

Structure of Bis(*N*-acetyl-*N*-benzylthiocarbamato)nickel(II)

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**Abstract.**  $[\text{Ni}(\text{C}_{10}\text{H}_{10}\text{NOS}_2)_2]$ ,  $M_r = 507.34$ , triclinic,  $P\bar{1}$ ,  $a = 7.4881$  (8),  $b = 19.6134$  (23),  $c = 7.4784$  (23) Å,  $\alpha = 90.78$  (1),  $\beta = 93.14$  (1),  $\gamma = 93.46$  (1)°,  $V = 1094.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.55$ ,  $D_x = 1.54$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha_1) = 0.70930$  Å,  $\mu = 1.275$  mm<sup>-1</sup>,  $F(000) = 524$ ,  $T = 295$  K,  $R = 0.062$ ,  $wR = 0.083$  for 3099 observed unique reflections. There are two independent centrosymmetric molecules in the unit cell. The Ni atoms occupy special positions, symmetry  $\bar{1}$ , and are planar-coordinated by four S atoms [Ni–S 2.195 (2)–2.206 (2) Å, S–Ni–S 78.60 (8)–78.82 (8)°]. The S<sub>2</sub>CNC<sub>2</sub> ligands are nearly planar, dimensions S–C 1.691 (9)–1.698 (9) Å, S–C–S 110.7 (5)–110.9 (5)°, C–N 1.37 (1)–1.38 (1), N–C(benzyl) 1.46 (1)–1.47 (1), N–C(acetyl) 1.42 (1)–1.44 (1) Å. The molecules are held together by van der Waals forces.

**Introduction.** In the past decade, a series of crystal structures of  $\text{Ni}(R_2\text{dtc})_2$  (dtc = dithiocarbamato) complexes were determined to delineate the effects of change of ligand substituent *R* on the ligand geometry and electron distribution (Coucovanis, 1979, and references therein). Since the accumulation of structural data of new dithiocarbamato compounds with different ligand substituents is highly desirable for comparison purposes, the investigation of the crystal structure of the title compound was undertaken.

**Experimental.** Crystal size 0.4 × 0.4 × 0.2 mm,  $D_m$  was measured by flotation in KI.H<sub>2</sub>O. Philips PW 1100 four-circle diffractometer, graphite-monochromatized Mo *K*α radiation. Cell parameters by least squares from setting angles of 59 reflections with 38° < 2θ < 48°. Data collection: θ/2θ scan, scan speed 0.06° s<sup>-1</sup>, scan width 2°,  $(\sin\theta/\lambda)_{\text{max}} = 0.59$  Å<sup>-1</sup>,  $-8 \leq h \leq 8$ ,  $-23 \leq k \leq 23$ ,  $-8 \leq l \leq 8$ . Three standard reflections measured every 60 min, no indication of deterioration. 9095 reflections measured over the whole sphere of reciprocal lattice averaged to 3451 unique reflections of which 352 had  $I < 2\sigma(I)$  and were considered as unobserved. No absorption correction was applied.

Structure solved by heavy-atom method. Least-squares refinement based on *F*,  $w = 1$ , anisotropic, H atoms from  $\Delta F$  synthesis and geometry, coordinates

refined, isotropic temperature factors, assigned the  $B_{\text{eq}}$  values of the atoms to which they were bonded. Final  $R = 0.062$ ,  $wR = 0.083$ ,  $S = 2.53$ ,  $(\Delta/\sigma)_{\text{max}} = 0.15$ ; residual electron density in final difference map within ±0.8 e Å<sup>-3</sup>; no extinction correction applied. Scattering factors for neutral atoms and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974). All computations were performed on a Univac 1106 computer with *DATRED* (Main, 1970) for data reduction, *BP70* (Ito & Sugawara, 1983) for best-plane calculations and *XRAY72* system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) for structure refinement and other calculations.

