

Research Article

Synthesis and Characterization of Novel Thiourea Derivatives and Their Nickel and Copper Complexes

Gün Binzet,¹ Gülten Kavak,² Nevzat Külcü,³ Süheyla Özbey,⁴
Ulrich Flörke,⁵ and Hakan Arslan³

¹ Department of Science Education, Faculty of Education, Mersin University, 33343 Mersin, Turkey

² Department of Physics, Faculty of Sciences, Dicle University, 21280 Diyarbakır, Turkey

³ Department of Chemistry, Faculty of Arts and Science, Mersin University, 33343 Mersin, Turkey

⁴ Department of Physics Engineering, Hacettepe University, Beytepe, 06800 Ankara, Turkey

⁵ Department of Chemistry, University of Paderborn, 33098 Paderborn, Germany

Correspondence should be addressed to Gün Binzet; polatgun@gmail.com and Hakan Arslan; hakan.arslan.acad@gmail.com

Received 29 May 2013; Accepted 28 July 2013

Academic Editor: Andrea Trabocchi

Copyright © 2013 Gün Binzet et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

New benzoyl thiourea derivatives and their nickel and copper complexes were synthesized. The structure of the synthesized compounds were confirmed by elemental analysis, FT-IR, and ¹H NMR techniques. Four of the synthesized compounds are analyzed by X-ray single crystal diffraction technique. Whereas *N,N*-dimethyl-*N'*-(4-fluorobenzoyl)thiourea, *N,N*-diethyl-*N'*-(4-fluorobenzoyl)thiourea, and *N,N*-di-*n*-butyl-*N'*-(4-fluorobenzoyl) thiourea crystallize in the monoclinic system, *bis*(*N,N*-di-*n*-propyl-*N'*-(4-fluorobenzoyl)thioureato) nickel(II) complex crystallizes in the triclinic system. These ligand molecules form dimers through strong intermolecular hydrogen bonds such as N-H...S, C-H...O, and N-H...O. Moreover, there are different types of intramolecular interactions in the crystal structures. *Bis*(*N,N*-dimethyl-*N'*-(4-fluorobenzoyl)thioureato) nickel(II) complex has a nearly square-planar coordination. The distance of nickel atom from the best plane through the coordination sphere is 0.029 Å.

1. Introduction

The role of benzoyl thioureas derivatives in coordination chemistry has been extensively studied and quite satisfactory elucidated. Because benzoyl thioureas have suitable C=O and C=S function groups, they can be considered as useful chelating agents due to their ability to encapsulate into their coordinating moiety metal ions [1]. Therefore, new thiourea derivatives and their structures have received attention of several research groups because of their complexation capacity [2–5]. Some derivatives are biologically active, such as antifungal [6, 7], antitumour [8–10], antiviral, antibacterial [11–13], pharmacological [14], herbicidal, and insecticidal properties [11–13]. In addition, some of the research groups have reported thermal behaviour [15–18] and the acidity constants [19] of ligands of some benzoylthiourea derivatives and their metal complexes [20–30].

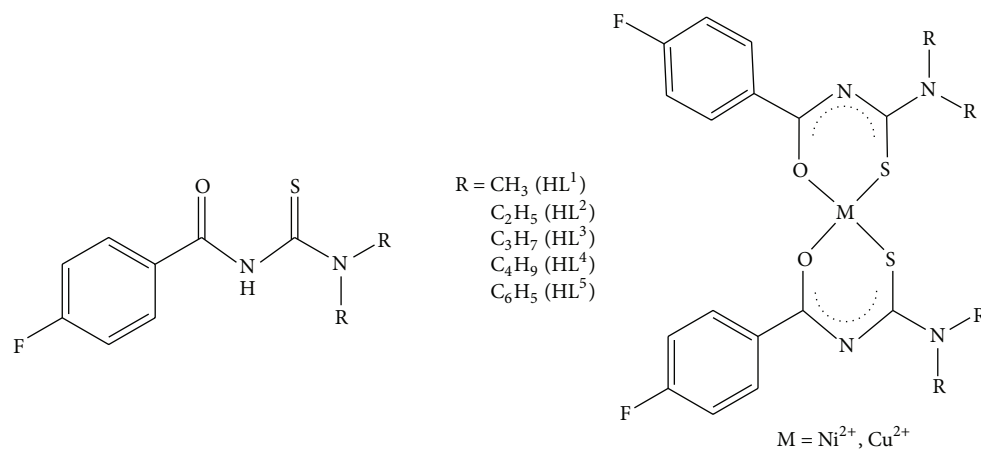
In addition, fluorine-containing organic compounds have been frequently applied to biorelated materials, medicines,

and agrochemicals because of their unique properties, such as high thermal stability and lipophilicity [20].

There are many reasons for the interest in such molecules. In the present study, we combined thiourea group with fluorine-containing organic compound and report the preparation and characterization of five new *N,N*-dialkyl-*N'*-(4-fluorobenzoyl) thiourea compounds (alkyl: methyl (HL¹), ethyl (HL²), *n*-propyl (HL³), *n*-butyl (HL⁴), and phenyl (HL⁵)) which include a fluorine atom and their Ni(II) and Cu(II) complexes (Scheme 1). The crystal and molecular structures of HL¹, HL², HL⁴, and Ni(L³)₂ were characterized by single crystal X-ray diffraction.

2. Experimental

2.1. Instrumentation. Melting points were recorded on electrothermal model 9200 apparatus. C, H, and N analyses were carried out on a Carlo Erba MOD 1106 elemental analyzer.



SCHEME 1: Synthesized compounds.

Infrared measurement was recorded in the range 400–4000 cm^{-1} on Satellite FT-IR equipped with a WINFIRST LITE software package from Mattson Instruments. The ^1H NMR spectrums were recorded in CDCl_3 solvent on Bruker-400 MHz spectrophotometer using tetramethylsilane as an internal reference. Single crystal X-ray diffraction data were collected on an Enraf-Nonius CAD 4 diffractometer and on a Bruker AXS SMART APEX CCD diffractometer using monochromated, MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation.

2.2. Reagents. 4-Fluorobenzoyl chloride, potassium thiocyanate, dimethylamine, diethylamine, di-*n*-propylamine, di-*n*-butylamine, and diphenylamine were purchased from Merck and used as received. Acetone and dichloromethane used without further purification. Ethanol was dried and distilled before the using.

2.3. General Procedure for the Synthesis of Ligands. A solution of 4-fluorobenzoyl chloride (0.01 mol, 0.12 mL) in anhydrous acetone (50 mL) was added dropwise to a suspension of dry potassium thiocyanate (0.01 mol, 9718 g) in acetone (50 mL), and the reaction mixture was refluxed for 45 min. After cooling to room temperature, a solution of secondary amine (0.01 mol) in anhydrous acetone (50 mL) was added, and the resulting mixture refluxed for 2 h. Hydrochloric acid (0.1 M, 300 mL) was added, and the solution was filtered. The solid product was washed with water and purified by recrystallization from an ethanol : dichloromethane mixture (1 : 3) (Scheme 2).

