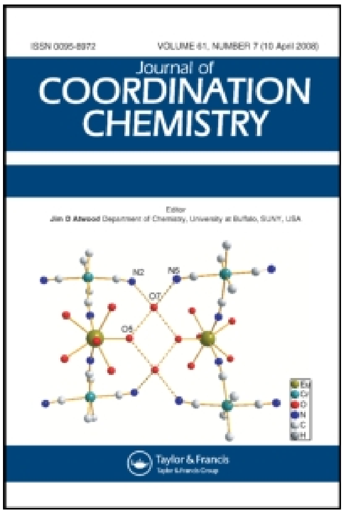

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Synthesis and characterization of nickel and copper complexes with 2,2-diphenyl-*N*-(alkyl(aryl)carbamothioyl) acetamide: The crystal structures of HL^1 and *cis*-$[Ni(L^1)_2]$

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2,2-diphenyl-*N*-(*R*-carbamothioyl)acetamide (R = diethyl, dipropyl, dibutyl, dihexyl, diphenyl and morpholine-4) and their Ni^{2+} and Cu^{2+} complexes have been synthesized and characterized by elemental analyses, IR spectroscopy and ^{1}H-NMR spectroscopy. The spectroscopic data are consistent with the ligand and the metal complexes containing two O, S chelated ligands. 2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamide, HL^1, and *bis*(2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamido)nickel(II), $Ni(L^1)_2$, were characterized by a single crystal X-ray diffraction study. HL^1 complex, $C_{19}H_{22}N_2OS$, crystallizes monoclinic, space group $P2_1/c$, with $Z = 4$, and unit cell parameters $a = 14.964(2)$, $b = 13.026(2)$, $c = 9.0123(15)$ Å, $\beta = 96.314(4)^\circ$. $Ni(L^1)_2$ complex, $C_{38}H_{42}N_4O_2S_2Ni$, crystallizes in monoclinic space group $P2_1/c$, with $Z = 4$, and unit cell parameters $a = 15.434(6)$, $b = 13.464(5)$, $c = 17.679(7)$ Å, $\beta = 108.477(11)^\circ$. The ligands coordinate bidentate to metal yielding neutral complexes of the type *cis*-$[ML_2]$.

Keywords: Synthesis; Thiourea; Complex; Single crystal structure

1. Introduction

Thioureas have long been known since their first synthesis by Neucki [1, 2] and are very versatile ligands, able to coordinate to a range of metal centers as either neutral ligands, monoanions or dianions [3–10]. In addition, the oxygen, nitrogen and sulfur donors provide a multitude of bonding possibilities. The coordination chemistry of substituted thioureas has led to some interesting practical applications, including liquid–liquid extraction, pre-concentration and highly efficient chromatographic separation, fluorimetric detection of the platinum group metals, and selective on-line pre-concentration of ultra-traces of Pd, followed by its determination using graphite furnace atom absorption spectrometry [11–13]. A number of thiourea derivatives and

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their metal complexes are associated with various biological activities. Some thiourea derivatives are useful as insecticides, herbicides, and plant-growth regulators [14, 15]. Thiourea derivatives have also been paid special attention because thiourea derivatives have antitumor and antifungal bioactivities [16].

We are pursuing investigations on the synthesis, characterization, crystal structure, thermal behavior and antimicrobial activity of new thiourea derivatives [8–11, 17–28]. Based upon the literature search, we could find no synthesis or characterization of the title compound type thiourea derivatives and their metal complexes. In this article, we report the preparation and characterization of six new ligands and their nickel and copper metal complexes. The crystal structures of 2,2-diphenyl-*N*-(diethylcarbamothioyl) acetamide and *bis*(2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamido)nickel(II) complex are also described.

2. Experimental

2.1. *Instrumentation*

The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra of the all synthesized compounds were registered using a Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000–525 cm^{-1}; number of scans: 250; resolution: 1 cm^{-1}). All ^{1}H-NMR spectra were recorded on a Bruker DPX-400 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Room temperature magnetic susceptibility measurements were carried out on a Sherwood-Scientific model Gouy magnetic balance (Calibrant: $Hg[Co(SCN)_4]$). C, H and N analyses were carried out on a Carlo Erba MOD 1106 elemental analyzer. Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer [29] using monochromated Mo-Kα radiation. The structures were solved [29] by direct and conventional Fourier methods with full-matrix least-squares refinement [29] based on F^2. All atoms other than hydrogen were refined anisotropically; hydrogen atoms were located from difference Fourier maps and refined at idealized positions with a "riding model" and $U(H) = 1.2\ U(C_{iso})$ and $1.5\ U(C_{iso})$ for methyl groups, respectively; H1 atom of NH group in HL^1 was allowed to refine freely. Further details concerning data collection and refinement are given in table 1.

2.2. *Synthesis of the ligands*

All chemicals used for the preparation of the ligands were of reagent grade. Some of the solvents were distilled before use. The ligands were prepared by a procedure similar to that reported in the literature [8, 30]. A solution of 2,2-diphenylacetyl chloride (0.005 mole) in acetone (50 cm^3) was added dropwise to a suspension of potassium thiocyanate (0.005 mole) in acetone (50 cm^3). The reaction mixture was heated (50°C) under reflux for 30 min, and then cooled to room temperature. A solution of secondary amine (0.005 mole) 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 mixture (1 : 1).

Table 1. Summary of crystallographic data and parameters of the HL^1 and $Ni(L^1)_2$.

