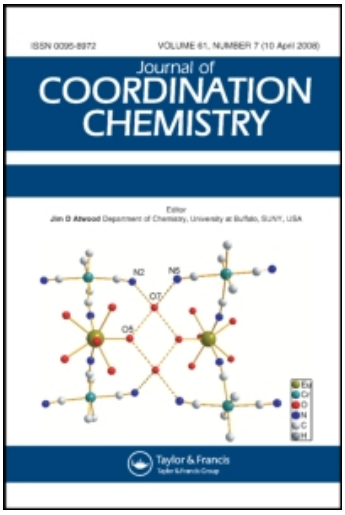


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# Synthesis and characterization of N -(alky(aryl)carbamothioyl)cyclohexanecarboxamide derivatives and their Ni(II) and Cu(II) complexes

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# Synthesis and characterization of *N*-(alky(aryl)carbamothioyl)-cyclohexanecarboxamide derivatives and their Ni(II) and Cu(II) complexes

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*N*-(*R*-carbamothioyl)cyclohexanecarboxamides (*R*: diethyl, di-*n*-propyl, di-*n*-butyl, diphenyl and morpholine-4) and their Ni(II) and Cu(II) complexes have been synthesized and characterized by elemental analyses, FT-IR and NMR methods. *N*-(diethylcarbamothioyl) cyclohexanecarboxamide, $HL^1$, $C_{12}H_{22}N_2OS$, crystallizes in the orthorhombic space group $P2_12_12_1$, with $Z=4$, and unit cell parameters, $a=6.6925(13)$ Å, $b=9.0457(18)$ Å, $c=22.728(5)$ Å. The conformation of the $HL^1$ molecule with respect to the thiocarbonyl and carbonyl moieties is twisted, as reflected by the torsion angles O1–C6–N2–C5, C6–N2–C5–N1 and S1–C5–N2–C6 of 1.68°, −67.47° and 115.50°, respectively. The structure of $HL^1$ also shows a delocalization of the $\pi$ electrons of the thiocarbonyl group over the C–N bonds. The ring puckering analysis shows that the cyclohexane ring has a chair conformation. The *bis*(*N*-(morpholine-4-carbonothioyl)cyclohexane carboxamido)nickel(II) complex, $Ni(L^5)_2$, $C_{24}H_{38}N_4NiO_4S_2$, crystallizes in the monoclinic space group $P2_1/c$, with $Z=4$, and unit cell parameters, $a=16.919(3)$ Å, $b=8.3659(17)$ Å, $c=19.654(4)$ Å, $\beta=107.43(3)°$. $Ni(L^5)_2$ is a *cis*-complex with a slightly distorted square-planar coordination of the central nickel by two oxygen and two sulfur atoms.

*Keywords*: Synthesis; Thiourea; Cyclohexanecarboxamide; Complex; Single crystal structure

## 1. Introduction

Thioureas are used as metal complexing agents with interesting applications such as liquid-liquid extraction, pre-concentration and highly efficient chromatographic separation, fluorimetric detection of platinum group metals, and the selective on-line pre-concentration of ultra-traces of transition metals, followed by its determination using graphite furnace atomic absorption spectrometry [1, 2]. Thiourea derivatives are potentially very versatile ligands, able to coordinate a range of metal centers as neutral ligands, monoanions or dianions [3–12]. In addition, the oxygen, nitrogen and sulfur

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donors provide a multitude of bonding possibilities. A number of thiourea derivatives and their metal complexes are also associated with various kinds of biological activities, insecticidal, herbicidal, antibacterial, antifungal, antitubercular, antithroid, antihelmintic, rodenticidal and plant-growth regulator properties [13–16].

Recently, we have pursued investigations on the synthesis, characterization, crystal structure, thermal behavior and antimicrobial activity of new thiourea derivatives [8–12, 17–29]. 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 full characterization of five new ligands and their nickel and copper metal complexes. The crystal structures of *N*-(diethylcarbamothioyl)cyclohexanecarboxamide and the *bis*(*N*-(morpholine-4-carbonothioyl)cyclohexanecarboxamido)nickel(II) complex are also described.



## 2. Experimental

### 2.1. *Instrumentation*

Room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra of all of the synthesized compounds were recorded using a Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism ($4000-525\,cm^{-1}$; number of scans: 250; resolution: $1\,cm^{-1}$). All $^1H$ NMR spectra were recorded on a Bruker DPX-400 spectrometer using $CDCl_3$ as the solvent and TMS as an 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 Rigaku Mercury AFC8S system with a Mercury CCD detector using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073\,\text{Å}$). The structure was solved by direct methods and refined by using full-matrix least-squares techniques (on $F^2$) [30]. Data were corrected for Lorentz and polarization effects and for absorption. The latter correction was made using REQABA, a multi-scan technique [31]. All non-hydrogen atoms were refined anisotropically. 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 quality. Some of the solvents were distilled before use. Ethanol was distilled by fractional distillation (78.3°C) using a small quantity of benzene. Acetone was dried by shaking with anhydrous calcium sulfate (Drierite) for several hours, followed by careful fractional distillation. The ligands were prepared by a procedure similar to that reported in the literature [8, 32]. A solution of cyclohexanecarbonyl chloride (0.005 mol) in acetone ($30\,cm^3$) was added dropwise to a suspension of potassium thiocyanate (0.005 mol) in acetone ($30\,cm^3$). The reaction mixture was heated (50°C) under reflux for 30 min and then cooled to room temperature. A solution of secondary

