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Synthesis, Characterization, Crystal Structure and Thermal Behavior of N'-(4-chlorobenzoyl)-N,N-di-n-butylthiourea and Its Nickel Complex

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We report the synthesis, structural characterization and thermal behavior of N'-(4-chlorobenzoyl)-N,N-di-n-butylthiourea (HL) and its nickel complex (NiL_2). Some physical properties of the prepared compounds were investigated using elemental analyses, IR, ^{1}H-NMR, and magnetic susceptibility. The molecular structures of HL and NiL_2 were determined by single crystal X-ray diffraction. HL is a monoclinic, space group $P2_1/c$ with $a = 10.7457(5)$ Å, $b = 15.5909(8)$ Å, $c = 10.4536(5)$ Å, $\beta = 104.398(1)°$, and $V = 1696.34(14)$ Å^{3}with $Z = 4$ for $d_{calc} = 1.280$ g/cm^3. NiL_2 is a triclinic, space group P-1 with $a = 8.561(3)$ Å, $b = 16.643(6)$ Å, $c = 25.723(9)$ Å, $\alpha = 77.448(6)°$, $\beta = 84.077(7)^o$, $\gamma = 88.684(6)°$, and $V = 3558(2)$ Å^{3}with $Z = 4$ for $D_{calc} = 1.326$ g/cm^3. The ligands coordinate to the metal atom in a bidentate manner, yielding an essentially neutral complex of the type ML_2. Thermal decomposition of related compounds was investigated by TG and DTA. The pyrolytic end product was identified by X-ray powder diffraction.

Key Words: Thioureas, synthesis, X-ray structure, thermal behavior, benzoylthiourea.

Introduction

N,N'-dialkyl-*N'*-benzoylthioureas are known for their use as metal complexing agents and they have been found to be useful ligands for the potential determination of transition metals by means of chromatography[1]. Metal complexes of these types of ligands containing oxygen and sulfur as donor atoms are known to possess antifungal and antibacterial activities[2]. On the other hand, some thiourea derivatives have been used in

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commercial fungicides. The derivative N-(o-nitrophenyl)-$N'-$(ethoxycarbonyl) thiourea was isolated from the leaves of the resistant *Pyricuiria oryzae cav.* rice variety and preliminary pharmacological tests showed it to have high antibacterial activity[3−6].

In previous studies[7−14], we described the synthesis, characterization, crystal structure, thermal behavior and antimicrobial activity of some benzoylthiourea derivatives and their metal complexes. In the present work, we report the preparation, characterization, structural and thermal properties of N'-(4-chlorobenzoyl)-N,N-di-n-butylthiourea and its nickel complex.

Experimental

Instrumentation and crystal structure determination

FT-IR spectra were recorded in the range 4000-400 cm^{-1} on a WinFirst Satellite spectrophotometer, using KBr pellets. All ^{1}H-NMR spectra were recorded on a Bruker DPX 300 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: $Hg[Co(SCN)_4]$). Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD[15] using monochromated MoK$_\alpha$ (λ = 0.71073 Å) radiation. Semi-empirical absorption corrections were applied.[15] The structures were solved[15] by direct and conventional Fourier methods. Full-matrix least-squares refinement[15] was based on F^2. All but non-H atoms were refined anisotropically; H atoms were refined at idealized positions with a riding model. There are 2 independent but identical molecules A and B in NiL_2. Further details concerning data collection and refinement are given in Table 1. The DTA and TG curves are obtained with a Shimadzu DTG-60H model simultaneously with DTA and TG apparatus. The heating rate and other characteristics are given below: heating rate-10 K.min^{-1}, atmosphere-nitrogen, flow rate of furnace atmosphere-60 mL.min^{-1}, crucible-Platinum, sample size-10 to 12 mg, and reference substance-α-Al_2O_3. X-ray powder diffraction analyses of the final residues were performed with a Siemens, F model diffractometer. The X-ray generator is a Phillips PW-1010 model, ranging from 20 to 40 kV and 6 to 50 mA while using CuK$_\alpha$ radiation (λ = 1.5406 Å).

Synthesis of the ligand

All chemicals used for the preparation of the ligand and nickel complex were of reagent grade quality. The ligand was prepared by a procedure similar to that reported in the literature[7,16]. A solution of 4-chlorobenzoylchloride (5.10^{-2} mol) in acetone (50 cm^3) was added dropwise to a suspension of potassium thiocyanate (5.10^{-2} mol) in acetone (30 cm^3). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of di-n-butlyamine (5.10^{-2} mol) in acetone (10 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 an ethanol:dichloromethane mixture (1:1).