Compound	HL^1	$Ni(L^1)_2$
Empirical formula	$C_{19}H_{22}N_2OS$	$NiC_{38}H_{42}N_4O_2S_2$
Formula weight	326.45	709.59
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	14.964(2)	15.434(6)
b	13.026(2)	13.464(5)
c	9.0123(15)	17.679(7)
β	96.314(4)	108.477(11)
V (Å^3)	1746.0(5)	3484(2)
Z	4	4
D_{Calcd} (Mg m^{-3})	1.242	1.353
Absorption coefficient (mm^{-1})	0.192	0.716
$F(000)$	696	1496
Crystal size (mm^3)	$0.22 \times 0.21 \times 0.03$	$0.38 \times 0.35 \times 0.04$
θ range for data collection (°)	1.37 to 27.88	1.94 to 23.79
Index ranges	$-19 \leq h \leq 19$ $-16 \leq k \leq 17$ $-11 \leq l \leq 11$	$-16 \leq h \leq 17$ $-14 \leq k \leq 14$ $-19 \leq l \leq 19$
Reflections collected	16140	18454
Independent reflections (R_{int})	4163 (0.0897)	4964 (0.0877)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	4163/212	4964/424
Goodness-of-fit on F^2	0.976	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$, $wR_2 = 0.1011$	$R_1 = 0.0654$, $wR_2 = 0.1725$
R indices (all data)	$R_1 = 0.0824$, $wR_2 = 0.1108$	$R_1 = 0.0940$, $wR_2 = 0.2004$
Largest diff. peak and hole (e Å^{-3})	0.304 and −0.290	0.761 and −0.582

2.2.1. 2,2-diphenyl-*N*-alkyl(aryl)carbamothioyl acetamide (HL^1). White. Yield: 85%, m.p.: 120–121°C. Anal. Calcd for $C_{19}H_{22}N_2OS$: C, 69.9; H, 6.8; N, 8.6. Found: C, 69.2; H, 6.74; N, 8.53%. FT-IR (KBr pellet, cm^{-1}): ν(N–H) 3190 (br), ν(Ph_2CH–) 3064–3027 (v), ν(C=O) 1712 (s). ^{1}H-NMR ($CDCl_3$): δ 10.65 (s, 1H, N*H*), 7.36–7.25 (m, 10H, Ar–*H*), 5.21 (s, 1H, C_6H_4CH), 3.84 (q, 2H, N–CH_2), 3.28 (q, 2H, N–CH_2), 1.16 (t, 3H, CH_3), 0.98 (t, 3H, CH_3).

2.2.2. 2,2-diphenyl-*N*-(dipropyl-carbamothioyl)acetamide (HL^2). White. Yield: 96%, m.p.: 107–108°C. Anal. Calcd for $C_{21}H_{26}N_2OS$: C, 71.1; H, 7.4; N, 7.9. Found: C, 70.6; H, 7.32; N, 7.85%. FT-IR (KBr pellet, cm^{-1}): ν(N–H) 3195 (br), ν(Ph_2CH–) 3059–3026 (v), ν(C=O) 1709 (s). ^{1}H-NMR ($CDCl_3$): δ 10.72 (s, 1H, N*H*), 7.35–7.26 (m, 10H, Ar–*H*), 5.21 (s, 1H, C_6H_4CH), 3.79 (t, 2H, N–CH_2), 3.15 (t, 2H, N–CH_2), 1.65 (h, 2H, CH_2), 1.39 (h, 2H, CH_2), 0.88 (t, 3H, CH_3), 0.53 (t, 3H, CH_3).

2.2.3. 2,2-diphenyl-*N*-(dibutyl-carbamothioyl)acetamide (HL^3). White. Yield: 89%, m.p.: 82–83°C. Anal. Calcd for $C_{23}H_{30}N_2OS$: C, 72.2; H, 7.9; N, 7.3. Found: C, 71.8; H, 7.8; N, 7.26%. FT-IR (KBr pellet, cm^{-1}): ν(N–H) 3191 (br), ν(Ph_2CH–) 3060–3029 (v), ν(C=O) 1703 (s). ^{1}H-NMR ($CDCl_3$): δ 10.71 (s, 1H, N*H*), 7.34–7.25 (m, 10H, Ar–*H*), 5.20 (s, 1H, C_6H_4CH), 3.83 (t, 2H, N–CH_2), 3.19 (t, 2H, N–CH_2), 1.57–1.63 (m, 4H, CH_2), 1.38–1.28 (m, 4H, CH_2), 0.89 (t, 3H, CH_3), 0.67 (t, 3H, CH_3).

2.2.4. 2,2-diphenyl-*N*-(dihexyl-carbamothioyl)acetamide (HL^4). White. Yield: 87%, m.p.: 80–81°C. Anal. Calcd for $C_{27}H_{38}N_2OS$: C, 73.9; H, 8.7; N, 6.4. Found: C, 73.0; H, 8.6; N, 6.3%. FT-IR (KBr pellet, cm^{-1}): ν(N–H) 3123 (br), ν(Ph$_2$CH–) 3063–3026 (v), ν(C=O) 1703 (s). ^{1}H-NMR (CDCl$_3$): δ 10.70 (s, 1H, N*H*), 7.34–7.24 (m, 10H, Ar–*H*), 5.20 (s, 1H, C$_6$H$_4$C*H*), 3.80 (t, 2H, N–C*H*$_2$), 3.17 (t, 2H, N–C*H*$_2$), 1.62 (p, 4H, C*H*$_2$), 1.37 (p, 4H, C*H*$_2$), 1.14 (p, 4H, C*H*$_2$), 1.02 (h, 4H, C*H*$_2$), 0.86 (t, 3H, C*H*$_3$), 0.80 (t, 3H, C*H*$_3$).

2.2.5. 2,2-diphenyl-*N*-(diphenyl-carbamothioyl)acetamide (HL^5). Yellow. Yield: 91%, m.p.: 154–155°C. Anal. Calcd for $C_{27}H_{22}N_2OS$: C, 76.7; H, 5.2; N, 6.6. Found: C, 76.5; H, 5.2; N, 6.6%. FT-IR (KBr pellet, cm^{-1}): ν(N–H) 3153 (br), ν(Ph$_2$CH–) 3058–3034 (v), ν(C=O) 1714 (s). ^{1}H-NMR (CDCl$_3$): δ 11.28 (s, 1H, N*H*), 7.33–7.16 (m, 20H, Ar–*H*), 5.05 (s, 1H, C$_6$H$_4$C*H*).