Table 1. Summary of crystallographic data and parameters of $HL^1$ and $Ni(L^5)_2$.

| Compound | $HL^1$ | $Ni(L^5)_2$ |
|---|---|---|
| Empirical formula | $C_{12}H_{22}N_2OS$ | $C_{24}H_{38}N_4O_4S_2Ni$ |
| Formula weight | 242.38 | 569.41 |
| Temperature (K) | 153(2) | 153(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | $P2_12_12_1$ | $P2_1/c$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 6.6925(13) | 16.919(3) |
| $b$ | 9.0457(18) | 8.3659(17) |
| $c$ | 22.728(5) | 19.654(4) |
| $\beta$ | 90 | 107.43(3) |
| $V$ (Å$^3$) | 1375.9(5) | 2654.2(9) |
| $Z$ | 4 | 4 |
| $D_c$ (Mg m$^3$) | 1.170 | 1.425 |
| Absorption coefficient (mm$^{-1}$) | 0.220 | 0.926 |
| $F(000)$ | 528 | 1208 |
| Crystal size (mm$^3$) | $0.48 \times 0.36 \times 0.29$ | $0.67 \times 0.38 \times 0.12$ |
| $\theta$ range for data collection (°) | 3.51–25.16 | 3.26–25.05 |
| Index ranges | $-7 \le h \le 8$, $-10 \le k \le 10$, $-27 \le l \le 23$ | $-15 \le h \le 20$, $-9 \le k \le 9$, $-23 \le l \le 22$ |
| Reflections collected | 7862 | 17990 |
| Independent reflections ($R_{int}$) | 2421 (0.0383) | 4662 (0.0369) |
| Absorption correction | Multi-scan (REQAB) | Multi-scan (REQAB) |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/parameters | 2421/147 | 4662/353 |
| Goodness-of-fit on $F^2$ | 1.073 | 1.085 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0385$, $wR_2 = 0.0934$ | $R_1 = 0.0399$, $wR_2 = 0.0929$ |
| $R$ indices (all data) | $R_1 = 0.0430$, $wR_2 = 0.0979$ | $R_1 = 0.0509$, $wR_2 = 0.1013$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.233 and −0.215 | 0.597 and −0.341 |



amine (0.005 mol) in acetone (30 m$^3$) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 100 cm$^3$) was added and the solution filtered. The solid product was washed with water and purified by recrystallization from ethanol:dichloromethane mixture (1 : 2).

**2.2.1. *N*-(diethylcarbamothioyl)cyclohexanecarboxamide [$HL^1$].** White. Yield: 76%. M.p.: 97–99°C. Anal. Calcd for $C_{12}H_{22}N_2OS$: C, 59.5; H, 9.1; N, 11.6. Found: C, 59.2; H, 9.1; N, 11.7%. FT-IR (cm$^{-1}$): $\nu$(NH) 3240(w), $\nu$(CH) 2976, 2926, 2853(s), $\nu$(C=O) 1661(s), $\nu$(C=S) 1312(s). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.00 (s, 1H, NH), 3.93 (t, 2H, $NCH_2$), 3.43 (t, 2H, $NCH_2$), 2.24 (tt, 1H, CH, ch), 1.89 (d, 1H, CH, ch), 1.84 (d, 1H, CH, ch), 1.78 (m, 1H, CH, ch), 1.74 (m, 1H, CH, ch), 1.67 (m, 1H, CH, ch), 1.64 (m, 1H, CH, ch), 1.41 (m, 4H, CH, ch), 1.32 (t, 3H, $CH_3$), 1.23 (t, 3H, $CH_3$).

**2.2.2. *N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamide [$HL^2$].** White. Yield: 85%. M.p.: 121–122°C. Anal. Calcd for $C_{14}H_{26}N_2OS$: C, 62.2; H, 9.7; N, 10.4. Found: C, 62.7; H, 9.6; N, 10.4%. FT-IR (cm$^{-1}$): $\nu$(NH) 3231(w), $\nu$(CH) 2959, 2924, 2856(w), $\nu$(C=O) 1655(s), $\nu$(C=S) 1313(s). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.89 (s, 1H, NH), 3.85 (t, 2H, $NCH_2$), 3.38 (t, 2H, $NCH_2$), 2.22 (tt, 1H, CH, ch), 1.89 (d, 1H, CH, ch), 1.79 (d, 1H, CH, ch), 1.78 (m, 1H, CH, ch), 1.75 (m, 1H, CH, ch),

1.66 (m, 1H, CH, ch), 1.62 (m, 1H, CH, ch), 1.42 (m, 4H, CH, ch), 1.32–1.12 (m, 4H, $NCH_2CH_2$), 0.94 (t, 3H, $CH_3$), 0.84 (t, 3H, $CH_3$).

