Inorganica Chimica Acta, 27 (1978) 27–30

The Crystal Structure of Bis(S-Methyl-N-Isopropylidendithiocarbazate)Nickel(II)

T. GLOWIAK and T. CISZEWSKA

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

Received June 14, 1977

The crystal structure of bis(S-methyl-N-isopropylidendithiocarbazate)nickel(II), $Ni[(CH_3)_2CNNCSSCH_3]_2$*, has been determined from three-dimensional X-ray diffractometer data. The triclinic crystals belong to the space group* $P\bar{1}$*:* $a = 7.198(3)$, $b = 18.548(4)$, $c = 7.025(3)$ Å, $\alpha = 94.02(5)$, $\beta = 114.85(5)$, $\gamma = 92.79(5)^\circ$. *The observed and calculated (Z = 2) densities are 1.51 and 1.50 gcm*$^{-3}$*, respectively. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares method to* $R_1 = 0.062$ *and* $R_2 = 0.069$ *using 1811 reflexions for which* $I > 1.96\ \sigma(I)$*. In the molecular, monomeric complex the nickel atom is four-coordinate and the stereochemistry around it is intermediate between planar and tetrahedral. The angle between the planes through Ni, S(1), N(1) and Ni, S(3), N(3) is 27.71°.*

Introduction

In recent years investigations of transition metal complexes with dithiocarbazic acid and its derivatives have given much information about their structure, magnetic properties and biological activity [1–6]. So far only the crystal structures of the two compounds: bis(ethyldithiocarbazate)nickel(II) [7] and (S,S-2-ethyldithiocarbazato)(S,N-2-methyl-methyldithiocarbazato)nickel(II) [8] have been investigated. The crystal structure of the title compound is the first stage of our investigation of the nickel complexes with dithiocarbazic acid derivatives.

Experimental

The compound $Ni[(CH_3)_2CNNCSSCH_3]_2$ was prepared as described previously [2]. The product was recrystallized from a mixture of chloroform and water yielding brown–green crystals. A single crystal of dimensions 0.1 × 0.1 × 0.1 mm was selected for data collection. The unit cell dimensions and intensity data were measured on a Syntex $P2_1$ four-circle diffractometer with a graphite monochromator using CuK_α radiation. The lattice parameters and orientation matrix used for data collection were obtained from the least-squares refinement of 15 reflexions. The parameters are: $a = 7.198(3)$ Å, $b = 18.548(4)$ Å, $c = 7.025(3)$ Å, $\alpha = 94.02(5)^\circ$, $\beta = 114.85(5)^\circ$, $\gamma = 92.79(5)^\circ$, $V = 845.8(2)$ Å^3. The density measured by flotation in a mixture of ethyl alcohol–carbon tetrachloride was 1.51 gcm^{-3}, the calculated density for Z = 2 was 1.50 gcm^{-3}. Intensities of 2209 reflexions were collected using the θ–2θ scan technique to $2\theta_{max} = 110^\circ$. The scan rate varied from 3.8 to 20.0 deg min^{-1} depending upon the intensity of reflexion. From a total collection 1811 reflexions were accepted for further calculations, being those for which I was greater than 1.96 σ(I). Intensities of a standard reflexion were measured every 15 reflexions and showed no significant change with time. The data were corrected for the Lorentz and polarization factors but not for absorption. The linear absorption coefficient was 59.0 cm^{-1} for CuK_α. The absorption factor varied from 1.56 to 1.52.

Structure Determination

The positions of the nickel and two sulphur atoms were determined from a three-dimensional Patterson synthesis. The Fourier map based on signs from those atoms showed the remaining two sulphur and three nitrogen atoms. All other non-H atoms were found from several difference Fourier maps. Refinement by the full-matrix least-squares method with individual isotropic thermal parameters reduced R to 0.112. Subsequent refinement with anisotropic thermal parameters reduced R to 0.082. At this stage a difference-Fourier synthesis showed the positions of seven H atoms. All the remaining H atoms were found from further difference-Fourier maps. The refinement with fixed parameters for H atoms (for all B = 5.0 Å^2) gave $R_1 = 0.062$ and $R_2 = 0.069$. The function minimized during the refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$.