**Discussion.** Final atomic parameters are given in Table 1\* and selected bond lengths and angles in Table 2. There are two independent centrosymmetric molecules in the unit cell with the Ni atoms occupying the special positions (0,0,0) and (0,½,0) respectively. A view of the asymmetric unit of the structure with the atomic numbering scheme is shown in Fig. 1. The Ni atoms are coordinated to four S atoms in a perfect square-planar arrangement because of the  $\bar{1}$  symmetry of the Ni sites. As in other related compounds the dithiocarbamato ligands, S<sub>2</sub>CNC<sub>2</sub>, are almost planar in both molecules with the Ni atoms deviating from the ligand planes by 0.131 (6) and 0.166 (7) Å respectively. The angles formed between the central NiS<sub>4</sub> plane on the one hand, and the planes of the dithiocarbamato ligand and the acetyl group on the other, do not exceed 16°. Hence, the major part of each molecule is essentially planar, with the two benzene rings roughly perpendicular to the molecular mean plane on opposite sides of it (Fig. 1), giving rise to a propeller-like shape. An analogous molecular conformation occurs also in bis(*N*-methyl-*N*-phenylthiocarbamato)nickel(II) (Martin, Newman, Robinson & White, 1972).

\* Lists of structure amplitudes, anisotropic temperature factors, positional parameters of H atoms, also bond lengths and angles involving H atoms and details of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42791 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

All the corresponding bond distances and angles in the two molecules agree to within  $3\sigma_{\text{combined}}$ . However, some differences between corresponding dihedral angles in the two molecules are significant. Mean bond distances and angles are: Ni—S 2.200 (2), S—C 1.695 (1), C—N 1.38 (1), N—C(benzyl) 1.47 (1), N—C(acetyl) 1.43 (1) Å, S—Ni—S 78.7 (1) and S—C—S 110.8 (1)°.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{Å}^2$ ) of the non-hydrogen atoms with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = 8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

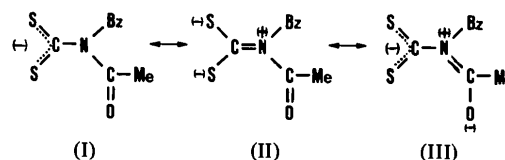
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Ni(1)	0	0	0	2.30 (4)
Ni(2)	0	½	0	2.84 (4)
S(1)	2500 (3)	-524 (1)	-171 (3)	2.81 (5)
S(2)	694 (3)	-175 (1)	2846 (3)	3.03 (6)
S(3)	-522 (3)	4422 (1)	-2545 (3)	3.41 (6)
S(4)	2736 (4)	4853 (1)	-782 (3)	3.62 (6)
O(1)	3016 (8)	-384 (3)	5781 (7)	3.4 (2)
O(2)	5393 (8)	4553 (4)	-3034 (9)	4.6 (2)
N(1)	3936 (8)	-763 (3)	3117 (8)	2.2 (2)
N(2)	2556 (9)	4204 (3)	-4094 (9)	2.9 (2)
C(1)	2554 (10)	-509 (4)	2098 (10)	2.4 (2)
C(2)	5432 (10)	-1032 (4)	2180 (11)	2.7 (2)
C(3)	5089 (11)	-1775 (4)	1552 (10)	2.5 (2)
C(4)	3674 (14)	-2194 (5)	2099 (13)	4.0 (3)
C(5)	3471 (18)	-2876 (6)	1491 (16)	5.5 (4)
C(6)	4675 (20)	-3128 (6)	381 (16)	5.9 (4)
C(7)	6042 (18)	-2722 (7)	-155 (15)	5.7 (4)
C(8)	6270 (13)	-2038 (6)	390 (13)	4.2 (3)
C(9)	3992 (10)	-733 (4)	5020 (10)	2.6 (2)
C(10)	5287 (13)	-1167 (6)	6002 (12)	4.1 (3)
C(11)	1743 (11)	4461 (4)	-2638 (11)	3.1 (2)
C(12)	1422 (12)	3970 (5)	-5666 (11)	3.3 (2)
C(13)	855 (11)	3217 (4)	-5720 (11)	2.8 (2)
C(14)	-151 (16)	2969 (6)	-7204 (15)	5.3 (3)
C(15)	-673 (18)	2278 (7)	-7382 (18)	6.6 (4)
C(16)	-227 (16)	1838 (6)	-6043 (19)	5.8 (4)
C(17)	733 (13)	2089 (5)	-4544 (16)	4.5 (3)
C(18)	1270 (12)	2771 (5)	-4368 (13)	4.0 (3)
C(19)	4476 (12)	4238 (5)	-4127 (13)	3.9 (3)
C(20)	5196 (15)	3836 (6)	-5595 (15)	5.2 (3)

