



Crystal and molecular structure of *bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel(II) complex

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ABSTRACT

We report the synthesis of *bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel(II) complex of an benzoylthiourea derivative formulated as $C_{24}H_{28}Br_2NiN_4O_2S_2$. The structure of compound has been determined by single-crystal X-ray diffraction analysis. It crystallizes in the monoclinic space group, $P2_1/c$ with unit cell dimensions of $a = 12.9099(17)$ Å, $b = 15.264(2)$ Å, $c = 14.0287(19)$ Å, $\beta = 92.140(4)^\circ$ and $V = 2762.5(6)$ Å³. In this compound, the nickel atom is coordinated by two sulphur and two oxygen atoms from two 4-bromo-*N*-(diethylcarbamothioyl)benzamide molecules forming an distorted square-planar geometry.

1. Introduction

In recent years, there has been considerable interest in benzoylthiourea compounds. This is due to the fact that these compounds have demonstrated remarkable pharmacological characteristics. Many benzoylthiourea compounds have been tested for their *in vitro* activity against a large variety of tumor lines and have been found to be as effective or better than traditional heavy metal anticancer drugs such as *cis*-platin [1]. Some acylthiourea derivatives exhibit antiviral [2], antibacterial [3], antifungal [4], antihelmintic [5,6], herbicidal [7], activities. 1,3-Dialkyl or diaryl thioureas exhibit significant antifungal activity against plant pathogens *Pyricularia oryzae* and *Drechslera oryzae* [8]. Furthermore, thiourea and its derivatives are a well-known class of excellent ligands for transition metals, which also exhibit redox activity with reducible metal ions to make the reaction systems complicated [9-11]. Moreover, ion selective electrodes for Pb(II) based on benzoylthioureido derivatives as ionophores have been formulated [12].

Our group has studied the synthesis [13-20], characterization, crystal structure [21-26], thermal behavior [26, 27] and antimicrobial activity [28, 29] of some substitute benzoylthiourea derivatives and their metal complexes. In the present work, we report the crystal structure of *bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel(II) complex.

2. Experimental

2.1. Instrumentation

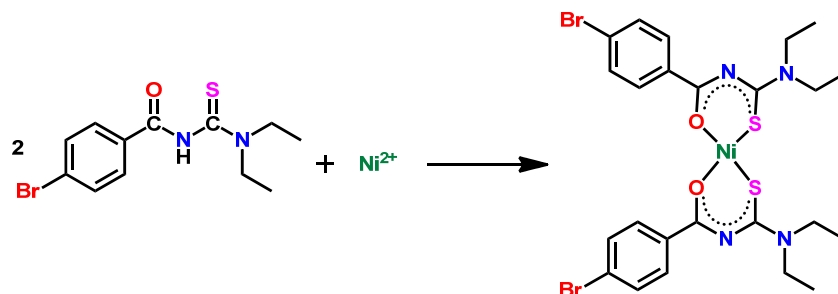
Melting points were measured on an Electrothermal model 9200 and are uncorrected. Elemental analyses were carried out

with a LECO CHNS-932 elemental analyzer. Fourier transform infrared spectra (FTIR) were recorded in KBr pellets using a WinFirst Satellite FTIR spectrometer. ¹H NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400 MHz using CDCl₃ as the solvent, with tetramethylsilane as internal standard. The crystallographic data of *bis*(4-bromo-*N*-(diethylcarbamothioyl) benzamido)nickel(II) complex were recorded on a Bruker AXS SMART-APEX diffractometer using MoK α radiation ($\lambda = 0.71073$ Å) at $T = 120(2)$ K. The structure was solved by direct methods and refined by least square cycles. The non-hydrogen atoms were refined anisotropically. All calculations were performed using the SHELXTL-97 package [30]. The crystallographic data for the complex are listed in Table 1.

2.2. Synthesis of *bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel(II) complex

All chemicals were used as obtained from Merck and analytical-grade solvents were used without further purification. The *bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel(II) complex was prepared according to the method described in the literature [16] (Scheme 1).

