

Crystal Structure of Nickel Bis-*N,N*-diethylphenylazothioformamide, $\text{Ni}[(\text{C}_6\text{H}_5)\text{NNCSN}(\text{C}_2\text{H}_5)_2]_2$

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Nickel bis-*N,N*-diethylphenylazothioformamide crystallizes in the tetragonal system, space group $P4_12_12$, $a = 10.38(2)\text{Å}$, $c = 22.60(4)\text{Å}$; $Z = 4$; three-dimensional X-ray data for a hemisphere of reflections with $\sin \theta/\lambda \leq 0.7$ were collected on a semiautomatic diffractometer. R -value 0.045 for 1592 significant reflections after least squares refinement. Nickel is tetrahedrally coordinated by sulfur and hydrazinic nitrogen atoms. The tetrahedron is slightly flattened so that the N—Ni—N angle is 144° ; the angle between the planes of the two ligands is 70.4° .

The compound under investigation was prepared by Jensen *et al.*¹ by oxidation of bis(1-phenyl-4,4-diethylthiosemicarbazidato)nickel(II), and also by reaction of the corresponding phenylazothioformamide with $\text{Ni}(\text{CO})_4$. The present investigation was part of the attempt to clarify the bonding in this and similar compounds, the result of which was described by Jensen, Bechgaard, and Pedersen.²

EXPERIMENTAL

The crystals are elongated tetragonal bipyramids (bounded by $\{101\}$). The one used for intensity measurements was $0.15 \times 0.15 \times 0.3\text{ mm}^3$ and mounted along the a -axis. Cell dimensions and space group were obtained from precession photographs taken with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{ Å}$). All reflections within a hemisphere ($h \geq 0$) with $\sin \theta/\lambda \leq 0.7$ were measured on an automatic Supper-Pace diffractometer using $\text{MoK}\alpha$ radiation obtained from a graphite monochromator.³ Corrections for Lorentz and polarization effects but not for absorption were applied and the four symmetry related reflections were averaged leaving 1592 independent, significant reflections [$I > 2\sigma(I)$].

CRYSTAL DATA

$\text{Ni}(\text{C}_{11}\text{H}_{15}\text{N}_3\text{S})_2$; $M = 501.4$;
Tetragonal; $a = 10.38(2)\text{ Å}$, $c = 22.60(4)\text{ Å}$; $V = 2435\text{ Å}^3$; $Z = 4$; $d_m = 1.37\text{ g/cm}^3$; $d_c = 1.38\text{ g/cm}^3$;
 $\mu_{\text{MoK}\alpha} = 9.9\text{ cm}^{-1}$;

Systematic absences: $00l: l \neq 4n$
 $h00: h \neq 2n$

Space group: $P4_12_12$ (No. 92) (or the enantiomorph, No. 96).

Final coordinates and temperature factor parameters are given in Tables 1 and 2. A list of observed and calculated structure factors can be obtained from the author.

STRUCTURE DETERMINATION AND REFINEMENT

The space group, unit cell and density indicated that Ni had to be on the diagonal two-fold axis in the tetragonal unit cell. The Patterson projection, $P(vw)$, was solved to give the nickel and sulfur positions and the Fourier based on this showed all the lighter atoms. The structure was refined by the method of least squares using the 3-dimensional data. The ALGOL program used on the GIER computer at Aarhus University works in the block diagonal approximation and allows anisotropic temperature factor refinement and extinction correction according to Zachariasen⁴ in the approximation given by Larson,⁵ formula 3. The final value of the extinction coefficient, g , was 2.4×10^{-7} . The hydrogen atoms were found in a difference Fourier synthesis calculated at $R = 0.07$, those of the methyl groups being

Table 1. Final atomic coordinates (in fractions) with standard deviations in terms of the last digit in parentheses. For hydrogen atoms the isotropic temperature factor parameters, B (\AA^2), are given.

	x	y	z	B
Ni	0.64663(7)	0.35397(7)	0.75000(0)	
S	0.4833(1)	0.3421(1)	0.68711(5)	
N1	0.5765(3)	0.2049(3)	0.7839(1)	
N2	0.4629(3)	0.1555(3)	0.7692(1)	
N3	0.2974(3)	0.1662(3)	0.7019(1)	
C1	0.4094(4)	0.2137(4)	0.7215(2)	
C2	0.2306(4)	0.0602(4)	0.7315(2)	
C3	0.1322(5)	0.1069(5)	0.7765(2)	
C4	0.2314(5)	0.2239(5)	0.6504(2)	
C5	0.2746(5)	0.1608(7)	0.5924(2)	
C6	0.6304(4)	0.1503(4)	0.8368(2)	
C7	0.5549(4)	0.0911(4)	0.8804(2)	
C8	0.6140(5)	0.0464(4)	0.9319(2)	
C9	0.7451(5)	0.0559(4)	0.9393(2)	
C10	0.8192(4)	0.1133(4)	0.8957(2)	
C11	0.7615(4)	0.1608(4)	0.8448(2)	
H1	0.4609(35)	0.0829(36)	0.8761(16)	3.3(0.8)
H2	0.5566(51)	0.0086(43)	0.9646(20)	6.8(1.3)
H3	0.7849(57)	0.0310(39)	0.9761(16)	4.1(0.9)
H4	0.9147(34)	0.1186(33)	0.9012(15)	3.1(0.8)
H5	0.8187(36)	0.2039(34)	0.8152(15)	3.3(0.8)
H6	0.2993(44)	0.0012(43)	0.7534(19)	5.9(1.1)
H7	0.1920(53)	0.0074(53)	0.7021(22)	7.6(1.4)
H8	0.2474(41)	0.3257(44)	0.6479(18)	5.5(1.2)
H9	0.1410(40)	0.2019(42)	0.6572(18)	5.0(1.0)
H10	0.2425(69)	0.0800(70)	0.5914(30)	13.3(2.4)
H11	0.3677(49)	0.1659(49)	0.5894(21)	7.5(1.3)
H12	0.2360(53)	0.2027(54)	0.5637(22)	8.5(1.5)
H13	0.0728(48)	0.0314(48)	0.7946(22)	7.6(1.4)
H14	0.0552(51)	0.1607(50)	0.7568(24)	8.4(1.5)
H15	0.1907(60)	0.1414(57)	0.8044(26)	10.6(1.7)

