

- LOWE, J. P. (1980). *J. Am. Chem. Soc.* **102**, 1262–1269.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- OUAHAB, L. (1985). Thèse de doctorat d'état, Rennes, France.
- OUAHAB, L., BATAIL, P., PERRIN, C. & GARRIGOU-LAGRANGE, C. (1986). *Mater. Res. Bull.* **21**, 1223–1230.
- PENICAUD, A., BATAIL, P., PERRIN, C., COULON, C., PARKIN, S. S. P. & TORRANCE, J. B. (1987). *J. Chem. Soc. Chem. Commun.* pp. 330–331.
- SCOTT, B. A., LA PLACA, S. J., TORRANCE, J. B., SILVERMAN, B. D. & WELBER, B. (1977). *J. Am. Chem. Soc.* **99**, 6631–6639.
- TEITELBAUM, R. C., MARKS, T. J. & JOHNSON, C. K. (1980). *J. Am. Chem. Soc.* **102**, 2986–2989.
- THAXTON, C. B. & JACOBSON, R. A. (1971). *Inorg. Chem.* **10**, 1460–1463.

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Amine(salicylaldehyde thiosemicarbazonato)nickel(II)

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Abstract. $[\text{Ni}(\text{C}_8\text{H}_7\text{N}_3\text{OS})(\text{NH}_3)]$, $M_r = 268.96$, monoclinic, $P2_1/c$, $a = 4.768$ (2), $b = 18.289$ (5), $c = 12.025$ (3) Å, $\beta = 105.75$ (4)°, $V = 1009.2$ (6) Å³, $Z = 4$, $D_m = 1.78$ (2), $D_x = 1.77$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 20.9$ cm⁻¹, $F(000) = 552$, room temperature, $R = 0.042$ for 1296 observed reflections. A molecule of salicylaldehyde thiosemicarbazone coordinates in a planar conformation to the central Ni atom through O, N and S atoms, interatomic distances being Ni–O = 1.844 (4), Ni–N = 1.856 (4) and Ni–S = 2.139 (2) Å. A fourth coordination site is occupied by the ammonia molecule, Ni–N = 1.919 (4) Å.

Introduction. The complex of nickel(II) with salicylaldehyde thiosemicarbazone forms two isomers differing by the unit-cell parameters and apparently by the packing of the molecules. The results of elemental analysis and IR spectrometry indicate that the two isomers are chemically identical (Gyepes, Pavelčík & Beňo, 1981). The main goal of this work was to determine the crystal and molecular structure of the complex because of its analytical importance. Salicylaldehyde thiosemicarbazones are widely used in analytical practice, e.g. for the gravimetric determination of Cd^{II}, spectrophotometric determination of Mn^{II} and separation of Mn^{II} and Ni^{II} by extraction (Holzbecher, 1972).

Experimental. Red-brown prismatic crystals with roughly hexagonal cross-section prepared by hot-mixing of equimolar methanolic solutions of salicylaldehyde thiosemicarbazone and nickel(II) nitrate in the presence of ammonia. Crystal dimensions approxi-

mately $0.01 \times 0.02 \times 0.04$ cm, D_m by flotation (thalous formate–malonate–water). Syntex $P2_1$ diffractometer, 15 reflections for lattice-parameter determination, $18 < 2\theta < 30^\circ$, absorption ignored, $2\theta_{\max} = 55^\circ$, hkl range $0,0,\bar{14}$ to $5,21,13$. Two standard reflections measured every 100 reflections showed no significant changes during intensity-data collection. 1788 reflections measured, 1296 of them observed with $I > 2.5\sigma(I)$. Ni-atom position found from Patterson map, other non-H atoms located from successive Fourier maps. H atoms from difference Fourier map and geometry. Full-matrix refinement of 45 positional parameters, 90 anisotropic thermal parameters and one overall scale factor for non-H atoms, H atoms not refined. Refinement based on F , $R = 0.042$, $wR = 0.038$, $S = 0.51$, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{\max} = 0.2$ in final refinement cycle for non-H atoms, $\Delta\rho$ in final difference Fourier synthesis $|0.4|$ e Å⁻³. All calculations performed at the Department of Crystal Structures, Institute of Chemistry, University of Wrocław on a Nova 1200 computer, XTL system (Syntex, 1973), atomic scattering factors from *International Tables for X-ray Crystallography* (1968).

