

2-Hydroxy-3-(4,5,6,7-tetrahydro-1*H*-imidazo[4,5-*c*]pyridin-5-ium-4-yl)-benzoate monohydrate

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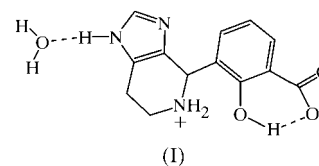
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The title molecule, C₁₃H₁₃N₃O₃·H₂O, is in the form of a monohydrated zwitterion. The tetrahydropyridinium ring adopts an envelope conformation and is nearly coplanar with the plane of the imidazoline ring. The water solvate molecule plays an important role as a bridge between zwitterions, forming molecular chains running along the *c* direction, which are interconnected by N—H···O hydrogen bonds into molecular ribbons. The crystal packing is further stabilized by another N—H···O and one O—H···N hydrogen bond, which interconnect the molecular ribbons.

Comment

Several approaches to the synthesis of discrete polynuclear complexes have been proposed. One involves compartmental organic ligands, which are able to hold one or more metal ions (Tuna *et al.*, 1999). The development of new bridging binuclear ligands is aimed at promoting efficient magnetic interactions between coordinated paramagnetic transition metal ions in metal complexes with varying *dⁿ* configurations. Complexes containing two or more adjacent metal centres offer an added chemical dimension over those containing a single metal centre. The metal centres not only act independently but can also act in a co-operative manner, leading to chemistry that differs appreciably from that displayed by their single metal-centre counterparts. The Schiff bases derived from 3-formylsalicylic acid and 2,6-diformyl-4-methylphenol can act as bridging binuclear ligands (Tanaka *et al.*, 1974). We have initiated (Nayar & Kurup, 2002) the synthesis of binuclear ligands derived from 3-formylsalicylic acid, which are useful for the preparation of hetero- and homo-binuclear complexes. The crystal structure determination of the title compound, 2-hydroxy-3-(4,5,6,7-tetrahydro-1*H*-imidazo[4,5-*c*]pyridin-5-

ium-4-yl)benzoate monohydrate, (I), was undertaken with a view to obtaining a clear understanding of the coordination geometry of this potential ligand.



Compound (I) is a monohydrated zwitterion, in which the positive and negative charges are localized on tetrahydropyridinium atom N3 and benzoate atom O1, respectively (Fig. 1). This is also confirmed by the geometric parameters (Table 1) and the unambiguous location and refinement of all H atoms in the structure. All bond lengths and angles have normal values (Allen *et al.*, 1987).

The zwitterion is composed of three rings, *viz.* the tetrahydropyridinium ring (C7/C8/C10–C12/N3), the imidazoline ring (C8–C10/N1/N2) and the benzoate aromatic ring (C1–C6). The tetrahydropyridinium ring adopts an envelop conformation, with atom C12 displaced by 0.279 (3) Å from the C7/C8/C10/C11/N3 plane. This plane is nearly coplanar with the plane of the imidazoline ring [dihedral angle 5.5 (1)°]. The dihedral angle between the mean plane of the tetrahydropyridinium and benzoate aromatic rings is 56.4 (1)°. The plane of the carboxylate group (O1/O2/C13/C1) is slightly twisted about the C–C bond with respect to its aromatic ring, by 14.0 (1)°. This relatively small twist angle is due to atom O1 being hydrogen bonded to the hydroxy group (O3–H103···O1), forming a six-membered O1–C13–C1–C6–O3–H103 ring (details are given in Table 2).

Within the asymmetric unit (Fig. 1), the water molecule is linked to the zwitterion and acts as a hydrogen-bond acceptor *via* an N2–H2···O1*W* hydrogen bond. In the crystal packing, the water molecule acts as a hydrogen-bond donor to the zwitterion *via* an O1*W*–H1*W*1···O2ⁱⁱⁱ hydrogen bond [symmetry code: (iii) *x*, *y*, 1 + *z*]. Therefore, the water molecule acts as a bridge between the zwitterions; in this manner, a C₂(12) chain (Bernstein *et al.*, 1995) is generated running along the *c* direction. Both N⁺–H bonds also play important roles in the

