

Structure of bis(di-n-butyldithiocarbamato)nickel(II)

^aJ. LOKAJ, ^bV. VRÁBEL, and ^bE. KELLÖ

^aDepartment of Microanalysis, Slovak Technical University,
CS-812 37 Bratislava

^bDepartment of Analytical Chemistry, Slovak Technical University,
CS-812 37 Bratislava

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Crystal and molecular structure of bis(di-n-butyldithiocarbamato)nickel(II), $\text{Ni}[\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2]_2$ has been determined by single-crystal X-ray diffraction methods and refined by diagonal-matrix least squares to a residual of 0.06 on 1080 "observed" reflections. Crystals are monoclinic with space group $P2_1/a$, $a = 1.6012(5)$ nm, $b = 0.7887(3)$ nm, $c = 1.0804(6)$ nm, $\beta = 118.48(3)^\circ$. The experimentally observed density is 1.27 g cm^{-3} and the calculated value of $Z = 2$ is 1.29 g cm^{-3} . In the structure the Ni atom occupies a special position in the centre of symmetry and is coordinated by two pairs of S atoms from two ligands in a plane: Ni—S $0.2201(3)$ nm and $0.2211(3)$ nm, S(1)—Ni—S(2) angle being $79.40(1)^\circ$. Ligand S_2CNC_2 is essentially planar.

Изучена кристаллическая и молекулярная структура бис(ди-н-бутилдителиокарбамато)никеля(II), $\text{Ni}[\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2]_2$ методом монокристаллической рентгеновской дифракции и уточнена с помощью метода наименьших квадратов с использованием диагонализированной матрицы до величины R-фактора 0,06 при 1080 «наблюдаемых» дифракциях. Кристаллы являются моноклинными и относятся к пространственной группе $P2_1/a$, $a = 1,6012(5)$ нм, $b = 0,7887(3)$ нм, $c = 1,0804(6)$ нм, $\beta = 118,48(3)^\circ$. Экспериментально наблюдаемая плотность равна $1,27 \text{ г см}^{-3}$, а рассчитанное значение при $Z = 2$ равно $1,29 \text{ г см}^{-3}$. В данной структуре атом Ni занимает особое положение в центре симметрии и плоскостно координирован с двумя парами атомов S из двух лигандов: связь Ni—S $0,2201(3)$ нм и $0,2211(3)$ нм, угол S(1)—Ni—S(2) равен $79,40(1)^\circ$. Лиганд S_2CNC_2 приблизительно плосок.

Dithiocarbamato anion (further dtc) easily forms complex compounds with many transition and nontransition metals. Crystal structures of these complexes have been investigated in a considerable extent in view of their utilization in chemical analysis, biological activity, and a great number of crystal and molecular types

which these compounds form, depending on the nature of the central metal atom and the substituent in the dtc ligand.

The type of the coordination bond, coordination symmetry, and geometry of dtc complexes is considerably sensitive to electron configuration of the central metal ion and the substituent in the ligand. Dtc complexes of transition metals, which do not undergo distortion resulting from Jahn—Teller theorem, are characterized by the equivalency of M—S and C—S bonds in the chelate ring.

Of the dtc complexes of transition metals in oxidation state II, nickel compounds with precise planar symmetry of the NiS₄ coordination core, required by crystallographic symmetry (atom Ni occupies the symmetry centre) [1—5], have been most extensively investigated. Small distortions of planar coordination have been observed in the unsubstituted dtc derivative of Ni (tetrahedral nature of distortion) [6] and in Ni (hexamethylene dtc)₂ (pyramidal deviation of Ni atom from the best plane constructed through four sulfur atoms) [7]. This paper deals with the structural study of Ni(di-n-butyl dtc)₂.

