

Synthesis, crystal structure and biological activity of a new complex, + bis(1,1-diethyl-3-(3-fluorobenzoyl)-thiourea)nickel(II)

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A new complex bis(1,1-diethyl-3-(3-fluorobenzoyl)-thiourea)nickel (II) (NiL_2) has been synthesized and characterized by IR, ^1H NMR, ^{13}C NMR spectra and elemental analysis. Structure of the complex has been determined by single crystal X-ray diffraction (CCDC 633339). The two ligand molecules adopt a *cis*-conformation bonded to the Ni(II) ion and the central nickel ion has four-coordination square-planar geometry contributed by two S and two carbonyl O atoms. Both the complex NiL_2 and its free ligand HL (1,1-diethyl-3-(3-fluorobenzoyl)-thiourea) exhibit powerful plant growth regulating activity towards the root of rape and compared with the free ligand HL. The complex NiL_2 displays more promoting activity in lower concentrations.

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Study of 1,1-dialkyl-3-benzoylthioureas has attracted considerable attention in view of their interesting properties^{1,2}. Owing to their pronounced affinity for coordination to the transition metal ions, many 1,1-dialkyl-3-benzoylthioureas have been utilized as the selective reagents for the extraction, concentration and separation of the noble metals³⁻⁶. Some thiourea derivatives and their complexes have been used as fungicides⁷⁻¹⁰, insecticides¹¹ and herbicides¹². To date, a plenty of 1,1-dialkyl-3-(X-benzoyl)thioureas (X = H, CH_3 , Cl, Br, I, NO_2 , CH_3O) and their corresponding complexes have been reported¹³⁻¹⁶. However, no paper has been published concerning the fluorine substituted 1,1-diethyl-3-benzoylthiourea and the corresponding complexes. In continuation of our studies on thiourea derivatives and their metal complexes¹⁷⁻¹⁹, we report herein a new ligand 1,1-diethyl-3-(3-fluorobenzoyl)thiourea (HL) and the corresponding nickel complex bis(1,1-diethyl-3-(3-fluorobenzoyl)-thiourea)nickel(II) (NiL_2). The complex has been characterized by single-crystal X-ray diffraction. We have also examined the biological

activity of NiL_2 and HL. Furthermore, we have found that complexation with Ni (II) ion can doubly enhance the promoting rate of the free ligand HL under the same conditions.

Experimental

SOCl_2 was distilled before use. All other chemical were reagent grade and used without further purification. Melting points were measured on X-4 digital melting-point apparatus and are uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer as KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on a varian Mercury plus-400MHz spectrometer with CDCl_3 as solvent. X-ray diffraction data were collected on a Bruker SMART diffractometer. Elemental analyses (C, H, N,) were performed on a Perkin-Elmer 2400 CHN instrument.

1,1-diethyl-3-(3-fluorobenzoyl)thiourea (HL)

3-Fluorobenzoyl chloride was obtained from the reaction of dried 3-fluorobenzoic acid (10 mmol) with freshly distilled SOCl_2 (20 mL) which was refluxed for 8 h, and then excessive SOCl_2 was evaporated. A mixture of NH_4SCN (10 mmol), TMEDA (0.1 mmol), $\text{CH}_3\text{COOC}_2\text{H}_5$ (8 mL) and the obtained 3-fluorobenzoyl chloride was stirred at room temperature for 5 h. Then, the mixture was filtered off to remove inorganic salts (NH_4Cl). Then the $\text{CH}_3\text{COOC}_2\text{H}_5$ solution of $\text{NH}(\text{C}_2\text{H}_5)_2$ (10 mmol) was added to the filtrate and stirred at room temperature for 5 h. Then, the solvent was distilled out and the product dried in air. The crude product was recrystallized using EtOH to give HL. Yield 60%; needle; m.pt. 85-87 °C; IR (KBr); ν 3291 (N-H), 1647 (C=O), 1282 (C=S), 1585,1521,1469 (ph); ^1H NMR (400 MHz, CDCl_3): δ 8.411 (s, 1H, NH), 7.253-7.618 (m, 4H, PhH), 3.593-4.038 (q, 4H, NCH₂), 1.290-1.372 (t, 6H, CCH₃); Elemental analysis: Anal. Calcd for HL: C, 56.67; H, 5.49; N, 11.01%. Found: C, 56.42; H, 5.56; N 10.89%.