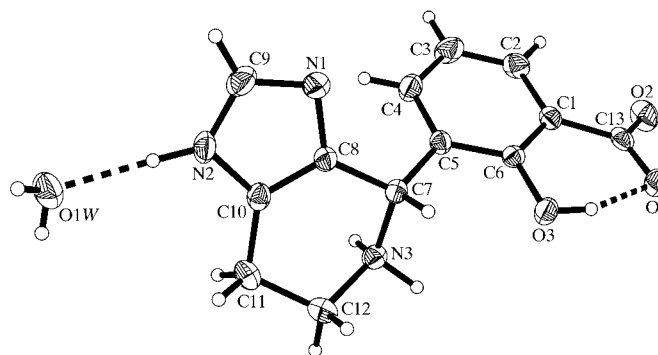


Figure 1

The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The dashed lines denote the intramolecular O—H···O and intermolecular N—H···O hydrogen bonds.

crystal packing; N3—H3B forms an N3—H3B···O2ⁱⁱ hydrogen bond to carboxylate atom O2 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, interconnecting two adjacent molecular chains into ribbons. The ribbons, as shown in Fig. 2, are comprised of $R_2^2(16)$ and $R_6^6(24)$ ring patterns of hydrogen bonds which are centered at $(n, \frac{1}{2}, \frac{1}{2} + n)$ and $(n, \frac{1}{2}, n)$, respectively ($n = \text{zero or integer}$). The ribbons are stacked one above the other along the b direction (Fig. 3) and are interconnected by two hydrogen bonds, *viz.* N3—H3A···O1ⁱ, formed from another N⁺—H bond of the zwitterion to carboxylate atom O1 at $(2 - x, 1 - y, 1 - z)$, and O1W—H2W1···N1^{iv}, formed from the water molecule to imidazoline atom N1 of the zwitterion at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$.

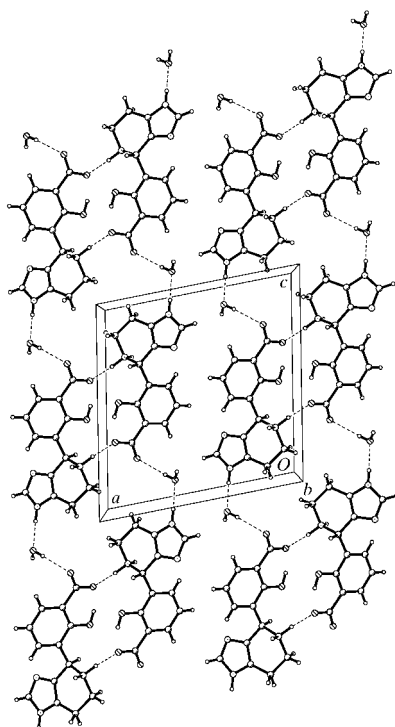


Figure 2
The packing of (I), viewed down the b axis, showing the molecular ribbons running along the c direction. The dashed lines denote the intermolecular hydrogen bonds.

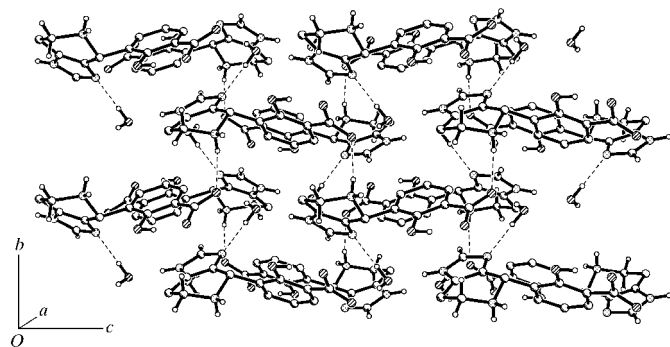


Figure 3
The packing of (I), viewed down the a axis, showing the two-dimensional molecular network along the b direction. The dashed lines denote the intermolecular N—H···O and O—H···N hydrogen bonds.

In the packing, across the center of symmetry, the C··· π distance for the C11—H11B··· π_{benzoate} contact is 3.776 (2) Å, while the distance between the centroids of the imidazoline and benzoate aromatic rings is 3.882 (4) Å. These rather long distances indicate that the C—H··· π and aromatic π — π interactions are weak.

Compound (I) crystallizes in a centrosymmetric space group and while Fig. 1 shows the enantiomorph of the zwitterion having an S chiral centre at C7, there are of course an equal number of molecules in the crystal with C7 having R chirality; there is clearly no implication that the condensation reaction of the achiral 3-formylsalicylic acid and histamine base gives rise to a chiral molecule.

