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New 1:1 and 2:1 salts in the ‘DL-norvaline–maleic acid’ system as an example of assembling various crystal structures from similar supramolecular building blocks

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Molecular salts and cocrystals of amino acids have potential applications as molecular materials with nonlinear optical, ferroelectric, piezoelectric, and other various target physical properties. The wide choice of amino acids and coformers makes it possible to design various crystal structures. The amino acid–maleic acid system provides a perfect example of a rich variety of crystal structures with different stoichiometries, symmetries and packing motifs built from the molecular building blocks, which are either exactly the same, or differ merely by protonation or as optical isomers. The present paper reports the crystal structures of two new salts of the DL-norvaline–maleic acid system with 1:1 and 2:1 stoichiometries, namely DL-norvalinium hydrogen maleate, $C_5H_{12}NO_2^+\cdot C_4H_3O_4^-$, (I), and DL-norvalinium hydrogen maleate–DL-norvaline, $C_5H_{12}NO_2^+\cdot C_4H_3O_4^-\cdot C_5H_{11}NO_2$, (II). These are the first examples of molecular salts of DL-norvaline with an organic anion. The crystal structure of (I) has the same $C_2^2(12)$ structure-forming motif which is common for hydrogen maleates of amino acids. The structure of (II) has dimeric cations. Of special interest is that the single crystals of (I) which are originally formed on crystallization from aqueous solution transform into single crystals of (II) if stored in the mother liquor for several hours.

1. Introduction

Molecular salts and cocrystals of amino acids are interesting mostly due to their potential applications as molecular materials with optical, piezoelectric, ferroelectric and other target physical properties (Fleck & Petrosyan, 2014). For example, large (several millimetres in each direction) crystals of L-alaninium hydrogen maleate [(L-AlaH$^+$)·M^-] (Alagar *et al.*, 2001*b*), L-argininium hydrogen maleate dihydrate [(L-ArgH$^+$)·M^-·2H$_2$O] (Sun *et al.*, 2007), L-phenylalaninium hydrogen maleate [(L-PheH$^+$)·M^-] (Alagar *et al.*, 2001*c*), L-histidinium hydrogen maleate hydrate [(L-HisH$^+$)·M^-·H$_2$O] (Fleck *et al.*, 2013), L-methioninium L-methionine hydrogen maleate (L-Met·L-MetH$^+$·M^-) (Natarajan *et al.*, 2010) and glycinium hydrogen maleate [(GlyH$^+$)·M^-] (Alagar *et al.*, 2001*a*) were obtained and the second harmonic generation (SHG) efficiency, investigated using the Kurtz–Perry powder method (Kurtz & Perry, 1968), was 0.27–1.5 times that of the SGH efficiency of KDP (potassium dideuterium phosphate) (Anbuchezhiyan *et al.*, 2009; Devaprasad & Madhavan, 2010; Yogam *et al.*, 2012; Gonsago *et al.*, 2012; Vasudevan *et al.*, 2013; Charoen-In *et al.*, 2010; Balasubramanian *et al.*, 2010; Natarajan *et al.*, 2008). The wide choice of amino acids and coformers makes it possible to design various crystal structures that

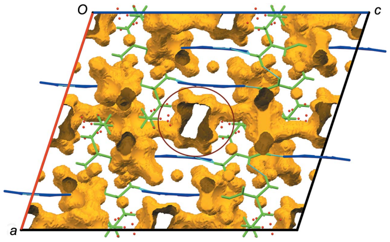
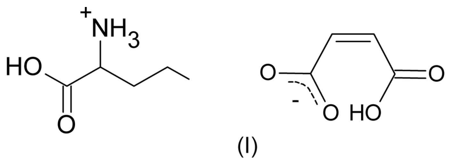


Table 1
Experimental details.

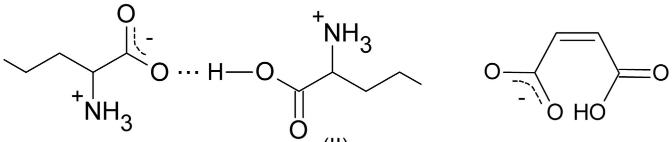
	(I)	(II)
Crystal data		
Chemical formula	$C_5H_{12}NO_2^+ \cdot C_4H_3O_4^-$	$C_5H_{12}NO_2^+ \cdot C_4H_3O_4^- \cdot C_5H_{11}NO_2$
M_r	233.22	350.37
Crystal system, space group	Monoclinic, *C*2/*c*	Orthorhombic, *Pnma*
Temperature (K)	293	293
a, *b*, *c* (Å)	19.6385 (15), 5.62705 (18), 23.6867 (10)	8.8572 (4), 27.3614 (11), 7.8306 (4)
α, β, γ (°)	90, 108.283 (6), 90	90, 90, 90
V (Å^3)	2485.4 (2)	1897.71 (15)
Z	8	4
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.11	0.10
Crystal size (mm)	0.25 × 0.15 × 0.10	0.50 × 0.25 × 0.20
Data collection		
Diffractometer	Agilent Xcalibur Ruby Gemini ultra	Agilent Xcalibur Ruby Gemini ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.866, 1.000	0.948, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13186, 2198, 1807	21923, 1975, 1731
R_{int}	0.051	0.053
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595	0.625
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.068, 0.166, 1.23	0.079, 0.146, 1.14
No. of reflections	2198	1975
No. of parameters	169	216
No. of restraints	12	298
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.15	0.15, −0.20

Computer programs: *CrysAlis PRO* (Agilent, 2014), *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

could be potentially important from a crystal engineering point of view. Moreover, in all the solvates of this system, in particular, hydrates can form on crystallization.



(I)



(II)

In addition to the abovementioned nonlinear optical properties, the 'amino acid–maleic acid' system provides a perfect example of a molecular salt in which the same small organic coformer (maleic acid) can cocrystallize with a large variety of molecules (amino acids). Maleic acid donates a proton to the amino acid and is present as a small and rigid maleate anion in all the crystalline maleates of amino acids. These structures can have various stoichiometries. The diversity of the stoichiometric ratios is determined by several factors:

(i) the symmetry non-equivalence of several amino acid cations;

(ii) the charge of the side chain of the amino acid;

(iii) the binding of several amino acid cations and zwitterions to form complex subunits known as dimeric or trimeric cations.

In particular, it is important to compare the crystal structures of chiral and racemic amino acid salts and cocrystals. Crystals of L- and DL-amino acids often have radically different properties (Chesalov *et al.*, 2008; Kolesov & Boldyreva, 2007; Bordallo *et al.*, 2007; Kolesnik *et al.*, 2005), and the same may hold for their salts and cocrystals (Boldyreva, 2014; Arkhipov *et al.*, 2013). Recently, the crystal structure of L-norvalinium hydrogen maleate–L-norvaline has been analyzed and shown to have dimeric L-Nva···L-NvaH$^+$ cations (Arkhipov *et al.*, 2015). In the present paper, we report the structures of racemic salts formed by DL-norvaline and maleic acid having different stoichiometries, namely DL-norvalinium hydrogen maleate, (I), and DL-norvalinium hydrogen maleate–DL-norvaline, (II).

2. Experimental

2.1. Synthesis and crystallization

Crystals of (I) were obtained by slow evaporation at room temperature from a drop of the saturated aqueous solution containing DL-norvaline and maleic acid in a 1:1 ratio (Rychkov *et al.*, 2014). Interestingly, crystallization from an

Table 2
Classification of hydrogen maleates according to their stoichiometry.