**2.2.3. *N*-(di-*n*-butylcarbamothioyl)cyclohexanecarboxamide [$HL^3$].** White. Yield: 89%. M.p.: 88–90°C. Anal. Calcd for $C_{16}H_{30}N_2OS$: C, 64.4; H, 10.1; N, 9.4. Found: C, 65.4; H, 10.2; N, 9.2%. FT-IR ($cm^{-1}$): $\nu$(NH) 3175(w), $\nu$(CH) 2961, 2930, 2872, 2859(s), $\nu$(C=O) 1655(vs), $\nu$(C=S) 1314(s). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.74 (s, 1H, NH), 3.93 (t, 2H, $NCH_2$), 3.44 (t, 2H, $NCH_2$), 2.23 (tt, 1H, CH, ch), 1.94 (d, 1H, CH, ch), 1.89 (d, 1H, CH, ch), 1.83 (m, 1H, CH, ch), 1.80 (m, 1H, CH, ch), 1.72 (m, 1H, CH, ch), 1.62 (m, 1H, CH, ch), 1.52–1.37 (m, 4H, $NCH_2CH_2$), 1.44 (m, 4H, CH, ch), 1.35–1.17 (m, 4H, $NCH_2CH_2CH_2$), 0.96 (t, 3H, $CH_3$), 0.93 (t, 3H, $CH_3$).

**2.2.4. *N*-(diphenylcarbamothioyl)cyclohexanecarboxamide [$HL^4$].** Yellow. Yield: 87%. M.p.: 152–154°C. Anal. Calcd for $C_{20}H_{22}N_2OS$: C, 71.0; H, 6.6; N, 8.3. Found: C, 71.1; H, 6.5; N, 8.2%. FT-IR ($cm^{-1}$): $\nu$(NH) 3242(w), $\nu$(Ar–CH) 3070, 3049(vw), $\nu$(CH) 2988, 2938, 2926, 2855(w), $\nu$(C=O) 1717(s), $\nu$(C=C) 1589(w), $\nu$(C=S) 1288(s). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.14 (s, 1H, NH), 7.40–7.25 (m, 10H, Ar–H ), 2.16 (tt, 1H, CH, ch), 1.68 (d, 2H, CH, ch), 1.65 (d, 2H, CH, ch), 1.61 (s, 2H, CH, ch), 1.14 (m, 4H, CH, ch).

**2.2.5. *N*-(morpholine-4-carbonothioyl)cyclohexanecarboxamide [$HL^5$].** White. Yield: 92%. M.p.: 164–166°C. Anal. Calcd for $C_{12}H_{20}N_2O_2S$: C, 56.2; H, 7.9; N, 10.9%. Found: C, 55.6; H, 8.0; N, 11.1%. FT-IR ($cm^{-1}$): $\nu$(NH) 3269(w), $\nu$(CH) 2972, 2955, 2926, 2851(s), $\nu$(C=O) 1676(vs), $\nu$(C=S) 1294(vs). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.43 (s, 1H, NH), 4.16 (m, 2H, $CH_2O$), 3.80 (m, 4H, $CH_2O$, $NCH_2$), 3.54 (m, 2H, $NCH_2$), 2.28 (tt, 1H, CH, ch), 1.91 (d, 1H, CH, ch), 1.87 (d, 1H, CH, ch), 1.81 (m, 1H, CH, ch), 1.78 (m, 1H, CH, ch), 1.70 (m, 1H, CH, ch), 1.68 (m, 1H, CH, ch), 1.44 (m, 4H, CH, ch).



### 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 [8, 32]. A solution of metallic acetate (0.01 mol) in ethanol (30 $cm^3$) was added dropwise to a solution of the ligand in a 1 : 2 ratio for all metal with a small excess of ligand in ethanol (30 $cm^3$) at room temperature, and the resulting mixture was stirred for 30 min. The solid complexes were filtered and recrystallized from an ethanol : dichloromethane mixture (1 : 2).

**2.3.1. *Bis*(*N*-(diethylcarbamothioyl)cyclohexanecarboxamido)nickel(II) [$Ni(L^1)_2$].** Purple. Yield: 83%. M.p.: 84–86°C. Anal. Calcd for $C_{24}H_{42}N_4O_2S_2Ni$: C, 53.2; H, 7.8; N, 10.3%. Found: C, 53.2; H, 7.8; N, 10.1%. FT-IR ($cm^{-1}$): $\nu$(CH) 2974, 2926, 2854(s), $\nu$(CN) 1522(w), $\nu$(CO) 1487(s). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 3.62 (m, 8H, $NCH_2$), 2.16 (m, 2H, CH, ch), 1.83 (s, 2H, CH, ch), 1.79 (s, 2H, CH, ch), 1.68 (s, 2H, CH, ch), 1.65 (s, 2H, CH, ch), 1.55 (m, 2H, CH, ch), 1.52 (m, 2H, CH, ch), 1.29 (m, 8H, CH, ch), 1.18 (t, 6H, $CH_3$), 1.09 (t, 6H, $CH_3$).

**2.3.2. *Bis*(*N*-(diethylcarbamothioyl)cyclohexanecarboxamido)copper(II) [Cu($L^1$)$_2$].** Green. Yield: 81%. M.p.: 71–73°C. Anal. Calcd for $C_{24}H_{42}N_4O_2S_2Cu$: C, 52.8; H, 7.7; N, 10.3%. Found: C, 51.7; H, 7.8; N, 10.2%. FT-IR ($cm^{-1}$): $\nu$(CH) 2972, 2924, 2854(s), $\nu$(CN) 1522(w), $\nu$(CO) 1489(vs).

