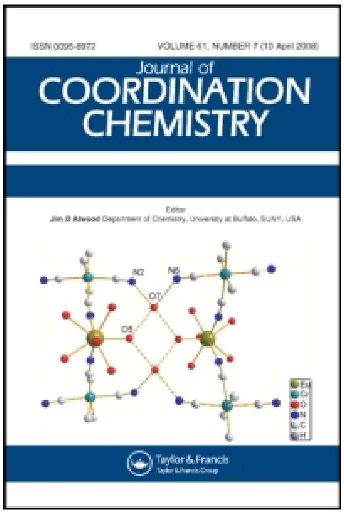

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You-Ming Zhang[a]; Hai-Xia Pang[a]; Cheng Cao[a]; Tai-Bao Wei[a]
[a] College of Chemistry and Chemical Engineering, Key Laboratory of Polymer Materials of Gansu Province, Lanzhou, Gansu 730070, P.R. China

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Synthesis and crystal structure of Cu(I) and Ni(II) complexes of 1,1-diethyl-3-(4-fluorobenzoyl)-thiourea

YOU-MING ZHANG, HAI-XIA PANG, CHENG CAO and TAI-BAO WEI*

College of Chemistry and Chemical Engineering, Key Laboratory of Polymer Materials
of Gansu Province, Lanzhou, Gansu 730070, P.R. China

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The reaction of 1,1-diethyl-3-(4-fluorobenzoyl)-thiourea (HL) with $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$ give two complexes, $Cu(HL)_3Cl$ (**1**) and NiL_2 (**2**). The crystal structures of these products were determined by single crystal X-ray diffraction. In **1**, three HL molecules are unidentate, coordinating through the sulfur, and the copper is tetrahedral with three S and one Cl. In **2**, two HL molecules are O and S donor bidentate and coordinate as anionic species with loss of the proton from the acyl-substituted nitrogen; the nickel is square-planar.

Keywords: Crystal structure; Thiourea derivative; Copper(I) complex; Nickel(II) complex

1. Introduction

1,1-Dialkyl-3-benzoylthioureas are excellent ligands to platinum group metals and many are used as selective reagents for extraction, concentration and separation of the noble metals [1–4]. Beyer and Koch reported a series of crystal Ni(II), Cu(II), Co(II), Pd(II), Pt(II) and Ru(III) complexes of such thiourea ligands [5–7]. In the structures of these complexes, 1,1-dialkyl-3-benzoylthioureas are O and S donor bidentate ligands and coordinate as anionic species with loss of the proton from the acyl-substituted nitrogen. Our interest in structures and coordination of acylthiourea complexes [8–11], more precise structural and conformational data are needed to understand these compounds. We have synthesized and characterized a series of new complexes of 1,1-dialkyl-3-(X-benzoyl)thioureas. In contrast to complexes reported [12, 13], **1** displays different coordination behavior and molecular structure with three unidentate HL molecules coordinating only through sulfur and the copper tetrahedral with three S and one Cl. Although with the same ligand as **1**, **2** is remarkably similar to *bis*(1,1-diethyl-3-benzoyl-thiourea)nickel(II) [12], with nickel in a square-planar geometry from two S and two carbonyl O atoms. In this article, we report the synthesis and crystal structure of $Cu(HL)_3Cl$ and NiL_2.

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*Corresponding author. Fax: +086-931-7971216. Email: weitaibao@126.com

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2. Experimental

2.1. *Synthesis*

2.1.1. Synthesis of Cu(HL)$_3$Cl. The 1,1-diethyl-3-(4-fluorobenzoyl)thiourea was prepared according to our previous work [14]. To 15 mL of ethanol containing HL (1.5 mmol) was added an ethanol solution of $CuCl_2 \cdot 2H_2O$ (0.5 mmol), the reaction mixture was filtered and left to crystallize by slow evaporation, then single crystals of Cu(HL)$_3$Cl were obtained after two weeks.. Yield, 30%; m.p. 171–172°C. Anal. Calcd for Cu(HL)$_3$Cl: C, 50.16; H, 5.26; N, 9.75%. Found: C, 50.31; H, 5.32; N, 9.50%.

