Hindawi
Journal of Chemistry
Volume 2018, Article ID 6108242, 8 pages
https://doi.org/10.1155/2018/6108242

Research Article

Crystal Structure and Cyclic Voltammetric Studies on the Metal Complexes of *N*-(Dimethylcarbamothioyl)-4-fluorobenzamide

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Received 31 October 2017; Accepted 26 December 2017; Published 30 April 2018

Academic Editor: Artur M. S. Silva

We synthesized *N*-(dimethylcarbamothioyl)-4-fluorobenzamide compound and its copper(II) and nickel(II) complexes. The structures of compounds have been characterized by elemental analysis and spectral data (IR, ^{1}H NMR). Furthermore, crystal and molecular structure of the synthesized complexes have been identified by using single crystal X-ray diffraction data. In the complexes formation the metal atom was coordinated via two sulfur atoms and two oxygen atoms. The single crystal structure of copper(II) and nickel(II) complex exhibits slightly distorted square planar geometry. The oxygen atoms are in a *cis* configuration. It appeared that the lengths of the thiocarbonyl and carbonyl bonds are longer than the average for C=S and C=O; meanwhile the C-N bonds in the complex ring appeared to be shorter than the average for C-N single bonds. These data show that C-O, C-S, and C-N bond lengths of the complexes suggest considerable electronic delocalization in the chelate ring. All bond lengths and angles obtained as a result of the analyses are found to be within experimental error limits. The obtained crystal analysis data shows that the structure of complex compounds is compatible with similar compounds in literature. Electrochemical behavior of complexes has been investigated by cyclic voltammetry technique in aprotic media. From the cyclic voltammetric investigation, both of the complexes have demonstrated electroactive properties.

1. Introduction

Benzoylthiourea derivatives are considered privileged compounds, because of their simple preparation with high yields [1–7]. The synthesis of new benzoylthiourea compounds also becomes widespread due to their potential application in biological [8–12] and analytical chemistry [13–17]. The ability of thiourea derivatives to complex with transition metal cations is well known [18, 19]. In general, thiourea derivative ligands consist of some substituents with different electron-donating or electron withdrawing groups and, therefore, may have interesting electrochemical properties. Due to these properties, the studies on the electrochemical properties of benzoyl thiourea derivatives are found in literature, albeit to a lesser extent [20–28]. The presence of hard O- and N- and soft S-donor atoms in the backbones of these ligands enables them to react readily with both, transition group and main group metal ions, yielding stable metal complexes [29]. The present paper reports the synthesis, characterization, and electrochemical properties on copper(II) and nickel(II) complexes of *N*-(dimethylcarbamothioyl)-4-fluorobenzamide compounds.

2. Experimental

2.1. Chemicals. All chemicals used in present study such as 4-fluorobenzoyl chloride, potassium thiocyanate, dimethyl amine, hydrochloric acid, nickel acetate, copper acetate, sodium hydroxide, tetrabutylammonium hexafluorophosphate, dichloromethane, and ethanol were purchased from Merck. All solvents and chemicals were of reagent grade quality and used without further purification.

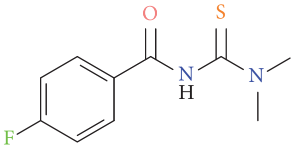


Figure 1

2.2. Instrumentation. C, H, and N analyses were carried out on a Carlo Erba MOD 1106 instrument. FT-IR (KBr pellets) spectra were recorded on a Shimadzu 435 spectrophotometer between 4000 and 400 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer, using CDCl$_3$ as solvent and TMS as internal standard. Single crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer using monochromated MoKα (λ = 0.71073 Å) radiation. The structures were solved by direct and conventional Fourier methods [30]. Full-matrix least-squares refinement was based on F^2 and hydrogen atoms derived from difference maps and refined at idealized positions riding at their parent C atoms [31]. Cyclic voltammetry experiments were carried out using a CHI 660E electrochemical workstation.

