Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Lamellar aggregation and hydrogen-bonding motifs in 3-(aminocarbonyl)-pyridinium perchlorate and hydrogen oxalate

S. Athimoolam* and S. Natarajan

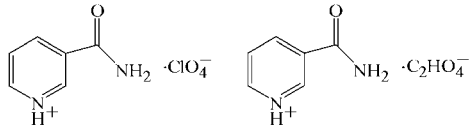
Department of Physics, Madurai Kamaraj University, Madurai 625 021, India
Correspondence e-mail: xrdsopmku@yahoo.com

Received 5 February 2007
Accepted 2 March 2007
Online 31 March 2007

In the title compounds, $C_6H_7N_2O^+\cdot ClO_4^-$, (I), and $C_6H_7N_2O^+\cdot C_2HO_4^-$, (II), the carboxamide plane is twisted from the plane of the protonated pyridine ring. Lamellar or sheet-like structural features are observed through N—H···O and O—H···O hydrogen-bonded motifs of cations and anions in (I) and (II), respectively. These sheets are aggregated through $C(4)$ and $C(5)$ chain motifs in (I) and (II), respectively. $R_1^2(4)$ ring motifs in (I) and $R_1^2(5)$ motifs in (II) are formed *via* pyridine–anion bifurcated N—H···O interactions. In (II), carboxamide groups form N—H···O dimers around the inversion centres of the unit cell, with $R_2^2(8)$ ring motifs. A 2_1 screw-related helical or ribbon-like structure along the *b* axis is formed in (II) through carboxamide and pyridinium N—H···O hydrogen bonds with the oxalate anions.

Comment

Intermolecular forces play an essential role in the formation of supramolecular organic systems. The phenomenon of hydrogen bonding has significance in the areas of molecular recognition, crystal-engineering research and organic synthons for supramolecular research (Desiraju, 1989). Carboxylic acids and amides are two commonly used functional groups in crystal engineering, because they generally form robust architectures *via* O—H···O and N—H···O hydrogen-bonded dimers. Thus, we are concerned with the biomolecular interactions, and preparation and X-ray analyses of crystalline complexes involving vitamins, and inorganic and organic acids (Athimoolam & Rajaram, 2005; Athimoolam & Natarajan, 2006*a*,*b*,*c*). The planar nicotinamide ligand is important since it has three potential sites for hydrogen-bonding interactions: (i) the pyridine N atom, (ii) the amine N atom and (iii) the carbonyl O atom. In addition, from the pharmacological viewpoint, nicotinamide is one of the two principal forms of the vitamin B complex. Nicotinamide, *via* its metabolites NAD (nicotinamide adenine dinucleotide) and NADP (nicotinamide adenine dinucleotide phosphate), is involved in a wide range of biological processes, including the production of energy, the synthesis of fatty acids, cholesterol and steroids, signal transduction, and maintenance of the integrity of the genome. It is also used in pharmacological doses as an antihyperlipidemic agent (Sampathkumar *et al.*, 2006). Complexes of nicotinamide with 3,5-dinitrosalicylate (Koman *et al.*, 2003) and nitrate (Gubin *et al.*, 1988) have already been reported. In addition, a few complexes of nicotinamide in the *iso* form have also been investigated (Aakeroy *et al.*, 2002), because of their relevance in the field of supramolecular reactions. To study the supramolecular geometry through hydrogen-bonding extension, nicotinamide was treated with perchloric acid [giving complex (I) with a tetrahedral anion] and oxalic acid [giving complex (II) with a planar anion]. Both complexes crystallize in the monoclinic centrosymmetric $P2_1/c$ space group.



(I) (II)

In both complexes, the asymmetric unit contains the protonated positively charged vitamin as a cation and the deprotonated negatively charged acid as an anion. As expected, the H atom from the inorganic/organic acid is transferred into the effective protonation site (pyridine N atom) of the nicotinamide in both complexes. Figs. 1 and 2 depict the molecular structures and displacement ellipsoid plots of complexes (I) and (II), respectively. Protonation on the N atom is confirmed by the C—N bond distances and C—N—C bond angle in both structures (Tables 1 and 3). From the Cambridge Structural Database (Version 5.27 of 2006; Allen, 2002), it is observed that protonation of the pyridine N atom leads to its going out of the ring and consequently to a slightly larger C—N—C bond angle (> 120°), which is also seen in the current structures. As a characteristic feature of the nicotinamide molecule, the twisting of the carboxamide group (–$CONH_2$) from the pyridine plane is observed in both structures. The twisting angles of the –$CONH_2$ plane from the