2.1.2. Synthesis of NiL$_2$. To 15 mL of ethanol containing HL (1 mmol) was added an ethanol solution of $NiCl_2 \cdot 6H_2O$ (0.5 mmol), then NaOAc (1 mmol) dissolved in ethanol was added, the reaction mixture was stirred at room temperature for 2 h, then filtered to give a violet solid, which was dried in air. Single crystals were obtained after two weeks by slow evaporation of an ethanol solution. Yield, 38%; m.p. 190–191°C. Anal. Calcd for NiL$_2$: C, 50.99; H, 4.99; N, 10.38%. Found: C, 50.82; H, 5.11; N, 10.52%.

2.2. *Physical measurements*

Melting points were measured on an X-4 digital melting-point apparatus and were uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer as KBr pellets. ^{1}H 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.

2.3. *Structure determination*

Intensity data were collected on a Bruker SMART diffractometer with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption correction was applied to the intensities by using the SADABS program [15]. The structure was solved by direct methods and full-matrix least-squares based on F^2 using the SHELXTL program package [16]. The data collection and refinement processes are summarized in table 1.

3. Results and discussion

3.1. *Description of the structures*

The molecular structures of the complexes are shown in figures 1 and 2. Selected bond distances and angles are listed in table 2. Hydrogen bonding parameters are given in table 3.

Table 1. Crystallographic data, data collection and refinement.

Compound	**1**	**2**
Formula	$C_{36}H_{45}ClCuF_3N_6O_3S_3$	$C_{24}H_{28}F_2N_4NiO_2S_2$
Formula weight	861.95	565.33
Temperature (K)	294(2)	294(2)
Crystal system	Monoclinic	Tetragonal
Space group	$P2(1)/n$	$I4(1)/a$
Crystal size (mm^3)	0.40 × 0.40 × 0.40	0.30 × 0.25 × 0.20
Unit cell parameters (Å, °)		
a	8.2012(7)	19.524(3)
b	20.1825(17)	19.524(3)
c	25.014(2)	13.804(2)
α	90.00	90.00
β	96.083(3)	90.00
γ	90.00	90.00
V (Å^3)	4117.1(6)	5262.0(13)
Z	4	8
Dx ($Mg\,m^{-3}$)	1.391	1.427
Wavelength (Å)	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.803	0.939
Absorption correction	Multi-scan	Multi-scan
$F(000)$	1792	2352
θ range for data collection (°)	2.2–25.9	2.8–24.0
Limiting indices	$-9 \leq h \leq 9$, $-24 \leq k \leq 20$, $-28 \leq I \leq 30$	$-23 \leq h \leq 23$, $-23 \leq k \leq 23$, $-15 \leq I \leq 16$
Reflections collected	22024	13748
Independent reflections [R_{int}]	7658 [0.027.0]	2451 [0.041]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	7658/497	2451/162
Goodness-of-fit on F^2	1.069	1.061
Final R indices [$I > 2\sigma$]	$R_1 = 0.0375$ $wR_2 = 0.0967$	$R_1 = 0.0492$ $wR_2 = 0.1120$
R indices (all data)	$R_1 = 0.0515$ $wR_2 = 0.1046$	$R_1 = 0.0674$ $wR_2 = 0.1234$
Largest diff. Peak and hole (e Å^3)	0.64.and −0.27	0.570 and –0.44

As presented in figure 1, Cu(I) ions of **1** are tetrahedrally coordinated by sulfur of three thiourea ligands and one Cl ion, Cu–S distances in the slightly distorted tetrahedral coordination are 2.2688, 2.2804 and 2.2956 Å, in agreement with Cu–S distances (2.238–2.361 Å) of Cu(I) complexes of substituted thiourea [17, 18]. The Cl(1)–Cu(1) bond length is 2.6064 Å and the Cl lies approximately on the line perpendicular to the basal S(1) S(2) S(3) plane as shown by the angles made by the Cl(1)–Cu(1) bond with the Cu(1)–S(1), Cu(1)–S(2) and Cu(1)–S(3) bonds. [S(3)–Cu(1)–Cl(1) = 102.51(3)°, S(1)–Cu(1)–Cl(1) = 100.10(3)°, S(2)–Cu(1)–Cl(1) = 100.36(3)°]. Three benzene rings are tilted with respect to each other; the dihedral angles are 69.2° (between the C(1)– and C(13)–containing rings), 84.8° (between the C(1)– and C(25)–containing rings) and 106.9° (between the C(13)– and C(25)–containing rings). The overall molecular structure resembles a turbine. Formation of intramolecular hydrogen bonds of Cl^- with N(1)–H(1′), N(2)–H(2′), N(5)–H(5′) evidently stabilize the molecular structure. As presented in figure 2, the two acylthiourea molecules of **2** adopt a *cis* conformation bonded to the central Ni(II) with the nickel a square-planar geometry with two S and two carbonyl O atoms. The Ni–S bond lengths of 2.1313 and 2.1314 Å agree with the corresponding distances in *bis*(1,1-diethyl-3-benzoylthiourea)nickel(II) [12], but the Ni–O distances of 1.878(2) Å are somewhat