N,N-dimethyl-*N'*-4-fluoro benzoyl thiourea, (HL¹): White. Yield: 78%. M.p.: 130–132°C. Anal. calcd. for $\text{C}_{10}\text{H}_{11}\text{FN}_2\text{OS}$ (%): C, 53.08; H, 4.90; N, 12.38. Found: C, 53.00; H, 4.81; N, 12.36. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{NH})$ 3231, $\nu(\text{CH})$ 2998, 2976, 2936, $\nu(\text{C}=\text{O})$ 1668, $\nu(\text{C}=\text{S})$ 1251, $\nu(\text{C}-\text{F})$ 758. ^1H NMR (400 MHz, CDCl_3): 8.58 (s, 1H, NH), 7.74 (d, 2H, Ar-H), 7.64 (d, 2H, Ar-H), 3.51 (s, 3H, N-CH₃), 3.26 (s, 3H, N-CH₃).

N,N-diethyl-*N'*-4-fluoro benzoyl thiourea, (HL²): White. Yield: 88%. M.p.: 138–140°C. Anal. calcd. for $\text{C}_{12}\text{H}_{15}\text{FN}_2\text{OS}$ (%): C, 56.67; H, 5.94; N, 11.01. Found: C, 56.59; H, 5.91; N,

10.91. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{NH})$ 3293, $\nu(\text{CH})$ 2998, 2977, 2933, $\nu(\text{C}=\text{O})$ 1647, $\nu(\text{C}=\text{S})$ 1275, $\nu(\text{C}-\text{F})$ 761. ^1H NMR (400 MHz, CDCl_3): 8.41 (s, 1H, NH), 7.88 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 4.04 (s, 2H, N-CH₂), 3.70 (s, 2H, N-CH₂), 1.38 (t, 3H, -CH₃), 1.32 (t, 3H, -CH₃).

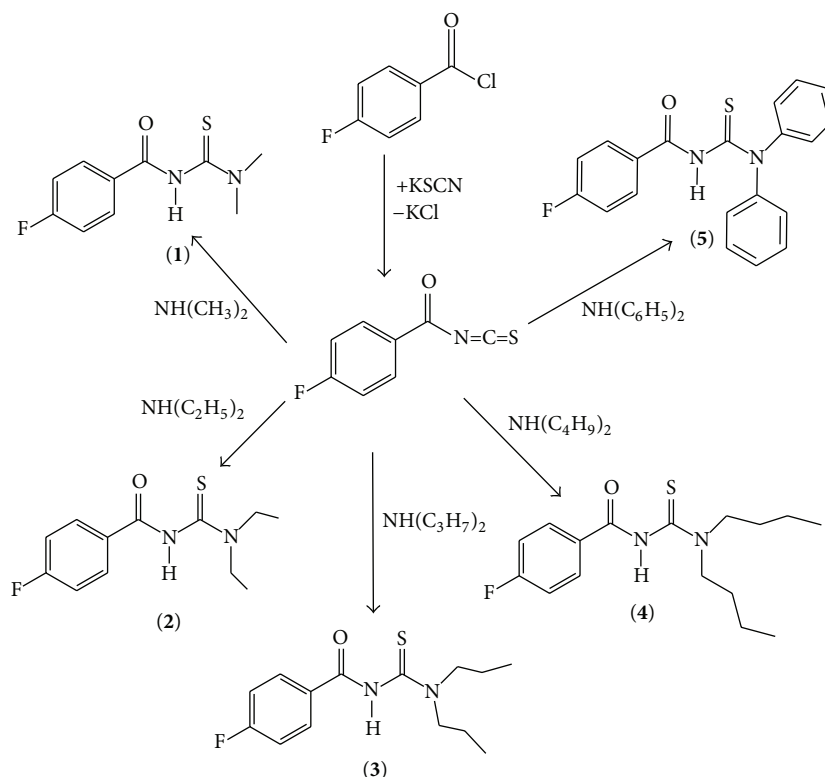
N,N-di-*n*-propyl-*N'*-4-fluoro benzoyl thiourea, (HL³): White. Yield: 67%. M.p.: 78–80°C. Anal. calcd. for $\text{C}_{14}\text{H}_{19}\text{FN}_2\text{OS}$ (%): C, 59.55; H, 6.78; N, 9.92. Found: C, 59.51; H, 6.67; N, 9.91. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{NH})$ 3271, $\nu(\text{CH})$ 2968, 2934, 2877, $\nu(\text{C}=\text{O})$ 1643, $\nu(\text{C}=\text{S})$ 1275, $\nu(\text{C}-\text{F})$ 753. ^1H NMR (400 MHz, CDCl_3): 8.42 (s, 1H, -NH), 7.86 (d, 2H, Ar-H), 7.15 (d, 2H, Ar-H), 3.92 (t, 2H, N-CH₂), 3.51 (t, 2H, N-CH₂), 1.83 (m, 2H, -CH₂-), 1.71 (m, 2H, -CH₂-), 1.02 (t, 3H, CH₃), 0.88 (t, 3H, -CH₃).

N,N-di-*n*-butyl-*N'*-4-fluoro benzoyl thiourea, (HL⁴): White. Yield 89%. M.p.: 89–91°C. Anal. calcd. for $\text{C}_{16}\text{H}_{23}\text{FN}_2\text{OS}$ (%): C, 61.90; H, 7.47; N, 9.02. Found: C, 61.82; H, 7.41; N, 9.00. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{NH})$ 3166, $\nu(\text{CH})$ 2958, 2934, 2871, $\nu(\text{C}=\text{O})$ 1685, $\nu(\text{C}=\text{S})$ 1296, $\nu(\text{C}-\text{F})$ 743. ^1H NMR (400 MHz, CDCl_3): 8.14 (s, 1H, -NH), 7.85 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 3.97 (s, 2H, N-CH₂), 3.52 (s, 2H, N-CH₂), 1.80 (m, 2H, -CH₂), 1.67 (m, 2H, -CH₂), 1.46 (m, 2H, -CH₂), 1.30 (m, 2H, -CH₂), 1.00 (t, 3H, -CH₃), 0.92 (t, 3H, -CH₃).

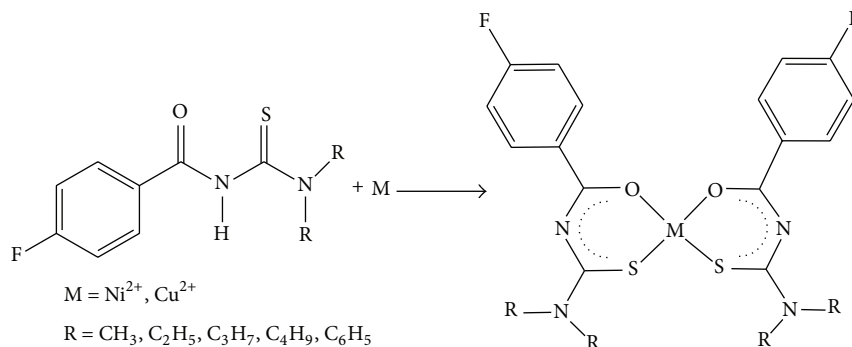
N,N-diphenyl-*N'*-4-fluoro benzoyl thiourea, (HL⁵): White. Yield 94%. M.p.: 149–151°C. Anal. calcd. for $\text{C}_{20}\text{H}_{15}\text{FN}_2\text{OS}$ (%): C, 68.55; H, 4.31; N, 7.99. Found: C, 68.48; H, 4.27; N, 7.92. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{NH})$ 3159, $\nu(\text{Ar}-\text{H})$ 3110, 3064, $\nu(\text{C}=\text{O})$ 1690, $\nu(\text{C}=\text{S})$ 1288, $\nu(\text{C}-\text{F})$ 755. ^1H NMR (400 MHz, CDCl_3): 8.64 (s, 1H, -NH), 7.65 (m, 2H, Ar-H), 7.68 (m, 8H, Ar-H), 7.28 (m, 2H, Ar-H), 7.09 (m, 2H, Ar-H).