2.3. Synthesis of the Ligand. *N*-(Dimethylcarbamothioyl)-4-fluorobenzamide compound was synthesized according to literature [18, 19]. A solution of 4-fluorobenzoyl chloride (0.5 mol) in dry acetone (30 mL) was added dropwise to a solution of potassium thiocyanate (0.5 mol) in dry acetone (30 mL). The reaction mixture was heated under reflux for 1 h and then cooled to room temperature. The dimethyl amine (0.1 mol) was added dropwise by stirring to the solution of 4-fluorobenzoyl isothiocyanate (0.1 mol) in dry acetone (30 mL). The reaction mixture was heated under reflux for 1 h. Then, the mixture was poured into cold 0.1 M HCl acid solution. Then, the white precipitated solid compound was filtered. After that crystallization of the crude product by using a mixture of dichloromethane : ethanol (in 1 : 2 ratio by volume) gave *N*-(dimethylcarbamothioyl)-4-fluorobenzamide as white crystals in 78% yield [18, 19].

N-(Dimethylcarbamothioyl)-4-fluorobenzamide, HL (See Figure 1). Color: White. Yield: 78%. M.p.: 130–132°C. Anal. calcd. for $C_{10}H_{11}FN_2OS$ (226.3 g/mol): C, 53.08; H, 4.90; N, 12.38. Found: C, 53.00; H, 4.81; N, 12.36%. FT-IR (KBr, ν, cm^{-1}): ν (NH) 3231; ν (CH) 2998, 2976, 2936; ν (C=O) 1668; ν (C=S) 1251, ν (C-F) 758. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 8.58 (s, 1H, N-H), 7.74 (d, 2H, Ar-H), 7.64 (d, 2H, Ar-H), 3.51 (s, 3H, N-CH$_3$), 3.26 (s, 3H, N-CH$_3$).

2.4. Synthesis of the Metal Complexes. Complex compounds were prepared according to the method described in literature [18, 19, 29, 32, 33]. A metal acetate solution in methanol was added dropwise to the ligand in a 1 : 2 molar ratio in methanol. Then, the pH was adjusted with 0.1 M NaOH or 0.1 M HCl for complex formation. The reaction mixture was stirred for 2 h at room temperature. The colored solid complexes were filtered and recrystallized from ethanol: dichloromethane (1 : 2, v : v) mixture [18, 19].