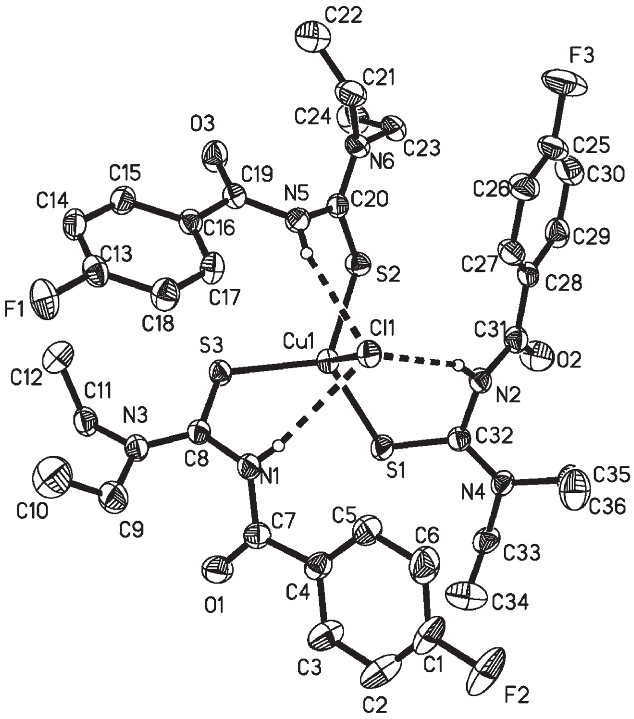

Figure 1. The molecular structure of $Cu(HL)_3Cl$.

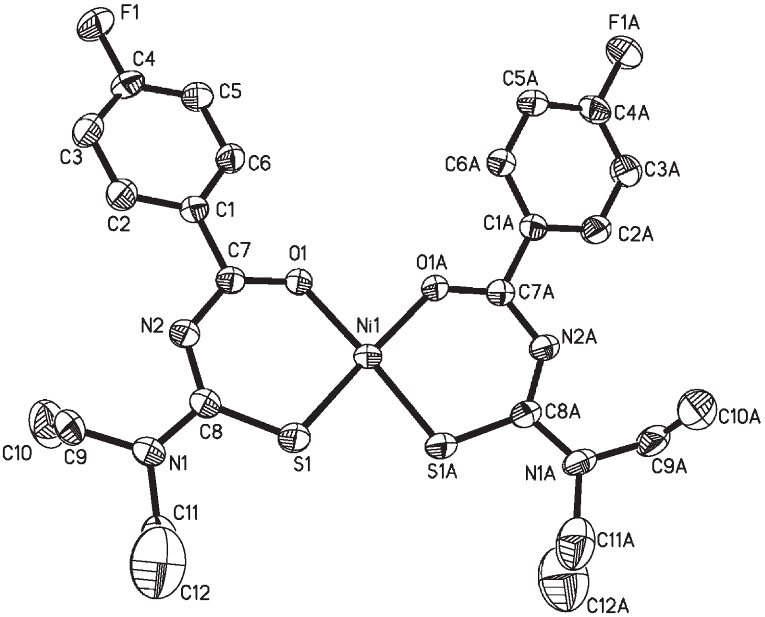

Figure 2. The molecular structure of NiL_2.