In the final cycle of refinement the maximum shift over error was 0.90 with an average shift over error of 0.15. The final atomic coordinates, temperature

TABLE I. Atomic Coordinates (× 10^4) and Thermal Parameters (× 10^2), with esd in Parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	4296(2)	2384(1)	2019(2)	468(8)	372(7)	439(8)	−5(6)	184(6)	5(6)
S(1)	5514(4)	1446(1)	3600(4)	349(13)	261(11)	322(12)	58(9)	55(10)	17(9)
S(2)	3696(5)	−60(1)	2275(5)	574(16)	239(12)	578(17)	52(11)	261(14)	87(11)
S(3)	6718(4)	3099(1)	4428(4)	352(13)	329(13)	370(13)	−77(10)	38(11)	−39(10)
S(4)	7581(5)	4633(2)	4304(5)	576(17)	358(14)	572(17)	−260(12)	251(14)	−122(12)
N(1)	2846(10)	1723(4)	−496(11)	263(35)	263(36)	262(37)	−2(28)	92(30)	−19(28)
N(2)	2471(11)	987(4)	−250(12)	322(39)	249(37)	308(39)	−11(29)	112(32)	5(29)
N(3)	2779(11)	3234(4)	1307(11)	340(40)	197(34)	288(36)	28(30)	138(32)	34(27)
N(4)	3952(13)	3921(4)	1771(12)	447(45)	217(36)	350(41)	−48(32)	152(36)	−28(30)
C(1)	3692(15)	833(5)	1598(17)	393(52)	175(41)	567(61)	26(37)	305(49)	−22(40)
C(2)	2102(17)	−555(5)	−237(19)	593(65)	239(47)	854(78)	−56(44)	438(60)	−72(49)
C(3)	5759(17)	3884(5)	3249(16)	551(64)	275(46)	429(57)	−138(44)	317(52)	−78(41)
C(4)	6208(21)	5359(6)	3025(18)	1078(95)	383(58)	544(68)	−334(61)	305(67)	−100(51)
C(5)	868(15)	3276(5)	645(13)	347(50)	335(48)	233(43)	72(39)	106(39)	2(35)
C(6)	−111(16)	3977(5)	316(17)	560(62)	270(49)	508(59)	106(45)	74(49)	6(43)
C(7)	−534(14)	2614(5)	272(16)	307(48)	326(48)	475(55)	−18(38)	130(42)	−19(40)
C(8)	2306(14)	1837(5)	−2423(15)	275(46)	432(53)	306(50)	86(39)	130(39)	8(40)
C(9)	1306(15)	1250(6)	−4201(16)	453(57)	557(61)	315(50)	10(47)	93(44)	−32(43)
C(10)	2734(16)	2574(6)	−2970(15)	614(64)	485(58)	303(49)	105(49)	217(47)	131(43)

Thermal parameters are in the form: $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2Bklb^*c^*)]$.

TABLE II. Atomic Coordinates (× 10^2) for the Hydrogen Atoms.

	x	y	z		x	y	z
H(1)	30	−5	−10	H(10)	47	53	29
H(2)	8	−3	−10	H(11)	67	59	38
H(3)	18	−11	−2	H(12)	60	53	15
H(4)	10	15	−55	H(13)	−15	27	10
H(5)	0	10	−43	H(14)	0	22	5
H(6)	22	9	−42	H(15)	−15	25	−10
H(7)	15	27	−40	H(16)	−14	38	−10
H(8)	35	25	−40	H(17)	6	44	−1
H(9)	35	30	−17	H(18)	−5	42	15

The isotropic temperature factor was taken as 5.0 $Å^2$.

factors and their estimated standard deviations are listed in Tables I and II. The atomic scattering factors for neutral-atoms were taken from Cromer and Waber (1974). A table of structure factors is available from the Editor.

All calculations were carried out on a NOVA minicomputer with programs supplied by Syntex.

Discussion

The structure may be described as isolated molecular units of $(S_4C_{10}N_4H_{18})_2Ni$, with only van der Waals interactions between them. Interatomic distances calculated indicate that there is neither hydrogen bonding, metal–metal interactions nor any metal-adjacent ligand bonding.