Table 2. Selected bond lengths (Å) and angles (°) and intermolecular contact distances shorter than the sum of the corresponding van der Waals radii

Ni(1)—S(1)	2.198 (2)	Ni(2)—S(3)	2.206 (2)
Ni(1)—S(2)	2.199 (2)	Ni(2)—S(4)	2.195 (2)
S(1)—C(1)	1.695 (8)	S(3)—C(11)	1.698 (9)
S(2)—C(1)	1.694 (8)	S(4)—C(11)	1.691 (9)
C(1)—N(1)	1.37 (1)	C(11)—N(2)	1.38 (1)
N(1)—C(2)	1.47 (1)	N(2)—C(12)	1.46 (1)
N(1)—C(9)	1.42 (1)	N(2)—C(19)	1.44 (1)
C(9)—O(1)	1.19 (1)	C(19)—O(2)	1.18 (1)
C(9)—C(10)	1.50 (1)	C(19)—C(20)	1.49 (2)
S(1)—Ni(1)—S(2)	78.82 (8)	S(3)—Ni(2)—S(4)	78.60 (8)
S(1)—C(1)—S(2)	110.9 (4)	S(3)—C(11)—S(4)	110.7 (5)
C(1)—N(1)—C(2)	117.9 (6)	C(11)—N(2)—C(12)	118.3 (7)
C(1)—N(1)—C(9)	121.6 (6)	C(11)—N(2)—C(19)	120.2 (7)
C(2)—N(1)—C(9)	120.3 (6)	C(12)—N(2)—C(19)	121.1 (7)
N(1)—C(9)—O(1)	120.6 (7)	N(2)—C(19)—O(2)	121.7 (8)
N(1)—C(9)—C(10)	117.2 (7)	N(2)—C(19)—C(20)	115.1 (8)
O(1)—C(9)—C(10)	122.2 (7)	O(2)—C(19)—C(20)	123.2 (9)
S(2)...S(2')	3.511 (3)	S(4)...S(4 <sup>iv</sup> )	3.537 (3)
O(1)...S(1 <sup>iv</sup> )	3.087 (6)	O(2)...S(3 <sup>v</sup> )	3.084 (7)
O(1)...S(2')	3.259 (7)	O(2)...S(4 <sup>iv</sup> )	3.275 (7)
O(1)...C(9 <sup>iv</sup> )	3.13 (1)	O(2)...C(19 <sup>iv</sup> )	3.21 (1)
C(9)...C(9 <sup>iii</sup> )	3.17 (1)	C(19)...C(19 <sup>iv</sup> )	3.35 (2)

Symmetry code: (i)  $-x, -y, 1-z$ ; (ii)  $x, y, 1+z$ ; (iii)  $1-x, -y, 1-z$ ; (iv)  $1-x, 1-y, -z$ ; (v)  $1+x, y, z$ ; (vi)  $1-x, 1-y, -1-z$ .

The dimensions of the  $\text{NiS}_4\text{C}_2$  group are in good agreement with those found in many di-*n*-alkyl complexes, *e.g.*  $\text{Ni}(\text{CS}_2\text{NET}_2)_2$  (Bonamico, Dessy, Mariani, Vaciego & Zambonelli, 1965),  $\text{Ni}(\text{CS}_2\text{N}^{\text{Pr}}\text{Pr}_2)_2$  (Peyronel & Pignedoli, 1967), and also in  $\text{Ni}(\text{CS}_2\text{-NMePh})_2$  (Martin *et al.*, 1972). This indicates that the ligand substituents of the title compound do not appreciably change the field experienced by the Ni atom relative to the above complexes. However, some differences are found in the geometry of the ligands themselves. Specifically, the lengths of the C—N bonds close to the  $\text{NiS}_4$  groups are significantly larger than those of the above-mentioned compounds, where they range from 1.30 (1) to 1.33 (1) Å. Moreover, in our case the lengths of the N—C bonds adjacent to the acetyl groups are significantly shorter than those which are adjacent to the benzyl groups and which are typical N—C single bonds [1.472 (5) Å, *International Tables for X-ray Crystallography* (1968)]. These differences may be attributed to the acetyl substituent of the dithiocarbamate ligand and can be readily explained if we assume the following resonance structures:



While (I) and (II) are sufficient for the description of the normal state of dithiocarbamate ligands, in the present case the structure type (III) should also be taken into account. This gives rise to a reduced contribution of (II) and hence to less double-bond character in the C—N bond of the  $\text{S}_2\text{CN}$  moiety. Further, it can be deduced from (III) that the N—C(acetyl) bond should also exhibit some double-bond character. This is also supported by the observed approximate coplanarity of the dithiocarbamate and acetyl groups. Bond distances and angles in the benzene rings are normal.

