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Synthesis and Structure of Bis(1,1-diethyl-3-(2-chlorobenzoyl)thioureido)nickel(II)

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Abstract

The Ni(II) complex of 1,1-diethyl-3-(2-chlorobenzoyl)thiourea (L) was synthesized and its crystal structure determined by X-ray crystallography. NiL_2 is monoclinic, space group P_21/c(#14), with $a = 8.229$, $b = 39.277$, $c = 8.485$ Å, $\beta = 96.8°$. The Ni(II) is coordinated in a planar fashion by two S and two O atoms in a *cis* arrangement. The Ni–S and Ni–O bond lengths are approximately 2.14 and 1.84 Å respectively, with the two bonds of each type differing only slightly. The S–Ni–S and O–Ni–O bond angles are 87.6° and 83.0° respectively, but with considerable expansion of the ligand bond angles in the chelate ring.

The crystal structure of the free ligand was also determined to compare free and complex bond lengths and angles. It is orthorhombic, space group P_bca(#61), with $a = 9.856$, $b = 10.128$ and $c = 26.848$ Å.

Introduction

We have recently begun to examine the coordination behavior of a series of *N*-acylthioureas that possess a number of interesting properties. These are O and S donor bidentate ligands that can coordinate as anionic species with loss of the proton from the acyl-substituted nitrogen. We discuss here the structure of one of them, bis(1,1-diethyl-3-(2-chlorobenzoyl)thioureido)nickel(II).

While numerous complexes of Ni(II) with substituted thioureas are known [1], complexation of thioureas with additional coordinating groups on the substituents has hardly been explored. Moreover, Ni(II) complexes with both O and S coordinating groups are not common. Casellato *et al.* [2] report a structure for one such complex containing the ligand $MeOCOCH_2CSCH_2OCOMe$ that is bidentate; two of these ligands coordinate Ni(II) in a neutral, diamagnetic planar complex with *cis* geometry (although with weak bonding of two other oxygen groups). As will be seen, the thiourea ligand discussed here has similar coordination properties.

Experimental

1,1-Diethyl-3-(2-chlorobenzoyl)thiourea (L) was prepared by the method of Ruffini [3]. Recrystallization from ethanol gave X-ray quality crystals. The nickel complex NiL_2 was formed in 30% yield as an insoluble material by refluxing 0.2 g of anhydrous $NiCl_2$ and 0.6 g of L in 135 ml chloroform for 5 days; the reaction proceeds much faster if an equivalent amount of base such as $(CH_3CH_2)_2NH$ is present. Purification was by chromatography through a Silica CC-7 Special column using a 70% ether, 30% hexane mixture, and the compound was recovered as purple needles on slow evaporation of the solvent. *Anal.* Found: C, 48.26; H, 4.73; S, 10.60; N, 9.32. Calc. for NiL_2: C, 48.00; H, 4.83; S, 10.70; N, 9.33%.

Infrared spectra were taken as KBr pellets on a Perkin-Elmer Model 298 infrared spectrophotometer, visible spectra were in chloroform solution using a Perkin-Elmer Model 330 UV–Vis spectrophotometer, and magnetic susceptibility was measured by the Gouy technique. Conditions for single-crystal X-ray diffraction are given in Table I.

Results and Discussion

The molecular structure of bis(1,1-diethyl-3-(2-chlorobenzoyl)thioureido)nickel(II) is shown in Fig. 1, atomic coordinates are listed in Table II, and selected bond lengths and bond angles are given in Table III.

The coordination geometry around the nickel atom is closely planar. The sulfur atoms are in the *cis* configuration in spite of the evident steric problem that produces an O–Ni–O bond angle of only approximately 83°; the S–Ni–S angle is about 87.6°. The S–S and O–O non-bonded separations

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TABLE I. Experimental Data for the X-ray Diffraction Studies

	NiL_2	L
Crystal system	monoclinic	orthorhombic
Space group	P_21/c(#14)	P_bca(#61)
Unit cell parameters		
a (Å)	8.229(1)	9.856(2)
b (Å)	39.277(5)	10.128(3)
c (Å)	8.485(1)	26.848(6)
α (°)	90.0	90.0
β (°)	96.8	90.0
γ (°)	90.0	90.0
Volume (Å^3)	2723.0(5)	2680.1(10)
Z	4	8
Density (calc.) (g cm^{-3})	1.46	1.342
Crystal dimensions (mm)	0.05 × 0.33 × 0.66	0.21 × 0.22 × 0.42
Diffractometer	Nicolet 3 Rm	Nicolet 3 Rm
Radiation	Mo Kα	Mo Kα
μMo (cm^{-1})	10.9	4.2
Omega scan range	$2° + (2\theta_{\alpha 1} - 2\theta_{\alpha 2})$	$2° + (2\theta_{\alpha 1} - 2\theta_{\alpha 2})$
$2\theta_{max}$ (°)	45	48
No. reflections	4153 (2761)	5596 (1905)
R, R_w (%)	4.54, 4.88	3.83, 4.53