**2.3.3. *Bis*(*N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamido)nickel(II) [Ni($L^2$)$_2$].** Purple. Yield: 85%. M.p.: 111–113°C Anal. Calcd for $C_{28}H_{50}N_4O_2S_2Ni$: C, 56.3; H, 8.4; N, 9.4%. Found: C, 56.9; H, 8.3; N, 9.3%. FT-IR ($cm^{-1}$): $\nu$(CH) 2972, 2926, 2860(vs), $\nu$(CN) 1516(s), $\nu$(CO) 1481(vs). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 3.56 (m, 8H, $NCH_2$), 2.20 (m, 2H, CH, ch), 1.87 (s, 2H, CH, ch), 1.83 (s, 2H, CH, ch), 1.70 (m, 4H, CH, ch), 1.59 (m, 4H, CH, ch), 1.33 (m, 8H, CH, ch), 1.24–1.21 (m, 8H, $NCH_2CH_2$), 0.90 (m, 12H, $CH_3$).

**2.3.4. *Bis*(*N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamido)copper(II) [Cu($L^2$)$_2$].** Green. Yield: 86%. M.p.: 78–80°C. Anal. Calcd for $C_{28}H_{50}N_4O_2S_2Cu$: C, 55.8; H, 8.4; N, 9.3%. Found: C, 56.8; H, 8.5; N, 9.2%. FT-IR ($cm^{-1}$): $\nu$(CH) 2963, 2932, 2852(s), $\nu$(CN) 1514(s), $\nu$(CO) 1481(vs).



**2.3.5. *Bis*(*N*-(di-*n*-butylcarbamothioyl)cyclohexanecarboxamido)nickel(II) [Ni($L^3$)$_2$].** Purple. Yield: 87%. M.p.: 89–91°C. Anal. Calcd for $C_{32}H_{58}N_4O_2S_2Ni$: C, 58.8; H, 8.9; N, 8.6%. Found: C, 57.9; H, 9.0; N, 8.6%. FT-IR ($cm^{-1}$): $\nu$(CH) 2963, 2924, 2876, 2853(s), $\nu$(CN) 1516(s), $\nu$(CO) 1485(s). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 3.58 (m, 8H, $NCH_2$), 2.20 (tt, 2H, CH, ch), 1.87 (s, 2H, CH, ch), 1.83 (s, 2H, CH, ch), 1.73 (m, 2H, CH, ch), 1.69 (m, 2H, CH, ch), 1.63 (m, 2H, CH, ch), 1.58 (m, 2H, CH, ch), 1.51 (m, 8H, $NCH_2CH_2$), 1.32 (m, 8H, CH, ch), 1.24 (m, 8H, $NCH_2CH_2CH_2$), 0.93 (m, 12H, $CH_3$).

**2.3.6. *Bis*(*N*-(di-*n*-butylcarbamothioyl)cyclohexanecarboxamido)copper(II) [Cu($L^3$)$_2$].** Green. Yield: 88%. M.p.: 80–82°C. Anal. Calcd for $C_{32}H_{58}N_4O_2S_2Cu$: C, 58.4; H, 8.9; N, 8.5%. Found: C, 58.1; H, 8.9; N, 8.3%. FT-IR ($cm^{-1}$): $\nu$(CH) 2955, 2930, 2872, 2851(s), $\nu$(CN) 1516(w), $\nu$(CO) 1487(vs).

**2.3.7. *Bis*(*N*-(diphenylcarbamothioyl)cyclohexanecarboxamido)nickel(II) [Ni($L^4$)$_2$].** Purple. Yield: 82%. M.p.: 252–254°C. Anal. Calcd for $C_{40}H_{42}N_4O_2S_2Ni$: C, 65.5; H, 5.8; N, 7.6%. Found: C, 65.2; H, 5.8; N, 7.7%. FT-IR ($cm^{-1}$): $\nu$(Ar–CH) 3064, 3045(vw), $\nu$(CH) 2990, 2930, 2916, 2847(s), $\nu$(C=C) 1587(w), $\nu$(CN) 1508(s), $\nu$(CO) 1489(s). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.30–7.22 (m, 20H, Ar–H), 2.09 (s, 2H, CH, ch), 1.63 (s, 4H, CH, ch), 1.59 (s, 4H, CH, ch), 1.53 (s, 4H, CH, ch), 1.15 (d, 8H, CH, ch).

**2.3.8. *Bis*(*N*-(diphenylcarbamothioyl)cyclohexanecarboxamido)copper(II) [Cu($L^4$)$_2$].** Green. Yield: 79%. M.p.: 196–198°C. Anal. Calcd for $C_{40}H_{42}N_4O_2S_2Cu$: C, 65.1; H, 5.7; N, 7.6%. Found: C, 65.3; H, 5.8; N, 7.5%. FT-IR ($cm^{-1}$): $\nu$(Ar–CH) 3066, 3047(vw), $\nu$(CH) 2957, 2939, 2920, 2855(w), $\nu$(C=C) 1595(w), $\nu$(CN) 1504(s), $\nu$(CO) 1489(vs).

