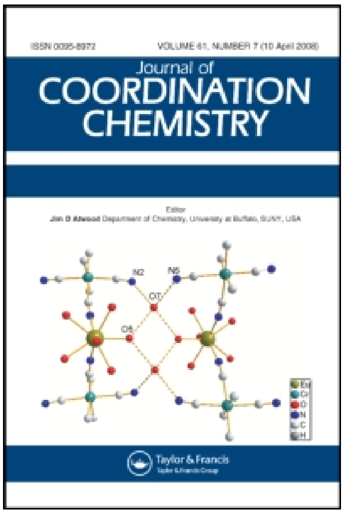

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Synthesis and characterization of Cu(II) and Ni(II) complexes of some 4-bromo- *N*-(di(alkyl/aryl)carbamothioyl) benzamide derivatives

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Synthesis and characterization of Cu(II) and Ni(II) complexes of some 4-bromo-*N*-(di(alkyl/aryl)carbamothioyl) benzamide derivatives

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4-Bromo-*N*-(di-R-carbamothioyl)benzamide (R = methyl, ethyl, *n*-propyl, *n*-butyl and phenyl) ligands and their Ni(II) and Cu(II) complexes have been synthesized and characterized by elemental analyses, FT-IR and ^{1}H-NMR spectroscopy. The crystal and molecular structure of *bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)nickel(II) has been determined from single crystal X-ray diffraction data. It crystallizes in the triclinic, space group $P\bar{1}$, $Z = 2$ with $a = 9.286(2)$ Å, $b = 13.215(3)$ Å, $c = 14.125(3)$ Å, $\alpha = 64.180(5)^\circ$, $\beta = 85.483(6)^\circ$, $\gamma = 83.067(5)^\circ$, $V = 1548.3(7)$ Å^3 and $D_{\mathrm{Calcd}} = 1.594\,\mathrm{mg\,m^{-3}}$. Loss of the N–H proton resonance and the N–H stretching vibration and the shift of the $\nu_{\mathrm{C=O}}$ and $\nu_{\mathrm{C=S}}$ stretching vibrations confirm formation of the metal complexes. These studies have shown that the metal complexes are neutral *cis*-[ML$_2$].

Keywords: Synthesis; Thiourea derivatives; Complex; Crystal structure

1. Introduction

Transition metal complexes such as nickel, copper, cobalt, palladium, platinum and ruthenium with N-, S-, and O-containing compounds have important biological activities. Thioureas act as ligands in these important compounds [1–9]. Although thiourea compounds have been known for more than a century, thioureas recently received much attention because of its applications in analytical and biological sciences [10–20]. The thiourea compounds have both sulfur and oxygen as soft and hard donors providing a multitude of bonding possibilities to thiourea derivatives [15–20]. Thioureas are useful as anti-tumor, anti-fungal, anti-bacterial, insecticidal, herbicidal, pesticidal reagents, and plant-growth regulators [1–9].

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Our team has focused on synthesis, characterization, crystal structure, thermal behavior, and antimicrobial activity of new thiourea derivatives [21–40]. In this article, a series of thiourea derivatives, 4-bromo-*N*-(dimethylcarbamothioyl)benzamide (HL^1), 4-bromo-*N*-(diethylcarbamothioyl)benzamide (HL^2) [35], 4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamide (HL^3) [36], 4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamide (HL^4), and 4-bromo-*N*-(diphenylcarbamothioyl)benzamide (HL^5), and their Cu(II) and Ni(II) complexes were synthesized and characterized. In addition, the crystal structure of *bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)nickel(II) is reported.

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 (FTIR) spectra were recorded in KBr pellets using a WinFirst Satellite FTIR spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400 MHz using $CDCl_3$ as the solvent, with tetramethylsilane as internal standard. Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer [41] using monochromated Mo-Kα radiation. The structures were solved [41] by direct and conventional Fourier methods with full-matrix least-squares refinement [41] based on F^2. All atoms other than hydrogen were refined anisotropically; hydrogens were located from difference Fourier maps and refined at idealized positions with a "riding model". Data collection and refinement details are given in table 1.