2.4. General Procedure for the Synthesis of Metal Complexes.

The metal complexes were prepared according to a described method [21–23]. A metal acetate solution in methanol was added dropwise to the ligand in a 1 : 2 molar ratio with a small excess of ligand in dichloromethane. The solid complex was filtered and recrystallized from ethanol : dichloromethane mixture (1 : 2) (Scheme 3).



SCHEME 2: Synthesis of the ligands.



SCHEME 3: Synthesis of the metal complexes.

Bis(N,N-dimethyl-*N'*-4-fluoro benzoyl thioureato) nickel(II), ($\text{Ni}(\text{L}^1)_2$): Purple. Yield: 86%. M.p.: 257-258°C. Anal. calcd. for $\text{C}_{20}\text{H}_{20}\text{F}_2\text{N}_4\text{NiO}_2\text{S}_2$, (%): C, 47.17; H, 3.96; N, 11.00. Found: C, 47.10; H, 3.87; N, 11.01. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{CH})$ 2929, 2853, $\nu(\text{CN})$ 1602, $\nu(\text{C}-\text{O})$, 1495, $\nu(\text{C}-\text{F})$, 760. ^1H NMR (400 MHz, CDCl_3): 8.13 (m, 4H, Ar-H), 7.06 (m, 4H, Ar-H), 3.42 (s, 6H, N-CH₃), 3.32 (s, 6H, N-CH₃).

Bis(N,N-diethyl-*N'*-4-fluoro benzoyl thioureato) nickel(II), ($\text{Ni}(\text{L}^2)_2$): Purple. Yield: 77%. M.p.: 139-140°C. Anal. calcd. for $\text{C}_{24}\text{H}_{28}\text{F}_2\text{N}_4\text{NiO}_2\text{S}_2$ (%): C, 50.99; H, 4.99; N, 9.91. Found: C, 50.76; H, 4.91; N, 9.90. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{CH})$ 2984, 2936, 2871, $\nu(\text{CN})$ 1598, $\nu(\text{C}-\text{O})$ 1494, $\nu(\text{C}-\text{F})$ 766. ^1H NMR (400 MHz, CDCl_3): 8.12 (m, 4H,

Ar-H), 7.06 (m, 4H, Ar-H), 3.79 (p, 8H, N-CH₂), 1.27 (m, 12H, -CH₃).

Bis(N,N-di-*n*-propyl-*N'*-4-fluoro benzoyl thioureato) nickel(II), ($\text{Ni}(\text{L}^3)_2$): Purple. Yield: 79%. M.p.: 155-156°C. Anal. calcd. for $\text{C}_{28}\text{H}_{36}\text{F}_2\text{N}_4\text{NiO}_2\text{S}_2$ (%): C, 54.12; H, 5.84; N, 9.02. Found: C, 53.97; H, 5.86; N, 9.07. FT-IR (KBr pellet, cm^{-1}): $\nu(\text{CH})$ 2963, 2929, 2871, $\nu(\text{CN})$ 1600, $\nu(\text{C}-\text{O})$ 1490, $\nu(\text{C}-\text{F})$ 764. ^1H NMR (400 MHz, CDCl_3): 8.11 (m, 4H, Ar-H), 7.05 (m, 4H, Ar-H), 3.68 (m, 8H, N-CH₂), 1.74 (m, 8H, CH₂), 0.96 (m, 12H, -CH₃).

Bis(N,N-di-*n*-butyl-*N'*-4-fluoro benzoyl thioureato) nickel(II), ($\text{Ni}(\text{L}^4)_2$): Purple. Yield: 75%. M.p.: 148-150°C. Anal. calcd. for $\text{C}_{32}\text{H}_{44}\text{F}_2\text{N}_4\text{NiO}_2\text{S}_2$ (%): C, 56.73; H, 6.55;

TABLE 1: Crystal data and the structure refinement details for HL¹, HL², HL⁴, and Ni(L³)₂.

Parameters	HL ¹	HL ²	HL ⁴	Ni(L ³) ₂
Crystal formula	C ₁₀ H ₁₁ FN ₂ OS	C ₁₂ H ₁₅ N ₂ SOF	C ₁₆ H ₂₃ N ₂ SOF	C ₂₈ H ₃₆ F ₂ N ₄ NiO ₂ S ₂
Formula weight (g/mol)	226.28	254.32	310.42	621.44
Crystal dimensions, (mm)	0.33 × 0.42 × 0.54	0.24 × 0.30 × 0.60	0.30 × 0.48 × 0.60	0.39 × 0.27 × 0.18
Temp, (K)	293(2)	293(2)	293(2)	120(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P 21/c	P 21/c	P 21/c	P-1
<i>a</i> , (Å)	10.917(3)	6.879(2)	10.4719(11)	10.272(3)
<i>b</i> , (Å)	5.572(5)	18.8034(19)	15.714(2)	12.377(3)
<i>c</i> , (Å)	18.073(5)	10.0498(12)	10.5497(11)	12.604(3)
α , (°)	90.00	90.00	90.00	68.014(5)
β , (°)	92.82(2)	93.161(17)	102.093(9)	87.123(6)
γ , (°)	90.00	90.00	90.00	83.438(6)
<i>Z</i> ; <i>D</i> _{calc} , (g/cm ⁻³)	4; 1.37	4; 1.30	4; 1.21	2; 1.398
Range of θ (°)	2.9/26.3	2.3/26.3	2.4/26.3	1.74/27.88
μ (MoK α) (mm ⁻¹)	0.283	0.247	0.201	0.843
Reflections collected	2338	2856	3637	13065
Reflections used in refinement	2221	2636	3448	6946
Number of refined parameters	143	158	205	353
<i>R</i> / <i>R</i> _w values	0.0380/0.1201	0.0410/0.1168	0.050/0.1538	0.0944/0.2878
GOF	1.0730	1.022	1.032	1.088
($\Delta\rho$) _{min} , ($\Delta\rho$) _{max} (e Å ⁻³)	-0.183, 0.195	-0.246, 0.181	-0.262, 0.328	-0.725, 2.197

N, 8.27. Found: C, 56.61; H, 6.44; N, 8.21. FT-IR (KBr pellet, cm⁻¹): ν (CH) 2956, 2929, 2866, ν (CN) 1600, ν (C–O) 1488, ν (C–F) 761. ¹H NMR (400 MHz, CDCl₃): 8.11 (m, 4H, Ar–H), 7.05 (m, 4H, Ar–H), 3.72 (m, 8H, N–CH₂), 1.68 (m, 8H, CH₂), 1.38 (m, 8H, CH₂), 0.96 (m, 12H, CH₃).

