normal and the respective values are in the ranges 1·361–1·408 Å and 117·5–121·6°. The three phenyl rings are non-coplanar; each of them is rotated so that they may be bonded to tin in the trigonal plane.

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Structure of a Nickel Complex with *p*-Nitrophenylazothiomethyl-*N*-phenylcarboximide Anion Radical

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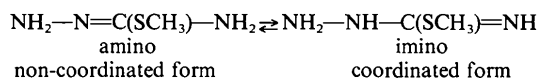(*Received 7 March* 1990; *accepted* 11 *February* 1991)

Abstract. $Ni[NO_2C_6H_4NNC(SCH_3)NC_6H_5]_2$, $M_r = 659\cdot3$, monoclinic, $P2_1/c$, $a = 11\cdot660\,(8)$, $b = 19\cdot428\,(6)$, $c = 13\cdot025\,(6)$ Å, $\beta = 90\cdot47\,(2)°$, $V = 2950\,(3)$ Å^3, $Z = 4$, $D_x = 1\cdot484$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1\cdot54178$ Å, $\mu = 26\cdot42$ cm^{-1}, $F(000) = 1360$, $T = 295$ K, $R = 0\cdot0470$, $wR = 0\cdot0533$ for 4264 reflections, $I \geq 2\sigma(I)$. The coordination of the Ni atom is tetrahedral. This is the first case of such a coordination polyhedron for nickel complexes with ligands derived from *S*-alkylisothiosemicarbazide.

Introduction. *S*-Alkylisothiosemicarbazides, R_1R_2-N(1)—N(2)=C(3)(SCH₃)—N(4)R_3R_4 (*L*), behave differently from those with a non-substituted sulfur atom R_1R_2—N—NH—CS—NR_3R_4. While the latter are coordinated by the metal *via* the S and N(1) atoms, the former use the N atoms N(1) and N(4)

(Malinowskii, Simonov, Gerbeleu, Yampol'skaya, Revenko & Shova, 1985).

It is known that the Ni^{II} complexes can form two types of coordination geometry with the *L* ligands: octahedral high-spin neutral or cationic complexes, such as [NiL₂(NO₂)₂] (Bourosh, Revenko, Simonov, Gerbeleu, Dvorkin & Malinowski, 1987) and [NiL₂im₂]I₂ (Revenko, Bourosh, Gerbeleu, Simonov, Virtosu & Malinowskii, 1989) and square-planar low-spin cationic complexes, such as [NiL₂]X₂ (Leovac, Babin, Canic & Gerbeleu, 1980) where $R_1 = R_2 = R_3 = R_4 = H$; $X = Cl$, Br, I.

In all these cases *L* is neutral and after coordination assumes the imino form

$$NH_2—N=C(SCH_3)—NH_2 \rightleftharpoons NH_2—NH—C(SCH_3)=NH$$
amino   imino
non-coordinated form   coordinated form

As has been shown (Simonov, Yampol'skaya, Shova, Gerbeleu, Bel'skii & Malinowskii, 1984) for the tridenate salicyladehyde S-methylisothiosemicarbazone copper complexes the isothiosemicarbazide moiety may behave like an anion, loosing a proton during the formation of the complex in alkaline medium.

Also reported (Simonov, Revenko, Bourosh, Gerbeleu, Virtosu, Indrichan, Tchumakov & Bel'skii, 1988) is the structure of an Ni^{II} complex with the ligand derived from 1-phenyl-substituted S-methylisothiosemicarbazide L^1 (e.g. L with $R_1 = C_6H_5$, $R_2 = R_3 = R_4 = H$).