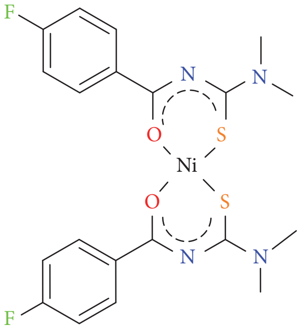


Figure 2

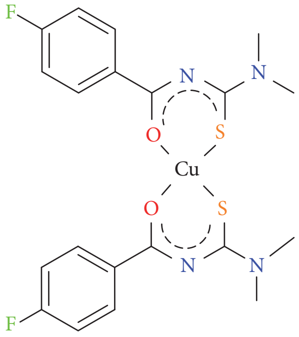


Figure 3

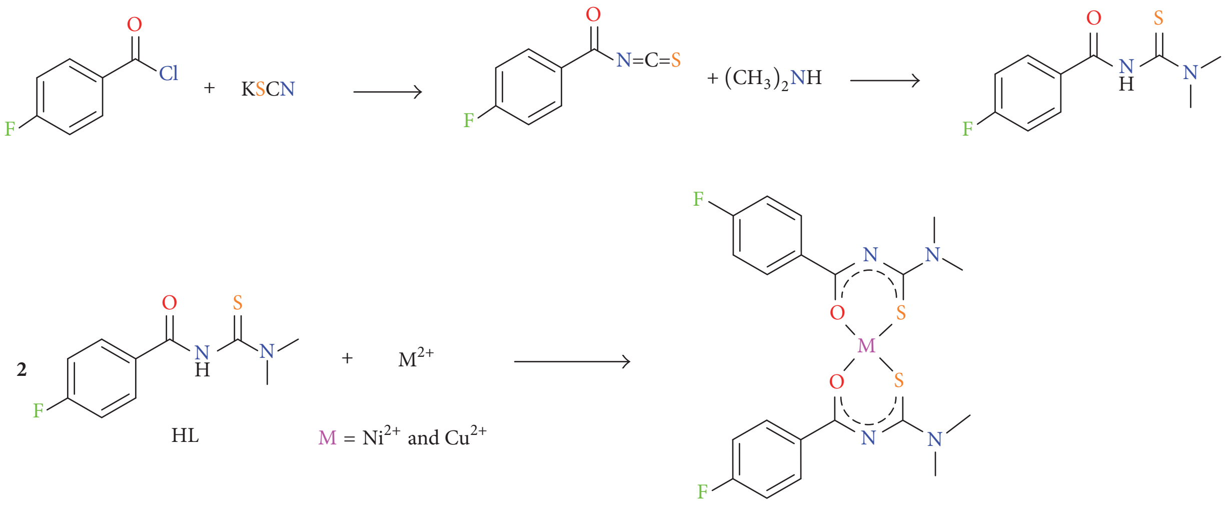
Bis(N,N-dimethyl-N′-4-fluorobenzoylthioureato) Nickel(II) (NiL$_2$) (See Figure 2). Color: Purple. Yield: 86 %. M.p.: 257-258°C. Anal. calcd. for $C_{20}H_{20}F_2N_4NiO_2S_2$ (509.2 g/mol): C, 47.17; H, 3.96; N, 11.00. Found: C, 47.10; H, 3.87; N, 11.01%. FT-IR (KBr, ν, cm^{-1}): ν (CH) 2929, 2853 (vw); ν (CN) 1602 (w); ν (C-O), 1495 (vs); ν (C-F), 760 (w). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 8.13 (m, 4H, Ar-H), 7.06 (m, 4H, Ar-H), 3.42 (s, 6H, N-CH$_3$), 3.32 (s, 6H, N-CH$_3$).

Bis(N,N-dimethyl-N′-4-fluorobenzoylthioureato) Copper(II) (CuL$_2$) (See Figure 3). Color: Green. Yield: 71 %. M.p.: 209-210°C. Anal. calcd. for $C_{20}H_{20}CuF_2N_4O_2S_2$ (514.1 g/mol): C, 46.73; H, 3.92; N, 10.90. Found: C, 46.61; H, 3.80; N, 10.77 %. FT-IR (KBr, ν, cm^{-1}): ν (CH), 2926, 2852 (vw); ν (CN) 1600 (w), ν (C-O) 1493 (vs); ν (C-F) 761 (w).

2.5. Cyclic Voltammetry. All experiments were conducted in CH$_2$Cl$_2$ with 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Electrochemical experiments were conducted in a three-component cell consisting of a Pt wire auxiliary electrode, a nonaqueous reference electrode (Ag/Ag$^+$), and a glassy carbon (GC) as working electrode in the range of −0.4 to +0.4 V and −0.4 to +1.6 V for Cu(II) and Ni(II) ions, respectively.

3. Results and Discussion

3.1. Synthesis. *N*-(Dimethylcarbamothioyl)-4-fluorobenzamide compound was synthesized in two steps. In the first step, 4-fluorobenzoyl chloride reacted with an equimolar amount of



Scheme 1: Synthesis reaction of the ligand and metal complexes.

potassium thiocyanate in dry acetone. At the end of the reaction 4-fluorobenzoyl isothiocyanate appeared. In the second step, 4-fluorobenzoyl isothiocyanate reacted with dimethylamine in dry acetone solution to synthesize *N*-(dimethylcarbamothioyl)-4-fluorobenzamide [18, 19].

Complexes were obtained with good yield by stirring the appropriate metal acetate with two equivalents of *N*-(dimethylcarbamothioyl)-4-fluorobenzamide for 2 hours in methanol [18, 19]. The reaction of complex is illustrated in Scheme 1. Ligand and its copper and nickel complex were characterized by different spectroscopic techniques including elemental analysis, IR, ^{1}H NMR spectroscopy, and single crystal X-ray diffraction study.

