

## DETERMINATION OF THE STRUCTURE OF BIS(PROPYLDITHIO-CARBAMATE)NICKEL(II)

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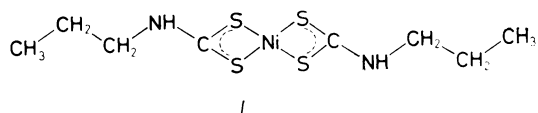
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The crystal and molecular structure of the title compound (C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>NiS<sub>4</sub>) was solved by the heavy atom method and the structure was refined anisotropically to a final *R* factor of *R* = 0.029 (*wR* = 0.037) for 715 observed reflections. The crystal is monoclinic, space group *P*2<sub>1</sub>/*c* with *a* = 948.3(2), *b* = 776.9(2), *c* = 1167.4(2) pm, β = 125.14(2)°, *Z* = 2. The molecule contains two four-membered NiSCS rings of approximately planar configuration with the Ni atom situated at a centre of symmetry. The molecules are arranged in chains along the *c*-axis of the unit cell.

The dithiocarbamates are ligands suitable for stabilization of high oxidation states of metals. From this point of view we have studied systematically bis(monoalkyl-dithiocarbamates)nickel(II) as starting materials. In a previous work<sup>1</sup> we prepared bis(propyldithiocarbamate)nickel(II) (*I*) as prototype. A magnetic study shows that



this complex is diamagnetic with square planar coordination around nickel(II). The aim of this work is to determine the structure of this compound and to compare it with the published structure of the bis(dipropyldithiocarbamate)nickel(II)<sup>2</sup>.

### EXPERIMENTAL

The complex was prepared by reaction of a 3.01 ml carbon disulphide and 4.24 ml propylamine in 15 ml ethanol with the solution of 5.94 g nickel(II) chloride hexahydrate in 20 ml water (molar ratio CS<sub>2</sub> : C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub> : NiCl<sub>2</sub>·6 H<sub>2</sub>O = 1 : 1 : 0.5). The dark green crystals obtained were

filtered off after 15 min, washed thoroughly with water and dried at 40°C. The single crystals for the structural purpose were obtained by recrystallization of the complex obtained from a mixture of benzene-tetrachloromethane (1 : 1). All reagents were of c.p. grade.

For  $C_8H_{16}N_2NiS_4$  (327.2) calculated 29.37% C, 4.93% H, 8.56% N, 17.93% Ni; found 29.17% C, 5.27% H, 8.13% N, 17.62% Ni. The elemental analysis was carried out on the CHN-Analyser (Laboratorní přístroje, Prague). The content of nickel was determined by chelometry.

The density of the crystals was estimated by flotation in a solution of KI at 295 K. Preliminary dimensions of the unit cell and the space group symmetry were determined from Weissenberg and precession patterns (conditions for reflection  $h0l$ :  $l = 2n$ ;  $0k0$ :  $k = 2n$ ). A single crystal with dimensions of  $0.3 \times 0.15 \times 0.1$  mm was selected for X-ray measurement on an Enraf-Nonius CAD 4 four-circle diffractometer. Graphite-monochromated  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) was used. The lattice parameters were refined from a set of 22 centered reflections  $5.22^\circ \leq \theta \leq 19.86^\circ$ . The intensities were measured using a  $\omega/2\theta$  scan at 296 K. A total of 1 338 independent reflections were obtained in the reciprocal space quadrants:  $-11 \leq h \leq 0$ ,  $-9 \leq k \leq 0$ ,  $-13 \leq l \leq 0$ ,  $\theta \leq 50^\circ$ .

On the basis of the condition  $I > 3\sigma(I)$  only 715 reflections were considered as observed. The scan speed varied between 1.6 and 16.5°/min. Two standard reflections (0 2 0 and 0 0 - 4) were measured every 2 hours and showed no significant intensity fluctuation (0.8%). The correction for absorption was neglected ( $\mu = 1.92$  mm<sup>-1</sup>). The non-hydrogen atoms were refined anisotropically, the H-atoms isotropically.

The structure was solved using of the Patterson function. An electron density map rescaled the positions of all non-hydrogen atoms. H-atoms coordinates were obtained from a difference electron-density map. In refinement the quantity  $\sum w(|F_o| - |F_c|)^2$  was minimized by full-matrix least squares. In the final refinement cycle, the maximal value was  $\Delta/\sigma = 0.01$ . The final *R*-factor values are:  $R = 0.029$ ,  $wR = 0.037$  where  $w = (\sigma^2 F_o + 0.02 F_o^2)^{-1}$ . The residual maximum on the final difference electron density map was 0.32 e/(100 pm)<sup>3</sup>. All calculations were carried out using the SDP system<sup>3</sup> on a PDP 11/73 computer.

## RESULTS AND DISCUSSION

The basic crystallographic data for the title compound are given in the Table I. The final parameters for non-hydrogen atoms are summarized in Table II. The important interatomic distances and angles are listed in Table III.

A perspective view of the molecule of *I* is given in Fig. 1. The thermal ellipsoids are drawn with 50% probability. Fig. 2 shows the molecular packing of the unit cell.

The structure is composed of isolated molecules, no evidence of H-bonding was found. The Ni atom which occupies the centre of symmetry is coordinated by four S atoms from two molecules of the ligand in a slightly distorted square planar arrangement, the S1—Ni—S2 angle being 79.9°.