The first step in this synthesis was the mixing of ethanolic solutions of $Ni(CH_3COO)_2.4H_2O$ and $L^1.HI$, but the expected product $NiL_2^1I_2$ (as was observed for L) has not been obtained. In order to increase the pH value of the solution, KOH has been added and dark-green stable crystals have been obtained. Their composition and structure were determined using magnetochemical data, NMR, X-ray diffraction and quantum-chemical calculations (Simonov, Revenko, Bourosh, Gerbeleu, Virtosu, Indrichan, Tchumakov & Bel'skii, 1988). The final formula of this product is $Ni(L^{1*}-2H)_2$. The ligand $(L^{1*}-2H)$ was formulated as a one-electron product of the oxidation of 1-phenyl-S-methylisothiosemicarbazide, the anion radical of phenylazothiomethylcarboximide: $C_6H_5-\bar{N}-N-C(SCH_3)=H$ $(L^{1*}-2H)$. The structure of the $Ni(L^{1*}-2H)_2$ is square-planar with Ni—N distances 1·835 (3)–1·854 (3) Å. These are evidently smaller than the values obtained for other complexes with S-alkylisothiosemicarbazides with such geometry (Malinowskii, Simonov, Gerbeleu, Yampol'skaya, Revenko & Shova, 1985). The steric hindrance due to the phenyl groups is minimized owing to the trans configuration of the complex. The values of the N4—C3 1·309 (4), N2—C3 1·346 (4) and N1—N2 1·354 (3) Å distances indicate an electron delocalization in the chelation rings and the complex was formulated (Revenko, Simonov, Virtosu, Gerbeleu, Bourosh, Bel'skii & Indrichan, 1988):
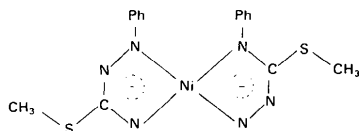
The further oxidation of the chelate $Ni(L^{1*}-2H)_2$ by iodine in chloroform solution yields the compound $Ni[C_6H_5NNC(SCH_3)NH]_2I_2$, where the ligand is the neutral molecule of phenylazothiomethylcarboximide. The structural investigation of this complex confirms the transfer of two electrons by iodine from the chelate molecule and the formation of a new octahedral compound with coordinated iodide ions (Revenko, Virtosu, Gerbeleu, Simonov, Bourosh & Sobolev, 1988).

In order to study the role of the steric hindrances in the stereochemistry of the complexes we have investigated the interaction of nickel acetate with 1-p-nitrophenyl-4-phenyl-S-methylisothiosemicarbazide $(L^2, p-NO_2-C_6H_4-NH-N=C(SCH_3)-NH-C_6H_5)$.

Experimental. The title compound $Ni(L^{2*}-2H)_2$ was prepared by the method described by Simonov, Revenko, Bourosh, Gerbeleu, Virtosu, Indrichan, Tchumakov & Bel'skii (1988). The crystallization from chloroform–ethanol mixture gave purple crystals. Crystal size was $0·15 \times 0·10 \times 0·30$ mm. Siemens AED diffractometer, monochromated Cu $K\alpha$ radiation, ω–2θ scan. Lattice parameters from setting angles of 22 reflections with $28 \leq \theta \leq 40°$, h: -14 to 14, k: 0 to 23, l: 0 to 15. 4264 observed reflections with $I \geq 2\sigma(I)$ ($2\theta \leq 140°$). Four standard reflections were measured for every 100 reflections and showed no significant variations. Lp correction, but no absorption correction was made. The structure was solved by means of the combination of heavy-atom and direct methods using SHELX programs (Sheldrick, 1976) and refined by a full-matrix least-squares method (on F) minimizing anisotropically for Ni, S, O, N, S, while the H atoms were refined isotropically. Final $R = 0·0470$ and $wR = 0·0533$, $w = \sigma^{-2}(F^2)$, $S = 1·72$, $(\Delta/\sigma)_{max} = 0·31$, max. height in the final difference map $0·39$ e Å^{-3}.

Final atomic coordinates with their e.s.d.'s are listed in Table 1.† Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV). All geometrical calculations performed with PARST (Nardelli, 1983) and CRYSRULER program system (Rizzoli, Sangermano, Calestani & Andreetti, 1987). Geometrical parameters of the complex are listed in Table 2.

