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# Synthesis and Molecular Structure of Salicylaldehyde *S*-methyl-isothiosemicarbazone, $C_9H_{11}N_3OS$

**Gy. Argay**[a], **A. Kálmán**[a,*], **B. Ribár**[b], **V. M. Leovac**[b], and **A. F. Petrović**[b]

[a] Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest-114, Hungary

[b] Faculty of Sciences, University of Novi Sad, YU-21000 Novi Sad, Yugoslavia

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The crystal structure of salicylaldehyde S-methylisothiosemicarbazone together with the synthesis applied are reported: $C_9H_{11}N_3OS$, monoclinic, $P2_1/n$, $a = 5.169(4)$, $b = 16.853(10)$, $c = 11.367(5)$ Å, $\beta = 92.48(1)°$, $V = 989.3(18)$ Å$^3$, $Z = 4$, $d_x = 1.405$ g cm$^{-3}$. The structure was solved by the heavy atom method and refined anisotropically to a residual $R = 0.046$. The molecule is practically co-planar. There is only one basic difference between the title compound $H_2L$ and its deprotonated and complexed forms reported hitherto: the nearly 180° difference in rotation about the formal double bond C1—N2. The molecules form hydrogen bonded dimers around $\bar{1}$.

*(Keywords: Crystal structure analysis; Salicylaldehyde S-methylisothiosemicarbazone)*

*Synthese und Molekülstruktur von Salizylaldehyd-S-methyl-isothiosemicarbazon,* $C_9H_{11}N_3OS$

Salicylaldehyd-*S*-methylisothiosemicarbazon wurde dargestellt und die Kristallstruktur vermessen: $C_9H_{11}N_3OS$, monoklin, $P2_1/n$, $a = 5{,}169(4)$, $b = 16{,}853(10)$, $c = 11{,}367(5)$ Å, $\beta = 92{,}48(1)°$, $V = 989{,}3(18)$ Å$^3$, $Z = 4$, $d_x = 1{,}405$ g cm$^{-3}$. Die Struktur wurde mit Hilfe der *Patterson*- und *Fourier*-Methode bestimmt und anisotropisch bis zu einem $R$-Wert von 0,046 verfeinert. Das Molekül ist praktisch eben, wobei ein grundlegender Unterschied zwischen der protonierten ($H_2L$) und der deprotonierten Form in den Komplexverbindungen besteht. Die Formen unterscheiden sich durch eine Drehung um ca. 180° um die $C_1$—$N_2$-Doppelbindung. Die Moleküle $H_2L$ sind durch Wasserstoffbindungen um das Symmetriezentrum zu einem Dimeren verknüpft.

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## Introduction

Salicylaldehyde *S*-methylisothiosemicarbazone ($H_2L$) takes part in the coordination to different transition metals as a quasi planar tridentate NNO ligand with a deprotonated OH group in the following structures: (*o*-phenatroline) (salicylaldehyde *S*-methylthiosemicarbazonato)copper(II)nitrate[1], (salicylaldehyde *S*-methylthiosemicarbazonato) (pyridine)copper(II)nitrate[2], (salicylaldehyde *S*-methylthiosemicarbazonato)copper(II)chloride[3], and tris(pyridine) (salicylaldehyde *S*-methylisothiosemicarbazonato)cobalt(II)-trichloro(pyridine)cobaltate(II)[4]. In these structures it is a monoanion ($HL^-$) while in ammonium(salicylaldehyde *S*-methylthiosemicarbazonato)dioxovanadate(V)monohydrate[5] it assumes a dianionic form ($L^{2-}$) by an additional deprotonation of the primary amine group. The latest structure analysis[4] substantiated the imido form of the thiosemicarbazide fragment [. . N—N(H)—C—(NH)—$SCH_3$] of the $HL^-$ ligand which had been suggested by *Divjaković* and co-workers[6]. The proton migration from N1 to N2 established by difference *Fourier* synthesis, is accompanied by a delocalization of the C1—N1 double bond on the N1-C1-C2 moiety. Consequently, C1—N1 and C1—N2 distances are practically equal and intermediate between single and double bonds. In order to give further evidence of this observation an X-ray study of the neutral ligand ($H_2L$) has also been performed.

