

Hydrogen-bonded networks in 5-chloropyridin-2-amine–fumaric acid (2/1) and 2-aminopyridinium DL-malate

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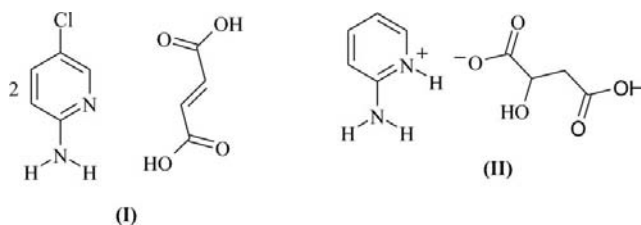
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Crystals of 5-chloropyridin-2-amine–(2*E*)-but-2-enedioate (2/1), $2C_5H_5ClN_2 \cdot C_4H_4O_4$, (I), and 2-aminopyridinium DL-3-carboxy-2-hydroxypropanoate, $C_5H_7N_2^+ \cdot C_4H_5O_5^-$, (II), are built from the neutral 5-chloropyridin-2-amine molecule and fumaric acid in the case of (I) and from ring-N-protonated 2-aminopyridinium cations and malate anions in (II). The fumaric acid molecule lies on an inversion centre. In (I), the neutral 5-chloropyridin-2-amine and fumaric acid molecules interact *via* hydrogen bonds, forming two-dimensional layers parallel to the (100) plane, whereas in (II), oppositely charged units interact *via* ionic and hydrogen bonds, forming a three-dimensional network.

Comment

As a continuation of our studies of hybrid crystals with acid–base ionic and hydrogen-bonding interactions whose utility has been described previously (Janczak & Perpétuo, 2002, 2003, 2009*a,b*; Marchewka *et al.*, 2003; Perpétuo & Janczak, 2003, 2006), in the present work we investigate the crystal structures of the 5-chloropyridin-2-amine–fumaric acid (2/1) adduct, (I), and 2-aminopyridinium DL-malate, (II).



The asymmetric unit of (I) consists of a neutral 5-chloropyridin-2-amine molecule and half of a centrosymmetric molecule of fumaric acid (Fig. 1*a*). Proton transfer does not take place from the fumaric acid to the ring N atom of

5-chloropyridin-2-amine, and the internal C2–N1–C6 angle [119.69 (13)°] is comparable with that in the neutral 5-chloropyridin-2-amine molecule [118.3 (1)°; Kvik & Backéus, 1974; Kvik *et al.*, 1976] and is in agreement with the valence shell electron pair repulsion model (VSEPR; Gillespie, 1992). The slightly increased C2–N1–C6 angle results from the relatively strong hydrogen bond diminishing the steric effect of the lone pair of electrons. The C–O bonds in the molecule of fumaric acid [C7–O1 = 1.3008 (18) Å and C7–O2 = 1.2220 (18) Å] are comparable with those found for pure fumaric acid (Bednowitz & Post, 1966) and in the adduct picoline *N*-oxide–fumaric acid (Gorres *et al.*, 1975), and with those observed in adducts with polyamines (Bowes *et al.*, 2003). The fumaric acid interacts with two neighbouring 5-chloropyridin-2-amine molecules *via* pairs of almost linear N–H···O and O–H···N hydrogen bonds (Table 1), which produce a binary graph set motif of $R_2^2(8)$ (Bernstein *et al.*, 1995), forming planar $(C_5H_5ClN_2) \cdot (C_4H_4O_4) \cdot (C_5H_5ClN_2)$ aggregates. Two such planar aggregates related by a *c*-glide plane are inclined by 76.08 (7)° with respect to each other [the dihedral angle is between the pyridine ring at (x, y, z) and that at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$]. These structural units, translated along the *c* axis, are linked *via* another N–H···O hydrogen bond between the amine group and atom O1 of fumaric acid,