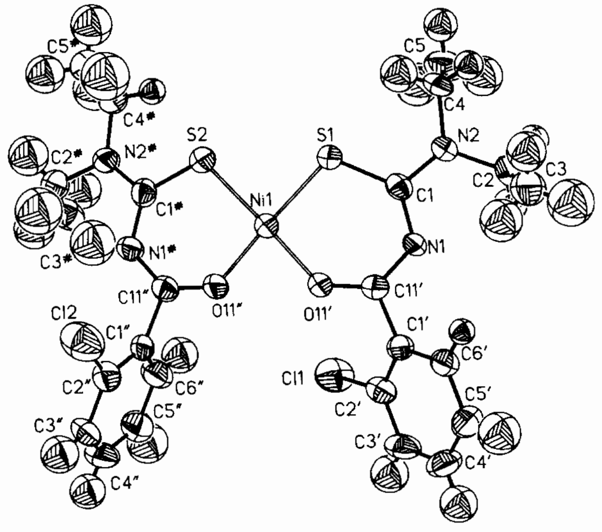

Fig. 1. Bis(1,1-diethyl-3-(2-chlorobenzoyl)thioureido)nickel(II). The atom labeling is consistent with Fig. 2 and the data tables.

are 2.97 and 2.45 Å respectively, compared to the sums of the van der Waals' radii of 3.6 and 3.0 Å [4]. Preference for the *cis* structure can be justified on the basis of greater Ni–S d–π bonding that can be present in the *cis* arrangement; each S atom can independently interact with a nickel d_{xz} or d_{yz} orbital. The Ni–S bond distance is similar to that found for a bidentate oxygen–sulfur donor recently reported [2].

For comparison, the molecular structure of the free ligand is shown in Fig. 2, with other pertinent structural data given in Tables IV and V.

The nitrogen to which the acyl group is attached is trigonal, exhibiting essentially the same C–N–C bond angle in the free ligand as in the complex, in which it has lost H^+. In the free ligand, the N–C bonds are of unequal length; both are shorter than average single bonds, but the acyl-substituted N–C distance is shorter than the other. In the complex form, both C–N bond lengths decrease and the difference becomes half as great as in the free ligand. At the same time, both the C–N and C–S bond lengths increase slightly on coordination; both remain shorter than typical single bonds, however, indicating considerable π-bonding character in the chelate ring. The S–C–N and O–C–N angles increase from near 120° to near 130° on coordination, reflecting considerable strain in achieving the required bite. When compared to unsubstituted thiourea [5], the C–S bond in the acyl compound is shorter (1.66 *versus* 1.72 Å) while the acyl-substituted N–C distance is longer (1.43 *versus* 1.33 Å).

The X-ray data show that there is little steric interaction among the organic substituent groups in the molecule of the complex, and no interactions between different nickel atoms in the crystal. The metal atoms are well separated from all other groups above and below the plane.

Pertinent features of the infrared spectra of ligand and complex include the loss of the N–H stretching frequency at 3200 cm^{-1} in the free ligand as the ligand loses the proton from the acyl-substituted nitrogen on forming the neutral complex, and the shift of the C=O stretching frequency from 1640 to 1605 cm^{-1} that accompanies coordination of this group. A ligand band at 730 cm^{-1} is probably

