

occurs frequently (L-alanine: Lehmann, Koetzle & Hamilton, 1972; DL-alanine: Donohue, 1950;  $\gamma$ -glycine: Iitaka, 1961; L-leucine: Harding & Howieson, 1976; DL-methionine: Mathieson, 1952; DL-norleucine: Mathieson, 1953; DL-valine: Mallikarjunan & Rao, 1969).

In the present crystal, the hydrogen-bonding pattern is different because the acceptor/donor ratio has been changed from 2/3 to 5/8 by the presence of water in this crystal structure. Each O atom accepts two hydrogen bonds. As there are only eight H atoms (six from two  $\text{NH}_3^+$  groups and two from  $\text{H}_2\text{O}$ ) able to form hydrogen bonding, two of these bonds must be bifurcated. The hydrogen-bonding pattern can be described as  $[(2 + 2 + 2 + 2)/(2 + 2 + 1 + 1 + 1 + 1 + 1)]$ . The bifurcated hydrogen bonds are weaker ( $\text{H}\cdots\text{O}$  distances are 2.3 to 2.4 Å) than others (1.9 to 2.05 Å) and one of them involves the water O atom (Table 3). This hydrogen-bond system can be classified as *B* under the assumption of 'equal' O atoms (type *A* = 'equal' H atoms).

We are grateful to NIH (GM 24864 and CA-23704) for financial support.

#### References

- BENEDETTI, E., PEDONE, C. & SIRIGU, A. (1973). *Acta Cryst.* B29, 730–733.
- DONOHUE, J. (1950). *J. Am. Chem. Soc.* 72, 949–953.
- ENRAF-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- GURU ROW, T. N. & PARTHASARATHY, R. (1981). *J. Am. Chem. Soc.* 103, 477–479.
- HARDING, M. M. & HOWIESON, R. M. (1976). *Acta Cryst.* B32, 633–634.
- IITAKA, Y. (1960). *Acta Cryst.* 13, 35–45.
- IITAKA, Y. (1961). *Acta Cryst.* 14, 1–10.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- JÖNSSON, P.-G. & KVICK, Å. (1972). *Acta Cryst.* B28, 1827–1833.
- KOETZLE, T. F., HAMILTON, W. C. & PARTHASARATHY, R. (1972). *Acta Cryst.* B28, 2083–2092.
- LAKSHMINARAYANAN, A. V., SASISEKHARAN, V. & RAMACHANDRAN, G. N. (1967). *Conformation of Biopolymers*, Vol. I, edited by G. N. RAMACHANDRAN, pp. 61–82. New York: Academic Press.
- LEHMANN, M. S., KOETZLE, T. F. & HAMILTON, W. C. (1972). *J. Am. Chem. Soc.* 94, 2657–2660.
- MALLIKARJUNAN, M. & RAO, S. T. (1969). *Acta Cryst.* B25, 296–303.
- MATHIESON, A. MCL. (1952). *Acta Cryst.* 5, 332–341.
- MATHIESON, A. MCL. (1953). *Acta Cryst.* 6, 399–403.
- PARTHASARATHY, R. (1969). *Acta Cryst.* B25, 509–518.
- ROSENFELD, R. E. JR & PARTHASARATHY, R. (1974). *J. Am. Chem. Soc.* 96, 1925–1930.
- ROSENFELD, R. E. JR, PARTHASARATHY, R. & DUNITZ, J. D. (1977). *J. Am. Chem. Soc.* 99, 4860–4862.
- TORII, K. & IITAKA, Y. (1970). *Acta Cryst.* B26, 1317–1326.
- TORII, K. & IITAKA, Y. (1971). *Acta Cryst.* B27, 2237–2246.
- TORII, K. & IITAKA, Y. (1973). *Acta Cryst.* B29, 2799–2807.