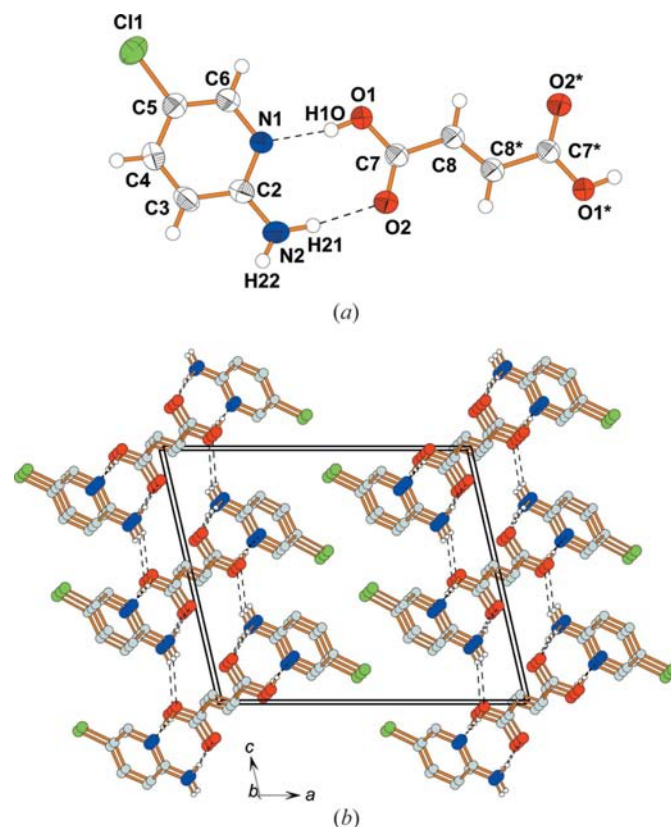


Figure 1
(*a*) The molecular structure of (I), showing the atom-labelling scheme [symmetry code: (*) $-x, 1 - y, -z$]. Displacement ellipsoids are shown at the 50% probability level and H atoms as spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. (*b*) The packing in (I), showing N–H···O and O–H···N hydrogen-bonded layers extending parallel to (100). H atoms bonded to C atoms have been omitted for clarity.

developing two-dimensional layers extending parallel to the (100) plane. The planar aggregates are stacked along the *b* axis (Fig. 1*b*).

The asymmetric unit of (II) consists of a protonated 2-aminopyridinium cation and a single deprotonated malate anion, linked by a pair of N—H···O hydrogen bonds which produces a binary graph set motif of $R_2^2(9)$ (Fig. 2*a*). The proton transfer from the carboxyl group to the ring N atom of 2-aminopyridine is manifested in the delocalization of the charge over both C—O bonds of the COO[−] group as well as in an increased internal C5—N1—C9 angle [124.0 (2)°] compared with that in neutral 2-aminopyridine [117.5 (3)°; Chao *et al.*, 1975]. The opening of the internal C—N—C angle results from a decrease of the steric effect of the lone pair of electrons and is consistent with the VSEPR model (Gillespie, 1992). The conformation of the carbon skeleton of the malate anion in (II) is *syn* [$\Psi = 173.68$ (18)°], with the carboxylate group (COO[−]) almost coplanar with atoms C2 and O5 [$\varphi_2 = -24.0$ (3)°]. The conformation of the carboxyl group (COOH) around the terminal C—C bond is clinal [$\chi = -55.4$ (3)°]. The Ψ , φ_2 and χ torsion angles in (II) ($\Psi = \text{C1—C2—C3—C4}$, $\varphi_2 = \text{O1—C1—C2—O5}$ and $\chi = \text{C2—C3—C4—O3}$) describe the conformation of the malate monoanion as well as the conformation of malic acid (van der Sluis & Kroon, 1985, 1989). In optimized malate the values of Ψ , φ_2 and χ are -177.8 , -3.9 and 61.7° , respectively, and thus the conformation of the carbon skeleton of optimized malate is *anti* (Janczak & Perpétuo, 2003). The optimized value of φ_2 is smaller than in (II) due to the presence in the optimized structure of an intramolecular O5—H5O···O1 hydrogen bond (O5—H5O = 0.95 Å, H5O···O1 = 1.87 Å and O5—H5O···O1 = 126°). In (II), malate anions related by translation along the *a* axis interact *via* O3—H3O···O1ⁱⁱ hydrogen bonds (symmetry code as in Table 2) between the carboxyl group (COOH) and the carboxylate group (COO[−]) of the neighbour to form chains along the *a* axis which can be described by the graph set motif of $C(7)$. These chains are interconnected by O5—H5O···O2ⁱ and symmetry-equivalent hydrogen bonds (Table 2) between the hydroxy groups and one O atom of the carboxylate groups (COO[−]), forming two-dimensional sheets extending parallel to (001) at $z = \frac{1}{4}$ and $\frac{3}{4}$ (Fig. 2*b*). Within the sheet, the malate anions are interconnected by two types of O—H···O hydrogen bonds: one type runs in the [100] direction to form the $C(7)$ chains described above, while the other type runs parallel to [010] and generates chains of anions with a graph set motif of $C(5)$. These chains intersect to yield a hydrogen-bonded tetramer within which the $R_4^4(22)$ motif can be discerned. Propagation by translation forms the two-dimensional layer (Fig. 2*c*). The 2-aminopyridinium cations are perpendicular to the anionic sheets and interact *via* N—H···O hydrogen bonds forming a three-dimensional network (Fig. 2*b*). The 2-aminopyridinium cation at (*x*, *y*, *z*) is related by inversion to that at (1 − *x*, 1 − *y*, −*z*) and to another at (1 − *x*, 2 − *y*, −*z*), with interplanar distances of 3.4010 (11) and 3.3999 (11) Å, and slip distances of 1.801 and 3.504 Å, respectively. The former involves a stabilizing π — π interaction between the rings