N,N-di-n-butyl-N'-(4-chloro-benzoyl)thiourea, (HL): White. Yield: 80%, m.p.: 89 °C. Anal. Calcd. for $C_{16}H_{23}N_2OSCl$: C, 58.7; H, 7.1; N, 8.6. Found: C, 58.1; H, 6.9; N, 8.5. IR (KBr pellet, cm^{-1}): ν(N-H) 3160 (br), ν(C = O) 1683 (s), ν(C = S) 1242 (s), ν (C-Cl) 757 (s). ^{1}H-NMR ($CDCl_3$): 8.93 (s, 1H, NH), 7.80-7.76 (d, 2H, C_6H_4Cl), 7.58-7.39 (d, 2H, C_6H_4Cl), 3.98-3.91 (t, 2H, NCH_2), 3.53-3.46 (t, 2H, NCH_2), 1.82-1.60 (m, 4H, CH_2), 1.489-1.218 (m, 4H, CH_2), 1.214-1.09 (t, 6H, CH_3).

Table 1. Summary of crystallographic data and parameters for HL and NiL_2.

Compound	HL	NiL_2
Empirical formula	$C_{16}H_{23}ClN_2OS$	$C_{32}H_{44}Cl_2N_4O_2S_2Ni$
Formula weight	326.87	710.44
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions		
a(Å)	10.7457(5)	8.561(3)
b(Å)	15.5909(8)	16.643(6)
c (Å)	10.4536(5)	25.723(9)
α (°)	90	77.448(6)
β (°)	104.398(1)	84.077(7)
γ (°)	90	88.684(6)
V (Å^3)	1696.34(14)	3558(2)
Z	4	4
D_c(Mg/m^3)	1.280	1.326
Absorption coefficient (mm^{-1})	0.349	0.846
F(000)	696	1496
Crystal size (mm^3)	0.40 x 0.35 x 0.30	0.45 x 0.20 x 0.18
θ range for data collection (°)	1.96 to 27.10	1.25 to 26.37
Index ranges	$-13 \leq h \leq 13$ $-19 \leq k \leq 19$ $-13 \leq l \leq 13$	$-10 \leq h \leq 10$ $-20 \leq k \leq 20$ $-24 \leq l \leq 32$
Reflections collected	18575	20936
Independent reflections (R_{int})	3733 (0.0330)	14186 (0.0952)
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	3733 / 196	14186 / 784
Goodness-of-fit on F^2	1.071	0.949
Final R indices [I > 2sigma(I)]	R1 = 0.0541, wR2 = 0.1477	R1 = 0.0901, wR2 = 0.1915
R indices (all data)	R1 = 0.0622, wR2 = 0.1533	R1 = 0.2108, wR2 = 0.2588
Largest diff. peak and hole (e.Å^{-3})	0.915 and -0.563	0.844 and -0.489

Synthesis of the complex

The complex was prepared according to the method described in the literature[7]. The nickel acetate solution in ethanol was added dropwise to the ligand in a 1:2 mole ratio with a small excess of ligand in dichloromethane. The solid complex was filtered and recrystallized from an ethanol:dichloromethane mixture (1:1).

Bis(N,N-di-n-butyl-N'-(4-chloro-benzoyl)thioureato)nickel(II) [NiL$_2$]: Pink. Yield: 82%, m.p.: 149 °C. Anal. Calcd. for $C_{32}H_{44}N_4O_2S_2Cl_2Ni$: C, 54.1; H, 6.2; N, 7.9. Found: C, 53.9; H, 6.1; N, 7.7. IR (KBr pellet, cm^{-1}): $\nu(C=O)$ 1581 (w), ν(C-Cl) 754 (s). ^{1}H-NMR ($CDCl_3$): 8.00-7.81 (m, 4H, C_6H_4Cl), 7.29-7.14 (m, 4H, C_6H_4Cl), 3.76-3.42 (t, 8H, NCH_2), 1.71-1.42 (m, 8H, CH_2), 1.38-1.10 (m, 8H, CH_2), 1.05-0.80 (t, 12H, CH_3).

Results and Discussion

In this work, we obtained and characterized the ligand (HL) and its Ni(II) complex. All compounds were characterized by elemental analysis, FT-IR spectroscopy, ^{1}H-NMR spectroscopy and single crystal X-ray diffraction methods. The thermal behavior of related compounds was investigated by DTA/TG.