*Acta Cryst.* (1986). C42, 623–625

## Structure of 5-Methoxysalicylaldehyde 4-Phenylthiosemicarbazone–Methanol (1/1)\*

BY M. SORIANO-GARCÍA,† J. VALDÉS-MARTÍNEZ, R. A. TOSCANO, J. GÓMEZ-LARA AND  
M. VILLALOBOS-PEÑALOZA

*Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México DF*

(Received 12 June 1985; accepted 12 November 1985)

**Abstract.**  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2\text{S}\cdot\text{CH}_4\text{O}$ ,  $\text{MeOPhSNO}$ ,  $M_r = 333.4$ , monoclinic,  $P2_1/c$ ,  $a = 10.543$  (2),  $b = 9.863$  (4),  $c = 17.977$  (6) Å,  $\beta = 103.38$  (2)°,  $V = 1819$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.22$  Mg m<sup>-3</sup>,  $\text{Mo K}\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.185$  mm<sup>-1</sup>,  $F(000) = 704$ ,  $T = 293$  K, final  $R = 0.089$  for 1696 reflections. The S atom is *trans* to the N atom of the hydrazine group. The angle between the normals to the planes of the phenyl ring and salicylidene group is 72.0 (11)°. There is no strong

interaction between the phenyl ring and the thioureide group. The molecular packing is dominated by a three-dimensional hydrogen-bonding system.

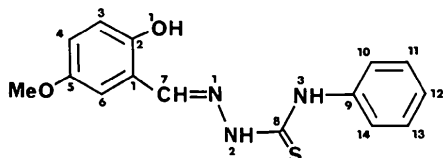
**Introduction.** Semicarbazides, thiosemicarbazides and their derivatives have been used as drugs whose action is attributed to their ability to form metal complexes (Petering & Van Giessen, 1965). Several metal complexes of semicarbazide and thiosemicarbazide have been the subject of chemical and structural studies (Ablov & Gerbeleu, 1965; Ryabova, Ponomarev, Zelentsov & Atovmyan, 1981; Biyushkin, Gerasimov

\* Contribution No. 772 of the Instituto de Química, UNAM.

† To whom correspondence should be addressed.

& Belov, 1981; Soriano-García, Toscano, Valdés-Martínez & Fernández-G., 1985; Soriano-García, Valdés-Martínez, Toscano & Gómez-Lara, 1985).

We have now prepared and carried out the crystal structure analysis of the title compound, in order to study its molecular geometry and the forces stabilizing the molecule, and to examine the conformational differences between the ligand and its Ni<sup>II</sup> complex.



**Experimental.** Crystals of MeOPhSNO prepared as described by Grammaticakis (1950) and Jensen, Anthoni, Kagi, Larsen & Pedersen (1968). Crystal 0.20 × 0.20 × 0.30 mm mounted on glass fibre along the needle axis. Nicolet R3 four-circle diffractometer, graphite-monochromatized MoK $\alpha$  radiation. Lattice parameters from 25 machine-centred reflections with  $7.9 < 2\theta < 20.4^\circ$ . 2715 reflections measured with  $3 < 2\theta < 45^\circ$  for two octants, of which 1696 had  $I > 2.5\sigma(I)$  and used in refinement. Index range  $h \pm 11$ ,  $k 0 \rightarrow 10$ ,  $l 0 \rightarrow 19$ .  $\omega$ -scan mode, variable scan speed, scan width  $1.0^\circ$  ( $\theta$ ). Two standard reflections (302; 311) monitored every 50 measurements; no significant variation. Lp correction, empirical absorption correction based on reflection intensity measurements at different azimuthal angles, max. transmission 0.96, min. 0.94.  $R_{\text{int}} = 0.076$ . Structure solved by direct methods with *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms anisotropic; H

atoms of CH and CH<sub>3</sub> groups riding on bonded C, H atoms attached to N and O atoms found on difference Fourier map at an advanced stage of anisotropic refinement and their coordinates refined; all H atoms assigned fixed isotropic temperature factor,  $U = 0.06 \text{ \AA}^2$ .  $\sum w(\Delta F)^2$  minimized,  $w = \{\sigma^2(F_o) + 0.01032(F_o)^2\}^{-1}$ . In the last cycle  $(\Delta/\sigma)_{\text{max}} = 0.073$ ; residual electron density within  $-0.359$  to  $1.022 \text{ e \AA}^{-3}$ ; final  $R = 0.089$  and  $wR = 0.136$ . Scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