Bis(1,1-diethyl-3-(3-fluorobenzoyl)-thiourea)nickel(II) (NiL_2)

To 15 mL of ethanol containing HL (1 mmol) was added an ethanol solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol). Then, NaOAc (1 mmol) dissolved in a minimum volume of water was added. The reaction mixture was stirred at room temperature for 2 h. It was then

filtered to give a violet solid, which was dried in air. Single crystals were obtained after two weeks by slow evaporation of EtOH solution of the complex NiL₂. We selected a block single crystal (0.39×0.24×0.05 mm³) to determine the crystal structure by X-ray diffraction.

Yield, 52%; violet crystal; m.pt. 130°C; IR (KBr): ν 1411 (C=O), 1257 (C=S), 1589, 1524, 1494 (Ph); ¹H NMR (400 MHz, CDCl₃): δ 7.14-7.91 (m, 8H, PhH), 3.74-3.82 (m, 8H, NCH₂), 1.22-1.55 (m, 12H, CCH₃); Elemental analysis: Anal. Calcd for NiL₂: C, 50.99; H, 4.99; N, 10.38%. Found: C, 50.81; H, 5.11; N, 10.50%.

Structure determination

Intensity data of the complex NiL₂ was collected on a Bruker SMART diffractometer with graphite monochromatic Mo K _{α} radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 4632 unique reflections were collected in the $2.2^\circ < \theta < 20.4^\circ$ range $-12 \leq h \leq 12$, $-22 \leq k \leq 22$, $-16 \leq l \leq 13$ with ϕ - ω scans mode. Empirical absorption correction

was applied to the raw intensities by using the SADABS program²⁰. The structure was solved by direct methods and full-matrix least-squares method based on F^2 using the SHELXTL program package²¹. The data collection and refinement processes for NiL₂ is summarized in Table 1.

Results and discussion

Crystal structure

The molecular structure of the complex NiL₂ is shown in Fig.1. Selected bond distances and angles are listed in Table. 2.

As presented in Fig. 1, the two acylthiourea molecules adopt a cis conformation bonded to the central Ni(II) ion. The nickel atom is in a closely four-coordination square-planar geometry contributed by two S and two carbonyl O atoms [O(2)-Ni(1)-S(1)=179.7(1)°, O(1)-Ni(1)-S(2)=176.4(1)]. The mean deviation from the plane of Ni(1), S(1), S(2), O(1) and O(2) is 0.0289 Å. The two Ni-S bond

Table 1 — Crystallographic data, data collection and refinement for NiL₂

Formula	C ₂₄ H ₂₈ F ₂ N ₄ NiO ₂ S ₂	Wavelength	0.71073 Å
Formula weight	565.33	Absorption coefficient	0.967 mm ⁻¹
Crystal colour	Violet	Absorption correction	multi-scan
Temperature (K)	294 (2)	F(000)	1176
Crystal system	Monoclinic	Range for data collection	2.2° ≤ θ ≤ 20.4°
Space group	P2(1)/n	Limiting indices	-12 ≤ h ≤ 12 -22 ≤ k ≤ 22
Crystal size (mm ³)	0.39 × 0.24 × 0.05		
Unit cell parameters			-16 ≤ l ≤ 13
<i>a</i>	10.5180 (3) Å	Reflections collected	13380
<i>b</i>	18.3839 (5) Å	Independent reflections [Rint]	4632 [0.055.000]
<i>c</i>	13.7411 (4) Å	Refinement method	Full-matrix least-squares on F^2
α	90.00°		
β	106.0440 (10)°	Data / parameters	4632 / 419
γ	90.00°	Goodness-of-fit on F^2	1.040
<i>V</i> (mm ³)	2553.51 (13) Å ³	Final <i>R</i> indices [$I > 2\sigma$]	$R_1 = 0.0510$, $wR_2 = 0.1074$
<i>Z</i>	4	<i>R</i> indices (all data)	$R_1 = 0.0873$, $wR_2 = 0.1257$
<i>D</i> _x	1.471 Mg m ⁻³	Largest diff. Peak and hole (e Å ⁻³)	0.450 and -0.46