The ligand shows ν_{N-H} vibrations at 3160 cm^{-1}, which disappear in the nickel complex, in the IR spectrum. The $\nu_{C=O}$ vibration frequency (1683 cm^{-1}) of the ligand decreases by ca. 102 cm^{-1} in the complex form; this is in good agreement with the literature data[7]. A shift to a higher frequency would also be expected for the $\nu_{C=S}$ vibration, but this vibration could not be assigned unambiguously because of overlap with other bands in that region. All this modification in the vibration frequencies in the complexation reaction confirms coordination through the oxygen and sulfur atoms. The N-H signal in the ^{1}H-NMR spectrum for the ligand at 8.93 ppm disappears upon the complexation reaction. This is in agreement with the IR spectrum. Magnetic moment showed that the nickel(II) complex is diamagnetic. The diamagnetic Ni(II) complex is consistent with a square planar geometry. This coordination of the nickel ion is confirmed by X-ray single crystal diffraction studies.

The molecular structures and packing diagrams of *N′*-(4-chlorobenzoyl)-*N*, *N*-di-*n*-butylthiourea, HL, and bis(*N′*-(4-chlorobenzoyl)-*N*, *N*-di-*n*-butylthioureato)nickel(II) complex, NiL_2, are depicted in Figures 1-4, respectively. Selected bond lengths and angles of the compounds are presented in Table 2. Atomic coordinates and equivalent isotopic displacement parameters for non-hydrogen atoms of HL and NiL_2 are given in Tables 3 and 4, respectively.

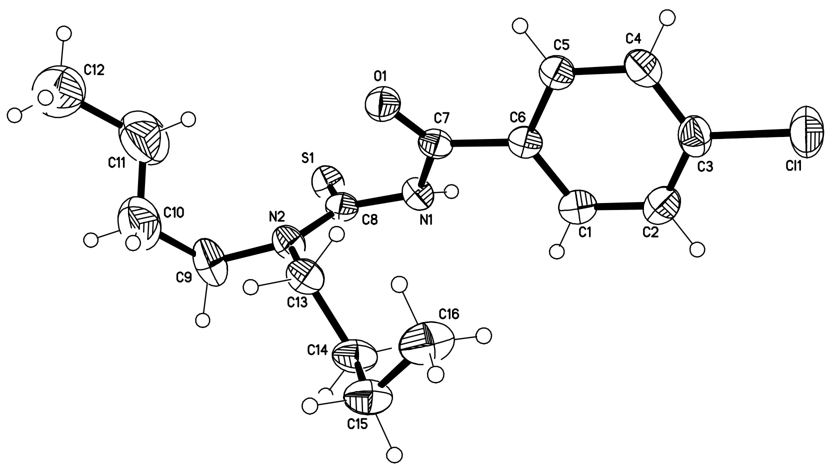

Figure 1. Molecular structure of HL. Thermal ellipsoids are shown at the 50% probability level.

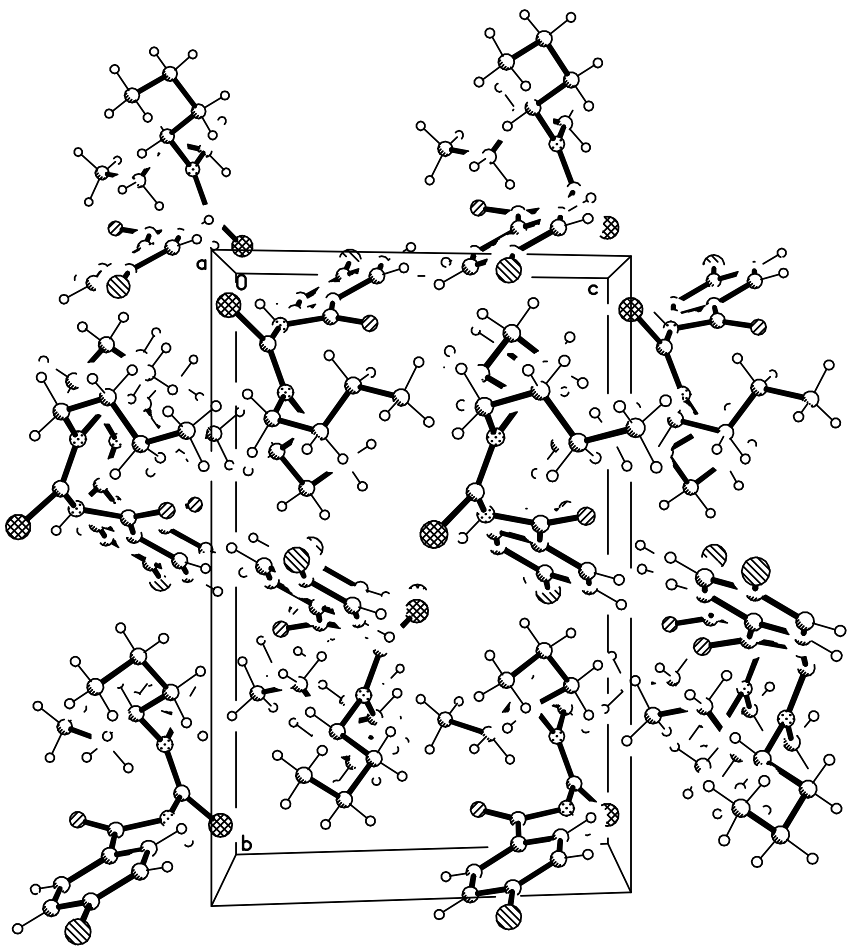

Figure 2. Crystal packing diagram of HL, view along [100].