Results. The molecular structure of the complex $Ni(L^{2*}-2H)_2$ is represented in Fig. 1. The coordination of the Ni atom is tetrahedral. This is the first example of an S-methylisothiosemicarbazide Ni^{II} complex series, when the coordination polyhedron of the Ni atom is represented as a tetrahedron. The endocyclic angles are 79·9 (1) and 80·5 (1)° and excyclic ones $-123·7$ (1) and 130·3 (1)°. The dihedral angle between the two metallocycle rings is 93·5 (1)°.

The distances Ni—N11 1·892 (2), Ni—N21 1·899 (2), Ni—N14 1·920 (2) and Ni—N24

$$Ni[NO_2C_6H_4NNC(SCH_3)NC_6H_5]_2$$

Table 1. Fractional atomic coordinates ($\times 10^4$)

	x	y	z
Ni	2742 (1)	3765 (1)	4593 (1)
S1	3427 (1)	1644 (1)	3612 (1)
S2	8313 (1)	4127 (1)	6166 (1)
O11	−493 (3)	3709 (2)	9380 (2)
O12	−959 (4)	2667 (2)	9226 (3)
O21	6566 (4)	4704 (4)	9232 (3)
O22	6762 (4)	3639 (2)	8855 (3)
N11	2033 (2)	3025 (1)	5286 (2)
N12	2230 (2)	2386 (1)	4943 (2)
N14	3398 (2)	3009 (1)	3854 (2)
N15	−500 (3)	3171 (2)	8918 (2)
N21	3460 (2)	4517 (1)	5273 (2)
N22	3095 (2)	5150 (1)	5052 (2)
N24	1955 (2)	4512 (1)	3957 (2)
N25	6384 (3)	4215 (2)	8686 (3)
C13	2992 (3)	2410 (1)	4159 (2)
C14	1336 (3)	3044 (1)	6159 (2)
C15	833 (4)	2459 (2)	6566 (3)
C16	237 (4)	2500 (2)	7468 (3)
C17	110 (3)	3132 (2)	7041 (2)
C18	582 (3)	3720 (2)	7538 (3)
C19	1186 (3)	3677 (2)	6643 (3)
C110	4285 (3)	3035 (2)	3091 (2)
C111	4013 (4)	3140 (2)	2067 (3)
C112	4874 (4)	3197 (2)	1358 (3)
C113	6017 (4)	3154 (2)	1859 (3)
C114	6277 (4)	3042 (2)	2678 (4)
C115	5416 (3)	2985 (2)	3383 (3)
C23	2285 (3)	5117 (1)	4309 (3)
C24	4238 (3)	4483 (1)	6095 (2)
C25	4479 (3)	5039 (2)	6733 (3)
C26	5215 (4)	4954 (2)	7572 (3)
C27	5690 (3)	4324 (2)	7757 (3)
C28	5490 (3)	3771 (2)	7118 (3)
C29	4768 (3)	3849 (2)	6289 (3)
C210	1027 (3)	4478 (1)	3220 (2)
C211	1260 (4)	4499 (2)	2178 (3)
C212	368 (4)	4453 (2)	1482 (3)
C213	−734 (4)	4379 (2)	1783 (4)
C214	−968 (4)	4357 (2)	2832 (4)
C215	−81 (3)	4407 (2)	3547 (3)
C1M	2731 (5)	1014 (2)	4374 (4)
C2M	2305 (5)	6520 (2)	4625 (4)

Table 2. Bond distances (Å) and bond angles (°)