4-bromo-*N*-(diethylcarbamothioyl)benzamide was dissolved in methanol (30 mL) and added dropwise to nickel(II) acetate, Ni(CH₃COO)₂, in methanol (30 mL) in a 1:2 ratio (Metal:Ligand) at pH > 7 and the mixture was stirred for 30 min at room temperature. During the time, the color of the 4-bromo-*N*-(diethylcarbamothioyl)benzamide is changed white to purple. The change in color was due to complete the reaction. The change in color was due to the interaction of NiCl₂·6H₂O with the 4-bromo-*N*-(diethylcarbamothioyl)benzamide.



Scheme 1

The solid complex was filtered and recrystallized from an ethanol:dichloromethane mixture (1:2) (Scheme 1). Purple precipitate was formed crystal suitable for X-ray single crystal diffraction.

Bis(4-bromo-N-(diethylcarbamothioyl)benzamido)nickel(II): Yield: 82%. M.p.: 248-250 °C. Anal. calcd. for $C_{24}H_{28}Br_2Ni_4O_2S_2$: C, 41.95; H, 4.11; N, 8.15. Found: C, 41.80; H, 4.05; N, 8.16 %. FT-IR (KBr, cm^{-1}): 2974, 2932, 2868 (CH); 1581 (CN), 1492 (C-O), 751 (C-Br). 1H NMR (400 MHz, $CDCl_3$, δ , ppm): 7.96 (d, 4H, Ar-H), 7.52 (d, 4H, Ar-H), 3.57 (m, 8H, N-CH₂), 1.48 (m, 12H, -CH₃).

Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$C_{24}H_{28}Br_2Ni_4O_2S_2$
Formula weight	687.15
Temperature / K	120(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
$a / \text{\AA}, b / \text{\AA}, c / \text{\AA}$	12.9099(17), 15.264(2), 14.0287(19)
β°	92.140(4)
Volume / \AA^3	2762.5(6)
Z	4
$\rho_{\text{calc.}} / \text{mg mm}^{-3}$	1.652
μ / mm^{-1}	3.775
F(000)	1384
Crystal size / mm^3	0.26 x 0.26 x 0.09
2 θ range for data collection	1.58 to 27.88°
Index ranges	-13 $\leq h \leq$ 16, -18 $\leq k \leq$ 20, -18 $\leq l \leq$ 18
Reflections collected	22583
Independent reflections	6579 [R(int) = 0.0607]
Data/restraints/parameters	6579/4/324
Goodness-of-fit on F^2	1.026
Final R indexes [$I > 2\sigma(I)$]	R1 = 0.0503, wR2 = 0.1146
Final R indexes [all data]	R1 = 0.0901, wR2 = 0.1301
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.731 / -0.612

3. Results and discussion

The reaction of nickel(II) acetate, $Ni(CH_3COO)_2$, with two equivalents of 4-bromo-N-(diethylcarbamothioyl)benzamide in methanol produces the potentially bidentate molecule *bis(4-bromo-N-(diethylcarbamothioyl)benzamido)nickel(II)* complex high yield (Scheme 1), as an air-stable purple solid. The single crystals of nickel(II) complex were grown by re-crystallization from an ethanol :dichloromethane solution mixture (1:2) at ambient temperature.

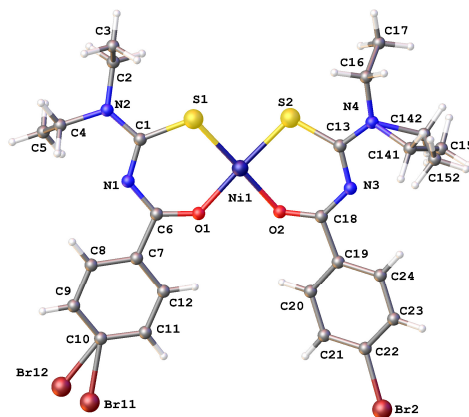
The ORTEP drawing of complex is illustrated in Figure 1 and some selected bond lengths and angles are listed in Table 1 and Table 2.

In this complex, the central Ni(II) atom is a *cis*-complex with slightly distorted square planar coordination. In this complex center nickel atom coordinated by two sulfur and two oxygen atoms from two ligands.