TABLE II. Atom Coordinates (×10^4) for NiL$_2$

Atom	x	y	z
Ni(1)	3626(1)	3688(1)	4786(1)
S(1)	3623(2)	3286(1)	6489(2)
S(2)	5928(2)	3847(1)	6017(2)
Cl(1)	1065(2)	3444(1)	244(2)
Cl(2)	3248(2)	4946(1)	3414(2)
C(1')	-862(5)	3342(1)	2620(5)
C(2')	-789(6)	3409(1)	1020(6)
C(3')	-2207(7)	3437(1)	-25(6)
C(4')	-3695(7)	3401(1)	498(7)
C(5')	-3801(7)	3326(1)	2062(7)
C(6')	-2391(6)	3294(1)	3106(6)
C(1")	4025(6)	4446(1)	1432(6)
C(2")	3371(6)	4767(1)	1554(6)
C(3")	2855(7)	4958(1)	201(7)
C(4")	3021(7)	4825(2)	-1255(8)
C(5")	3642(8)	4504(2)	-1394(7)
C(6")	4157(7)	4314(2)	-49(6)
N(1)	614(4)	3090(1)	4918(4)
N(2#)	8420(4)	4195(1)	5139(5)
O(11')	1634(4)	3568(1)	3700(4)
N(2)	1604(4)	2802(1)	7122(4)
N(1#)	6087(4)	4297(1)	3521(5)
C(11')	612(5)	3335(1)	3839(7)
O(11")	3563(4)	4022(1)	3242(4)
C(2)	129(6)	2583(1)	6853(6)
C(4)	2774(6)	2713(1)	8495(5)
C(4#)	9445(7)	4034(1)	6493(6)
C(11")	4587(6)	4235(1)	2890(6)
C(1)	1828(6)	3055(1)	6127(5)
C(1#)	6827(6)	4123(1)	4796(6)
C(5#)	9351(8)	4233(2)	8026(7)
C(5)	3967(8)	2442(2)	8090(8)
C(3)	-1369(9)	2732(2)	7458(7)
C(3#)	9575(8)	4327(2)	2636(7)
C(2#)	9196(7)	4456(2)	4241(7)

TABLE III. Selected Bond Lengths (Å) and Angles (°) for NiL$_2$

Bond length		Bond angle	
Ni(1)-S(1)	2.138(2)	S(1)-Ni(1)-O(11')	94.4(1)
Ni(1)-S(2)	2.142(1)	S(2)-Ni(1)-O(11")	95.0(1)
Ni(1)-O(11')	1.842(3)	Ni(1)-O(11')-C11')	134.7(3)
Ni(1)-O(11")	1.848(4)	N(1)-C(11')-O(11')	130.2(4)
O(11')-C(11')	1.256(6)	C(11")-N(1)-C(1)	122.7(4)
N(1)-C(11')	1.326(6)	N(1)-C(1)-S(1)	128.3(3)
N(1)-C(1)	1.350(5)	C(1)-S(1)-Ni(1)	109.6(2)
C(1)-S(1)	1.728(5)	S(1)-Ni(1)-S(2)	87.6(1)
		O(11')-Ni(1)-O(11")	83.0(2)

a mode involving the C=S stretch; it also shifts to lower energy, 700 cm^{-1}, as would be anticipated on complex formation [6].

TABLE IV. Atomic Coordinates (×10^4) for Ligand

Atom	x	y	z
S(1)	9526(1)	1608(1)	6664(1)
C(1)	7950(2)	1253(2)	6496(1)
N(1)	7584(2)	1366(2)	5983(1)
C(11')	7436(2)	290(2)	5685(1)
O(11')	7491(2)	-829(1)	5849(1)
C(1')	7243(2)	561(2)	5142(1)
C(2')	6218(2)	1338(2)	4939(1)
Cl(2)	4961(1)	2011(1)	5319(1)
C(3')	6122(3)	1546(2)	4433(1)
C(4')	7058(3)	985(2)	4123(1)
C(5')	8074(3)	188(2)	4308(1)
C(6')	8157(2)	-34(2)	4815(1)
N(2)	6949(2)	896(2)	6798(1)
C(2)	5534(3)	701(3)	6637(1)
C(3)	4732(3)	1973(3)	6674(1)
C(4)	7201(3)	701(2)	7332(1)
C(5)	7577(3)	-704(3)	7445(1)

TABLE V. Selected Bond Lengths (Å) and Angles (°) for Ligand

Bond	Length	Bond	Angle
S_1-C_1	1.658(2)	S_1-C_1-N_1	118.7(2)
C_1-N_1	1.428(2)	C_1-N_1-C_{11}'	122.1(1)
N_1-C_{11}'	1.360(2)	N_1-C_{11}'-O_{11}'	121.8(2)
C_{11}'-O_{11}'	1.218(2)		
C_1-N_2	1.327(3)		

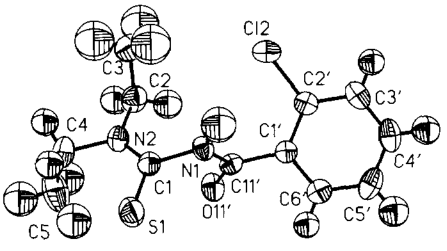

Fig. 2. Uncoordinated 1,1-diethyl-3-(2-chlorobenzoyl)thiourea.

The complex is diamagnetic at room temperature, and exhibits an electronic spectrum typical of square planar Ni(II) [7]; there is a ligand peak at 19 600 cm^{-1} ($\epsilon = 236$ l m^{-1} cm^{-1}) showing some structure. We have not attempted to resolve this peak and fit it to an energy level diagram.

Supplementary Material

Complete X-ray data are available from Prof. Bailey.

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