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Synthesis and crystal structure of a nickel complex with the bidentate ligand derived from condensation of acetylferrocene and *S*-benzylthiocarbamate

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NICKEL COMPLEX WITH THE BIDENTATE LIGAND DERIVED FROM CONDENSATION OF ACETYLFERROCENE AND *S*-BENZYL DITHIOCARBAZATE

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Reaction of the bidentate ligand (**HL**) generated from condensation of acetylferrocene and *S*-benzyl dithiocarbazate with nickel chloride hexahydrate afforded a new nickel complex $\text{Ni}(\text{HL})_2\text{Cl}_2$. Both compounds have been characterized by elemental analyses, ^1H NMR, IR and UV spectroscopies. Single-crystal X-ray analysis of the complex indicates that **HL** as a neutral bidentate ligand coordinates to the nickel atom via the imine nitrogen and thione sulfur atoms and the coordination geometry of the central metal is tetrahedral.

Keywords: Ferrocene; Dithiocarbazate; Ligand; Complex; Nickel; Crystal structure

INTRODUCTION

Metal complexes of *S*-alkyldithiocarbazate have been studied over the past two decades [1] not only because of their interesting coordination chemistry but also because of their pronounced biological activity against microbes, viruses and cancer cells [2–6]. Since the discovery of ferrocene in 1951, a considerable number of ferrocene derivatives have been prepared directly or indirectly from ferrocene and their properties have been investigated extensively. Among them, some have been reported to display biological activity and act as β -lactamase inhibitors [7,8]. Herein I report the synthesis and crystal structure of a nickel complex with the bidentate ligand (**HL**) derived from condensation of acetylferrocene and *S*-benzyl dithiocarbazate.

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EXPERIMENTAL

Reagents and General Procedures

All chemicals were of analytical grade and used without further purification. *S*-benzyl-dithiocarbamate and acetylferrocene were synthesized according to literature methods [2,9]. Progress of the reactions was monitored by TLC (silica gel H). ¹H NMR spectra were determined with an FT-80A and a Bruker Avance 300 spectrometer using TMS as an external standard in DMSO-*d*₆ and CDCl₃. IR spectra (KBr disks) were recorded on a Nicolet-5DX spectrophotometer in the range 400–4000 cm⁻¹. UV spectra were recorded with a Shimadzu UV-240 spectrophotometer using a solution in DMF. Analyses for C, H and N were carried out on an Elementa Vario EL III microanalytical instrument. Melting points were measured on a Yanagimoto instrument and were uncorrected.

Synthesis of the Ligand

S-Benzylthiocarbamate (1.98 g, 10 mmol) was added to a solution of acetylferrocene (2.28 g, 10 mmol) and a catalytic amount of *p*-TsOH (*ca* 10 mg) in 20 ml of benzene. The mixture was refluxed for 1 h in a Dean-Stark apparatus to remove water and then cooled to room temperature. The red crystals that formed were filtered off, washed with cold ethanol and dried *in vacuo*. Yield of **HL**: 2.76 g (87%), mp 146–147°C [10,11]. Anal. Calcd. for C₂₀H₂₀FeN₂S₂(%): C, 58.83; H, 4.94; N, 6.86. Found: C, 58.80; H, 4.83; N, 6.94. IR (KBr disk): $\nu(\text{NH})$ 3166 (s), $\nu(\text{C}=\text{N})$ 1594 (s), $\nu(\text{C}=\text{S})$ 1194 (w), $\nu(\text{C}-\text{S})$ 1037 (m), $\nu(\text{N}-\text{N})$ 961 (m) cm⁻¹. UV (nm, in DMF): λ_{max} ($\epsilon \times 10^4$) 282 (1.2) (B-band), 331 (2.2) (K-band), 442 (0.29) (CT-band). ¹H NMR (80 MHz, DMSO-*d*₆): δ 2.25 (s, 3H, CH₃), 4.2 (s, 5H, C₅H₅), 4.4 (d, 2H, CH₂), 4.4 [d, 2H, 2 (H³, H⁴) of C₅H₄ ring], 4.65 [d, 2H, 2 (H², H⁵) of C₅H₄ ring], 7.35 (m, 5H, C₆H₅), 12.2 (s, 1H, NH).