For HL essential bond lengths viz. S(1)-C(8) = 1.677(2) Å, C(8)-N(1) = 1.410(3) Å, N(1)-C(7) = 1.382(3) Å and C(7)-O(1) = 1.215(3) Å are similar to the corresponding bond lengths in the cited compound[10]. The conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is twisted, as reflected by the torsion angles C(8)-N(1)-C(7)-O(1) and C(7)-N(1)-C(8)-S(1) of –1.1(3) and 120.7(2)°, respectively. The packing shows intermolecular hydrogen bridges N(1)-H(1)...S(1)(-x+1, -y, -z), which give rise to the formation of dimers. Geometric parameters are N..S 3.409(2) Å, H. . . S 2.63(3) Å and N-H..S 162.9(2)°; N-H is 0.81(3) Å.

The structure of the nickel complex shows the Ni atom with 4-fold coordination set up by 2 oxygen and 2 sulfur atoms [S(11)-Ni(1)-O(12) 174.7(2)° and O(11)-Ni(1)-S(12) 174.36(19)°]. The S_2O_2 plane is nearly planar with a dihedral angle between the S(11)-Ni(1)-O(11) and S(12)-Ni(1)-O(12) planes of 173.4(1)° and a distance of Ni from the best plane of 0.001(1) Å. The bond lengths of the carbonyl C(107)-O(11) 1.288(9) Å; C(127)-O(12) 1.262(8) Å and thiocarbonyl C(108)-S(11) 1.738(8) Å; C(128)-S(12) 1.735(7) Å groups lie between those for double and single bonds, a feature known from related structures[7,17]. Similar observations are true for C-N bonds. This is due to the strong delocalization in the chelate ring. All the other bond lengths fall within the expected range. According to all of the results, our studies have shown that *bis*(*N′*-

(4-chlorobenzoyl)-N,N-di-n-butylthioureato)nickel(II) complex preferentially forms neutral *cis*-[ML_2] type complex as presented in Figure 3. The molecular structure is close to that of related Ni complexes[7,17,18] and shows similar short C-O and C-S bonds, indicating the known π-bonding character in the chelate rings.

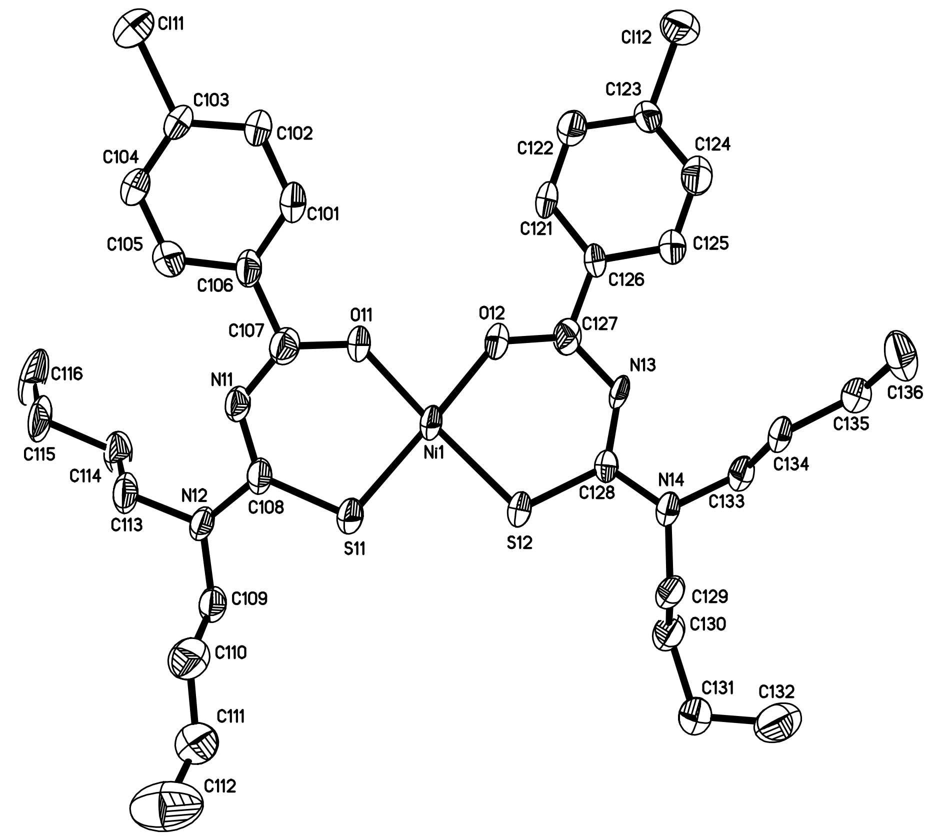

Figure 3. The molecular structure (molecule A) of NiL_2 with the hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