There are also two hydrates belonging to the A^+B^- class, *viz.* (L-ArgH$^+$)·M^-·2H$_2$O (CSD refcode GIHGEK; Sun *et al.*, 2007) and (L-HisH$^+$)·M^-·H$_2$O (CSD refcode TENVUF; Fleck *et al.*, 2013), and two other hydrates related to the nA^+nB^- class, *viz.* (L-HisH$^+$)$_2$·(M^-)$_2$·3H$_2$O (CSD refcode VAZJUD; Gonsago *et al.*, 2012) and (L-IleH$^+$)$_2$·(M^-)$_2$·H$_2$O (CSD refcode VUKQEZ; Arkhipov *et al.*, 2015).

Composition	Stoichiometry class	Numerical order	CSD refcodes and references to original work
(GlyH$^+$)·M^-	A^+B^-	1	RENBAN (Rajagopal *et al.*, 2001*a*)
(L-AlaH$^+$)·M^-			BOQTEG (Alagar *et al.*, 2001*b*)
(L-PheH$^+$)·M^-			EDAXIQ (Alagar *et al.*, 2001*c*)
(DL-PheH$^+$)·M^-			VAGVIJ (Alagar *et al.*, 2003)
(DL-ValH$^+$)·M^-			QURSUR (Alagar *et al.*, 2001*a*)
(L-SerH$^+$)·M^-			REZPET (Arkhipov *et al.*, 2013)
(DL-SerH$^+$)·M^-			REZPAP (Arkhipov *et al.*, 2013)
(DL-MetH$^+$)·M^-			MOCXUX (Alagar *et al.*, 2002)
(SarH$^+$)·M^-			MIYBAX01 (Ilczyszyn *et al.*, 2003)
(L-ValH$^+$)·M^-			NUZMIG (Rychkov *et al.*, 2016)
(DL-ThrH$^+$)·M^-			ETEYOR (Rajagopal *et al.*, 2004)
(β-AlaH$^+$)·M^-			EDASUX (Rajagopal *et al.*, 2001*b*)
(BacH$^+$)·M^-			LUSXII (Báthori & Kilinkissa, 2015)
(L-LysH$^+$)·M^-			XADTOL (Pratap *et al.*, 2000)
(DL-ArgH$^+$)·M^-			Ravishankar *et al.* (1998)
(BetH$^+$)·M^-			NASQED01 (Haussühl & Schreuer, 2001)
(L-HisH$_2$$^{2+}$)·($M^-$)$_2$	$A^{n+}nB^-$	2	TENVOZ (Fleck *et al.*, 2013)
L-Met·L-MetH$^+$·M^-	$A_2{}^+B^-$	3	Natarajan *et al.* (2010)
L-Nva·L-NvaH$^+$·M^-			VUKQID (Arkhipov *et al.*, 2015)
(L-HisH$^+$)$_2$·(M^-)$_2$	nA^+nB^- (n = 2, 3, *etc.*)	4	XADTIF (Pratap *et al.*, 2000)
(L-LeuH$^+$)$_3$·(M^-)$_3$			VUKQAV (Arkhipov *et al.*, 2015)

equimolar drop of the solution of DL-norvaline and maleic acid first gives crystals of (I), which, if kept in the mother liquor for a few hours, are transformed into larger crystals of another phase, denoted (II), with a 2:1 stoichiometry of DL-norvaline and maleic acid. One can suppose that phase (I) nucleates and grows faster than phase (II), although the latter is the thermodynamically more stable form. The case is very similar to that observed when crystallizing tolazamide polymorphs (I) and (II) (Boldyreva *et al.*, 2015), as well as to other solution-assisted polymorphic transformations (Munroe *et al.*, 2014; Kobari *et al.*, 2014). The crystals of (II), grown from a small drop were thin and not suitable for single-crystal X-ray structural analysis. Larger crystals of (II) were obtained using slow evaporation from a crystallization vessel.

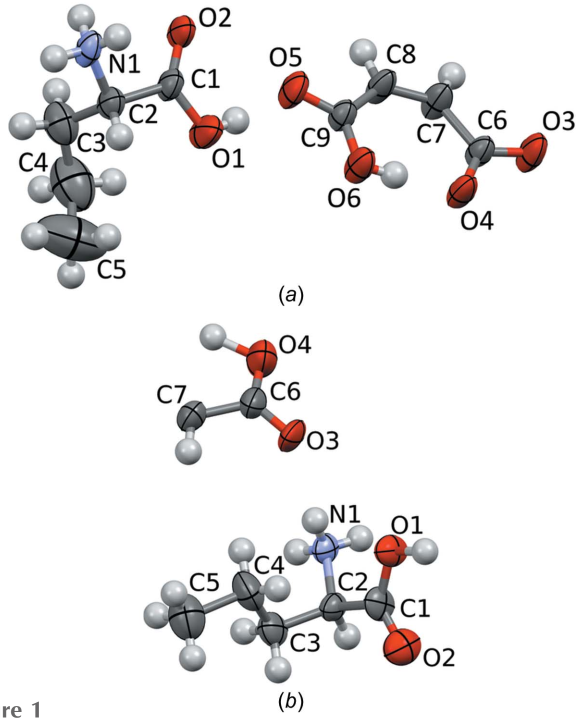


Figure 1
The asymmetric units of (*a*) (I) and (*b*) (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level. For (I), only the major-disorder form of the molecules are shown. For (II), half of the maleate anion belongs to the asymmetric unit, as it sits on a mirror plane.

2.2. Crystal structure solution and refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Suitable crystals of (I) and (II) was selected under a microscope in polarized light and mounted by means of MiTeGen Micro-Grippers using MiTeGen LV Cryo Oil (LVCO-1) on an Agilent Xcalibur diffractometer. The *n*-propyl group (including the H atoms) of the DL-norvalinium cation of the structure of (I) (C4*A*/C5*A*) is disordered (the minor-disorder sites are labelled C4*B*/C5*B*). The occupation ratio of the disordered sites refined to 0.865 (8):0.135 (8). For the C5*B*/C4*B*/C3 atoms, the U^{ij} values were restrained to be within 0.02 Å^2 (within 0.04 Å^2 for the terminal atom). All H atoms were located initially in a difference Fourier map. The positions of all H atoms were subsequently geometrically optimized and refined using a riding model, with the following assumptions and constraints: N—H = 0.89 Å, O—H = 0.82 Å and C—H = 0.93 (anion), 0.98 (methine), 0.97 (methylene) or 0.96 Å (methyl), with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(parent atom) for the methyl and OH groups, and 1.2$U_{\rm eq}$(parent atom) otherwise.

The selection of a good-quality single crystal of (I) was not easy because the brittle crystals were easily damaged. The crystal eventually selected for the X-ray diffraction experiment contained four domains. Data reduction was carried out in three different ways: (i) taking into account the reflections from the largest domain only (one orientation matrix and 59% of all reflections); (ii) processing the diffraction data as from a multiple crystal (four different orientation matrices) using reflections from all four domains; (iii) processing the diffraction data as from a multiple crystal using four different orientation matrices but taking into consideration the reflection from largest domain (50% of all reflections). According to the $F^2/\sigma(F^2)$ and $R_{\rm int}$ parameters, the first method gave the best results.