Synthesis of the Complex

A solution of NiCl₂·6H₂O (0.119 g, 0.5 mmol) in 5 ml of absolute ethanol was added dropwise to a stirred solution of the ligand **HL** (0.408 g, 1 mmol) in 20 ml of acetone. The mixture was refluxed for 0.5 h and then cooled to room temperature. The resulting solid was filtered off and recrystallized from a mixture of dichloromethane and petroleum ether to afford the brown complex Ni(**HL**)₂Cl₂. Yield: 0.582 g (90%). Mp 241°C. Anal. Calcd. for C₄₀H₄₀Fe₂N₄S₄NiCl₂(%): C, 50.77; H, 4.26; N, 5.92. Found: C, 50.93; H, 4.19; N, 5.86. IR (KBr disk): $\nu(\text{NH})$ 3439 (w, br), $\nu(\text{C}=\text{N})$ 1552 (vs), $\nu(\text{C}=\text{S})$ 1105 (m), $\nu(\text{C}-\text{S})$ 1030 (m), $\nu(\text{N}-\text{N})$ 992 (vs) cm⁻¹. UV (nm, in DMF): λ_{max} ($\epsilon \times 10^4$) 277 (3.45) (B-band), 365 (0.87) (K-band), 458 (0.10) (CT-band). ¹H NMR (300 MHz, CDCl₃): δ 1.86 (s, 6H, 2CH₃), 4.17 (s, 10H, 2C₅H₅), 4.28 [s, 4H, 2 (H³, H⁴) of C₅H₄ rings], 4.33 [s, 4H, 2 (H², H⁵) of C₅H₄ rings], 5.31 (s, 4H, CH₂), 7.35 (m, 10H, 2C₆H₅), 6.91 (s, 2H, 2NH). Single crystals for X-ray determination were obtained by slow evaporation of a solution of the complex in dichloromethane and petroleum ether.

Crystal Structure Determination

A black single crystal of the complex Ni(**HL**)₂Cl₂ was mounted on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$)

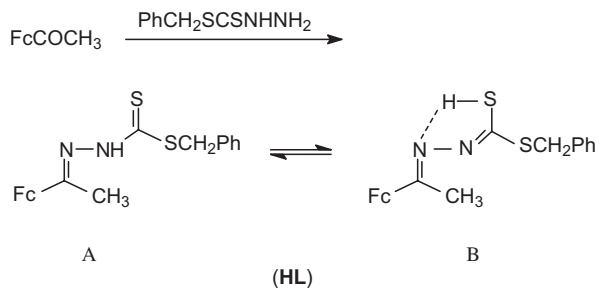
TABLE I Crystallographic data for the complex

Formula	C ₄₀ H ₄₀ Cl ₂ Fe ₂ N ₄ NiS ₄
Formula weight	946.31
Crystal size (mm)	0.4 × 0.3 × 0.3
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>
Unit cell dimensions	
<i>a</i> (Å)	10.790(2)
<i>b</i> (Å)	17.400(4)
<i>c</i> (Å)	21.900(4)
α (°)	90.00
β (°)	91.84(3)
γ (°)	90.00
<i>V</i> (Å ³)	4109.5(14)
<i>Z</i>	4
<i>D</i> _c (g cm ⁻³)	1.530
<i>F</i> (000)	1944
<i>T</i> (K)	293(2)
μ (Mo K α) (mm ⁻¹)	1.518
Scan mode	$\omega - 2\theta$
θ range (°)	1.50 to 24.97
Limiting indices	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 20, -26 ≤ <i>l</i> ≤ 26
Reflections collected	7627
Independent reflections	7216
No. of parameters refined	482
Absorption correction	Multiscan
Final <i>R</i> indices [<i>I</i> > 2.0 σ (<i>I</i>)]	<i>R</i> = 0.0546, <i>R</i> _w = 0.1535
<i>R</i> indices (all data)	<i>R</i> = 0.1083, <i>R</i> _w = 0.1827
Goodness-of fit	0.979
Largest peak and hole (e Å ⁻³)	1.176 and -0.497

