Crystal structures of 2-aminopyridine citric acid salts: $C_5H_7N_2^+ \cdot C_6H_7O_7^-$ and $3C_5H_7N_2^+ \cdot C_6H_5O_7{}^{3-}$

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2-Aminopyridine and citric acid mixed in 1:1 and 3:1 ratios in ethanol yielded crystals of two 2-aminopyridinium citrate salts, viz. $C_5H_7N_2^+ \cdot C_6H_7O_7^-$ (I) (systematic name: 2-aminopyridin-1-ium 3-carboxy-2-carboxymethyl-2-hydroxypropanoate), and $3C_5H_7N_2^+ \cdot C_6H_5O_7{}^{3-}$ (II) [systematic name: tris(2-aminopyridin-1-ium) 2-hydroxypropane-1,2,3-tricarboxylate]. The supramolecular synthons present are analysed and their effect upon the crystal packing is presented in the context of crystal engineering. Salt I is formed by the protonation of the pyridine N atom and deprotonation of the central carboxylic group of citric acid, while in II all three carboxylic groups of the acid are deprotonated and the charges are compensated for by three 2-aminopyridinium cations. In both structures, a complex supramolecular three-dimensional architecture is formed. In I, the supramolecular aggregation results from $N_{amino}-H \cdots O_{acid}$, $O_{acid} \cdots H-O_{acid}$, $O_{alcohol}-H \cdots O_{acid}$, $N_{amino}-H \cdots O_{alcohol}$, $N_{py}-H \cdots O_{alcohol}$ and $C_{ar}-H \cdots O_{acid}$ interactions. The molecular conformation of the citrate ion (CA^{3-}) in II is stabilized by an intramolecular $O_{alcohol}-H \cdots O_{acid}$ hydrogen bond that encloses an $S(6)$ ring motif. The complex three-dimensional structure of II features $N_{amino}-H \cdots O_{acid}$, $N_{py}-H \cdots O_{acid}$ and several $C_{ar}-H \cdots O_{acid}$ hydrogen bonds. In the crystal of I, the common charge-assisted 2-aminopyridinium–carboxylate heterosynthon exhibited in many 2-aminopyridinium carboxylates is not observed, instead chains of $N-H \cdots O$ hydrogen bonds and hetero $O-H \cdots O$ dimers are formed. In the crystal of II, the 2-aminopyridinium–carboxylate heterosynthon is sustained, while hetero $O-H \cdots O$ dimers are not observed. The crystal structures of both salts display a variety of hydrogen bonds as almost all of the hydrogen-bond donors and acceptors present are involved in hydrogen bonding.
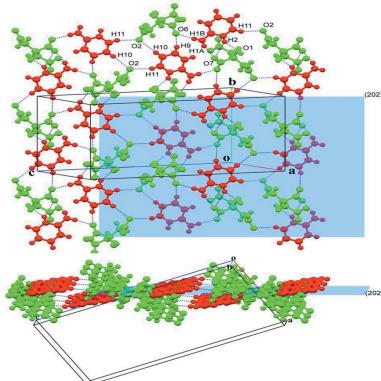
1. Chemical context

Systematic structural and statistical analysis focusing on the identification of robust supramolecular synthons or patterns are essential for crystal engineering and the design of new solid-state structures with desired properties. Organic crystals, especially salts, are now considered as potential materials for optical applications because of their flexibility in molecular design (Jayanalina et al., 2015a), thermal stability and delocalized clouds of π electrons (Jayanalina et al., 2015b). An analysis of the Cambridge Structural Database (Groom et al., 2016) by Bis & Zaworotko (2005) revealed that 77% of compounds that contain both the 2-aminopyridine and carb-

oxylic acid moieties generate 2-aminopyridine–carboxylic acid supramolecular heterosynthons rather than carboxylic acid or 2-aminopyridine supramolecular homosynthons. In the absence of other competing functionalities, the occurrence of heterosynthons increased to 97%. Several salts and co-crystals containing 2-aminopyridine or 2-acetaminopyridine and a carboxylic acid moiety have been reported (Jayanalina *et al.*, 2015*a*,*b*; Bis & Zaworotko, 2005; Aakeröy *et al.*, 2006; Jasmine *et al.*, 2015; Jin *et al.*, 2001). In all of these reported structures, the charge-assisted 2-aminopyridinium-carboxylate or neutral 2-acetaminopyridine–carboxylic heterosynthon is observed, as suggested by statistical analysis. Keeping this in mind, the crystal structure analyses of two 2-aminopyridinium citrate salts, $C_5H_7N_2^+ \cdot C_6H_7O_7^-$ (**I**) and $3C_5H_7N_2^+ \cdot C_6H_5O_7^{3-}$ (**II**), were undertaken in order to study the packing patterns and identify the supramolecular synthons present in each salt.
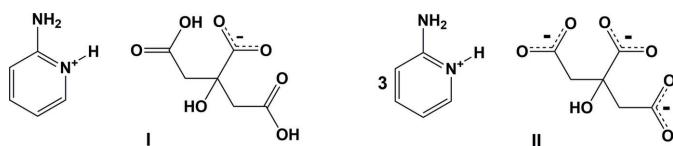
2. Structural commentary

The carboxylic groups in citric acid have pKa values of 3.128 (central –COOH group), 4.762 and 6.396 (terminal –COOH groups). Thus, an equimolar mixing of citric acid and 2-aminopyridine resulted in the formation of salt **I** (2-AMP⁺·CA⁻), whose structure is illustrated in Fig. 1. Here, the pyridine N atom is protonated and the central carboxylic group of the acid is deprotonated. The two C—O bond lengths of the central carboxylic group have values of 1.235 (3) Å for C6—O7 and 1.264 (3) Å for C6—O6, indicating partial double-bond character for both bonds. However, the two C—O bonds in each of the terminal carboxylic groups have different bond lengths [1.207 (3) Å for C3=O2 and 1.327 (3) Å for C3—O3, and 1.209 (3) Å for C5=O5 and 1.319 (3) Å for C5—O4], indicating double-bond character for one C—O bond and single-bond character for the other. These

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O6^{i}	0.82	1.86	2.681 (4)	177
N1—H1$A\cdots$O1^{ii}	0.86	2.09	2.895 (4)	156
N2—H2$C\cdots$O1^{ii}	0.86	2.34	3.076 (5)	144
N2—H2$D\cdots$O2	0.86	2.09	2.935 (5)	168
O3—H3$\cdots$O7^{i}	0.82	1.75	2.547 (4)	164
O4—H4$\cdots$O6^{iii}	0.82	1.82	2.601 (4)	158
C9—H9$\cdots$O3^{iv}	0.93	2.57	3.351 (5)	142

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

observations clearly confirm the deprotonation of the central carboxylic group (C6/O6/O7). The two terminal carboxylic groups in **I** have different conformations. In one of them (C5/O4/O5) the O—H and C=O bonds are in a *syn* conformation while in the other (C3/O2/O3), they have an *anti* conformation (Fig. 1). In the asymmetric unit of **I**, the 2-aminopyridinium cation, 2-AMP⁺, and the citrate anion, CA⁻, are linked *via* N$_{amino}$—H$\cdots$O$_{acid(t1)}$ hydrogen bonds [acid(t1) = C3/O2/O3], *viz.* N2—H2$D\cdots$O2 (Table 1 and Fig. 1).

