

Related literature. Two structures of the glycinate nickel compounds [diaquabis(glycinato-*O,N*)-nickel(II) (Castellano, Nascimento & Calvo, 1982); bis(glycinato-*N,O*)(2,2'-bipyridyl-*N,N'*)nickel(II) 5·5 hydrate (Žák, Głowiak, Kameníček & Březina, 1990)] are known. The coordination polyhedron around Ni can be approximated as an octahedron formed by the glycine O1 atom and by five water O atoms characterized by an average Ni—O distance of 2·056 (6) Å and O—Ni—O angle of 90 (2)° (with e.s.d.'s of arithmetic means in parentheses). This distance is significantly smaller than those in diaquabis(glycinato-*O,N*)nickel(II) [2·08 (1) Å; Castellano, Nascimento & Calvo, 1982], bis(glycinato-*N,O*)(2,2'-bipyridyl-*N,N'*)nickel(II) 5·5 hydrate [2·081 (2) Å; Žák, Głowiak, Kameníček & Březina, 1990] or in nickel oxide [2·084 (1) Å; Wyckoff, 1965]. Total bond valence of Ni—O calculated according to Brown & Altermatt (1985) equals 2·02 (theoretical value = 2·00). The glycine molecule is in its zwitterionic non-planar form: the N atom lies -0·335 Å out of the C1—C2—O1—O2 best plane located 0·002, -0·009, 0·003 and 0·003 Å from the defining atoms (see e.g. Solans, Franco & Miravittles, 1985). A comparison of this structure with glycine (Jönsson & Kvik, 1972) and triglycine sulfate (Solans, Franco & Miravittles, 1985; Žukov, Tafajenko & Fetisov, 1990) shows that the geometry of the amino acid is not significantly altered by coordination. The interplay among the distances and angles in the carboxylate group follows closely the relationships described by Borthwick (1980). Bond lengths and angles in the

sulfate anion are in the usual ranges. The O12 atom in the water molecule is 4·939 (2) Å from the Ni atom. The closest non-H atom of O12 is O8ⁱ ($i = \bar{x}, 0·5 + y, -0·5 - z$) located at a distance of 2·694 (2) Å. An inspection of the crystal packing shows that the bonding between the complex cation and the sulfate anion is predominantly ionic with the shortest distance O6—O9 = 2·664 (2) Å. All H atoms of water molecules and of the NH₃ group form hydrogen bonds with average distances and angles O^d—H^d = 0·87 (6), H^d...O^a = 1·9 (1), O^d...O^a = 2·76 (8) Å, O^d—H^d...O^a = 163 (7)° and N^d—H^d = 0·91 (2), H^d...O^a = 2·0 (1), N^d...O^a = 2·89 (10) Å and N^d—H^d...O^a = 166 (10)° (*d* indicates donor and *a* acceptor atoms).

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Semicarbazones and Thiosemicarbazones. XIV. Bis(2-methylthiosemicarbazide)-nickel(II) Nitrate

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Abstract. C₄H₁₄N₆NiS₂·2NO₃, *M_r* = 393·0, triclinic, *P*1̄, *a* = 7·114 (3), *b* = 7·760 (2), *c* = 6·718 (3) Å, α = 93·10 (3), β = 101·60 (3), γ = 76·49 (3)°, *V* = 353·2 Å³, *Z* = 1, *D_x* = 1·85 g cm⁻³, λ(Mo *K*α) = 0·71073 Å, μ = 1·85 cm⁻¹, *F*(000) = 202, *T* = 293 K, final *R* = 0·046 for 1180 reflections with *F* > 3σ(*F*).

The Ni^{II} ion lies in a square-planar environment in a *trans* configuration. The ligands are coordinated as bidentate through the S and hydrazine N atoms. The influence of the methyl group on N(2) is mainly reflected in the Ni—S distance [2·177 (1) Å] which is longer, and the Ni—N and C—S bond lengths [1·894 (3) and 1·716 (4) Å, respectively], which are shorter than those reported for similar compounds.