$$U_{\text{eq}} = (U_{11} \times U_{22} \times U_{33})^{1/3}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
S	-212 (2)	1610 (2)	755 (1)	54 (1)
N(1)	2755 (5)	1618 (5)	-222 (3)	39 (2)
N(2)	1586 (6)	1370 (6)	-16 (4)	45 (2)
N(3)	1704 (6)	3340 (6)	661 (4)	46 (2)
O(1)	5164 (5)	2769 (5)	-122 (3)	64 (2)
O(2)	6164 (6)	-1297 (6)	-1980 (4)	75 (2)
O(3)	6787 (6)	-126 (6)	5218 (3)	63 (2)
C(1)	4365 (6)	766 (7)	-846 (3)	37 (2)
C(2)	5322 (7)	1741 (7)	-593 (4)	43 (2)
C(3)	6510 (7)	1680 (7)	-800 (4)	51 (3)
C(4)	6749 (7)	658 (8)	-1266 (4)	50 (3)
C(5)	5804 (7)	-327 (7)	-1535 (4)	48 (3)
C(6)	4634 (6)	-263 (7)	-1323 (4)	41 (2)
C(7)	3141 (6)	721 (7)	-624 (4)	39 (2)
C(8)	1117 (6)	2153 (7)	467 (4)	40 (2)
C(9)	1387 (7)	4274 (8)	1186 (4)	46 (3)
C(10)	1119 (7)	5604 (8)	966 (4)	53 (3)
C(11)	841 (8)	6557 (8)	1465 (5)	65 (3)
C(12)	817 (8)	6147 (10)	2197 (5)	73 (4)
C(13)	1087 (9)	4838 (11)	2422 (5)	73 (4)
C(14)	1370 (7)	3892 (8)	1920 (4)	56 (3)
C(15)	5270 (11)	-2332 (12)	-2260 (7)	111 (6)
C(16)	7302 (20)	84 (19)	6042 (7)	259 (15)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

S—C(8)	1.689 (7)	N(1)—N(2)	1.388 (9)
N(1)—C(7)	1.267 (9)	N(2)—C(8)	1.339 (10)
N(3)—C(8)	1.333 (9)	N(3)—C(9)	1.413 (10)
O(1)—C(2)	1.355 (9)	O(2)—C(5)	1.356 (10)
O(2)—C(15)	1.402 (13)	O(3)—C(16)	1.470 (13)
C(1)—C(2)	1.393 (9)	C(1)—C(6)	1.399 (10)
C(1)—C(7)	1.437 (10)	C(2)—C(3)	1.388 (11)
C(3)—C(4)	1.371 (11)	C(4)—C(5)	1.395 (10)
C(5)—C(6)	1.374 (11)	C(9)—C(10)	1.380 (11)
C(9)—C(14)	1.375 (10)	C(10)—C(11)	1.378 (12)
C(11)—C(12)	1.382 (13)	C(12)—C(13)	1.363 (14)
C(13)—C(14)	1.378 (13)		
N(2)—N(1)—C(7)	116.8 (6)	N(1)—N(2)—C(8)	123.8 (6)
C(8)—N(3)—C(9)	125.5 (7)	C(5)—O(2)—C(15)	117.9 (8)
C(2)—C(1)—C(6)	117.8 (6)	C(2)—C(1)—C(7)	124.0 (6)
C(6)—C(1)—C(7)	118.1 (6)	O(1)—C(2)—C(1)	122.4 (7)
O(1)—C(2)—C(3)	116.7 (6)	C(1)—C(2)—C(3)	120.8 (6)
C(2)—C(3)—C(4)	120.1 (7)	C(3)—C(4)—C(5)	120.4 (7)
O(2)—C(5)—C(6)	114.8 (7)	O(2)—C(5)—C(6)	126.0 (6)
C(4)—C(5)—C(6)	119.2 (7)	C(1)—C(6)—C(5)	121.7 (6)
N(1)—C(7)—C(1)	124.4 (6)	S—C(8)—N(2)	118.3 (5)
S—C(8)—N(3)	124.5 (6)	N(2)—C(8)—N(3)	117.2 (7)
N(3)—C(9)—C(10)	119.5 (7)	N(3)—C(9)—C(14)	121.3 (7)
C(10)—C(9)—C(14)	119.2 (7)	C(9)—C(10)—C(11)	121.4 (8)
C(10)—C(11)—C(12)	118.3 (8)	C(11)—C(12)—C(13)	120.8 (9)
C(12)—C(13)—C(14)	120.5 (9)	C(9)—C(14)—C(13)	119.7 (8)