The asymmetric unit of salt **II**, illustrated in Fig. 2, consists of one citrate trianion, CA³⁻ [(C₅H₅O₇)³⁻], and three 2-AMP⁺ cations (2-AMP1, 2-AMP2 and 2-AMP3), wherein the pyridine N atom of each 2-AMP unit is protonated and all three carboxylic groups of the acid are deprotonated. This is supported by the observation that the C—O bonds of all the three carboxylic groups have similar bond lengths, in the range 1.231 (2)–1.266 (2) Å, which is an indication of the partial double-bond character of all of the C—O bonds resulting from deprotonation. The molecular conformation of the CA³⁻ anion is stabilized by an intramolecular O$_{alcohol}$—H$\cdots$O$_{acid(t1)}$ hydrogen bond, namely O1—H1$O\cdots$O3, that closes an *S*(6) ring motif (Table 2, Fig. 2).


Figure 1
A view of the molecular structure of salt **I**, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines [Table 1; acid(t1) = C3/O2/O3; acid(t2) = C5/O4/O5; acid(c) = C6/O6/O7].
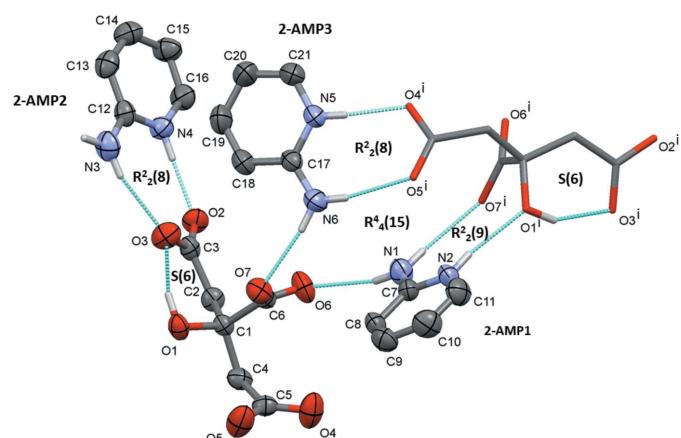
Figure 2
A view of the molecular structure of salt **II**, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular and some intermolecular interactions are shown as dashed lines [Table 2; acid(t1) = C3/O2/O3; acid (t2) = C5/O4/O5; acid(c) = C6/O6/O7; symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$]. For clarity, C-bound H atoms have been omitted.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$O\cdots$O3	0.91 (3)	1.84 (3)	2.681 (2)	152 (3)
N3—H3$A\cdots$O3	0.86	2.07	2.905 (3)	164
N4—H4$\cdots$O2	0.86	1.81	2.666 (2)	175
N1—H1$B\cdots$O6	0.86	2.07	2.893 (2)	161
N6—H6$B\cdots$O7	0.86	2.09	2.928 (2)	164
N1—H1$A\cdots$O7^{i}	0.86	2.12	2.948 (2)	162
N2—H2$\cdots$O1^{i}	0.86	2.00	2.760 (2)	144
N2—H2$\cdots$O7^{i}	0.86	2.55	3.304 (2)	144
C9—H9$\cdots$O6^{ii}	0.93	2.60	3.372 (2)	141
C10—H10$\cdots$O2^{ii}	0.93	2.51	3.419 (3)	167
C11—H11$\cdots$O2^{iii}	0.93	2.41	3.294 (3)	160
N3—H3$B\cdots$O4^{iv}	0.86	2.09	2.851 (2)	146
C13—H13$\cdots$O6^{iv}	0.93	2.40	3.301 (3)	163
N5—H5$\cdots$O4^{i}	0.86	1.77	2.591 (2)	160
N6—H6$A\cdots$O5^{i}	0.86	2.07	2.916 (2)	169
C20—H20$\cdots$O7^{v}	0.93	2.60	3.463 (3)	155
C21—H21$\cdots$O3^{v}	0.93	2.43	3.334 (3)	164

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) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $x+1, y, z$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

In the asymmetric unit of salt **II**, the three 2-AMP$^+$ cations are in different environments and interact with the CA^{3-} anion in different ways [Fig. 2 and Table 2; acid(t1) = C3/O2/O3; acid(t2) = C5/O4/O5; acid(c) = C6/O6/O7]. The first cation, 2-AMP1, interacts with the anion via a discrete N_{amino}—H$\cdots$O$_{acid(c)}$ hydrogen bond, namely N1—H1$B\cdots$O6. The second cation, 2-AMP2, interacts with the CA^{3-} anion via a charge-assisted 2-aminopyridinium-carboxylate $R_2^2(8)$ heterosynthon consisting of N_{amino}—H$\cdots$O$_{acid(t1)}$ (N3—H3$A\cdots$O3) and N_{py}—H$\cdots$O$_{acid(t1)}$ (N4—H4$\cdots$O2) hydrogen bonds. The third cation, 2-AMP3, interacts with the anion via a discrete N_{amino}—H$\cdots$O$_{acid(c)}$ hydrogen bond, namely N6—H6$B\cdots$O7.

3. Supramolecular features

Full details of the hydrogen-bonding interactions in the crystal of salt **I** are given in Table 1, and illustrated in Figs. 3 and 4. In the crystal of **I**, the cations and anions of adjacent units are interconnected by a C_{ar}—H$\cdots$O$_{acid(t1)}$ interactions, viz. C9—H9$\cdots$O3, while adjacent anions related by b-glide symmetry form chains running along the b-axis direction, consisting of an $R_2^2(8)$ heterosynthon of O$_{acid(c)}\cdots$H—O$_{acid(t1)}$ and O$_{alcohol}$—H$\cdots$O$_{acid(c)}$ hydrogen bonds, namely O3—H3$\cdots$O7^{i} and O1—H1$\cdots$O6^{i}; see Fig. 3 and Table 1. The 2-AMP$^+$ and CA$^-$ ions further aggregate to form sheets parallel to the ac plane (Fig. 4). The sheets consist of chains of O$_{acid(t2)}$—H$\cdots$O$_{acid(c)}$ hydrogen bonds, namely O4—H4$\cdots$O6^{iii}, running along the a-axis direction and linking the twofold-symmetry-related CA$^-$ anions (Table 1, Fig. 4). Adjacent chains are connected by 2-AMP$^+$ ions via N_{amino}—H$\cdots$O$_{acid(t1)}$=C hydrogen bonds, namely N2—H2$D\cdots$O2, and an $R_2^1(6)$ heterosynthon of N_{amino}—H$\cdots$O$_{alcohol}$ and N_{py}—H$\cdots$O$_{alcohol}$ hydrogen bonds, N2—H2$C\cdots$O1^{ii} and N1—H1$A\cdots$O1^{ii}, respectively, is formed (Table 1, Fig. 4). Overall, a three-dimensional supramolecular architecture is observed. All of the strong hydrogen-bond acceptors and hydrogen-bond donors in **I** are involved in
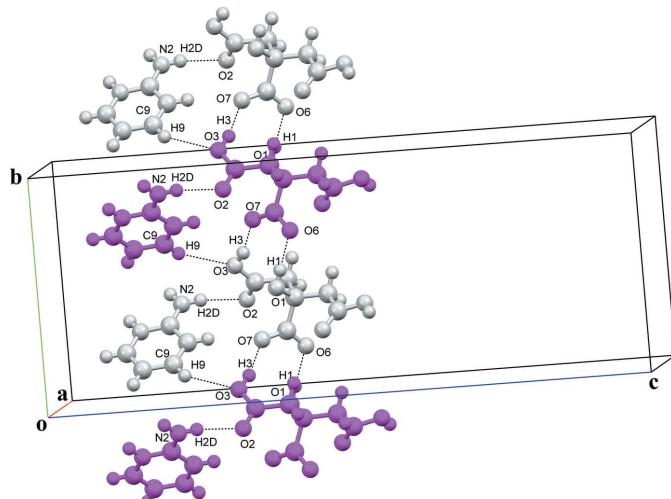
Figure 3
A partial view along the a axis of the crystal packing of salt **I**, showing the chains of CA$^-$ anions running along the b-axis direction. Attached to the chains and bridging two anions are the 2-AMP$^+$ cations. The various intermolecular interactions are shown as dashed lines (Table 1).

hydrogen bonding. However, the most reproducible charge-assisted 2-aminopyridinium–carboxylate heterosynthon, found in the crystal structures of many 2-aminopyridinium carboxylates (Bis & Zaworotko, 2005), is not present; instead chains of N—H$\cdots$O hydrogen bonds and hetero O—H$\cdots$O dimers are observed.

