

## Structure of Ammine[salicylaldehyde 4-phenylthiosemicarbazonato(2-)]nickel(II), $[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_3\text{OS})(\text{NH}_3)]^*$

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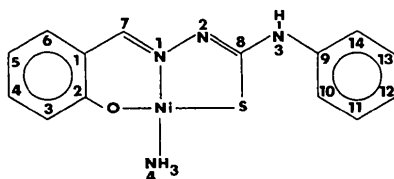
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**Abstract.**  $M_r = 345.1$ , monoclinic,  $P2_1/c$ ,  $a = 6.380$  (4),  $b = 29.260$  (5),  $c = 8.112$  (3) Å,  $\beta = 101.67$  (4)°,  $V = 1483$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.55$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 1.450$  mm<sup>-1</sup>,  $F(000) = 712$ ,  $T = 293$  K, final  $R = 0.064$  for 1452 observed reflections. The Ni<sup>II</sup> ion lies in a square-planar environment surrounded by the O and N of the azomethine group, the S atom, and the N of the ammonia molecule at distances of 1.858 (6), 1.844 (7), 2.166 (2) and 1.921 (7) Å. The variation in the Ni–N distances, the coplanarity of the salicylidene ring and the thiosemicarbazone moiety, and the rotation of the phenyl ring are probably a consequence of inter-related effects which seek to maximize the  $\pi$  character of the Ni–S bond and optimize crystal packing.

**Introduction.** Thiosemicarbazone and thiosemicarbazone derivatives have been studied because of their pharmacological activity against tuberculosis (Domagk, Behnisch, Mietzsch & Schmidt, 1946). They have also been found to be active against certain kinds of tumours (Petering, Buskirk & Underwood, 1964), smallpox and vaccinia (Bauer & Sadler, 1966), and have been suggested as possible fungicides (Bennis, Gingras & Bayley, 1960). Their activity has frequently been thought to be due to their ability to chelate trace metals (Liebermeister, 1950; Petering & Van Giessen, 1965).

Only a few studies of the coordination chemistry of transition-metal chelates of thiosemicarbazones (Campbell, 1975), and thiosemicarbazone derivatives (Casellato, Vigato & Vidali, 1977) have been performed. Consequently, we have prepared and performed the crystal structure analysis of the title compound, Ni(phsno)NH<sub>3</sub>.



**Experimental.** Ni(phsno)NH<sub>3</sub> was prepared from the 4-phenylthiosemicarbazone and nickel(II) nitrate hexahydrate in methanolic ammonia solution, following the procedure of Gyepes, Pavelčik & Beňo (1981). Prismatic crystal 0.10 × 0.18 × 0.32 mm. Nicolet R3 four-circle diffractometer, graphite-monochromated Mo K $\alpha$ . Lattice parameters from 25 machine-centred reflections with  $5.3 < 2\theta < 20.3^\circ$ . 2092 reflections with  $3 < 2\theta < 45^\circ$  for two octants. 1452 independent reflections with  $I > 2.5\sigma(I)$ . Index range  $h \pm 6, k 0/30, l 0/8$ .  $\omega$ -scan mode, variable scan speed, scan width  $1.0^\circ$  ( $\theta$ ). Two standard reflections monitored every 50 measurements; no significant variation. Lp correction, absorption ignored.  $R_{\text{int}} = 0.043$ . Structure solved by direct methods using *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms treated anisotropically, H atoms riding on the bonded C with fixed isotropic temperature factor  $U = 0.06$  Å<sup>2</sup>.  $\sum w(\Delta F)^2$  minimized,  $w = |\sigma^2(F_o) + 0.00169(F_o)^2|^{-1}$ .  $(\Delta/\sigma)_{\text{max}} < 0.04$ . Residual electron density within  $\pm 0.7$  e Å<sup>-3</sup>. Isotropic-extinction parameter  $X = 0.00108$ . Final  $R = 0.064$ ,  $wR = 0.079$ . Scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The shape of the molecule and the atomic numbering are indicated in Fig. 1. Final atomic parameters are given in Table 1‡ and bond distances and angles in Table 2.

For the purpose of overall geometrical description, the Ni(phsno)NH<sub>3</sub> molecule can be considered as made up of four parts, the salicylidene, phenyl and chelate rings and the thiosemicarbazone moiety.

The Ni<sup>II</sup> ion lies in an approximate square-planar coordination environment; all atoms are tetrahedrally displaced from the mean coordination plane by 0.011 (9) Å. The angles S–Ni–N(1) and S–Ni–N(4) are close to 90° at 87.7 (2) and 91.5 (2)°, respectively.

‡ Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39858 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Ni—N distances [1.844 (7) and 1.921 (7) Å] are not significantly different from those found by Gyepes *et al.* (1981) in the nickel(II) chelate of salicylaldehyde semicarbazone ammine and this indicates that the presence of an additional phenyl group at N(3) does not appreciably influence the geometry in the coordination plane. It has been pointed out by Curtis (1979) that the Ni—N distances appear to be dependent on the nature of the N donor atom, *i.e.* amine or imine and also the number of atoms in the chelate rings encompassing the Ni—N bond. Ni—N(amine) is longer than Ni—N(imine), in good agreement with the above observation.