2.2. *Synthesis of the ligands*

A solution of 4-bromobenzoyl chloride (0.005 M) in acetone (50 cm^3) was added dropwise to a suspension of potassium thiocyanate (0.005 M) in anhydrous acetone (50 cm^3) [21, 26, 34]. The reaction mixture was heated under reflux for 30 min and then cooled to room temperature. A solution of secondary amine (dimethylamine, diethylamine, di-*n*-propylamine, di-*n*-butylamine and diphenylamine) (0.005 M) in acetone (30 cm^3) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 300 cm^3) was added and the solution filtered. The solid product was washed with water and purified by recrystallization from ethanol : dichloromethane (1 : 2).

2.2.1. 4-Bromo-*N*-(dimethylcarbamothioyl)benzamide, HL^1. White. Yield: 79%, m.p.: 176–178°C. Calcd for $C_{10}H_{11}BrN_2OS$: C, 41.82; H, 3.86; N, 9.75. Found: C, 41.80; H, 3.84; N, 9.77%. FT-IR (cm^{-1}): ν(NH) 3201 (w); ν(CH) 2922, 2901 (w); ν(C=O) 1697 (s); ν(C=S) 1275 (m); ν(C–Br) 752 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.65 (s, 1H, –N*H*), 7.72 (d, 2H, Ar–*H*), 7.61 (d, 2H, Ar–*H*), 3.51 (s, 3H, N–CH_3), 3.25 (s, 3H, N–CH_3).

2.2.2. 4-Bromo-*N*-(diethylcarbamothioyl)benzamide, HL^2. White. Yield: 89%, m.p.: 144–146°C. Calcd for $C_{12}H_{15}BrN_2OS$: C, 45.72; H, 4.80; N, 8.89. Found: C, 45.68; H,

Table 1. Crystal data and structure refinement of [(Ni(L^3)$_2$].

Empirical formula	$C_{28}H_{36}Br_2N_4O_2S_2Ni$
Formula weight	743.26
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.286(2)
b	13.215(3)
c	14.125(3)
α	64.180(5)
β	85.483(6)
γ	83.067(5)
Volume (Å^3)	1548.3(7)
Z	2
Calculated density (mg m^{-3})	1.594
Absorption coefficient (mm^{-1})	3.374
$F(000)$	756
Crystal size (mm^3)	0.43 × 0.38 × 0.03
θ range for data collection (°)	1.60–27.88
Limiting indices	$-11 \leq h \leq 12$; $-17 \leq k \leq 17$; $-18 \leq l \leq 16$
Reflections collected	13920
Independent reflections	7335 [$(R_{int}) = 0.0823$]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/parameters	7335/352
Goodness-of-fit on F^2	0.913
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.1090$
R indices (all data)	$R_1 = 0.0744$, $wR_2 = 0.1182$
Largest difference peak and hole (e Å^{-3})	0.924 and −0.869

4.91; N, 8.69%. FT-IR (cm^{-1}): ν(NH) 3275 (w); ν(CH) 2975, 2931, 2868 (vw); ν(C=O) 1641 (s); ν(C=S) 1285 (m); ν(C–Br) 752 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.51 (s, 1H, N*H*), 7.62 (d, 2H, Ar–*H*), 7.60 (d, 2H, Ar–*H*), 4.02 (s, 2H, N–C*H*$_2$), 3.59 (s, 2H, N–C*H*$_2$), 1.36 (s, 3H, C*H*$_3$) 1.30 (s, 3H, C*H*$_3$).

