds between carboxyl groups of the (cdoH)⁻ group. Atoms H2 and H6 are at half-occupancy and are disordered with respect to centres of symmetry. [Symmetry codes: (′) $-x + 2$, $-y + 2$, $-z$; (″) $-x + 1$, $-y + 1$, $-z + 1$.]

carboxylic acid centres, as well as with respect to a centre of inversion. As shown in Fig. 4, the H-atom position is disordered between opposite sides of the centre of inversion with occupancies of 0.5. Thus, there are two asymmetric hydrogen bonds, *viz.* O2—H2···O2′ and O6—H6···O6″ (see Fig. 4 for symmetry codes). The O···O distances and linear geometry correspond to very short hydrogen bonds (Table 2). On average, each (cdoH)⁻ anion acts as an acceptor, using either O2 or O6, and as a donor, using either H2 or H6. A similar but apparently symmetrically hydrogen-bonded species was reported in the structure of [Zn(phen)₃]₄[H(Hpydc)₂]-(NO₃)₇·26H₂O (phen is 1,10-phenanthroline and Hpydc is 6-carboxypyridine-2-carboxylate; Moghimi *et al.*, 2005). In this case, the unique H atom resides on a centre of symmetry, bridging two carboxylates, and leads to the formation of a discrete anion with an O···O distance of 2.493 (3) Å. In (II),
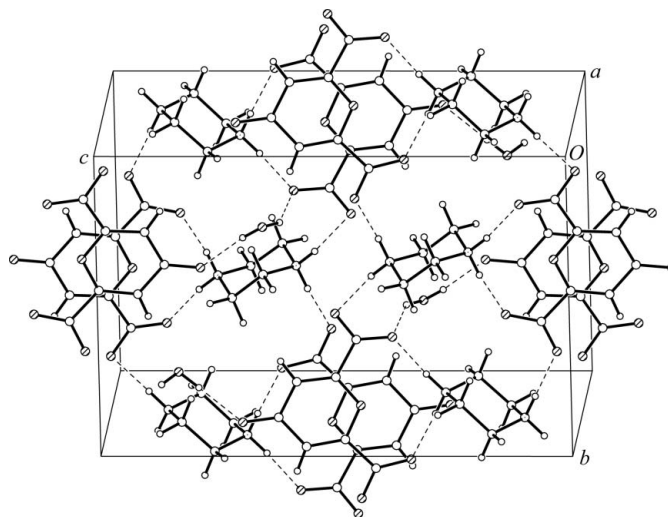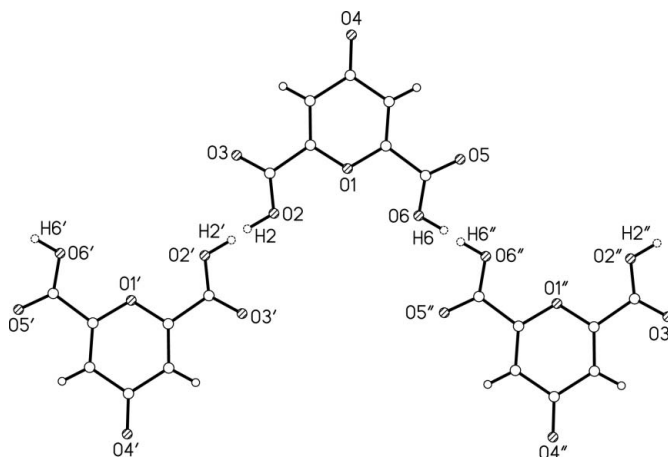
each of the N—H donor groups is hydrogen bonded to a different C=O group of the anion (see Table 2 for details). The N···N vector of the (pipzH₂)²⁺ cation is perpendicular to the chain of anions, yielding a three-dimensional hydrogen-bonding motif (Fig. 5), different from the orientation in (I) where the N···N vector is in the plane of the anions.