Experimental and results

Crystals of the Ni[S₂CN(C₄H₉)₂]₂ compound (relative molecular mass 467.45) with the following elemental analysis were prepared using the procedure previously described [5]

	C	H	N	S
$w_i(\text{calc.})/\%$	46.24	7.76	5.99	27.43
$w_i(\text{found})/\%$	45.80	7.20	5.72	28.52

Crystals are needles of green colour with monoclinic symmetry. The dimensions of the unit cell found from the rotation and Weissenberg patterns were refined by the least-square fit on the Syntex P2₁ diffractometer. The 12 precisely centred reflections yielded the following values: $a = 1.601(5)$ nm, $b = 0.7887(3)$ nm, $c = 1.0804(6)$ nm, $\beta = 118.48(3)^\circ$. The experimentally observed density of 1.27 g cm⁻³ (measured by flotation in bromoform—ethanol mixture) agrees well with the value calculated, assuming two formulae units per unit cell ($D_c = 1.29$ g cm⁻³). Systematic absence of reflections of the $h01$ type for $h = 2n + 1$ and of the type $0k0$ for $k = 2n + 1$ indicated space group $P2_1/a$ (C_{2h}^5 , No. 14). The diffraction intensities were collected on the Syntex P2₁ diffractometer by the Θ — 2Θ scan technique with a take-off angle of 1.5° and CuK α radiation using crystal of dimensions 0.4 mm \times 0.2 mm \times 0.15 mm. The scan rate was variable and was determined by a fast (20° min⁻¹) 2 s prescan. If more than 30 net counts were found, a slow scan was carried out; if not, the reflections were regarded as unobserved. Calculated speeds for the slow scan based on the net intensity gathered in the prescan ranged from 28° min⁻¹ to 4.5° min⁻¹. Background counts were measured for half the total scan time at each end of the scan range. Two standard reflections were measured periodically; no significant fluctuation in the intensities was noticed. The intensities were corrected for Lorentz and polarization factors

but not for absorption ($\mu R = 0.7$). From a total of 1231 monitored reflections 1080 were classified as "observed". Only observed reflections were used to solve the structure. From the formula unit number and the space group it follows that the Ni atom occupies a special position at the centre of symmetry. Three-dimensional Patterson synthesis, using all the data available, is in accordance with this position and enabled the localization of the sulfur atoms. The Ni atom was localized to (0, 0, 0) and the other atoms to general positions. The successive three-dimensional Fourier synthesis gave the positions of all nonhydrogen atoms, the isotropic thermal coefficient being assumed to be 0.035 nm^2 . The structure parameters were refined by the diagonal-matrix least squares, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized; a unit weighting scheme was employed. After three refinement cycles using isotropic thermal parameters factor R converged to the value of 0.15. The introduction of anisotropic thermal parameters for all nonhydrogen atoms decreased R after two cycles to 0.075. Hydrogen atoms were calculated assuming sp^3 hybridization and that of terminal methyl groups using staggered conformation. Hydrogen atoms were not refined. Their introduction into the structure decreased R to 0.06 and R_w to 0.085.

Table 1

Final fractional atomic coordinates for nonhydrogen atoms with e.s.d.'s in parentheses

Atom	10^4x	10^4y	10^4z
Ni	0	0	0
S(1)	1015(2)	1824(3)	1501(3)
S(2)	463(2)	1345(3)	-1363(3)
N(1)	1654(6)	3892(10)	154(9)
C(1)	1126(7)	2567(14)	110(11)
C(2)	2197(7)	4837(13)	1479(11)
C(3)	1629(7)	6258(13)	1662(11)
C(4)	2189(8)	7034(15)	3175(13)
C(5)	2228(12)	5946(21)	4298(14)
C(6)	1678(7)	4416(13)	-1151(11)
C(7)	1005(8)	5904(14)	-1883(11)
C(8)	963(9)	6242(14)	-3326(12)
C(9)	283(10)	7702(17)	-4129(13)

Scattering factors were taken from *International Tables for X-ray Crystallography* [8]. All crystallographic calculations were performed with the NRC program package [9] on a Siemens 4004/150 computer. Atomic coordinates of nonhydrogen atoms are listed in Table 1, those of hydrogen atoms in Table 2, bond distances and angles in Table 3. A projection of the unit-cell contents down y and numbering of the atoms are shown in Fig. 1. The values of observed and calculated structure factors are filled with the authors.