2.2.3. 4-Bromo-*N*-(di-*n*-propylcarbamothioyl)benzamide, HL^3. White. Yield: 88%, m.p.: 118–120°C. Calcd for $C_{14}H_{19}BrN_2OS$: C, 48.98; H, 5.58; N, 8.16. Found: C, 48.74; H, 5.44; N, 8.36%. FT-IR (cm^{-1}): ν(NH) 3207 (w); ν(CH) 2962, 2947, 2871 (w); ν(C=O) 1685 (s); ν(C=S) 1261 (m); ν(C–Br) 750 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.38 (bs, 1H, –N*H*), 7.64 (d, 2H, Ar–*H*), 7.62 (d, 2H, Ar–*H*), 3.95 (bs, 2H, N–C*H*$_2$), 3.50 (s, 2H, N–C*H*$_2$), 1.84 (m, 2H, -C*H*$_2$–), 1.67 (m, 2H, –C*H*$_2$–), 1.04 (bs, 3H, C*H*$_3$), 0.91 (bs, 3H, C*H*$_3$).

2.2.4. 4-Bromo-*N*-(di-*n*-butylcarbamothioyl)benzamide, HL^4. White. Yield: 89%, m.p.: 102–104°C. Calcd for $C_{16}H_{23}BrN_2OS$: C, 51.75; H, 6.24; N, 7.54. Found: C, 51.71; H, 6.21; N, 7.51%. FT-IR (cm^{-1}): ν(NH) 3241 (s); ν(CH) 2957, 2929, 2871 (s); ν(C=O) 1643 (s); ν(C=S) 1268 (s); ν(C–Br) 751 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.37 (s, 1H, –N*H*), 7.71 (d, 2H, Ar–*H*), 7.64 (d, 2H, Ar–*H*), 3.98 (t, 2H, N–C*H*$_2$), 3.52 (t, 2H, N–C*H*$_2$), 1.81 (m, 2H, C*H*$_2$), 1.67 (m, 2H, C*H*$_2$), 1.45 (m, 2H, C*H*$_2$), 1.31(m, 2H, C*H*$_2$), 1.00 (t, 3H, C*H*$_3$), 0.92 (t, 3H, C*H*$_3$).

2.2.5. 4-Bromo-*N*-(diphenylcarbamothioyl)benzamide, HL^5. White. Yield: 90%, m.p.: 158–160°C. Calcd for $C_{20}H_{15}BrN_2OS$: C, 58.40; H, 3.68; N, 6.81. Found: C, 58.35; H, 3.61; N, 6.77%. FT-IR (cm^{-1}): ν(NH) 3156 (w); ν(Ar–H) 3110, 3056 (w); ν(C=O) 1694 (s); ν(C=S) 1252 (s); ν(C–Br) 751 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.71 (s, 1H, –N*H*), 7.95 (d, 2H, Ar–*H*), 7.68 (d, 2H, Ar–*H*), 7.54 (t, 2H, N–Ar–*Hb*), 7.49 (t, 2H, N–Ar–*Hb′*), 7.36 (t, H, N–Ar–*Hc*), 7.28 (t, H, N–Ar–*Hc′*), 7.11 (d, 2H, N–Ar–*Ha*), 6.95 (d, 2H, N–Ar–*Ha′*).

2.3. *Synthesis of the complexes*

A solution of metallic acetate (0.01 M) in methanol (30 cm^3) was added dropwise to a solution of the ligand in a 1 : 2 ratio for both nickel and copper with a small excess of ligand in ethanol (30 cm^3) at room temperature, and the resulting mixture was stirred for 30 min [21, 26, 34]. The solid complexes were filtered and recrystallized from an ethanol : dichloromethane mixture (1 : 2).

