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SPECTROSCOPIC CHARACTERIZATION AND CRYSTAL STRUCTURE OF *cis*-bis(*N*-(2-BENZOYL)-*N*′,*N*′-DIPHENYLTHIOUREATO-*k*²O,S)NICKEL(II)

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The title compound [Ni(C$_{20}$H$_{15}$N$_2$OS)$_2$] is prepared by the reaction of metal acetate with the corresponding acylthiourea derivative. The complex is characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, and its structure is determined by single crystal X-ray diffraction. The Ni(II) ion is coordinated by the S and O atoms of two *N*-benzoyl-*N*′,*N*′-diphenylthiourea ligands in a slightly distorted square-planar coordination geometry. The two O and two S atoms are mutually *cis* to each other. The substance crystallizes triclinic (*P*-1 space group) with cell dimensions $a = 10.7262(9)$, $b = 12.938(3)$, $c = 14.2085(12)$ Å, $\alpha = 74.650(4)$, $\beta = 78.398(4)$, $\gamma = 68.200(5)°$, and two formula units in the unit cell. The structure is very close to the related *N*-(2-furoyl) Ni complex reported previously.

K e y w o r d s : nickel(II) complex, acylthiourea derivatives, spectroscopic analysis, crystal structure, molecular assembly, Hirshfeld surface.

INTRODUCTION

In recent years, thiourea derivatives have been a subject of investigations because of their applications in analytical and biological sciences, as well as due to their ability to form stable metal complexes [1]. A class of substituted thioureas widely studied is known as *N*-acyl-*N*′,*N*′-dialkylthiourea, synthesized for the first time by Neucki in 1873 [2]. In the field of coordination chemistry, *N*-acyl-*N*′,*N*′-dialkylthioureas coordinated with transition metals were first explored by Beyer and co-workers [3] and later by König *et al.* [4]. Many *N*-acyl-*N*′,*N*′-disubstituted thiourea complexes involving metals such as nickel, copper, cobalt, cadmium, palladium, platinum, and ruthenium have been studied, [5—10]. Thioureas coordinate to a metal via both sulfur and oxygen providing a multitude of bonding possibilities [1, 11]. Over recent years, many transition metal complexes with *N*-benzoyl-*N*′,*N*′-disubstituted thioureas have been reported [12—15] because this kind of ligands display a remarkably rich coordination chemistry. Usually the ligand is coordinated to the metal center forming a very stable bidentate complexe (*cis* conformation preferred) with a six-membered ring chelate structure, the complex stoichiometry generally being 1:2 or 1:3 (M:L, with M = metal ion and L = ligand), according to the oxidation state of the metal ion.

The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions. Metal complexes of these ligands containing oxygen and sulfur as donor atoms are known to possess useful activities as anti-tumor, anti-fungal, anti-bacterial, insecticidal, herbicidal, pesticidal reagents and plant-growth regulators [16, 17].

We have recently begun to examine the coordination behavior of a series of substituted acylthio-urea derivatives [5—7, 13—15]. In this paper, we study the binding of N-benzoyl-N',N'-diphenyl-thiourea to the Ni(II) ion. The complex was characterized by the elemental analysis, IR, ^{1}H and ^{13}C-NMR spectra, and X-ray structural analysis.

EXPERIMENTAL

All reagents and solvents used were purchased from commercial sources of analytical grade. Elemental analysis (C, H, N, and S) were performed on a Perkin-Elmer 2400 CHN instrument. The infrared spectrum was recorded on a Nicolet NEXUS 670 IR spectrophotometer using KBr discs. ^{1}H and ^{13}C NMR spectra were recorded on an Advance 300 Bruker spectrometer with $CDCl_3$ as the solvent at frequencies of 250 MHz and 62.9 MHz respectively, using TMS as the standard. The as-signment of the signals in the ^{13}C NMR spectra was supported by the DEPT-135° spectrum.