All atoms of (II) (except for the C atom of the carboxyl group of the maleate anion, the H atom of the carboxyl group

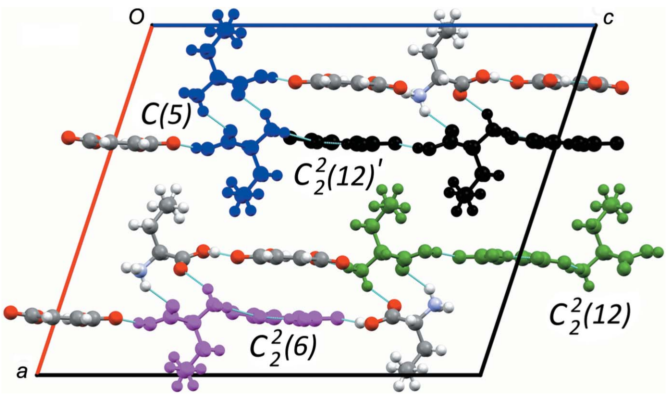


Figure 2
The crystal structure of fragments of (I), showing (*a*) $C^2_2(12)$ chains linked to each other *via* $C^2_2(6)$ chains and (*b*) $C^2_2(12)'$ chains linked to each other *via* $C(5)$ chains.

of the dimeric DL-norvalinium–DL-norvaline cation and another H atom of the carboxyl group of the maleate anion) are disordered. The sites with smaller occupancies are defined as *B*. The occupancy ratio for the disordered sites was refined as 0.556 (11):0.444 (11) for the maleate anion and 0.741 (5):0.259 (5) for the dimeric DL-norvalinium–DL-norvaline cation. The amino acid cations at the sites with higher and lower occupancies are stereoisomers. The H1 atom lies on the inversion centre and the H4 atom lies on the mirror plane; therefore, the corresponding site occupancies are equal to 0.5. The C1*B*—C2*B*, O1*B*—C1*B*, O1—H1 and O4—H4 distances were fixed at 1.480 (2), 1.400 (2), 1.289 (2) and 1.202 (2) Å, respectively. The anisotropic displacement parameters of all the atoms were refined with a rigid-bond restraint. For all non-H atoms, the U^{ij} values were restrained to be within 0.04 Å^2 (within 0.08 Å^2 for the terminal atom). All H atoms were located initially in a difference Fourier map. The positions of all H atoms (except for the H1 and H4 atoms, for which O—H distances were restrained) were subsequently geometrically optimized and refined using a riding model, with the following assumptions and constraints: N—H = 0.89 Å and C—H = 0.93 (anion), 0.98 (methine), 0.97 (methylene) or 0.96 Å (methyl), with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C,O})$ for the methyl and OH groups, and $1.2U_{\rm eq}({\rm C,N})$ otherwise.

3. Results and discussion

Currently, 25 crystal structures of molecular salts of maleic acid with amino acids have been reported, with 23 having been documented in the Cambridge Structural Database (CSD; Groom *et al.*, 2016) and two structures having no refcodes [DL-argininium hydrogen maleate (Ravishankar *et al.*, 1998) and L-methioninium L-methionine hydrogen maleate (Natarajan *et al.*, 2010)]. All these structures can be divided into three classes.

(1) Hydrogen maleates with a 1:1 stoichiometry containing one amino acid and one maleate anion in the asymmetric unit. The majority of all known hydrogen maleates belong to this class.

(2) Hydrogen maleates with a 1:2 stoichiometry containing one amino acid dication and two maleate anions in the asymmetric unit. Currently only one structure can be assigned to this class (see Table 2, refcode TENVOZ).

(3) Hydrogen maleates with dimeric amino acid cations and maleate anions consequently having a 2:1 stoichiometry.

(4) Hydrogen maleates with a 1:1 stoichiometry containing more than one of each chemical species (amino acid cation and maleate anion) in the asymmetric unit (Table 2).

The title salts, (I) and (II), are the first examples of molecular salts of DL-norvaline with a carboxylic acid (Fig. 1). Maleic acid is known as a common coformer. Due to its compact flat shape, stabilized by an intramolecular hydrogen bond (Table 3) and the presence of several hydrogen-bond acceptors, maleic acid can easily be embedded into different crystalline environments. Salt (I) crystallizes in the centrosymmetric space group *C*2/*c*. The asymmetric unit of (I) contains one norvaline cation and one maleate anion, so that it

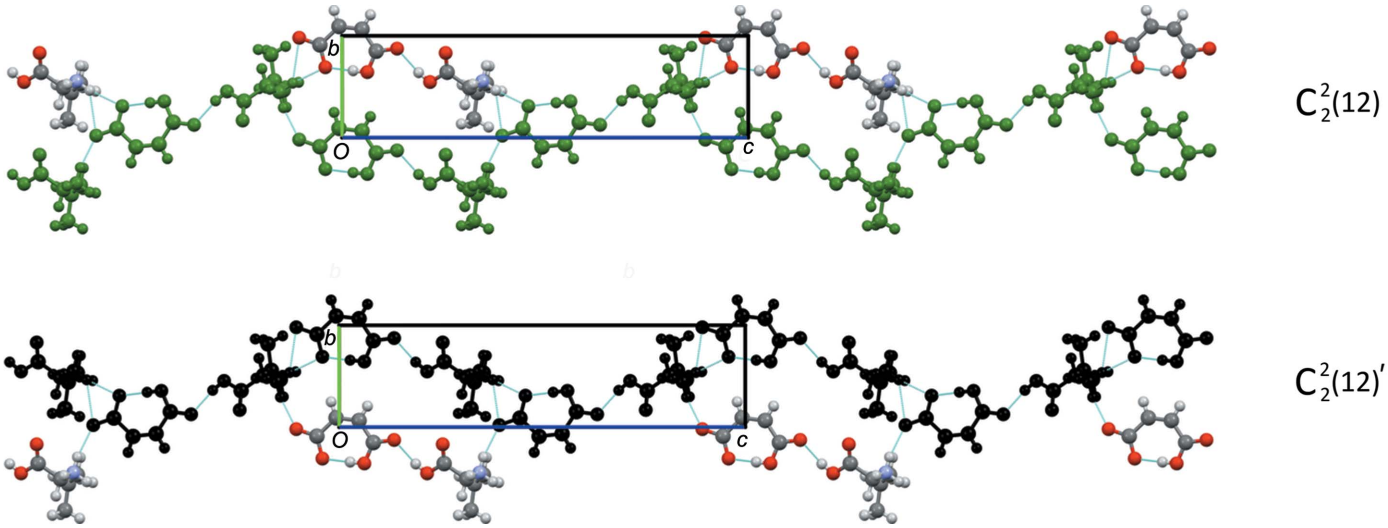


Figure 3
The $C^2_2(12)$ and $C^2_2(12)'$ chains in (DL-NvaH$^+$)·M^-, (I).