2.2.6. 2,2-diphenyl-*N*-(morpholine-4-carbamothioyl)acetamide (HL^6). Yellow. Yield: 83%, m.p.: 150–151°C. Anal. Calcd for $C_{19}H_{20}N_2O_2S$: C, 67.0; H, 5.9; N, 8.2. Found: C, 66.6; H, 5.9; N, 8.1%. FT-IR (KBr pellet, cm^{-1}): ν(N–H) 3265 (br), ν(Ph$_2$CH–) 3055–3028 (v), ν(C=O) 1688 (s). ^{1}H-NMR CDCl$_3$): δ 10.96 (s, 1H, N*H*), 7.36–7.22 (m, 10H, Ar–*H*), 5.28 (s, 1H, C$_6$H$_4$C*H*), 4.05–3.65 (m, 4H, O–C*H*$_2$), 3.57–3.36 (m, 4H, N–C*H*$_2$).

2.3. *Synthesis of the complexes*

Metallic salts used for the preparation of the complexes were obtained from Merck. Metallic complexes were prepared according to the method described in the literature [8, 30]. A solution of the metallic acetate (0.01 mole) in ethanol (30 cm^3) was added dropwise to a solution of the ligand in a 1 : 2 ratio with a small excess of ligand in ethanol (50 cm^3) at room temperature and the resulting mixture was stirred for 30 min. The solid complexes were filtered and recrystallized from ethanol:dichloromethane mixture (1 : 3).

2.3.1. *Bis*(2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamido)nickel(II) (Ni(L^1)$_2$). Purple. Yield: 75%, m.p.: 171–172°C. Anal. Calcd for $C_{38}H_{42}N_4O_2S_2Ni$: C, 64.3; H, 6.0; N, 7.9. Found: C, 63.95; H, 5.91; N, 7.8%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3058–3021 (v), ν(C–N) 1529 (s). ^{1}H-NMR (CDCl$_3$): δ 7.19–7.35 (m, 20H, Ar–*H*), 5.19 (s, 2H C$_6$H$_4$C*H*), 3.83 (q, 4H, N–C*H*$_2$), 3.28 (q, 4H, N–C*H*$_2$), 1.22 (t, 3H, C*H*$_3$), 1.15 (t, 3H, C*H*$_3$), 0.97 (t, 3H, C*H*$_3$), 0.84 (t, 12H, C*H*$_3$).

2.3.2. *Bis*(2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamido)copper(II) (Cu(L^1)$_2$). Green. Yield: 77%, m.p.: 140–141°C. Anal. Calcd for $C_{38}H_{42}N_4O_2S_2Cu$: C, 63.9; H, 5.9; N, 7.8. Found: C, 63.2; H, 5.9; N, 7.7%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$C*H*–) 3058–3019 (v), ν(C–N) 1529 (s).

2.3.3. *Bis*(2,2-diphenyl-*N*-(dipropylcarbamothioyl)acetamido)nickel(II) (Ni(L^2)$_2$). Purple. Yield: 76%, m.p.: 136–137°C. Anal. Calcd for $C_{42}H_{50}N_4O_2S_2Ni$: C, 65.9; H, 6.6; N, 7.3. Found: C, 64.7; H, 6.5; N, 7.3%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3058–3028 (v), ν(C–N) 1519 (s). ^{1}H-NMR (CDCl$_3$): δ 7.34–7.26 (m, 20H, Ar–*H*), 5.18, (s, 2H, C$_6$H$_4$C*H*), 3.77 (t, 4H, N–C*H*$_2$), 3.14 (t, 4H, N–C*H*$_2$), 1.63 (h, 4H, C*H*$_2$), 1.38 (h, 4H, C*H*$_2$), 0.86 (t, 6H, C*H*$_3$), 0.51(t, 6H, C*H*$_3$).

2.3.4. *Bis*(2,2-diphenyl-*N*-(dipropylcarbamothioyl)acetamido)copper(II) (Cu(L^2)$_2$). Green. Yield: 72%, m.p.: 129–130°C. Anal. Calcd for $C_{42}H_{50}N_4O_2S_2Cu$: C, 65.5; H, 6.5; N, 7.3. Found: C, 65.1; H, 6.5; N, 7.1%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3057–3026 (v), ν(C–N) 1519 (s).

2.3.5. *Bis*(2,2-diphenyl-*N*-(dibutylcarbamothioyl)acetamido)nickel(II) (Ni(L^3)$_2$). Purple. Yield: 70%, m.p.: 73–74°C. Anal. Calcd for $C_{46}H_{58}N_4O_2S_2Ni$: C, 67.2; H, 7.1; N, 6.8. Found: C, 67.1; H, 7.0; N, 6.8%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3058–3024 (v), ν(C–N) 1519 (s). ^{1}H-NMR (CDCl$_3$): δ 7.20–7.36 (m, 20H, Ar–*H*), 5.18 (s, 2H, C$_6$H$_4$C*H*), 3.80 (t, 4H, N–C*H*$_2$), 3.18 (t, 4H, N–C*H*$_2$) 1.61–1.58 (m, 8H, C*H*$_2$), 1.34–1.23 (m, 8H, C*H*$_2$), 0.88 (t, 6H, C*H*$_3$), 0.67 (t, 6H, C*H*$_3$).

2.3.6. *Bis*(2,2-diphenyl-*N*-(dibutylcarbamothioyl)acetamido)copper(II) (Cu(L^3)$_2$). Green. Yield: 73%, m.p.: 70–71°C. Anal. Calcd for $C_{46}H_{58}N_4O_2S_2Cu$: C, 66.8; H, 7.1; N, 6.8. Found: C, 66.5; H, 7.0; N, 6.7%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3058–3025 (v), ν(C–N) 1519 (s).