2.3.1. *Bis*(4-bromo-*N*-(dimethylcarbamothioyl)benzamido)nickel(II), [Ni(L^1)$_2$]. Purple. Yield: 85%, m.p.: 244–246°C. Calcd for $C_{20}H_{20}Br_2N_4O_2S_2Ni$: C, 38.07; H, 3.19; N, 8.88. Found: C, 38.01; H, 3.15; N, 8.81%. FT-IR (cm^{-1}): ν(CH) 2923, 2853 (vw); ν(CN) 1580 (w); ν(C–O), 1500 (vs); ν(C–Br), 751 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 8.00 (d, 4H, Ar–*H*), 7.52 (d, 4H, Ar–*H*), 3.39 (bs, 6H, N–C*H*$_3$), 3.33 (bs, 6H, N–C*H*$_3$).

2.3.2. *Bis*(4-bromo-*N*-(dimethylcarbamothioyl)benzamido)copper(II), [Cu(L^1)$_2$]. Green. Yield: 76%, m.p.: 222–224°C. $C_{20}H_{20}Br_2N_4O_2S_2Cu$: C, 37.78; H, 3.17; N, 8.81. Found: C, 37.97; H, 3.20; N, 8.79%. FT-IR (cm^{-1}): ν(CH), 2925, 2852 (vw); ν(CN) 1580 (w), ν(C–O) 1499 (vs); ν(C–Br) 756 (w).

2.3.3. *Bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)nickel(II), [Ni(L^2)$_2$]. Purple. Yield: 82%, m.p.: 248–250°C. Calcd for $C_{24}H_{28}Br_2N_4O_2S_2Ni$: C, 41.95; H, 4.11; N, 8.15. Found: C, 41.80; H, 4.05; N, 8.16%. FT-IR (cm^{-1}): ν(CH) 2974, 2932, 2868 (w); ν(CN) 1581 (w); ν(C–O) 1492 (vs); ν(C–Br) 751 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.96 (d, 4H, Ar–*H*), 7.52 (d, 4H, Ar–*H*), 3.57 (m, 8H, N–C*H*$_2$), 1.48 (m, 12H, –C*H*$_3$).

2.3.4. *Bis*(4-bromo-*N*-(diethylcarbamothioyl)benzamido)copper(II), [Cu(L^2)$_2$]. Green. Yield: 76%, m.p.: 204–206°C. Calcd for $C_{24}H_{28}Br_2N_4O_2S_2Cu$: C, 41.66; H, 4.08; N, 8.10. Found: C, 41.80; H, 4.04; N, 8.04%. FT-IR (cm^{-1}): ν(CH) 2977, 2931, 2865 (vw), ν(CN) 1579 (w), ν(C–O) 1490 (vs); ν(C–Br) 754 (w).

2.3.5. *Bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)nickel(II), [Ni(L^3)$_2$]. Purple. Yield: 78%, m.p.: 198–200°C. Calcd. for $C_{28}H_{36}Br_2N_4O_2S_2Ni$: C, 45.25; H, 4.88; N, 7.54. Found: C, 45.05; H, 4.80; N, 7.50%. FT-IR (cm^{-1}): ν(CH) 2941, 2928, 2868 (w), ν(CN) 1577 (w), ν(C–O) 1492 (vs); ν(C–Br) 753 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.95 (d, 4H, Ar–*H*), 7.57 (d, 4H, Ar–*H*), 3.7 (m, 8H, N–C*H*$_2$), 1.57 (m, 8H, C*H*$_2$), 0.95 (m, 12H, –C*H*$_3$).

2.3.6. *Bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)copper(II), [Cu(L^3)$_2$]. Green. Yield: 76%, m.p.: 164–166°C. Calcd for $C_{28}H_{36}Br_2N_4O_2S_2Cu$: C, 44.95; H, 4.85; N, 7.49. Found: C, 44.99; H, 4.82; N, 7.55%. FT-IR (cm^{-1}): ν(CH) 2942, 2929, 2870 (w); ν(CN) 1578 (w); ν(C–O) 1490 (vs); ν(C–Br) 755 (w).