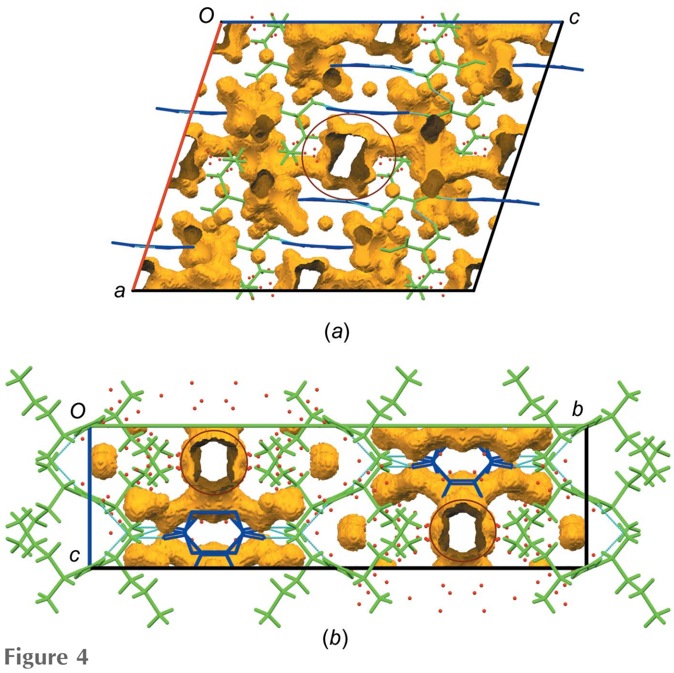


Figure 4
Visualization of the voids in the structures of (*a*) (I) and (*b*) (II) using the *Mercury* program (Macrae *et al.*, 2008). The channel along the *b* direction is highlighted by the dark-red circle. Voids were found using the 'contact surface' method with a probe radius of 0.5 Å and a grid size of 0.1 Å. The major-disorder form of the DL-norvalinium cation and DL-norvalinium–DL-norvaline dimeric cation are coloured green, the maleate anion is blue and red dots correspond to the minor-disorder forms of the components.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O6—H6⋯O4	0.82	1.60	2.421 (2)	178
O1—H1⋯O5	0.82	1.80	2.612 (3)	171
N1—H1A⋯O2^{i}	0.89	2.11	2.864 (3)	142
N1—H1B⋯O4^{ii}	0.89	2.01	2.898 (3)	172
N1—H1C⋯O3^{iii}	0.89	1.97	2.850 (3)	168

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, -y+1, z+\frac{1}{2}$; (iii) $x, -y, z+\frac{1}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O2^{i}	0.89	1.94	2.807 (8)	165
N1—H1B⋯O3	0.89	2.08	2.92 (4)	157
N1—H1C⋯O3^{ii}	0.89	1.90	2.79 (4)	178
O1—H1⋯O1^{iii}	1.28 (1)	1.28 (1)	2.568 (13)	180 (1)
O4—H4⋯O4^{iv}	1.21 (1)	1.21 (1)	2.418 (9)	173 (8)

Symmetry codes: (i) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, -y+\frac{3}{2}, z$.

belongs to the first (most populated) class of the aforementioned classification (Fig. 1) (Table 2).

The crystal structure of (I) can be compared with those of two polymorphs of pure DL-norvaline, *i.e.* at 203 (the β-form) and 183 K (the α-form) (Görbitz, 2011). Both compounds have layered structures; the H_3N^+ group of the norvaline zwitterions are linked to three COO^- groups of other zwitterions by hydrogen bonds, forming three 'head-to-tail' chains. Similar chains (but composed of norvalinium cations) are present also in the structure of (I) [$C(5)$ motifs along the crystallographic *b* direction]. One can also see $C_2^2(6)$ chains along the *b* direction formed by hydrogen bonds between the NH_3^+ group of one norvalinium cation and the COO^- group of another cation (Fig. 2 and Table 4). Almost all the amino acid maleates contain $C_2^2(12)$ chains (Rychkov *et al.*, 2016), and (I) is no exception; it also has $C_2^2(12)$ chains formed by norvalinium cations and maleate anions assembling along the *c* direction. In addition, there are $C_2^2(12)'$ chains in (I) formed by two types of hydrogen bonds: (i) between the COOH group of a norvalinium cation and the COOH group of a maleate anion, and (ii) between the H_3N^+ group of a norvalinium cation and the COO^- group of a maleate anion (Fig. 3). The second type of hydrogen bond involves one of the O atoms of the COO^- group of a maleate anion which is participating in an intramolecular hydrogen bond within a maleate anion (Fig. 3 and Table 3). The $C_2^2(6)$, $C_2^2(12)$ and $C_2^2(12)'$ chains form half a layer, and two such half-layers are connected by $C(5)$ chains, with each forming a complete layer so that a two-dimensional hydrogen-bonding network parallel to the (100) plane is formed (Fig. 2). The side chains of DL-norvaline are directed to the outer surfaces of the layers and thus adjacent layers interdigitate to give hydrophobic layers with well-defined channels lie parallel to the hydrophobic layers (Fig. 4).

The molecular salt (II) crystallizes in a centrosymmetric *Pnma* space group. The unit cell of (II) contains dimeric DL-norvalinium–DL-norvaline cations (a zwitterion of norvaline and a norvalinium cation connected by a strong O—H⋯O hydrogen bond) and maleate anions in the 1:1 ratio. The salt (II) could be assigned to the third class according to Table 2. The structure of (II) contains two $C_3^3(17)$ heteromolecular chains along the crystallographic *b* direction formed by dimeric DL-norvalinium–DL-norvaline cations and maleate anions. Similar hydrogen-bonded chains were observed in the structure of L-norvalinium hydrogen maleate–L-norvaline (Arkhipov *et al.*, 2015) (Fig. 5*a*). Head-to-tail $C(5)$ chains of dimeric DL-norvalinium–DL-norvaline cations propagate along the *c* direction normal to the $C_3^3(17)$ chains. Another amino acid $C_2^2(9)$ chain along the *a* direction is formed by the dimeric DL-norvalinium–DL-norvaline cations. These three types of chains have common norvaline molecules and are connected with each other by hydrogen bonds to form a three-dimensional hydrogen-bonded network. Comparing the structures of (I) and (II), one can see that the same components form different types of crystal structures: a layered structure in (I) and a three-dimensional hydrogen-bonded structure in (II). The structure of (II) also has channels along the crystallographic *a* direction; the volume of the voids in (II) (12.1%, 230.42 $Å^3$) is about a half of that in (I) (Fig. 4).

The DL-norvaline–maleic acid system is interesting from a crystal engineering point of view: the same molecules form salts with different types of crystal structures. DL-Norvaline can form salts with maleic acid with either a layered structure as in (I) or a three-dimensional hydrogen-bonded structure as in (II). The molecular salts (I) and (II) belong to different stoichiometric classes (Table 2). DL-Norvalinium hydrogen

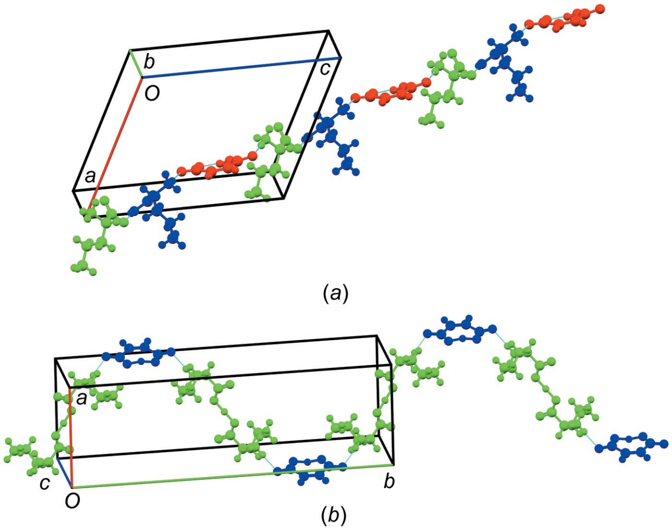


Figure 5
Comparison of the heteromolecular hydrogen-bonded chains in the structures of (*a*) L-norvalinium hydrogen maleate–L-norvaline (Arkhipov *et al.*, 2015) and (*b*) DL-norvalinium hydrogen maleate–DL-norvaline, (II).

maleate, (I), and DL-norvalinium hydrogen maleate–DL-norvaline, (II), are the first examples of molecular salts of DL-norvaline with a carboxylic acid. The presence of the dimeric cation of DL-norvaline in the structure of (II) makes it possible to form a three-dimensional network of hydrogen bonds, the structural type which is not common for the maleates of amino acids with a large hydrophobic side chain. Despite the large number of hydrogen maleates documented in the literature, the prediction of whether a selected L-amino acid or a DL-racemate will cocrystallize with maleic acid is still difficult to make. For example, for norvaline, both L- and DL-norvalinium hydrogen maleates (with different stoichiometries) have been reported (Arkhipov *et al.*, 2015). For alanine, only L-alaninium hydrogen maleate has been described (Alagar *et al.*, 2001*a*), with no maleates of the racemic DL-form reported. In contrast, for threonine, DL-threoninium hydrogen maleate exists (Rajagopal *et al.*, 2004), but no maleate of the L-form has been reported. Moreover, the crystallization of DL-alaninium hydrogen maleate is probably impossible because of the resolution of alanine enantiomers in a racemic solution on addition of maleic acid with the formation of L-alaninium hydrogen maleate and D-alaninium hydrogen maleate (Asai *et al.*, 1975). Such ‘stereoselective’ cocrystallization is hard to explain using the traditional synthon approach (Desiraju, 1995). It is quite possible that the number of hydrogen maleates of amino acids obtained is proportional to the time spent searching for them, similar to what McCrone (1965) supposed for polymorphs.