TABLE II Selected bond distances (Å) and angles (°) for the complex

<i>Bond distances</i>			
Ni–N(1)	1.924(5)	C(3)–N(4)	1.274(7)
Ni–N(2)	1.928(5)	C(3)–S(2)	1.739(6)
Ni–S(3)	2.154(2)	C(3)–S(4)	1.741(7)
Ni–S(4)	2.151(2)	C(4)–S(2)	1.814(7)
Fe(1)–C(31)	2.029(7)	C(5)–C(6)	1.505(8)
Fe(1)–C(41)	2.041(5)	N(2)–C(6)	1.293(7)
Fe(2)–C(53)	2.042(6)	N(2)–N(3)	1.407(6)
Fe(2)–C(63)	2.018(7)	C(7)–N(3)	1.271(7)
C(1)–C(2)	1.499(8)	C(7)–S(3)	1.729(6)
N(1)–C(2)	1.303(7)	C(7)–S(1)	1.756(6)
N(1)–N(4)	1.406(6)	C(8)–S(1)	1.806(8)
<i>Bond angles</i>			
N(1)–Ni–N(2)	100.4(2)	N(2)–Ni–S(3)	86.3(2)
N(1)–Ni–S(3)	164.8(1)	N(2)–Ni–S(4)	165.4(1)
N(1)–Ni–S(4)	86.4(1)	S(3)–Ni–S(4)	90.29(7)

at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares methods based on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. All computations were carried out using the *SHLXTL* program package [12]. An ORTEP drawing was made with ORTEP-3 for Windows [13]. Crystal structure data and refinement details are summarized in Table I. Selected bond distances and angles are listed in Table II.



SCHEME 1 Synthesis of the ligand.



SCHEME 2 Synthesis of the complex.

RESULTS AND DISCUSSION

Reaction of acetylferrocene and *S*-benzylthiocarbamate in refluxing benzene with removal of water affords the ligand **HL** as bright red crystals in a good yield (Scheme 1). **HL** reacts with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to form the brown complex $\text{Ni}(\text{HL})_2\text{Cl}_2$ (Scheme 2). The ligand and its nickel complex were characterized by elemental analyses, ^1H NMR, IR and UV spectroscopies.

In the IR spectrum of the ligand, bands at *ca* 3166, 1594, 1194, 1037 and 962 cm^{-1} can be assigned to $\nu(\text{NH})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{S})$, $\nu(\text{C}-\text{S})$ and $\nu(\text{N}-\text{N})$, respectively. However, in solution the ligand shows an absorption at 2538 cm^{-1} that is due to the $\nu(\text{S}-\text{H})$ band [1]. Therefore, the ligand remains in the thioketo form in the solid state, but in solution it may exist as an equilibrium mixture of both the thioketo and thiol tautomeric forms as shown in Scheme 1 [1,2]. The IR spectrum of the complex shows the $\nu(\text{NH})$ band at 3439 cm^{-1} , indicating that the ligand is coordinated to the nickel ion in a neutral form (A in Scheme 1), and this is further supported by the ^1H NMR spectrum. Furthermore, shifts of $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ bands in the spectrum of the ligand to lower frequencies, 1552 and 1105 cm^{-1} , respectively, in the complex, suggest that **HL** is a bidentate ligand containing azomethine nitrogen and thione sulfur donor atoms, in agreement with the X-ray analysis as described below [1,14].

In the UV spectra of the ligand and its complex, three absorptions attributed to B, K and CT bands are observed, respectively. Interestingly, the B-band exhibits a hypsochromic shift whereas the K-band undergoes a bathochromic shift compared with that of the free ligand [15,16]. However, against theoretical expectation, the tetrahedral complex shows no d-d absorption, because the weak d-d transition is obscured by other intense absorptions [15,16].

^1H NMR signals of the complex, except the CH_2Ph groups, show high-field shifts compared with those of the ligand, which may result from the fact that these hydrogen atoms lie in shielding cone-shaped areas of benzene and/or cyclopentadienyl rings, as shown in Fig. 1 [17]. As the complex displays slightly broad absorptions, it may be paramagnetic and therefore the coordination geometry of the metal ion is planar distorted. The four donor atoms about the $\text{Ni}(\text{II})$ ion are tetrahedral [18]. This conclusion is firmly supported by the crystal structure of the complex.