Synthesis of the complex. N-benzoyl-N',N'-diphenylthiourea ligand was synthesized by convert-ing benzoyl chloride into benzoyl isothiocyanate and then condensing with an appropriate amine [18]. To an ethanol solution (30 ml) containing the ligand (0.66 g, 2 mmol) was added an ethanol solution of $Ni(CH_3 \sim COO)_2 \sim 4H_2O$ (0.25 g, 1 mmol). The solution was stirred at room temperature for 2 h, and at once a solution of NaOH (1 N) was added to adjust pH to the neutral value. The mixture was filtered and the filtrate was evaporated under reduced pressure to give a red solid that was washed with acetone. Suitable X-ray quality crystals were obtained by slow evaporation of a chloroform/hexane solution (1:1, v/v) of the complex.

***cis*-bis(N-(2-benzoyl)-N',N'-diphenylthioureato-k^2O,S)nickel(II).** Brown. Yield, 74.0 %. TF (°C), 276—277. Anal. Calcd. for $C_{40}H_{30}N_4NiO_2S_2$ (%): C, 66.59; H, 4.19; N, 7.76; S, 8.89. Found: C, 66.46; H, 4.15; N, 7.81; S, 8.95. IR (KBr): ν = 3060 (CH), 3028 (CH), 1587 (C=C), 1513, 1417 (CN), 1254 (CS) cm^{-1}. ^{1}H NMR (CDCl$_3$), ppm: δ = 7.22—7,25 (m, 4H, Ph); 7.28 (d, J = 7.93 Hz, 1H, Ph); 7.33 (d, J = 7.32 Hz, 1H); 7,35—7,43 (m, 2H, Ph); 7.76 (d, J = 6.66 Hz, 2H, Ph); ^{13}C NMR (CDCl$_3$), ppm: 127.10, 128.56, 129.12, 129.49, 131.18, 131.63, 136.37, 136.45, 142.96 (C—Ph); 173.71 (CO); 175.48 (CS).

X-ray crystallography. X-ray diffraction data collection of the complex was performed on an Enraf-Nonius Kappa—CCD diffractometer (95 mm CCD camera on a φ-goniostat) using graphite-monochromated MoK_α radiation (0.71073 Å). The final unit cell parameters were based on all reflec-tions. Data collections were carried out using the COLLECT program [19]; integration and scaling of the reflections were performed with the HKL Denzo—Scalepack system of programs [20]. Gaussian absorption correction was applied [21]. The structure was solved by direct methods with SHELXS-97 [22]. The model was refined by full-matrix least squares on F^2 with SHELXL-97 [22]. All hydrogen atoms were stereochemically positioned and refined with the riding model. The aromatic hydrogen atoms were set isotropic with a thermal parameter 20 % greater than the equivalent isotropic displace-ment parameter of the atom to which each one was bonded. The WinGX [23] program was used to prepare the material for publication. Structural analysis and figures were made using the ORTEP-3 [24] and MERCURY [25] softwares. The Cambridge Structural Database was used to compare the structure of the complex with the others [26]. Further details concerning data collection and refine-ment are given in Table 1.

RESULTS AND DISCUSSION

IR and NMR spectra. Regarding the IR spectra, the complex displays strong bands in the region of 1590—1250 cm^{-1}, which are characteristic of N-benzoyl-N',N'-diphenylthioureas and N-furoyl-N',N'-diphenylthioureas [27]. No absorption was detected, however, in the range between 1700 cm^{-1} and 1650 cm^{-1}, where the uncoordinated ligand is supposed to exhibit C=O stretching vibrations [18]. This absorption shifts to lower frequencies is a clear proof of complex formation with a large degree of electron delocalization within the chelate rings. N-benzoyl-N',N'-diphenylthiourea show the N—H stretching band near 3200 cm^{-1}, which is not present in the corresponding metal complex, in agree-ment with the presence of a deprotonated ligand in this chelate. The bands that center near 1500 cm^{-1},

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Crystal data and structure refinement parameters obtained for the complex