In the crystal of **II**, all of the strong hydrogen-bond donors and acceptors are utilized in a supramolecular association. Full details of the hydrogen-bonding interactions are given in Table 2, and illustrated in Figs. 2, 5 and 6. A number of the C_{ar}—H groups are also involved in C—H$\cdots$O hydrogen bonds (Table 2). However, in contrast to **I**, the alcoholic OH group is
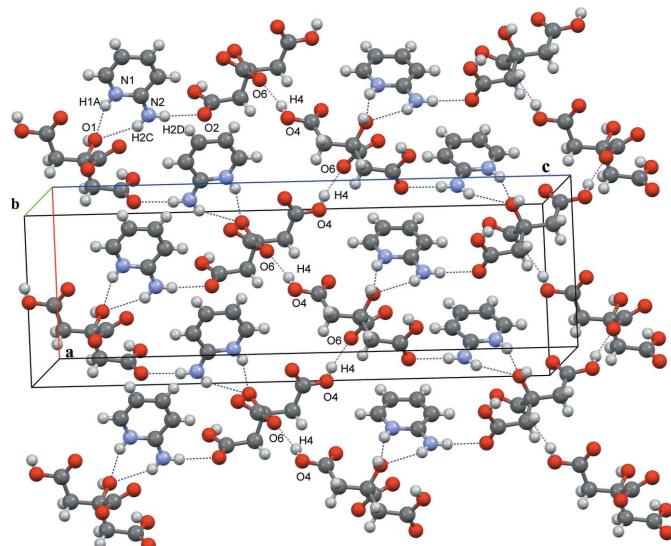
Figure 4
A partial view along the b axis of the crystal packing of salt **I**, illustrating the layer-like structure. Red and blue dashed lines denote the various intermolecular interactions (Table 1).
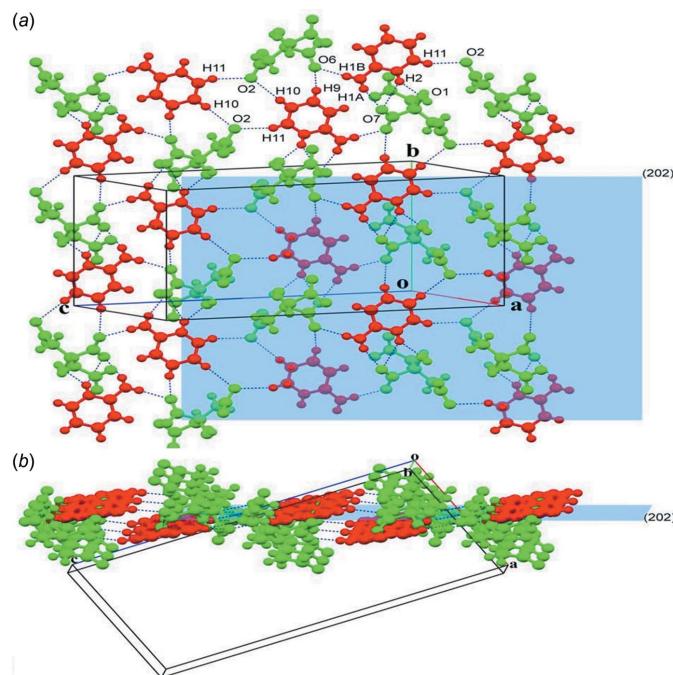
Figure 5
(a) Partial crystal packing of salt **II**, involving citrate (green) and 2-AMP1 (red) ions, showing the layer-like structure lying in plane (202). (b) An alternative view, along the b axis, of the layer-like structure. The hydrogen bonds and other intermolecular interactions are shown as dashed lines (Table 2).

Figure 6
(a) Partial crystal packing of salt **II**, involving citrate (green) and 2-AMP2 (blue) ions. Red dashed lines denote various intermolecular interactions and solid blue lines denote intramolecular hydrogen bonds (Table 2). (b) Partial crystal packing of salt **II**, involving citrate (green) and 2-AMP3 (yellow) ions. Dashed lines denote various intermolecular interactions (Table 2).

not involved in intermolecular hydrogen bonding as it is locked into an intramolecular O1—H1O···O3$_{acid(t1)}$ hydrogen bond. The CA^{3-} anion and the first 2-AMP$^+$ cation (2-AMP1) form sheets lying parallel to the (101) plane (Fig. 5a and 5b). The sheet consists of alternating CA^{3-} and 2-AMP$^+$ ions, forming chains via C11—H11···O2^{iii} interactions, with adjacent anti-parallel chains linked by C10—H10···O2^{ii}, N1—H1A···O7^i, N1—H1B···O6, N2—H2···O7^i and N2—H2···O1^i hydrogen bonds (Table 2, Fig. 5). On the other hand, the citrate and the second 2-AMP$^+$ ions (2-AMP2) propagate alternately along the a-axis direction to form ribbons (Fig. 6a) consisting of alternating $R_2^2(8)$ heterosynthons of N3—H3A···O3 and N4—H4···O2 hydrogen bonds (Table 2) and $R_2^2(11)$ heterosynthons of N3—H3B···O4 and C13—H13···O6 hydrogen bonds (Table 2). Finally, the third 2-AMP$^+$ ions (2-AMP3) are interlinked to the adjacent citrate ions, forming ribbons of alternating $R_2^2(8)$ heterosynthons, of N5—H5···O4^i and N6—H6A···O5^i hydrogen bonds (Table 2), and $R_2^2(10)$ heterosynthons of C21—H21···O3^{vi} and C20—H20···O7^{vi} interactions (Table 2) along the a-axis direction (Fig. 6b). Adjacent ribbons are further interconnected by N6—H6B···O7 hydrogen bonds to form corrugated sheets parallel to the ab plane (Table 2, Fig. 6b). Overall a complex supramolecular three-dimensional structure is formed.

4. Database survey

A survey of the Cambridge Structural Database (CSD, Version 5.39, last update May 2018; Groom et al., 2016)

revealed 80 organic structures involving a citric acid moiety in the form of solvates/hydrates, salts/salt hydrates and co-crystals. 25 structures among these are salts/salt hydrates of citric acid (deprotonated to different extents) with various organic cations. It is observed that most of the organic citrates appear as their hydrates, with the exception of a few (including **I** and **II**). The most common hydrogen bonds observed in these hydrated salts are N$_{amine}$—H···O$_{citric}$, N$_{amine}$—H···O$_{water}$ and O$_{water}$—H···O$_{citric}$, forming different supramolecular architectures. In the absence of a water molecule, the most common hydrogen bonds are N$_{amine}$—H···O$_{citric}$ and O$_{citric}$—H···O$_{citric}$. However, the nature of these supramolecular synthons varies from one structure to another, depending on the nature of the organic cations.