2.3.7. *Bis*(2,2-diphenyl-*N*-(dihexylcarbamothioyl)acetamido)nickel(II) (Ni(L^4)$_2$). Purple. Yield: 76%, m.p.: 90–91°C. Anal. Calcd for $C_{54}H_{74}N_4O_2S_2Ni$: C, 69.4; H, 8.0; N, 6.0. Found: C, 69.2; H, 7.8; N, 5.9%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3059–3024 (v), ν(C–N) 1525 (s). ^{1}H-NMR (CDCl$_3$): δ 7.33–7.24 (m, 20H, Ar–*H*), 5.18 (s, 2H, C$_6$H$_4$C*H*), 3.79 (t, 4H, N–C*H*$_2$), 3.16 (t, 4H, N–C*H*$_2$), 1.60–1.55 (m, 8H, C*H*$_2$), 1.35–1.25 (m, 8H, C*H*$_2$), 1.15–1.10 (m, 8H, C*H*$_2$), 1.03–0.99 (m, 8H, C*H*$_2$), 0.84–0.77 (m, 12H, C*H*$_3$).

2.3.8. *Bis*(2,2-diphenyl-*N*-(dihexylcarbamothioyl)acetamido)copper(II) (Cu(L^4)$_2$). Green. Yield: 72%, m.p.: 63–64°C. Anal. Calcd for $C_{54}H_{74}N_4O_2S_2Cu$: C, 69.1; H, 7.9; N, 6.0. Found: C, 68.9; H, 7.9; N, 5.9%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3060–3023 (v), ν(C–N) 1525 (s).

2.3.9. *Bis*(2,2-diphenyl-*N*-(diphenylcarbamothioyl)acetamido)nickel(II) (NiL^5)$_2$). Purple. Yield: 80%, m.p.: 240–241°C. Anal. Calcd for $C_{54}H_{42}N_4O_2S_2Ni$: C, 71.9; H, 4.7; N, 6.2. Found: C, 71.7; H, 4.6; N, 6.1%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3058–3029 (v), ν(C–N) 1514 (s). ^{1}H-NMR (CDCl$_3$): δ 7.37–7.06 (m, 40H, Ar–*H*), 5.02 (s, 2H, C$_6$H$_4$C*H*).

2.3.10. *Bis*(2,2-diphenyl-*N*-(diphenylcarbamothioyl)acetamido)copper(II) (Cu(L^5)$_2$). Green. Yield: 78%, m.p.: 179–180°C. Anal. Calcd for $C_{54}H_{42}N_4O_2S_2Cu$: C, 71.5; H, 4.7; N, 6.2. Found: C, 71.5; H, 4.6; N, 6.1%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3057–3029 (v), ν(C–N) 1515 (s).

2.3.11. *Bis*(2,2-diphenyl-*N*-(morpholine-4-carbamothioyl)acetamido)nickel(II) (Ni(L^6)$_2$). Purple. Yield: 74%, m.p.: 231–232°C. Anal. Calcd for $C_{38}H_{38}N_4O_4S_2Ni$: C, 61.9; H, 5.2; N, 7.6. Found: C, 61.6; H, 5.1; N, 7.5%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3054–3023 (v), ν(C–N) 1523 (s). ^{1}H-NMR (CDCl$_3$): δ 7.32–7.17 (m, 20H, Ar–*H*), 5.25 (s, 2H, C_6H_4CH), 4.03–3.77 (m, 8H, O–C*H*$_2$), 3.58–3.30 (m, 8H, N–C*H*$_2$).

2.3.12. *Bis*(2,2-diphenyl-*N*-(morpholine-4-carbamothioyl)acetamido)copper(II) (Cu(L^6)$_2$). Green. Yield: 72%, m.p.: 168–169°C. Anal. Calcd for $C_{38}H_{38}N_4O_4S_2Cu$: C, 61.5; H, 5.2; N, 7.5. Found: C, 61.3; H, 5.1; N, 7.5%. FT-IR (KBr pellet, cm^{-1}): ν(Ph$_2$CH–) 3057–3021 (v), ν(C–N) 1518 (s).

3. Results and discussion

All the ligands were prepared according to the method of Douglass and Dains [31] and obtained in yields ranging from 83–96%. The synthesis involves the reaction of a 2,2-diphenylacetyl chloride with potassium thiocyanate in acetone followed by condensation of the 2,2-diphenylacetyl isothiocyanate with the appropriate secondary amine. The ligands were purified by re-crystallisation from ethanol:dichloromethane mixture (1 : 1) and characterized by elemental analysis, ^{1}H-NMR and IR spectroscopy. The analytical and spectroscopic data are consistent with the proposed structures given in figure 1.

The main vibrational bands of the related compounds are given in the experimental section. Medium peak at 3190, 3195, 3191, 3123, 3153, and 3265 cm^{-1} for HL^1, HL^2, HL^3, HL^4, HL^5, and HL^6, respectively, is attributed to the stretching vibration of N–H group adjacent to carbonyl group. Notable features of the infrared spectra of the metal complexes are the disappearance of the N–H stretching vibrations. These results agree with both ligand and complex structure and complexation reaction. A strong absorption (1712, 1709, 1703, 1703, 1714, and 1688 cm^{-1} for HL^1, HL^2, HL^3, HL^4, HL^5, and HL^6, respectively) in IR spectra of the ligands is ascribed to the stretching vibrational of the carbonyl groups. Another notable feature of the infrared spectra of the metal complexes is shifts of the carbonyl stretching vibration bands to higher frequencies upon complexation of the thiourea ligands. The deprotonation induces a delocalization of carbonyl stretching vibration in agreement with the literature [8–11] confirming coordination through the oxygen. A shift to higher frequency would also be expected for the thiocarbonyl stretching vibration band but this vibration could not be assigned unambiguously.