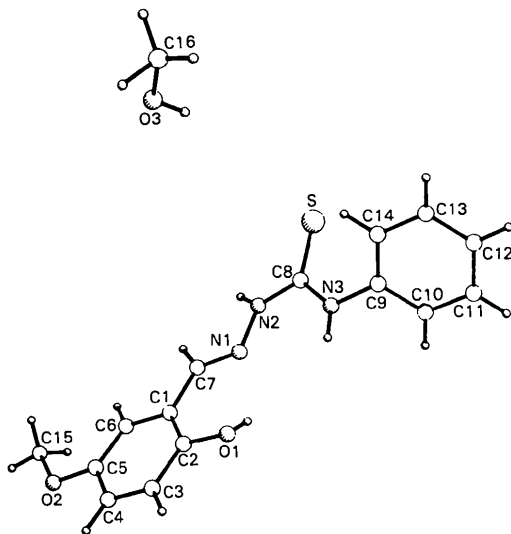


Fig. 1. A molecule of MeOPhSNO showing the atom labelling.

All computations performed on a Nova 4S computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs. C(16) of the methanol molecule shows evidence of disorder [thermal parameter  $U_{33} = 0.37(3) \text{ \AA}^2$ ]; C(15) of the methoxy-carbonyl group may also be affected by disorder (see thermal parameters in Table 1). The high final  $R$  is probably due to this disorder.

**Discussion.** A perspective drawing of the MeOPhSNO molecule is shown in Fig. 1. The final atomic coordinates are given in Table 1.\* Bond lengths and interbond angles are listed in Table 2.

The S atom in the thiosemicarbazone fragment is *trans* with respect to the hydrazinic  $-\text{HN}_2$  group, N(1), while in chelation with  $\text{Ni}^{\text{II}}$  (Soriano-García, Toscano *et al.*, 1985) it assumes the *cis* configuration. The S—C(8)—N(2)—N(1) torsion angle is  $-172.0(5)^\circ$ .

As is clearly seen in Fig. 1, the phenyl rings C(1)—C(6) and C(9)—C(14) are not coplanar, but form a dihedral angle of  $72.0(11)^\circ$ . The thiosemicarbazone fragment forms dihedral angles of  $10.4(11)$  and  $61.8(11)^\circ$  with the salicylidene group and C(9)—C(14) phenyl ring.

The distribution of bond lengths in the thiosemicarbazone fragment indicates delocalization of the  $\pi$  electrons. However, it is not altogether planar; maximum deviations from the plane are  $-0.113(10)$ ,

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, the results of mean-plane calculations and hydrogen-bonding details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42635 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

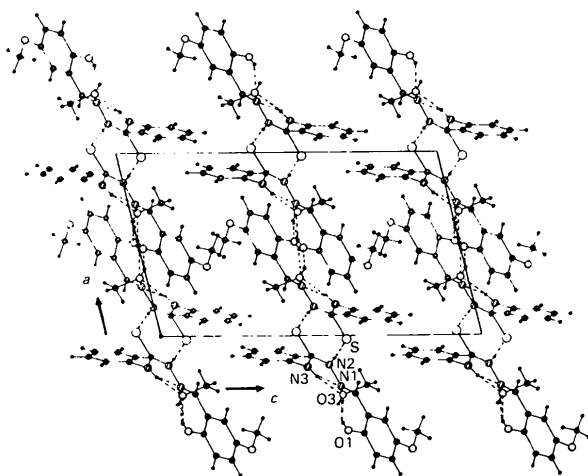


Fig. 2. Packing arrangement of the MeOPhSNO molecules as viewed along **b**. Broken lines indicate the intra- and intermolecular hydrogen bonds.