## Experimental

*Synthesis.* 5.0 g of *S*-methylisothiosemicarbazide · HI[7] dissolved in 20 ml of water was mixed to 25 ml of salicylaldehyde diluted with 5 ml of ethanol. This reaction mixture was then neutralized by adding 4 g of $Na_2CO_3 \cdot 10\,H_2O$ solved in 15 ml of water dropwise under permanent stirring. Cooling of the neutralized mixture resulted in a yellowish crystalline precipitant which was filtered and rinsed intensively first with water and after the negative reaction for iodine with ethanol and ether, as well. The yield was 4.3 $H_2L$ (95%). Crystals suitable for X-ray analysis were obtained by recrystallizing 0.5 g of $H_2L$ from 25 ml of warmed methanol. M.p.: 440 K. The crystals are soluble in warm methanol, less soluble in ethanol but insoluble in water and ether.

*CHN analysis.* Calculated for $C_9H_{11}N_3OS$ ($M = 209.24$): C 51.66, H 5.29, N 20.07. Found: C 51.38, H 5.34, N 20.15%.

*X-ray analysis.* A crystal with dimensions of 0.1 × 0.15 × 0.25 mm was mounted on a Syntex P$\bar{1}$ four-circle diffractometer equipped with a graphite monochromator. Cell dimensions were obtained by least-squares from the setting angles of 15 carefully centered reflections whose approximate positions had previously been obtained from a random peak search. The monoclinic symmetry was checked from oscillation and *Weissenberg* photographs.

Intensities of all reflections within $\theta < 25°$ were determined in the $\omega$-$2\theta$ scan mode using $MoK_\alpha$ ($\lambda = 0.7107$ Å) radiation. After conventional data reduction of 2 395 unique observations 1 719 with $F_0 > 3.0\,\sigma\,(F_0)$ were taken as observed. No absorption correction was applied [$\mu(\mathrm{MoK}_\alpha) = 2.8\,\mathrm{cm}^{-1}$].

The position of the S atom was located in a *Patterson* map. The subsequent structure factor and *Fourier* calculations started from $R = 0.55$ revealed the positions of all the non-hydrogen atoms. Full-matrix least squares refinement of positional and vibrational parameters reduced $R$ to 0.076. At this stage the coordinates of H atoms were located in a difference electron density map. Further anisotropic refinement of non-hydrogen atoms—while the hydrogen atoms were treated isotropically—improved $R$ to the final 0.046 ($R_w = 0.058$, $R_{tot} = 0.069$). Scattering factors were taken from International Tables for X-ray Crystallography[8]. The calculations have been carried out on a PDP-11/34 minicomputer in Budapest using the SDP-34 program system provided by Enraf-Nonius.

## Results and Discussion

Fractional atomic coordinates and isotropic tensor components are listed in Table 1 for non-hydrogen atoms. The isotropic tensor components were calculated as one third part of the trace of the orthogonalized $u_{ij}$ tensor. The parameters for H atoms are given in Table 2. Bond distances, angles and the relevant torsion angles are listed in Table 3.

As shown by the row of the *antiperiplanar*[9] (~ 180°) torsion angles (Table 3) about the consecutive bonds: C1—N2, N2—N3, N3—C3, C3—C4, and C4—C5 of which four assume the same sign (—), the nearly planar $H_2L$ molecule (Fig. 1) is slightly twisted about an axis

Table 1. *Fractional atomic coordinates ( × 10⁴) and thermal parameters for non-hydrogen atoms. The e.s.d.'s are given in parentheses*

| $y$ | $z$ | $v03n_x$<br>$B_{eq}$ | | |
|---|---|---|---|---|
| S | 3 769 (2) | 227 (1) | 1 618 (1) | 4.1 (1) |
| O | 997 (6) | —1 393 (2) | 1 147 (2) | 4.9 (1) |
| N 1 | 5 949 (6) | 675 (2) | 3 701 (3) | 4.1 (1) |
| N 2 | 2 663 (6) | —229 (2) | 3 786 (2) | 3.7 (1) |
| N 3 | 996 (6) | —695 (2) | 3 094 (2) | 3.3 (1) |
| C 1 | 4 155 (7) | 212 (2) | 3 153 (3) | 3.2 (1) |
| C 2 | 6 280 (9) | 890 (3) | 1 192 (4) | 5.0 (2) |
| C 3 | —631 (7) | —1 108 (2) | 3 674 (3) | 5.3 (1) |
| C 4 | —2 435 (7) | —1 663 (2) | 3 103 (3) | 3.0 (1) |
| C 5 | —4 105 (7) | —2 102 (2) | 3 786 (3) | 3.5 (1) |
| C 6 | —5 814 (8) | —2 644 (2) | 3 297 (3) | 3.8 (1) |
| C 7 | —5 883 (8) | —2 756 (2) | 2 096 (3) | 4.2 (2) |
| C 8 | —4 260 (8) | —2 338 (2) | 1 394 (3) | 4.2 (2) |
| C 9 | —2 535 (7) | —1 793 (2) | 1 882 (3) | 3.4 (1) |