The ^{1}H-NMR spectra of the compounds are consistent with the structural results. The ^{1}H-NMR spectra show multiplets at 7.4–7.2 ppm for phenyl protons in the ligands. The ^{1}H-NMR spectra of compounds show the aromatic protons with slightly variations in their position. The aryl proton signals are shifted to lower field (0.1–0.2 ppm) relatively to those in the free ligand. The α-methylene protons of the HL^1, HL^2, HL^3, and HL^4 ligands show two signals at ca 3.8 and 3.2 ppm and the β-methylene protons of the HL^2, HL^3, and HL^4 ligands show two signals at ca 1.6 and 1.4 ppm. Irradiation at 3.8–3.2 or 1.6–1.4 ppm shows clearly that two alkyl (diethyl, dipropyl, dibutyl and dihexyl) groups are non-equivalent, probably due to the restricted rotation about the thiocarbonyl-nitrogen bond. HL^1, HL^2, HL^3, HL^4, HL^5, and HL^6

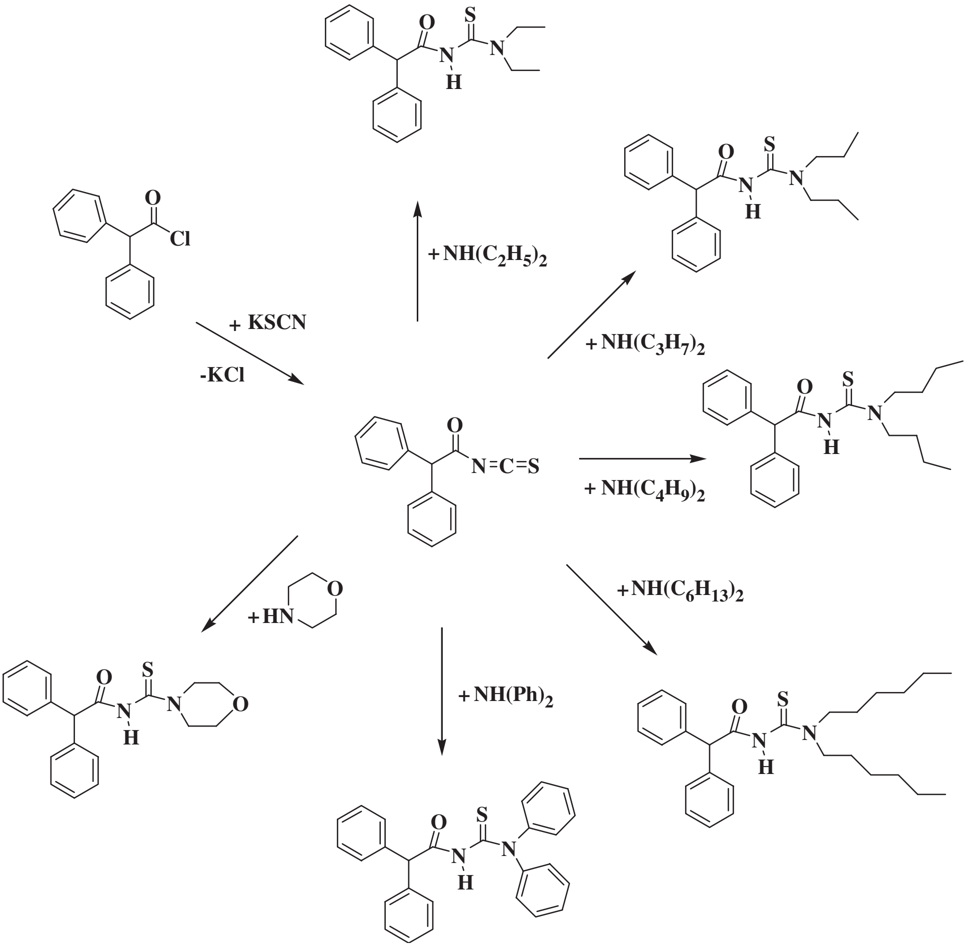

Figure 1. Synthesis of the ligands.

show a peak at 10.65, 10.72, 10.71, 10.70, 11.28, and 10.96 ppm, respectively, corresponding to the proton of the N–H group. This peak does not appear in the Ni complexes (Ni(L^1)$_2$, Ni(L^2)$_2$, Ni(L^3)$_2$, Ni(L^4)$_2$, Ni(L^5)$_2$, and Ni(L^6)$_2$) that contains the deprotonated ligand, in accord with the presence of imine in these compounds [8, 10]. These data are in agreement with the IR spectra.

The magnetic susceptibility values of the complexes show diamagnetic d^8 configuration of Ni^{2+} complexes, while the Cu^{2+} complexes are paramagnetic. The measured values for the Cu(L^1)$_2$, Cu(L^2)$_2$, Cu(L^3)$_2$, Cu(L^4)$_2$, Cu(L^5)$_2$, and Cu(L^6)$_2$ complexes are 1.75, 1.78, 1.74, 1.76, 1.77, and 1.75 B.M., respectively. These values show that the Ni^{2+} and Cu^{2+} complexes are distorted square-planar. All data agree with Arslan *et al.* [9, 10] and Duta and Syamal [32] results.

The molecular structure of 2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamide and *bis*(2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamido)nickel(II) are depicted in figures 2 and 3, respectively. Selected bond lengths and angles are presented in table 2.

The bond lengths of the carbonyl and thiocarbonyl groups of the 2,2-diphenyl-*N*-(diethyl-carbamothioyl)acetamide have typical double-bond character

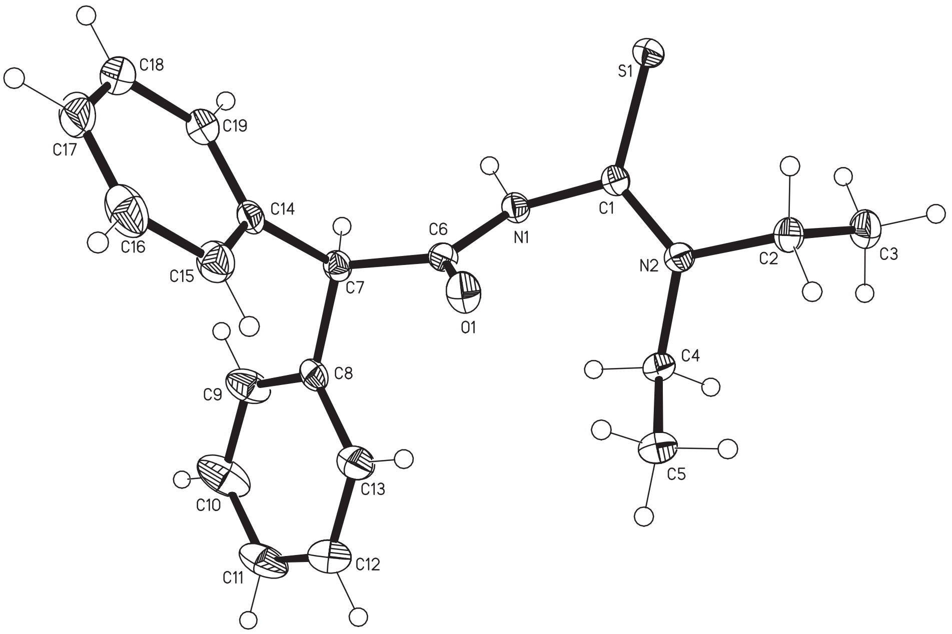

Figure 2. Molecular structure of HL^1. Thermal ellipsoids are shown at the 50% probability level.