There are several other notable differences between the two structures. Although both (I) and (II) feature alternating inversion-related π–π stacking interactions, these differ in their details, as viewed from top to bottom in Fig. 6. If the stacking planes are represented by the six-membered C1–C5/O1 ring, in (I), the perpendicular distances between stacking planes alternate between 3.2856 (5) and 3.4334 (5) Å, with slippage distances of 2.46 and 2.18 Å, and centroid–centroid distances between 4.1071 (7) and 4.0644 (7) Å, respectively. In
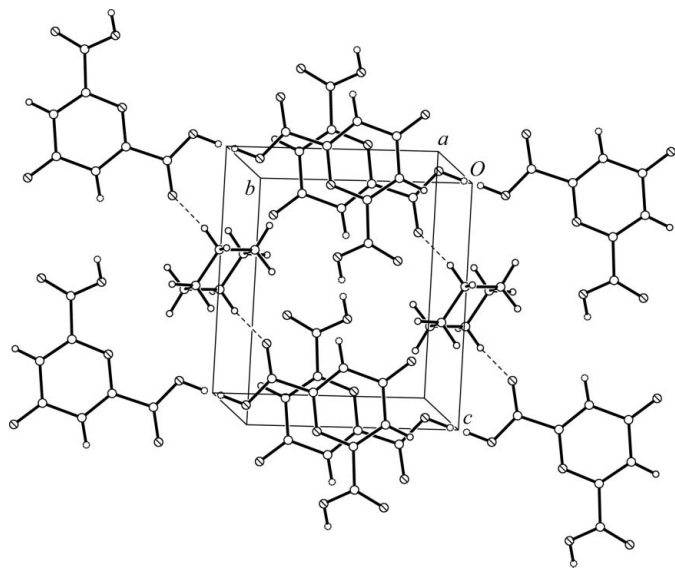
organic compounds

Figure 5
A view, approximately down the *a* axis, of the packing of (II). N—H···O hydrogen-bonding interactions are shown as dashed lines.
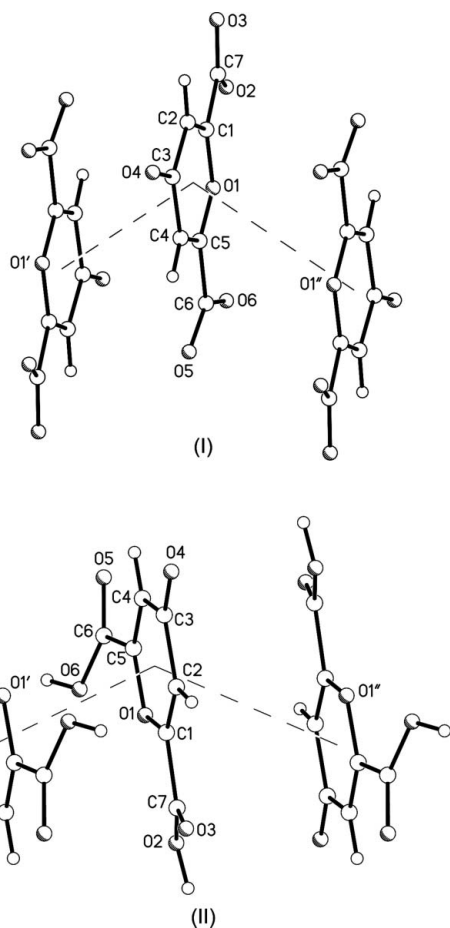

(I)

(II)

Figure 6
Stacking of the aromatic anions, showing the alternation of inversion-related π–π interactions. [Symmetry codes, for (I): (′) −*x*, −*y* + 1, −*z*; (″) −*x* + 1, −*y* + 1, −*z*; for (II): (′) −*x* + 1, −*y* + 1, −*z*; (″) −*x* + 2, −*y* + 1, −*z*.]

(II), the corresponding values are 3.2771 (3) and 3.3451 (3) Å for perpendicular distances, 1.35 and 2.04 Å for slippage

distances, and 3.5449 (4) and 3.9201 (4) Å for centroid–centroid distances.