**2.3.9. *Bis*(*N*-(morpholine-4-carbonothioyl)cyclohexanecarboxamido)nickel(II) [Ni($L^5$)$_2$].** Purple. Yield: 78%. M.p.: 195–197°C. Anal. Calcd for $C_{24}H_{38}N_4O_4S_2Ni$: C, 50.6; H, 6.7; N, 9.8%. Found: C, 50.9; H, 6.8; N, 9.9%. FT-IR ($cm^{-1}$): $\nu$(CH) 2989, 2968, 2927, 2853(s), $\nu$(CN) 1514(s), $\nu$(CO) 1471(vs). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 3.97 (s, 4H, $CH_2O$), 3.92 (s, 4H, $CH_2O$), 3.66 (s, 4H, $NCH_2$), 3.64 (s, 4H, $NCH_2$), 2.17 (m, 2H, CH, ch), 1.81 (s, 2H, CH, ch), 1.77 (s, 2H, CH, ch), 1.66 (s, 4H, CH, ch), 1.57 (s, 4H, CH, ch), 1.25 (m, 8H, CH, ch).

**2.3.10. *Bis*(*N*-(morpholine-4-carbonothioyl)cyclohexanecarboxamido)copper(II) [Cu($L^5$)$_2$].** Green. Yield: 83%. M.p.: 147–149°C. $C_{24}H_{38}N_4O_4S_2Cu$: C, 50.2; H, 6.7; N, 9.8%. Found: C, 49.7; H, 6.7; N, 9.9%. FT-IR ($cm^{-1}$): $\nu$(CH) 2987, 2966, 2926, 2848(s), $\nu$(CN) 1510(vs), $\nu$(CO) 1471(vs).

## 3. Results and discussion



Cyclohexanecarbonyl isothiocyanate was synthesized through reaction of cyclohexanecarbonyl chloride and potassium thiocyanate in acetone [33]. The final compounds ($HL^1$, $HL^2$, $HL^3$, $HL^4$, and $HL^5$) were obtained by reaction of the appropriate secondary amine (diethylamine, di-*n*-propylamine, di-*n*-butylamine, diphenylamine and morpholine) with cyclohexanecarbonyl isothiocyanate. The ligands were purified by re-crystallization from an ethanol : dichloromethane mixture (1 : 2) and obtained in yields ranging from 76–92%. The reaction of the ligands with metal salts at room temperature with ethanol as solvent yielded the new complexes. The proposed structures given in figure 1 are consistent with the analytical and spectroscopic data.

The main vibrational bands of the investigated compounds are given in the experimental section. Absorptions at 3240, 3231, 3175, 3242 and 3269 $cm^{-1}$ for $HL^1$, $HL^2$, $HL^3$, $HL^4$ and $HL^5$ are attributed to stretching of an N–H adjacent to carbonyl. The FT-IR spectra of the complexes show significant changes when compared with the FT-IR spectra of the corresponding ligands. The most striking changes are the N–H stretching frequency at ~3200 $cm^{-1}$ in the free ligands, disappear completely, in agreement with both ligand and complex structure and the complexation reaction. Another striking change is observed for the carbonyl stretching vibrations. A strong absorption (1661, 1655, 1655, 1717 and 1676 $cm^{-1}$ for $HL^1$, $HL^2$, $HL^3$, $HL^4$ and $HL^5$, respectively) in FT-IR spectra of the ligands is ascribed to the stretching of the carbonyl groups, which shifts to higher frequencies upon complexation of the thiourea ligands because the deprotonation induces delocalization of the carbonyl stretching vibration [8–12]. The same trend is observed for thiocarbonyl stretching vibration frequencies, which are observed at approximately 1300 $cm^{-1}$ in the free ligands, and shift to higher frequency after complexation; unfortunately, this vibration could not be assigned unambiguously. This is also in agreement with the crystal structure determined for the Ni($L^5$)$_2$ complex and suggests that the oxygen atom of the carbonyl group and the sulfur atom of thiocarbonyl group are involved in coordination.

The $^1$H NMR data of the compounds obtained in $CDCl_3$ solution are given in the experimental section and are consistent with the structural results. All proton signals of the ligands shift to lower fields upon binding to metal ions as expected. $HL^1$, $HL^2$, $HL^3$,

