Crystal structure of pyridine-2-carbaldehyde thiosemicarbazonium chloride hydrate, $[C_7H_9N_4S]Cl \cdot H_2O$

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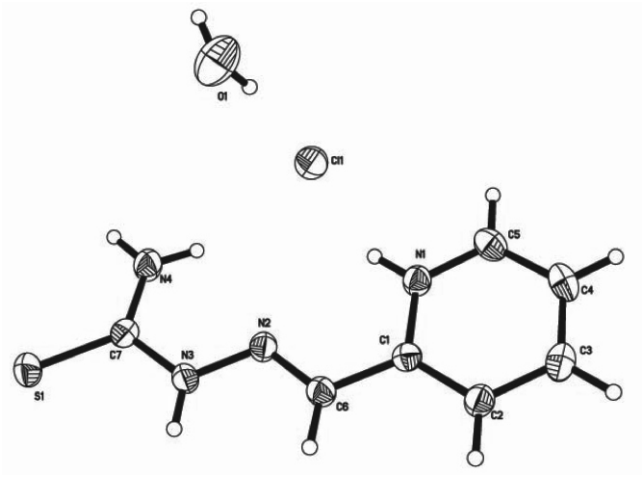

Abstract

$C_7H_{11}ClN_4OS$, monoclinic, $P2_1/n$ (no. 14), a = 4.9525(9) Å, b = 13.859(2) Å, c = 15.799(3) Å, β = 98.011(2)°, V = 1073.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.096, T = 296 K.

Source of material

The title compound was synthesized from pyridine-2-carbaldehyde thiosemicarbazone and concentrated hydrochloric acid in 75 % yield according to the reported method [1]. Yellow crystals suitable for X-ray diffraction study were obtained from a methanol solution.

Experimental details

All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors U_{iso}(H) = 1.2 U_{eq}(C,N) and 1.5 U_{eq}(O), respectively, and included in the final refinement with d(C—H) = 0.93 Å.

Discussion

The development of receptors for recognizing cation, neutral, and anion species has attracted much attention in molecular recognition study and supramolecular chemistry [2,3]. In particular, the design and synthesis of receptors capable of binding anionic guests is of crucial importance due to its potential applications in environmental and biological processes [4]. In general, most positively charged anion receptors have amide, pyrrole, urea, ammonium, or guanidinium groups as binding sites, which form N–H···anion hydrogen bonds [5].

The asymmetric unit of the title crystal structure consists of a pyridine-2-carbaldehyde thiosemicarbazone cation, a chloride anion, and a lattice water molecule. The N1 and N2 atoms are *cis* with respect to the C1—C6 bond, while the S1 and N2 atoms are *trans* with respect to the C7—N3 bond. The distance d(C7—S1) = 1.667(2) Å is intermediate between the values of 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond. The bond lengths d(C6—N2), d(C7—N3), and d(C7—N4) match well with the literature values [6]. The thiosemicarbazone cation exhibits high planarity with the maximum deviation of 0.126(2) Å at N3. The chloride ion plays an important role in stablizing the crystal structure. Pyridine-2-carbaldehyde thiosemicarbazone cations are connected into an infinite chain along [100] by four intermolecular hydrogen bonding interactions: N1–H1···Cl1, N4–H4A···Cl1, N4–H4B···O1 (x+1,y,z), and O1–H1W···Cl1. The chains are mutually linked by hydrogen bond N3–H3A···Cl1 ($-x$+3/2,y–1/2,$-z$+3/2), forming a layer in (001) plane. The layers are further assembled by hydrogen bond O1–H2W···Cl1 ($-x$+1,–y+2,$-z$+1), leading to the formation of a 3D suparmolecular architecture.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.11 × 0.15 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.25 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7062, 1957
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1333
$N(param)_{refined}$:	135
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.1546	0.6684	0.9118	0.051
H(3)	4*e*	–0.1192	0.7798	0.9689	0.059
H(4)	4*e*	–0.1444	0.9364	0.9178	0.062
H(5)	4*e*	0.1091	0.9797	0.8126	0.058
H(6)	4*e*	0.4890	0.6302	0.8067	0.047
H(1)	4*e*	0.3685	0.8697	0.7628	0.048
H(3A)	4*e*	0.7785	0.6076	0.7126	0.049
H(4A)	4*e*	0.7810	0.8267	0.6390	0.062
H(4B)	4*e*	0.9536	0.8119	0.5701	0.062
H(1W)	4*e*	0.270(9)	0.930(3)	0.550(1)	0.17(2)
H(2W)	4*e*	0.21(1)	0.949(2)	0.464(2)	0.15(2)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.2938(5)	0.7594(2)	0.8291(2)	0.038(1)	0.034(1)	0.033(2)	–0.002(1)	0.003(1)	–0.001(1)
C(2)	4*e*	0.1451(5)	0.7317(2)	0.8920(2)	0.044(2)	0.043(1)	0.040(2)	–0.001(1)	0.011(1)	0.000(1)
C(3)	4*e*	–0.0192(5)	0.7982(2)	0.9260(2)	0.045(2)	0.064(2)	0.041(2)	–0.002(1)	0.012(1)	–0.005(1)
C(4)	4*e*	–0.0335(5)	0.8913(2)	0.8958(2)	0.044(2)	0.051(2)	0.060(2)	0.008(1)	0.011(2)	–0.015(1)
C(5)	4*e*	0.1168(5)	0.9169(2)	0.8334(2)	0.050(2)	0.038(1)	0.057(2)	0.004(1)	0.005(2)	–0.006(1)
C(6)	4*e*	0.4707(5)	0.6944(2)	0.7899(2)	0.042(2)	0.034(1)	0.042(2)	0.001(1)	0.010(1)	–0.001(1)
C(7)	4*e*	0.8930(5)	0.6965(2)	0.6296(2)	0.040(2)	0.043(1)	0.034(2)	–0.001(1)	0.005(1)	0.001(1)
Cl(1)	4*e*	0.5598(2)	0.98380(5)	0.67659(5)	0.0761(5)	0.0382(4)	0.0577(5)	–0.0032(3)	0.0133(4)	–0.0019(3)
N(1)	4*e*	0.2747(4)	0.8519(1)	0.8020(1)	0.043(1)	0.038(1)	0.042(1)	–0.0017(9)	0.012(1)	–0.001(1)
N(2)	4*e*	0.6004(4)	0.7277(1)	0.7318(1)	0.040(1)	0.038(1)	0.035(1)	0.0003(9)	0.008(1)	–0.0021(9)
N(3)	4*e*	0.7602(4)	0.6663(1)	0.6948(1)	0.047(1)	0.035(1)	0.045(1)	0.005(1)	0.018(1)	0.001(1)
N(4)	4*e*	0.8736(4)	0.7891(1)	0.6107(1)	0.069(2)	0.041(1)	0.051(2)	0.001(1)	0.027(1)	0.003(1)
O(1)	4*e*	0.1990(6)	0.9096(2)	0.5025(2)	0.101(2)	0.097(2)	0.069(2)	–0.031(2)	0.020(2)	–0.001(2)
S(1)	4*e*	1.0623(2)	0.61531(5)	0.57955(5)	0.0593(5)	0.0526(4)	0.0519(5)	0.0100(3)	0.0249(4)	0.0001(3)

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