Similarly, the crystal structures of several salts with 2-AMP$^+$ as the cation are reported. Single-crystal structures of ten salts that contain both a 2-aminopyridine and a carboxylic acid moiety have been reported (Bis & Zaworotko, 2005). They include: 2-aminopyridinium 4-aminobenzoate, 2-aminopyridinium isophthalate, bis(2-aminopyridinium) terephthalate, 2-amino-5-methylpyridinium benzoate, bis(2-amino-5-methylpyridinium) 5-tertbutylisophthalate, 2-amino-5-methylpyridinium terephthalate, bis(2-amino-5-methylpyridinium) 2,6-naphthalenedicarboxylate, bis(2-amino 5-methylpyridinium) adipate adipic acid, bis(2-amino-5-methylpyridinium) 2,5-thiophenedicarboxylate 2,5-thiophenedicarboxylic acid, and indomethacin 2-amino-5-methylpyridinium. In all the reported structures, the most reproducible pattern is the charge-assisted 2-aminopyridinium–carboxylate heterosynthon seen in salt **II**. Similarly, in the crystal structure of

Table 3
Experimental details.

	I	II
Crystal data		
Chemical formula	$C_5H_7N_2{}^+{\cdot}C_6H_7O_7{}^-$	$3C_5H_7N_2{}^+{\cdot}C_6H_5O_7{}^{3-}$
M_r	286.24	474.48
Crystal system, space group	Orthorhombic, $Pbca$	Monoclinic, $P2_1/n$
Temperature (K)	296	296
a, b, c (Å)	9.000 (11), 10.721 (13), 27.21 (3)	10.0297 (17), 10.6564 (14), 21.986 (4)
α, β, γ (°)	90, 90, 90	90, 101.426 (9), 90
V (Å^3)	2625 (5)	2303.3 (7)
Z	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.12	0.11
Crystal size (mm)	$0.27 \times 0.22 \times 0.19$	$0.22 \times 0.19 \times 0.17$
Data collection		
Diffractometer	Bruker APEXII	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.968, 0.977	0.977, 0.982
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8086, 2977, 2143	13120, 5242, 3779
R_{int}	0.099	0.056
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.195, 1.06	0.052, 0.149, 1.05
No. of reflections	2977	5242
No. of parameters	184	311
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})	0.29, −0.30	0.27, −0.21

Computer programs: *APEX2*, *SAINT-Plus* and *XPREP* (Bruker, 2009), *SHELXT2016* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b) and *Mercury* (Macrae *et al.*, 2008).

2-amino-3-methylpyridinium *ortho*-phthalate (Jin *et al.*, 2001), the two 2-amino-3-methylpyridinium ions are interconnected to the *ortho*-phthalate ion *via* a charge-assisted 2-amino-pyridinium–carboxylate heterosynthon. This robust pattern is also observed in the crystal structures of 2-aminopyridinium 6-chloronicotinate (Jasmine *et al.*, 2015) and 2-amino-5-chloropyridinium pyridine-2-carboxylate monohydrate (Jayanalina *et al.*, 2015a). Single-crystal structures of ten co-crystals that contain 2-acetaminopyridine and a carboxylic acid moiety: 2-acetaminopyridine/fumaric acid have been reported by Aakeröy *et al.* (2006). They include: 2-acetaminopyridine/succinic acid, 2-acetaminopyridine/glutaric acid, 2-acet-aminopyridine /adipic acid, 2-acetaminopyridine/pimelic acid, 2-acetaminopyridine/suberic acid, 2-acetamino-pyridine/azelaic acid, 2-acetaminopyridine/sebacic acid, 2-acetamino-pyridine/3,5-dimethylbenzoic acid, and 2-acetaminopyridine/5-nitroisophthalic acid. Although these are neutral compounds wherein there is no transfer of proton from carboxylic acid to the 2-acetaminopyridine moiety, the most repetitive pattern observed in these structures is the neutral 2-acetaminopyridine–carboxylic acid $R_2^2(8)$ heterosynthon. This is very similar to the charge-assisted 2-aminopyridinium–carboxylate heterosynthon except for the positioning of the hydrogen atom, on either the O or N atom.

The crystal structure of 2-amino 5-chloropyridinium-L-tartarate (Jayanalina *et al.*, 2015b) shows that despite of the presence of other competing functionalities on the carboxylic acid (two alcoholic OH groups in tartaric acid), the most

frequent 2-aminopyridinium–carboxylate heterosynthon is still observed. However, the presence of the alcoholic OH group in citric acid has resulted in a deviation from the regular trend as the charge-assisted 2-aminopyridinium–carboxylate heterosynthon is not observed in **I**; instead chains of N—H$\cdots$O hydrogen bonds and hetero O—H$\cdots$O dimers are observed. The 2-aminopyridinium–carboxylate heterosynthon is sustained in the crystal structure of **II** because of the non-availability of the alcoholic OH group for intermolecular hydrogen bonding.

Hence, the study of the crystal structure of 2-amino-pyridinium citrate, mixed in a 2:1 ratio, would be highly significant in understanding the packing-pattern trends observed in this family of salts. Unfortunately, despite a number of attempts, we have not been able to obtain good-quality single crystals of this salt.

5. Synthesis and crystallization

A solution of citric acid (3 mmol, 0.576 g) in ethanol (15 ml) was added to an ethanolic solution (15 ml) of 2-aminopyridine (3 mmol, 0.282 g). The resulting solution was heated and the hot solution was filtered. Slow evaporation of the solution resulted in the formation of colourless prismatic crystals of salt **I** (m.p. 493 K). Single crystals of salt **II** were obtained from a similar procedure; an ethanolic solution (15 ml) of citric acid (3 mmol, 0.576 g) was mixed with an ethanolic solution (15 ml) of 2-aminopyridine (9 mmol, 0.846 g).

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. In salt **I**, the OH H atom (H1) was positioned geometrically and refined as riding: O—H = 0.82 Å with $U_{iso}(H) = 1.5U_{eq}(O)$. In salt **II**, the OH H atom (H1O) was located in a difference-Fourier map and freely refined. In both salts, the other H atoms were positioned geometrically and refined as riding: N—H = 0.86 Å, C—H = 0.93–0.97 Å with $U_{iso}(H) = 1.2U_{eq}(N, C)$.

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supporting information

Crystal structures of 2-aminopyridine citric acid salts: $C_5H_7N_2^+ \cdot C_6H_7O_7^-$ and $3C_5H_7N_2^+ \cdot C_6H_5O_7^{3-}$

Shet M. Prakash, S. Naveen, N. K. Lokanath, P. A. Suchetan and Ismail Warad

Computing details

For both structures, data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* and *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2009); program(s) used to solve structure: SHELXT2016 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015b).

2-Aminopyridin-1-ium 3-carboxy-2-carboxymethyl-2-hydroxypropanoate (I)

Crystal data
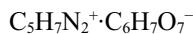
$C_5H_7N_2^+ \cdot C_6H_7O_7^-$	$D_x = 1.448$ Mg m^{-3}
$M_r = 286.24$	Melting point: 493 K
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2ab	Cell parameters from 143 reflections
$a = 9.000\ (11)$ Å	$\theta = 3.1$–$27.5°$
$b = 10.721\ (13)$ Å	$\mu = 0.12$ mm^{-1}
$c = 27.21\ (3)$ Å	$T = 296$ K
$V = 2625\ (5)$ Å^3	Prism, colourless
$Z = 8$	$0.27 \times 0.22 \times 0.19$ mm
$F(000) = 1200$	