Table 2. *Fractional atomic coordinates ( $\times 10^3$) and temperature factors for hydrogen atoms. The e.s.d.'s are given in parentheses*

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| H2A | 610(8) | 149(2) | 163(3) | 4.8(9) |
| H2B | 786(7) | 72(2) | 139(3) | 3.8(8) |
| H2C | 602(9) | 99(3) | 45(4) | 6.9(12) |
| H3 | −70(7) | −109(2) | 456(3) | 3.9(8) |
| H5 | −413(7) | −202(2) | 462(3) | 4.5(9) |
| H6 | −689(7) | −294(2) | 380(3) | 4.0(8) |
| H7 | −702(7) | −312(2) | 181(3) | 4.6(9) |
| H8 | −422(7) | −242(2) | 58(3) | 4.5(9) |
| HO | −12(7) | −117(2) | 148(3) | 3.3(8) |
| H1A | 616(7) | 64(2) | 434(3) | 4.5(9) |
| H1B | 713(9) | 104(3) | 324(4) | 7.6(12) |

Table 3. *Structural data*

Bond Length (Å)

| | | | | | |
|---|---|---|---|---|---|
| S—C1 | 1.748(3) | N3—C3 | 1.284(5) | C6—C7 | 1.377(5) |
| S—C2 | 1.795(5) | C3—C4 | 1.454(5) | C7—C8 | 1.376(5) |
| C1—N1 | 1.344(5) | C4—C5 | 1.398(5) | C8—C9 | 1.380(5) |
| C1—N2 | 1.309(4) | C4—C9 | 1.404(5) | C9—O | 1.357(4) |
| N2—N3 | 1.395(4) | C5—C6 | 1.372(5) | | |

Bond Angles (°)

| | | | | | |
|---|---|---|---|---|---|
| C1—S—C2 | 103.0(3) | N3—C3—C4 | 122.3(5) | C6—C7—C8 | 120.9(6) |
| S—C1—N1 | 120.1(5) | C3—C4—C5 | 119.5(5) | C7—C8—C9 | 120.5(6) |
| S—C1—N2 | 120.8(5) | C3—C4—C9 | 122.5(5) | C4—C9—C8 | 119.8(6) |
| N1—C1—N2 | 119.1(5) | C5—C4—C9 | 118.0(5) | C4—C9—O | 122.2(5) |
| C1—N2—N3 | 112.4(5) | C4—C5—C6 | 122.0(6) | C8—C9—O | 118.0(5) |
| N2—N3—C3 | 114.7(5) | C5—C6—C7 | 118.8(6) | | |

Relevant Torsion Angles (°)

| | | | |
|---|---|---|---|
| N1—C1—N2—N3 | −177.9(7) | C3—C4—C5—C6 | −178.8(7) |
| C1—N2—N3—C3 | −176.6(6) | C2—S—C1—N2 | −178.7(4) |
| N2—N3—C3—C4 | −176.3(7) | O—C9—C4—C3 | −1.8(6) |
| N3—C3—C4—C5 | 179.3(6) | C9—C4—C3—N3 | 0.8(6) |

bisecting the terminal N1—C1 and C5—C6 bonds of the zigzaged molecular skeleton. This feature of the molecule is apparently permitted by the existing p$\pi$-p$\pi$ interaction between the conjugated double bonds and the whole amidine (isothiosemicarbazide) moiety. The conspicuous differences between the conformation of the title compound $H_2L$ and those of its ionized (once or twice deprotonated) chelating forms are the different (~ 180°) amounts of rotations about the C1—N2 and C1—S bonds. If C1—N2 can be regarded as a double bond then $H_2L$ and its deprotonated forms are related as geometrical isomers, namely in $H_2L$ N3 and S atoms are eclipsed relative to the C1—N2 bond (isomer *Z*) while in the chelating ligands they are in *anti* positions (isomer *E*). The latter is essential for the tridentate ligands to allow an optimal geometry for chelation (Fig. 2 a). However, in $H_2L$ the isomer *E* involving automatically close intramolecular contact N1H...N3 would be disfavoured by the presence of the intramolecular OH...N3 hydrogen bond.

