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Pyridine-2-carbaldehyde Thiosemicarbazone Hydrochloride Monohydrate, $2C_7H_9N_4S^+.2Cl^-.2H_2O$

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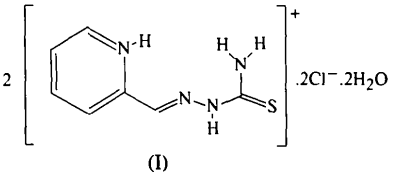
Abstract

The structure of the title compound comprises $C_7H_9N_4S^+$ cations [2-(thiosemicarbazonomethyl)pyridinium], Cl^- anions and a water molecule of crystallization which stabilizes the crystal lattice through a network of hydrogen bonds. There are two independent molecules in the asymmetric unit, the organic moieties of which show great planarity. Spectroscopic studies carried out in both the solid state and aqueous solution are in accordance with the existence of a π-delocalized system along each organic cation.

Comment

Thiosemicarbazones are a large group of organic derivatives having a wide range of biological activities. It has been shown that α-N-heterocyclic thiosemicarbazones possess antitumor properties, partially related to their ability to inhibit the enzyme ribonucleoside diphosphate reductase (RDR), which is essential in DNA synthesis (Moore, Zedek, Agrawal & Sartorelli, 1970). These drugs and their respective metallic complexes act either as chelating agents of the Fe atoms of the active site in the enzyme mentioned or by destroying the tyrosine radical present in a subunit of this protein (Thelander & Gräslund, 1983), thus inhibiting, in both cases, the catalytic activity of the enzyme. In an attempt to obtain a high affinity for the target enzyme RDR, it was decided to attempt to increase the water solubility of thiosemicarbazones for easier administration to patients. For this purpose, cationic salts of these compounds were prepared, but few of their structures have been solved (Kuroda, Neidle & Wilman, 1984).

The crystal structure of the title compound, (I), consists of $C_7H_9N_4S^+$ cations and an arrangement of Cl^- anions and water molecules of crystallization. The two crystallographically independent cations have very similar geometries. The occurrence of crystallographically non-equivalent molecules in the unit cells of organic crystals has been discussed (Gautham, 1992). Pyridine-2-carbaldehyde thiosemicarbazone monohydrate (Byushkin, Chumakov, Samus & Baka, 1987) has one molecule in the asymmetric unit and a different conformation from that of the cationic form; atoms N1 and N2 are *anti* with respect to the C5—C6 bond.



(I)

The atomic distances and angles of the title compound are very similar, within experimental error, to those in pyridine-2-carbaldehyde thiosemicarbazone, except for angles C6—N2—N3, C1—N1—C5, C5—C6—N2, N1—C1—C2 and N1—C5—C4 (Table 2), which have values of 114.7 (3), 117.3 (3), 121.2 (3), 123.5 (3) and 122.4 (3)°, respectively, in the neutral molecule. This could be due to the protonation of the pyridine N atom and the influence of new hydrogen bonds that are formed. The geometries of the pyridine and thiosemicarbazone moieties show that the molecules can be considered to have delocalized systems, similar to those of other aryl thiosemicarbazones (Palenik, Rendle & Carter, 1974).

The thiosemicarbazone side chain is almost planar and bends away from the pyridinium plane, showing slight positive shifts for molecule *A* (Fig. 1) and even smaller negative shifts for molecule *B*. The maximum deviations from the calculated mean planes are 0.289 (2) Å for atom S*A* and −0.117 (5) Å for atom N3*B*. The pyridinium planes of the two molecules are at an angle of 6.4 (2)° with respect to each other.

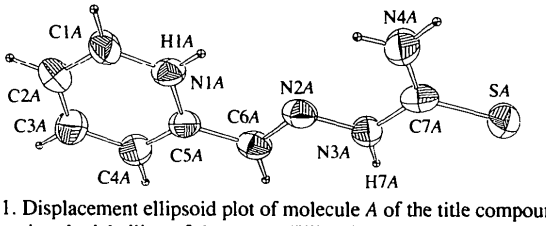


Fig. 1. Displacement ellipsoid plot of molecule *A* of the title compound showing the labelling of the atoms. Ellipsoids are drawn at the 50% probability level with isotropic H-atoms represented as spheres of arbitrary radii.

Analysis of the molecular packing confirms the stabilization of the lattice by two hydrogen bonds, N3*A*—H7*A*···O*W*2 and N1*B*—H1*B*···Cl2(x, $\frac{1}{2}-y$, $z-\frac{1}{2}$), in which Cl^- anions and water molecules play an important role. However, there is no hydrogen bonding be-

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tween the organic moieties, in contrast to the packing of the neutral compound which involves N3—H7···N1 contacts. The title molecule also diverges from the tendency to form N—H···S contacts seen in other thiosemicarbazones (Mathew & Palenik, 1971).