Data collection

Bruker APEXII diffractometer	8086 measured reflections
Radiation source: sealed X-ray tube	2977 independent reflections
Graphite monochromator	2143 reflections with $I > 2\sigma(I)$
phi and φ scans	$R_{int} = 0.099$
Absorption correction: multi-scan (SADABS; Bruker, 2009)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
	$h = -11 \rightarrow 9$
	$k = -13 \rightarrow 13$
$T_{min} = 0.968$, $T_{max} = 0.977$	$l = -12 \rightarrow 35$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.066$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.195$	
$S = 1.06$	Hydrogen site location: inferred from neighbouring sites
2977 reflections	
184 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.1065P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ 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	$U_{iso}*/U_{eq}$
C1	0.2827 (2)	0.40538 (18)	0.41150 (7)	0.0284 (4)
C2	0.4265 (2)	0.47554 (18)	0.39605 (8)	0.0314 (5)
H2A	0.419854	0.561864	0.406495	0.038*
H2B	0.511292	0.438155	0.412406	0.038*
C3	0.4500 (2)	0.47082 (18)	0.34102 (8)	0.0329 (5)
C4	0.2668 (3)	0.4112 (2)	0.46729 (8)	0.0348 (5)
H4A	0.354470	0.374637	0.482187	0.042*
H4B	0.262245	0.497923	0.477316	0.042*
C5	0.1315 (3)	0.3448 (2)	0.48646 (8)	0.0383 (5)
C6	0.2956 (2)	0.26921 (17)	0.39304 (7)	0.0280 (4)
C7	0.4276 (3)	0.3173 (2)	0.19589 (9)	0.0397 (5)
C8	0.3305 (3)	0.2475 (2)	0.22619 (9)	0.0479 (6)
H8	0.333716	0.255755	0.260195	0.057*
C9	0.2320 (3)	0.1677 (3)	0.20452 (11)	0.0546 (7)
H9	0.167956	0.121120	0.224075	0.066*
C10	0.2259 (3)	0.1548 (3)	0.15313 (10)	0.0523 (7)
H10	0.158588	0.100241	0.138646	0.063*
C11	0.3192 (3)	0.2228 (2)	0.12526 (10)	0.0469 (6)
H11	0.316651	0.215571	0.091216	0.056*
N1	0.4170 (2)	0.30207 (19)	0.14690 (7)	0.0411 (5)
H1A	0.475232	0.344774	0.128331	0.049*
N2	0.5275 (2)	0.3966 (2)	0.21382 (8)	0.0521 (5)
H2C	0.584424	0.437389	0.194183	0.062*
H2D	0.535185	0.406964	0.245054	0.062*
O1	0.15695 (16)	0.45874 (12)	0.38791 (6)	0.0337 (4)
H1	0.147677	0.531534	0.396642	0.051*
O2	0.5321 (2)	0.39665 (16)	0.32168 (7)	0.0520 (5)
O3	0.3748 (2)	0.55002 (14)	0.31300 (6)	0.0444 (4)
H3	0.334824	0.602731	0.330373	0.067*
O4	0.1087 (2)	0.3705 (2)	0.53325 (7)	0.0570 (5)
H4	0.031941	0.336621	0.542459	0.085*
O5	0.0527 (2)	0.27613 (19)	0.46272 (7)	0.0620 (6)
O6	0.37012 (18)	0.19472 (13)	0.41930 (6)	0.0405 (4)
O7	0.23360 (18)	0.24341 (13)	0.35387 (5)	0.0367 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0314 (10)	0.0247 (9)	0.0289 (10)	−0.0017 (8)	−0.0027 (8)	−0.0002 (7)
C2	0.0336 (10)	0.0277 (9)	0.0330 (11)	−0.0039 (8)	0.0026 (9)	−0.0010 (8)
C3	0.0370 (11)	0.0259 (9)	0.0357 (11)	−0.0037 (8)	0.0063 (9)	−0.0014 (8)
C4	0.0407 (11)	0.0327 (11)	0.0311 (11)	−0.0065 (9)	0.0047 (9)	−0.0054 (8)
C5	0.0435 (12)	0.0366 (11)	0.0349 (11)	−0.0043 (10)	0.0063 (10)	0.0000 (9)
C6	0.0301 (9)	0.0228 (9)	0.0311 (10)	−0.0014 (7)	−0.0007 (8)	0.0008 (7)
C7	0.0381 (11)	0.0425 (12)	0.0385 (12)	0.0097 (10)	0.0049 (10)	−0.0016 (9)
C8	0.0482 (13)	0.0588 (15)	0.0366 (13)	0.0082 (11)	0.0096 (11)	0.0059 (11)
C9	0.0454 (14)	0.0573 (16)	0.0611 (17)	0.0027 (12)	0.0126 (13)	0.0104 (13)
C10	0.0455 (14)	0.0552 (15)	0.0563 (16)	0.0027 (12)	0.0013 (12)	0.0001 (12)
C11	0.0443 (13)	0.0553 (14)	0.0412 (13)	0.0107 (12)	−0.0018 (11)	−0.0019 (11)
N1	0.0379 (10)	0.0478 (11)	0.0375 (11)	0.0055 (9)	0.0070 (8)	0.0048 (8)
N2	0.0530 (12)	0.0609 (13)	0.0422 (11)	−0.0033 (11)	0.0095 (10)	−0.0061 (10)
O1	0.0339 (8)	0.0232 (7)	0.0441 (9)	0.0033 (6)	−0.0046 (6)	−0.0015 (6)
O2	0.0625 (11)	0.0472 (10)	0.0462 (10)	0.0155 (9)	0.0142 (9)	−0.0037 (8)
O3	0.0641 (11)	0.0364 (9)	0.0326 (8)	0.0135 (8)	0.0050 (8)	0.0007 (6)
O4	0.0542 (10)	0.0787 (13)	0.0381 (10)	−0.0225 (10)	0.0135 (8)	−0.0070 (9)
O5	0.0683 (12)	0.0697 (12)	0.0481 (11)	−0.0336 (11)	0.0144 (10)	−0.0148 (9)
O6	0.0507 (9)	0.0252 (7)	0.0456 (9)	0.0038 (7)	−0.0156 (7)	0.0019 (6)
O7	0.0470 (9)	0.0276 (8)	0.0355 (8)	0.0002 (6)	−0.0087 (7)	−0.0036 (6)

Geometric parameters (Å, °)

C1—O1	1.421 (3)	C7—N1	1.346 (3)
C1—C4	1.526 (3)	C7—C8	1.416 (4)
C1—C6	1.548 (3)	C8—C9	1.365 (4)
C1—C2	1.555 (3)	C8—H8	0.9300
C2—C3	1.513 (3)	C9—C10	1.406 (4)
C2—H2A	0.9700	C9—H9	0.9300
C2—H2B	0.9700	C10—C11	1.346 (4)
C3—O2	1.207 (3)	C10—H10	0.9300
C3—O3	1.327 (3)	C11—N1	1.357 (3)
C4—C5	1.503 (3)	C11—H11	0.9300
C4—H4A	0.9700	N1—H1A	0.8600
C4—H4B	0.9700	N2—H2C	0.8600
C5—O5	1.209 (3)	N2—H2D	0.8600
C5—O4	1.319 (3)	O1—H1	0.8200
C6—O7	1.235 (3)	O3—H3	0.8200
C6—O6	1.264 (3)	O4—H4	0.8200
C7—N2	1.330 (3)		
O1—C1—C4	110.98 (18)	O6—C6—C1	116.87 (18)
O1—C1—C6	107.03 (16)	N2—C7—N1	119.3 (2)
C4—C1—C6	111.61 (16)	N2—C7—C8	122.8 (2)
O1—C1—C2	110.23 (17)	N1—C7—C8	117.9 (2)