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

1			
C(7)–O(1)	1.212(3)	C(32)–S(1)	1.689(2)
C(19)–O(3)	1.217(3)	Cl(1)–Cu(1)	2.6064(7)
C(31)–O(2)	1.222(3)	Cu(1)–S(3)	2.2688(7)
C(8)–S(3)	1.689(2)	Cu(1)–S(1)	2.2804(8)
C(20)–S(2)	1.689(2)	Cu(1)–S(2)	2.2956(7)
C(8)–S(3)–Cu(1)	111.24(8)	S(1)–Cu(1)–Cl(1)	100.10(3)
C(20)–S(2)–Cu(1)	108.58(8)	S(3)–Cu(1)–S(1)	116.53(3)
C(32)–S(1)–Cu(1)	107.42(9)	S(3)–Cu(1)–S(2)	113.97(3)
S(3)–Cu(1)–Cl(1)	102.51(3)	S(2)–Cu(1)–S(1)	118.89(3)
S(2)–Cu(1)–Cl(1)	100.36(3)		
2			
Ni(1)–O(1)	1.878(2)	C(4)–F(1)	1.363(4)
Ni(1)–O(1A)	1.878(2)	C(7)–O(1)	1.268(4)
Ni(1)–S(1A)	2.1313(12)	C(7)–N(2)	1.322(4)
Ni(1)–S(1)	2.1314(12)	C(8)–N(1)	1.331(5)
C(11)–N(1)	1.637(8)	C(8)–N(2)	1.340(5)
C(9)–N(1)	1.466(6)	C(8)–S(1)	1.714(4)
O(1)–C(7)–N(2)	129.9(3)	C(9)–N(1)–C(11)	114.0(4)
N(1)–C(8)–N(2)	115.3(3)	C(7)–N(2)–C(8)	124.5(3)
N(1)–C(8)–S(1)	116.8(3)	O(1)–Ni(1)–O(1A)	87.01(14)
N(2)–C(8)–S(1)	127.9(3)	O(1)–Ni(1)–S(1A)	174.67(9)
N(1)–C(9)–C(10)	112.3(5)	O(1)–Ni(1)–S(1)	95.23(7)
C(12)–C(11)–N(1)	97.2(7)	S(1)–Ni(1)–S(1A)	82.96(7)
C(8)–N(1)–C(9)	121.0(4)	C(7)–O(1)–Ni(1)	132.1(2)
C(8)–N(1)–C(11)	122.6(4)	C(8)–S(1)–Ni(1)	109.56(13)

Table 3. Hydrogen bonding distances (Å) and angles (°).

D–H ... A	D–H	H ··· A	D ··· A	D–H ··· A	Symmetry code
1					
N1–H1′ ··· Cl1	0.724	2.593	3.306	168.71	–
N2–H2′ ··· Cl1	0.745	2.523	3.231	159.42	–
N5–H5′ ··· Cl1	0.777	2.476	3.226	162.99	–
C33A–H33A ··· Cl1B	0.970	2.815	3.583	136.70	$x+1/2, -y+3/2, z+1/2$

longer, indicating fluorine decreases the electron delocalization of the O atom. The angle between planes (Ni(1), S(1), O(1)) and (Ni(1), S(1A), O(1A)) is 6.7°. This structure is also very similar to the nickel complexes [12].

In **2**, the O–C bond distance of 1.268(4) Å is shorter than 1.43 Å (C–O single bond length) and longer than double bond length. The S–C bond [1.714(4) Å] is also longer than a double bond. This may be due to existence of a conjugated system of O(1)–C(7)–N(2)–C(8)–S(1). In **1**, the O–C bond distance is 1.21 Å, characteristic of C=O double bonds, but the C–S bond length (1.689 Å) remains longer than typical double bonds and shorter than the C–S bond lengths (1.741 Å) of typically *bis*-S,O chelated Cu(II) complexes [6].

In **1**, molecules are connected into chains by intermolecular hydrogen bonds C(33A)–H(33A) ··· Cl (1B), as shown in figure 3. In **2**, molecules vertically intersect and the dihedral angle between the coordination planes of the two molecules is 90°. This can be observed in the packing of NiL_2 projected along the *c*-axis (figure 4).

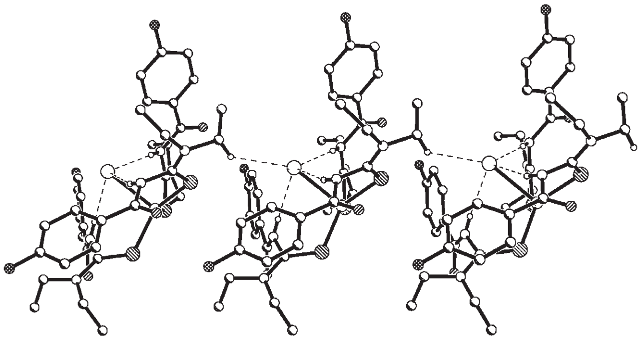

Figure 3. Complex molecules are connected into a chain by intermolecular hydrogen bonds for **1**. Some of the H atoms have been omitted for clarity.