Table 2

Calculated fractional atomic coordinates for hydrogen atoms

Atom	10 ⁴ x	10 ⁴ y	10 ⁴ z
H(1) (C(2))	2422	3926	2358
H(2) (C(2))	2850	5358	1515
H(3) (C(3))	1475	7242	867
H(4) (C(3))	955	5767	1546
H(5) (C(4))	2919	7301	3363
H(6) (C(4))	1862	8289	3164
H(7) (C(5))	2546	4733	4325
H(8) (C(5))	2611	6570	5337
H(9) (C(5))	1480	5715	4116
H(10) (C(6))	2418	4857	- 838
H(11) (C(6))	1512	3364	- 1845
H(12) (C(7))	305	5557	- 2069
H(13) (C(7))	1254	7036	- 1252
H(14) (C(8))	1696	6521	- 3133
H(15) (C(8))	729	5077	- 3957
H(16) (C(9))	553	8880	- 3482
H(17) (C(9))	291	7923	- 5125
H(18) (C(9))	- 417	7431	- 4302

Table 3

Bond distances and angles with e.s.d.'s in parentheses

Bond	Bond length/nm	Bond	Bond length/nm
Ni —S(1)	0.2201(3)	C(3)—C(4)	0.1554(17)
Ni —S(2)	0.2211(3)	C(4)—C(5)	0.1536(20)
S(1)—C(1)	0.1720(11)	N(1)—C(6)	0.1470(14)
S(2)—C(1)	0.1742(11)	C(6)—C(7)	0.1523(17)
C(1)—N(1)	0.1329(13)	C(7)—C(8)	0.1532(17)
N(1)—C(2)	0.1479(14)	C(8)—C(9)	0.1569(20)
C(2)—C(3)	0.1558(16)		

Atoms	Angle/°	Atoms	Angle/°
S(1)—Ni —S(2)	79.4(1)	C(2)—Ni —C(6)	120.8(8)
Ni —S(1)—C(1)	86.2(4)	N(1)—C(2)—C(3)	112.2(8)
Ni —S(2)—C(1)	85.3(4)	C(2)—C(3)—C(4)	109.7(10)
S(1)—C(1)—S(2)	109.0(6)	C(3)—C(4)—C(5)	120.3(12)
S(1)—C(1)—N(1)	126.1(8)	N(1)—C(6)—C(7)	112.3(9)
C(1)—N(1)—C(2)	118.6(9)	C(7)—C(8)—C(9)	118.0(9)
C(1)—N(1)—C(6)	120.5(9)		