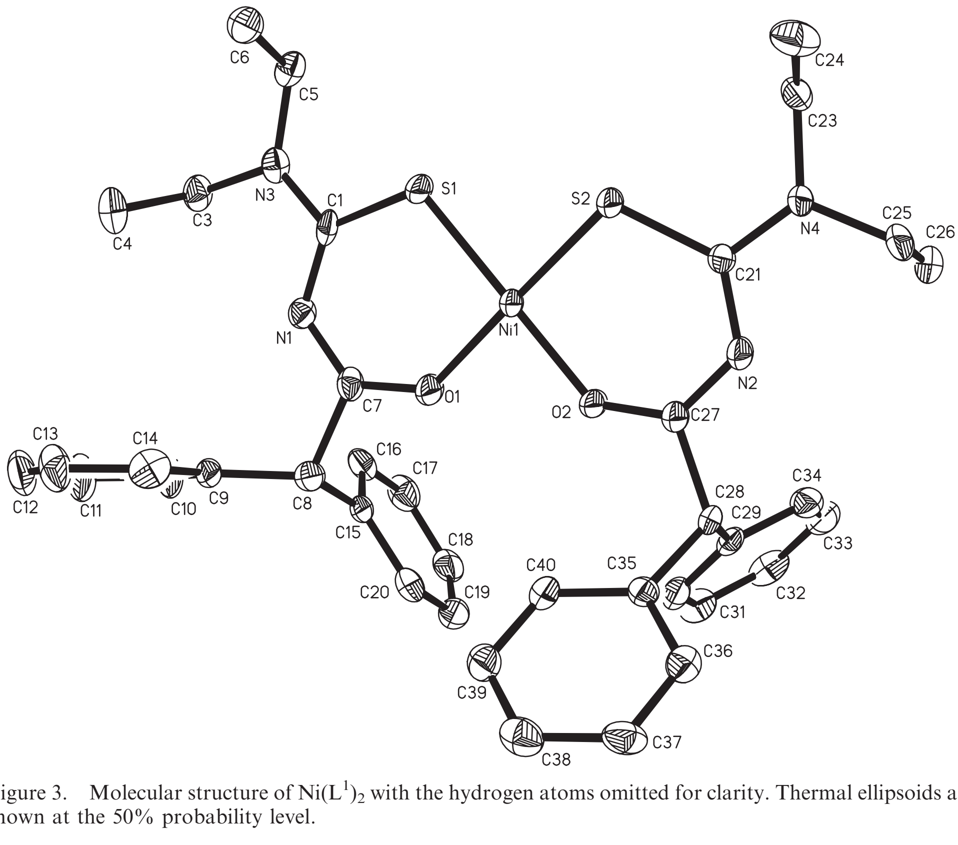

Figure 3. Molecular structure of Ni(L^1)$_2$ with the hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°).

Compound				
HL^1	S(1)–C(1)	1.6877(17)	N(2)–C(2)	1.478(2)
	O(1)–C(6)	1.207(2)	N(2)–C(4)	1.483(2)
	N(1)–C(6)	1.391(2)	C(6)–C(7)	1.529(2)
	N(1)–C(1)	1.411(2)	C(7)–C(14)	1.520(2)
	N(2)–C(1)	1.323(2)	C(7)–C(8)	1.531(2)
	C(6)–N(1)–C(1)	121.74(15)	O(1)–C(6)–N(1)	122.37(16)
	C(1)–N(2)–C(2)	120.41(14)	O(1)–C(6)–C(7)	123.48(16)
	C(1)–N(2)–C(4)	123.66(15)	N(1)–C(6)–C(7)	114.15(15)
	C(2)–N(2)–C(4)	115.15(14)	C(14)–C(7)–C(6)	109.51(14)
	N(2)–C(1)–N(1)	117.35(15)	C(14)–C(7)–C(8)	112.68(14)
	N(2)–C(1)–S(1)	124.63(13)	C(6)–C(7)–C(8)	112.06(14)
	N(1)–C(1)–S(1)	118.02(13)		
$Ni(L^1)_2$	Ni(1)–O(1)	1.852(4)	N(2)–C(27)	1.320(7)
	Ni(1)–O(2)	1.862(4)	N(2)–C(21)	1.342(7)
	Ni(1)–S(1)	2.1327(16)	N(3)–C(1)	1.332(7)
	Ni(1)–S(2)	2.1509(16)	N(3)–C(5)	1.458(7)
	S(1)–C(1)	1.742(6)	N(3)–C(3)	1.486(7)
	S(2)–C(21)	1.738(5)	N(4)–C(21)	1.345(7)
	O(1)–C(7)	1.261(6)	N(4)–C(25)	1.473(7)
	O(2)–C(27)	1.265(6)	N(4)–C(23)	1.480(7)
	N(1)–C(7)	1.320(7)	C(7)–C(8)	1.543(8)
	N(1)–C(1)	1.351(7)	C(27)–C(28)	1.536(7)
	O(1)–Ni(1)–O(2)	83.75(16)	C(27)–O(2)–Ni(1)	133.4(4)
	O(1)–Ni(1)–S(1)	95.41(12)	C(7)–N(1)–C(1)	123.5(4)
	O(2)–Ni(1)–S(1)	177.16(14)	C(1)–N(3)–C(5)	122.9(5)
	O(1)–Ni(1)–S(2)	175.14(15)	C(1)–N(3)–C(3)	119.3(5)
	O(2)–Ni(1)–S(2)	94.72(12)	C(5)–N(3)–C(3)	117.6(4)
	S(1)–Ni(1)–S(2)	86.34(6)	N(3)–C(1)–N(1)	116.1(5)
	C(1)–S(1)–Ni(1)	108.5(2)	N(3)–C(1)–S(1)	116.6(4)
	C(21)–S(2)–Ni(1)	107.72(19)	O(1)–C(7)–N(1)	130.2(5)
	C(7)–O(1)–Ni(1)	133.0(4)	O(1)–C(7)–C(8)	112.7(5)

