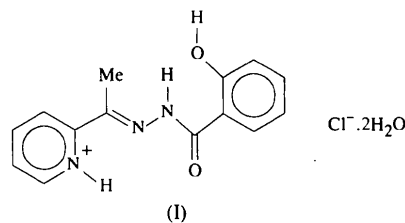


- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Subotkowski, W., K.-Subotkowska, L. & Shine, H. J. (1993). *J. Am. Chem. Soc.* **115**, 5073–5076.
- Suh, I. H., Kim, K. J., Choo, G. H., Lee, J. H., Choh, S. H. & Kim, M. J. (1993). *Acta Cryst.* **A49**, 369–371.



Acta Cryst. (1997). **C53**, 1322–1323

2-[1-(Salicyloylhydrazone)ethyl]pyridinium Chloride Dihydrate at 173 K

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Abstract

The approximately planar molecule of the title compound, C₁₄H₁₄N₃O₂⁺·Cl⁻·2H₂O, is in an *E* conformation with respect to the C=N bond, with a C—C=N—N torsion angle of 179.5(1)°. The maximum possible number of hydrogen bonds are formed in the crystal. The pyridinium H atom forms a hydrogen bond to a water molecule which is hydrogen bonded to the carbonyl O atom, requiring the pyridine ring to be rotated 180° compared to the unprotonated 2-formylpyridine analog. There is an intramolecular hydrogen bond involving the NH group on the chain and the hydroxyl O atom on the phenyl ring which, in turn, is hydrogen bonded to a Cl⁻ ion. Finally, a water molecule and chloride ion form a hydrogen-bonded square around a center of symmetry, with O···Cl distances of 3.199(2) and 3.206(2) Å, and endocyclic angles of 91.17(4) and 88.83(4)° at the O and Cl atoms, respectively.

Comment

Although Schiff base complexes of salicylaldehyde have been extensively studied, there are few reports utilizing the related salicyloylhydrazide. As part of a program which uses tridentate ligands to complex various metal ions, we synthesized 2-acetylpyridine salicyloylhydrazone. In the course of our studies, we isolated colorless crystals of the chloride salt dihydrate of the protonated ligand, (I). The structure was determined to establish the conformation of the protonated species for comparison with the related 2-formylpyridine salicyloylhydrazone reported by Domiano, Musatti, Pelizzi & Predieri (1974) (henceforth DMPP).

The cation shown in Fig. 1 can be viewed as an approximately planar molecule consisting of three planar segments: the pyridine ring, the hydroxybenzene ring and the hydrazone link between the two rings. Relative to the plane of the pyridine ring (N1, C1–C5), the remaining atoms, with the exception of C6', all lie on one side. The deviations include a twist of 4.03(8)° of the chain C6=N2–N3–C7(=O1)—C8, with respect to the pyridine ring. The chain is also twisted by 1.75(9)° relative to the benzene ring (C8–C13). The twists and distortions in our protonated form are all slightly less than in the unprotonated form reported by DMPP. The hydrogen bonding shown in Fig. 2,

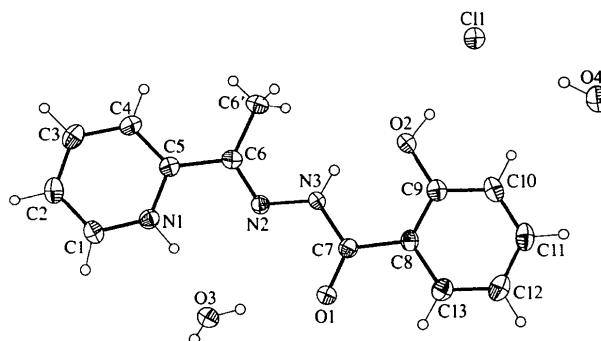


Fig. 1. The molecular structure of (I) with 50% probability ellipsoids and the atom-numbering scheme.

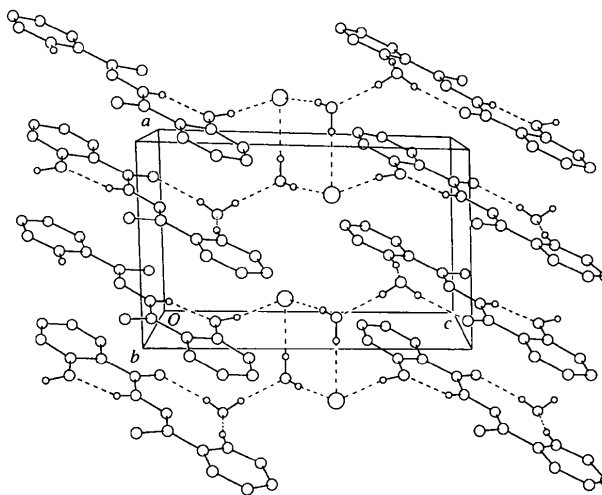


Fig. 2. View of the packing of (I) in the *ab* plane.

involving a water molecule, N—H1' and O1, is probably the main factor in the increased planarity of the cation relative to the formyl derivative of DMPP.