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Experimental. The title compound, $[\text{Ni}(\text{2-MeTSC})_2(\text{NO}_3)_2]$, was prepared by the reaction of $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ and 2-methylthiosemicarbazide in ethanol; suitable crystals were obtained by slow evaporation of the solution. Crystal $0.14 \times 0.26 \times 0.44$ mm mounted on glass fiber. Nicolet R3 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters from 25 reflections with $5.4 < 2\theta < 20.4^\circ$. 1349 reflections measured (unique 1243, $R_{\text{int}} 0.01$) with $3 < 2\theta < 50^\circ$ for half sphere, of which 1180 had $F > 3\sigma(F)$ and were used in refinement. Index range $h: 0 \rightarrow 8, k: \pm 9, l: \pm 7$. $\theta: 2\theta$ scan mode, variable scan speed ($4\text{--}30^\circ \text{ s}^{-1}$), scan width $2.2 + (K\alpha_1 - K\alpha_2)^\circ$. Two standard reflections ($0\bar{3}1, \bar{1}\bar{1}2$) monitored every 50 measurements; no significant variation. Lp corrections. Structure solved by heavy-atom method. Least-squares refinement (on F) of all non-H atoms anisotropic; H atoms of CH_3 group and N(1) atom riding on bonded C and N, H atoms attached to N(3) found on difference Fourier map at an advanced stage of

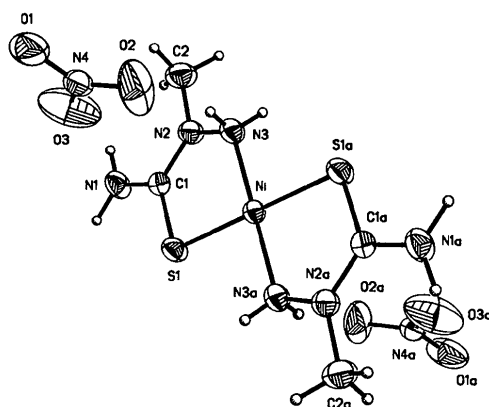


Fig. 1. The molecular conformation of $[\text{Ni}(\text{2MeTSC})_2](\text{NO}_3)_2$, showing the atom numbering.

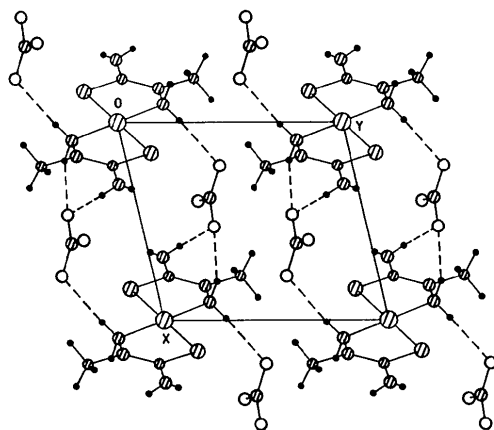


Fig. 2. The crystal structure of $[\text{Ni}(\text{2MeTSC})_2](\text{NO}_3)_2$. Broken lines indicate hydrogen bonds.

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Ni	10000	0	10000	25 (1)
S(1)	8433 (1)	-1163 (1)	7342 (1)	33 (1)
O(1)	2210 (5)	4101 (4)	9615 (7)	76 (2)
O(2)	5306 (6)	3207 (7)	10726 (7)	96 (2)
O(3)	4021 (9)	2735 (6)	7682 (7)	102 (2)
N(1)	6821 (5)	585 (5)	3940 (5)	39 (1)
N(2)	8284 (5)	2184 (4)	6547 (5)	31 (1)
N(3)	9080 (5)	2214 (4)	8669 (5)	31 (1)
N(4)	3844 (4)	3313 (4)	9380 (4)	34 (1)
C(1)	7802 (5)	662 (5)	5809 (5)	28 (1)
C(2)	7779 (7)	3852 (5)	5471 (6)	45 (1)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Ni—S(1)	2.177 (1)	Ni—N(3)	1.894 (3)
S(1)—C(1)	1.716 (4)	O(1)—N(4)	1.217 (5)
O(2)—N(4)	1.223 (5)	O(3)—N(4)	1.222 (6)
N(1)—C(1)	1.313 (4)	N(2)—N(3)	1.425 (4)
N(2)—C(1)	1.348 (5)	N(2)—C(2)	1.451 (5)
S(1)—Ni—N(3)	87.9 (1)	N(1)—C(1)—N(2)	120.3 (3)
Ni—S(1)—C(1)	97.4 (1)	N(3)—N(2)—C(1)	116.0 (3)
N(3)—N(2)—C(2)	117.3 (3)	C(1)—N(2)—C(2)	125.9 (3)
Ni—N(3)—N(2)	117.0 (2)	O(1)—N(4)—O(2)	122.3 (4)
O(1)—N(4)—O(3)	117.7 (4)	O(2)—N(4)—O(3)	119.8 (4)
S(1)—C(1)—N(1)	120.2 (3)	S(1)—C(1)—N(2)	119.6 (2)

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, $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$, with final $g = 0.003$ (where g is a 'fudge factor' refined each cycle to prevent unrealistic weight). In the last cycle $(\Delta/\sigma)_{\text{max}} = 0.025$; residual electron density within -0.70 to 0.93 e \AA^{-3} ; final $R = 0.046$ and $wR = 0.060$, $S = 1.345$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations performed on a Nova 45 with *SHELXTL* (Sheldrick, 1983). The shape of the molecule and the atomic numbering are indicated in Fig. 1.* The packing of the molecules in the unit cell is shown in Fig. 2. Final atomic parameters are given in Table 1 and bond distances and angles in Table 2.