Bis(*N,N*-diphenyl-*N'*-4-fluoro benzoyl thioureato) nickel(II), (Ni(L⁵)₂): Purple. Yield: 89%. M.p.: 317–318°C. Anal. calcd. for C₄₀H₂₈F₂N₄NiO₂S₂ (%): C, 63.42; H, 3.73; N, 7.40. Found: C, 63.30; H, 3.66; N, 7.33. FT-IR (KBr pellet, cm⁻¹): ν (Ar–CH) 3100, 3086, ν (CN) 1599, ν (C–O) 1500, ν (C–F) 695. ¹H NMR (400 MHz, CDCl₃): 7.80–6.90 (m, 28H, Ar–H).

Bis(*N,N*-dimethyl-*N'*-4-fluoro benzoyl thioureato) copper(II), (Cu(L¹)₂): Green. Yield: 71%. M.p.: 209–210°C. Anal. calcd. for C₂₀H₂₀CuF₂N₄O₂S₂ (%): C, 46.73; H, 3.92; N, 10.90. Found: C, 46.61; H, 3.80; N, 10.77. FT-IR (KBr pellet, cm⁻¹): ν (CH), 2926, 2852, ν (CN) 1600, ν (C–O) 1493, ν (C–F) 761.

Bis(*N,N*-diehtyl-*N'*-4-fluoro benzoylthioureato) copper(II), (Cu(L²)₂): Green. Yield: 68%. M.p.: 143–144°C. Anal. calcd. for (%): C₂₄H₂₈CuF₂N₄O₂S₂: C, 50.56; H, 4.95; N, 9.83. Found: C, 50.39; H, 4.95; N, 9.81. FT-IR (KBr pellet, cm⁻¹): ν (CH) 2985, 2933, 2868, ν (CN) 1598, ν (C–O) 1492, ν (C–F) 765.

Bis(*N,N*-di-*n*-propyl-*N'*-4-fluoro benzoyl thioureato) copper(II), (Cu(L³)₂): Green. Yield: 76%. M.p.: 101–102°C. Anal. calcd. for C₂₈H₃₆CuF₂N₄O₂S₂ (%): Found: C, 53.70; H, 5.79; N, 8.95. Bulunan: C, 53.61; H, 5.71; N, 8.98. FT-IR (KBr pellet, cm⁻¹): ν (CH) 2961, 2928, 2869, ν (CN) 1600, ν (C–O) 1485, ν (C–F) 766.

Bis(*N,N*-di-*n*-butyl-*N'*-4-fluorobenzoyl thioureato) copper(II), (Cu(L⁴)₂): Green. Yield: 70%. M.p.: 112–113°C. Anal. calcd. for C₃₂H₄₄CuF₂N₄O₂S₂ (%): C, 56.32; H, 6.50; N, 8.21. Found: C, 56.19; H, 6.41; N, 8.20. FT-IR (KBr pellet, cm⁻¹): ν (CH) 2958, 2929, 2857, ν (CN) 1600, ν (C–O) 1488, ν (C–F) 766.

Bis(*N,N*-diphenyl-*N'*-4-fluoro benzoyl thioureato) copper(II), (Cu(L⁵)₂): Green. Yield: 86%. M.p.: 223–224°C. Anal. calcd. for C₄₀H₂₈CuF₂N₄O₂S₂ (%): C, 63.02; H, 3.70; N, 7.35. Found: C, 62.72; H, 3.68; N, 7.15. FT-IR (KBr pellet, cm⁻¹): ν (Ar–CH) 3101, 3086, ν (CN) 1596, ν (C–O) 1498, ν (C–F) 698.

2.5. X-Ray Crystallography. The crystal structure of the synthesized four new compounds was solved by direct methods using SHELXS-97, and refinements were performed with SHELXL-97 [31]. Full-matrix least-squares refinement is based on F². All nonhydrogen atoms were refined anisotropically. In three compounds, the hydrogen atom of N1 was found in difference Fourier map and refined isotropically. All other hydrogen atoms were positioned geometrically to their idealized positions, C–H = 0.93 (aromatic), 0.96 (CH₃), and 0.97 (CH₂) Å, and refined with a “riding model” with isotropic displacement parameters. Crystal data and details of the structural determinations for ligands (HL¹, HL², and HL⁴) and complex, Ni(L³)₂, are given in Table 1.

3. Results and Discussion

3.1. Synthesis and Characterisation. 4-Fluorobenzoyl isothiocyanate was produced by reaction of 4-fluorobenzoyl chloride

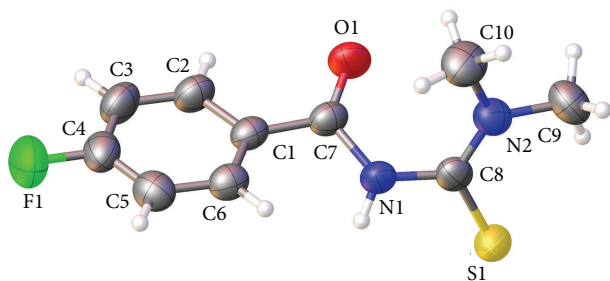


FIGURE 1: Molecular structure of HL¹. Anisotropic displacement ellipsoids are shown at the 50% probability level.

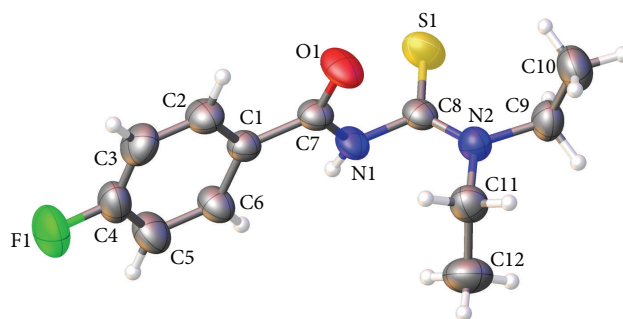


FIGURE 2: Molecular structure of HL². Anisotropic displacement ellipsoids are shown at the 50% probability level.

with an equimolar amount of potassium thiocyanate in dry acetone. All benzoylthiourea derivatives (HL¹–HL⁵) were synthesized from 4-fluorobenzoyl isothiocyanate and secondary amines in dry acetone. Scheme 2 outlines the synthesis of the series of thiourea derivatives. The ligands were purified by recrystallization from an ethanol:dichloromethane mixture (1:2) and obtained in yields ranging from 67 to 94%. ¹H NMR spectra, FT-IR spectra, and elemental analysis data of all synthesized compounds confirm the proposed structures.