C6–O1 = 1.207(2) Å, C1–S1 = 1.6877(17) Å. The bond lengths of all C–N bonds C6–N1 = 1.391(2) Å, C1–N1 = 1.411(2) Å, C1–N2 = 1.323(2) Å, C2–N2 = 1.478(2) Å, and C4–N2 = 1.483(2) Å are shorter than the normal C–N single bond length and longer than the normal C=N double bond length (1.25 Å). These results are in agreement with expected delocalization in the 2,2-diphenyl-*N*-(diethyl-carbamothioyl) acetamide and confirmed by C1–N1–C6 = 121.74(15)°, C1–N2–C4 = 123.66(15)° showing sp^2 hybridization on N1 and N2. The conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is twisted, as reflected by the torsion angles O1–C6–N1–C1, C6–N1–C1–N2, and S1–C1–N1–C6 of −8.13°, 62.95° and −117.74°, respectively. The crystal packing shows intermolecular contacts N1–H1 ··· S1^i, with N–H 0.89 Å, H–S 2.54 Å, N–H–S 171° and C7–H7A ··· S1^i, with C–H 0.98 Å, H–S 2.83 Å, C–H–S 156° [symmetry code: (i) $-x$, $1-y$, $-z$] forming centrosymmetric dimers that are stacked along [001] (figure 4). Possible intramolecular interactions are C2–H2B ··· S1 with C–H 0.97 Å, H–S 2.63 Å, C–H–S 105°; C4–H4B ··· N1 with C–H 0.97 Å, H–N 2.36 Å, C–H–N 108°; C5–H5B ··· O1 with C–H 0.96 Å, H–O 2.39 Å, C–H–O 130°; C13–H13A ··· O1 with C–H 0.93 Å, H–O 2.43 Å, C–H–O 125°.

Bis(2,2-diphenyl-*N*-(diethylcarbamothioyl)acetamido)nickel(II) presents a planar square environment about nickel with the ligands coordinating in a relatively undistorted manner (O(2)–Ni(1)–S(1) = 177.16(14)°, O(1)–Ni(1)–S(2) = 175.14(15)°, O(1)–Ni(1)–S(1) = 95.41(12)° and O(2)–Ni(1)–S(2) = 94.72(12)°). The distance of