HL and its nickel complex were studied by thermogravimetric analysis from ambient temperature to 1300 K in nitrogen atmosphere. DTA/TG/DTG diagrams of HL and NiL_2 complex are shown in Figures 5 and 6, respectively. From the TG curve of HL, it appeared that the sample decomposes in 2 stages over the temperature range 403 to 802 K. The first decomposition occurs between 403 and 459 K, with a mass loss of 10.4%; the second decomposition starts at 459 K, and ends at 802 K, with an 88.9% mass loss. From the corresponding DTA profile, 3 endothermic peaks are noted, the first between 355 and 390 K, with a maximum at 362 K; the second between 390 and 443 K, with a maximum at 425 K; and the third between 443 and 600 K, with a maximum at 508 K. The first endothermic effect is related to the melting of HL (362 K). The other effects are due to the decomposition of the related compound. The TG curve of NiL_2 complex shows an initial mass loss in the temperature range 501-612 K, corresponding to the decomposition of the complex to $Ni(SCN)_2$.The mass loss at this stage is attributed to the evolved moieties di-n-butylbenzamide (theoretical mass loss: 75.4%, experimental mass loss: 75.7%). These agree with the literature data[19]. The last decomposition step occurs in the temperature range 612-1273 K and it corresponds to the formation of

Ni_3S_2 (theoretical mass loss: 88.7%, experimental mass loss: 88.4%). This end product was confirmed with XRD data. The X-ray powder diffraction pattern of the end product of complex can be seen in Figure 7. The DTA curve shows 2 endothermic effects, at 422 and 549 K. The first endothermic effect is due to melting of the complex and second to decomposition of the complex to $Ni(SCN)_2$. This agrees with the calculated mass loss and XRD data.

