

## The Crystal and Molecular Structure of Bis(1,1-diethyl-3-benzoylthioureato)nickel(II)

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The crystal and molecular structure of *cis*-bis(1,1-diethyl-3-benzoylthioureato)nickel(II) was determined from three-dimensional X-ray diffraction data. The crystals belong to the monoclinic space group  $P2_1/c$  (No. 14). The cell parameters are  $a = 10.49(1)$ ,  $b = 18.47(1)$ ,  $c = 14.72(1)$  Å,  $\beta = 118.80(7)^\circ$ , and  $Z = 4$ . The structure was refined to a final  $R$ -value of 3.58%. 1,1-Diethyl-3-benzoylthiourea is bidentate and coordinates through its S and O atoms, forming a 6-membered ring. The average Ni–S and Ni–O bond lengths are 2.134 and 1.860 Å, respectively, and the interchelate S–S distance is 2.881(2) Å. Coordination around the nickel atom is square planar. One of the four ethyl groups is disordered. The molecules in the unit cell are arranged in pairs, the Ni–Ni distance being 4.05 Å.

The structures of several metal complexes of thiourea and its derivatives have been determined during the past decades.<sup>1–12</sup> Among these are nickel complexes of substituted thioureas. Depending on the nature of the substituent groups, thiourea acts as a unidentate or bidentate ligand.<sup>1,13–16</sup> The title ligand, 1,1-diethyl-3-benzoylthiourea, acts as a bidentate ligand coordinating through the sulfur atom and the benzoyl oxygen atom. The structures of its palladium and copper complexes have been determined earlier.<sup>17,18</sup> Palladium forms a planar complex, and one modification of the copper complex is tetrahedral.

The present determination of the structure of the nickel complex was carried out to obtain information on the coordination around the nickel atom and on the unusual residual paramagnetism ( $\mu = 0.61$  B.M.) of the complex measured earlier.<sup>19</sup> The only reason for such magnetic behaviour in this

type of coordination compounds known from literature<sup>20</sup> is<sup>a</sup> described by the formation of interallogonic systems consisting of planar and tetrahedral structural units in the ratio of 2:1.

### EXPERIMENTAL

**Data collection.** The reddish brown crystals have been synthesized earlier.<sup>19</sup> The compound was recrystallized twice from hot ethanol. A needle-formed crystal was transferred to the Syntex P2<sub>1</sub> automatic four-circle diffractometer. Graphite monochromatized MoK $\alpha$ -radiation was used for data collection. The unit cell parameters were calculated by least squares refinement of 15 reflections. The intensities of 2671 independent reflections were collected ( $5^\circ < 2\theta < 50^\circ$ ) at room temperature using the  $\theta/2\theta$ -scan technique with the scan rate varying from 1.0 to 15.0° min<sup>-1</sup> depending on the peak intensity. The intensity of one standard reflection, recorded after every 50 measurements to monitor the crystal stability, remained essentially constant throughout data collection. Out of 2671 measured reflections 1927 were observed on the basis of  $I > 3\sigma(I)$ . The data were corrected for Lorentz and polarization factors but not for absorption ( $\mu(\text{MoK}\alpha) = 9.66$  cm<sup>-1</sup>).

**Structure determination.** The phase problem was solved by the MULTAN 78 direct methods.<sup>21</sup> The phases of the 232  $E$ -values larger than 1.3 were calculated. Refinement was carried out with programs of the X-Ray System.<sup>22</sup> The scattering factors for Ni, S, O, N and C were those of Cromer and Mann<sup>23</sup> and for H atoms those of Stewart, Davidson and Simpson.<sup>24</sup> MULTAN gave the coordinates of Ni and the atoms of its coordination circle as well as those of six carbon atoms. During refinement one of the ethyl groups was found to be disordered.

The location of its carbon and hydrogen atoms was difficult and one of the hydrogens was not found. The high thermal parameters of C9 and C10 are due to this disorder. The positions of the other atoms could be located satisfactorily. In the final least squares cycles of block-diagonal refinement, non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters. After the last cycle the final *R*-value was 3.58%. The final difference Fourier map showed no peaks above 0.3 e/Å<sup>3</sup>. The calculations were carried out on a UNIVAC 1100/60 computer.

## DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The molecular structure of bis(1,1-diethyl-3-benzoyl-thioureato)nickel(II) is shown in Fig. 1 and the packing of the molecules in Fig. 2.