The reaction of the ligands with nickel acetate or copper acetate at room temperature with ethanol as solvent yielded the new complexes (ML₂, M=Cu, or Ni). All the new metal complexes were recrystallized from ethanol:dichloromethane mixture (1:1). The proposed structures given in Scheme 1 are consistent with the analytical and spectroscopic data.

FT-IR spectra were taken with KBr pellets between 4000 and 400 cm⁻¹. In the FT-IR spectra of the synthesized benzoylthiourea derivatives show sharp and strong absorption band at 3231, 3293, 3271, 3166, and 3159 cm⁻¹ for HL¹, HL², HL³, HL⁴, and HL⁵ attributed to the stretching vibration of N–H group, respectively [11, 12, 21, 22, 24–28].

The strong C=O stretching vibration band was observed in the range of 1643–1690 cm⁻¹, which is in agreement with the literature data [11, 12, 21, 22, 24–28]. In addition, synthesized compounds show weak intensity C=S stretching vibration in the 1251–1296 cm⁻¹ range [11, 12, 21, 22, 24–28].

All IR spectra of metallic complexes are practically similar. The N–H stretching vibration, present in the ligand around ~3200 cm⁻¹, disappears in the complex spectra. At the same time, a new peak appeared in the range 1485–1500 cm⁻¹, which was attributed to the absorption of C–O stretching vibration band. In the spectra of complexes, there is another intense absorption band at 1596–1602 cm⁻¹ corresponding to the C–N fragment. All this conclusions are in agreement with the literature [11, 12, 21, 22, 24–28].

The ¹H NMR spectra of the ligands are consistent with their structures. The ¹H NMR spectrum of ligands exhibited broad signals at 8.58, 8.41, 8.42, 8.14, and 8.64 for HL¹, HL², HL³, HL⁴, and HL⁵, respectively, due to NH protons. This peak does not appear in Ni(II) and Cu(II) complexes. These data are in agreement with the IR spectra and literature

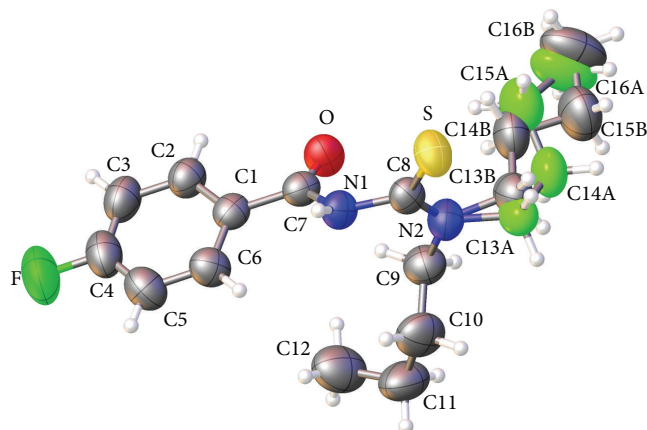


FIGURE 3: Molecular structure of HL⁴. Anisotropic displacement ellipsoids are shown at the 50% probability level.

data [11, 12, 21, 23]. All other proton signals are appeared in appropriate place.

3.2. X-Ray Crystal Structures. We used X-ray single crystal diffraction method to determine and confirm the structure of the synthesized compounds. Only four of the synthesized compounds were suitable for X-ray single crystal diffraction. The molecular structures of HL¹, HL², HL⁴, and Ni(L³)₂ are depicted in Figures 1, 2, 3, and 4, respectively. Selected bond lengths and angles are listed in Tables 2 and 3.

In each ligand, F atom is coplanar with the C1–C6 ring. The C2–C1–C7–O1 torsion angles set up by aromatic ring and the carbonyl group are 25.3(3), 5.0(3), and –20.3(4)°, for HL¹, HL², and HL⁴, respectively. The molecules of compounds HL¹ and HL⁴ are effectively nonplanar, as shown by the values of the N1–C7–C1–C6 torsion angle, respectively, (Table 2); this angle defines the rotation of the aryl ring relative to the rest of the molecule. Within the thiourea moieties of compounds HL¹, HL², and HL⁴, the geometry at the carbon atoms is ideally planar, with a sum of the bond angles at C8 in HL¹, HL², and HL⁴ of 360.0(2), 360.0(2), and 359.9(2)°, respectively. The S1 atom is out of the plane of the N–C–N thiourea bridge by 0.051(1) Å in HL¹, 0.029(1) Å in HL², and 0.075(1) Å in compound HL⁴. The thiourea moiety

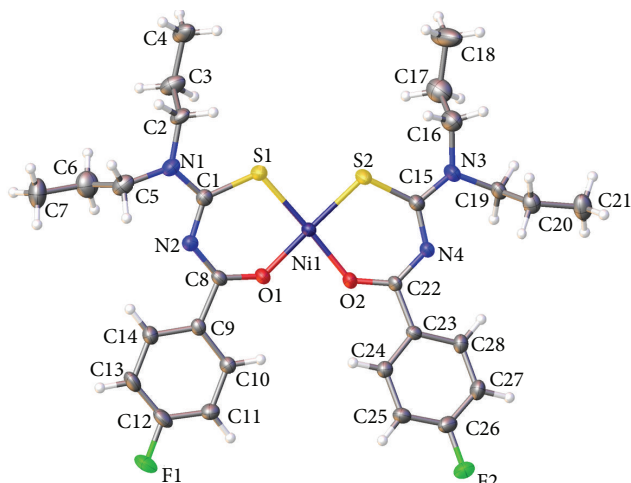


FIGURE 4: Molecular structure of $\text{Ni}(\text{L}^3)_2$. Anisotropic displacement ellipsoids are shown at the 50% probability level.

TABLE 2: Selected geometric parameters of (HL^1 , HL^2 , and HL^4).

Bond lengths, Å	HL^1	HL^2	HL^4
C(1)–C(7)	1.481(3)	1.490(3)	1.487(4)
C(7)–O(1)	1.212(2)	1.225(2)	1.219(3)
N(1)–C(7)	1.398(2)	1.349(3)	1.383(3)
N(1)–C(8)	1.393(2)	1.432(3)	1.406(3)
S(1)–C(8)	1.683(2)	1.658(2)	1.673(3)
C(8)–N(2)	1.322(2)	1.319(3)	1.324(3)
Bond angles, °			
N1–C7–C1	115.42(16)	117.35(17)	116.0(2)
O1–C7–N1	121.49(18)	120.50(2)	122.0(2)
N1–C8–S1	119.29(14)	119.27(15)	118.6(2)
N2–C8–N1	117.05(17)	114.16(18)	116.6(2)
N2–C8–S1	123.62(15)	126.55(16)	124.8(2)
Torsion angles, °			
C6–C1–C7–N1	27.8(3)	4.2(3)	155.1(2)
C2–C1–C7–O1	25.3(3)	5.0(3)	–20.3(4)
O1–C7–N1–C8	–1.6(3)	–5.9(3)	–0.9(4)
C7–N1–C8–N2	55.0(3)	89.4(2)	–62.5(3)

is almost perpendicular to the phenyl ring plane with an angle of 80.9(1), 89.0(1) and 84.6(1)° for HL^1 , HL^2 , and HL^4 , respectively. In all ligands, the fluorobenzoyl ring and one of the methyl, ethyl, and *n*-butyl groups are *trans* to S1, but the other methyl, ethyl, and *n*-butyl groups are *cis* with respect to N2–C8 thiourea bond.