2.3.7. *Bis*(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido)nickel(II), [Ni(L^4)$_2$]. Purple. Yield: 82%, m.p.: 158–160°C. Calcd for $C_{32}H_{44}Br_2N_4O_2S_2Ni$: C, 48.08; H, 5.55; N, 7.01. Found: C, 47.79; H, 5.50; N, 6.90%. FT-IR (cm^{-1}): ν(CH) 2956, 2930, 2863 (w); ν(CN) 1578 (w), ν(C–O) 1493 (vs); ν(C–Br) 753 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.96 (d, 4H, Ar–*H*), 7.52 (d, 4H, Ar–*H*), 3.7 (m, 8H, N–CH_2), 1.68 (m, 8H, CH_2), 1.40 (m, 8H, CH_2), 0.98 (m, 12H, CH_3).

2.3.8. *Bis*(4-bromo-*N*-(di-*n*-butylcarbamothioyl)benzamido)copper(II), [Cu(L^4)$_2$]. Green. Yield: 76%, m.p.: 120–122°C. Calcd for $C_{32}H_{44}Br_2N_4O_2S_2Cu$: C, 47.79; H, 5.51; N, 6.97. Found: C, 48.08; H, 5.44; N, 7.04%. FT-IR (cm^{-1}): ν(CH) 2954, 2930, 2864 (w); ν(CN) 1579 (w), ν(C–O) 1493 (vs); ν(C–Br) 757 (w).

2.3.9. *Bis*(4-bromo-*N*-(diphenylcarbamothioyl)benzamido)nickel(II), [Ni(L^5)$_2$]. Purple. Yield: 82%, m.p.: 292–294°C. Calcd for $C_{40}H_{28}Br_2N_4O_2S_2Ni$: C, 54.64; H, 3.21; N, 6.37. Found: C, 54.50; H, 3.18; N, 6.33%. FT-IR (cm^{-1}): ν(Ar–CH) 3100, 3086 (vw); ν(CN) 1581 (w); ν(C–O) 1491 (vs); ν(C–Br) 695 (w). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60–7.25 (m, 28H, Ar–*H*).

2.3.10. *Bis*(4-bromo-*N*-(diphenylcarbamothioyl)benzamido)copper(II), [Cu(L^5)$_2$]. Green. Yield: 76%, m.p.: 250–252°C. Calcd for $C_{40}H_{28}Br_2N_4O_2S_2Cu$: C, 54.34; H, 3.19; N, 6.34. Found: C, 54.31; H, 3.15; N, 6.33%. FT-IR (cm^{-1}): ν(Ar–CH) 3101, 3086 (vw); ν(CN) 1580 (w); ν(C–O) 1492 (vs); ν(C–Br) 698 (w).

3. Results and discussion

The thiourea derivatives were synthesized from 4-bromobenzoyl isothiocyanate and secondary amines in dry acetone. Figure 1 outlines the synthesis of the series of thiourea derivatives. ^{1}H-NMR spectra, FT-IR spectra and elemental analysis data of all synthesized compounds confirm the proposed structures. Synthesized compounds were soluble in ethanol and dichloromethane in varying degrees.

The sharp and strong absorptions at 3201, 3275, 3207, 3241 and 3156 cm^{-1} for HL^1, HL^2, HL^3, HL^4, and HL^5 correspond to N–H stretches. These sharp and strong ν_{NH} disappear in the corresponding complexes (Supplementary material, figure S1). The strong $\nu_{C=O}$ are observed at 1697, 1641, 1685, 1643, and 1694 cm^{-1} for HL^1, HL^2, HL^3, HL^4, and HL^5. The $\nu_{C=O}$ stretching vibrations in the corresponding complexes shift to lower wavenumber, in agreement with the disappearing ν_{NH} and the suggested molecular structures in figure 1. The same trend is observed for $\nu_{C=S}$ which shifts to lower wavenumber. Unfortunately, the shifted $\nu_{C=S}$ stretching vibration bands could not be assigned clearly because of overlap with other vibration bands in this region.