Empirical formula	$[NiC_{40}H_{30}N_4O_2S_2]$
Formula weight	721.51
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	10.7262(9), 12.938(3), 14.2085(12);
a, b, c, Å; α, β, γ, deg.	74.650(4), 78.398(4), 68.200(5)
Volume, Å^3	1753.8(5)
Z	2
Density calculated, Mg/m^3	1.366
μ, mm^{-1}	0.713
F(000)	748
Crystal size, mm^3	0.072×0.042×0.031
θ range deg.	3.11—25.00
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $-15 \le l \le 15$
Reflections collected	9392
Independent reflections	5011 [R(int) = 0.0838]
Completeness to θ$_{max}$, %	99.4
Max. and min. transmission	0.978 and 0.926
Data / restraints / parameters	6179 / 0 / 442
Goodness-of-fit on F^2	0.976
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0505$, $wR2 = 0.0910$
R indices (all data)	$R1 = 0.1102$, $wR2 = 0.1065$
Δρ$_{max}$ and Δρ$_{min}$, e·Å^{-3}	0.251 and -0.385

1400 cm^{-1}, and 1250 cm^{-1} can be attributed to absorptions of the CN and CS groups engaged in partial double bonds and confirm the complex formation, while those bands are absent in the IR spectra of the free ligand.

Additional support for the above assignments is obtained from the ^{1}H NMR spectra of this complex. The experimental NMR data of the complex correspond to those of similar compounds [28]. The absence of the singlet corresponding to the proton of NH acylthioureide groups around 8.70 ppm [18] corroborates the coordination of the ligand to metal through these groups. As far as ^{13}C NMR spectra is concerned, the signals in 182.76 ppm (C=S) and 162.63 ppm (C=O), typical of the free ligand, are absent. Two new peaks, assigned to quaternary carbon atoms, were found about 175.5 ppm (CS) and 173.7 ppm (CO) instead, which is in accordance with the proposed structure for the complex. The effects of circulating π electrons of the chelate rings could account for the opposite displacements that have been found with respect to the free ligand, especially in the carbon atoms corresponding to the thiocarbonyl and carbonyl groups, with shifts to lower and higher frequencies respectively.

Single crystal X-ray analysis. The molecular structure of the complex showing the atom numbering scheme is given in Fig. 1. Selected bond lengths and angles are listed in Table 2. In the structure, two *N*-benzoyl-*N′*,*N′*-diphenylthiourea molecules are bonded to the central Ni(II) ion in *cis* positions. The coordination geometry is a slightly distorted square-plane as reflected by O1—Ni1—S2 and O2—Ni1—S1 bond angles (Table 2). The dihedral angle between S1—Ni1—O1 and S2—Ni1—O2 planes is 5.1(2)°.

The Ni—S (1.862(3) Å and 1.865(3) Å) bond distances are equal within experimental error [26]. The Ni—S and Ni—O bond lengths lie within the range of those found in the related structures [5, 14]. The distance of the nickel atom from the best plane through the coordination sphere is −0.013(1) Å. The chelate ring systems Ni1—O1—C1—N1—C2—S1 and Ni1—O2—C21—N3—
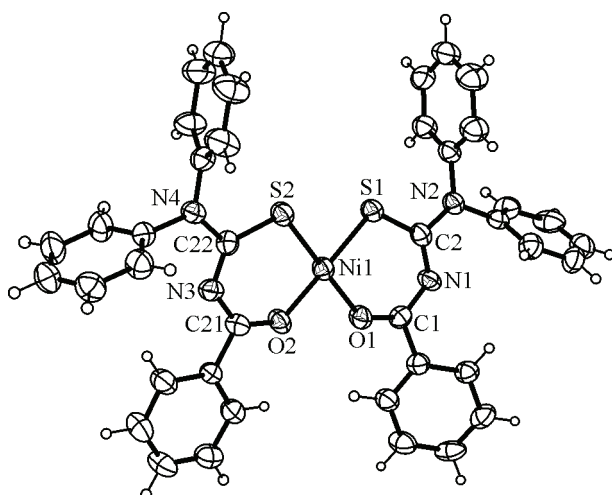
Fig. 1. Molecular structure of the title compound with selected atoms labeled. Displacement ellipsoids are drawn at the 30 % probability level

C22—S2 are nearly planar with the largest deviations from the best plane being 0.047(2) Å for O1 and –0.037(3) Å for O2 respectively. The dihedral angle between these chelate planes is 6.66(13)°. The molecular structure is very close to the related *N*-(2-furoyl) Ni complex reported previously [5], and shows a dihedral angle of 28.1(2)° between the phenyl planes of the benzoyl groups, in comparison with the corresponding angle of 24.2(2)° between the furanic planes of the furoyl Ni complex.