Bond distances and bond angles of the thiourea group agree well with those expected from other thiourea derivatives [22, 28–30, 32–34]. The C7–O1 and C8–S1 bonds both show typical double-bond character with bond lengths of 1.212(2) for HL^1 , 1.225(2) for HL^2 , and 1.219(3) for HL^4 and 1.683(2) for HL^1 , 1.658(2) for HL^2 , and 1.673(3) Å for HL^4 , respectively. The C8–N2 and C7–N1 bonds also indicate a partial double bond character. These bonds due to their

TABLE 3: Some selected geometrical parameters of compound $\text{Ni}(\text{L}^3)_2$.

Bond lengths, Å	
Ni–O1	1.854(4)
Ni–S1	2.1454(18)
O1–C8	1.271(8)
S1–C1	1.729(7)
N2–C1	1.342(8)
N1–C1	1.345(9)
N2–C8	1.340(8)
Bond angles, °	
O2–Ni–O1	83.6(2)
O2–Ni–S2	94.91(15)
O1–Ni–S1	94.24(15)
C8–O1–Ni	132.6(4)
O1–C8–N2	130.3(6)
N2–C1–S1	128.9(5)
C1–S1–Ni	108.7(2)
C1–N2–C8	122.2(6)

vicinity to the carbonyl group and methyl, ethyl, and *n*-butyl groups are slightly shorter in compound HL^2 and HL^4 , but C7–N1 bond is almost the same as compared to the C8–N1 in compound HL^1 . The elongation of C8–N1 relative to C8–N2 and C7–N1 in compound HL^2 and HL^4 is in agreement with other thiourea derivatives [3, 32, 35–39]. All the other bond lengths fall within the expected ranges [34]. The conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is twisted, as reflected by the torsion angles C8–N1–C7–O1 and C7–N1–C8–S1 of –1.6(3) and –127.0(2), –5.9(3) and 91.8(2), and –0.9(4) and 120.4(2)° for HL^1 , HL^2 , and HL^4 , respectively.

There are different kinds of interactions in the benzoyl thiourea compounds, but N–H···S, C–H···O, and N–H···O intermolecular hydrogen bonds play a dominant role in the stabilities of crystal structures. The molecules of HL^1 , HL^2 , and HL^4 are packed in a centrosymmetric manner through weak N–H···S and C–H···O hydrogen bonding. In compound HL^1 , crystal packing shows dimeric units formed through the N2–H2···S1 and C2–H7···O1 hydrogen bonds. The short C9–H9C···S1, C10–H10A···O1, and C10–H10C···N2 distances of 2.50, 2.44, and 2.44 Å point out the presence of intramolecular hydrogen interactions. In compound HL^2 , crystal packing shows intermolecular N1–H1N···O1 hydrogen bonds and molecules again form dimers. Intramolecular C9–H9A···S1 hydrogen bonds are also similar to those in compound HL^1 . In compound HL^4 , the crystal packing shows intermolecular N1–H1N···S1 and C2–H2···O hydrogen bonds and molecules again form dimers. Intramolecular C–H···O and C–H···S hydrogen bonds are also similar to those in compounds HL^1 and HL^2 . Hydrogen bonding and short contact geometry for three compounds HL^1 , HL^2 , and HL^4 are given in Table 4.

TABLE 4: Hydrogen bonding geometry (Å, °) for HL¹, HL², HL⁴, and Ni(L³)₂ compounds.

Compound	D-H...A	D-H	H...A	D...A	D-H...A
HL ¹	N2-H2...S1 ⁱ	0.83(2)	2.68(2)	3.470(4)	159.8(19)
	C2-H7...O1 ⁱⁱ	0.93	2.38	3.189(4)	146
	C9-H9C...S1	0.96	2.50	3.020(4)	114
	C10-H10A...O1	0.96	2.44	2.818(4)	103
	C10-H10C...N2	0.96	2.44	2.801(4)	102
HL ²	N1-H1N...O1 ⁱⁱⁱ	0.83(3)	2.10(3)	2.880(2)	157(2)
	C9-H9A...S1	0.97	2.59	3.054(2)	109
HL ⁴	N1-H1N...S1 ^{iv}	0.82(3)	2.65(3)	3.442(2)	165(3)
	C2-H2...O ^v	0.93	2.49	3.290(4)	144
	C9-H9A...O	0.97	2.27	3.009(4)	132
	C13A-H13B...S	1.04	2.51	3.084(18)	114
	C13A-H13D...S	0.97	2.57	3.084(18)	113
Ni(L ³) ₂	C2-H2B...S1	0.99	2.51	2.918(8)	104
	C10-H10A...O1	0.95	2.35	2.679(8)	100
	C13-H16A...S2	0.99	2.52	2.963(9)	107

Symmetry codes: ⁱ1 - x, 2 - y, -z; ⁱⁱ - x, 2 - y, -z; ⁱⁱⁱx, 1/2 - y, -1/2 + z; ^{iv}1 - x, -y, -z; ^v1 - x, -y, 1 - z.

All of the structural data of the nickel complex agree with the elemental analysis, FT-IR spectroscopy, and ¹H NMR spectroscopy data. *Bis*(*N,N*-dimethyl-*N'*-4-floro benzoyl thioureato) nickel(II) complex has a nearly square-planar coordination at the nickel atom. The distance of nickel atom from the best plane through the coordination sphere is 0.029 Å. The bond lengths of the carbonyl and thiocarbonyl groups lie between those for double and single bonds, a feature which is known from related structures (O1-C8: 1.271(8) Å; O2-C22: 1.271(7) Å; S1-C1: 1.729(7) Å; S2-C15: 1.745(7) Å) [11, 12, 21, 22, 40, 41] (Table 3). The bond length C1-N2 is 1.342(8) and N(2)-C(8) 1.340(8) Å. The bond length is C-N shorter than a normal single C-N bond. This is due to strong delocalization in the chelate rings [42-44].

4. Conclusions

In this work, five flourobzoyl thiourea ligands and their Ni(II) and Cu(II) complexes have been synthesized and characterized by elemental analysis, IR spectroscopy, and ¹H NMR. Crystal and molecular structures of three synthesized ligands and one metal complex 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 thiourea derivatives. The bond lengths and angles also agree well with other thiourea derivatives. In the crystal structure, intermolecular N-H...S, C-H...O, and N-H...O hydrogen bonds seem to be effective in the stabilization of the structure. In all ligands, molecules form dimers through strong intermolecular hydrogen bonds.

Disclosure

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with

the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-811681 (HL¹), CCDC-811682 (HL²), CCDC-811683 (HL⁴), and CCDC-865984 Ni(L³)₂. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgments

This study is a part of Gun Binzet's Ph.D. thesis and was supported by Mersin University Research Fund (Project no. BAP-FBE KB (GB) 2006-1 DR).