Another interesting point related to the hydrogen maleates of L-amino acids is the presence of dimeric cations in some of the structures. Up to now, this complex structural subunit has been observed in two hydrogen maleates of amino acids, namely in L-norvalinium hydrogen maleate–L-norvaline (Arkhipov *et al.*, 2015) and in L-methioninium L-methionine hydrogen maleate (Natarajan *et al.*, 2010). DL-Norvalinium hydrogen maleate–DL-norvaline, (II), is the first example of a racemic maleate containing the dimeric cation of an amino acid.

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New 1:1 and 2:1 salts in the `DL-norvaline–maleic acid′ system as an example of assembling various crystal structures from similar supramolecular building blocks

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014) for (I); *CrysAlis PRO* (Rigaku OD, 2015) for 2dl_nv_mal. Cell refinement: *CrysAlis PRO* (Agilent, 2014) for (I); *CrysAlis PRO* (Rigaku OD, 2015) for 2dl_nv_mal. Data reduction: *CrysAlis PRO* (Agilent, 2014) for (I); *CrysAlis PRO* (Rigaku OD, 2015) for 2dl_nv_mal. For both compounds, program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b). Molecular graphics: OLEX2 (Dolomanov *et al.*, 2009) for (I); *Mercury* (Macrae *et al.*, 2008) for 2dl_nv_mal. For both compounds, software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

(I) *DL*-Norvalinium hydrogen maleate

Crystal data

$C_5H_{12}NO_2^+\cdot C_4H_3O_4^-$
$M_r = 233.22$
Monoclinic, $C2/c$
$a = 19.6385\ (15)$ Å
$b = 5.62705\ (18)$ Å
$c = 23.6867\ (10)$ Å
$\beta = 108.283\ (6)°$
$V = 2485.4\ (2)$ Å^3
$Z = 8$

$F(000) = 992$
$D_x = 1.247$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3032 reflections
$\theta = 1.8$–$25.1°$
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Block, clear light colourless
0.25 × 0.15 × 0.1 mm

Data collection

Agilent Xcalibur Ruby Gemini ultra diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.3457 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{min} = 0.866$, $T_{max} = 1.000$

13186 measured reflections
2198 independent reflections
1807 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$
$h = -23\rightarrow23$
$k = -6\rightarrow6$
$l = -28\rightarrow28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.166$

$S = 1.23$
2198 reflections
169 parameters
12 restraints

Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 1.2674P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O2	0.30316 (12)	0.1684 (3)	0.75497 (7)	0.0587 (6)	
O4	0.33415 (13)	0.3088 (3)	0.45870 (8)	0.0634 (6)	
O6	0.34166 (13)	0.3563 (3)	0.56205 (8)	0.0653 (6)	
H6	0.3388	0.3428	0.5269	0.098*	
O5	0.33741 (12)	0.1258 (4)	0.63532 (8)	0.0640 (6)	
O3	0.32140 (14)	0.0195 (3)	0.39432 (8)	0.0733 (7)	
O1	0.35365 (15)	0.4538 (4)	0.71650 (9)	0.0797 (8)	
H1	0.3461	0.3614	0.6884	0.120*	
N1	0.29849 (14)	0.4474 (4)	0.84537 (9)	0.0530 (6)	
H1A	0.2541	0.4754	0.8218	0.064*	
H1B	0.3073	0.5355	0.8781	0.064*	
H1C	0.3030	0.2943	0.8553	0.064*	
C9	0.33889 (16)	0.1511 (4)	0.58407 (10)	0.0472 (7)	
C1	0.33256 (16)	0.3576 (5)	0.75847 (11)	0.0493 (7)	
C6	0.32998 (17)	0.0889 (5)	0.44513 (11)	0.0517 (7)	
C2	0.35023 (16)	0.5090 (5)	0.81368 (11)	0.0513 (7)	
H2	0.3446	0.6770	0.8022	0.062*	
C8	0.33796 (19)	−0.0648 (5)	0.54893 (11)	0.0602 (9)	
H8	0.3401	−0.2063	0.5697	0.072*	
C7	0.33452 (19)	−0.0911 (5)	0.49233 (12)	0.0637 (9)	
H7	0.3350	−0.2480	0.4802	0.076*	
C3	0.4257 (2)	0.4676 (7)	0.85504 (15)	0.0804 (11)	
H3AA	0.4303	0.5434	0.8928	0.097*	0.865 (8)
H3AB	0.4325	0.2983	0.8623	0.097*	0.865 (8)
H3BC	0.4217	0.3299	0.8784	0.097*	0.135 (8)
H3BD	0.4525	0.4145	0.8292	0.097*	0.135 (8)
C4A	0.4845 (3)	0.5576 (11)	0.8329 (2)	0.1011 (19)	0.865 (8)
H4AA	0.5301	0.5092	0.8608	0.121*	0.865 (8)
H4AB	0.4800	0.4808	0.7952	0.121*	0.865 (8)
C4B	0.473 (2)	0.624 (7)	0.8964 (16)	0.114 (9)	0.135 (8)
H4BA	0.4527	0.6638	0.9274	0.136*	0.135 (8)
H4BB	0.5181	0.5409	0.9150	0.136*	0.135 (8)
C5A	0.4863 (4)	0.8168 (15)	0.8244 (5)	0.143 (3)	0.865 (8)
H5AA	0.4440	0.8653	0.7934	0.214*	0.865 (8)