The lengths of C—O, C—S, and C—N bonds in the chelate ring are between characteristic single and double bond lengths [26], which are shorter than single and longer than double bonds. These results can be explained by the existence of delocalization in the chelate ring, which is also supported by IR and NMR data. Fig. 2 shows the packing arrangement of the complex with two molecules in the unit cell. The crystal assembly of this complex is formed by sheets along the [111] direction (Fig. 3). To stabilize the structure there are weak non-classical C…H—C intermolecular interactions, such as van der Waals forces and π—π stacking. It is known that the non-classical interactions can provide good structural motifs for the construction of extended architectures and stabilize the crystal structures of Ni(II) complexes [29].

These weak intermolecular interactions of the complex were analyzed using the Hirshfeld surfaces and the corresponding 2D fingerprint plots [30]. The d_{norm} (normalized contact distance) surface

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Selected bond lengths and angles (Å, deg.) *for the complex*

Ni1—O1	1.862(3)	C1—O1	1.255(4)	C2—N1	1.330(4)
Ni1—O2	1.865(3)	C1—N1	1.332(4)	C2—N2	1.362(4)
Ni1—S1	2.1445(11)	C1—C3	1.478(5)	C2—S1	1.720(4)
Ni1—S2	2.1530(11)				

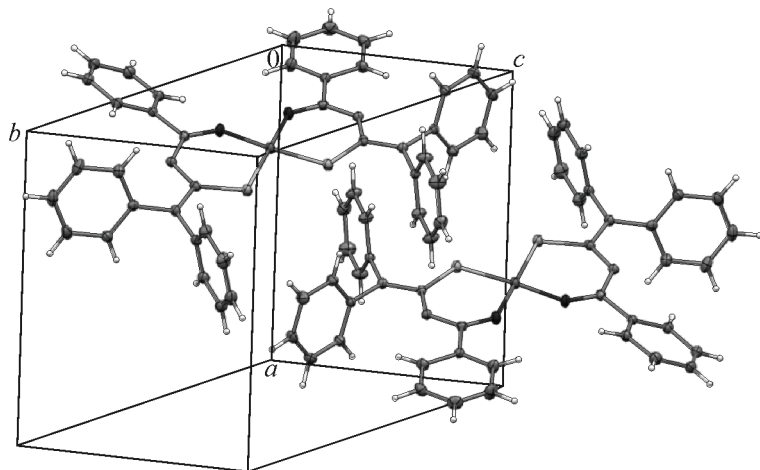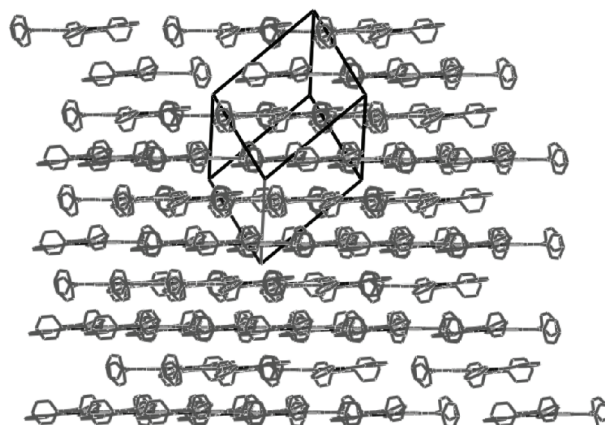| O1—Ni1—O2	83.36(11)	O2—Ni1—S1	176.66(9)	O2—Ni1—S2	95.68(9)
O1—Ni1—S1	95.57(8)	O1—Ni1—S2	175.57(9)	S1— Ni1—S2	85.62(4)

Fig. 2. View of the unit cell of the title complex

Fig. 3. Crystal packing representation with the molecules forming sheets along the [111] direction

and the breakdown of the fingerprint plots (new techniques and tools incorporated in the CrystalExplorer computer program [31]) were used for decoding and quantifying the intermolecular interactions in the crystal lattice. From this analysis, it immediately emerges that the title compound noticeably contributes to C…H—C interactions (35.9 % Hirshfeld surface area), more than other contacts, as obtained from the crystal structure of the complex.

Supplementary Material. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 816028. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

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