The bond lengths of the carbonyl O1-C6 1.263(5) \AA ; O2-C18 1.268(5) \AA and thiocarbonyl S1-C1 1.744(4) \AA ; S2-C13 1.745(4) \AA groups lie between those for double and single bonds. The same behavior is observed for C-N bond lengths. C-N bond lengths for the investigated complex is shorter than the average single C-N bond length of 1.48 \AA , being C1-N1 = 1.335(5) \AA , C6-

N1= 1.325(6) \AA , C1-N2 = 1.334(6) \AA , thus showing varying degrees of double bond character [13-27,33,34].

Two carbon atoms of one of the terminal ethyl groups were modelled as disordered over two sites, the ratio of refined occupancies being 0.5:0.5 for C141/C151: C142/C152. The C141-C151 and C141-N4 bond lengths were restrained to be equal to the C142-C152 and C142-N4 bond lengths, respectively with an effective standard deviation of 0.003 \AA . H atoms were placed in calculated positions and refined as riding, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ or 1.5 U_{eq} (methyl C). One Br atom is disordered over two positions with a refined site-occupancy ratio of 0.509(5):0.491 (5).

**Figure 1.** A perspective view of the title compound, with atom-numbering scheme.

The crystal structure is stabilized by weak C-H...S and C-H...Br hydrogen-bonding interactions (Table 4).

Table 2. Bond lengths for the title compound.

Atom	Atom	Length, \AA
Ni1	O1	1.852(3)
Ni1	O2	1.854(3)
Ni1	S1	2.1356(12)
Ni1	S2	2.1405(12)
Br2	C22	1.899(4)
Br11	C10	1.980(6)
S1	C1	1.744(4)
S2	C13	1.745(4)
O1	C6	1.263(5)
O2	C18	1.268(5)
N1	C1	1.335(5)
N1	C6	1.325(6)
N2	C1	1.334(6)
N2	C2	1.466(6)
N2	C4	1.487(5)
N3	C13	1.345(5)
N3	C18	1.314(5)
N4	C13	1.322(6)
N4	C141	1.519(8)

Table 3. Bond angles for the title compound.

Atom	Atom	Atom	Angle, °
O1	Ni1	O2	84.05(14)
O2	Ni1	S2	93.39(10)
O1	Ni1	S2	177.42(10)
O2	Ni1	S1	178.89(10)
O1	Ni1	S1	94.90(10)
S1	Ni1	S2	87.66(4)
C1	S1	Ni1	107.99(16)
C13	S2	Ni1	105.87(17)
C6	O1	Ni1	133.4(3)
C18	O2	Ni1	131.9(3)
C6	N1	C1	123.9(4)
C1	N2	C2	124.3(4)
C1	N2	C4	120.4(4)
C2	N2	C4	115.3(4)
C6	N1	C1	123.9(4)
C1	N2	C2	124.3(4)
C1	N2	C4	120.4(4)
C2	N2	C4	115.3(4)
N2	C1	N1	115.6(4)
N2	C1	S1	116.5(3)
N1	C1	S1	127.9(4)
O1	C6	N1	129.4(4)
O1	C6	C7	114.8(5)
N1	C6	C7	115.8(4)
N4	C13	N3	115.6(4)
N4	C13	S2	116.5(3)
N3	C13	S2	127.8(4)
C20	C19	C24	119.8(4)
C20	C19	C18	119.1(4)
C24	C19	C18	121.0(4)

Table 4. Hydrogen bonds for the title compound.

D	H	A	d(D-H), Å	d(H-A), Å	d(D-A), Å	D-H-A, °
C(2)	H(2B)	S(1)	0.99	2.56	2.965(5)	105
C(16)	H(16A)	S(2)	0.99	2.53	2.951(6)	106
C(3)	H(3A)	Br(12) ⁱ	0.98	2.87	3.633(6)	135

Symmetry code: *i*: -1+x, 1/2-y, -1/2+z.

4. Conclusion

In this work, *bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel (II) complex has been synthesized according to the previous reports. The crystal of nickel(II) complex is suitable for X-ray single crystal diffraction analysis. In this nickel complex, the nickel atom is coordinated by two S atoms and two O atoms from two 4-bromo-*N*-(diethylcarbamothioyl)benzamide molecules.

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Supplementary material

CCDC-848930 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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