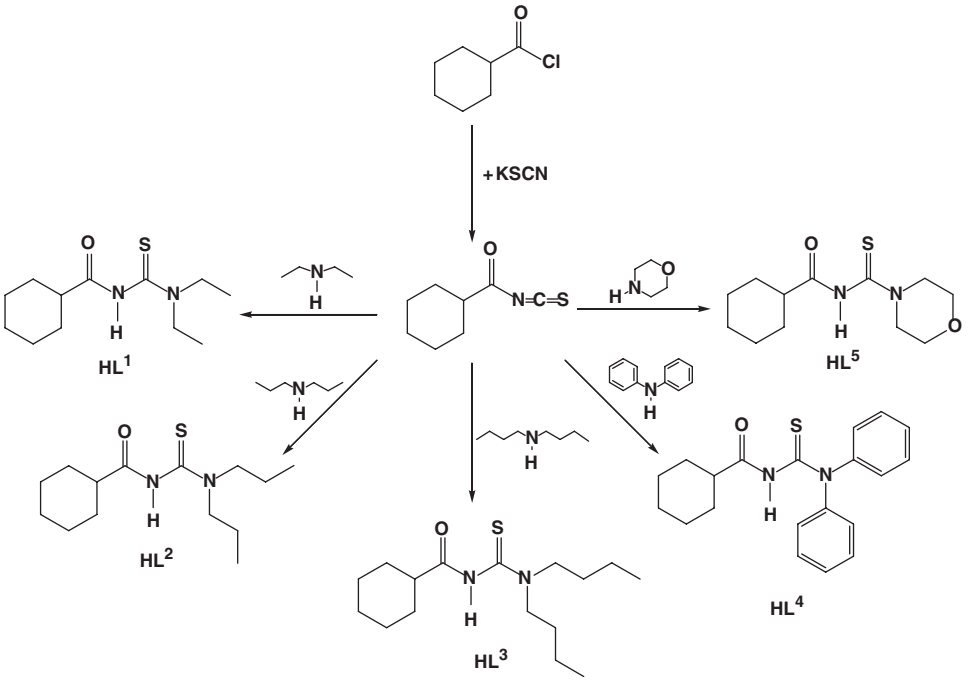


Figure 1. Synthesis of the ligands.



$HL^4$ and $HL^5$ show a peak at 8.00, 7.89, 7.74, 8.14 and 8.43 ppm, respectively, corresponding to the proton of the N–H group. This peak does not appear in the nickel complexes that contain the deprotonated ligand, indicating an imine in these compounds [8, 12], in agreement with the FT-IR spectra and X-ray single crystal diffraction data. The α-methylene protons of $HL^1$, $HL^2$ and $HL^3$ show two signals at ca 3.9 and 3.4 ppm. Irradiation at 3.9 and 3.4 ppm shows clearly that the two alkyls are non-equivalent, probably due to restricted rotation about the thiocarbonyl-nitrogen bond. The $^1$H NMR spectra of $HL^4$ shows multiplets at 7.4–7.2 ppm for phenyl protons. The $^1$H NMR spectra of nickel complex show the aromatic protons with slight variations in their position. The aryl proton signals are shifted to lower field (0.05–0.10 ppm) relative to those in free $HL^4$.

The magnetic susceptibility values of the complexes show that the $d^8$ configuration of Ni(II) complexes is diamagnetic, while the Cu(II) complexes are paramagnetic. The measured values for $Cu(L^1)_2$, $Cu(L^2)_2$, $Cu(L^3)_2$, $Cu(L^4)_2$ and $Cu(L^5)_2$ are 1.74, 1.75, 1.75, 1.79 and 1.76 B.M., respectively. The magnetic susceptibilities also show that the Ni(II) and Cu(II) complexes are distorted square planar. All these data agree with Arslan *et al*. [9–11] and Duta and Syamal [34].

The crystal structure (figure 2) and unit cell diagram (Supplementary Material) of *N*-(diethylcarbamothioyl)cyclohexanecarboxamide are shown [35], and selected bond lengths and angles are listed in table 2. As presented in figure 2, the conformation of $HL^1$ with respect to the thiocarbonyl and carbonyl moieties is twisted, as reflected by the torsion angles O1–C6–N2–C5, C6–N2–C5–N1 and S1–C5–N2–C6 of 1.68°, −67.47° and 115.50°, respectively. By comparison, the corresponding torsion angles for

3-[4-(3, 3-diethylthioureidocarbonoyl)-benzoyl]-1,1-diethylthiourea [29] are 5.63°, −71.19° and 108.27°, respectively, as obtained from the crystal structure of this compound. It is clear that the geometry of the central carbonyl and thiourea moiety is in agreement with most thiourea derivatives [18, 21, 22]. In the structure of the *N*-(diethylcarbamothioyl)cyclohexanecarboxamide, the overall bond lengths and angles

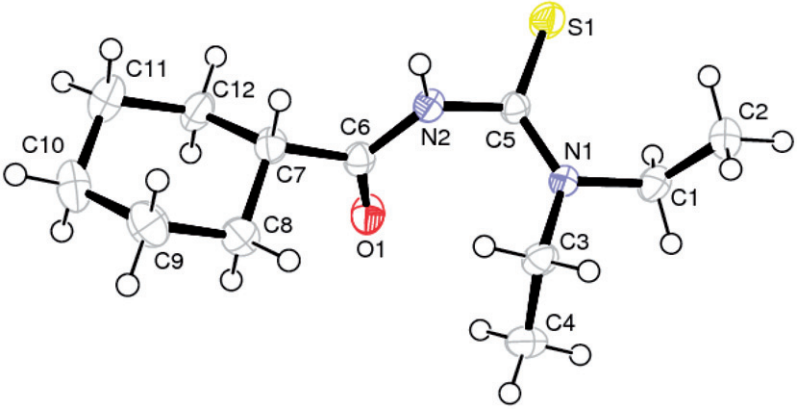


Figure 2. Molecular structure of $HL^1$. Thermal ellipsoids are shown at the 50% probability level.