(Janiak, 2000; Hunter *et al.*, 2001). In the second interaction, the rings do not overlap, but the 2-amino group of each cation is parallel to and eclipsed with the ring of the other.

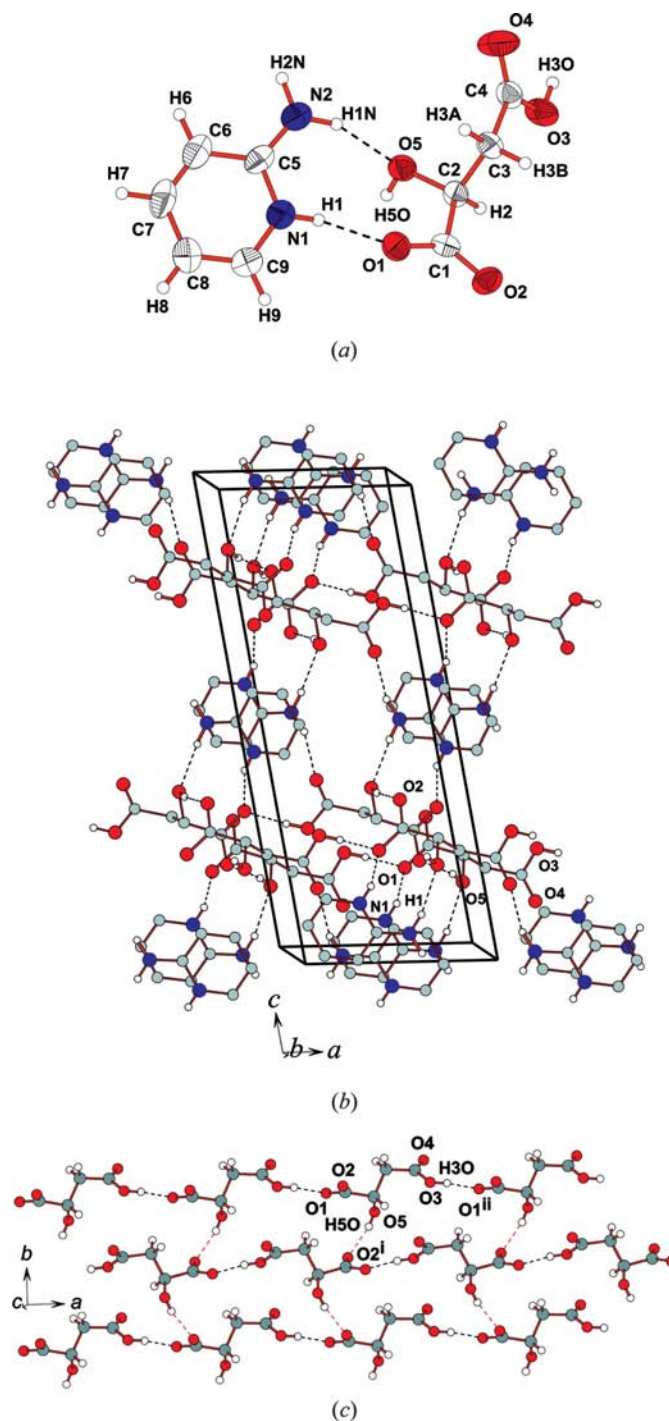


Figure 2
(*a*) The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms as spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. (*b*) A view of the hydrogen-bonded three-dimensional network in (II). H atoms bonded to C atoms have been omitted for clarity. (*c*) The O—H···O hydrogen-bonded two-dimensional layer of malate anions, showing the binary graph set motif $R_4^4(22)$. [Symmetry codes: (i) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 + x, y, z$.]