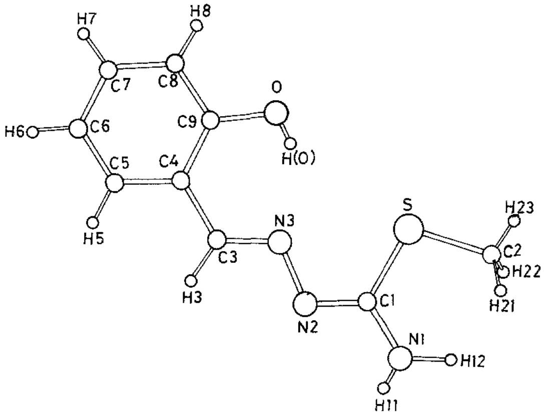

Fig. 1. A perspective view of the molecule with atomic numbering

| | O...N | H...N | ∢OH...N |
|---|---|---|---|
| OH...N3 | 2.67 (1) | 2.06 (3) Å | 148 (3)° |

This sterical hindrance may only be eliminated by an unlikely rotation of 180° about the strong N3—C3 double bond turning the OH group toward the other bi-coordinated N atom (Fig. 2 b) and forming thus an other conformation stabilized by an OH...N2 intramolecular hydrogen bond. The existing OH...N3 hydrogen bond also forces the S—C2 (methyl) bond from its favourable position (*synperiplanar*[9] with the N1—N2 bond) into an *antiperiplanar* arrangement to allow chelation of the $HL^-$ and $L^{2-}$ ligands. However, this results in an eclipsed conformation of the terminal C1—N1 and S—C2 bonds which in turn prevents H12 from attaining to a hydrogen bond. Consequently, the primary amine group of the title compound [N 1(H)$_2$] can maintain only an intermolecular hydrogen bond *via* H 11 with the only remaining acceptor atom (N 2) of a symmetry related molecule. This can either be

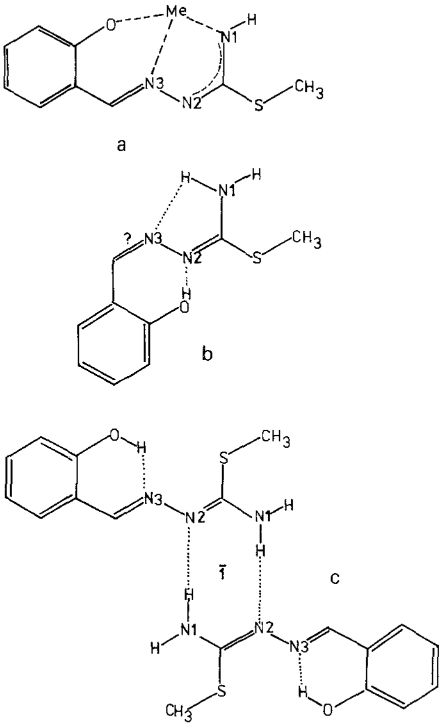

Fig. 2. *a* The conformation of the deprotonated molecule in chelated form (isomer *E*); *b* an unlikely conformation of the title compound which permits an intramolecular N 1H . . . N 3 hydrogen bond; *c* dimer of the centre of symmetry related H$_2$*L* molecules bound by N 1H . . . N 2 intermolecular hydrogen bond pairs

formed as an infinite hydrogen bond helix around a twofold screw axis or about a centre of symmetry as in the case of the title compound (Fig. 2 c). The hydrogen bond parameters of the dimer associates formed in the lattice of the title compound are as follows

| | N . . . N | H . . . N | NH . . . N |
|---|---|---|---|
| N 1—H 11 . . . N 2[$\bar{x},\bar{y},\bar{z},$] | 3.01 (1) | 2.30 (3) Å | 165 (2)° |

To summarize, the internal rotations shown by the molecules of the title compound H$_2$*L* and of its ionized forms ligated to transition metals are governed directly by the optimal conditions of forming either intra- and intermolecular hydrogen bonds as in $H_2L$ or chelates as in the metal complexes[1–5].

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