The carbonyl bond lengths support the existence of deprotonated acid molecules. In particular, the C—O distances indicate full delocalization in (I) and are equal within the s.u. values. In (II), the C—O bonds bearing the H atoms is *ca* 0.05 Å longer than the C=O bonds (see Tables 3 and 4).

The 4-oxo group of the furan ring is expected to be a strong hydrogen-bond acceptor, but is only engaged in a classical hydrogen bond to water in the structure of (I). In the structure of (II), there are no remaining donors for this purpose and it remains only weakly involved in C—H interactions.

Experimental

For the preparation of compound (I), 4-oxo-4*H*-pyran-2,6-dicarboxylic acid (2.02 g, 10 mmol; Acros, chelidonic acid) was dissolved in methanol (200 ml) by heating. To this solution was added a solution of piperazine (0.86 ml, 10 mmol) in methanol (10 ml). After cooling, a light-yellow precipitate was collected. The precipitate was redissolved in water and allowed to evaporate slowly, producing crystals suitable for X-ray diffraction [m.p. 467 K (decomposition)]. Elemental analysis calculated for $C_{18}H_{18}N_2O_{12}$: C 47.54, H 3.96, N 6.16%; found: C 47.09, H 3.91, N 6.08%. IR (KBr, ν, cm^{-1}): 1339 (*s*), 1397 (*s*), 1644 (*s*), 2446 (*br*), 2999 (*br*), 3075 (*w*), 3236 (*s*), 3424 (*s*), 3620 (*s*); ^{1}H NMR (D$_2$O): δ 3.439 (3H, pipH$_2$), 6.939 (2H, cdo); ^{13}C NMR (D$_2$O): δ 184.5, 159.1, 115.8, 40.2; UV: 223 nm.

Compound (II) was obtained when we attempted to synthesize a nickel(II) complex with (cdo)$^{2-}$. To a solution of (I) (1 mmol, 0.27 g) in water was added a solution of Ni(NO$_3$)$_2$·6H$_2$O (0.14 g, 0.5 mmol) (molar ratio of 2:1) in water (25 ml). After one week, a light-yellow precipitate was collected. This was redissolved in water and allowed to evaporate slowly, yielding the crystals used for data collection [m.p. 489 K (decomposition)]. IR (KBr, ν, cm^{-1}): 1338 (*br*), 1383 (*s*), 1459 (*w*), 1642 (*br*), 2489 (*br*), 3075 (*w*), 3238 (*w*), 3622 (*br*).

Compound (I)

Crystal data

$C_4H_{12}N_2{}^{2+}\cdot C_7H_2O_6{}^{2-}\cdot H_2O$	$V = 1250.27\,(9)$ Å^3
$M_r = 288.26$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 6.8003\,(3)$ Å	$\mu = 0.13$ mm^{-1}
$b = 11.3961\,(5)$ Å	$T = 87$ K
$c = 16.1548\,(7)$ Å	$0.42 \times 0.14 \times 0.06$ mm
$\beta = 92.968\,(2)°$	

Data collection

Bruker SMART APEX DUO diffractometer	59584 measured reflections
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2006)	4609 independent reflections
	4303 reflections with $I > 2\sigma(I)$
$T_{min} = 0.948$, $T_{max} = 0.993$	$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.099$	
$S = 1.12$	
4609 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
189 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
3 restraints	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H7$A\cdots$O4	0.87 (2)	1.94 (2)	2.8049 (14)	172 (2)
O7—H7$B\cdots$O2^{i}	0.89 (2)	2.27 (2)	3.0533 (16)	147 (2)
N1—H1$A\cdots$O3^{ii}	0.92	1.88	2.7796 (12)	166
N1—H1$B\cdots$O5^{iii}	0.92	1.80	2.7126 (12)	170
N2—H2$B\cdots$O2	0.92	1.77	2.6815 (12)	171
N2—H2$A\cdots$O6	0.92	1.84	2.7519 (13)	168
N1—H1$A\cdots$O2^{ii}	0.92	2.56	3.1115 (13)	119
N2—H2$B\cdots$O1	0.92	2.49	2.9436 (12)	110