The atomic coordinates with their standard deviations for non-hydrogen and hydrogen atoms are given in Table 1. Tables of observed and calculated structure factors and of final thermal parameters are available from the authors on request.

Intramolecular distances and angles with their standard deviations are shown in Table 2.

The central Ni atom is coordinated to two 1,1-diethyl-3-benzoylthiourea molecules through their oxygen and sulfur atoms and the stereochemistry of the complex is *cis*. The coordination around nickel is square planar. The angle between planes (Ni, S1, O1) and (Ni, S2, O2) is 3.33°.

There is no significant difference between the Ni–S1 and Ni–S2 bond lengths of 2.123(2) and 2.144(1) Å, respectively. The Ni–O1 and Ni–O2 bond lengths of 1.863 and 1.856 Å, respectively, are equal within error limits. Both Ni–S and Ni–O distances are comparable with

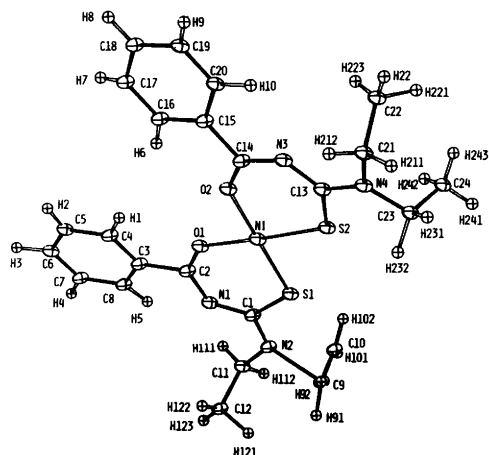


Fig. 1. An ORTEP drawing of bis(1,1-diethyl-3-benzoyl-thioureato)nickel(II), including atomic labeling scheme.

those of the square planar nickel(II)- $\beta$ -thioxo-ketonates<sup>25–27</sup> and the Ni–S distances agree with the corresponding distances in bis(dithio-biureato)nickel(II),<sup>10</sup> but are somewhat shorter than those in the dithiolato complex (Ni–S = 2.253–2.338 Å)<sup>28</sup> and the *N,N'*-diallylthiourea complex (Ni–S = 2.221 Å).<sup>1</sup> The chelate ring bond distances show delocalization of  $\pi$ -electrons, and agree with those found in the thiourea complexes determined earlier.<sup>1–12</sup>

The bond distance C–N between the diethyl-amino substituent and the chelate ring is shorter than a normal single C–N bond length, C1–N2 being 1.332 Å and C13–N4 1.345 Å. This shortening of the C–N bond lengths is in agreement both with the bond distances of thiourea complexes determined earlier<sup>1–12</sup> and with the <sup>1</sup>H NMR results

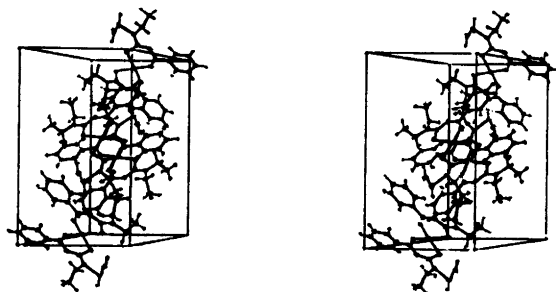


Fig. 2. Stereoview of the packing perpendicular to the *ab* plane.

Table 1. Final positional parameters for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>Ni including hydrogen atoms.