The phenyl ring C(9)—C(14) is planar within the limits of experimental error. The phenyl ring of the salicylidene part of the molecule, however, deviates considerably from planarity; maximum deviations are  $-0.025$  (9) Å for both C(2) and C(6). The non-planarity of this ring could be attributed to coordination effects.

The distribution of bond lengths in the thiosemicarbazone moiety indicates complete delocalization of the  $\pi$  electrons. The thioureide group exhibits a partial double-bond character in one of the C—N bonds [C(8)—N(2) 1.333 (10) Å] as compared with the other C—N bond. The C(8)—S bond [1.717 (9) Å] is almost of the same magnitude as the double bond in thiosemicarbazide, 1.713 (5) Å (Hansen & Hazell, 1969) and thiosemicarbazide hydrochloride, 1.692 (3) Å (Coghi, Manotti Lanfredi & Tiripicchio, 1976).

The phenyl rings C(1)—C(6) and C(9)—C(14) make dihedral angles of 3.7 (9) and 130.4 (9)°, respectively, with the planar chelate ring. The dihedral angle between the two phenyl rings is 133.1 (10)°. Hence the amount of conjugation expected to occur between the phenyl ring C(9)—C(14) and the salicylaldehyde thiosemicarbazone part of the molecule will be small.

The packing of the molecules in the unit cell is shown in Fig. 2. The crystal structure consists of rows of molecule along the *b* axis. There is a short N—H...N contact involving N(3), which is 3.01 (1) Å from N(2) of an adjacent molecule ( $-x, 1-y, 1-z$ ). The

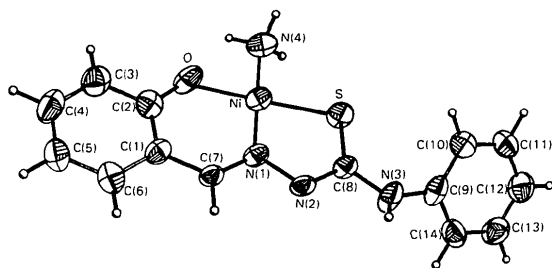


Fig. 1. The molecular conformation of Ni(phpno)NH<sub>3</sub>, showing the atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

H(3A)...N(2) distance of 2.37 Å together with the N(3)—H(3A)...N(2) angle of 157.8° suggest that a weak N—H...N bond may be present. Apart from the above interaction, the molecules of different rows are held together in the crystal by both van der Waals and crystal-packing forces.

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

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ni	5063 (2)	5712 (1)	2710 (1)	37 (1)
S	4199 (4)	5004 (1)	2165 (3)	45 (1)
N(1)	2778 (10)	5750 (2)	3777 (7)	36 (2)
N(2)	1497 (9)	5372 (2)	3917 (8)	38 (2)
N(3)	790 (11)	4632 (2)	3179 (9)	52 (3)
N(4)	7415 (11)	5666 (2)	1568 (8)	49 (3)
O	5980 (9)	6311 (2)	3125 (7)	52 (2)
C(1)	3157 (12)	6552 (3)	4515 (9)	39 (3)
C(2)	5040 (14)	6631 (3)	3906 (10)	43 (3)
C(3)	6067 (14)	7061 (3)	4196 (11)	53 (3)
C(4)	5138 (15)	7402 (3)	5032 (11)	59 (4)
C(5)	3267 (15)	7329 (3)	5594 (12)	59 (4)
C(6)	2301 (15)	6914 (3)	5337 (11)	50 (3)
C(7)	2105 (12)	6125 (2)	4400 (9)	35 (3)
C(8)	2084 (12)	5000 (3)	3180 (9)	35 (3)
C(9)	878 (15)	4209 (3)	2330 (10)	43 (3)
C(10)	2665 (15)	3940 (3)	2504 (10)	47 (3)
C(11)	2569 (15)	3526 (3)	1689 (11)	56 (4)
C(12)	693 (16)	3373 (3)	715 (12)	60 (4)
C(13)	-1103 (15)	3634 (3)	537 (11)	59 (4)
C(14)	-998 (15)	4047 (3)	1353 (11)	52 (4)