The compound loses water at 414 K. A diffuse reflectance spectrum shows two absorption bands at 280 and 320 nm (with a shoulder around 330 nm), which are assigned to $n \rightarrow \pi^*$ transitions of the ring and the thiosemicarbazone chain. These data only exhibit very slight differences from those obtained in solution at low pH, with bands at 270 and 325 nm and a shoulder at 335 nm (Beraldo & Tosi, 1986).

Experimental

Pyridine-2-carbaldehyde thiosemicarbazone was prepared according to the method of Anderson, Duca & Scudi (1951). This compound (1 mmol, 0.18 g) was dissolved in 40 ml of ethanol containing 3 ml of concentrated hydrochloric acid. The powder obtained was recrystallized from an acid–ethanol solution. The density D_m was measured by flotation in $CHCl_3/CHBr_3$.

Crystal data

$2C_7H_9N_4S^+.2Cl^-.2H_2O$
$M_r = 469.4$
Monoclinic
$P2_1/c$
$a = 9.036\ (1)$ Å
$b = 19.834\ (1)$ Å
$c = 12.160\ (1)$ Å
$\beta = 100.81\ (1)°$
$V = 2140.6\ (3)$ Å^3
$Z = 4$
$D_x = 1.46$ Mg m^{-3}
$D_m = 1.459\ (3)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–13°$
$\mu = 0.517$ mm^{-1}
$T = 293$ K
Prismatic
0.4 × 0.35 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6676 measured reflections
6237 independent reflections
2862 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0443$

$\theta_{max} = 30°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 27$
$l = 1 \rightarrow 17$
2 standard reflections monitored every 250 reflections
intensity decay: insignificant

Refinement

Refinement on F^2
$R(F) = 0.064$
$wR(F^2) = 0.1631$
$S = 1.113$
6237 reflections
254 parameters
H atoms refined isotropically

$w = 1/[\sigma^2(F_o^2) + (0.100P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
N1*A*	0.2696 (5)	0.3440 (2)	0.8906 (4)	3.2 (1)
C1*A*	0.2185 (7)	0.2823 (3)	0.9014 (5)	3.8 (2)
C2*A*	0.2577 (8)	0.2302 (4)	0.8394 (6)	4.4 (2)
C3*A*	0.3534 (8)	0.2423 (3)	0.7659 (6)	4.2 (2)
C4*A*	0.4043 (7)	0.3075 (3)	0.7557 (5)	3.9 (2)
C5*A*	0.3636 (6)	0.3584 (3)	0.8180 (5)	2.9 (2)
C6*A*	0.4108 (7)	0.4288 (3)	0.8113 (5)	3.2 (2)
N2*A*	0.3583 (5)	0.4725 (2)	0.8690 (4)	3.0 (1)
N3*A*	0.3988 (6)	0.5380 (2)	0.8631 (4)	3.2 (1)
C7*A*	0.3458 (6)	0.5846 (3)	0.9253 (4)	2.9 (2)
N4*A*	0.2562 (6)	0.5634 (3)	0.9922 (5)	4.3 (2)
S*A*	0.3936 (2)	0.6663 (1)	0.9152 (1)	3.8 (1)
N1*B*	0.2321 (5)	0.5582 (2)	0.5652 (4)	2.9 (1)
C1*B*	0.3274 (7)	0.5886 (3)	0.5091 (5)	3.5 (2)
C2*B*	0.3488 (7)	0.6562 (3)	0.5160 (5)	3.7 (2)
C3*B*	0.2701 (7)	0.6933 (3)	0.5816 (5)	3.6 (2)
C4*B*	0.1710 (7)	0.6611 (3)	0.6384 (5)	3.5 (2)
C5*B*	0.1536 (6)	0.5923 (3)	0.6297 (4)	2.7 (1)
C6*B*	0.0559 (6)	0.5540 (3)	0.6910 (5)	3.1 (2)
N2*B*	0.0478 (5)	0.4911 (2)	0.6774 (4)	2.8 (1)
N3*B*	−0.0424 (6)	0.4563 (2)	0.7357 (4)	3.6 (1)
C7*B*	−0.0591 (7)	0.3892 (3)	0.7222 (5)	3.0 (2)
N4*B*	0.0175 (5)	0.3595 (2)	0.6533 (4)	3.2 (1)
S*B*	−0.1777 (2)	0.3475 (1)	0.7891 (2)	4.5 (1)
Cl1	0.1448 (2)	0.0810 (1)	0.5820 (1)	4.6 (1)
Cl2	0.2807 (2)	0.0890 (1)	1.0130 (1)	4.0 (1)
O*W*1	−0.0317 (5)	0.2152 (2)	0.6116 (4)	5.3 (2)
O*W*2	0.6081 (6)	0.5493 (3)	0.7115 (4)	5.8 (2)

Table 2. *Selected geometric parameters* (Å, °)