H5AB	0.5280	0.8578	0.8135	0.214*	0.865 (8)
H5AC	0.4881	0.8961	0.8607	0.214*	0.865 (8)
C5B	0.488 (4)	0.829 (11)	0.872 (3)	0.166 (18)	0.135 (8)
H5BA	0.4471	0.8746	0.8392	0.249*	0.135 (8)
H5BB	0.5285	0.8054	0.8581	0.249*	0.135 (8)
H5BC	0.4988	0.9530	0.9014	0.249*	0.135 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0956 (16)	0.0514 (12)	0.0351 (10)	−0.0135 (11)	0.0289 (9)	−0.0092 (8)
O4	0.1220 (19)	0.0344 (10)	0.0397 (10)	−0.0056 (10)	0.0336 (10)	0.0026 (7)
O6	0.1231 (19)	0.0385 (11)	0.0417 (11)	−0.0051 (11)	0.0364 (12)	−0.0074 (8)
O5	0.1054 (17)	0.0600 (12)	0.0355 (10)	0.0015 (11)	0.0350 (10)	−0.0014 (8)
O3	0.139 (2)	0.0517 (12)	0.0381 (11)	−0.0037 (12)	0.0405 (12)	−0.0057 (8)
O1	0.129 (2)	0.0787 (16)	0.0470 (12)	−0.0372 (14)	0.0501 (13)	−0.0171 (10)
N1	0.0863 (18)	0.0445 (13)	0.0319 (11)	0.0082 (11)	0.0240 (11)	−0.0036 (9)
C9	0.0698 (19)	0.0395 (14)	0.0354 (14)	0.0031 (12)	0.0208 (12)	0.0009 (10)
C1	0.0698 (19)	0.0502 (17)	0.0322 (13)	−0.0032 (14)	0.0221 (12)	−0.0026 (11)
C6	0.087 (2)	0.0372 (14)	0.0364 (14)	−0.0011 (13)	0.0279 (13)	−0.0007 (11)
C2	0.072 (2)	0.0471 (15)	0.0380 (14)	−0.0066 (13)	0.0210 (13)	−0.0077 (11)
C8	0.111 (3)	0.0333 (14)	0.0418 (15)	0.0039 (15)	0.0321 (15)	0.0065 (11)
C7	0.124 (3)	0.0296 (13)	0.0429 (15)	0.0042 (15)	0.0347 (16)	−0.0041 (11)
C3	0.082 (3)	0.088 (3)	0.065 (2)	0.002 (2)	0.0144 (19)	−0.0186 (18)
C4A	0.072 (3)	0.129 (5)	0.096 (3)	−0.002 (3)	0.019 (3)	−0.028 (3)
C4B	0.114 (16)	0.106 (16)	0.104 (16)	−0.005 (15)	0.012 (14)	−0.044 (14)
C5A	0.112 (5)	0.122 (6)	0.195 (9)	−0.031 (4)	0.050 (6)	−0.010 (6)
C5B	0.15 (3)	0.15 (3)	0.17 (3)	−0.03 (3)	0.01 (3)	−0.05 (3)

Geometric parameters (Å, º)

O2—C1	1.202 (3)	C7—H7	0.9300
O4—C6	1.274 (3)	C3—H3AA	0.9700
O6—H6	0.8200	C3—H3AB	0.9700
O6—C9	1.275 (3)	C3—H3BC	0.9700
O5—C9	1.231 (3)	C3—H3BD	0.9700
O3—C6	1.226 (3)	C3—C4A	1.498 (6)
O1—H1	0.8200	C3—C4B	1.43 (3)
O1—C1	1.308 (3)	C4A—H4AA	0.9700
N1—H1A	0.8900	C4A—H4AB	0.9700
N1—H1B	0.8900	C4A—C5A	1.474 (9)
N1—H1C	0.8900	C4B—H4BA	0.9700
N1—C2	1.482 (4)	C4B—H4BB	0.9700
C9—C8	1.469 (4)	C4B—C5B	1.36 (7)
C1—C2	1.507 (4)	C5A—H5AA	0.9600
C6—C7	1.490 (4)	C5A—H5AB	0.9600
C2—H2	0.9800	C5A—H5AC	0.9600
C2—C3	1.517 (5)	C5B—H5BA	0.9600

C8—H8	0.9300	C5B—H5BB	0.9600
C8—C7	1.329 (4)	C5B—H5BC	0.9600

C9—O6—H6	109.5	H3AA—C3—H3AB	107.5
C1—O1—H1	109.5	H3BC—C3—H3BD	105.7
H1A—N1—H1B	109.5	C4A—C3—C2	115.2 (3)
H1A—N1—H1C	109.5	C4A—C3—H3AA	108.5
H1B—N1—H1C	109.5	C4A—C3—H3AB	108.5
C2—N1—H1A	109.5	C4B—C3—C2	130.3 (16)
C2—N1—H1B	109.5	C4B—C3—H3BC	104.7
C2—N1—H1C	109.5	C4B—C3—H3BD	104.7
O6—C9—C8	120.8 (2)	C3—C4A—H4AA	108.3
O5—C9—O6	121.7 (2)	C3—C4A—H4AB	108.3
O5—C9—C8	117.6 (2)	H4AA—C4A—H4AB	107.4
O2—C1—O1	125.0 (2)	C5A—C4A—C3	115.9 (5)
O2—C1—C2	122.4 (2)	C5A—C4A—H4AA	108.3
O1—C1—C2	112.6 (2)	C5A—C4A—H4AB	108.3
O4—C6—C7	119.1 (2)	C3—C4B—H4BA	108.7
O3—C6—O4	122.4 (2)	C3—C4B—H4BB	108.7
O3—C6—C7	118.5 (2)	H4BA—C4B—H4BB	107.6
N1—C2—C1	107.4 (2)	C5B—C4B—C3	114 (3)
N1—C2—H2	109.3	C5B—C4B—H4BA	108.7
N1—C2—C3	108.9 (2)	C5B—C4B—H4BB	108.7
C1—C2—H2	109.3	C4A—C5A—H5AA	109.5
C1—C2—C3	112.7 (3)	C4A—C5A—H5AB	109.5
C3—C2—H2	109.3	C4A—C5A—H5AC	109.5
C9—C8—H8	114.7	H5AA—C5A—H5AB	109.5
C7—C8—C9	130.6 (2)	H5AA—C5A—H5AC	109.5
C7—C8—H8	114.7	H5AB—C5A—H5AC	109.5
C6—C7—H7	114.6	C4B—C5B—H5BA	109.5
C8—C7—C6	130.8 (2)	C4B—C5B—H5BB	109.5
C8—C7—H7	114.6	C4B—C5B—H5BC	109.5
C2—C3—H3AA	108.5	H5BA—C5B—H5BB	109.5
C2—C3—H3AB	108.5	H5BA—C5B—H5BC	109.5
C2—C3—H3BC	104.7	H5BB—C5B—H5BC	109.5
C2—C3—H3BD	104.7		

O2—C1—C2—N1	−26.0 (4)	N1—C2—C3—C4A	−170.8 (3)
O2—C1—C2—C3	93.9 (4)	N1—C2—C3—C4B	−90 (2)
O4—C6—C7—C8	5.0 (6)	C9—C8—C7—C6	−0.4 (7)
O6—C9—C8—C7	−5.4 (6)	C1—C2—C3—C4A	70.1 (4)
O5—C9—C8—C7	175.1 (4)	C1—C2—C3—C4B	151 (2)
O3—C6—C7—C8	−174.1 (4)	C2—C3—C4A—C5A	63.3 (7)
O1—C1—C2—N1	154.9 (3)	C2—C3—C4B—C5B	−57 (5)
O1—C1—C2—C3	−85.1 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O4	0.82	1.60	2.421 (2)	178
O1—H1···O5	0.82	1.80	2.612 (3)	171
N1—H1*A*···O2^{i}	0.89	2.11	2.864 (3)	142
N1—H1*B*···O4^{ii}	0.89	2.01	2.898 (3)	172
N1—H1*C*···O3^{iii}	0.89	1.97	2.850 (3)	168

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+3/2; (ii) *x*, −*y*+1, *z*+1/2; (iii) *x*, −*y*, *z*+1/2.