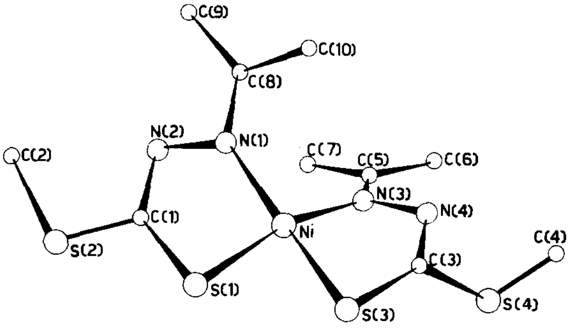

Figure 1. Perspective view of the molecule seen down *a*.

Each Ni atom is bonded to two molecules of S-methyl-N-isopropylidendithiocarbazate through N and S atoms of the bidentate ligand molecule (Fig. 1). The resulting arrangement of the Ni^{2+} is slightly nonplanar with tetrahedral deformation. The entire molecule has a "twisted stepped" structure: the planes calculated through S(1), C(1), N(2), N(1), (b) and S(3), C(3), N(4), N(3), (c) are not parallel but form an angle of 24.39°, the Ni atom being displaced by −0.531(2) Å from plane (b) and 0.581(1) Å from plane (c).

All bond lengths and angles within the molecule and their estimated standard deviations are listed in Tables III and IV. The Ni–S distance (mean value 2.153 Å) and the Ni–N distance (mean value 1.934 Å) are similar to the respective distances reported for other Ni^{2+} complexes: 2.149 Å and 1.930 Å in bis(thiosemicarbazido)Ni(II) sulfate (β-form) *cis*-isomer [9], 2.155 Å and 1.911 Å in bis(thiosemi-

TABLE III. Interatomic Distances (Å).

Ni–S(1)	2.152(3)	C(2)–H(1)	1.00
Ni–S(3)	2.154(3)	C(2)–H(2)	1.02
Ni–N(1)	1.933(7)	C(2)–H(3)	1.00
Ni–N(3)	1.935(7)	C(4)–H(10)	1.04
S(1)–C(1)	1.752(11)	C(4)–H(11)	1.00
S(3)–C(3)	1.752(10)	C(4)–H(12)	1.02
C(1)–N(2)	1.287(13)	C(6)–H(16)	1.01
C(3)–N(4)	1.288(15)	C(6)–H(17)	1.02
N(2)–N(1)	1.415(10)	C(6)–H(18)	1.03
N(4)–N(3)	1.432(10)	C(7)–H(13)	1.03
C(1)–S(2)	1.758(9)	C(7)–H(14)	0.92
C(3)–S(4)	1.748(11)	C(7)–H(15)	0.87
S(2)–C(2)	1.800(12)	C(9)–H(4)	1.00
S(4)–C(4)	1.775(13)	C(9)–H(5)	1.00
N(1)–C(8)	1.279(12)	C(9)–H(6)	1.00
N(3)–C(5)	1.262(14)	C(10)–H(7)	0.92
C(8)–C(9)	1.496(14)	C(10)–H(8)	1.08
C(8)–C(10)	1.498(15)	C(10)–H(9)	1.02
C(5)–C(6)	1.494(14)		
C(5)–C(7)	1.486(14)		

TABLE IV. Bond Angles (deg).

S(1)–Ni–S(3)	91.75(12)
S(1)–Ni–N(3)	159.63(25)
S(1)–Ni–N(1)	86.71(24)
N(1)–Ni–N(3)	101.92(32)
N(1)–Ni–S(3)	160.18(25)
S(3)–Ni–N(3)	86.18(24)
Ni–S(1)–C(1)	93.79(36)
S(1)–C(1)–S(2)	125.65(81)
C(1)–N(2)–N(1)	110.65(78)
N(2)–N(1)–Ni	118.05(55)
Ni–N(1)–C(8)	128.96(67)
C(8)–N(1)–N(2)	112.67(76)
N(1)–C(8)–C(9)	122.56(91)
N(1)–C(8)–C(10)	120.05(90)
C(9)–C(8)–C(10)	117.35(89)
S(1)–C(1)–S(2)	113.83(59)
S(2)–C(1)–N(2)	120.48(79)
C(1)–S(2)–C(2)	101.76(53)
Ni–S(3)–C(3)	93.79(38)
S(3)–C(3)–N(4)	125.42(85)
C(3)–N(4)–N(3)	110.10(81)
N(4)–N(3)–Ni	117.10(56)
Ni–N(3)–C(5)	128.51(67)
N(4)–N(3)–C(5)	114.07(77)
N(3)–C(5)–C(6)	123.52(90)
N(3)–C(5)–C(7)	120.30(88)
C(6)–C(5)–C(7)	116.08(86)
S(3)–C(3)–S(4)	111.72(61)
N(4)–C(3)–S(4)	122.86(84)
C(3)–S(4)–C(4)	103.23(58)

TABLE V. Molecular Planes for $Ni[(CH_3)_2CNNCSSCH_3]_2$.