C4—C1—C2	109.12 (17)	C9—C8—C7	118.7 (3)
C6—C1—C2	107.80 (17)	C9—C8—H8	120.6
C3—C2—C1	111.57 (17)	C7—C8—H8	120.6
C3—C2—H2A	109.3	C8—C9—C10	121.1 (3)
C1—C2—H2A	109.3	C8—C9—H9	119.5
C3—C2—H2B	109.3	C10—C9—H9	119.5
C1—C2—H2B	109.3	C11—C10—C9	118.9 (3)
H2A—C2—H2B	108.0	C11—C10—H10	120.6
O2—C3—O3	118.9 (2)	C9—C10—H10	120.6
O2—C3—C2	122.6 (2)	C10—C11—N1	119.9 (3)
O3—C3—C2	118.45 (18)	C10—C11—H11	120.0
C5—C4—C1	113.69 (18)	N1—C11—H11	120.0
C5—C4—H4A	108.8	C7—N1—C11	123.5 (2)
C1—C4—H4A	108.8	C7—N1—H1A	118.3
C5—C4—H4B	108.8	C11—N1—H1A	118.3
C1—C4—H4B	108.8	C7—N2—H2C	120.0
H4A—C4—H4B	107.7	C7—N2—H2D	120.0
O5—C5—O4	123.5 (2)	H2C—N2—H2D	120.0
O5—C5—C4	125.3 (2)	C1—O1—H1	109.5
O4—C5—C4	111.2 (2)	C3—O3—H3	109.5
O7—C6—O6	125.90 (19)	C5—O4—H4	109.5
O7—C6—C1	117.22 (17)		
O1—C1—C2—C3	−59.0 (2)	C2—C1—C6—O7	−97.6 (2)
C4—C1—C2—C3	178.89 (16)	O1—C1—C6—O6	−159.64 (18)
C6—C1—C2—C3	57.5 (2)	C4—C1—C6—O6	−38.0 (3)
C1—C2—C3—O2	−98.1 (3)	C2—C1—C6—O6	81.8 (2)
C1—C2—C3—O3	80.5 (2)	N2—C7—C8—C9	−179.6 (2)
O1—C1—C4—C5	58.9 (2)	N1—C7—C8—C9	0.5 (3)
C6—C1—C4—C5	−60.4 (2)	C7—C8—C9—C10	−0.2 (4)
C2—C1—C4—C5	−179.39 (17)	C8—C9—C10—C11	0.0 (4)
C1—C4—C5—O5	11.1 (3)	C9—C10—C11—N1	0.1 (4)
C1—C4—C5—O4	−169.0 (2)	N2—C7—N1—C11	179.6 (2)
O1—C1—C6—O7	21.0 (2)	C8—C7—N1—C11	−0.5 (3)
C4—C1—C6—O7	142.6 (2)	C10—C11—N1—C7	0.2 (4)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O6[i]	0.82	1.86	2.681 (4)	177
N1—H1A⋯O1[ii]	0.86	2.09	2.895 (4)	156
N2—H2C⋯O1[ii]	0.86	2.34	3.076 (5)	144
N2—H2D⋯O2	0.86	2.09	2.935 (5)	168
O3—H3⋯O7[i]	0.82	1.75	2.547 (4)	164
O4—H4⋯O6[iii]	0.82	1.82	2.601 (4)	158
C9—H9⋯O3[iv]	0.93	2.57	3.351 (5)	142

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

Tris(2-aminopyridin-1-ium) 2-hydroxypropane-1,2,3-tricarboxylate (II)

Crystal data
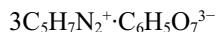
$3C_5H_7N_2{}^+ \cdot C_6H_5O_7{}^{3-}$	$F(000) = 1000$
$M_r = 474.48$	$D_x = 1.368$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.0297$ (17) Å	Cell parameters from 132 reflections
$b = 10.6564$ (14) Å	$\theta = 3.1$–27.5°
$c = 21.986$ (4) Å	$\mu = 0.11$ mm^{-1}
$\beta = 101.426$ (9)°	$T = 296$ K
$V = 2303.3$ (7) Å^3	Prism, colourless
$Z = 4$	$0.22 \times 0.19 \times 0.17$ mm

Data collection

Bruker APEXII diffractometer	13120 measured reflections
Radiation source: sealed X-ray tube	5242 independent reflections
Graphite monochromator	3779 reflections with $I > 2\sigma(I)$
phi and φ scans	$R_{int} = 0.056$
Absorption correction: multi-scan (SADABS; Bruker, 2009)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$T_{min} = 0.977$, $T_{max} = 0.982$	$h = -13\rightarrow12$
	$k = -13\rightarrow13$
	$l = -28\rightarrow16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.052$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.149$	$w = 1/[\sigma^2(F_o{}^2) + (0.0673P)^2 + 0.409P]$
$S = 1.05$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
5242 reflections	$(\Delta/\sigma)_{max} < 0.001$
311 parameters	$\Delta\rho_{max} = 0.27$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

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}
O1	0.40837 (15)	0.54865 (11)	0.08093 (6)	0.0423 (3)
H1O	0.489 (3)	0.506 (3)	0.0879 (12)	0.071 (8)*
O2	0.52383 (14)	0.18918 (12)	0.03079 (6)	0.0466 (3)
O3	0.59153 (14)	0.36464 (13)	0.08316 (7)	0.0527 (4)
O4	0.00785 (17)	0.50955 (14)	0.11124 (8)	0.0651 (5)
O5	0.13362 (17)	0.67594 (14)	0.10506 (9)	0.0661 (5)
O6	0.25602 (17)	0.28972 (13)	0.14580 (6)	0.0542 (4)
O7	0.36839 (14)	0.45764 (12)	0.18962 (6)	0.0449 (3)

C1	0.31580 (17)	0.44500 (15)	0.07766 (7)	0.0322 (4)
C2	0.35607 (19)	0.34310 (16)	0.03557 (8)	0.0377 (4)
H2A	0.295896	0.271947	0.035888	0.045*
H2B	0.339938	0.375355	−0.006509	0.045*
C3	0.50118 (19)	0.29614 (16)	0.05164 (8)	0.0368 (4)
C4	0.17245 (19)	0.49234 (18)	0.04858 (8)	0.0410 (4)
H4A	0.179056	0.544641	0.013183	0.049*
H4B	0.116466	0.420505	0.033149	0.049*
C5	0.10047 (18)	0.56668 (17)	0.09152 (8)	0.0393 (4)
C6	0.31417 (17)	0.39294 (15)	0.14353 (8)	0.0334 (4)
N1	0.14007 (18)	0.20220 (15)	0.24858 (8)	0.0510 (4)
H1A	0.137464	0.124190	0.258293	0.061*
H1B	0.156634	0.223370	0.213063	0.061*
N2	0.09288 (17)	0.25593 (15)	0.34395 (7)	0.0458 (4)
H2	0.093048	0.175597	0.351991	0.055*
C7	0.11865 (18)	0.29025 (17)	0.28856 (8)	0.0381 (4)
C8	0.1228 (2)	0.42056 (17)	0.27643 (9)	0.0451 (4)
H8	0.138649	0.448570	0.238434	0.054*
C9	0.1037 (2)	0.50434 (19)	0.32022 (11)	0.0535 (5)
H9	0.108433	0.589807	0.312368	0.064*
C10	0.0768 (2)	0.4638 (2)	0.37722 (11)	0.0603 (6)
H10	0.062386	0.521166	0.407137	0.072*
C11	0.0723 (2)	0.3385 (2)	0.38754 (10)	0.0558 (5)
H11	0.054862	0.309350	0.425062	0.067*
N3	0.8662 (2)	0.27826 (16)	0.08313 (9)	0.0557 (5)
H3A	0.785814	0.310176	0.076107	0.067*
H3B	0.936026	0.325756	0.094377	0.067*
N4	0.77000 (16)	0.08491 (14)	0.05893 (8)	0.0430 (4)
H4	0.692251	0.121911	0.051585	0.052*
C12	0.8824 (2)	0.15464 (18)	0.07656 (8)	0.0421 (4)
C13	1.0095 (2)	0.0933 (2)	0.08716 (9)	0.0504 (5)
H13	1.089615	0.138975	0.098593	0.060*
C14	1.0135 (2)	−0.0336 (2)	0.08043 (10)	0.0558 (5)
H14	1.097062	−0.074390	0.087536	0.067*
C15	0.8939 (2)	−0.1037 (2)	0.06300 (11)	0.0551 (5)
H15	0.897109	−0.190487	0.058988	0.066*
C16	0.7740 (2)	−0.04213 (18)	0.05220 (10)	0.0485 (5)
H16	0.693459	−0.086724	0.040050	0.058*
N5	0.62921 (16)	0.12553 (15)	0.31762 (7)	0.0441 (4)
H5	0.587297	0.102488	0.346297	0.053*
N6	0.46530 (18)	0.27662 (17)	0.28874 (8)	0.0514 (4)
H6A	0.426137	0.251756	0.318032	0.062*
H6B	0.431257	0.337666	0.265102	0.062*
C17	0.57809 (19)	0.22085 (17)	0.28005 (8)	0.0393 (4)
C18	0.6471 (2)	0.2548 (2)	0.23248 (10)	0.0499 (5)
H18	0.613328	0.318660	0.204882	0.060*
C19	0.7631 (3)	0.1936 (2)	0.22721 (12)	0.0640 (6)
H19	0.808573	0.216020	0.195845	0.077*