Table 2. Mean square vibration amplitudes, U_{ij} , in $\text{\AA}^2 \times 10^{-4}$. Standard deviations in parentheses. The expression for the temperature factor is: $\exp[-2\pi^2(U_{11}(ha^*)^2 + \dots + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	389(2)	389(2)	417(3)	-101(2)	0(0)	0(0)
S	476(5)	544(6)	476(5)	-145(4)	-56(4)	129(5)
N1	328(15)	348(15)	381(16)	-53(12)	-10(14)	-12(14)
N2	362(15)	355(15)	438(16)	-98(12)	-29(14)	-11(14)
N3	389(16)	588(22)	473(18)	-93(16)	-80(15)	75(18)
C1	343(19)	434(21)	407(20)	-34(16)	11(17)	-4(18)
C2	434(23)	501(25)	633(27)	-195(18)	-54(21)	21(22)
C3	662(32)	833(35)	658(28)	-269(27)	68(27)	-2(29)
C4	493(27)	620(31)	558(23)	-66(17)	-94(20)	64(22)
C5	648(32)	1328(54)	558(27)	42(35)	-36(26)	-22(34)
C6	401(19)	326(16)	418(19)	-2(15)	-17(16)	-53(15)
C7	421(22)	491(23)	511(23)	-80(19)	13(19)	20(21)
C8	703(31)	556(26)	483(24)	-116(25)	-19(24)	113(22)
C9	758(32)	452(24)	510(25)	-7(22)	-197(24)	6(21)
C10	493(25)	409(22)	683(28)	27(19)	-157(23)	-62(22)
C11	374(19)	447(22)	486(22)	-63(17)	-23(18)	15(19)

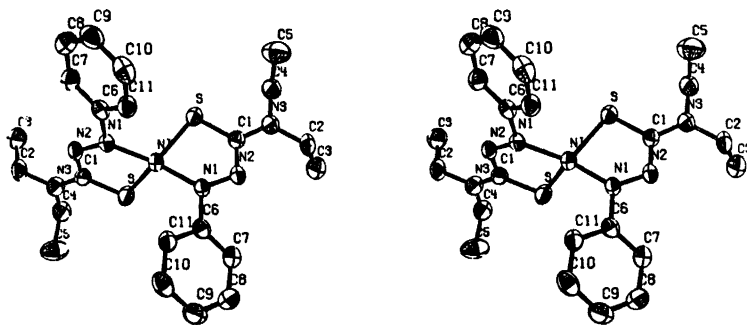


Fig. 1. Stereo view of a molecule of nickel bis-*N,N*-diethylphenylazothioformamide.

fitted to small positive regions with considerable uncertainty. These groups have large thermal movements compared to the rest of the molecule. Because no absorption correction had been made, and because we could not hope that a simple model like rigid body or riding motion would account for the thermal movements of this molecule, the temperature factors were not examined except to check that they looked reasonable. The weights in the refinement were $w = [\sigma(F)]^{-2} = \{\sigma_c(F^2) + (1+k)F^2\}^{-1} - |F|^{-2}$ where $\sigma_c(F^2)$, the standard deviation from counting statistics, was supplemented with a contribution kF^2 to take account of other possible errors; k was adjusted during refinement so that the average of $w(|F_o| - |F_c|)^2$ was independent of $|F|$, ($k=0.016$). The final value of $R = \sum |F_o| - |F_c| / \sum |F_o|$ was 0.045.