Discussion. Final positional and equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1,* interatomic distances and bond angles in

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51455 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates* ($\times 10^4$; $\times 10^5$ for Ni) and *equivalent isotropic thermal parameters* (\AA^2) with *e.s.d.'s in parentheses*

B_{eq} is defined as a one-third of the trace of the orthogonalized B_{ij} matrix.

	x	y	z	B_{eq}
Ni	4112 (15)	8525 (4)	15045 (5)	2.47 (4)
S	-2215 (3)	-63 (1)	1693 (1)	3.4 (1)
O	2694 (7)	1608 (2)	1230 (3)	3.0 (3)
N(1)	2392 (8)	738 (2)	3053 (3)	2.4 (3)
N(2)	1391 (9)	248 (2)	3751 (3)	2.8 (3)
N(3)	-2038 (10)	-630 (2)	3747 (4)	3.5 (4)
N(4)	-1984 (10)	1040 (3)	-30 (4)	3.7 (4)
C(1)	4871 (11)	1918 (3)	1959 (4)	2.5 (4)
C(2)	6261 (12)	2518 (3)	1597 (5)	3.5 (5)
C(3)	8658 (13)	2840 (3)	2311 (5)	4.0 (5)
C(4)	9757 (12)	2600 (3)	3427 (5)	3.6 (5)
C(5)	8454 (11)	2030 (3)	3827 (4)	2.8 (4)
C(6)	5978 (11)	1683 (3)	3120 (4)	2.6 (4)
C(7)	4642 (12)	1113 (3)	3593 (4)	2.6 (4)
C(8)	-807 (11)	-136 (3)	3173 (4)	2.9 (4)

Table 2. *Some interatomic distances* (\AA) and *bond angles* ($^\circ$) with *e.s.d.'s in parentheses*

Ni—O	1.844 (4)	C(5)—C(6)	1.406 (7)
Ni—N(1)	1.856 (4)	C(6)—C(1)	1.418 (7)
Ni—S	2.139 (2)	C(6)—C(7)	1.419 (7)
Ni—N(4)	1.919 (4)	C(7)—N(1)	1.290 (7)
O—C(1)	1.293 (6)	N(1)—N(2)	1.398 (6)
C(1)—C(2)	1.412 (8)	N(2)—C(8)	1.296 (7)
C(2)—C(3)	1.363 (8)	C(8)—N(3)	1.364 (7)
C(3)—C(4)	1.373 (8)	C(8)—S	1.728 (5)
C(4)—C(5)	1.367 (8)		
O—Ni—N(1)	95.73 (16)	N(1)—C(7)—C(6)	126.2 (5)
N(1)—Ni—S	87.62 (13)	C(7)—C(6)—C(1)	122.0 (5)
S—Ni—N(4)	91.69 (15)	C(1)—C(6)—C(5)	119.1 (5)
N(4)—Ni—O	85.39 (18)	C(5)—C(6)—C(7)	118.9 (5)
Ni—S—C(8)	95.45 (18)	C(6)—C(5)—C(4)	121.3 (5)
S—C(8)—N(2)	122.8 (4)	C(5)—C(4)—C(3)	119.9 (5)
N(2)—C(8)—N(3)	119.0 (5)	C(4)—C(3)—C(2)	120.7 (6)
N(3)—C(8)—S	118.2 (4)	C(3)—C(2)—C(1)	121.7 (5)
C(8)—N(2)—N(1)	112.5 (4)	C(2)—C(1)—C(6)	117.3 (5)
N(2)—N(1)—Ni	120.7 (3)	C(6)—C(1)—O	123.4 (5)
Ni—N(1)—C(7)	124.9 (4)	O—C(1)—C(2)	119.3 (5)
C(7)—N(1)—N(2)	114.2 (4)	C(1)—O—Ni	127.6 (3)

Table 2. A perspective view of the molecule is shown in Fig. 1.