This work illustrates the utility of 2-aminopyridine and its 5-chloro derivative for the formation of two- or three-dimensional hydrogen-bonded networks formed with cocrystallization partners, *i.e.* fumaric or DL-malic acid. A search of the Cambridge Structural Database (Version 5.31 of November 2009; Allen, 2002) for structures containing 2-aminopyridine cocrystallized with anionic partners gives over 70 structures with a large number of inorganic and organic anions, but for 5-chloropyridin-2-amine yields only ten structures. Generally, the dimensionality of the networks in these crystals is determined by the conformation of the cocrystallization partners.

Experimental

Suitable crystals of (I) and (II) were obtained by slow evaporation of solutions of 5-chloropyridin-2-amine in 5% fumaric acid and of 2-aminopyridine in 5% DL-malic acid.

Compound (I)

Crystal data

$2C_5H_5ClN_2 \cdot C_4H_4O_4$	$V = 798.1 (3) \text{ \AA}^3$
$M_r = 373.24$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.806 (3) \text{ \AA}$	$\mu = 0.44 \text{ mm}^{-1}$
$b = 5.066 (1) \text{ \AA}$	$T = 295 \text{ K}$
$c = 11.705 (2) \text{ \AA}$	$0.38 \times 0.27 \times 0.18 \text{ mm}$
$\beta = 102.87 (3)^\circ$	

Data collection

Kuma KM-4 diffractometer with an area CCD detector	8665 measured reflections
Absorption correction: numerical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	2063 independent reflections
$T_{\min} = 0.855$, $T_{\max} = 0.928$	1651 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.009$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.117$	
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
2063 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
119 parameters	

Compound (II)

Crystal data

$C_5H_7N_2^+ \cdot C_4H_5O_5^-$	$V = 1068.2 (4) \text{ \AA}^3$
$M_r = 228.21$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.6190 (15) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 7.4730 (15) \text{ \AA}$	$T = 295 \text{ K}$
$c = 19.042 (4) \text{ \AA}$	$0.35 \times 0.26 \times 0.21 \text{ mm}$
$\beta = 99.85 (3)^\circ$	

Data collection

Kuma KM-4 diffractometer with an area CCD detector	13230 measured reflections
Absorption correction: numerical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	2730 independent reflections
$T_{\min} = 0.962$, $T_{\max} = 0.974$	1436 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.055$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H1O \cdots N1	0.83 (1)	1.80 (1)	2.6136 (16)	168 (2)
N2–H21 \cdots O2	0.95 (2)	1.94 (2)	2.880 (2)	172.1 (19)
N2–H22 \cdots O1 ⁱ	0.82 (2)	2.36 (2)	3.146 (2)	162 (2)

Symmetry code: (i) $x, -y - \frac{1}{2}, z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5–H5O \cdots O2 ⁱ	0.82 (2)	1.89 (2)	2.699 (2)	167 (2)
O3–H3O \cdots O1 ⁱⁱ	0.86 (2)	1.72 (2)	2.581 (2)	172 (3)
N1–H1 \cdots O1	0.91 (2)	1.85 (2)	2.706 (2)	156 (2)
N2–H1N \cdots O5	0.93 (2)	2.06 (1)	2.911 (2)	152 (2)
N2–H2N \cdots O4 ⁱⁱⁱ	0.93 (2)	1.95 (1)	2.845 (3)	161 (2)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.084$	
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
2730 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
160 parameters	

H atoms involved in hydrogen bonds in both structures were located in difference Fourier maps and refined with independent positional parameters but with distance restraints applied to O1–H1O in (I) [0.83 (1) \AA] and to N2–H1N and N2–H2N in (II) [0.93 (2) \AA]. H atoms bonded to C atoms in both structures were placed at calculated positions and refined as riding, with C–H = 0.93 \AA in (I), and C2–H2 = 0.98 \AA , C3–H = 0.97 \AA and pyridinium C–H = 0.93 \AA in (II). $U_{\text{iso}}(\text{H})$ values for all H atoms in both structures were constrained to xU_{eq} of their respective carrier atoms, with $x = 1.2$ for all H atoms in (I), and with $x = 1.2$ for pyridinium ring H atoms and $x = 1.5$ for all other H atoms in (II).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3217). Services for accessing these data are described at the back of the journal.

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