$0.104(10)$  and  $-0.077(11) \text{ \AA}$  for N(2), S and N(3) respectively.

The thioureide group exhibits a high degree of electron delocalization. The C—S distance of  $1.689(7) \text{ \AA}$  is similar to that found for thiourea [ $1.72(1) \text{ \AA}$ ; Truter, 1967] and in most of the thiosemicarbazides and thiosemicarbazones reported (Palenik, Rendle & Carter, 1974; Nandi, Chaudhuri, Mazumdar & Ghosh, 1984). The C—S distance in the free ligand is shorter by  $0.072 \text{ \AA}$  than the corresponding distance in its  $\text{Ni}^{\text{II}}$  complex. The dihedral angle between the plane of the phenyl ring C(9)—C(14) and the thioureide group is  $57.6(11)^\circ$ , while the phenyl ring C(1)—C(6) is inclined at  $14.4(11)^\circ$  to the thioureide group. This alternating position of the phenyl rings *versus* the thioureide group gives efficient packing of the molecules in the crystal. The packing arrangement is illustrated in Fig. 2. Details of the hydrogen-bonding scheme have been deposited.

The MeOPhSNO molecules in the cell are connected by pairs of intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds across a centre of inversion and intramolecular  $\text{O}-\text{H}\cdots\text{N}$  and  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds lend conformational stability to the molecules in the crystal. The dimer-like units are joined by hydrogen bonds *via* a molecule of methanol.

We are greatly indebted to Consejo Nacional de Ciencia y Tecnología de México, CONACYT, for financial support, Proyecto No. PCCBBNA-021262. We thank Mr Abelardo Cuellar for his technical assistance.

#### References

- ABLOV, A. V. & GERBELEU, N. V. (1965). *Russ. J. Inorg. Chem.* **10**, 33–37.
- BIYUSHKIN, V. N., GERASIMOV, V. I. & BELOV, N. V. (1981). *Sov. Phys. Crystallogr.* **26**, 183–187.
- GRAMMANTICAKIS, P. (1950). *Bull. Soc. Chim. Fr.* pp. 504–510.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JENSEN, K. A., ANTHONI, U., KAGI, B., LARSEN, CH. & PEDERSEN, C. TH. (1968). *Acta Chem. Scand.* **22**, 1–50.
- NANDI, A. K., CHAUDHURI, S., MAZUMDAR, S. K. & GHOSH, S. (1984). *Acta Cryst.* **C40**, 1193–1196.
- PALENIK, G. J., RENDLE, D. F. & CARTER, W. S. (1974). *Acta Cryst.* **B30**, 2390–2395.
- PETERING, H. G. & VAN GIESSEN, G. J. (1965). *Biochem. Copper Proc. Symp.*, pp. 197–208. New York: Harriman.
- RYABOVA, N. A., PONOMAREV, V. L., ZELENTOV, V. V. & ATOVMIYAN, L. O. (1981). *Sov. Phys. Crystallogr.* **26**, 53–57.
- SHELDRIK, G. M. (1981). *SHELXTL*, revision 3. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen.
- SORIANO-GARCÍA, M., TOSCANO, R. A., VALDÉS-MARTÍNEZ, J. & FERNÁNDEZ-G., J. M. (1985). *Acta Cryst.* **C41**, 498–500.
- SORIANO-GARCÍA, M., VALDÉS-MARTÍNEZ, J., TOSCANO, R. A. & GÓMEZ-LARA, J. (1985). *Acta Cryst.* **C41**, 500–502.
- TRUTER, M. R. (1967). *Acta Cryst.* **22**, 556–559.