	Molecule *A*	Molecule *B*
N1—C1	1.323 (8)	1.337 (8)
N1—C5	1.364 (8)	1.336 (8)
C1—C2	1.366 (10)	1.355 (9)
C2—C3	1.376 (11)	1.377 (10)
C3—C4	1.385 (9)	1.385 (10)
C4—C5	1.354 (9)	1.376 (8)
C5—C6	1.468 (8)	1.468 (9)
C6—N2	1.262 (8)	1.260 (8)
N2—N3	1.356 (7)	1.364 (7)
N3—C7	1.338 (8)	1.345 (8)
C7—N4	1.319 (8)	1.321 (8)
C7—S	1.687 (6)	1.680 (6)
C1—N1—C5	121.9 (5)	122.4 (5)
N1—C1—C2	120.9 (6)	120.8 (6)
C1—C2—C3	119.1 (6)	118.7 (6)
C2—C3—C4	118.8 (6)	119.7 (6)
C3—C4—C5	121.0 (6)	119.6 (6)
N1—C5—C4	118.3 (5)	118.8 (5)
C4—C5—C6	124.5 (5)	123.0 (5)
N1—C5—C6	117.2 (5)	118.2 (5)
C5—C6—N2	118.7 (5)	118.1 (5)
C6—N2—N3	119.7 (5)	117.3 (5)
N2—N3—C7	120.2 (5)	120.1 (5)
N3—C7—S	119.8 (4)	119.7 (4)
N3—C7—N4	117.1 (5)	117.3 (5)
N4—C7—S	123.0 (4)	123.0 (4)

D—H···*A*	*D*···*A*	*D*—H···*A*
N3*A*—H7*A*···O*W*2	2.887 (14)	164.1 (6)
N1*B*—H1*B*···Cl2'	3.038 (5)	155.1 (6)

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

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Melaminium Diperchlorate Hydrate

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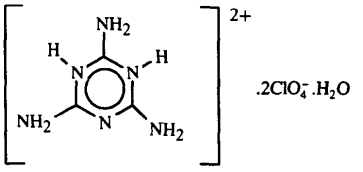
Abstract

The structure of the new melaminium salt, 2,4,6-triamino-1,3,5-triazine-1,3-diium diperchlorate hydrate, $C_3H_8N_6^{2+}.2ClO_4^-.H_2O$, has been characterized using low-temperature X-ray diffraction data (100 K). Melaminium diperchlorate has a high density (ρ_c = 1.94 Mg m^{-3}), is extensively hydrogen bonded and contains a water dimer.

Comment

The asymmetric unit of melaminium diperchlorate, (I), consists of two well defined perchlorate anions, a well defined aromatic ring protonated at two of the three ring N atoms and a partially disordered water molecule.



(I)

There is an extensive hydrogen-bonding network throughout the lattice (Fig. 1). Both perchlorate anions have the expected tetrahedral geometry, with bond lengths ranging from 1.430 (2) (Cl1—O1) to 1.458 (1) Å (Cl1—O4). The bond angles range from 108.78 (7) (O3—Cl1—O4) to 110.86 (8)° (O6—Cl2—O7). Protonation of the ring N atoms distorts the bond lengths in the aromatic ring. The two shortest bonds [N3—C3 1.320 (2) and N3—C1 1.333 (2) Å] are those furthest from the protonated ring N atoms. The two longest bonds [N2—C3 1.378 (2) and N1—C1 1.376 (2) Å] are those connected to the shortest bonds. This has the effect of opening up the ring bond angles at atoms C1 and C3, thus creating the largest bond angles in the ring [N2—C3—N3 122.2 (2) and N1—C1—N3 122.1 (1)°]. The amine groups do not appear to be affected in any systematic way by the distortion of the ring.

The bond length most likely to be affected, N5—C2 [1.304 (2) Å], lies midway between N4—

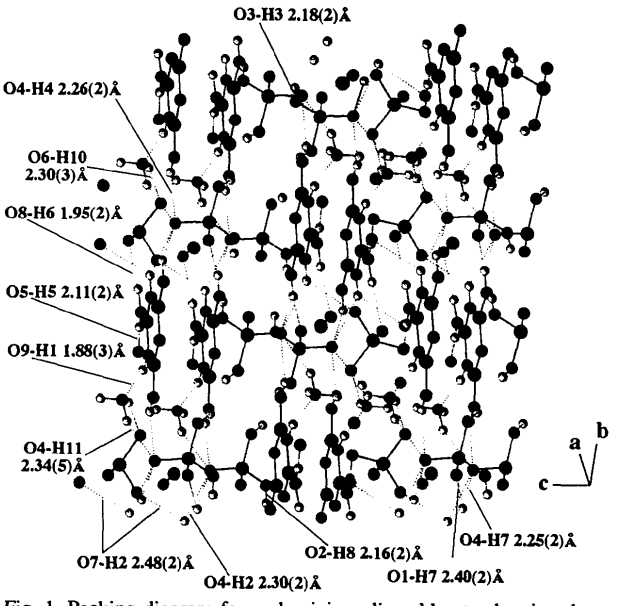


Fig. 1. Packing diagram for melaminium diperchlorate showing three unit cells in the *a* direction and two unit cells in the *b* and *c* directions, with hydrogen bonds (O···H < 2.5 Å) shown.

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