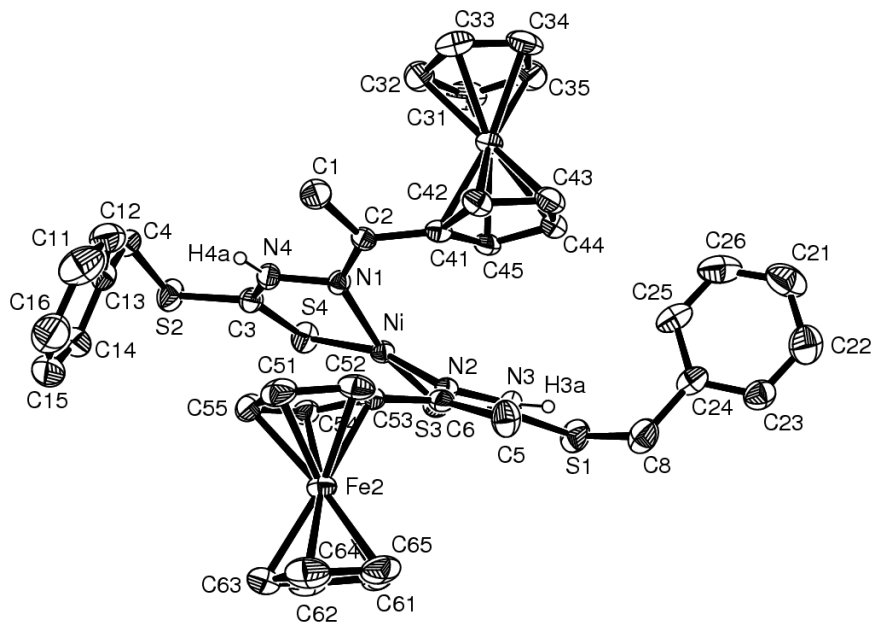


FIGURE 1 Crystal structure of the complex. Two Cl anions are omitted for clarity.

As shown in Fig. 1, the complex consists of two neutral bidentate ligands (**HL**), each of which coordinates to the Ni(II) ion via the imine nitrogen and thione sulfur atoms, and two disordered chlorides. The coordination geometry of the central metal ion is a distorted tetrahedron, the angles of N(1)–Ni–S(3) and N(2)–Ni–S(4) being 164.8(1) and 165.4(1)°, respectively. Interestingly, both ferrocenyl groups in the complex are *anti* to each other, thus minimizing steric repulsion between them [16]. The bond distances Ni–N and Ni–S [mean 1.926(5) and 2.152(2) Å] are very close to the values reported for a *trans* four-coordinate nickel complex containing *S*-benzylthiocarbazate [19]. The N–N bond distance [mean 1.406(6) Å] is equal to that of *S*-benzylthiocarbazate [20]. More double-bond character is present in the C–N bond of the HNCS₂ moiety as judged from its bond distance of 1.273(7) Å. This indicates a pronounced lone pair delocalization between carbon and nitrogen. More interestingly, formal C=S and C–S bonds in the HNCS₂ moiety also display remarkable electron delocalization. In addition, evidence of delocalization is further supported by the fact that the hybridized states of C and N atoms are all sp². It has been found that thioamides with –NHC(=S)– groups can coordinate to a metal ion in neutral and/or deprotonated forms, but so far no complexes containing neutral *S*-alkyl dithioamide ligands with –NHC(=S)–SR groups have been reported [14]. It should be noted that protons of thioamide NHCS₂ functional groups are not removed on complexation; although this is unusual, similar cases occur for metal complexes of thiosemicarbazone ligands [19,21].

The C=N bond distance [mean 1.298(7) Å] is longer than the single bond distance, suggesting that the imine nitrogen is involved in coordination, which is in agreement with above spectral evidence. The average distances of iron to carbon with and without side-chains [2.039(6) and 2.033(7) Å] in the ferrocenyl groups are shorter than the

2.045 Å in ferrocene [22]. In addition, no intermolecular hydrogen bonding about the NH groups in the complex is observed because of the steric hindrance from the methyl and benzyl groups.

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Supplementary Data

Crystallographic data (CCDC No. 221761) have been deposited with the Cambridge Crystallographic Data Centre and are available on request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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