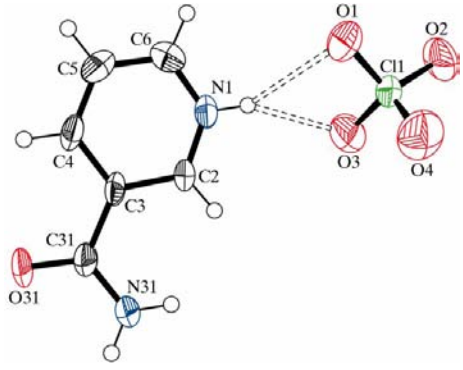


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

 DOI: 10.1107/S0108270107010098

pyridine ring plane are 7.4 (2) and 6.3 (1)° for (I) and (II), respectively. The deviation of the amide N atom from the pyridine ring plane is slightly larger [0.196 (1) and 0.193 (3) Å] than that of the O atom [0.071 (2) and 0.050 (3) Å] in the carboxamide unit in both structures, which can be correlated with the hydrogen-bonding interaction of the amide group.

The packing diagrams of the two complexes are given in Figs. 3 and 4. Similar to most of the crystal structures of planar vitamins and their complexes solved in our laboratory (Athimoolam & Rajaram, 2005; Athimoolam & Natarajan, 2006*a*,*b*,*c*), both structures can be described in terms of planar or lamellar features. In structure (I), the 3-(aminocarbonyl)-pyrdinium cations are connected through N—H···O hydrogen bonds involving the carboxamide groups (Table 2), forming slabs or lamellar sheets stacked almost parallel to the ($\bar{4}04$) and ($40\bar{4}$) planes of the unit cell. As a result, during the X-ray intensity data collection, the ($\bar{2}02$) and ($20\bar{2}$) parallel planes gave strong reflections. These slabs or sheets are separated by a distance of 3.524 (2) Å and subtend an angle of 37.9 (2)° to the *ab* plane of the unit cell. According to the nomenclature suggested by Etter *et al.* (1990), this molecular aggregation is described by a *C*(4) motif forming an infinite chain, which runs along the *b* axis of the unit cell (Fig. 5). Similarly, in structure (II), the oxalate anions are connected through O—H···O hydrogen-bond motifs (Table 4), forming a lamellar structure or anionic slabs separated by a distance of 3.142 (3) Å and subtending an angle of 2.9 (2)° to the *ac* plane of the unit cell. These anionic slabs are almost parallel to the (040) and ($0\bar{4}0$) planes of the unit cell, causing the (020) and ($0\bar{2}0$) reflections to have strong X-ray intensities, as in structure (I). These O—H···O hydrogen bonds involving the

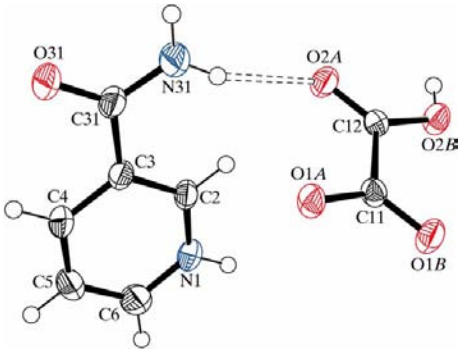


Figure 2
The molecular structure of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

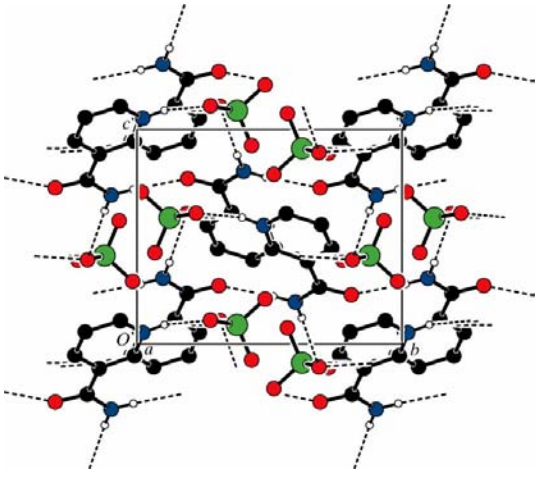


Figure 3
The packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

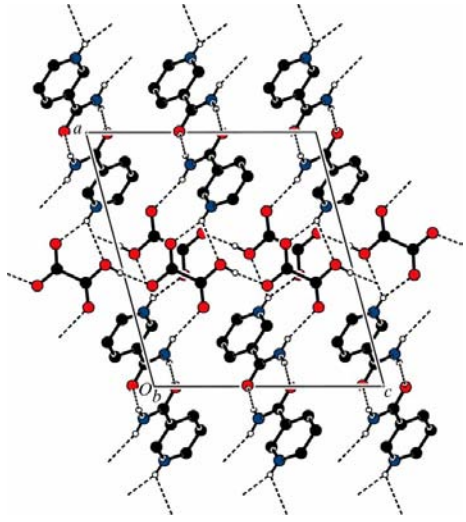


Figure 4
The packing of (II), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