The FT-IR data of the prepared compounds are consistent with the proposed structures. In the FT-IR spectra of the ligand, the N-H stretching vibration is observed at *ca* 3200 cm^{-1} as an intense broad band. This absorption band disappears upon metal complex formation. The delocalization of the ν C=O stretching vibration causes a negative shift. The ν C=O stretching vibration can be observed in the ligand at 1695 cm^{-1}, and the ν CO stretching vibration of the corresponding Ni(II) and Cu(II) complexes appears at 1445 and 1493 cm^{-1}, respectively. This is in close agreement with other previously studied thiourea derivatives [18, 19, 29, 32–35].

The ^{1}H NMR spectra of all compounds are compatible with their expected structures. The ^{1}H NMR spectra of the ligands are consistent with their structures. In the ^{1}H NMR spectra, the N-H signal present in the ligand at δ 8.58 ppm disappears in the complexes. The aryl proton signals are shifted to lower field [18, 19, 29, 32–35].

3.2. Crystal Structure Analysis. Crystals of the synthesized compounds suitable for single crystal X-ray diffraction analysis were obtained by recrystallization from dichloromethane : methanol (1 : 2, $v : v$) mixture at room temperature. The ORTEP views of *bis*(*N*,*N*-dimethyl-*N*′-4-fluorobenzoylthioureato) nickel(II) (NiL_2) and *bis*(*N*,*N*-dimethyl-*N*′-4-fluorobenzoylthioureato) copper(II) (CuL_2) with atom numbering schemes are depicted in Figures 4 and 5, respectively. Further details concerning data collection and refinement are given in Table 1. Selected bond lengths and angles of NiL_2 and CuL_2 are listed in Table 2. The crystal structures (Figures 4 and 5) of the complexes confirm that the *N*-(dimethylcarbamothioyl)-4-fluorobenzamide ligand is a bidentate chelating ligand, coordinating with the copper or nickel atom through the thiocarbonyl and carbonyl groups [29, 32–35]. Both structures are isotypic with very related geometric parameters. The planes of the dimethylamino groups as well as those of the *p*-fluorophenyl rings are almost parallel to the carbamothioyl moieties as shown from the torsion angles C-N-C-N and O-C-C-C with average 1.3(5) and 1.5(2) Å and 4.9(5) and 6.4(3) Å for NiL_2 and CuL_2, respectively. The coordination around the metal centers deviates slightly from square planarity with S-M-S 85.26(6)° and 88.62(2)° and O-M-O 85.0(1)° and 85.97(6)° (Ni and Cu).

The lengths of the thiocarbonyl and carbonyl bonds are longer than the average for C=S and C=O, while the C-N bonds in the complex ring are all shorter than the average for C-N single bonds, indicating the expected delocalization in the chelate ring. All other bond lengths and angles are in expected ranges. Related structures are known from SOBRIL (*bis*(1,1-diethyl-3-(4-fluorobenzoyl)thiourea)-nickel(II)) [35] or FIKSUP (*bis*(*N*-4-fluorobenzoylpiperidine-1-carbothioimidato)-copper(II)) [36]. There are no intermolecular interactions shorter than Van der Waals radii.

3.3. Electrochemistry. The electrochemical behaviors of copper(II) and nickel(II) complexes have been investigated in aprotic solvents by cyclic voltammetry. According to the obtained results, both Cu(II) and Ni(II) complexes have shown electroactive properties. Cyclic voltammogram of CuL_2 and NiL_2 in dichloromethane are shown in Figure 6. The results indicate that CuL_2 undergoes one-electron reversible redox waves in potential range of 400 to −400 mV. It can be seen from the cyclic voltammogram of Cu(II) complex in DCM at a scan rate of 0.1 V/s that a well-defined redox

Table 1: Crystal data and structure refinement for NiL_2 and CuL_2 complexes.