Table 2 — Selected bond distances (Å) and bond angles (°) for the complex NiL₂

Bond lengths					
Ni1-O1	1.854(3)	C8-N1	1.345(5)	C19-O2	1.260(4)
Ni1-O2	1.862(2)	C8-N2	1.339(5)	C8-S1	1.721(4)
Ni1-S1	2.1318(11)	C9-N2	1.474(5)	C20-S2	1.724(4)
Ni1-S2	2.1374(12)	C2-F1	1.225(6)	C14-F2	1.363(4)
C7-O1	1.265(4)	C4-F1'	1.283(6)	C7-N1	1.321(4)
Bond angles					
O1-Ni1-O2	85.78(11)	C7-O1-Ni1	133.8(3)	N1-C7-C6	115.0(3)
O1-Ni1-S1	94.53(8)	C19-O2-Ni1	132.4(2)	N2-C8-N1	115.0(4)
O2-Ni1-S1	179.68(9)	C7-N1-C8	122.9(3)	N2-C8-S1	116.6(3)
O1-Ni1-S2	176.44(10)	C8-N2-C9	123.1(4)	N1-C8-S1	128.4(3)
O2-Ni1-S2	94.81(8)	C8-N2-C11	121.4(4)	O1-C7-N1	130.4(4)
S1-Ni1-S2	84.87(4)	C20-S2-Ni1	109.15(13)	C8-S1-Ni	109.94(15)

lengths [2.1318(11) Å, 2.1374(12) Å] are clearly longer than the two Ni-O bond lengths [1.854(3) Å, 1.862(2) Å] because of the divergent geometry of the two arms, in order to allow the sulfur atom to approach the metal atom within reasonable bonding distance. These values agree well with Ni(II) complexes of substituted thiourea^{13,14}. In the title complex NiL₂, the bond length of O(1)-C(7) is 1.265(4) Å, which is shorter than 1.43 Å (C-O single bond length) and longer than 1.23 Å (C=O double bond length). Moreover, the bond S(1)-C(8) [1.721(4) Å] is longer than double bond. In fact, the N(1)-C(7) [1.321(4) Å], N(1)-C(8) [1.345(5) Å] and

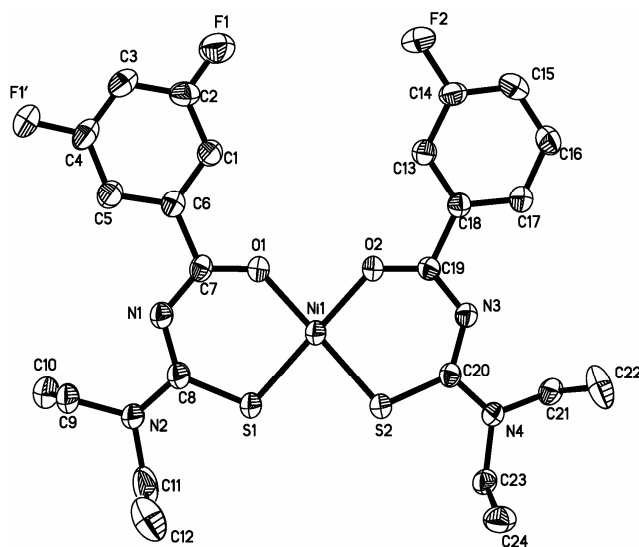


Fig.1 — The molecular structure of C₂₄H₂₈F₂N₄NiO₂S₂ (H atoms have been omitted for clarity).

N(2)-C(8) [1.339(5) Å] are within the range of C=N bond distances. This exhibits the existence of a conjugated system of O(1)-C(7)-N(1)-C(8)-S(1)-N(2). The fluorine and hydrogen atoms at C(2) and C(4) reveal disorder due to the rotation of the C(6)-C(7) bond. On the other hand, the molecules form centrosymmetric pairs in the unit cell. The molecules in the dimmers lie almost directly above each other, and the Ni-Ni distance is 3.936 Å which is shorter than the Ni-Ni distance (4.05 Å) of bis(1,1-diethyl-3-benzoylthiourea)nickel(II)¹³. The Ni-Ni connections form an angle of 88.7° with the coordination plane of Ni(1), S(1), S(2), O(1) and O(2), which is also observed in related complexes²². The view of the molecules forming centrosymmetric pairs is shown in Fig. 2.