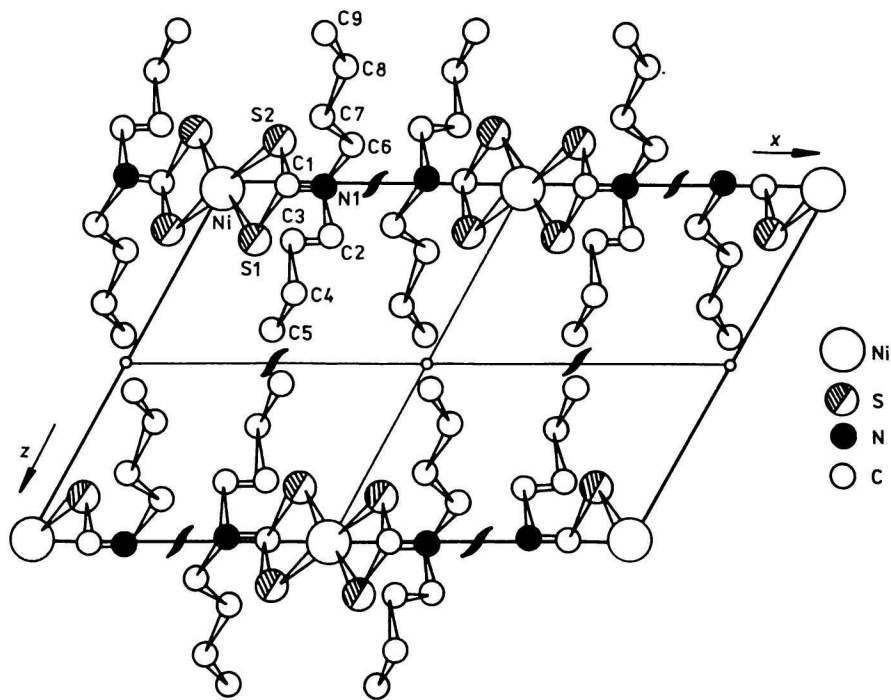


Fig. 1. Cell contents viewed down y and numbering of the atoms.

Discussion

The crystal structure consists of discrete centrosymmetric molecules $\{\text{Ni}[\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2]_2\}$, with Ni atom lying at centres of symmetry. The Ni atom is coordinated with two pairs of S atoms from two ligands; the geometry of the NiS_4 coordination core is thus planar and the two pairs of Ni—S distances (0.2201 nm and 0.2211 nm) are almost identical. These distances agree fairly well with similar lengths reported for other structures [5, 10, 11] and are well within the range of 0.21–0.23 nm found in many square-planar diamagnetic Ni(II) complexes. The Ni—S bond distances are by 0.03 nm shorter than in six-coordinated paramagnetic complexes of Ni(II) with thiourea (0.24–0.26 nm) [12, 13], which reflects significant different bond radii for diamagnetic and paramagnetic Ni ions [14].

In dithiophosphato and dithiophosphinato nickel(II) complexes [15–17] the average bond length of S—P 0.20 nm in the chelate ring (single bond length S—P 0.214 nm and double one S=P 0.194 nm) indicates that in these complexes there also exists the delocalized π -system through three atoms of the four-membered

chelate ring; besides, owing to the bulkier phosphorus atom (compared with the carbon atom), four sulfur atoms in the NiS₄ coordination core are directed nearer to the square corners, confirming the S—Ni—S chelate angle increase from the average value of 79°, observed in dtc complexes and xanthates, to the value of 88°, similarly as in 1,2-dithiolenes of Ni(II) (90°).

In spite of these facts the Ni—S bond lengths in these complexes are, similarly as in xanthate complexes, significantly longer than in analogical Ni(II) complexes (Table 4). From Table 4 it follows that the ligand geometry is practically insensitive to a change of substituent, in contrast to the geometry of the NiS₄ coordination core. The considerably distorted S—C—S bond angles (with respect to the value of 90°) result from the strain in the four-membered ring. Distortions have also been found in other metal dithiocarbamates, related xanthates [18—21], and dithiobenzoates [22]. The average value of the S—C—S bond angle is approximately 110°, irrespective of the nature of the central metal atom, its charge, number of ligands bonded to the central atom, and monomeric or dimeric nature of the complex [7, 21—25].

As shown in Tables 5 and 6, the S₂CNC₂ ligand fragment is substantially planar and conforms to the mm symmetry. The Ni atom is somewhat out of the plane as

Table 4
Some bond distances and angles in planar diamagnetic
bis(1,1-dithiolato)chelates of Ni(II)