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

| | | | |
|---|---|---|---|
| **$HL^1$** | | | |
| S(1)–C(5) | 1.664(2) | N(1)–C(5) | 1.337(3) |
| O(1)–C(6) | 1.228(3) | N(1)–C(1) | 1.480(3) |
| N(2)–C(6) | 1.363(3) | N(1)–C(3) | 1.479(3) |
| N(2)–C(5) | 1.428(3) | C(6)–C(7) | 1.518(3) |
| C(6)–N(2)–C(5) | 125.27(17) | N(1)–C(5)–S(1) | 125.04(16) |
| C(5)–N(1)–C(1) | 119.29(18) | N(2)–C(5)–S(1) | 118.74(15) |
| C(5)–N(1)–C(3) | 125.13(18) | O(1)–C(6)–N(2) | 121.74(19) |
| C(1)–N(1)–C(3) | 114.97(18) | O(1)–C(6)–C(7) | 122.84(19) |
| N(1)–C(5)–N(2) | 116.16(18) | N(2)–C(6)–C(7) | 115.40(18) |
| **$Ni(L^5)_2$** | | | |
| Ni(1)–O(1) | 1.8579(19) | N(3)–C(19) | 1.329(3) |
| Ni(1)–O(3) | 1.869(2) | N(3)–C(20) | 1.334(4) |
| Ni(1)–S(1) | 2.1405(9) | N(2)–C(8) | 1.347(3) |
| Ni(1)–S(2) | 2.1468(9) | N(2)–C(9) | 1.466(3) |
| S(1)–C(8) | 1.730(3) | N(2)–C(12) | 1.467(3) |
| S(2)–C(20) | 1.732(3) | N(4)–C(20) | 1.341(4) |
| O(1)–C(7) | 1.265(3) | N(4)–C(24) | 1.487(6) |
| O(3)–C(19) | 1.262(3) | N(4)–C(21) | 1.557(7) |
| N(1)–C(7) | 1.335(3) | C(7)–C(1) | 1.526(3) |
| N(1)–C(8) | 1.343(3) | C(13)–C(19) | 1.511(4) |
| O(1)–Ni(1)–O(3) | 84.14(8) | C(7)–O(1)–Ni(1) | 133.44(18) |
| O(3)–Ni(1)–S(2) | 94.85(6) | C(19)–N(3)–C(20) | 124.4(2) |
| O(1)–Ni(1)–S(2) | 178.90(6) | C(20)–N(4)–C(24) | 124.9(3) |
| O(3)–Ni(1)–S(1) | 179.19(6) | C(20)–N(4)–C(21) | 119.7(3) |
| O(1)–Ni(1)–S(1) | 95.19(6) | C(24)–N(4)–C(21) | 105.8(4) |
| S(1)–Ni(1)–S(2) | 85.83(3) | N(4)–C(20)–N(3) | 115.3(3) |
| C(20)–S(2)–Ni(1) | 107.40(10) | N(4)–C(20)–S(2) | 116.6(2) |
| C(8)–S(1)–Ni(1) | 109.63(9) | O(3)–C(19)–N(3) | 128.9(3) |
| C(19)–O(3)–Ni(1) | 132.64(18) | O(3)–C(19)–C(13) | 116.3(2) |

in the thiourea are normal, with a thiocarbonyl bond distance of 1.664(2) Å and carbonyl bond distance of 1.228(3) Å, both typical of double bonds. However, the C–N bond lengths, C6–N2 = 1.363(3) Å, C5–N2 = 1.428(3) Å, C5–N1 = 1.337(3) Å, for the investigated compound are all shorter than the average single C–N bond length of 1.48 Å, thus showing varying degrees of double bond character in these C–N bonds [36]. These results are in agreement with the expected delocalization in the *N*-(diethylcarbamothioyl)cyclohexanecarboxamide and confirmed by C5–N2–C6 = 125.27(17)° and C5–N1–C3 = 125.13(18)° showing $sp^2$ hybridization on the N1 and N2 atoms. But, both C1–N1 = 1.480(3) Å and C3–N2 = 1.479(3) Å have typical C–N single bond lengths. These results are confirmed by FT-IR and $^1$H-NMR data. The cyclohexane ring exhibits a puckered conformation, with puckering parameters [37] $q_2 = 0.039(3)$ Å, $q_3 = 0.585(3)$ Å, $Q_T = 0.586(3)$ Å, $\theta = 2.9(3)°$ and $\varphi = 32(4)°$. The largest deviations from the mean plane are 0.260(3) Å for C8 and 0.257(3) Å for C7. This ring puckering analysis shows that the cyclohexane ring has a chair conformation with equatorial substitution at C7 for C6. In the crystal structure, the molecules are packed as dimers via intermolecular contact N2–H2···O1$^i$, with N–H 0.91 Å, H–O 1.96 Å, N–H–O 161° [symmetry code: (*i*) $1-x, -1/2+y, -1/2-z$]. Possible intramolecular interactions are C1–H1A···S1 with C–H 0.96 Å, H–S 2.67 Å, C–H–S 102°; C4–H4A···O1 with C–H 0.96 Å, H–O 2.47 Å, C–H–O 130°; C3–H3A···N2 with C–H 0.96 Å, H–O 2.38 Å, C–H–N 108°.