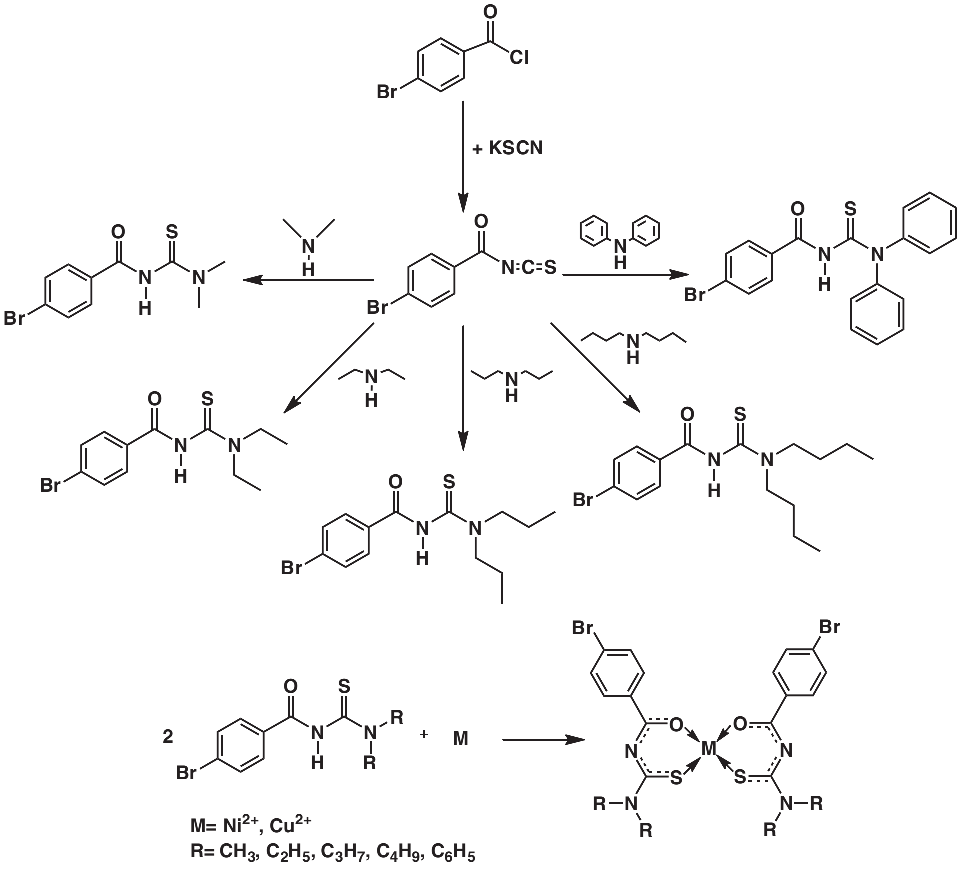

Figure 1. Synthesis of the compounds.

Proton NMR spectra were obtained from deuterated chloroform solutions and the NH resonances at 8.65, 8.51, 8.38, 8.37, and 8.71 ppm were assigned for HL^1, HL^2, HL^3, HL^4, and HL^5, respectively. The disappearing NH resonance in the ^{1}H-NMR spectra of the complexes correlates to complex formation. The other hydrogen resonances given in the experimental section confirm the suggested molecular structure of the synthesized ligands and their metal complexes.

The molecular structure of *bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido) nickel(II) is shown in figure 2; selected bond lengths and angles for *bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)nickel(II) are listed in table 2.