Parameters	NiL_2	CuL_2
Empirical formula	$C_{20}H_{20}F_2NiN_4O_2S_2$	$C_{20}H_{20}F_2CuN_4O_2S_2$
Formula weight	509.23	514.06
Temperature (K)	120(2)	120(2)
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	11.339(7)	11.3504(16)
b (Å)	8.255(5)	8.5070(12)
c (Å)	22.051(17)	22.164(3)
β (∘)	103.934(18)	103.828(3)
Volume ($Å^3$)	2003(2)	2078.1(5)
Z	4	4
Calculated density (mg/m^3)	1.689	1.643
Absorption coefficient (mm^{-1})	1.223	1.296
$F(000)$	1.048	1052
Crystal size (mm^3)	0.47 × 0.43 × 0.02	0.42 × 0.33 × 0.23
Radiation	Mo$K\alpha$	Mo$K\alpha$
Θ range for data collection	1.85 to 27.87∘	1.85 to 27.88°
Index ranges	$-14 \le h \le 14$ $-10 \le k \le 10$ $-29 \le l \le 24$	$14 \le h \le 14$ $-11 \le k \le 10$ $-25 \le l \le 29$
Reflections collected	17259	17633
Independent reflections	4776 [$R_{int} = 0.1266$]	4953 [$R_{int} = 0.0279$]
Data/parameters	4776/284	4953/284
Goodness-of-fit on F^2	0.947	1.057
Final R indexes ($I \ge 2\sigma(I)$)	$R1 = 0.0554$, w$R2 = 0.1186$	$R1 = 0.0311$, w$R2 = 0.0792$
Final R indexes (all data)	$R1 = 0.0864$, w$R2 = 0.1285$	$R1 = 0.0378$, w$R2 = 0.0829$
Largest difference peak and hole (e·$Å^{-3}$)	0.926/−0.892	0.461/−0.256

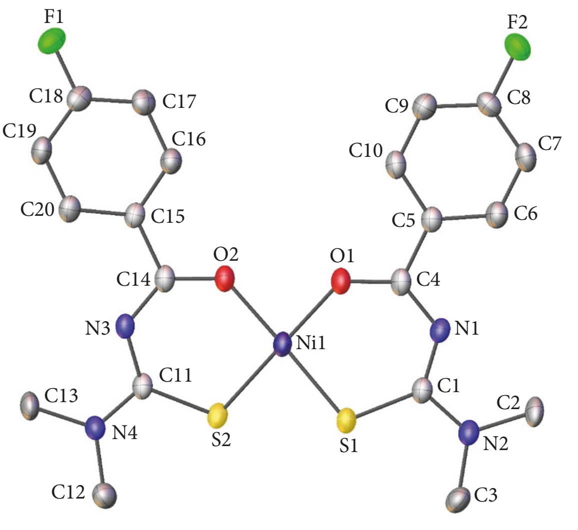


Figure 4: Molecular structure of NiL_2 with anisotropic displacement ellipsoids drawn at 50% probability level. H-atoms omitted for clarity.