C20	0.8150 (2)	0.0974 (2)	0.26828 (13)	0.0686 (7)
H20	0.895861	0.056931	0.265660	0.082*
C21	0.7437 (2)	0.0652 (2)	0.31185 (11)	0.0580 (6)
H21	0.774715	−0.000586	0.338719	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0546 (8)	0.0294 (6)	0.0474 (7)	−0.0046 (6)	0.0211 (6)	−0.0017 (5)
O2	0.0522 (8)	0.0363 (7)	0.0538 (8)	0.0038 (6)	0.0162 (6)	−0.0095 (6)
O3	0.0496 (8)	0.0504 (8)	0.0574 (8)	0.0004 (6)	0.0084 (6)	−0.0184 (7)
O4	0.0731 (10)	0.0523 (8)	0.0824 (11)	−0.0157 (8)	0.0453 (9)	−0.0252 (8)
O5	0.0646 (10)	0.0438 (8)	0.0986 (13)	−0.0062 (7)	0.0371 (9)	−0.0227 (8)
O6	0.0796 (10)	0.0415 (7)	0.0443 (8)	−0.0156 (7)	0.0187 (7)	0.0038 (6)
O7	0.0567 (8)	0.0452 (7)	0.0320 (6)	0.0011 (6)	0.0070 (6)	−0.0052 (6)
C1	0.0407 (9)	0.0277 (7)	0.0297 (8)	0.0003 (7)	0.0104 (7)	−0.0011 (6)
C2	0.0463 (10)	0.0357 (8)	0.0328 (8)	0.0013 (7)	0.0118 (7)	−0.0069 (7)
C3	0.0493 (10)	0.0334 (8)	0.0312 (8)	−0.0005 (7)	0.0162 (7)	−0.0022 (7)
C4	0.0486 (10)	0.0422 (9)	0.0321 (8)	0.0086 (8)	0.0074 (8)	0.0000 (7)
C5	0.0413 (9)	0.0377 (9)	0.0371 (9)	0.0069 (8)	0.0035 (7)	−0.0036 (7)
C6	0.0391 (9)	0.0303 (8)	0.0325 (8)	0.0048 (7)	0.0111 (7)	0.0001 (7)
N1	0.0642 (11)	0.0406 (8)	0.0532 (10)	−0.0002 (8)	0.0238 (8)	0.0016 (7)
N2	0.0544 (10)	0.0389 (8)	0.0478 (9)	0.0046 (7)	0.0187 (7)	0.0134 (7)
C7	0.0362 (9)	0.0380 (9)	0.0420 (9)	0.0023 (7)	0.0123 (7)	0.0074 (7)
C8	0.0523 (11)	0.0387 (9)	0.0466 (10)	0.0012 (8)	0.0154 (9)	0.0131 (8)
C9	0.0613 (13)	0.0362 (9)	0.0639 (13)	0.0037 (9)	0.0147 (10)	0.0054 (9)
C10	0.0729 (15)	0.0564 (13)	0.0546 (12)	0.0095 (11)	0.0200 (11)	−0.0082 (11)
C11	0.0659 (13)	0.0634 (13)	0.0431 (11)	0.0075 (11)	0.0228 (10)	0.0079 (10)
N3	0.0647 (11)	0.0406 (9)	0.0642 (11)	−0.0118 (8)	0.0184 (9)	−0.0069 (8)
N4	0.0404 (8)	0.0371 (8)	0.0514 (9)	0.0001 (7)	0.0089 (7)	−0.0042 (7)
C12	0.0513 (11)	0.0418 (9)	0.0351 (9)	−0.0075 (8)	0.0129 (8)	−0.0021 (8)
C13	0.0447 (11)	0.0613 (12)	0.0446 (11)	−0.0089 (9)	0.0077 (9)	−0.0067 (9)
C14	0.0462 (11)	0.0624 (13)	0.0577 (13)	0.0107 (10)	0.0076 (9)	−0.0019 (11)
C15	0.0558 (12)	0.0418 (10)	0.0655 (14)	0.0063 (9)	0.0071 (10)	−0.0038 (10)
C16	0.0475 (11)	0.0384 (9)	0.0585 (12)	−0.0054 (8)	0.0080 (9)	−0.0078 (9)
N5	0.0424 (8)	0.0461 (9)	0.0445 (8)	0.0010 (7)	0.0099 (7)	0.0143 (7)
N6	0.0518 (10)	0.0561 (10)	0.0475 (9)	0.0107 (8)	0.0129 (8)	0.0170 (8)
C17	0.0409 (9)	0.0383 (9)	0.0374 (9)	−0.0019 (7)	0.0041 (7)	0.0047 (7)
C18	0.0559 (12)	0.0475 (10)	0.0476 (11)	0.0002 (9)	0.0130 (9)	0.0140 (9)
C19	0.0646 (14)	0.0676 (15)	0.0682 (15)	0.0001 (12)	0.0331 (12)	0.0167 (12)
C20	0.0558 (13)	0.0658 (14)	0.0919 (18)	0.0140 (11)	0.0331 (13)	0.0234 (14)
C21	0.0491 (12)	0.0547 (12)	0.0709 (14)	0.0092 (10)	0.0136 (10)	0.0230 (11)

Geometric parameters (Å, º)