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

Ni—S	2.166 (2)	Ni—N(1)	1.844 (7)
Ni—N(4)	1.921 (7)	Ni—O	1.858 (6)
S—C(8)	1.717 (9)	N(1)—N(2)	1.393 (9)
N(1)—C(7)	1.316 (10)	N(2)—C(8)	1.333 (10)
N(3)—C(8)	1.357 (10)	N(3)—C(9)	1.423 (10)
O—C(2)	1.339 (11)	C(1)—C(2)	1.407 (12)
C(1)—C(6)	1.418 (12)	C(1)—C(7)	1.414 (10)
C(2)—C(3)	1.415 (12)	C(3)—C(4)	1.404 (13)
C(4)—C(5)	1.378 (14)	C(5)—C(6)	1.358 (12)
C(9)—C(10)	1.368 (13)	C(9)—C(14)	1.378 (12)
C(10)—C(11)	1.377 (12)	C(11)—C(12)	1.369 (13)
C(12)—C(13)	1.360 (14)	C(13)—C(14)	1.375 (12)
S—Ni—N(1)	87.7 (2)	S—Ni—N(4)	91.5 (2)
N(1)—Ni—N(4)	179.0 (3)	S—Ni—O	176.0 (2)
N(1)—Ni—O	96.2 (3)	N(4)—Ni—O	84.6 (3)
Ni—S—C(8)	95.9 (3)	Ni—N(1)—N(2)	121.5 (5)
Ni—N(1)—C(7)	125.5 (5)	N(2)—N(1)—C(7)	112.9 (6)
N(1)—N(2)—C(8)	113.0 (6)	C(8)—N(3)—C(9)	127.4 (8)
Ni—O—C(2)	126.3 (6)	C(2)—C(1)—C(6)	118.7 (7)
C(2)—C(1)—C(7)	123.4 (7)	C(6)—C(1)—C(7)	117.9 (8)
O—C(2)—C(1)	123.2 (7)	O—C(2)—C(3)	117.6 (8)
C(1)—C(2)—C(3)	119.2 (8)	C(2)—C(3)—C(4)	119.0 (9)
C(3)—C(4)—C(5)	121.8 (8)	C(4)—C(5)—C(6)	119.1 (9)
C(1)—C(6)—C(5)	122.2 (9)	N(1)—C(7)—C(1)	125.1 (7)
S—C(8)—N(2)	121.9 (6)	S—C(8)—N(3)	122.9 (6)
N(2)—C(8)—N(3)	115.0 (7)	N(3)—C(9)—C(10)	124.2 (7)
N(3)—C(9)—C(14)	117.5 (8)	C(10)—C(9)—C(14)	118.1 (8)
C(9)—C(10)—C(11)	120.1 (8)	C(10)—C(11)—C(12)	120.9 (9)
C(11)—C(12)—C(13)	119.9 (9)	C(12)—C(13)—C(14)	119.0 (8)
C(9)—C(14)—C(13)	122.0 (9)		

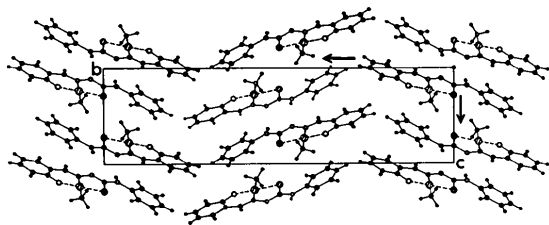


Fig. 2. The crystal structure projected along *a*. Broken lines indicate the Ni coordination bonds.

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## Structure of Bis[salicylaldehyde thiosemicarbazonato(1-)]chromium(III) Perchlorate Trihydrate, [Cr(C<sub>8</sub>H<sub>8</sub>N<sub>3</sub>OS)<sub>2</sub>]ClO<sub>4</sub>·3H<sub>2</sub>O\*

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**Abstract.**  $M_r = 593.9$ , monoclinic,  $P2_1/c$ ,  $a = 12.868$  (4),  $b = 14.630$  (6),  $c = 13.363$  (4) Å,  $\beta = 107.58$  (2)°,  $V = 2398.2$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.64$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.801$  mm<sup>-1</sup>,  $F(000) = 1220$ ,  $T = 293$  K, final  $R = 0.048$  for 2568 reflections. The Cr<sup>III</sup> ion is octahedrally coordinated by the two tridentate ligands, in the meridional configuration. The O and S atoms of the salicylidene-iminato groups are each arranged *cis* in the Cr octahedron while the imine N atoms are *trans*. Hydrogen-bond formation occurs between the amine groups and water molecules. The perchlorate ions are linked to the complex cation by a hydrogen bond involving a molecule of water. Water molecules lie in

well defined positions in the lattice and play an important role in the crystal packing.

**Introduction.** Semicarbazides, thiosemicarbazides and their derivatives have been the subject of many studies owing to their potential use as drugs whose action is related to chelation of trace metals (Petering & Van Giessen, 1965).

Derivatives of semicarbazide and thiosemicarbazide with trivalent metallic ions have been studied and postulated as octahedral with two ligand molecules acting in a tridentate manner (Ablov & Gerbelev, 1965). Owing to thione-thiol equilibrium the thiosemicarbazides (Walter & Schlichting, 1973) neutralize either one or two charges of the metallic ion. Several of these possibilities have been proposed and confirmed by crystallographic techniques (Ryabova, Ponomarev,

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