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Salicylaldehyde Semicarbazone–Acetic Acid Hydrogen-Bonded Complex

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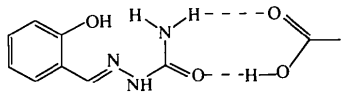
Abstract

The crystals of $C_8H_9N_3O_2.C_2H_4O_2$ consist of a one-to-one ratio of salicylaldehyde semicarbazone and acetic acid. Each molecule of salicylaldehyde semicarbazone is joined to an acetic acid molecule by a double hydrogen bond. This arrangement is very similar to the typical carboxylic acid dimer. The crystal structure exhibits a three-dimensional network of hydrogen bonds involving all of the possible hydrogen-bond donors and acceptors in both molecules.

Comment

The use of semicarbazones and thiosemicarbazones as anti-cancer and anti-viral agents has been known for many years (West *et al.*, 1993; Padhye & Kauffman, 1985). In 1956, the activity of pyridine-2-carboxaldehyde thiosemicarbazone in the lymphoid-leukaemia-1210 test was reported (Ali & Livingstone, 1974). In 1990, the compounds 2-acetylpyridine semicarbazone and thiosemicarbazone were reported to show activity against type-2 herpes simplex viral infections (Sidwell, Huffman, Schafer & Shipman, 1990). While these semicarbazones and thiosemicarbazones were shown to be effective while acting alone, the carcinostatic activity of kethoxal bis(thiosemicarbazone) was enhanced by the presence of Cu and Zn ions (Ali & Livingstone, 1974).

Bismuth drugs have been well documented for hundreds of years and several bismuth complexes, including the subsalicylate and citrate, are currently used to treat gastric disorders (Baxter, 1992). The synthesis of bismuth complexes with semicarbazone ligands seems a natural progression given their well noted activities. Crystals obtained in an unsuccessful attempt to synthesize a bismuth complex with salicylaldehyde semicarbazone (SASC) yielded a unique crystal structure of this ligand with a single molecule of acetic acid (HAc). This arrangement displays a high degree of hydrogen bonding involving SASC in a conformation that is stable enough to prevent the formation of the metal complex.



SASC–HAc

A displacement-ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1991) of the molecules with the atom-labelling scheme is presented in Fig. 1. The structure of SASC has been determined previously (Valdés-Martínez, Toscano, Salcedo, Cea-Olivares & Meléndez, 1990). We report the crystal structure of the title compound SASC–HAc, crystallized in a 1:1 ratio. All of the structural features of SASC are similar to those of the previously reported structure. The carbonyl group is in the *anti* conformation with respect to N7, a conformation observed in similar compounds (Soriano-García, Valdés-Martínez & Toscano, 1988; Chattopadhyay, Mazumdar, Banerjee, Ghosh & Mak, 1988; Soriano-García, Valdés-Martinez, Toscano, Gomez-Lara & Villalobos-Penalosa, 1986; Naik & Palenik, 1974; Nardelli, Fava & Giraldi, 1965). Bond lengths and angles of the C1–C8 chain suggest π-electron delocalization along the chain. This delocalization is also supported by the torsion angles along the chain: C2—C1—C7—N7 = −2.3 (4), C1—C7—N7—N8 = −179.5 (3), C7—N7—N8—C8 = 172.0 (2), N7—N8—C8—N8*b* = 7.4 (4) and N7—N8—C8—O8*a* = −172.1 (2)°. The least-squares plane of the semicarbazone moiety forms an angle of 5° with the plane of the phenyl ring.

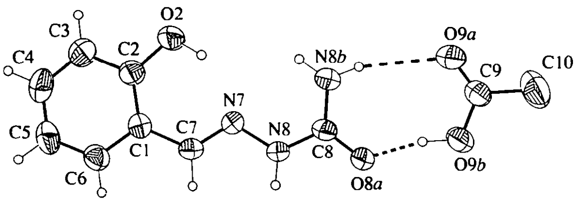


Fig. 1. Molecular structure with 50% probability ellipsoids, showing the atom-numbering scheme.