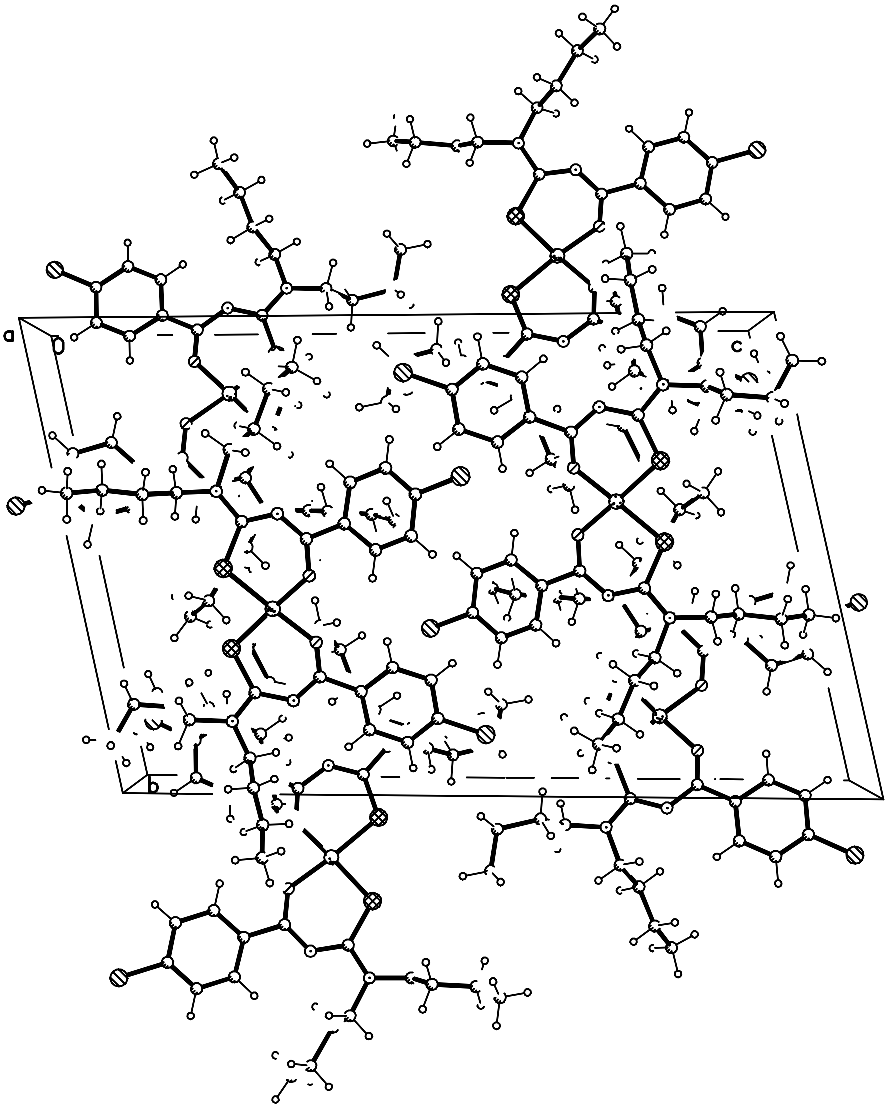

Figure 4. Crystal packing diagram of NiL_2, view along [100].

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

Compound				
	Bond lengths and angles			
	N(1)-C(7)	1.382(3)	C(9)-N(2)	1.473(3)
	N(1)-C(8)	1.410(3)	C(13)-N(2)	1.474(3)
	N(2)-C(8)	1.328(3)	C(7)-C(6)	1.493(3)
	C(8)-S(1)	1.677(2)	C(7)-O(1)	1.215(3)
HL				
	O(1)-C(7)-N(1)	123.1(2)	S(1)-C(8)-N(2)	125.43(17)
	C(7)-N(1)-C(8)	124.21(19)	C(8)-N(2)-C(9)	121.0(2)
	N(1)-C(8)-S(1)	118.04(16)	C(9)-N(2)-C(13)	114.30(18)
	Bond lengths and angles (in parentheses for molecule B with labeling 2xx)			
	Ni(1)-S(11)	2.149(2) (2.133(2))	N(11)-C(108)	1.324(9) (1.336(10))
	Ni(1)-O(11)	1.862(5) (1.863(5))	S(11)-C(108)	1.738(8) (1.737(8))
	O(11)-C(107)	1.288(9) (1.283(9))	C(107)-C(106)	1.482(10) (1.490(11))
	C(107)-N(11)	1.297(9) (1.301(10))	C(108)-N(12)	1.353(9) (1.341(10))
	Ni(1)-S(12)	2.154(2) (2.148(2))	N(12)-C(113)	1.463(9) (1.469(10))
	Ni(1)-O(12)	1.851(5) (1.843(5))	N(12)-C(109)	1.462(9) (1.468(11)
NiL_2				
	O(11)-Ni(1)-S(11)	96.5(2) (95.2(2))	C(108)-S(11)-Ni(1)	107.2(3) (109.3(3))
	S(11)-Ni(1)-S(12)	86.43(9) (85.7(1))	C(107)-O(11) Ni(1)	130.6(5) (132.6(6))
	O(11)-Ni(1)-S(12)	174.4(2) (177.5(2))	N(11)-C(108)-S(11)	127.9(6) (127.7(6))
	S(11)-Ni(1)-O(12)	174.7(2) (177.6(2))	S(11)-C(108)-N(12)	117.6(6) (116.4(7))
	O(11)-C(107)-N(11)	130.5(8) (130.0(8))	C(113)-N(12)-C(109)	117.0(6) (115.1(7))
	C(107)-N(11)-C(108)	124.7(6) 124.6(7))	O(11)-C(107)-C(106)	113.1(7) (114.7(8))

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for HL. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	-555(1)	-272(1)	2996(1)	58(1)
S(1)	6720(1)	746(1)	203(1)	34(1)
O(1)	5501(2)	982(1)	3625(2)	33(1)
N(1)	4830(2)	1010(1)	1373(2)	28(1)
N(2)	6306(2)	2125(1)	1564(2)	32(1)
C(1)	2269(2)	728(2)	1629(2)	34(1)
C(2)	1064(2)	474(2)	1733(2)	38(1)
C(3)	951(2)	48(2)	2857(3)	37(1)
C(4)	2009(2)	-128(2)	3877(2)	36(1)
C(5)	3205(2)	128(2)	3768(2)	32(1)
C(6)	3353(2)	555(1)	2646(2)	28(1)
C(7)	4665(2)	857(1)	2622(2)	27(1)
C(8)	5967(2)	1340(1)	1118(2)	28(1)
C(9)	7439(3)	2549(2)	1294(3)	49(1)
C(10)	8474(4)	2765(3)	2481(4)	74(1)
C(11)	8952(4)	2042(3)	3284(4)	83(1)
C(12)	10223(4)	2241(3)	4443(4)	80(1)
C(13)	5534(2)	2679(1)	2213(2)	33(1)
C(14)	4373(3)	3067(2)	1269(2)	39(1)
C(15)	3668(3)	3678(2)	1992(3)	43(1)
C(16)	3062(3)	3231(2)	2961(3)	51(1)