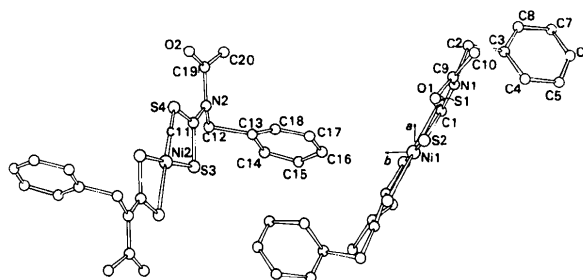


Fig. 1. View of the asymmetric unit of the structure along [001].

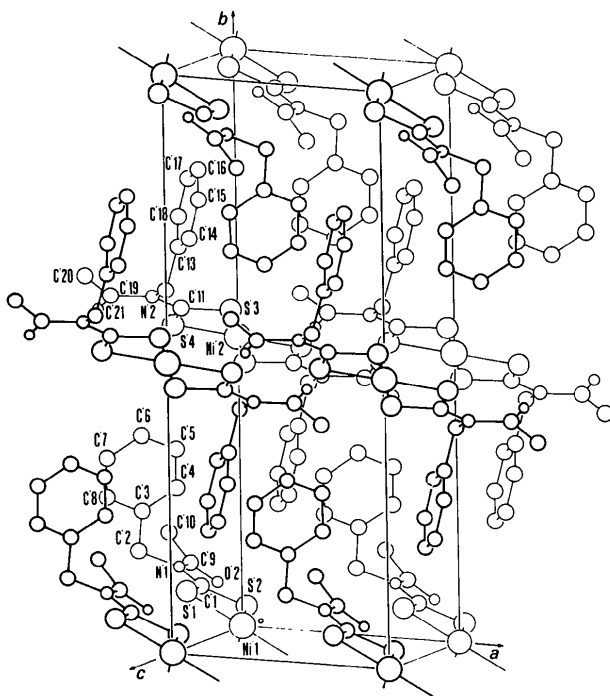


Fig. 2. Clinographic projection of the structure along *c*, showing the molecular packing.

Some very short intramolecular contact distances involving H atoms occur [S(1)···H1(C2) 2.54 (10), S(3)···H2(C12) 2.51 (11), N(1)···H(C4) 2.54 (11) and N(2)···H(C18) 2.54 (11) Å], the S···H and N···H van der Waals distances being 3.00 and 2.75 Å, respectively (Bondi, 1964)]. Since the observed *X*···

H—C angles (*X* = S, N) are less than 117° these close contacts probably do not involve hydrogen bonding. There are no unusual intermolecular *X*···H interactions and the crystal cohesion is thus dominated by normal van der Waals forces. A clinographic projection of the structure showing the molecular packing is shown in Fig. 2.

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### Structure of Dichloro[2,5-dimethyl-1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-diazahexane-*N,N',N'',N'''*]cadmium(II)

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**Abstract.** [CdCl<sub>2</sub>(C<sub>16</sub>H<sub>28</sub>N<sub>6</sub>)], *M<sub>r</sub>* = 487.76, orthorhombic, *Pbcn*, *a* = 15.936 (2), *b* = 8.4044 (8), *c* = 15.454 (2) Å, *V* = 2069.8 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* =

1.565 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 13.1 cm<sup>-1</sup>, *F*(000) = 989.1, *T* = 295 K, molecular symmetry *C*<sub>2v</sub>, *R* = 0.031 for 1747 significant reflections. The coordination of the cadmium atoms is distorted octahedral, although no unusual bond lengths or angles occur [Cd—Cl 2.501 (1) Å, Cd—N 2.478 (3) and 2.431 (3) Å]. The coordination geometry is similar to

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