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 C24H28Br2NiN4O2S2. The structure of compound has been determined by single-crystal X-ray diffraction analysis. It crystallizes in the monoclinic space group, P21/c with unit cell dimensions of a = 12.9099(17) Å, b = 15.264(2) Å, c = 14.028(19) Å, β = 92.140(4)° and V = 2782.5(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 pharmacological characteristics. Many benzoylthiourea compounds have been tested for their in vitro activity against a large variety of tumor lines and have found to be as effective or better than traditional heavy metal anticancer drugs such as cis-platin [1]. Some benzoylthiourea derivatives exhibit antiviral [2], antinftuel [3], antifungal [4], antimalarial [5,6], and herbicidal [7], activities. 1,3-Dialkyl or diaryl thioeureas exhibit significant antifungal activity against plant pathogens Pyricularia oryzae and Drechslera oryzae [8]. Furthermore, thioeurea 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 MoKα radiation (λ = 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)benzamid 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 the reaction. The change in color was due to the interaction of NiCl2·6H2O with the 4-bromo-N-(diethylcarbamothioyl) benzamide.
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.

**Scheme 1**

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

<table>
<thead>
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<th>Atom</th>
<th>Atom</th>
<th>Length, Å</th>
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<tbody>
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</tr>
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3. Results and discussion

The reaction of nickel(II) acetate, Ni(CH₃COO)₂, with two equivalents of 4-bromo-N-(diethylcarbamothioyl)benzamido)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 recrystallization 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 carboxyl O1-C6 1.263(5) Å; O2-C18 1.268(5) Å and thiocarbonyl S1-C1 1.744(4) Å; S2-C13 1.745(4) Å 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 Å, being C1-N1 = 1.335(5) Å, C6-
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.

Acknowledgements

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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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