Atom	X	Y	Z	Atom	X	Y	Z
Ni	.4902(1)	.0506(0)	.8747(0)	H1	.078(4)	.409(2)	.315(3)
S1	.4745(1)	.0358(1)	1.2057(1)	H2	.832(5)	.391(5)	.259(3)
S2	.7223(1)	.0640(1)	.9486(1)	H3	.367(5)	.951(2)	.386(3)
O2	.7122(3)	-.0419(2)	1.1962(2)	H4	.289(5)	.031(2)	.483(3)
O2	.5383(3)	.8737(1)	.0542(2)	H5	.029(5)	.046(3)	.438(3)
N1	.7750(4)	.0486(2)	.3215(2)	H6	.274(5)	.304(2)	.443(3)
N2	.3647(4)	.6230(2)	.1419(3)	H7	.841(6)	.705(3)	.025(4)
N3	.6919(3)	.1624(2)	.0776(2)	H8	.704(5)	.871(2)	.370(3)
N4	.9199(4)	.1209(2)	.1223(2)	H9	.541(5)	.353(2)	.219(3)
C1	.3595(5)	.5694(2)	.2005(3)	H10	.329(5)	.765(2)	.335(3)
C2	.2000(5)	.4963(2)	.2298(3)	H91	.469(5)	.236(2)	.341(3)
C3	.0418(2)	.4828(2)	.1944(3)	H92	.467(6)	.175(3)	.242(4)
C4	.0029(5)	.4363(2)	.2508(3)	H101	.485(5)	.143(2)	.438(3)
C5	.1423(5)	.9242(2)	.2792(3)	H102	.417(4)	.081(2)	.356(3)
C6	.2518(5)	.9575(2)	.3660(3)	H111	.844(5)	.125(2)	.473(3)
C7	.7869(5)	.5033(3)	.0774(3)	H112	.735(5)	.173(2)	.495(3)
C8	.9322(5)	.5160(2)	.1060(3)	H121	.281(5)	.763(3)	.117(4)
C9	.5403(5)	.6805(4)	.1878(5)	H122	.829(5)	.214(3)	.357(4)
C10	.5454(9)	.6327(4)	.1278(4)	H123	.902(5)	.247(3)	.468(4)
C11	.7658(5)	.1572(3)	.4407(3)	H211	.928(5)	.642(2)	.225(3)
C12	.1874(6)	.7233(3)	.0933(4)	H212	.093(4)	.664(2)	.251(3)
C13	.7758(5)	.1190(2)	.0560(3)	H221	.901(5)	.747(2)	.381(3)
C14	.4521(4)	.6650(2)	.4785(3)	H222	.946(6)	.766(3)	.235(5)
C15	.5236(5)	.7230(2)	.4479(3)	H223	.921(5)	.265(3)	.155(3)
C16	.3259(5)	.2690(2)	.4995(3)	H231	.891(4)	.571(2)	.321(3)
C17	.7417(5)	.7850(3)	.4751(4)	H232	.019(5)	.542(2)	.415(3)
C18	.6576(6)	.8322(2)	.3950(4)	H241	.150(4)	.088(2)	.030(3)
C19	.4927(5)	.3243(2)	.1582(3)	H242	.007(5)	.871(2)	.033(3)
C20	.5596(5)	.2711(2)	.1317(3)	H243	.125(4)	.163(2)	.072(3)
C21	.9750(6)	.1641(2)	.2180(3)				
C22	.0049(6)	.2399(3)	.2039(4)				
C23	.0275(5)	.0795(2)	.1068(3)				
C24	.0789(5)	.1183(2)	.0403(4)				

concerning the hindered rotation of the diethyl-amino groups about the C–N bond ( $\Delta G = 76.1 \text{ kJ mol}^{-1}$ ).<sup>29</sup> The atoms of the chelate rings are nearly coplanar. The distances of the atoms from the least squares ring planes are given in Table 3. The angle between these planes is  $3.50^\circ$ .

One ethyl group attached to N2 is disordered. Such disorder was also observed in the previously determined planar palladium complex of the title ligand,<sup>17</sup> but not in the tetrahedral copper complex.<sup>18</sup> This kind of disorder is quite common in terminal alkyl groups of dialkylthiocarbamate complexes.<sup>30–32</sup>

The interchelate distance between S1 and S2 (2.881(2) Å) in the present nickel complex is shorter than the corresponding distance in the palladium

and copper complexes (3.12 and 3.14 Å),<sup>17,18</sup> and is much shorter than the sum of van der Waals radii (3.70 Å).<sup>33</sup>

Gray *et al.*<sup>34</sup> have suggested that a relatively short interligand S–S distance (3.18–2.98 Å) could indicate some residual S–S interaction. Also Amma *et al.*<sup>10</sup> have concluded that there is some residual S–S interchelate bonding in bis(dithio-biureato)nickel(II) in which the interchelate S–S distance is 3.220 Å and the intrachelate S–S distance is 2.895 Å. In our nickel complex the interchelate S–S distance is one of the shortest non-bonded S–S distances observed.<sup>2,10,34–40</sup>

In the unit cell the molecules form centrosymmetric pairs. The molecules in the dimers lie almost directly above each other, and the Ni–Ni distance

Table 2. Interatomic distances (Å) and angles (°) with standard deviations.