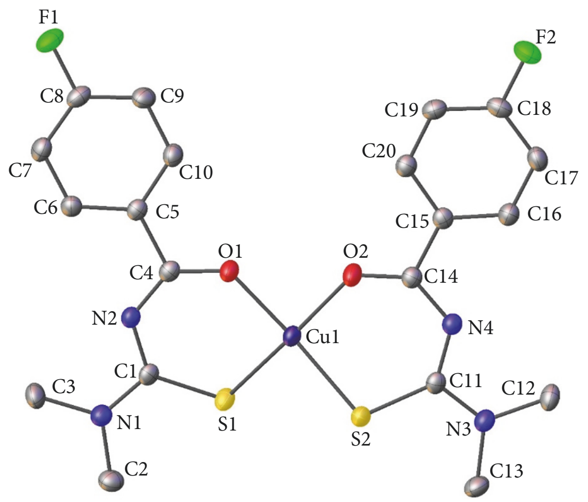
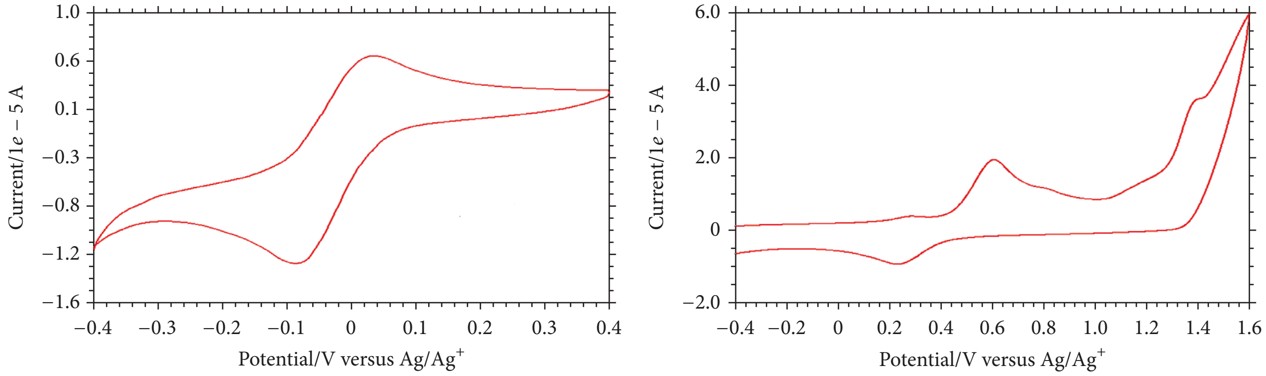


Figure 5: Molecular structure of CuL_2 with anisotropic displacement ellipsoids drawn at 50% probability level. H-atoms omitted for clarity.

process exists. The Cu(II) complex has exposed the observed reduction peak at $E_{pc} = -0.085$ V which indicates the formation of Cu(II)/Cu(I) and corresponding oxidation peak at $E_{pa} = 0.025$ V versus Ag/Ag^+ indicates C(I)/Cu(II) couple [37–40]. The peak separation (ΔE_p) of this couple is found to be 0.110 V which is in accordance with the reversibility of

Table 2: Bond lengths and angles for NiL_2 and CuL_2 complexes.

Atom	Atom	Bond lengths, Å	Atom	Atom	Atom	Bond angles, ∘
			NiL_2			
Ni(1)	O(2)	1.848(3)	O(2)	Ni(1)	O(1)	85.05(12)
Ni(1)	O(1)	1.849(3)	O(2)	Ni(1)	S(2)	94.91(9)
Ni(1)	S(2)	2.1241(15)	O(1)	Ni(1)	S(2)	174.84(9)
Ni(1)	S(1)	2.1254(16)	O(2)	Ni(1)	S(1)	174.78(8)
S(2)	C(11)	1.716(4)	O(1)	Ni(1)	S(1)	95.26(9)
N(3)	C(14)	1.305(4)	S(2)	Ni(1)	S(1)	85.26(6)
N(3)	C(11)	1.324(4)	C(4)	O(1)	Ni(1)	131.4(2)
O(2)	C(14)	1.264(4)	C(14)	O(2)	Ni(1)	131.2(2)
N(4)	C(11)	1.329(4)	C(11)	N(4)	C(12)	123.4(3)
N(4)	C(12)	1.445(5)	C(11)	N(4)	C(13)	120.0(3)
N(4)	C(13)	1.458(5)	C(12)	N(4)	C(13)	116.6(3)
C(14)	C(15)	1.480(5)	N(3)	C(11)	N(4)	115.1(3)
C(15)	C(16)	1.378(5)	N(4)	C(11)	S(2)	117.0(3)
C(15)	C(20)	1.383(5)	C(1)	S(1)	Ni(1)	107.56(13)
F(1)	C(18)	1.345(4)	C(11)	S(2)	Ni(1)	107.29(13)
			CuL_2			
Cu(1)	O(1)	1.9232(13)	O(1)	Cu(1)	O(2)	85.97(6)
Cu(1)	O(2)	1.9293(14)	O(1)	Cu(1)	S(2)	169.33(5)
Cu(1)	S(2)	2.2349(5)	O(2)	Cu(1)	S(2)	93.81(4)
Cu(1)	S(1)	2.2384(6)	O(1)	Cu(1)	S(1)	93.37(4)
S(1)	C(1)	1.7360(18)	O(2)	Cu(1)	S(1)	170.37(5)
F(1)	C(8)	1.363(2)	S(2)	Cu(1)	S(1)	88.62(2)
O(1)	C(4)	1.269(2)	C(4)	O(1)	Cu(1)	131.65(12)
N(1)	C(1)	1.336(2)	C(1)	N(1)	C(2)	123.31(16)
N(1)	C(2)	1.459(2)	C(1)	N(1)	C(3)	120.18(16)
N(1)	C(3)	1.470(2)	C(2)	N(1)	C(3)	116.51(16)
N(2)	C(4)	1.318(2)	C(4)	N(2)	C(1)	125.43(16)
N(2)	C(1)	1.343(2)	N(1)	C(1)	N(2)	114.81(16)
C(4)	C(5)	1.498(2)	N(1)	C(1)	S(1)	117.42(14)
C(5)	C (10)	1.392(3)	N(2)	C(1)	S(1)	127.71(14)
C(5)	C(6)	1.393(3)	O(1)	C(4)	N(2)	130.40(17)