DESCRIPTION OF THE STRUCTURE

The coordination around nickel is a somewhat flattened tetrahedron of two sulfur and two nitrogen atoms as illustrated in Fig. 1. The dimensions of the azothioformamide determine that the in-ring N-Ni-S angles are smaller than the tetrahedral value. The other angles around Ni are normal except the N-Ni-N angle, which is as big as 144° . The angle between the two ligand planes is 70.4° compared to 90° in a regular tetrahedron. In primary zinc dithizonate⁶ the interplanar angle is 85° , and the N-Zn-N angle is 110° , *i.e.* much closer to regular tetrahedral coordination. In bis(acetophenone thioacetylhydrazonato)-nickel(II)⁷ the interplanar angle is 21.6° and the N-Ni-N angle is 101.6° , *i.e.* close to *cis*-planar configuration; a planar structure is also reported for nickel dithizonate.⁸ The steric requirements of the present complex seem similar to those of these two compounds and do not explain why it does not assume either

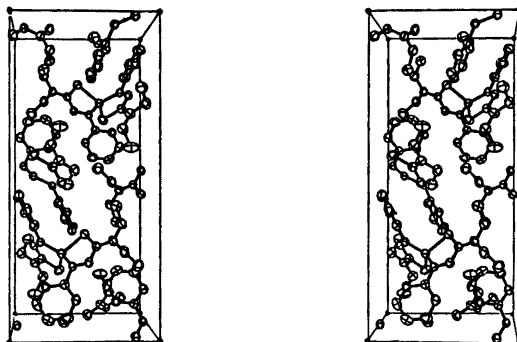


Fig. 2. Stereo view of the contents of a unit cell down the *a* axis.

Table 3. Bond lengths (Å) and angles (°). Standard deviations in parentheses.

Ni-S	2.215(2)	C2-H6	1.06(5)
Ni-N1	1.869(3)	C2-H7	1.05(5)
S-C1	1.723(4)	C4-H8	1.07(5)
N1-N2	1.328(4)	C4-H9	0.98(4)
N2-C1	1.356(5)	C3-H13	1.08(5)
N3-C1	1.338(5)	C3-H14	1.07(5)
N3-C2	1.463(6)	C3-H15	0.95(6)
N3-C4	1.478(6)	C5-H10	0.90(8)
C2-C3	1.521(7)	C5-H11	0.97(5)
C4-C5	1.531(7)	C5-H12	0.88(5)
N1-C6	1.435(5)	C7-H1	0.98(4)
C6-C7	1.401(6)	C8-H2	1.03(5)
C7-C8	1.395(6)	C9-H3	0.96(4)
C8-C9	1.375(7)	C10-H4	1.00(4)
C9-C10	1.385(6)	C11-H5	1.00(4)
C10-C11	1.387(6)		
C11-C6	1.377(5)		
S-Ni-S	119.5(1)	C1-N3-C2	122.6(3)
S-Ni-N1	85.5(1)	C1-N3-C4	120.9(4)
S-Ni-N1	112.9(1)	C2-N3-C4	116.4(3)
N1-Ni-N1	144.2(1)	N3-C2-C3	112.6(4)
Ni-S-C1	95.3(1)	N3-C4-C5	111.4(4)
Ni-N1-N2	124.2(2)	N1-C6-C7	122.7(3)
Ni-N1-C6	121.0(2)	N1-C6-C11	117.6(3)
C6-N1-N2	113.7(3)	C7-C6-C11	119.7(4)
N1-N2-C1	113.0(3)	C6-C7-C8	119.1(4)
N2-C1-S	121.5(3)	C7-C8-C9	120.9(4)
N2-C1-N3	117.0(3)	C8-C9-C10	119.6(4)
S-C1-N3	121.5(3)	C9-C10-C11	120.2(4)
		C10-C11-C6	120.5(4)

a regular tetrahedral arrangement or a nearly planar one. In zinc dithizonate the phenyl groups are coplanar with the rest of the ligand, in bis(acetophenone thioacetylhydrazonato) nickel the phenyl groups form an angle of 26° with the rest of the ligand making the two phenyl groups parallel. In the present compound the corresponding angle is 29° but in such a direction that the two phenyl groups get closer together; this deformation must be due to intermolecular packing forces, see Fig. 2. It is worth noticing that similar compounds without a bulky group at this nitrogen atom are too unstable to be isolated^{1,2} whereas the present compound is very stable so the extra steric strain seems to be easily offset by some stabilizing effect.

The Ni-S and Ni-N bonds (Table 3) are longer than those of planar thiosemicarbazide complexes of divalent nickel⁸⁻¹¹ but shorter than the distances expected from tetrahedral divalent nickel. In a diamagnetic, tetrahedral

Ni⁰ complex,¹² [(C₆H₅)₂Nb(SMe)₂] Ni(BF₄)₂·2H₂O, the Ni-S distances (2.20 Å) are similar to the ones found in the present investigation. The ligand can be derived from thiosemicarbazide by removal of two protons from N1 and N2 (and substitution of bulky groups for other hydrogen atoms). As could be anticipated, this leads to a short N-N bond (1.33 Å) though not as short as expected for a localized double bond. The N2-C bond is significantly longer than in the thiosemicarbazides probably because of the participation of N2 in a nearly double bond to N1. The C-S and C-N3 bonds are also long although the differences are hardly significant. The coordination is so far from regular that simple ligand field considerations cannot predict the electronic structure, but Bechgaard¹³ has presented a qualitative molecular orbital diagram in accordance with the observed spectra and magnetic properties, according to which the highest occupied orbital is a π* orbital of the ligand.

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