Another unusual feature of the structure is an almost square Cl—H₂O grouping about a center of symmetry. The water forms two O—H...Cl hydrogen bonds to the two Cl⁻ ions. Angles Cl1...O4...Cl1ⁱⁱ and O4...Cl1...O4ⁱⁱ are very close to 90° at 91.17(4) and 88.83(4)°, respectively [symmetry code: (ii) $-x, 2-y, 1-z$]. There is an O3—H3B...O4 hydrogen bond which links the Cl—H₂O grouping to the cation. The result of the hydrogen bonding is a double infinite chain of hydrogen-bonded molecules.

Experimental

Colorless crystals of (I) were obtained as one of the products from the reaction of antimony trioxide dissolved in concentrated HCl with 2-acetylpyridine and salicyloylhydrazide, a 1:1 molar ratio of Sb to ligand. The crystals were grown by slow evaporation of an aqueous ethanol (pH 1) solution.

Crystal data

C₁₄H₁₄N₃O₇·Cl⁻·2H₂O

$M_r = 327.76$

Triclinic

$P\bar{1}$

$a = 7.6381(2) \text{ \AA}$

$b = 8.0844(1) \text{ \AA}$

$c = 12.5955(4) \text{ \AA}$

$\alpha = 99.042(1)^\circ$

$\beta = 93.042(2)^\circ$

$\gamma = 92.225(2)^\circ$

$V = 766.14(3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.421 \text{ Mg m}^{-3}$

D_m not measured

Data collection

SMART platform diffractometer

ω scans

Absorption correction:

empirical (SHELXTL;

Sheldrick, 1995)

$T_{\min} = 0.848, T_{\max} = 0.973$

3874 measured reflections

Refinement

Refinement on F^2

$R(F) = 0.036$

$wR(F^2) = 0.108$

$S = 1.094$

2646 reflections

272 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.3882P]$

where $P = (F_o^2 + 2F_c^2)/3$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2788 reflections

$\theta = 1.64\text{--}26.34^\circ$

$\mu = 0.27 \text{ mm}^{-1}$

$T = 173(2) \text{ K}$

Needle

$0.23 \times 0.13 \times 0.10 \text{ mm}$

Colorless

2677 independent reflections

2377 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 26.34^\circ$

$h = -7 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -14 \rightarrow 13$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Extinction correction:

SHELXTL

Extinction coefficient:

0.018(3)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters ($\text{\AA}, ^\circ$)

O1—C7	1.228(2)	C5—C6	1.479(2)
N2—C6	1.288(2)	C6—C6'	1.496(3)
N2—N3	1.365(2)	C7—C8	1.496(2)
N3—C7	1.367(2)		
C6—N2—N3	117.2(1)	C5—C6—C6'	121.2(2)
N2—N3—C7	118.8(2)	O1—C7—N3	122.1(2)
N2—C6—C5	113.9(2)	O1—C7—C'8	122.1(2)
N2—C6—C6'	124.9(2)	N3—C7—C8	115.8(2)

Table 2. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1'...O3	0.92(2)	1.80(2)	2.703(2)	167(2)
O2—H2'...Cl1	0.90(3)	2.13(3)	3.020(1)	170(3)
N3—H3'...O2	0.86(2)	1.90(2)	2.615(2)	140(2)
O3—H3A...O1	0.79(3)	2.08(3)	2.852(2)	167(2)
O3—H3B...O4'	0.83(3)	1.92(2)	2.749(2)	173(3)
O4—H4A...Cl1	0.83(3)	2.38(3)	3.199(2)	172(3)
O4—H4B...Cl1''	0.87(3)	2.35(3)	3.206(2)	169(3)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, 2 - y, 1 - z$.

A system of Siemens SMART platform equipped with a CCD area detector, a graphite monochromator and Mo $K\alpha$ radiation from a sealed tube was used for data collection. The selected crystal was mounted on a thin glass fiber and bathed in a cold nitrogen stream maintained at 173(2) K for the duration of data collection. Three sets of 20 frames each were collected covering three perpendicular sectors of space. Reflections from these frames, usually 50–400, were used to obtain an initial set of cell parameters and an orientation matrix for data collection. A hemisphere of data, 1381 frames, 0.3° in ω , was measured in four separate runs with a 30 s exposure time per frame. This data collection strategy provides data with a high degree of redundancy. The first 50 frames were remeasured at the end of data collections in order to monitor crystal and instrument stability and to enable crystal decay corrections. Crystallographic raw data frames were integrated, all reflections were extracted, reduced, and Lp-corrected using program SAINT (Siemens, 1995). A large number of reflections, up to a maximum of 8192, was used to refine the cell parameters.

Data collection: SMART (Siemens, 1995). Cell refinement: SMART and SAINT. Data reduction: SHELXTL (Sheldrick, 1995). Program(s) used to solve structure: SHELXTL. Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1045). Services for accessing these data are described at the back of the journal.

References

- Domiano, P., Musatti, A., Pelizzi, C. & Predieri, G. (1974). *Cryst. Struct. Commun.* **3**, 531–534.
- Sheldrick, G. M. (1995). SHELXTL. Version 5. *Structure Determination Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). SMART and SAINT. *Data Collection and Processing Software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.