(a)

(b)

Figure 6: Cyclic voltammogram (a) of CuL_2 and (b) of NiL_2 in dichloromethane containing 0.1 M TBAHFP. Scan rate 100 mV/s.

Cu(II)/Cu(I) couple. A similar study reported that thiourea Cu complexes showed the reduction of Cu(II)/Cu(I) redox system undergoing an irreversible process with peak separation (ΔE_p) of about 0.200 V [21]. Duan et al. indicated that some modified thiourea derivatives undergo one-electron quasi-reversible and reversible redox reactions [41]. Ni(II) complex shows a quasi-reversible redox wave and an irreversible oxidation peak in in potential range of −0.4 to +1.6 V. Cyclic voltammogram indicates that Ni(II) complex in DCM undergoes Ni(II)/Ni(III) oxidation at $E_{\mathrm{pa}} = 0.59$ V with corresponding reduction at $E_{\mathrm{pc}} = 0.25$ V [42, 43]. The peak separation (ΔE_p) is 0.34 V for Ni(II)/Ni(III) redox couple.

Ni(II) complex also exhibits an irreversible oxidation peak at +1.38 V that is considered to be ligand moiety.

4. Conclusions

In this work, *N*-(dimethylcarbamothioyl)-4-fluorobenzamide ligand and its Ni(II) and Cu(II) complexes have been synthesized and evaluated for their electroactive properties. The chemical structure of compounds was characterized by elemental analysis, FT-IR, and ^{1}H NMR spectroscopy techniques. When the FT-IR spectra of the compounds were examined, characteristic peaks (ν C=O, ν C-O, ν C=S, ν C-S, and ν N-H stretching modes) were observed which should be present in similar benzoylthiourea derivatives such as 2,2-diphenyl-*N*-(dipropyl-carbamothioyl)acetamide, 2,2-diphenyl-*N*-(dibutyl-carbamothioyl)acetamide, *bis*(2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamido)nickel(II), *N*,*N*-diethyl-*N*′-benzoylthiourea, *N*,*N*-dipropyl-*N*′-benzoylthiourea, *cis-bis*(*N*,*N*-dimethyl-*N*′-4-chlorobenzoyl-thioureato)palladium(II), *N*-(dibenzylcarbamothioyl)-3-methylbutanamide, *cis-bis*[4-fluoro-*N*-(diethylcarbamothioyl)benzamido-κ^2O,S]platinum(II), *N*-(di-*n*-propyl carbamothioyl) cyclohexanecarboxamide, 4-chloro-*N*-[*N*-(6-methyl-2-pyridyl)carbamothioyl]benzamide, 4-bromo-*N*-(dimethylcarbamothioyl)benzamide, and *bis*(4-bromo-*N*-(dimethylcarbamothioyl)benzamido)nickel(II) which is consistent with the literature [1, 4–7, 32, 34, 44, 45]. Besides these, the crystal and molecular structure of synthesized complexes were analyzed by X-ray single crystal diffraction method. The comparative analysis was performed with literature data. The structure of these compounds is consistent with the structure of other benzoylthiourea derivatives. The bond lengths and angles also agree well with other thiourea derivatives. The electrochemical behaviors of copper(II) and nickel(II) complexes have been investigated in aprotic solvents by cyclic voltammetry. Cu(II) complex showed reversible behavior in potential range of 400 to −400 mV while Ni(II) complex showed quasi-reversible behavior in potential of 1600 to −400 mV. According to the obtained results, both Cu(II) and Ni(II) complexes have shown electroactive properties.