The structure of *I* which is the first solved structure of bis(monoalkylthiocarbamate)nickel(II) can be compared with those<sup>4</sup> of  $[Ni(S_2C.N(C_2H_5)_2)_2]$  (*II*) and  $[Ni(S_2C.N(C_3H_7)_2)_2]$  (*III*). Whilst all equivalent ring distances and angles of *I*, *II*, *III* are equal within experimental errors, the C1—N distance of the present complex 129.5 pm is significantly shorter (133 pm for *II*, *III*). This fact can be attributed to

TABLE I  
Basic crystallographic data of bis(propyldithiocarbamate)nickel(II)

$a = 948.3(2)$ pm	$\beta = 125.14(2)^\circ$	Space group $P2_1/c$
$b = 776.9(2)$ pm	$V = 703.4(4) \cdot 10^6$ pm <sup>3</sup>	$\rho_c = 1.545$ g cm <sup>-3</sup>
$c = 1167.4(2)$ pm	$Z = 2$	$\rho_o = 1.54$ g cm <sup>-3</sup>

TABLE II  
The fractional coordinates of the non-hydrogen atoms ( $\cdot 10^4$ ) and their equivalent displacement parameters  $B_{eq}$  ( $\cdot 10^2$  pm<sup>2</sup>)  $B_{eq} = \frac{4}{3} (\sum_i \sum_j \beta_{ij} a_i a_j)$

Atoms	$x/a$	$y/b$	$z/c$	$B_{eq}$
Ni	5 000	5 000	5 000	3.77(2)
S1	2 921(1)	4 659(2)	5 291(1)	4.57(3)
S2	6 219(1)	6 146(2)	7 083(1)	4.71(3)
N	3 878(3)	6 345(5)	7 647(3)	4.73(9)
C1	4 273(4)	5 781(6)	6 820(4)	3.9(1)
C2	2 250(5)	6 141(7)	7 490(4)	5.5(1)
C3	2 524(5)	5 544(7)	8 834(4)	5.7(1)
C4	0 871(5)	5 514(9)	8 735(5)	7.5(2)

TABLE III  
The interatomic distances (pm) and angles ( $^\circ$ )

Bond	Distance	Atoms	Angle
Ni-S1	220.2(1)	S1-Ni-S2	79.92(4)
Ni-S2	219.3(1)	Ni-S1-C1	84.3(2)
S1-C1	171.9(4)	Ni-S2-C1	84.7(1)
S2-C1	171.1(4)	C1-N-C2	127.6(3)
N-C1	129.5(7)	S1-C1-S2	110.7(3)
N-C2	145.5(6)	N-C2-C3	111.6(3)
C2-C3	150.8(8)	C2-C3-C4	112.1(3)
C3-C4	150.5(8)		

the larger induction effect of  $\text{NR}_2$  group compared to  $\text{NHR}$  group. The  $P2_1/c$  space group of the present structure is the same as for *II*, while for *III* the space group  $R\bar{3}$  was found.

The title compound was successfully employed<sup>5</sup> as a starting material for the preparation of Ni(III) complexes of the  $[\text{Ni}(\text{C}_4\text{H}_8\text{NS}_2)_2]\text{X}$ , where  $\text{X} = \text{Br}^-$ ,  $\text{ClO}_4^-$ .

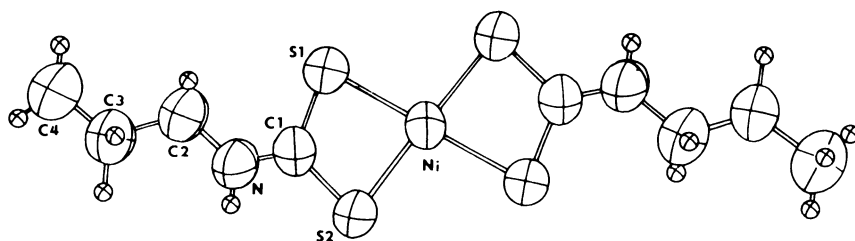


FIG. 1  
Perspective view of *I*

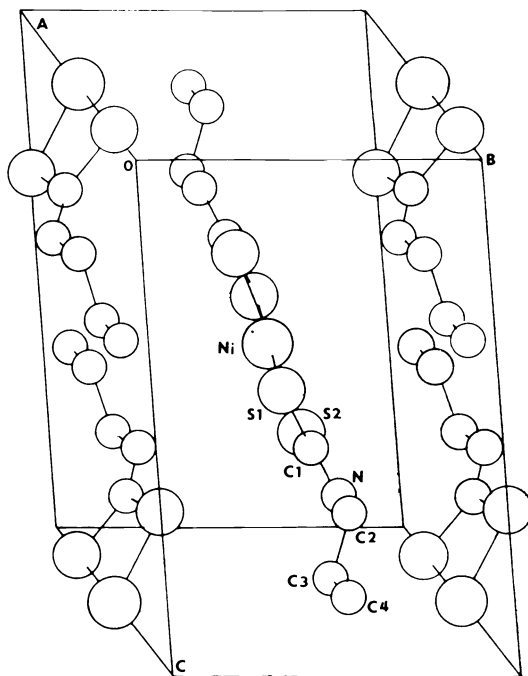


FIG. 2  
The molecular packing (viewed along the *a* axis)

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