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for NiL_2. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	6048(1)	1509(1)	2532(1)	43(1)
Cl(11)	9002(4)	3957(2)	-644(1)	82(1)
Cl(12)	3569(3)	-1331(2)	393(1)	73(1)
S(11)	6550(3)	2413(1)	2974(1)	47(1)
S(12)	5658(3)	663(1)	3296(1)	51(1)
O(11)	6537(7)	2169(3)	1853(2)	52(2)
O(12)	5455(7)	787(3)	2133(2)	53(2)
N(11)	7253(8)	3455(3)	1989(3)	42(2)
N(12)	6908(8)	4034(4)	2706(2)	45(2)
N(13)	4512(8)	-410(3)	2740(2)	43(2)
N(14)	4500(8)	-833(4)	3624(3)	46(2)
C(101)	7688(11)	2588(5)	801(3)	58(3)
C(102)	8123(11)	2832(5)	253(3)	59(3)
C(103)	8423(11)	3654(5)	40(3)	57(3)
C(104)	8330(11)	4213(5)	356(3)	54(2)
C(105)	7903(11)	3981(5)	890(3)	55(2)
C(106)	7556(10)	3159(4)	1127(3)	46(2)
C(107)	7077(10)	2909(5)	1709(3)	50(2)
C(108)	6894(10)	3340(4)	2514(3)	47(2)
C(109)	6575(11)	4047(5)	3273(3)	52(2)
C(110)	8001(12)	4069(6)	3553(4)	71(3)
C(111)	7615(16)	4133(7)	4134(4)	90(4)
C(112)	8845(15)	4260(10)	4432(5)	131(6)
C(113)	7212(11)	4827(5)	2333(3)	54(2)
C(114)	5840(11)	5188(5)	2033(4)	60(3)
C(115)	6328(12)	5986(5)	1623(4)	69(3)
C(116)	5066(14)	6338(6)	1286(4)	100(4)
C(121)	4716(11)	196(5)	1283(3)	52(2)
C(122)	4423(10)	-118(5)	849(3)	52(2)
C(123)	3896(10)	-921(5)	937(3)	44(2)
C(124)	3656(10)	-1384(5)	1447(4)	54(2)
C(125)	3957(10)	-1073(5)	1879(3)	48(2)
C(126)	4478(10)	-260(4)	1801(3)	43(2)
C(127)	4847(10)	79(4)	2255(3)	44(2)
C(128)	4838(10)	-234(4)	3205(3)	41(2)
C(129)	4757(10)	-806(5)	4173(3)	47(2)
C(130)	3251(12)	-615(5)	4497(3)	62(3)
C(131)	3372(13)	-842(5)	5112(3)	71(3)
C(132)	3156(14)	-1724(6)	5326(4)	85(3)
C(133)	3861(10)	-1608(4)	3554(3)	49(2)
C(134)	5141(11)	-2143(4)	3349(3)	49(2)
C(135)	4516(12)	-2938(5)	3262(3)	64(3)
C(136)	5804(14)	-3481(6)	3079(4)	90(4)

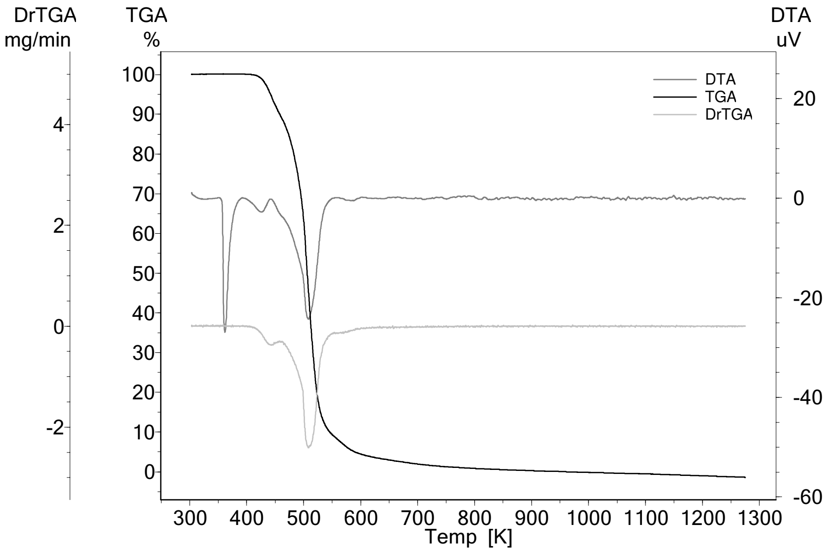

Figure 5. DTA/TG/DTG diagram of N'-(4-chlorobenzoyl)-N,N-di-n-butylthiourea.

