Crystal Structure of [1-(1*H*-Benzoimidazol-2-yl)-ethanone thiosemicarbazone]₂Nickel, [C₂₀H₂₂N₁₀S₂Ni]

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The title compound, [C₂₀H₂₂N₁₀S₂Ni], crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 10.9319(9)\text{Å}$, $b = 12.0083(9)\text{Å}$, $c = 13.4978(11)\text{Å}$, $\alpha = 87.057(7)^\circ$, $\beta = 85.841(7)^\circ$, $\gamma = 63.820(6)^\circ$, $V = 1585.6(2)\text{Å}^3$, $Z = 2$. The structure was refined to a final R value of 0.0498 for 4798 reflections [$I > 2\sigma(I)$]. The nickel atom is in a regular octahedral environment by four nitrogen atoms and two sulfur atoms.

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Thiosemicarbazones and their metal complexes have received considerable attention because of their biological properties.¹ They also contain N=C–C=N structure unit, which forms a strong

chelate ring giving possible electron delocalization associated with extended conjugation that may effect the nature of the formed complex. The biological activity of these compounds was attributed to their interaction with enzymes, such as ribonucleotide reductases, the RNA dependent DNA polymerase, the formation of oxygen active species, and the reaction with cell thiols.^{2–5} The title complex is shown in Fig. 1 and Fig. 2.

Fig. 1 Chemical diagram of the title compound.

Fig. 2 Molecular structure of the title compound with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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Table 1 Crystal and experimental data

Formula:	C ₂₀ H ₂₂ N ₁₀ S ₂ Ni
Formula weight:	525.29
Crystal system:	triclinic
Space group:	$P\bar{1}$
Z :	2
a :	10.9319(9)Å
α :	87.057(7)°
b :	12.0083(9)Å
β :	85.841(7)°
c :	13.4978(11)Å
γ :	63.820(6)°
V :	1585.6(2)Å ³
D_x :	1.100 g/cm ³
$\mu(\text{Mo } K\alpha)$:	0.766 mm ⁻¹
T :	293 K
Crystal color:	prism, dark red
$\lambda(\text{Mo } K\alpha)$:	0.71073 Å
R :	0.0498
wR :	0.1323
No. of reflections measured:	6949
No. of reflections used:	4798 [$I > 2\sigma(I)$]
No. of parameters:	306
Goodness-of-fit:	0.974
$(\Delta/\sigma)_{\text{max}}$:	0.011
$(\Delta\rho)_{\text{max}}$:	0.864 eÅ ⁻³
$(\Delta\rho)_{\text{min}}$:	-0.608 eÅ ⁻³
$2\theta_{\text{max}}$:	54.26°
Measurements:	Stoe IPDS-2 diffractometer
Program system:	X-AREA software
Structure determination:	SHELXS-97
Refinement:	SHELXL-97
Hydrogen atoms:	geometrically located
Refinement:	full-matrix least-squares on F^2
Deposit number:	CCDC 270038

Table 2 Final atomic coordinates and equivalent anisotropic thermal parameters for non-hydrogen

Atom	x	y	z	$U_{eq}(\text{\AA}^2)$
Ni	0.75092(5)	0.59053(4)	0.20729(3)	0.0392(6)
N1	0.5391(3)	0.4037(3)	0.1254(2)	0.0392(14)
N2	0.5981(3)	0.5541(2)	0.15385(19)	0.0442(7)
N3	0.8516(3)	0.4030(2)	0.1838(2)	0.0402(6)
N4	0.9857(3)	0.3392(3)	0.2008(2)	0.0419(6)
N5	1.1839(4)	0.3344(4)	0.2440(3)	0.0503(7)
N6	0.6687(4)	0.9312(3)	0.0268(3)	0.0678(10)
N7	0.6128(3)	0.8644(3)	0.1742(2)	0.0631(10)
N8	0.6306(3)	0.7724(2)	0.24263(19)	0.0461(7)
N9	0.6817(3)	0.5750(2)	0.35370(19)	0.0414(6)
N10	0.5607(3)	0.6813(3)	0.4855(2)	0.0484(7)
S1	0.97316(10)	0.55323(9)	0.26056(9)	0.0578(3)
S2	0.78618(11)	0.68705(8)	0.05260(7)	0.0546(3)
C1	0.4225(4)	0.5135(3)	0.1167(2)	0.0422(7)
C2	0.4620(4)	0.6076(3)	0.1344(2)	0.0412(7)
C3	0.3656(4)	0.7321(3)	0.1301(3)	0.0485(8)
C4	0.2360(4)	0.7567(4)	0.1104(3)	0.0566(9)
C5	0.1981(4)	0.6613(4)	0.0937(3)	0.0580(9)
C6	0.2911(4)	0.5391(4)	0.0969(3)	0.0520(9)
C7	0.6399(4)	0.4322(3)	0.1478(2)	0.0423(7)
C8	0.7811(4)	0.3462(3)	0.1626(2)	0.0439(7)
C9	0.8318(5)	0.2094(3)	0.1557(3)	0.0602(10)
C10	1.0522(4)	0.4018(3)	0.2339(3)	0.0515(8)
C11	0.6852(4)	0.8347(3)	0.0852(2)	0.0460(8)
C12	0.4672(4)	0.9215(3)	0.3635(3)	0.0585(10)
C13	0.5647(3)	0.7978(3)	0.3281(2)	0.0404(7)
C14	0.5999(3)	0.6855(3)	0.3894(2)	0.0407(7)
C15	0.6975(4)	0.4924(3)	0.4323(3)	0.0461(8)
C16	0.7701(4)	0.3641(4)	0.4380(3)	0.0566(9)
C17	0.7664(5)	0.3058(4)	0.5275(3)	0.0678(11)
C18	0.6923(5)	0.3730(5)	0.6101(3)	0.0711(12)
C19	0.6172(5)	0.4994(4)	0.6060(3)	0.0633(11)
C20	0.6219(4)	0.5577(3)	0.5157(3)	0.0487(8)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$$