As can be seen from Fig. 1 the molecule of salicylaldehyde thiosemicarbazone acts as a tridentate ligand which coordinates to the central Ni atom through the O, N(1) and S atoms. The fourth coordination site is occupied by the ammonia molecule.

The molecule of the complex is nearly planar. The atoms deviating most from the mean plane are S [0.213 (2)], N(3) [-0.136 (5)] and N4 [-0.131 (5) \AA]. The arrangement of the molecules in the unit cell is shown in Fig. 2. The packing is apparently determined by the N(3)—H(6) \cdots N(2)(-x, -y, -z + 1) and N(4)—H(9) \cdots S(-x-1, -y, -z) contacts. The corresponding distances, 3.022 (6) and 3.441 (5) \AA respectively, are comparable with the sums of the accepted van der Waals radii, namely 3.0 and 3.35 \AA (Pauling, 1967).

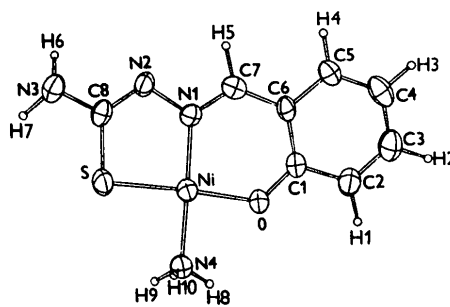


Fig. 1. Perspective view of the molecule showing the numbering of atoms.

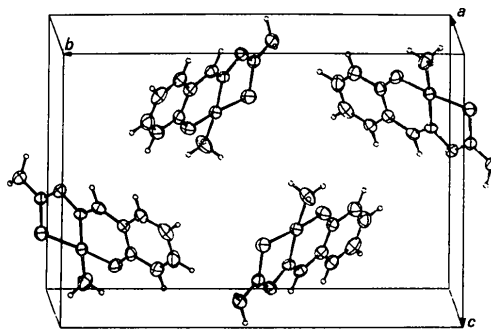


Fig. 2. Packing of the molecules.

The mean value of the interatomic distance in the aromatic ring is 1.390 (8) \AA (expected value 1.395 \AA) where the three bonds closer to the central atom [C(5)—C(6), C(6)—C(1), C(1)—C(2)] are a little longer than the mean while the remainder are shorter. Such a distribution of π electrons (compared with the benzene ring) is evidently caused by the electron-donating effect of the O atom and by the electron-withdrawing effect of the N(1) \cdots C(7) group. In consequence of these effects the interatomic distances O—C(1) and C(6)—C(7) [1.293 (6) and 1.419 (7) \AA respectively] are shorter than the expected values for single bonds (Sutton, 1965).

From the values of the bond distances along the chain O—C(1)—C(6)—C(7)—N(1)—N(2)—C(8)—N(3) it appears that there is π conjugation.

References

- GYEPES, E., PAVELČÍK, F. & BEŇO, A. (1981). *Collect. Czech. Chem. Commun.* **46**, 975–981.
- HOLZBECHER, Z. (1972). *Chem. Listy*, **66**, 7–20.
- International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- PAULING, L. (1967). *The Chemical Bond*, 4th ed., p. 152. Ithaca: Cornell Univ. Press.
- SUTTON, L. E. (1965). *Tables for Interatomic Distances and Configuration in Molecules and Ions*. Spec. Publ. No. 18. London: The Chemical Society.
- Syntax (1973). *XTL Structure Determination System*. Syntax Analytical Instruments, Cupertino, California, USA.