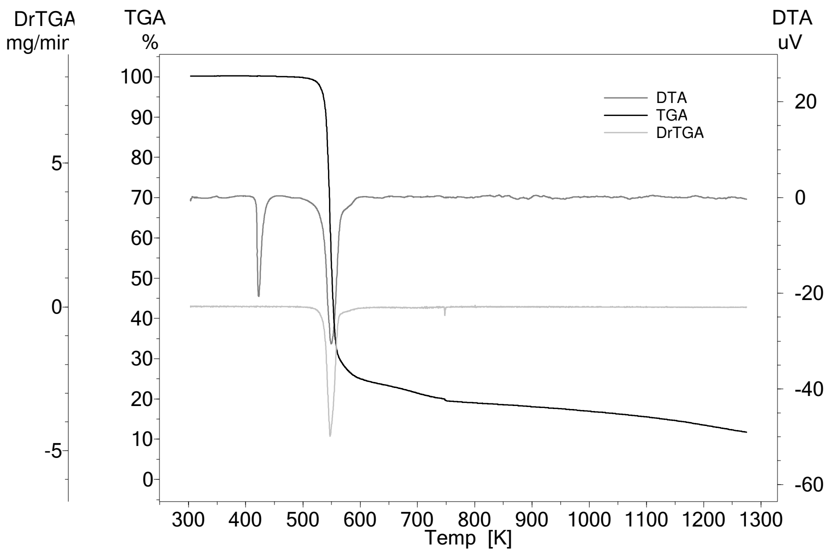

Figure 6. DTA/TG/DTG diagram of *cis*-bis(N'-(4-chlorobenzoyl)-N,N-di-n-butylthioureato)nickel(II) complex.

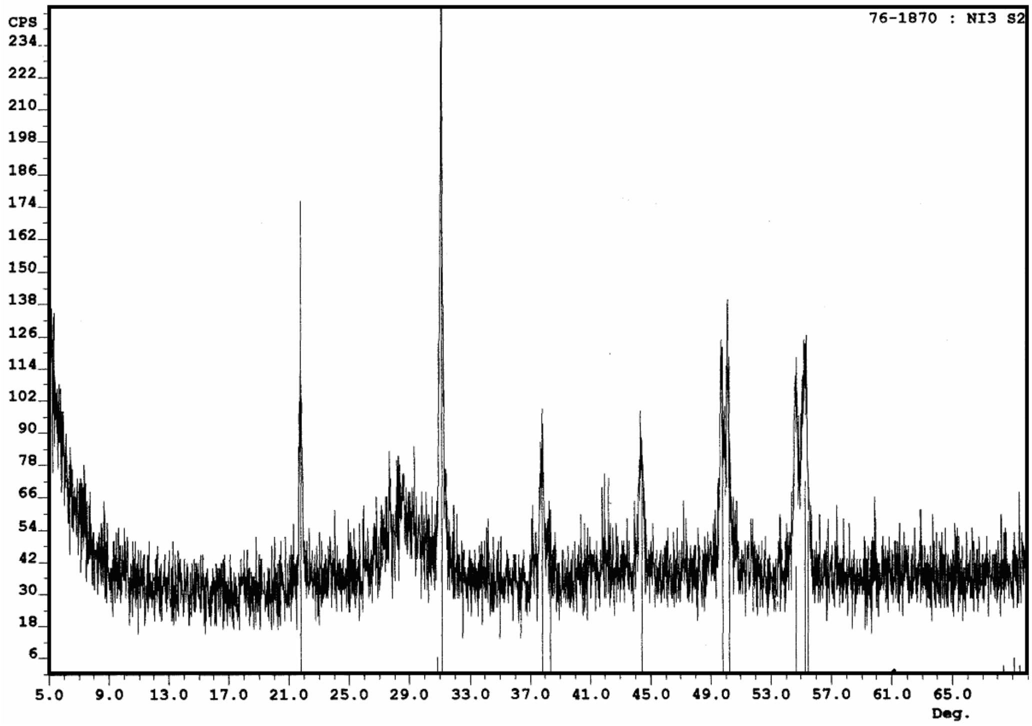

Figure 7. X-ray powder diffraction pattern of Ni_3S_2 (76-1870).

Supplementary material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with quotation number CCDC-270646 for HL and CCDC-270647 for NiL_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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