Disclosure

A part of this work was presented as a poster (P-261) at the 5th National Inorganic Chemistry Congress 2015 in Mersin, Turkey.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This academic work was linguistically supported by the Mersin Technology Transfer Office Academic Writing Center of Mersin University. This study was supported by the Research Fund of Mersin University in Turkey with Project no. BAP-2015-AP4-1198.

Supplementary Materials

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication no. CCDC-1457502 for NiL$_2$ and no. 1459297 for CuL$_2$. Copies of available material can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, by emailing data_request@ccdc.cam.ac.uk, or contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033. *(Supplementary Materials)*

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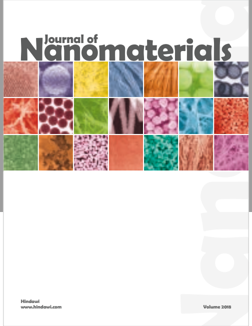
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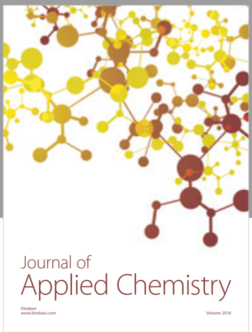
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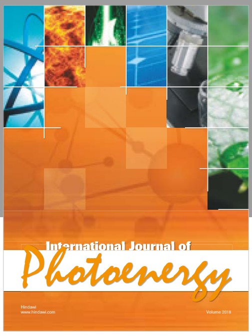
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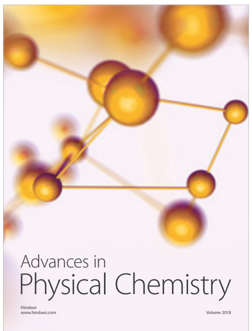
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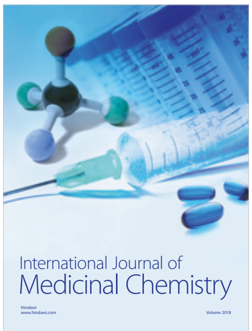
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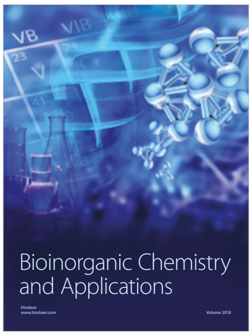
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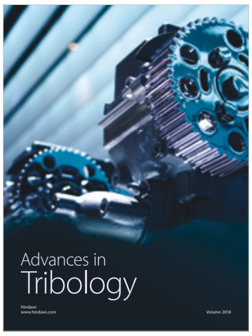
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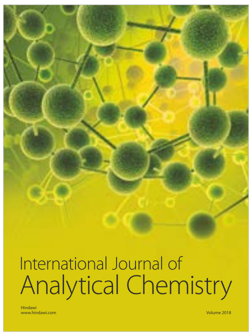
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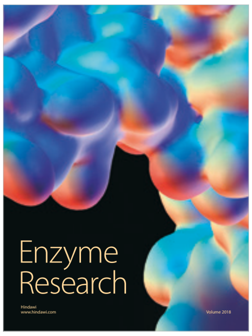
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