References

- [1] R. Vivas-Reyes, E. Espinosa-Fuentes, J. Forigua, A. Arias, R. Gaitán, and E. Arguello, "Theoretical study of a series of *N*-(*N*-propyl)-*N'*-(*para*-R-benzoyl)-thioureas with *trans*[pt(py)₂cl₂] through chemistry reactivity descriptors based on density functional theory," *Journal of Molecular Structure: THEOCHEM*, vol. 862, no. 1-3, pp. 92-97, 2008.
- [2] K. H. König, M. Schuster, B. Steinbrech, G. Schneeweis, and R. Schodder, "N, N-Dialkyl-*N'*-benzoylthioharnstoffe als selektive Extraktionsmittel zur Abtrennung und Anreicherung von Platinmetallen," *Fresenius' Zeitschrift für Analytische Chemie*, vol. 321, no. 5, pp. 457-460, 1985.
- [3] J. R. Sabino, S. Cunha, R. M. Bastos, and I. Vencato, "*N*-(benzylaminothiocarbonyl)benzamide," *Acta Crystallographica E*, vol. 62, no. 9, pp. o3918-o3920, 2006.
- [4] T. Yesilkaynak, G. Binzet, F. M. Emen, U. Flörke, N. Külcü, and H. Arslan, "Theoretical and experimental studies on *N*-(6-methylpyridin-2-yl-carbamothioyl)biphenyl-4-carboxamide," *European Journal of Chemistry*, vol. 1, no. 1, pp. 1-5, 2010.
- [5] C. Y. Panicker, H. T. Varghese, A. George, and P. K. V. Thomas, "FT-IR, FT-Raman and ab-initio studies of 1,3-diphenyl thiourea," *European Journal of Chemistry*, vol. 1, no. 3, pp. 173-178, 2010.

- [6] R. del Campo, J. J. Criado, R. Gheorghe et al., "*N*-benzoyl-*N'*-alkylthioureas and their complexes with Ni(II), Co(III) and Pt(II)—crystal structure of 3-benzoyl-1-butyl-1-methylthiourea: activity against fungi and yeast," *Journal of Inorganic Biochemistry*, vol. 98, no. 8, pp. 1307–1314, 2004.
- [7] R. Del Campo, J. J. Criado, E. García et al., "Thiourea derivatives and their nickel(II) and platinum(II) complexes: antifungal activity," *Journal of Inorganic Biochemistry*, vol. 89, no. 1-2, pp. 74–82, 2002.
- [8] C. Sacht and M. S. Datt, "Synthesis and characterisation of mixed-ligand platinum(II)-sulfoxide complexes, [PtCl(DMSO)(L)], for potential use as chemotherapeutic agents (HL = *N,N*-dialkyl-*N'*-(3-*R*-benzoyl)thiourea)," *Polyhedron*, vol. 19, no. 11, pp. 1347–1354, 2000.
- [9] C. I. Sacht, M. S. Datt, S. Otto, and A. Roodt, "Chiral and achiral platinum(II) complexes for potential use as chemotherapeutic agents: crystal and molecular structures of *cis*-[Pt(L¹)₂] and [Pt(L¹)Cl(MPSO)] [HL¹ = *N,N*-diethyl-*N'*-benzoylthiourea]," *Journal of the Chemical Society, Dalton Transactions*, no. 5, pp. 727–733, 2000.
- [10] W. Hernandez, E. Spodine, L. Beyer et al., "Synthesis, characterization and antitumor activity of copper(II) complexes, [CuL₂] [HL¹-3=*N,N*-Diethyl-*N'*-(*R*-benzoyl)thiourea (*R*=H, *o*-Cl and *p*-NO₂)]," *Bioinorganic Chemistry and Applications*, vol. 3, no. 3-4, pp. 299–316, 2005.
- [11] G. Binzet, H. Arslan, U. Flörke, N. Külcü, and N. Duran, "Synthesis, characterization and antimicrobial activities of transition metal complexes of *N,N*-dialkyl-*N'*-(2-chlorobenzoyl)thiourea derivatives," *Journal of Coordination Chemistry*, vol. 59, no. 12, pp. 1395–1406, 2006.
- [12] M. F. Emen, H. Arslan, N. Külcü, U. Flörke, and N. Duran, "Synthesis, characterization and antimicrobial activities of some metal complexes with *N'*-(2-chloro-benzoyl)thiourea ligands: the crystal structure of *fac*-[CoL3] and *cis*-[PdL2]," *Polish Journal of Chemistry*, vol. 79, no. 10, pp. 1615–1626, 2005.
- [13] S. Saeed, N. Rashid, M. Ali, and R. Hussain, "Synthesis, characterization and antibacterial activity of nickel (II) and copper (II) complexes of *N*-(alkyl(aryl)carbamoithoyl)-4-nitrobenzamide," *European Journal of Chemistry*, vol. 1, no. 3, pp. 200–205, 2010.
- [14] S. Saeed, N. Rashid, M. Ali, R. Hussain, and P. G. Jones, "Synthesis, spectroscopic characterization, crystal structure and pharmacological properties of some novel thiophene-thiourea core derivatives," *European Journal of Chemistry*, vol. 1, no. 3, pp. 221–227, 2010.
- [15] S. Saeed, N. Rashid, P. Jones, and R. Hussain, "Thermomechanical studies of thermally stable metal-containing epoxy polymers from diglycidyl ether of bisphenol A and amino-thiourea metal complexes," *European Journal of Chemistry*, vol. 2, no. 1, pp. 77–82, 2011.
- [16] N. Özpozan, H. Arslan, T. Özpozan, M. Merdivan, and N. Külcü, "Thermal decomposition kinetics of some metal complexes of *N,N*-diethyl-*N'*-benzoylthiourea," *Journal of Thermal Analysis and Calorimetry*, vol. 61, no. 3, pp. 955–965, 2000.
- [17] G. Avşar, N. Külcü, and H. Arslan, "Thermal behaviour of copper(II), nickel(II), cobalt(II) and palladium(II) complexes of *N,N*-dimethyl-*N'*-benzoylthiourea," *Turkish Journal of Chemistry*, vol. 26, no. 4, pp. 607–615, 2002.
- [18] N. Ozpozan, T. Ozpozan, H. Arslan, F. Karipçin, and N. Külcü, "Thermal behaviours of Co(II), Ni(II), Cu(II)), and Pb(II) complexes of *N,N*-dipropyl-*N'*-benzoylthiourea," *Thermochimica Acta*, vol. 336, no. 1-2, pp. 97–103, 1999.
- [19] G. Binzet, B. Zeybek, E. Kılıç, N. Külcü, and H. Arslan, "Determination of the ionization constants of some benzoyl thiourea derivatives in dioxane-water mixture," *Journal of Chemistry*, vol. 2013, Article ID 201238, 7 pages, 2013.
- [20] X. Xu, X. Qian, Z. Li, Q. Huang, and G. Chen, "Synthesis and insecticidal activity of new substituted *N*-aryl-*N'*-benzoylthiourea compounds," *Journal of Fluorine Chemistry*, vol. 121, no. 1, pp. 51–54, 2003.
- [21] G. Binzet, *Synthesis and characterization of benzoylthiourea derivatives and their metal complexes [Ph.D. thesis]*, Mersin University, Mersin, Turkey, 2009.
- [22] G. Kavak, S. Özbey, G. Binzet, and N. Külcü, "Synthesis and single crystal structure analysis of three novel benzoylthiourea derivatives," *Turkish Journal of Chemistry*, vol. 33, no. 6, pp. 857–868, 2009.
- [23] G. Binzet, N. Külcü, U. Flörke, and H. Arslan, "Synthesis and characterization of Cu(II) and Ni(II) complexes of some 4-bromo-*N*-(di(alkyl/aryl)carbamoithoyl) benzamide derivatives," *Journal of Coordination Chemistry*, vol. 62, no. 21, pp. 3454–3462, 2009.
- [24] Z. Weiqun, L. Baolong, Z. Liming et al., "Structural and spectral studies on *N*-(4-chloro)benzoyl-*N'*-(4-tolyl) thiourea," *Journal of Molecular Structure*, vol. 690, no. 1–3, pp. 145–150, 2004.
- [25] A. Saeed, A. Mumtaz, and U. Flörke, "Synthesis, characterization and crystal structure of 1-(4-methylbenzoyl)-3-(4-aminosulfonylphenyl)thiourea," *European Journal of Chemistry*, vol. 1, no. 2, pp. 73–75, 2010.
- [26] G. Kurt, F. Sevgi, and B. Mercimek, "Synthesis, characterization, and antimicrobial activity of new benzoylthiourea ligands," *Chemical Papers*, vol. 63, no. 5, pp. 548–553, 2009.
- [27] D. S. Mansuroğlu, H. Arslan, D. Vanderveer, and G. Binzet, "Synthesis and characterization of *N*-(2,2-diphenylacetyl)-*N'*-substituted thiourea derivatives: the crystal structure of *N*-(2,2-diphenylacetyl)-*N'*-(4-chloro phenyl)-thiourea," *Phosphorus, Sulfur and Silicon and the Related Elements*, vol. 184, no. 12, pp. 3221–3230, 2009.
- [28] H. Arslan, U. Flörke, and N. Külcü, "*N'*-(4-chlorobenzoyl)-*N*, *N*-diphenylthiourea," *Acta Crystallographica E*, vol. 59, pp. o641–o642, 2003.
- [29] G. Binzet, U. Flörke, N. Külcü, and H. Arslan, "Crystal structure of 3-(2-chlorobenzoyl)-1,1-diphenylthiourea, (C₆H₅)₂N(CS)(NH)(CO)(C₆H₄Cl)," *Zeitschrift für Kristallographie—New Crystal Structures*, vol. 219, no. 4, pp. 395–397, 2004.
- [30] H. Arslan, U. Flörke, and N. Külcü, "The crystal and molecular structure of 1-(2-chloro-benzoyl)-3-*p*-tolyl- thiourea," *Turkish Journal of Chemistry*, vol. 28, no. 6, pp. 673–678, 2004.
- [31] G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, University of Göttingen, Göttingen, Germany, 1997.
- [32] A. Saeed and M. Parvez, "The crystal structure of 1-(4-chlorophenyl)-3-(4-methylbenzoyl)thiourea," *Central European Journal of Chemistry*, vol. 3, no. 4, pp. 780–791, 2005.
- [33] H. Arslan, N. Külcü, and U. Flörke, "Normal coordinate analysis and crystal structure of *N,N*-dimethyl-*N'*-(2-chlorobenzoyl)thiourea," *Spectrochimica Acta A*, vol. 64, no. 4, pp. 1065–1071, 2006.
- [34] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, "Tables of bond lengths determined by x-ray and neutron diffraction—part 1: bond lengths in organic compounds," *Journal of the Chemical Society, Perkin Transactions 2*, no. 12, pp. S1–S19, 1987.