The molecular structure of 4-bromo-*N*-(diethylcarbamothioyl)benzamide and 4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamide are in agreement with the suggested molecular structure for the synthesized ligands (figure 1) [35, 36]. The carbonyl {1.230(2) Å for HL^2 and 1.218(3) Å for HL^3} and thiocarbonyl {1.6638(18) Å for HL^2 and 1.673(3) Å for HL^3} bond lengths indicate double bonds [30, 31, 35–39]. The C–N bond lengths for the HL^2 and HL^3 compounds are all shorter than the average single C–N bond length of 1.48 Å, N1–C6 = 1.355(2) Å, N1–C1 = 1.435(2) Å, N2–C1 = 1.325(2) Å for HL^2 and N11–C108 = 1.389(3) Å, N11–C101 = 1.416(3) Å,

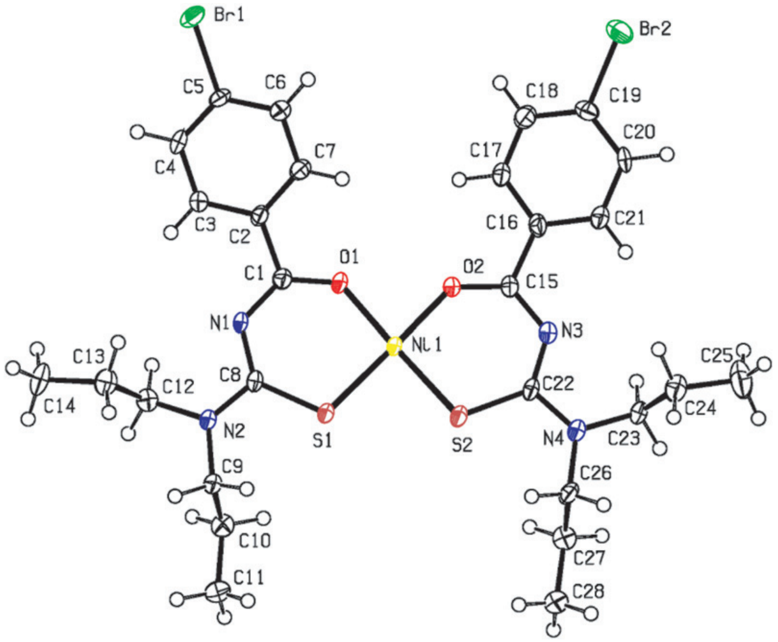

Figure 2. The crystal structure of *bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)nickel(II). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected bond lengths (Å) and angles (°) of $[Ni(L^3)_2]$.

Ni1–O2	1.858(3)	C15–N3	1.329(5)
Ni1–O1	1.861(3)	C22–N3	1.325(5)
Ni1–S1	2.1427(11)	C22–N4	1.355(5)
Ni1–S2	2.1448(11)	N4–C23	1.472(5)
S1–C8	1.741(4)	N2–C8	1.339(5)
S2–C22	1.735(4)	N3–C15	1.329(5)
O1–C1	1.275(4)	N1–C8	1.335(5)
O2–C15	1.276(4)	N1–C1	1.328(5)
O2–Ni1–O1	83.71(11)	C1–O1–Ni1	132.7(3)
O2–Ni1–S1	177.47(9)	C15–O2–Ni1	133.2(2)
O1–Ni1–S1	94.70(9)	O2–C15–C16	114.8(3)
O2–Ni1–S2	95.34(8)	O2–C15–N3	129.0(3)
O1–Ni1–S2	175.89(10)	N3–C22–N4	115.1(3)
S1–Ni1–S2	86.38(4)	N4–C22–S2	116.6(3)
C8–S1–Ni1	109.10(13)	C22–N4–C26	123.8(3)
C22–S2–Ni1	108.75(13)	C15–N3–C22	124.1(3)

N12–C101 = 1.323(3) Å for HL^3, thus showing varying degrees of double bond character in these C–N bonds [30, 31, 42–48]. This indicates partial electron delocalization within the (OC)–N–(CS)–N fragment of both ligands. These results are in agreement with the literature [30, 31, 35–39, 42–48].