The presence of acetic acid in the crystal provides an extensive network of three-dimensional hydrogen bonding. H2 and H8*b* are involved in intermolecular hydrogen bonds with O9*a*, and intramolecular hydrogen bonds with N7. These intramolecular hydrogen bonds seem to be strong enough to prevent metal complex formation. Evidently, the presence of H2 and H8*b* and their interactions with the lone pair of electrons on N7 render these electrons inaccessible to the metal ions. There are three moieties in the structure that have both donor and acceptor sites, *i.e.* H8—N8—C8—O8*a*, H8*a*—N8*b*—C8—O8*a* and H9*b*—O9*b*—C9—O9*a*. Interactions among these groups provide the strongest hydrogen bonds in this structure. One of these interactions involves the H8—N8—C8—O8*a* moiety where molecules of SASC form cyclic dimers around crystallographic centers of inversion.

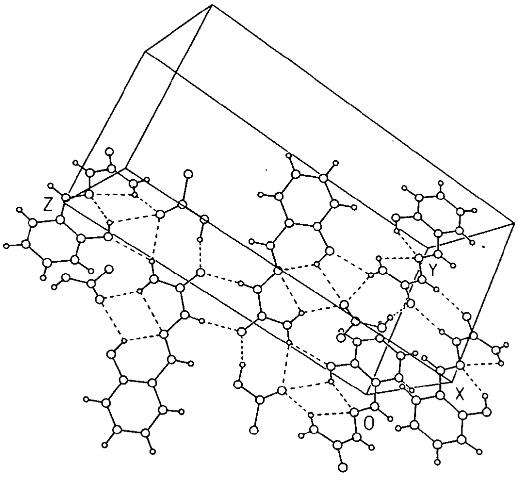


Fig. 2. Packing diagram showing the hydrogen-bonding network.

Experimental

All materials used, including salicylaldehyde, semicarbazide hydrochloride, sodium acetate, bismuth subcarbonate and glacial acetic acid, were obtained commercially and used without further purification. The SASC ligand was synthesized by adding 0.94 ml of salicylaldehyde to a solution of approximately 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate in 8 ml of H_2O. The resulting white precipitate was recrystallized once from H_2O. Analysis calculated (found) for $C_8H_9N_3O_2$: C 53.63 (53.43), H 5.06% (5.00%), N 23.45 (23.85). Crystals of SASC–HAc were obtained during a procedure in which 0.138 g (0.270 mmol) of $(BiO)_2CO_3$ was dissolved in 30 ml of glacial HAc and combined with 0.232 g (1.29 mmol) of SASC. Large colorless crystals, obtained upon evaporation of the clear colorless solution, appeared to lose solvent molecules after drying in air. Recrystallization from HAc produced large colorless crystals, one of which was used in this crystal structure analysis.

Crystal data

$C_8H_9N_3O_2.C_2H_4O_2$
$M_r = 239.23$
Monoclinic
$P2_1/n$
$a = 7.182\,(1)$ Å
$b = 8.947\,(1)$ Å
$c = 18.277\,(2)$ Å
$\beta = 91.89\,(1)°$
$V = 1173.8\,(2)$ Å^3
$Z = 4$
$D_x = 1.354$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 10$–11°
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Plate
0.36 × 0.23 × 0.19 mm
Colorless

Data collection

Seimens *P*3*m*/*V* diffractometer
ω scans
Absorption correction: analytical
$T_{\min} = 0.962$, $T_{\max} = 0.986$
3115 measured reflections
2711 independent reflections
1309 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.012$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = -23 \rightarrow 23$
4 standard reflections monitored every 100 reflections intensity decay: 1%

Refinement

Refinement on *F*
$R = 0.042$
$wR = 0.041$
$S = 1.19$
1309 reflections
198 parameters
All H-atom parameters refined except for methyl H atoms

$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: none
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)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	$U_{\rm eq}$
O2	0.3581 (3)	0.4840 (2)	0.33965 (9)	0.0683 (8)
O8*a*	−0.0242 (3)	−0.0740 (2)	0.40836 (8)	0.0530 (6)
N8*b*	0.1206 (4)	0.0580 (3)	0.32124 (12)	0.0605 (10)
O9*a*	0.0698 (3)	−0.2661 (2)	0.24866 (10)	0.0732 (8)
O9*b*	−0.1086 (3)	−0.3203 (2)	0.34046 (10)	0.0687 (8)
N7	0.1864 (3)	0.2779 (2)	0.42151 (10)	0.0406 (7)
N8	0.1075 (3)	0.1430 (2)	0.43959 (11)	0.0487 (8)
C1	0.2754 (3)	0.5222 (3)	0.46468 (12)	0.0388 (8)
C2	0.3502 (4)	0.5715 (3)	0.39979 (12)	0.0458 (9)
C3	0.4231 (5)	0.7148 (3)	0.3950 (2)	0.0612 (11)