(2dl_nv_mal) *DL*-Norvalinium hydrogen maleate–*DL*-norvaline (1/1)

Crystal data

$C_5H_{12}NO_2^+\cdot C_4H_3O_4^-\cdot C_5H_{11}NO_2$
M_r = 350.37
Orthorhombic, *Pnma*
a = 8.8572 (4) Å
b = 27.3614 (11) Å
c = 7.8306 (4) Å
V = 1897.71 (15) Å^3
Z = 4
F(000) = 752
D_x = 1.226 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6447 reflections
θ = 2.3–27.7°
µ = 0.10 mm^{-1}
T = 293 K
Block, clear light colourless
0.5 × 0.25 × 0.2 mm

Data collection

Agilent Xcalibur Ruby Gemini ultra diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.3457 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.948, T_{max} = 1.000
21923 measured reflections
1975 independent reflections
1731 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 26.4°, θ_{min} = 3.0°
h = −11→11
k = −34→34
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.079
$wR(F^2)$ = 0.146
S = 1.14
1975 reflections
216 parameters
298 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 2.5627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\mathrm{iso}}*/U_{\mathrm{eq}}$	Occ. (<1)
O1	0.3996 (7)	0.5283 (3)	0.4353 (8)	0.0588 (14)	0.733 (5)
O2	0.2253 (12)	0.4842 (4)	0.5382 (11)	0.0673 (19)	0.733 (5)
N1	0.1895 (3)	0.58452 (10)	0.2864 (4)	0.0436 (9)	0.733 (5)
H1A	0.209236	0.566396	0.194754	0.052*	0.733 (5)
H1B	0.271973	0.601006	0.316357	0.052*	0.733 (5)
H1C	0.115546	0.605455	0.262507	0.052*	0.733 (5)
C1	0.2668 (10)	0.5162 (3)	0.486 (2)	0.053 (2)	0.733 (5)
C6	0.4597 (4)	0.69058 (10)	0.2591 (5)	0.0667 (9)	
C3	0.0925 (9)	0.5831 (2)	0.5848 (10)	0.0563 (15)	0.733 (5)
H3A	0.015017	0.605821	0.547903	0.068*	0.733 (5)
H3B	0.047697	0.561615	0.669252	0.068*	0.733 (5)
C2	0.1420 (5)	0.55218 (16)	0.4302 (6)	0.0450 (10)	0.733 (5)
H2	0.054865	0.533011	0.392004	0.054*	0.733 (5)
O4	0.4852 (12)	0.70580 (16)	0.1052 (7)	0.082 (3)	0.532 (13)
C4	0.2156 (11)	0.6112 (4)	0.6672 (11)	0.078 (2)	0.733 (5)
H4A	0.258051	0.633807	0.584784	0.093*	0.733 (5)
H4B	0.295023	0.588785	0.701321	0.093*	0.733 (5)
C7	0.4209 (11)	0.7257 (3)	0.3969 (11)	0.055 (2)	0.532 (13)
H7	0.391943	0.711475	0.499571	0.066*	0.532 (13)
O4B	0.5932 (11)	0.70603 (18)	0.1975 (19)	0.112 (5)	0.468 (13)
N1B	0.0750 (11)	0.5607 (3)	0.3297 (13)	0.054 (3)	0.267 (5)
H1BA	0.116614	0.543114	0.246574	0.065*	0.267 (5)
H1BB	0.034246	0.587671	0.285670	0.065*	0.267 (5)
H1BC	0.003694	0.543223	0.381236	0.065*	0.267 (5)
O1B	0.425 (2)	0.5365 (8)	0.503 (2)	0.067 (5)	0.267 (5)
O2B	0.229 (4)	0.4803 (10)	0.593 (3)	0.066 (5)	0.267 (5)
C2B	0.1906 (15)	0.5742 (4)	0.4535 (19)	0.054 (3)	0.267 (5)
H2B	0.259337	0.597557	0.399015	0.064*	0.267 (5)
C7B	0.3551 (12)	0.7257 (3)	0.3272 (18)	0.068 (3)	0.468 (13)
H7B	0.271968	0.711838	0.381295	0.082*	0.468 (13)
C1B	0.271 (3)	0.5271 (8)	0.473 (7)	0.049 (4)	0.267 (5)
C3B	0.117 (4)	0.5995 (9)	0.605 (4)	0.086 (6)	0.267 (5)
H3BA	0.052294	0.625599	0.563819	0.103*	0.267 (5)
H3BB	0.053207	0.576156	0.664850	0.103*	0.267 (5)
C4B	0.223 (4)	0.6193 (12)	0.723 (4)	0.107 (7)	0.267 (5)
H4BA	0.240324	0.596531	0.815453	0.129*	0.267 (5)
H4BB	0.318602	0.625157	0.665381	0.129*	0.267 (5)
O3	0.453 (5)	0.6486 (10)	0.284 (6)	0.073 (7)	0.532 (13)
O3B	0.440 (5)	0.6447 (12)	0.290 (6)	0.063 (5)	0.468 (13)
C5	0.1602 (13)	0.6408 (3)	0.8296 (14)	0.096 (3)	0.733 (5)
H5A	0.089387	0.665441	0.794706	0.145*	0.733 (5)
H5B	0.245280	0.656078	0.883680	0.145*	0.733 (5)
H5C	0.112409	0.618901	0.908534	0.145*	0.733 (5)
C5B	0.170 (5)	0.6600 (9)	0.782 (5)	0.129 (11)	0.267 (5)
H5BA	0.103300	0.674308	0.698621	0.193*	0.267 (5)

H5BB	0.251346	0.682068	0.804935	0.193*	0.267 (5)
H5BC	0.114773	0.653731	0.885012	0.193*	0.267 (5)
H1	0.500000	0.500000	0.500000	0.193*	
H4	0.483 (9)	0.750000	0.115 (11)	0.193*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.044 (3)	0.052 (3)	0.080 (4)	0.016 (2)	0.004 (2)	0.021 (3)
O2	0.058 (2)	0.061 (4)	0.083 (6)	0.005 (2)	0.002 (4)	0.030 (4)
N1	0.0397 (17)	0.0352 (15)	0.056 (2)	0.0090 (13)	−0.0013 (15)	0.0050 (14)
C1	0.045 (3)	0.051 (4)	0.061 (5)	0.023 (3)	0.001 (3)	0.019 (5)
C6	0.064 (2)	0.0354 (15)	0.101 (3)	0.0003 (13)	0.0253 (19)	−0.0043 (17)
C3	0.048 (3)	0.052 (3)	0.069 (4)	0.018 (2)	0.009 (3)	0.006 (3)
C2	0.040 (2)	0.034 (2)	0.061 (3)	0.0051 (18)	0.001 (2)	0.008 (2)
O4	0.115 (7)	0.047 (2)	0.084 (3)	0.000 (3)	0.028 (4)	−0.011 (2)
C4	0.072 (4)	0.080 (4)	0.081 (5)	0.010 (3)	0.014 (4)	−0.023 (4)
C7	0.066 (5)	0.035 (3)	0.065 (4)	−0.001 (3)	0.007 (4)	0.003 (3)
O4B	0.070 (5)	0.043 (3)	0.223 (12)	0.004 (3)	0.081 (7)	0.000 (4)
N1B	0.050 (6)	0.041 (5)	0.070 (6)	0.009 (4)	−0.002 (5)	0.010 (4)
O1B	0.044 (6)	0.057 (7)	0.101 (14)	0.013 (5)	0.003 (7)	0.017 (9)
O2B	0.074 (7)	0.059 (6)	0.064 (11)	0.029 (5)	0.017 (8)	0.050 (7)
C2B	0.050 (6)	0.029 (5)	0.083 (8)	0.012 (5)	−0.006 (6)	0.008 (5)
C7B	0.048 (5)	0.038 (3)	0.119 (9)	0.000 (4)	0.027 (5)	−0.002 (5)
C1B	0.053 (7)	0.035 (8)	0.059 (10)	0.006 (6)	0.014 (6)	0.026 (7)
C3B	0.084 (13)	0.090 (14)	0.083 (10)	0.037 (11)	−0.002 (9)	−0.005 (9)
C4B	0.127 (15)	0.103 (14)	0.092 (15)	0.041 (12)	−0.025 (13)	−0.013 (10)
O3	0.071 (14)	0.023 (4)	0.124 (11)	0.004 (5)	0.026 (9)	0.005 (5)
O3B	0.050 (6)	0.032 (6)	0.108 (12)	0.002 (6)	0.019 (7)	−0.007 (7)
C5	0.098 (5)	0.094 (7)	0.097 (6)	0.020 (5)	0.004 (4)	−0.023 (5)
C5B	0.20 (3)	0.071 (14)	0.12 (2)	0.029 (16)	0.020 (18)	0.002 (12)