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O2^{i}	0.93 (4)	1.52 (4)	2.4549 (11)	177 (6)
O6—H6$\cdots$O6^{ii}	0.91 (4)	1.53 (4)	2.4395 (11)	177 (5)
N1—H1$A\cdots$O3	0.92	1.94	2.8032 (8)	156
N1—H1$B\cdots$O5^{iii}	0.92	2.09	2.8419 (8)	138

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

Compound (II)

Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_7H_3O_6^{-}$
$M_r = 454.34$
Triclinic, $P\bar{1}$
$a = 6.7880$ (3) Å
$b = 8.0650$ (4) Å
$c = 8.5675$ (4) Å
$\alpha = 90.377$ (2)°
$\beta = 94.110$ (2)°

$\gamma = 104.538$ (3)°
$V = 452.70$ (4) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.14$ mm^{-1}
$T = 87$ K
$0.36 \times 0.34 \times 0.22$ mm

Data collection

Bruker SMART APEXII
  diffractometer
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 1996)
  $T_{min} = 0.956$, $T_{max} = 0.976$

7496 measured reflections
2971 independent reflections
2806 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.092$
$S = 1.06$
2971 reflections
153 parameters

H atoms treated by a mixture of
  independent and constrained
  refinement
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

For (I), the crystal was a three-component rotational twin. Twin integration was carried out using *SAINT* (Bruker, 2010) and the absorption correction was applied using *TWINABS* (Sheldrick, 2006). The final reflection file used all components and composites. The excess 447 reflections were discounted in the least-squares instruction in order not to underestimate the s.u. values. In addition, 33 reflections were specifically omitted that were likely affected by overlap of twin domains. The twin laws were as follows: transforms $h1.1(1) \rightarrow h1.2(2)$ (-0.99994 0.00089 0.00046/ -0.00252 -1.00000 -0.00009/ 0.24863 -0.00003 0.99994); transforms $h1.1(1) \rightarrow h1.3(3)$ (-1.00020 -0.00071 -0.04193/ 0.00208 -1.00000 -0.00066/ 0.00948 -0.00126 1.00020); transforms $h1.2(2) \rightarrow h1.3(3)$ (0.98972 0.00160

Table 3
Selected bond lengths (Å) for (I).

O2—C7	1.2575 (13)	O5—C6	1.2518 (13)
O3—C7	1.2518 (13)	O6—C6	1.2520 (14)
O4—C3	1.2417 (14)		

Table 4
Selected bond lengths (Å) for (II).

O2—C7	1.2794 (9)	O5—C6	1.2303 (9)
O3—C7	1.2330 (9)	O6—C6	1.2850 (9)
O4—C3	1.2373 (8)		

-0.04239/ -0.00474 0.99999 -0.00057/ 0.23919 0.00144 1.00015). Refined twin parameters for the three components are: 0.6036 (10)/ 0.2707 (10)/0.1257 (11).

For both (I) and (II), H atoms bonded to C and N atoms were refined as riding, with C—H = 0.95–0.99 Å and N—H = 0.92 Å, and with U_{iso}(H) = $1.2U_{eq}$(C,N). For (I), the H atoms of the hydrate molecule were located in a difference map and subsequently refined with restraints of O—H = 0.84 (2) Å and H$\cdots$H = 1.34 (4) Å, and with U_{iso}(H) = $1.5U_{eq}$(O). In the structure of (II), there are two short hydrogen bonds between the protonated carboxyl groups and the unprotonated carboxylate groups of an inversion-related (cdoH)$^{-}$ anion. Electron-density maps show that these are asymmetric hydrogen bonds and the H atom does not reside on the centre of symmetry. Each of these H atoms (H2 and H6) is at half-occupancy for charge balance and in order to model the disorder. These two H atoms were freely refined.

For both compounds, data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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