Related literature. The crystal and molecular structure of Ni^{II} dithiosemicarbazide sulfate has been reported (Grönbæk & Rasmussen, 1962; Hazell, 1968). The so-called α -isomer is a trihydrate with a *trans*-planar structure [Ni—S length $2.16 (1) \text{ \AA}$]

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen bonds and short contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54387 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Grönbæk & Rasmussen, 1962). The β -isomer contains two independent sets of complex ions, one of *cis*- and another of *trans*-planar configuration (Hazell, 1968). The Ni—S bond of the *cis* complex is significantly shorter than that of the *trans* complex [2.149 (1) and 2.169 (1) Å, respectively]. The molecular structures of *cis* and *trans* nickel dithiosemicarbazide dinitrate have been determined [Hazell (1972), Ni—S bond lengths 2.150 (5) and 2.185 (1) Å respectively].

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2-Thia[3]ferrocenophane S-Oxide

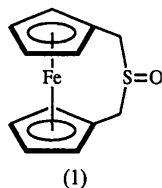
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Abstract. [Fe(η^5 -C₅H₄CH₂SOCH₂- η^5 -C₅H₄)], M_r = 260.1, $P2_1/c$, a = 13.195 (2), b = 7.476 (2), c = 10.541 (2) Å, β = 95.00 (2)°, V = 1035.9 (7) Å³, Z = 4, D_x = 1.668 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ = 16.13 cm⁻¹, $F(000)$ = 536, T = 299 K, R = 0.028 for 2465 observed data (of 3017 unique data). The η^5 -cyclopentadienyl ligands each exhibit a maximum deviation of 0.006 (2) Å from planarity. The bridging C atoms lie out of these planes by 0.114 (2) and 0.079 (2) Å toward Fe. The Fe atom lies 1.635 (1) Å from each plane. The two rings form a dihedral angle of 5.9 (5)°, and the Cp centroid—Fe—Cp centroid angle is 175.7°. The S=O distance is 1.501 (2) Å.

Experimental. The title compound (1) was prepared by 3-chloroperbenzoic acid oxidation of 2-thia[3]ferrocenophane (Ando, Hanyu, Kumamoto & Takata, 1986) and recrystallized from refluxing ethanol to afford yellow–orange needles, m.p. 474.5–475 K.



A needle fragment of dimensions 0.28 × 0.38 × 0.45 mm, was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Cell dimensions

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were determined at 299 K by a least-squares fit to setting angles of 25 reflections having $19 > \theta > 12^\circ$. One quadrant of data having $1 < \theta < 30^\circ$, $0 \leq h \leq 18$, $0 \leq k \leq 10$, $-14 \leq l \leq 14$ was measured by ω - 2θ scans at speeds ranging from 0.45 to 4.0° min⁻¹ to measure all significant data with approximately equal precision. Three standard reflections (500, 040, 004) exhibited only a random fluctuation in intensity so no correction for decay was applied. Data reduction included corrections for background, Lorentz, polarization and absorption. Absorption corrections were based on ψ scans, with maximum transmission coefficients 91.56%.

The space group was determined by systematic absences $h0l$ with l odd, and $0k0$ with k odd. The structure was solved by heavy-atom methods and refined by full-matrix least squares based on F , with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Determination Package* (Frenz, 1980), scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974), and data having $I > 3\sigma(I)$. Heavy-atom coordinates were refined with anisotropic thermal parameters; H-atom coordinates were located by ΔF synthesis and were refined with isotropic thermal parameters. Final R = 0.028 (R = 0.041 for all 3017 data), wR = 0.038, S = 1.810 for 185 variables. Largest shift was 0.02σ in the final cycle, maximum and minimum residual density 0.45 and -0.37 e Å⁻³, extinction coefficient $g = 8.9(5) \times 10^{-7}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c .

The fractional coordinates of the title compound are given in Table 1. Fig. 1 is a perspective drawing showing the atom numbering, and Fig. 2 is a unit-

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