Geometric parameters (Å, º)

O1—C1	1.286 (11)	N1B—H1BA	0.8900
O1—H1	1.284 (6)	N1B—H1BB	0.8900
O2—C1	1.034 (15)	N1B—H1BC	0.8900
N1—H1A	0.8900	N1B—C2B	1.457 (17)
N1—H1B	0.8900	O1B—C1B	1.41 (2)
N1—H1C	0.8900	O1B—H1	1.20 (2)
N1—C2	1.492 (6)	O2B—C1B	1.63 (4)
C1—C2	1.544 (7)	C2B—H2B	0.9800
C6—O4	1.295 (6)	C2B—C1B	1.481 (18)
C6—C7	1.486 (8)	C2B—C3B	1.52 (3)
C6—O4B	1.345 (6)	C7B—C7B$^{\rm i}$	1.331 (17)
C6—C7B	1.437 (9)	C7B—H7B	0.9300
C6—O3	1.17 (3)	C3B—H3BA	0.9700
C6—O3B	1.29 (3)	C3B—H3BB	0.9700

C3—H3A	0.9700	C3B—C4B	1.42 (3)
C3—H3B	0.9700	C4B—H4BA	0.9700
C3—C2	1.541 (8)	C4B—H4BB	0.9700
C3—C4	1.481 (10)	C4B—C5B	1.29 (4)
C2—H2	0.9800	C5—H5A	0.9600
O4—H4	1.212 (7)	C5—H5B	0.9600
C4—H4A	0.9700	C5—H5C	0.9600
C4—H4B	0.9700	C5B—H5BA	0.9600
C4—C5	1.586 (12)	C5B—H5BB	0.9600
C7—C7^{i}	1.327 (14)	C5B—H5BC	0.9600
C7—H7	0.9300		

C1—O1—H1	110.8 (7)	C2B—N1B—H1BA	109.5
H1A—N1—H1B	109.5	C2B—N1B—H1BB	109.5
H1A—N1—H1C	109.5	C2B—N1B—H1BC	109.5
H1B—N1—H1C	109.5	C1B—O1B—H1	112.4 (17)
C2—N1—H1A	109.5	N1B—C2B—H2B	108.1
C2—N1—H1B	109.5	N1B—C2B—C1B	100.8 (18)
C2—N1—H1C	109.5	N1B—C2B—C3B	109.4 (15)
O1—C1—C2	113.7 (8)	C1B—C2B—H2B	108.1
O2—C1—O1	131.8 (9)	C1B—C2B—C3B	121 (2)
O2—C1—C2	113.5 (9)	C3B—C2B—H2B	108.1
O4—C6—C7	120.5 (4)	C6—C7B—H7B	114.0
O4B—C6—C7B	119.3 (5)	C7B^{i}—C7B—C6	131.9 (4)
O3—C6—O4	119 (2)	C7B^{i}—C7B—H7B	114.0
O3—C6—C7	120 (2)	O1B—C1B—O2B	106 (2)
O3B—C6—O4B	120 (2)	O1B—C1B—C2B	109.0 (19)
O3B—C6—C7B	120 (2)	C2B—C1B—O2B	129 (3)
H3A—C3—H3B	107.6	C2B—C3B—H3BA	109.0
C2—C3—H3A	108.6	C2B—C3B—H3BB	109.0
C2—C3—H3B	108.6	H3BA—C3B—H3BB	107.8
C4—C3—H3A	108.6	C4B—C3B—C2B	113 (3)
C4—C3—H3B	108.6	C4B—C3B—H3BA	109.0
C4—C3—C2	114.7 (6)	C4B—C3B—H3BB	109.0
N1—C2—C1	113.0 (6)	C3B—C4B—H4BA	110.0
N1—C2—C3	110.3 (4)	C3B—C4B—H4BB	110.0
N1—C2—H2	108.0	H4BA—C4B—H4BB	108.4
C1—C2—H2	108.0	C5B—C4B—C3B	108 (3)
C3—C2—C1	109.3 (8)	C5B—C4B—H4BA	110.0
C3—C2—H2	108.0	C5B—C4B—H4BB	110.0
C6—O4—H4	105 (4)	C4—C5—H5A	109.5
C3—C4—H4A	109.0	C4—C5—H5B	109.5
C3—C4—H4B	109.0	C4—C5—H5C	109.5
C3—C4—C5	112.7 (8)	H5A—C5—H5B	109.5
H4A—C4—H4B	107.8	H5A—C5—H5C	109.5
C5—C4—H4A	109.0	H5B—C5—H5C	109.5
C5—C4—H4B	109.0	C4B—C5B—H5BA	109.5
C6—C7—H7	114.8	C4B—C5B—H5BB	109.5

C7^{i}—C7—C6	130.4 (3)	C4B—C5B—H5BC	109.5
C7^{i}—C7—H7	114.8	H5BA—C5B—H5BB	109.5
H1BA—N1B—H1BB	109.5	H5BA—C5B—H5BC	109.5
H1BA—N1B—H1BC	109.5	H5BB—C5B—H5BC	109.5
H1BB—N1B—H1BC	109.5		
O1—C1—C2—N1	17.9 (14)	N1B—C2B—C1B—O1B	147 (3)
O1—C1—C2—C3	−105.4 (12)	N1B—C2B—C1B—O2B	−83 (4)
O2—C1—C2—N1	−151.9 (12)	N1B—C2B—C3B—C4B	−173 (2)
O2—C1—C2—C3	84.9 (15)	C2B—C3B—C4B—C5B	144 (3)
C2—C3—C4—C5	−177.9 (7)	C1B—C2B—C3B—C4B	71 (3)
O4—C6—C7—C7^{i}	−7.7 (7)	C3B—C2B—C1B—O1B	−92 (3)
C4—C3—C2—N1	−67.1 (8)	C3B—C2B—C1B—O2B	38 (4)
C4—C3—C2—C1	57.7 (9)	O3—C6—C7—C7^{i}	−180 (3)
O4B—C6—C7B—C7B^{i}	8.4 (9)	O3B—C6—C7B—C7B^{i}	174 (3)

Symmetry code: (i) *x*, −*y*+3/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2^{ii}	0.89	1.94	2.807 (8)	165
N1—H1*B*···O3	0.89	2.08	2.92 (4)	157
N1—H1*C*···O3^{iii}	0.89	1.90	2.79 (4)	178
O1—H1···O1^{iv}	1.28 (1)	1.28 (1)	2.568 (13)	180 (1)
O4—H4···O4^{i}	1.21 (1)	1.21 (1)	2.418 (9)	173 (8)

Symmetry codes: (i) *x*, −*y*+3/2, *z*; (ii) −*x*+1/2, −*y*+1, *z*−1/2; (iii) *x*−1/2, *y*, −*z*+1/2; (iv) −*x*+1, −*y*+1, −*z*+1.