Ni—N11	1·892 (2)	C14—C15	1·385 (5)
Ni—N14	1·920 (2)	C14—C19	1·394 (4)
Ni—N21	1·899 (2)	C15—C16	1·372 (6)
Ni—N24	1·903 (2)	C16—C17	1·382 (5)
S1—C13	1·728 (3)	C17—C18	1·374 (5)
S2—C23	1·738 (3)	C18—C19	1·369 (5)
S1—C1M	1·776 (5)	C110—C111	1·385 (5)
S2—C2M	1·774 (4)	C111—C112	1·374 (6)
O11—N15	1·207 (4)	C24—C29	1·400 (4)
O12—N15	1·187 (5)	C24—C25	1·391 (5)
O21—N25	1·204 (5)	C25—C26	1·394 (6)
O22—N25	1·222 (5)	C26—C27	1·364 (5)
N11—N12	1·339 (3)	C27—C28	1·377 (5)
N11—C14	1·404 (4)	C28—C29	1·371 (5)
N12—C13	1·360 (4)	C210—C215	1·371 (5)
N14—C13	1·317 (4)	C210—C211	1·387 (5)
N14—C110	1·441 (4)	C211—C212	1·378 (6)
N15—C17	1·465 (5)	C212—C213	1·355 (7)
N21—N22	1·334 (3)	C213—C214	1·396 (7)
N21—C24	1·399 (4)	C214—C215	1·389 (6)
N22—C23	1·348 (4)	C112—C113	1·389 (7)
N24—C23	1·318 (4)	C113—C114	1·377 (6)
N24—C210	1·442 (4)	C114—C115	1·371 (6)
N25—C27	1·466 (5)	C115—C110	1·373 (5)

N21—Ni—N24	80·0 (1)	C15—C16—C17	119·3 (4)
N14—Ni—N24	124·9 (1)	N15—C17—C16	119·1 (3)
N14—Ni—N21	130·3 (1)	C16—C17—C18	121·6 (4)
N11—Ni—N24	125·2 (1)	N15—C17—C18	119·2 (3)
N11—Ni—N21	123·7 (1)	C17—C18—C19	118·9 (3)
N11—Ni—N14	80·5 (5)	C14—C19—C18	120·4 (3)
C13—S1—C1M	103·1 (2)	N14—C110—C115	120·0 (3)
Ni—N11—C14	128·7 (2)	N14—C110—C111	120·6 (3)
Ni—N11—N12	117·9 (2)	C111—C110—C115	119·4 (3)
N12—N11—C14	113·4 (2)	C110—C111—C112	119·7 (4)
N11—N12—C13	109·5 (2)	C111—C112—C113	120·7 (4)
Ni—N14—C110	127·6 (2)	C112—C113—C114	119·0 (5)
Ni—N14—C13	112·3 (2)	C113—C114—C115	120·2 (4)
C13—N14—C110	120·1 (3)	C110—C115—C114	121·0 (4)
O11—N15—O12	123·1 (4)	N22—C23—N24	119·5 (3)
O12—N15—C17	118·4 (3)	N21—C24—C29	117·6 (3)
O11—N15—C17	118·5 (3)	N21—C24—C25	123·2 (3)
Ni—N21—C24	127·0 (2)	C25—C24—C29	119·3 (3)
Ni—N21—N22	118·0 (2)	C24—C25—C26	119·8 (3)
N22—N21—C24	114·4 (2)	C25—C26—C27	119·4 (4)
N21—N22—C23	109·4 (2)	N25—C27—C26	119·7 (4)
Ni—N24—C210	127·7 (2)	C26—C27—C28	121·8 (4)
Ni—N24—C23	113·0 (2)	N25—C27—C28	118·4 (3)
C23—N24—C210	119·2 (3)	C27—C28—C29	119·3 (3)
O21—N25—O22	123·6 (4)	C24—C29—C28	120·4 (3)
O22—N25—C27	118·4 (4)	N24—C210—C211	119·9 (3)
O21—N25—C27	117·9 (4)	N24—C210—C215	120·1 (3)
N12—C13—N14	119·7 (3)	C215—C210—C211	120·0 (4)
S1—C13—N14	121·9 (3)	C210—C215—C214	119·8 (4)
S1—C13—N12	118·4 (2)	C215—C214—C213	120·2 (5)
N11—C14—C19	117·7 (3)	C214—C213—C212	118·7 (5)
N11—C14—C15	122·6 (3)	C213—C212—C211	122·0 (4)
C15—C14—C19	119·7 (3)	C212—C211—C210	119·3 (4)
C14—C15—C16	120·0 (3)		
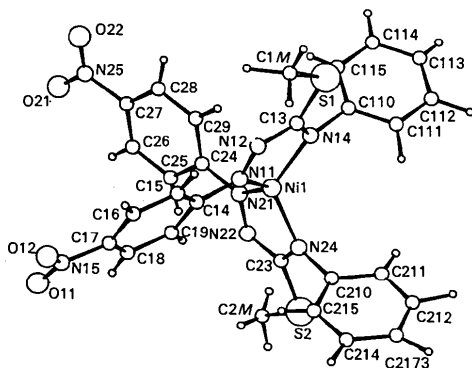
Fig. 1. Diagram showing the complex and corresponding atom numbering.