Spectral properties

Comparing the IR spectra of HL, all the stretching vibrations of the complex NiL₂ show corresponding change. The NH stretching vibration at 3291 cm⁻¹ in the free ligand disappears in the complex NiL₂, mainly due to the ligand losing the proton from the acyl-substituted nitrogen upon forming the neutral complex. The band at 1647 cm⁻¹ is assigned to C=O stretching vibration in the compound HL. In the complex, it is not observed at the same wavenumber. But, a strong peak appears at 1411 cm⁻¹ corresponding to coordinated carbonyl. At the same time, the C=S band at 1282 cm⁻¹ for the free ligand shifts to 1257 cm⁻¹. All the low-frequency shifts indicate the coordination of the metal by the S and O atoms.

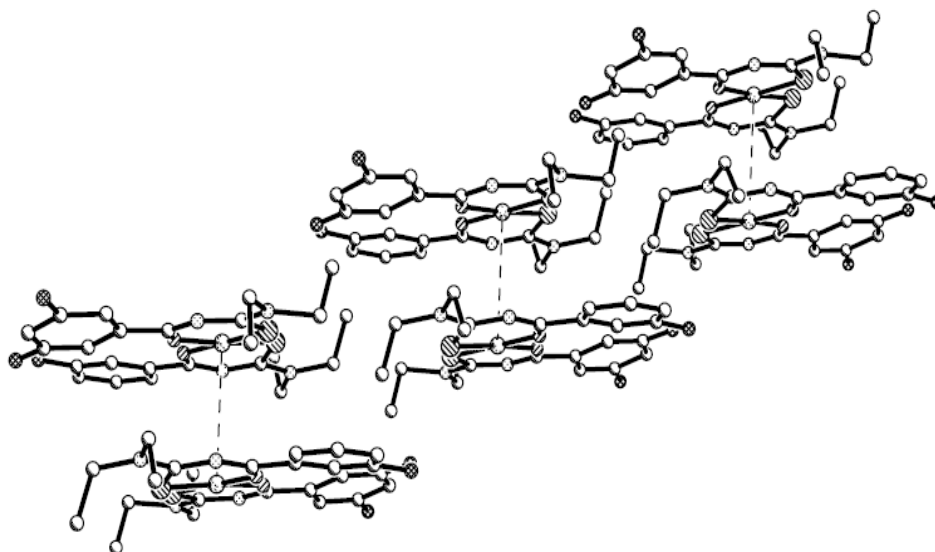


Fig.2 — A view of the molecules form centrosymmetric pairs (H atoms have been omitted for clarity).

Table 3 — ^{13}C NMR spectra of the compounds HL and NiL_2

Compound	Assignment											
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂
HL	115.07	162.56	119.83	130.50	123.23	134.82	163.93	178.84	47.97	13.24	47.68	11.42
NiL_2	115.95	163.71	118.40	129.37	124.75	139.12	171.07	172.66	46.22	13.11	45.64	12.45

As presented in Table 3, the carbon atom of the thiocarbonyl group appears at 178.84 ppm in compound HL shifts to 172.66 ppm in the complex NiL_2 as a consequence of coordination. Compare with the ^1H NMR spectra of the uncomplexed ligand HL, the proton peak of the N-H group at 8.41 ppm disappears in the complex NiL_2 . This is in agreement with the IR spectra and the X-ray single crystal diffraction studies.

Biological activity

We investigated the ligand HL and the complex NiL_2 for plant growth regulating activities by plate culture method¹⁹. The compounds were dissolved in H_2O : DMF (99.5:0.5, v/v) solvents, and 0.1 g Tween-80 was added to promote the compounds to dissolve. The root lengths of rape were measured after four days. The percentage plant growth activity was calculated according to the following equation:

$$\text{Percentage plant growth activity} = (N - N_0) / N_0 \times 100\%$$

where N is the root length cultured in compound solution and N_0 is the root length cultured in the distilled water under the same condition. The results are shown in Table 4. The heteroauxing has been used to compare with the compounds HL and NiL_2 .