- [35] H. Arslan, U. Flörke, and N. Külcü, "The crystal and molecular structure of 1-(biphenyl-4-carbonyl)-3-p-tolyl-thiourea," *Acta Chimica Slovenica*, vol. 51, no. 4, pp. 787–792, 2004.
- [36] R. D. Campo, J. J. Criado, R. Gheorghe et al., "*N*-benzoyl-*N'*-alkylthioureas and their complexes with Ni(II), Co(III) and Pt(II)—crystal structure of 3-benzoyl-1-butyl-1-methylthiourea: activity against fungi and yeast," *Journal of Inorganic Biochemistry*, vol. 98, no. 8, pp. 1307–1314, 2004.
- [37] M. K. Rauf, A. Badshah, and M. Bolte, "1-benzyl-3-(2-methylbenzo-yl)thio-urea," *Acta Crystallographica E*, vol. 63, no. 4, pp. o1679–o1680, 2007.
- [38] S. Shanmuga Sundara Raj, K. Puviarasan, D. Velmurugan, G. Jayanthi, and H.-K. Fun, "N-H···S hydrogen bonding in *N*-benzoyl-*N'*-methyl-*N'*-phenylthiourea and *N*-benzoyl-*N'*-(3,4-dimethylphenyl)thiourea," *Acta Crystallographica C*, vol. 55, no. 8, pp. 1318–1320, 1999.
- [39] G. Binzet, U. Flörke, N. Külcü, and H. Arslan, "Crystal and molecular structure of bis(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel(II) complex," *European Journal of Chemistry*, vol. 3, no. 1, pp. 37–39, 2012.
- [40] G. Binzet, U. Flörke, N. Külcü, and H. Arslan, "Crystal and molecular structure of bis(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido) copper(II) complex," *European Journal of Chemistry*, vol. 3, no. 2, pp. 211–213, 2012.
- [41] H. Arslan, D. Vanderveer, F. Emen, and N. Külcü, "Crystal structure of cis-bis(*N,N*-dimethyl-*N'*-4-chlorobenzoylthioureato)palladium(II), Pd(C₁₀H₁₀ClN₂OS)₂," *Zeitschrift für Kristallographie—New Crystal Structures*, vol. 218, no. 4, pp. 479–480, 2003.
- [42] H. Arslan, N. Külcü, and U. Flörke, "Synthesis and characterization of copper (II), nickel (II) and cobalt (II) complexes with novel thiourea derivatives," *Transition Metal Chemistry*, vol. 28, no. 7, pp. 816–819, 2003.
- [43] L. R. Gomes, L. M. N. B. F. Santos, B. Schröder, Ch. Wagner, and J. N. Low, "Bis[*N,N*-diisobutyl-*N'*-(2-thienylcarbonyl)thioureato]nickel(II)," *Acta Crystallographica E*, vol. 63, pp. m953–m955, 2007.
- [44] G. Avşar, H. Arslan, H.-J. Haupt, and N. Külcü, "Crystal structure of cis-bis(*N,N*-dimethyl-*N'*-benzoylthioureato)palladium(II)," *Turkish Journal of Chemistry*, vol. 27, no. 3, pp. 281–285, 2003.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