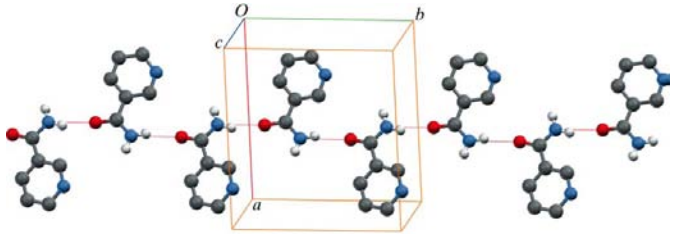


Figure 5
Lamellar sheets formed by the 3-(aminocarbonyl)pyridinium cation in (I) through the *C*(4) motif. Hydrogen bonds are shown as dashed lines.

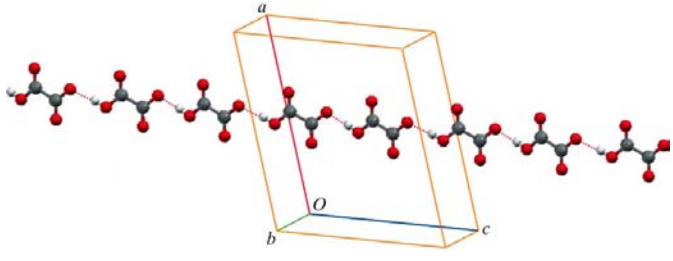


Figure 6
Slabs of oxalate anions in (II), formed through *C*(5) motifs of O—H···O hydrogen bonds. Hydrogen bonds are shown as dashed lines.

dicarboxylic acid units form a $C(5)$ graph-set motif extending infinitely along the c axis of the unit cell (Fig. 6).

In both structures, the N atom of the pyridine ring forms a bifurcated hydrogen bond with the O atoms of the anions, leading to $R_1^2(4)$ and $R_1^2(5)$ graph-set motifs in (I) and (II), respectively. The perchlorate anions in (I) are sandwiched between the slabs of cations and form a closed hydrogen-bonding network [$R_3^2(12)$ motif]. In structure (II), the carboxamide groups form inversion-related closed dimers through N—H···O hydrogen bonds around the inversion centres of the unit cell with an $R_2^2(8)$ graph-set motif (Fig. 7). This is similar to the carboxyl group dimerization in many organic compound assemblies. A helical or ribbon structure is observed in (II), formed through the carboxamide and pyridinium N—H···O hydrogen bonds with the oxalate anions. The 2_1 screw-related ribbon structure is extended along the b axis of the unit cell (Fig. 8).

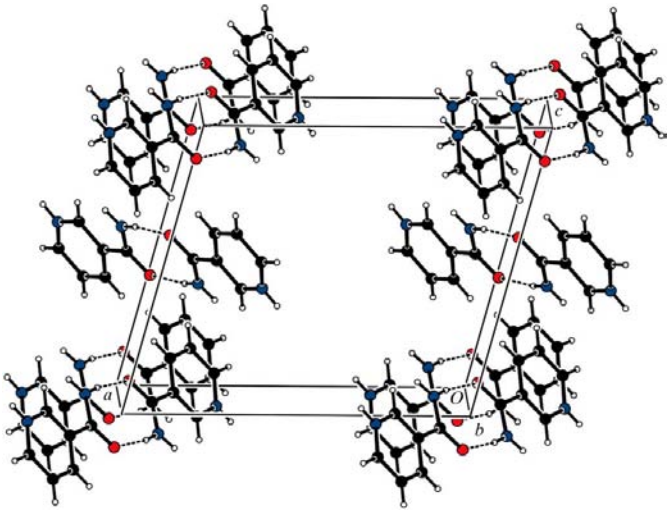


Figure 7
Inversion-related dimers of carboxamide units, with the $R_2^2(8)$ graph-set motif, around inversion centres of the unit cell in (II). Hydrogen bonds are shown as dashed lines.

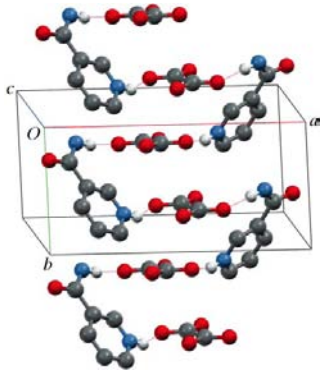


Figure 8
The ribbon-like structure of (II), formed through pyridine/carboxamide N—H···O bonds, with the oxalate anion extending along the b axis. Hydrogen bonds are shown as dashed lines.