The crystalline ligand (0.125 g, 0.538 mmol) was dissolved in 40 ml ethanol, NiCl_2 (0.0349 g, 0.269 mmol) was dissolved in wet ethanol. The NiCl_2 solution was added to the ligand solution. The mixture was refluxed on a hot plate at 60–70°C for 6 h. It was left for crystallization. The structure was solved by direct methods, and refined on F^2 by full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically, and all of the hydrogens were fixed as a riding model over their parent atoms with $U_{iso}(H) = 1.3U_{eq}(C)$. The average Ni–N and Ni–S bond lengths are [2.070(10) and 2.425(4) Å], respectively. The nickel ion is linked to the azomethinic nitrogen N3 and the thioamide sulfur S1 atoms. The bond distances are 2.061(9) Å and 2.425(4) Å, respectively. The azomethinic nitrogens [N3 and N8] are placed in a *trans* position. The *trans* angle involving the azomethinic nitrogens, 171.95(12)°, most closely approaches 180°.

The coordination about the nickel ion is not completely regular; the bond angles at the Ni(II) atom range from [78.3(4) to 105.6(3)°]. The best plane is defined by atoms S1, C7, C8, C10, N2, N3 and N4 [maximum deviation 0.0873(7)°], and Ni(II) is located only 0.003(4)° from this plane. The planes, Ni, N8, N9,

Table 3 Selected bond distances (Å) and angles (°)

N2–Ni	2.091(10)	N9–Ni	2.086(10)
N3–Ni	2.061(9)	N3–N4	1.352(4)
S1–Ni	2.425(4)	N7–N8	1.358(4)
S2–Ni	2.425(4)	C10–S1	1.683(14)
N8–Ni	2.041(10)	C11–S2	1.682(14)
S1–Ni–S2	91.52(15)	N2–Ni–N9	90.6(4)
N3–Ni–S1	81.2(3)	N8–Ni–S2	81.51(8)
N9–Ni–S1	91.2(3)	N3–Ni–S2	105.11(8)
N8–Ni–N2	97.3(4)	N2–Ni–S2	93.82(8)
N3–Ni–N2	78.3(4)	N8–Ni–N9	78.4(4)
N8–Ni–S1	103.29(8)	N3–Ni–N9	94.8(4)
C8–N3–Ni–N8	45.0(9)	C8–N3–Ni–S2	–99.7(2)
C10–S1–Ni–N2	3.5(3)	C10–S1–Ni–S2	–102.04(14)
N6–C11–S2–Ni	178.0(3)	S1–Ni–S2–C11	–103.61(14)

C13, C14 and Ni, S1, N3, N4, C10 have mean plane deviations of 0.023(4) and –0.013(5), respectively. These two coordination planes are at an angle of 88.8(3)° from each other, close to the idealized 90° for a regular octahedron. Angles generated at the nickel center by the chelating donor points (N and S) differ slightly in the two coordinating ligands. It appears that the angles at the nickel center in the chelate rings are controlled to some extent by the ligand geometry. The bond distances and angles around the nickel atom are in agreement with the literature values.^{3–5} The angle between the mean planes of Ni, S2, N7, N8, C11 and Ni, N8, N9, C13, C14 is 1.66(4)° and that between mean planes of Ni, S1, N3, N4, C10 and Ni, N2, N3, C7, C8 is 4.41(4)°, respectively.

The crystal data and the other relevant parameters are given in Table 1. The final atomic coordinates, the bond distances and angles are presented in Tables 2 and 3.

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