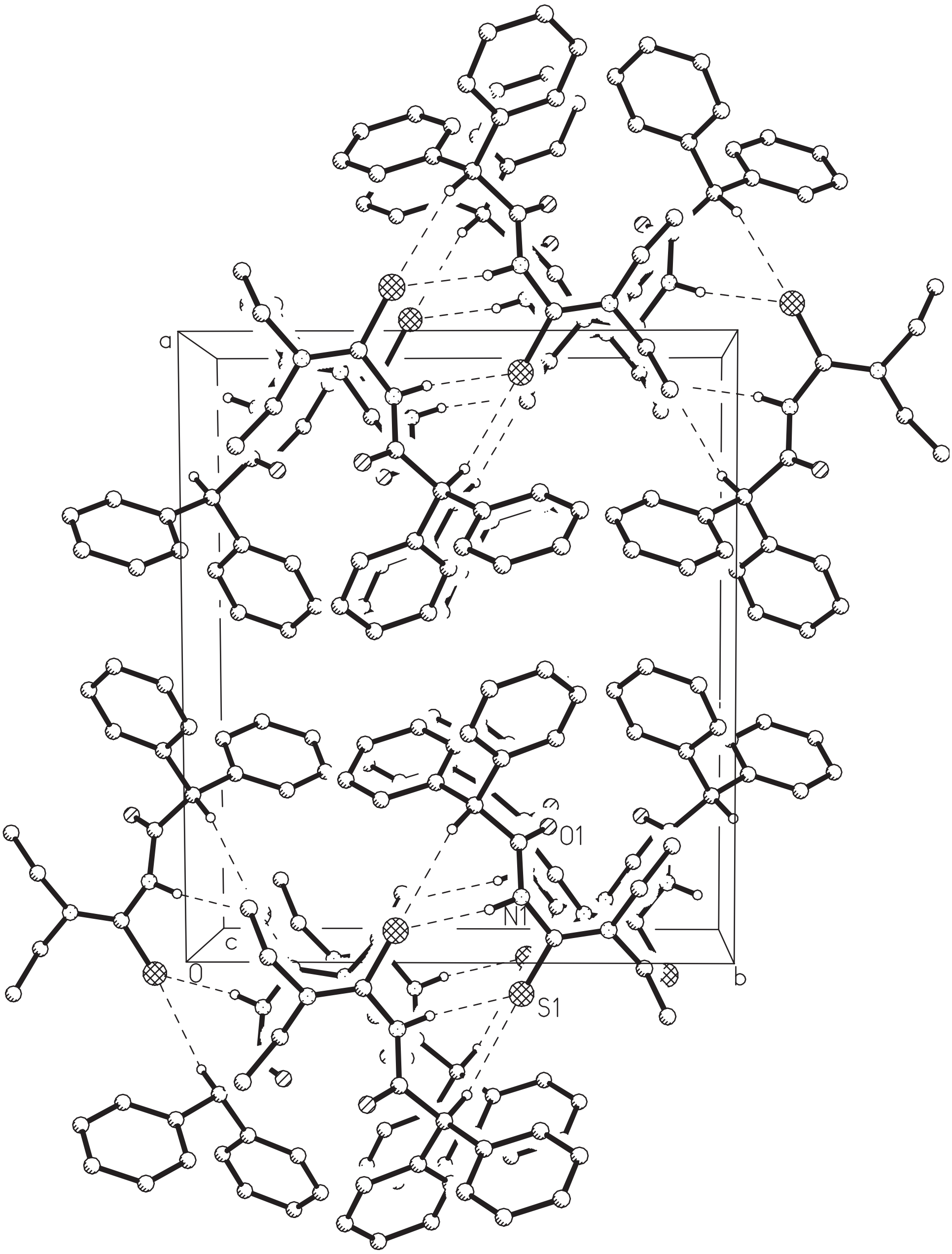

Figure 4. Packing diagram for HL^1 viewed along [001] with hydrogen bonds as dotted lines; H-atoms not involved omitted.

nickel from the best plane through the coordination sphere is 0.016 Å. The chelate ring systems, Ni–O–C–N–C–S, are nearly planar as well with the largest deviations from the best plane being 0.136 Å for C21 atom. The dihedral angle between these chelate planes of 6.1° indicates weak distortion from square planar towards tetrahedral geometry. With respect to the chelating ligands the molecule shows *cis*-arrangement. The bond lengths of the carbonyl O(1)–C(7) 1.261(6) Å; O(2)–C(27) 1.265(6) Å and thiocarbonyl S(1)–C(1) 1.742(6) Å; S(2)–C(21) 1.738(5) Å groups lie between those for double and single bonds, a feature which is known from related structures [8, 9, 11, 26]. The bond distance C–N between the diethylamino substituent and the chelate ring is shorter than a normal single C–N bond, C1–N1 being 1.351(7) Å and N(3)–C(1) 1.332(7) Å. This shortening of the C–N bond lengths is in agreement with the bond distances of thiourea complexes determined earlier [8, 9, 11], due to the strong delocalization in the chelate ring. All the other bond lengths fall within the expected range. According to all

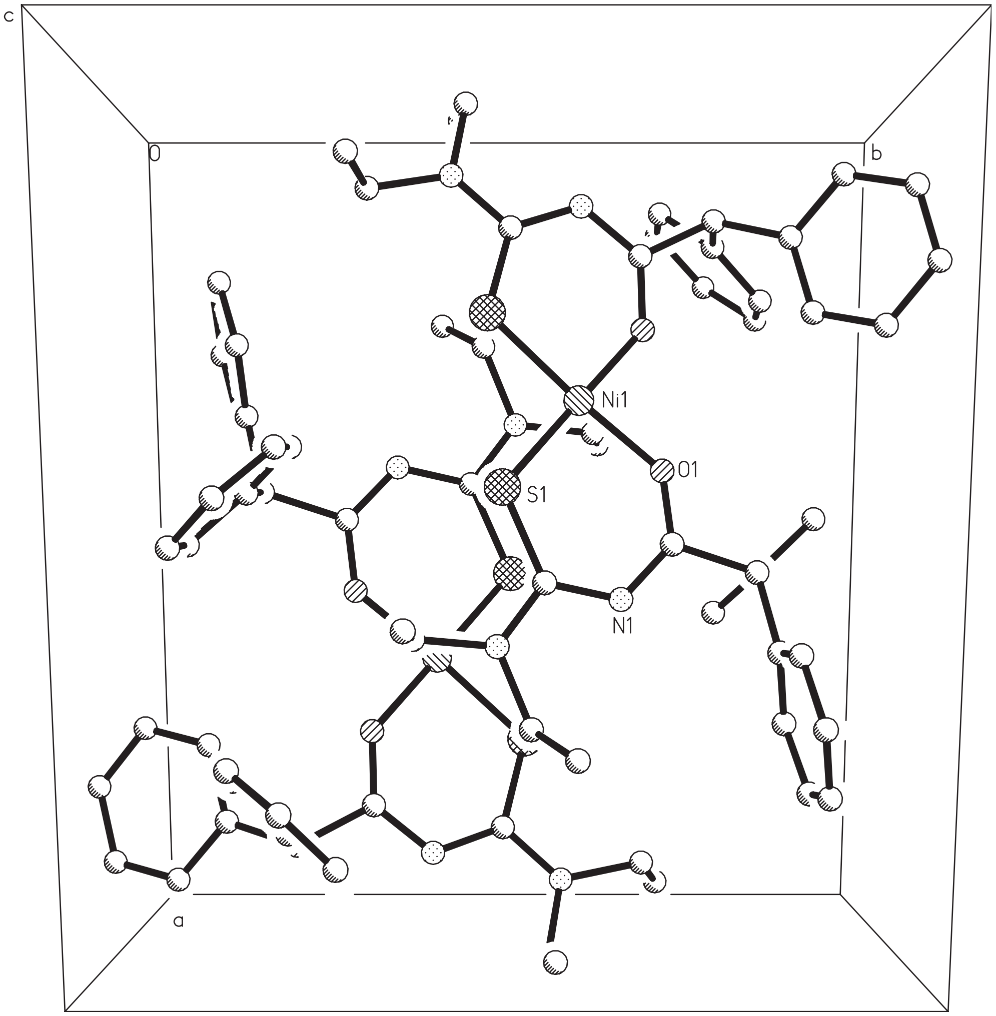

Figure 5. Packing diagram for Ni(L^1)$_2$ viewed along [001]; H-atoms omitted.

of the results, our studies show that *bis*(2,2-diphenyl-*N*-(diethylcarbamothioyl) acetamido)nickel(II) preferentially forms neutral *cis*-[$Ni(L^1)_2$] type complex as presented in figure 3. The crystal packing is shown in figure 5, there are no intermolecular D–H $\cdots$ A contacts.

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-661584 for HL^1 and CCDC-661585 for $Ni(L^1)_2$ and can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; Email: deposit@ccdc.cam.ac.uk].

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