including its deprotonation and dehydrogenation. During this interaction the formation of an anion radical (L^{2*}-2H) takes place. The coordination of (L^{2*}-2H) by the Ni^{II} stablizes this intermediate state and produces the chelate Ni(L^{2*}-2H)$_2$, which is diamagnetic.

In the square-planar series of these complexes diamagnetism is the result of delocalization of the π-electron density of both chelate rings *via* the Ni atom. In the tetrahedral state Ni^{II} has two lone electrons and is generally paramagnetic. In the case of Ni(L^{2*}-2H)$_2$ each lone nickel electron participates in delocalization with 5π electrons of the ligand system and forms two pseudoaromatic metallocycles. The fundamental state of the complex is that of a singlet.

1·905 (2) Å are longer than those found in the square-planar complex (Simonov, Revenko, Bourosh, Gerbeleu, Virtosu, Indrichan, Tchumakov & Bel'skii, 1988). The final ΔF synthesis clearly shows evidence that none of the H atoms are bonded to any of the N atoms. All this suggests that the ligand L^2 is subject to the same modifications observed for L^1,

The *p*-nitrophenyl rings make dihedral angles of 9·5 (1) and 89·1 (1)° with the chelation rings, while the phenyl radicals make angles of −88·4 (1) and 14·4 (1)°.

The presence of the bulky groups in the 1 and 4 positions causes the formation of the tetrahedral complexes.

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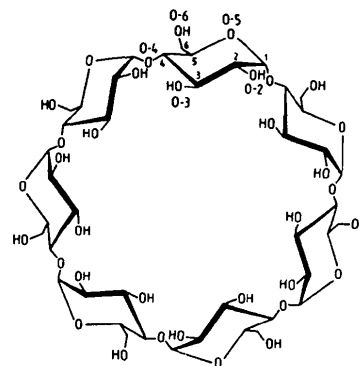# β-Cyclodextrin–Potassium Hydroxide–Water (1/1/8)

By P. CHARPIN, I. NICOLIS, F. VILLAIN, C. DE RANGO AND A. W. COLEMAN

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Abstract. $C_{42}H_{70}O_{35}.K^+.OH^-.8H_2O$, $M_r = 1335·24$, monoclinic, $P2_1$, $a = 15·223$ (5), $b = 10·578$ (3), $c = 20·204$ (6) Å, $\beta = 108·37$ (7)°, $V = 3087$ Å^3, $Z = 2$, $D_x = 1·436$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 1·876$ mm^{-1}, $F(000) = 1420$, $T = 295$ K, final $R = 0·080$ for 4774 observed reflections. The cyclodextrin molecules are stacked, as monomeric entities, inclined at 43·4° along the twofold screw axis, forming a classical herringbone scheme. Three O atoms, attributed to water molecules, are found inside the cyclodextrin cavity, two of them being hydrogen bonded to the two primary hydroxyl groups which are in a *gauche–trans* conformation. Six others, present as doublets or singlets of water molecules, are located between the cyclodextrin entities and ensure the packing *via* hydrogen bonding. The potassium ion is incorporated in an interstitial site and coordinated to six non-water O atoms which belong to four different cyclodextrin units, in a distorted trigonal-prism environment. It is suggested that the balancing negative charge is localized inside the cavity, one of the three water molecules being in fact a hydroxyl anion.

Introduction. Cyclodextrins, cyclic oligosaccharides consisting of six, seven or eight α-1→4-linked glucose units, have attracted interest owing to their ability to form inclusion compounds with a wide variety of 'guest' molecules; such complexes are used in the pharmaceutical and food industries. (Szetjli, 1989). However, their interaction with metals has

β-Cyclodextrin