O1—C1	1.435 (2)	C11—H11	0.9300
O1—H1O	0.92 (3)	N3—C12	1.339 (3)
O2—C3	1.266 (2)	N3—H3A	0.8600

O3—C3	1.259 (2)	N3—H3B	0.8601
O4—C5	1.257 (2)	N4—C12	1.342 (2)
O5—C5	1.231 (2)	N4—C16	1.363 (2)
O6—C6	1.251 (2)	N4—H4	0.8601
O7—C6	1.257 (2)	C12—C13	1.410 (3)
C1—C2	1.532 (2)	C13—C14	1.362 (3)
C1—C4	1.538 (2)	C13—H13	0.9300
C1—C6	1.554 (2)	C14—C15	1.400 (3)
C2—C3	1.513 (3)	C14—H14	0.9300
C2—H2A	0.9700	C15—C16	1.349 (3)
C2—H2B	0.9700	C15—H15	0.9300
C4—C5	1.520 (2)	C16—H16	0.9300
C4—H4A	0.9700	N5—C21	1.344 (3)
C4—H4B	0.9700	N5—C17	1.345 (2)
N1—C7	1.332 (3)	N5—H5	0.8600
N1—H1A	0.8600	N6—C17	1.325 (3)
N1—H1B	0.8601	N6—H6A	0.8599
N2—C7	1.345 (2)	N6—H6B	0.8600
N2—C11	1.347 (3)	C17—C18	1.411 (3)
N2—H2	0.8740	C18—C19	1.359 (3)
C7—C8	1.416 (2)	C18—H18	0.9300
C8—C9	1.354 (3)	C19—C20	1.397 (3)
C8—H8	0.9300	C19—H19	0.9300
C9—C10	1.401 (3)	C20—C21	1.348 (3)
C9—H9	0.9300	C20—H20	0.9300
C10—C11	1.356 (3)	C21—H21	0.9300
C10—H10	0.9300		
C1—O1—H1O	99.9 (17)	N2—C11—C10	120.6 (2)
O1—C1—C2	109.29 (14)	N2—C11—H11	119.7
O1—C1—C4	108.09 (14)	C10—C11—H11	119.7
C2—C1—C4	108.54 (13)	C12—N3—H3A	120.0
O1—C1—C6	110.73 (13)	C12—N3—H3B	120.0
C2—C1—C6	111.26 (13)	H3A—N3—H3B	120.0
C4—C1—C6	108.84 (14)	C12—N4—C16	122.68 (17)
C3—C2—C1	116.74 (14)	C12—N4—H4	118.6
C3—C2—H2A	108.1	C16—N4—H4	118.7
C1—C2—H2A	108.1	N3—C12—N4	117.58 (19)
C3—C2—H2B	108.1	N3—C12—C13	124.28 (19)
C1—C2—H2B	108.1	N4—C12—C13	118.14 (18)
H2A—C2—H2B	107.3	C14—C13—C12	119.12 (19)
O3—C3—O2	124.07 (17)	C14—C13—H13	120.4
O3—C3—C2	119.39 (15)	C12—C13—H13	120.4
O2—C3—C2	116.53 (16)	C13—C14—C15	121.2 (2)
C5—C4—C1	115.63 (14)	C13—C14—H14	119.4
C5—C4—H4A	108.4	C15—C14—H14	119.4
C1—C4—H4A	108.4	C16—C15—C14	118.25 (19)
C5—C4—H4B	108.4	C16—C15—H15	120.9

C1—C4—H4B	108.4	C14—C15—H15	120.9
H4A—C4—H4B	107.4	C15—C16—N4	120.57 (19)
O5—C5—O4	123.87 (18)	C15—C16—H16	119.7
O5—C5—C4	120.28 (18)	N4—C16—H16	119.7
O4—C5—C4	115.85 (16)	C21—N5—C17	122.15 (18)
O6—C6—O7	125.52 (17)	C21—N5—H5	118.9
O6—C6—C1	116.25 (15)	C17—N5—H5	118.9
O7—C6—C1	118.22 (15)	C17—N6—H6A	120.0
C7—N1—H1A	120.0	C17—N6—H6B	120.0
C7—N1—H1B	120.0	H6A—N6—H6B	120.0
H1A—N1—H1B	120.0	N6—C17—N5	118.87 (17)
C7—N2—C11	123.42 (17)	N6—C17—C18	123.38 (17)
C7—N2—H2	117.2	N5—C17—C18	117.74 (18)
C11—N2—H2	119.4	C19—C18—C17	119.63 (19)
N1—C7—N2	119.41 (17)	C19—C18—H18	120.2
N1—C7—C8	123.51 (17)	C17—C18—H18	120.2
N2—C7—C8	117.08 (17)	C18—C19—C20	120.8 (2)
C9—C8—C7	119.94 (18)	C18—C19—H19	119.6
C9—C8—H8	120.0	C20—C19—H19	119.6
C7—C8—H8	120.0	C21—C20—C19	117.6 (2)
C8—C9—C10	120.79 (19)	C21—C20—H20	121.2
C8—C9—H9	119.6	C19—C20—H20	121.2
C10—C9—H9	119.6	N5—C21—C20	122.0 (2)
C11—C10—C9	118.1 (2)	N5—C21—H21	119.0
C11—C10—H10	120.9	C20—C21—H21	119.0
C9—C10—H10	120.9		
O1—C1—C2—C3	54.58 (19)	C7—C8—C9—C10	−1.4 (3)
C4—C1—C2—C3	172.25 (15)	C8—C9—C10—C11	0.9 (4)
C6—C1—C2—C3	−68.0 (2)	C7—N2—C11—C10	0.0 (3)
C1—C2—C3—O3	−22.8 (2)	C9—C10—C11—N2	−0.2 (4)
C1—C2—C3—O2	158.57 (16)	C16—N4—C12—N3	−178.41 (19)
O1—C1—C4—C5	−77.58 (19)	C16—N4—C12—C13	1.4 (3)
C2—C1—C4—C5	163.99 (15)	N3—C12—C13—C14	178.4 (2)
C6—C1—C4—C5	42.8 (2)	N4—C12—C13—C14	−1.3 (3)
C1—C4—C5—O5	75.6 (2)	C12—C13—C14—C15	0.3 (3)
C1—C4—C5—O4	−104.5 (2)	C13—C14—C15—C16	0.8 (4)
O1—C1—C6—O6	−167.93 (15)	C14—C15—C16—N4	−0.8 (3)
C2—C1—C6—O6	−46.2 (2)	C12—N4—C16—C15	−0.3 (3)
C4—C1—C6—O6	73.39 (19)	C21—N5—C17—N6	−179.5 (2)
O1—C1—C6—O7	13.2 (2)	C21—N5—C17—C18	1.6 (3)
C2—C1—C6—O7	135.00 (16)	N6—C17—C18—C19	179.3 (2)
C4—C1—C6—O7	−105.44 (17)	N5—C17—C18—C19	−1.8 (3)
C11—N2—C7—N1	178.85 (19)	C17—C18—C19—C20	0.0 (4)
C11—N2—C7—C8	−0.5 (3)	C18—C19—C20—C21	2.0 (4)
N1—C7—C8—C9	−178.14 (19)	C17—N5—C21—C20	0.5 (4)
N2—C7—C8—C9	1.2 (3)	C19—C20—C21—N5	−2.3 (4)

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*O*⋯O3	0.91 (3)	1.84 (3)	2.681 (2)	152 (3)
N3—H3*A*⋯O3	0.86	2.07	2.905 (3)	164
N4—H4⋯O2	0.86	1.81	2.666 (2)	175
N1—H1*B*⋯O6	0.86	2.07	2.893 (2)	161
N6—H6*B*⋯O7	0.86	2.09	2.928 (2)	164
N1—H1*A*⋯O7[i]	0.86	2.12	2.948 (2)	162
N2—H2⋯O1[i]	0.86	2.00	2.760 (2)	144
N2—H2⋯O7[i]	0.86	2.55	3.304 (2)	144
C9—H9⋯O6[ii]	0.93	2.60	3.372 (3)	141
C10—H10⋯O2[ii]	0.93	2.51	3.419 (3)	167
C11—H11⋯O2[iii]	0.93	2.41	3.294 (3)	160
N3—H3*B*⋯O4[iv]	0.86	2.09	2.851 (2)	146
C13—H13⋯O6[iv]	0.93	2.40	3.301 (3)	163
N5—H5⋯O4[i]	0.86	1.77	2.591 (2)	160
N6—H6*A*⋯O5[i]	0.86	2.07	2.916 (3)	169
C20—H20⋯O7[v]	0.93	2.60	3.463 (3)	155
C21—H21⋯O3[v]	0.93	2.43	3.334 (3)	164

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