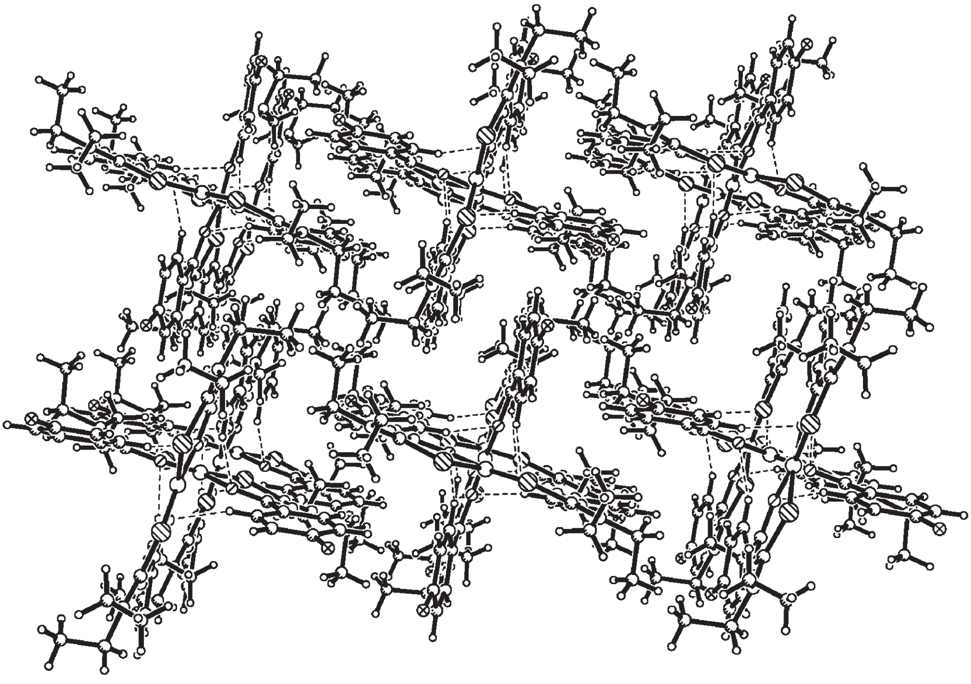

Figure 4. Packing diagram of NiL_2.

3.2. *Spectral properties*

The IR spectra of **1** show two bands at 3444 and 3167 cm^{-1}, which are ascribed to N–H stretching frequencies. A strong band at 1683 cm^{-1} is assigned to the C=O vibration, while C=S is observed at 1268 cm^{-1}, which has a red shift of 10 cm^{-1} compared with 1278 cm^{-1} in free thiourea HL. This indicates coordination of the thionyl group with Cu(I). The IR spectra of **2** show that the NH stretching vibration at 3290 cm^{-1} in the free ligand disappears in NiL_2 and the C=O band at 1646 cm^{-1} is not observed in the complex, the C=S band at 1278 $\mathrm{cm^{-1}}$ in the free ligand has shifted to 1216 $\mathrm{cm^{-1}}$ and the low-frequency shifts indicate coordination of the metal by S and O.

The ^{1}H NMR spectra of the complexes are in agreement with the results of the IR spectra and the X-ray single crystal diffraction. The N–H at 8.71 ppm in the free ligand shifts to 10.28 ppm in **1** and disappears in **2**. The methyl protons are observed at δ $1.18 \sim 1.60$ ppm in both compounds. Two resonances at 3.46 and 3.76 ppm are due to protons of the methylene groups. The proton peaks of benzene are at 7.02 and 8.14 ppm and similar in the two complexes.

4. Conclusion

In many syntheses of copper complexes, irreversible Cu(II)/Cu(I)$^-$ redox was observed [19, 20]. In preparation of **1**, copper was reduced from Cu(II) to Cu(I); some HL ligands act as reducing agents, then the Cu(I)$^-$ was coordinated by other HL. In preparation of **2**, HL lost the proton from the acyl-substituted nitrogen by reaction with NaOAc and coordinates to Ni(II) as an anionic species forming the neutral complex. HL is a general bidentate ligand coordinating through the S and O atoms in **2**, whereas in **1** it is a relatively rare unidentate ligand coordinating only through the S. Koch and co-workers have reported monodentate S coordination of related ligands to Pt(II) [21, 22]. This significant difference in coordination behavior and molecular structure of **1** and **2** may be because in **1** the Cu(I)$^-$ ion is a soft acid, forming a more stable complex with the soft sulfur than the harder oxygen, but in **2**, the Ni(II) is intermediate and can be bonded not only to soft S but also to hard O.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 640898 and 633234. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/deposit

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