The *bis*(*N*-(morpholine-4-carbonothioyl)cyclohexanecarboxamido)nickel(II) complex which was used for single crystal X-ray diffraction was found to crystallize in the monoclinic space group $P2_1/c$. The molecular structure of the nickel complex with the atomic numbering scheme is shown in figure 3. Selected bond lengths and angles are given in table 2. The crystal structure of Ni($L^5$)$_2$ confirms that the *N*-(morpholine-4-carbonothioyl)cyclohexanecarboxamide ligand is a bidentate chelating ligand, coordinating to the nickel through the thiocarbonyl and carbonyl groups. As shown in figure 3,

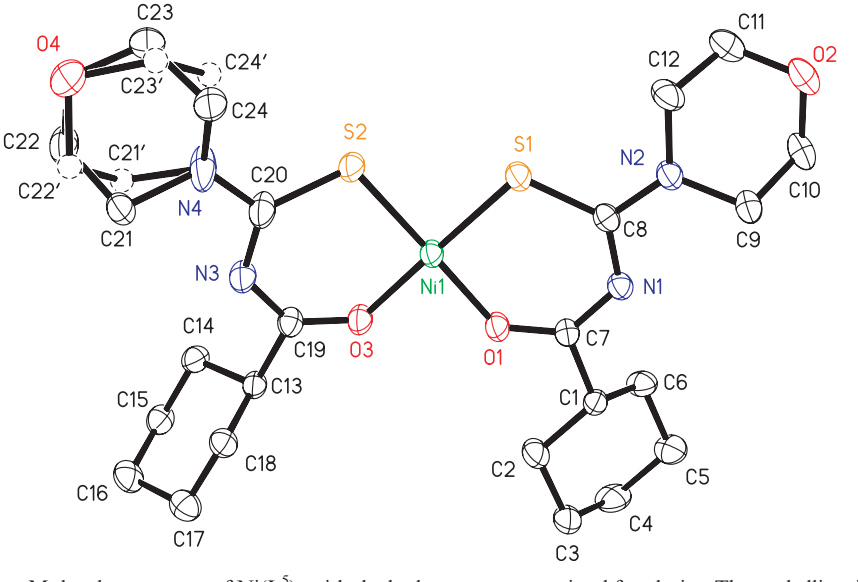


Figure 3. Molecular structure of Ni($L^5$)$_2$ with the hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

the nickel is four-coordinate square-planar contributed by two sulfurs and two oxygens (O3–Ni–S1 = 179.19(6)°, O1–Ni–S2 = 178.90(6)°, O1–Ni–S1 = 95.19(6)° and O3–Ni–S2 = 94.85(6)°). The distance of nickel atom from the best plane through the coordination sphere is 0.000 Å. The thioureas are bonded in O, S-chelating mode, forming a six-membered Ni–O–C–N–C–S ring system. The chelate ring systems are nearly planar with the largest deviations from the best plane being 0.011 Å for N1. The dihedral angle between these chelate planes of 11.10° indicates slight distortion from square planar towards tetrahedral geometry. With respect to the chelating ligands, the molecule shows a *cis*-arrangement. C–O, C–S and C–N bond lengths of the complex suggest considerable electronic delocalization in the chelate rings. The bond lengths of the carbonyl O1–C7 1.265(3) Å; O3–C19 1.262(3) Å and thiocarbonyl S1–C8 1.730(3) Å; S2–C20 1.732(3) Å groups lie between those for double and single bonds, similar to related structures [8–11], while both C–O and C–S bond lengths are typical of double bonds in the free ligand [18, 21, 22, 29]. The same behavior is observed for C–N bond lengths. The C–N bond distance is shorter than a normal single C–N bond length, C7–N1 1.335(3) Å and N1–C8 1.343(3) Å. This shortening of the C–N bond lengths is in agreement with bond distances of thiourea complexes determined earlier [8, 10, 11]. One 6-membered morpholine ring (O2–C10–C9–N2–C12–C11) in the nickel complex exhibits a puckered conformation, with puckering parameters [37] $q_2 = 0.041(3)$ Å, $q_3 = 0.549(3)$ Å, $Q_T = 0.550$ (3) Å, $\theta = 4.6(3)°$ and $\varphi = 13(5)°$. The largest deviations from the mean plane are 0.252(3) Å for O2 and 0.237(2) Å for C10. These data show that the morpholine ring adopts a chair conformation. The other morpholine ring of the nickel complex is disordered, with occupancies for the major and minor conformers of 0.566(8) and 0.434(8), respectively. Disordered atoms are indicated by the dotted circle on the morpholine group in figure 3. The morpholine ring adopts a chair conformation in both major ($Q_T = 0.731(7)$ Å) and minor conformer ($Q_T = 0.809(8)$ Å); the cyclohexane ring occurs at the northern pole for the major conformer and southern pole type for the minor conformer. The cyclohexane ring in the nickel complex exhibits a puckered conformation similar to the cyclohexane ring of the free ligand, with puckering parameters [37] $q_2 = 0.005(3)$ Å, $q_3 = -0.576(3)$ Å, $Q_T = 0.575(3)$ Å, $\theta = 180.0(3)°$ and $\varphi = 229(36)°$. These data show that the cyclohexane ring adopts a chair conformation.



## 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-673148 for $HL^1$ and CCDC-673147 for $Ni(L^5)_2$ and can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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