Experimental

3-Formylsalicylic acid (H_2fsa) was prepared according to Duff & Bills (1932). The Schiff base was obtained by mixing H_2fsa (0.332 g, 2 mmol) and histamine base (0.223 g, 2 mmol) in absolute ethanol and refluxing the resulting solution for 1 h under a nitrogen atmosphere (Andruh *et al.*, 1993; Simmons *et al.*, 1980), producing a yellow solution. After 3 d, yellow crystals were collected from the reaction mixture by filtration and dried. Single crystals of (I) suitable for X-ray diffraction analysis were grown by slow evaporation from water over a period of a few weeks at room temperature.

Crystal data

$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3 \cdot \text{H}_2\text{O}$
 $M_r = 277.28$
Monoclinic, $P2_1/c$
 $a = 12.4975$ (13) Å
 $b = 7.7837$ (8) Å
 $c = 13.1320$ (14) Å
 $\beta = 100.402$ (2)°
 $V = 1256.4$ (2) Å³
 $Z = 4$

$D_x = 1.466$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2247 reflections
 $\theta = 3.1$ – 28.3 °
 $\mu = 0.11$ mm⁻¹
 $T = 293$ (2) K
Block, colorless
 $0.46 \times 0.20 \times 0.12$ mm

Data collection

Siemens SMART CCD area-detector
 ω scans
Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.890$, $T_{\text{max}} = 0.987$
7773 measured reflections

3103 independent reflections
2079 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 28.3$ °
 $h = -13 \rightarrow 16$
 $k = -10 \rightarrow 10$
 $l = -17 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.157$
 $S = 1.06$
3103 reflections
241 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 0.2851P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Selected interatomic distances (Å).

O1—C13	1.273 (3)	N2—C10	1.366 (3)
O2—C13	1.250 (3)	N3—C12	1.501 (3)
O3—C6	1.353 (2)	N3—C7	1.520 (3)
N1—C9	1.319 (3)	C10—C11	1.488 (3)
N1—C8	1.387 (3)	C11—C12	1.521 (3)
N2—C9	1.339 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2A...O1W	0.92 (3)	1.87 (3)	2.783 (3)	178 (2)
N3—H3A...O1 ⁱ	1.02 (3)	1.71 (3)	2.720 (2)	174 (2)
N3—H3B...O2 ⁱⁱ	0.89 (2)	2.02 (2)	2.864 (2)	159 (2)
O1W—H1W1...O2 ⁱⁱⁱ	0.76 (4)	2.14 (4)	2.897 (3)	171 (3)
O1W—H2W1...N1 ^{iv}	0.89 (3)	1.96 (3)	2.844 (3)	170 (4)
O3—H103...O1	0.90 (3)	1.64 (3)	2.513 (2)	161 (3)
C12—H12A...O1 ^{iv}	0.98 (3)	2.48 (3)	3.325 (3)	145 (2)
C12—H12B...O3 ^v	0.96 (2)	2.51 (2)	3.447 (3)	166 (2)

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

All H atoms were located in difference Fourier maps and were refined isotropically. The C—H, N—H and O—H bond-length ranges are 0.90 (3)–1.01 (3), 0.89 (3)–1.01 (3) and 0.76 (4)–0.90 (3) Å, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1090). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Andruh, M., Ramade, I., Godjovi, E., Guillou, O., Kahn, O. & Trombe, J. C. (1993). *J. Am. Chem. Soc.* **115**, 1822–1829.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Duff, J. C. & Bills, E. J. (1932). *J. Chem. Soc.* p. 1987.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Nayar, C. R. & Kurup, M. R. P. (2002). SIF Users' Symposium, Synthesis and Characterization of Binuclear Zinc(II) Complexes, Indian Institute of Science, Bangalore, India, p. O-09.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINTE*. Siemens AXS Inc., Madison, Wisconsin, USA.
- Simmons, M. G., Merrill, C. L. & Wilson, L. T. (1980). *J. Chem. Soc. Dalton Trans.*, pp. 1827–1837.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Tanaka, M., Okawa, H., Tamura, T. & Kida, S. (1974). *Bull. Chem. Soc. Jpn.* **47**, 1669–1672.
- Tuna, F., Patron, L., Journaux, Y., Andruh, M., Plass, W. & Trombe, J.-C. (1999). *J. Chem. Soc. Dalton Trans.* pp. 539–545.