Ni-S1	2.123(2)	S1-Ni-S2	84.9(1)	C6-C7-C8	121.2(4)
Ni-O1	1.863(3)	S1-Ni-O1	94.5(1)	C3-C8-C7	119.8(5)
Ni-S2	2.144(1)	O1-Ni-O2	86.2(1)	N2-C9-C10	74.2(6)
Ni-O2	1.856(3)	S2-Ni-O2	94.4(1)	N2-C11-C12	113.6(4)
S1-C1	1.731(4)	Ni-S1-C1	109.7(2)	C13-N3-C14	123.6(3)
O1-C2	1.252(4)	Ni-O1-C2	134.1(3)	C13-N4-C21	119.8(4)
N1-C1	1.339(6)	Ni-C2-C13	108.7(2)	C13-N4-C23	123.3(3)
N1-C2	1.327(6)	Ni-O2-C14	133.1(3)	C21-N4-C23	116.9(3)
N2-C1	1.332(7)			S2-C13-N3	127.6(3)
N2-C9	1.940(10)	C1-N1-C2	122.8(3)	S2-C13-N4	115.7(4)
N2-C11	1.465(5)	C1-N2-C9	120.5(3)	N3-C13-N4	116.6(3)
C2-C3	1.496(7)	C1-N2-C11	123.1(4)	O2-C14-N3	130.0(4)
C3-C4	1.386(7)	C9-N2-C11	113.6(4)	O2-C14-N15	115.0(3)
C3-C8	1.397(5)	S1-C1-N1	128.6(4)	N3-C14-C15	115.0(3)
C4-C5	1.381(7)	S1-C1-N2	116.4(4)	C14-C15-C16	120.4(3)
C5-C6	1.384(6)	N1-C1-N2	115.0(3)	C14-C15-C20	120.7(4)
C6-C7	1.379(8)	O1-C2-N1	130.1(4)	C16-C15-C20	118.9(4)
C7-C8	1.388(7)	O1-C2-C3	115.6(4)	C15-C16-C17	121.2(4)
C9-C10	1.274(11)	N1-C2-C3	114.2(3)	C16-C17-C18	119.2(5)
C11-C12	1.489(8)	C2-C3-C4	119.4(3)	C17-C18-C19	119.8(5)
S2-C13	1.732(4)	C2-C3-C8	121.7(4)	C18-C19-C20	120.7(4)
O2-C14	1.265(4)	C4-C3-C8	118.9(4)	C15-C20-C19	120.0(4)
N3-C13	1.335(6)	C3-C3-C5	120.4(4)	N4-C21-C22	113.2(4)
N3-C14	1.324(5)	C4-C5-C6	121.1(5)	N4-C23-C24	113.1(4)
N4-C13	1.345(5)	C5-C6-C7	118.6(5)		
N4-C21	1.475(5)				
N4-C23	1.467(7)				
C14-C15	1.496(6)				
C15-C20	1.393(5)				
C16-C17	1.376(8)				
C17-C18	1.388(6)				
C18-C19	1.386(7)				
C19-C20	1.368(7)				
C21-C22	1.469(5)				
C23-C24	1.508(8)				
S1-S2	2.881(2)				

Table 3. The distance of the chelate ring atoms from the least squares plane.

Atom	Distance (Å)
Ni	0.03
O1	-0.03
C2	0.00
N1	0.02
C1	0.00
S1	-0.02
Ni	-0.11
O2	0.04
C14	0.06
N3	-0.04
C13	-0.08
S2	0.13

is 4.05 Å. The Ni-Ni line forms an angle of 77.6° with the coordination plane (Ni, O1, O2, S1, S2). In *N,N'*-ethylenebis(salicylideneiminato)nickel(II)<sup>41</sup> and *N,N'*-ethylenebis[(2-hydroxy-1-naphthyl)methaniminato]-nickel(II)<sup>42</sup> the very small Ni-Ni distances (3.21 and 3.324 Å, respectively) have led to a pairing of the molecules while an Ni-Ni chain exists in bis(dimethylglyoximato)nickel(II),<sup>43</sup> with an Ni-Ni distance of 3.25 Å.

The unusual paramagnetism of the present compound is not directly explainable from the geometry of the complex molecule.

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