Bis(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)nickel(II) is a *cis*-complex with slightly distorted square planar coordination of nickel by two oxygens and two sulfurs. The Ni–O bond distances {1.858(3) Å and 1.861(3) Å} are equal within

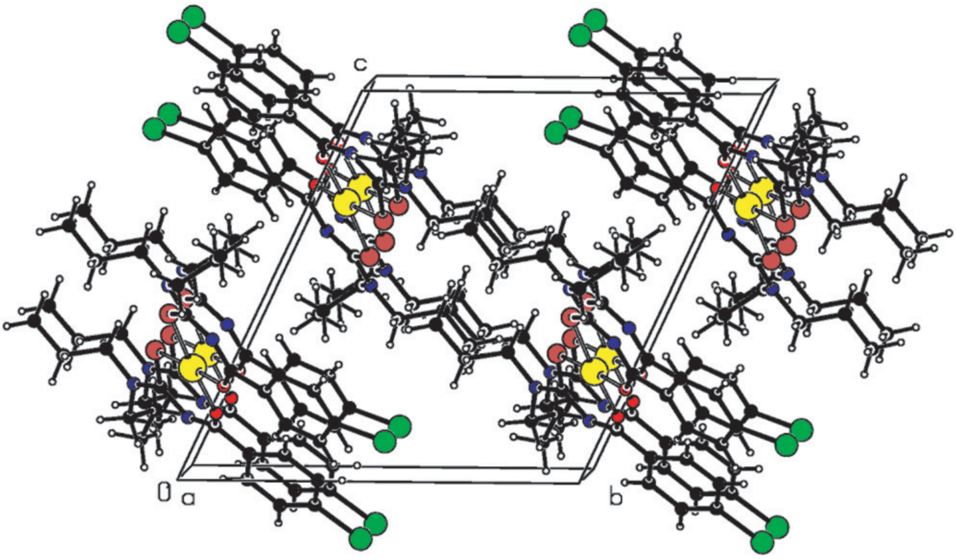

Figure 3. Unit cell diagram of *bis*(4-bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido)nickel(II).

experimental error. As expected, the Ni–O bond distance is shorter than Ni–S bond distances {2.1427(11) Å and 2.1448(11) Å}. The distance of nickel, sulfur, and oxygen atoms from the best plane through the coordination sphere is 0.018(1) Å, −0.047(1) Å and 0.055(3) Å, respectively. The chelate ring systems, Ni–O1–C1–N1–C8–S1 and Ni–O2–C15–N3–C22–S2, are nearly planar as well with the largest deviations from the best plane being 0.093(4) Å for C1 and −0.068(1) Å for S2, respectively. The dihedral angle between these chelate planes is 5.37(12)°. The bond distances of the C–N {C1–N1: 1.328(5); C8–N1: 1.335(5); N3–C15: 1.329(5) and N3–C22: 1.335(5) Å} in the chelate ring are all shorter than the average C–N single bond distance [42]. In addition, the bond distances of the C–S {S1–C8: 1.741(4) and S2–C22: 1.735(4) Å) and C–O (C1–O1: 1.275(4) and C15–O2: 1.276(4) Å} in the chelate ring are longer than average C=S and C=O double bond distances of thiourea derivatives [35, 36]. These results indicate extensive delocalization of electrons within the chelate rings. All di-*n*-propyl groups in the nickel complex are twisted in a + and − antiperiplanar conformation with −180° (H25A), +180° (H28A), −180° (H11A) and +180° (H14A). The unit cell diagram of the nickel complex is shown in figure 3. The crystal packing shows the molecules stacked in parallel sheets along [100]. Although there is no intermolecular D–H ⋯ A contacts, the crystal structure has two intramolecular interactions: C9–H9B ⋯ S1, with H ⋯ S 2.52 Å and C–H ⋯ S 106°; and C26–H26A ⋯ S2, with H ⋯ S 2.48 Å and C–H ⋯ S 110°.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with quotation number CCDC-720899 for [Ni(L^3)$_2$] and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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