The results reveal that both the two compounds HL and NiL_2 exhibit inhibitory activities against roots of rape in higher concentration (100 ppm) and powerful promoting activities in lower concentrations (1 ppm). Especially the complex NiL_2 , its promoting rate to the root can attain 57.14% in 1 ppm, in contrast to the free ligand, it is apparent that complexation with Ni(II) ion can doubly enhance the promoting activity of the ligand HL under the same condition. This mainly can be due to the reason that complex formed by thiourea derivative ligand with nickel(II) is stronger than the corresponding alkaline salts formed by it with Ca (II) (calcium is a major component of pectin, the strengthening agent of plant cell walls). The kidnap metals which thiourea derivative ligand seeks is nickel(II) other than calcium; so, the nickel(II) complex NiL_2 does not appear to affect the

Table 4 — Plant growth regulating activity data (rape)

Compounds	% Plant growth activity				
	100 ppm	10 ppm	1 ppm	0.1 ppm	0.01 ppm
HL	-75.12	10.71	28.57	17.86	2.51
NiL_2	-35.71	51.20	57.14	35.71	3.57
Heteroauxing	-100	-93.92	-50.00	-28.57	3.57

normal physiology of the plant and dose not affect the micronutrient Ni(II) availability for plant growth²³; but, the free ligand dose. Thus, free ligand complexation with ion Ni(II) ion is more beneficial to plant growth.

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References

- Irving A, Koch K R & Matoetoe M, *Inorg Chim Acta*, 206 (1993) 193.
- Schuster M, *Fr Z Anal Chem*, 342 (1992) 791.
- Dominguez M, Antico E, Beyer L, Aguirre A, Garcia-Granda S & Salvado V, *Polyhedron*, 21 (2002) 1429.
- Mangaka Matoetoe, *M. Sc. Thesis*, University of Cape Town, 1989.
- Koch K R, Hallale O, Bourne S A, Miller J & Bacsá J, *J Mol Struct*, 561 (2001) 185.
- Koch K R, *Coord Chem Rev*, 216-217 (2001) 473.
- Campo R, Criado J J, Garcia E, Hermosa M R, Sanchez A J, Manzano J L, Monte E, Rodriguez-Fernandez E & Sanz F, *J Inorg Biochem*, 89 (2002) 74.
- Criado J J, Rodriguez-Fernandez E, Garcia E, Hermosa M R & Monte E, *J Inorg Biochem*, 69 (1998) 113.
- Zhang Y M, Wei T B & Gao L M, *Synth Commun*, 31 (2001) 3099.
- Campo R D, Criado J J, Gheorghe R, Gonzalez F J, Hermosa M R, Sanz F, Manzano J L, Monte E & Rodriguez-Fernandez E, *J Inorg Biochem*, 98 (2004) 1307.
- Madan V K, Taneja A D & Kudesia V P, *J Indian Chem Soc*, 68 (1991) 162.

- 12 Li Z H, Zhang Y, Peng Z H & Wang Y G, *Huaxueshiji*, 24 (2002) 214.
- 13 Knuuttila P, Knuuttila H, Hennig H & Beyer L, *Acta Chem Scand A*, 36 (1982) 541.
- 14 Juranic N, Hoyer E, Dietze F & Beyer L, *Inorg Chim Acta*, 162 (1989) 161.
- 15 Sacht C & Datt M S, *Polyhedron*, 19 (2000) 1347.
- 16 Sosa-Albertus M & Piris M, *J Mol Struct* 598 (2001) 261.
- 17 Zhang Y M, Yang L Z, Lin Q & Wei T B, *Chin J Org Chem*, 26 (2006) 138.
- 18 Zhang Y M, Yang L Z, Lin Q & Wei T B, *Trans Met Chem*, 30 (2005) 944.
- 19 Xie S J, Ke S Y, Wei T B, Duan L P & Guo Y L, *J Chin Chem Soc*, 51 (2004) 1013.
- 20 Sheldrick G M, *SADABS: Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen Germany, 1996.
- 21 Sheldrick G M, *SHELXTL: Structure Determination Software Program*, Bruker Analytical X-ray System, Inc, Madison, WI, 1997.
- 22 Balley R A & Rothaupt K L, *Inorg Chim Acta*, 147 (1988) 233.
- 23 Vidhyasekaran P, *Fungal Pathogenesis in Plants and Crops* (Marcel Dekker, New York) 1997.