(a) Plane through Ni, S(1), N(1)

$0.9633x + 0.1317y - 0.2339z - 2.4623 = 0$

(b) Plane through Ni, S(3), N(3)

$0.7302x + 0.2559y - 0.6335z - 1.9516 = 0$

(c) Plane through S(1), C(1), N(2), N(1)

$0.5969x - 0.2884y - 0.7487z - 1.3192 = 0$

Distances of atoms from plane (Å)

Ni	−0.531(2)	N(2)	−0.009(8)
S(1)	−0.000(3)	C(1)	0.015(11)
S(2)	0.131(3)	C(2)	0.486(12)
N(1)	0.004(7)	C(8)	0.499(10)

(d) Plane through S(3), C(3), N(3), N(4)

$0.2285x - 0.2281y - 0.9464z + 0.6611 = 0$

Distances of atoms from plane (Å)

Ni	0.581(1)	N(3)	−0.005(7)
S(3)	0.001(3)	N(4)	0.013(8)
S(4)	−0.080(3)	C(3)	−0.022(10)

Angles between planes

a–b	27.71°
c–d	24.39°

carbazidato)Ni(II) [10], 2.150 Å and 1.935 Å in bis(acetophenonethioacethydrazonato)Ni(II) [11]. In the ligand molecules all bonds are similar to those in bis(acetophenonethioacethydrazonato)Ni(II) and they can be described as single or double bonds. The presence of the two double bonds C═N in the ligand molecule confirms the results of previous investigations [2] that the deprotonated tautomeric form of the ligand takes part in the bonding. The lengths of other bonds and the angles in the organic ligand are only slightly different from those found in other similar compounds [9, 11].

The angle between the planes through Ni, S(1), N(1) and Ni, S(3), N(3) is 27.71°. This angle is 0° for a perfectly planar arrangement and 90° for a perfectly tetrahedral one. The respective angle in bis(acetophenonethioacethydrazonato)nickel(II) is 19°. Other compounds of nickel containing similar chelate rings but without large groups at the nitrogen atom directly bound with the nickel atom are planar or nearly planar [9, 10, 12].

It was found by R. G. Hazell [13] that Ni(bis-N,N-diethylphenylazothioformamide) is quite stable, contrary to the similar compounds without a bulky group at this nitrogen atom which are unstable and difficult to be isolated.

References

1 M. Akbar Ali, S. E. Livingstone, and D. J. Philiphs, *Inorg. Chim. Acta, 5,* 119 (1971).

2 M. Akbar Ali, S. E. Livingstone, and D. J. Philiphs, *Inorg. Chim. Acta, 5,* 493 (1971).

3 M. Akbar Ali, S. E. Livingstone, and D. J. Philiphs, *Inorg. Chim. Acta, 19,* 5 (1976).
4 M. Akbar Ali, and S. E. Livingstone, *Coordination Chem. Rev., 13,* 101 (1974).
5 C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, *J. Inorg. Nucl. Chem., 33,* 3815 (1971).
6 D. Gattegno, and A. M. Giuliani, *J. Inorg. Nucl. Chem., 36,* 1553 (1974).
7 L. Gastaldi, and P. Porta, *Cryst. Struct. Commun., 2(3),* 467 (1973).
8 L. Gastaldi, and P. Porta, *Cryst. Struct. Commun., 1(4),* 693 (1975).
9 R. G. Hazell, *A. Chem. Scand., 22,* 2171 (1968).
10 L. Cavalca, M. Nardelli, G. Fava, *A. Cryst., 15,* 1139 (1962).
11 S. Larsen, *A. Chem. Scand., A28,* 779 (1974).
12 R. Gronbaek, and S. E. Rassmussen, *A. Chem. Scand., 16,* 2325 (1962).
13 R. G. Hazell, *A. Chem. Scand., A30,* 322 (1976).