Complex		Distance/nm			Angles/°	
		Ni—S	S—C or S—P	C—Y*	S—M—S	S—C—S or S—P—S
Ni(H ₂ dtc) ₂	[6]	0.2220(1)	0.169(2)	0.138(3)	78.5(2)	112.0(1)
Ni(Et ₂ dtc) ₂	[1]	0.2202(2)	0.171(1)	0.133(1)	79.2(2)	110.6(6)
Ni(Pr ₂ dtc) ₂	[2]	0.2203(2)	0.171(1)	0.133(1)	79.2(1)	110.6(6)
Ni(pmdtc) ₂	[5]	0.2206(4)	0.171(1)	0.132(1)	79.0(1)	110.5(6)
Ni(hmdtc) ₂	[7]	0.2203(5)	0.172(2)	0.135(2)	81.0(2)	110.5(7)
Ni(MePhdtc) ₂	[4]	0.2203(3)	0.172(1)	0.130(1)	79.3(1)	109.5(6)
Ni(Pr ₁ dtc) ₂	[3]	0.2181(3)	0.171(1)	0.133(2)	79.2(2)	109.4(5)
Ni(HMedtc) ₂	[10]	0.2199(3)	0.171(1)	0.130(2)	79.2(2)	109.8(7)
Ni(Me ₂ dtc) ₂	[11]	0.2207(2)	0.172(8)	0.134(9)	79.2(7)	109.9(4)
Ni(allyl ₂ dtc) ₂	[26]	0.2204(2)	0.172(8)	0.129(1)	79.2(1)	109.3(4)
Ni(S ₂ COEt) ₂	[20]	0.2235(6)	0.169(2)	0.138(2)	79.5(1)	116.6(3)
Ni(S ₂ PMe ₂) ₂	[15]	0.2240(5)	0.200(1)		87.7(2)	101.6(3)
Ni(S ₂ PPh ₂) ₂	[16]	0.2238(5)	0.201(1)		88.3(2)	101.3(3)
Ni(S ₂ POEt ₂) ₂	[17]	0.2233(4)	0.199(1)		88.5(1)	103.1(2)

* Y = N or O.

Table 5

Values of the coefficients in the equation of planes in the form $AX + BY + CZ = D$ and designation of the atoms through which the plane was constructed by the least-squares method

Plane	Atoms defining the plane							A	B	C	$D/10^3$ pm
1	Ni	S(1)	S(2)	C(1)	N(1)	C(2)	C(6)	-0.7466	0.6205	-0.2399	-0.0582
2	S(1)	S(2)	C(1)	N(1)	C(2)	C(6)		-0.7582	0.6061	-0.2404	-0.1284
3	S(1)	S(2)	C(1)	N(1)				-0.7587	0.6025	-0.2475	-0.1353

Table 6

Deviation d of some atoms from the plane expressed in orthogonal space

Plane	Ni	S(1)	S(2)	C(1)	N(1)	C(2)	C(6)
	d/pm						
1	5.8	-2.9	-4.9	-2.1	1.2	4	2.6
2	12.8	1.0	1.1	-1	8	-1.4	8
3	13.5	0.09	0.09	-3	1	-3.2	8

Table 7

Shortest packing distance (0.4 nm)

S(1)	C(7) ^I	0.391(1)	C(2)	C(9) ^{III}	0.398(2)
S(2)	C(2) ^{II}	0.397(1)	C(3)	C(6) ^{III}	0.391(2)
S(2)	C(3) ^I	0.370(1)	C(4)	C(5) ^{IV}	0.389(2)
S(2)	C(4) ^I	0.394(1)	C(4)	C(6) ^{III}	0.389(2)
C(1)	C(3) ^I	0.399(2)	C(5)	C(8) ^V	0.390(2)
C(1)	C(6) ^{II}	0.396(2)	C(8)	C(8) ^I	0.399(3)
C(2)	C(8) ^{III}	0.386(2)	C(9)	C(9) ^{VI}	0.396(3)

Symmetry code

I \bar{x} , $1 - y$, \bar{z}

II $1/2 - x$, $y - 1/2$, \bar{z}

III $1/2 - x$, $1/2 + y$, \bar{z}

IV $1/2 - x$, $1/2 + y$, $1 - z$

V x , y , $1 + z$

VI \bar{x} , $2 - y$, $\bar{z} - 1$

a consequence of the folding of the ligand about the line through the two S atoms. However, there are some complexes in which the deviation of the metal atom from the ligand plane is much larger [5, 26] and thus may be a measure of the steric crowding due to packing. This is also reflected in packing distances (Table 7) that can be compared with those in the complex $[\text{Ni}(\text{diallyl})(\text{dtc})_2]$ [26]. In the butyl ligand all bond lengths correspond to single bonds with an average value of 0.1554 nm.

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