C4	0.4206 (4)	0.8087 (3)	0.4540 (2)	0.0640 (12)
C5	0.3481 (4)	0.7625 (3)	0.5187 (2)	0.0600 (11)
C6	0.2776 (4)	0.6209 (3)	0.5239 (2)	0.0501 (10)
C7	0.1979 (3)	0.3738 (3)	0.47329 (13)	0.0410 (8)
C8	0.0658 (3)	0.0377 (3)	0.38916 (12)	0.0433 (9)
C9	−0.0372 (4)	−0.3490 (3)	0.27748 (14)	0.0540 (10)
C10	−0.0993 (5)	−0.4960 (3)	0.2465 (2)	0.087 (2)

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

C2—O2	1.352 (3)	C2—C1	1.390 (3)
C8—O8*a*	1.247 (3)	C6—C1	1.397 (3)
C8—N8*b*	1.327 (3)	C7—C1	1.450 (3)
C9—O9*a*	1.202 (3)	C3—C2	1.389 (4)
C9—O9*b*	1.301 (3)	C4—C3	1.368 (4)
N8—N7	1.378 (3)	C5—C4	1.372 (5)
C7—N7	1.279 (3)	C6—C5	1.369 (4)
C8—N8	1.345 (3)	C10—C9	1.494 (4)
N8—N7—C7	115.3 (2)	C6—C5—C4	119.4 (3)
C8—N8—N7	122.2 (2)	C1—C6—C5	121.7 (3)
C2—C1—C6	117.8 (2)	N7—C7—C1	123.4 (2)
C6—C1—C7	119.3 (2)	O8*a*—C8—N8*b*	123.0 (2)
C7—C1—C2	122.9 (2)	O8*a*—C8—N8	118.3 (2)
C3—C2—O2	117.2 (2)	N8*b*—C8—N8	118.6 (2)
C3—C2—C1	120.3 (2)	C10—C9—O9*a*	124.3 (3)
O2—C2—C1	122.5 (2)	C10—C9—O9*b*	112.8 (3)
C4—C3—C2	120.1 (3)	O9*a*—C9—O9*b*	122.8 (2)
C5—C4—C3	120.7 (3)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
O2—H2···N7	0.90 (3)	1.93 (3)	143 (3)
O2—H2···O9*a*^{i}	0.90 (3)	2.47 (3)	104 (2)
N8*b*—H8*a*···O9*a*	0.88 (3)	2.37 (3)	158 (3)
N8*b*—H8*a*···O2*a*^{ii}	0.88 (3)	2.42 (3)	126 (3)
N8*b*—H8*b*···N7	0.92 (3)	2.38 (3)	102 (2)
N8*b*—H8*b*···O9*a*^{i}	0.92 (3)	2.20 (3)	151 (2)
N8—H8···O8*a*^{iii}	0.87 (2)	2.07 (2)	172 (2)
O9*b*—H9*b*···O8*a*	1.01 (3)	1.61 (3)	164 (3)

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

The methyl H atoms of C10 are found to be disordered. The refined structure includes two sets of idealized methyl H atoms with fixed displacement parameters. Their site-occupation factors refined to 0.60 (2) and 0.40 (2), respectively. The ω-scan width was symmetrically over 1.2° about the $\alpha_{1,2}$ maximum and the background was offset 1.0 and −1.0° in ω from the $K\alpha_{1,2}$ maximum. The scan speed was a variable 3–6° min^{-1} (depending upon intensity). The linear absorption coefficient was calculated using values from the *International Tables for X-ray Crystallography* (1974).

Programs used: *SHELXTL-Plus* (Sheldrick, 1991) for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics, and *SHELX76* (Sheldrick, 1976) for structure refinement (full-matrix least-squares).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: CR1161). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3,5,6-Tetrachloro-4-hydroxyphenyl *N*-(4-Chlorophenyl)benzenecarboximidate

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Abstract

When 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil) is reacted with *N*-benzylidene-*p*-chloroaniline, its quinoidal structure is converted to a phenolic derivative, the title compound ($C_{19}H_{10}Cl_5NO_2$). The C—O bond distances, 1.345 (5) and 1.389 (5) Å, indicate that they are hydroxyl and ether bonds, respectively. The N—C bond lengths are 1.272 (5) and 1.433 (5) Å, which

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