Experimental

Compounds (I) and (II) were crystallized from aqueous mixtures of nicotinamide with perchloric acid and oxalic acid, respectively, in the stoichiometric ratio 1:1 in each case, at room temperature by slow evaporation.

Compound (I)

Crystal data

$C_6H_7N_2O^+\cdot ClO_4^-$
M_r = 222.59
Monoclinic, $P2_1/c$
a = 11.273 (5) Å
b = 9.858 (4) Å
c = 8.077 (5) Å
β = 99.43 (3)°
V = 885.5 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.43 mm^{-1}
T = 293 (2) K
0.21 × 0.17 × 0.15 mm

Data collection

Nonius MACH3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.929, T_{max} = 0.946
1895 measured reflections
1562 independent reflections
1038 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.220
S = 1.04
1562 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C2	1.319 (6)	C31—O31	1.224 (5)
N1—C6	1.324 (7)	C31—N31	1.304 (7)
C2—N1—C6	125.2 (4)		
C4—C3—C31—O31	5.0 (8)	C2—C3—C31—N31	8.3 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.39	3.058 (6)	135
N1—H1···O3	0.86	2.16	2.971 (6)	156
N31—H31A···O3^{i}	0.86	2.29	3.138 (7)	170
N31—H31B···O31^{ii}	0.86	2.09	2.927 (6)	165

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

Compound (II)

Crystal data

$C_6H_7N_2O^+\cdot C_2HO_4^-$
M_r = 212.16
Monoclinic, $P2_1/c$
a = 12.8295 (7) Å
b = 6.3148 (5) Å
c = 11.1883 (9) Å
β = 104.950 (12)°
V = 875.75 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 293 (2) K
0.22 × 0.19 × 0.14 mm

Data collection

Nonius MACH3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.962, T_{max} = 0.983
2383 measured reflections
1916 independent reflections
1457 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.109
S = 1.06
1916 reflections
137 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

O1*A*—C11	1.2535 (17)	N1—C2	1.331 (2)
O1*B*—C11	1.2380 (18)	N1—C6	1.332 (2)
C12—O2*A*	1.2142 (18)	C31—O31	1.2299 (18)
C12—O2*B*	1.2938 (17)	C31—N31	1.323 (2)
C2—N1—C6	123.05 (14)		
C4—C3—C31—O31	−6.8 (2)	C2—C3—C31—N31	−5.7 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*B*—H2*B*···O1*A*^{i}	0.82	1.72	2.531 (2)	172
N1—H1···O1*B*^{ii}	0.86	1.90	2.681 (2)	149
N31—H31*A*···O31^{iii}	0.86	2.10	2.953 (2)	172
N31—H31*B*···O2*A*	0.86	2.18	3.018 (2)	163

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

All H atoms were positioned geometrically and refined using a riding model [C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å, and U_{iso}(H) = 1.2–1.5U_{eq}(parent atom)].

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *ORTEP-3* (Farrugia, 1997), *MERCURY* (Version 1.4.1; Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

The authors thank the Department of Science and Technology, Government of India, for establishing the single-crystal diffractometer facility at the School of Physics, Madurai Kamaraj University, through the FIST programme. The authors also thank the UGC for a SAP programme.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3074). Services for accessing these data are described at the back of the journal.

References

Aakeroy, C. B., Beatty, A. M. & Helfrich, B. A. (2002). *J. Am. Chem. Soc.* **124**, 14425–14432.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Athimoolam, S. & Natarajan, S. (2006*a*). *Acta Cryst.* C**62**, o612–o617.
Athimoolam, S. & Natarajan, S. (2006*b*). *Acta Cryst.* E**62**, o4027–o4029.
Athimoolam, S. & Natarajan, S. (2006*c*). *Acta Cryst.* E**62**, o4219–o4221.
Athimoolam, S. & Rajaram, R. K. (2005). *Acta Cryst.* E**61**, o2764–o2767.
Bruker (2000). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*. Amsterdam: Elsevier.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gubin, A. I., Nurakhmetov, N. N., Buranbaev, M. Zh. & Mul'kina, R. I. (1988). *Kristallografiya* (*Russ.*) (*Crystallogr. Rep.*), **33**, 504–507.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Koman, M., Martiška, L., Valigura, D. & Glowiak, T. (2003). *Acta Cryst.* E**59**, o441–o442.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sampathkumar, K., Selvam, M., Sooraj, Y. S., Gowthaman, S. & Ajeshkumar, R. N. P. (2006). *Int. Urol. Nephrol.* **38**, 171–174.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.