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Synthesis and molecular structure of a novel ferrocene-containing macrocyclic acyl thiourea derivative

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Abstract

Reaction of 1,1′-bis[carbonyl isothiocyanate]ferrocene with 1,2-phenylenediamine affords both polymeric and macrocyclic products. The structure of the macrocyclic product was determined by single crystal X-ray diffraction analysis and compared with those of other ferrocene-containing acyl thiourea derivatives obtained previously. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene derivatives; Hydrogen bonding; Acyl thiourea; Crystal structures

1. Introduction

The synthesis, structure, electrochemistry and coordination behaviors of ferrocenophanes have attracted considerable attention in recent years [1–6]. Most of the ferrocenophanes reported to date feature crown ether or cryptand-like structures in which a ferrocenyl group acts as a redox spectator and provides a molecular ball-bearing skeleton [6].

With the presence of several electron-donating atoms, acyl thiourea compounds are known for their coordination particularly with transition metals [7–12]. Koch et al. studied the crystal structure of a series of acylthioureas and their complexes with platinum-group metals. The nature of the intramolecular hydrogen bond in these compounds was elucidated [8–13]. Beer et al. reported a ferrocenyl-containing acyl thiourea containing a strong intramolecular hydrogen bond and proposed that the hydrogen bond prevents it from binding $H_2PO_4^-$ as a host [14].

Since we reported the crystal and molecular structure of *N*-(ferrocenylcarbonyl)-*N*′-naphthyl thiourea in 1994 [15], our research group has been engaged in the synthesis, structural elucidation, electrochemistry, intramolecular hydrogen bonding studies and coordination behavior towards transition metals of a series of ferrocene-containing acyl thiourea derivatives [16–18]. Intramolecular hydrogen bonding between acyl and hydrogen atom on N′ (ferrocene-containing mono-substituted acyl thiourea derivatives **1** and ferrocene-containing disubstituted acyl thiourea derivatives **2**) was found to be common in this kind of compound (Scheme 1). A planar six-membered ring was often observed. While in the absence of hydrogen atom on N′, another inter-side chain hydrogen bond forms between carbonyl and hydrogen on *N*-(1-[*N*-formyl-*N*′,*N*′-disubstituted thiourea]-1′-[*N*′,*N*′-disubstituted amide]ferrocene derivatives **3**. In continuation of our interest, we have synthesized the novel ferrocenophane which incorporates an aromatic and acyl thiourea subunit in the bridging chain in addition to the ferrocene moiety. In an attempt to synthesize a new ferrocene-containing macrocyclic acyl thiourea by the reaction of 1,1′-bis[formylisothiocyanate]ferrocene with aromatic diamines, a contest between polymerization and cyclization was observed in the case of 1,2-phenylenediamine. We report herein a new synthesis, characterization, crystal structure and intramolecular hydrogen bonding studies of the unique ferrocene-containing macrocyclic acyl thiourea derivative.

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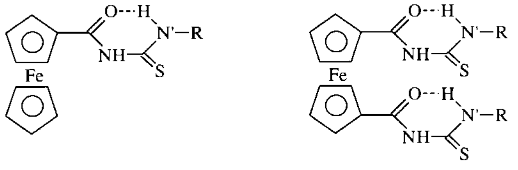
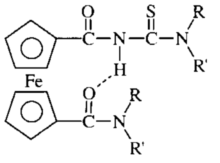
2. Results and discussion

The reaction of 1,1′-bis[formylisothiocyanate]ferrocene with 1,2-phenylenediamine affords both polymeric and cyclic products as described in Scheme 2.

Due to the poor solubility of the polymer, it precipitated from the reaction mixture. It is noteworthy that red crystals of the cyclic structure were obtained on concentration and cooling of the filtrate. The cyclic product appears to be the first example of the ferrocene-containing macrocyclic acyl thiourea to the best of our knowledge. Under the same reaction conditions, only polymer forms were isolated in the cases of 1,3- and 1,4-pheylenediamine. In 1,2-phenylenediamine, the distance of the two nitrogen atoms is comparable to that of the cyclopentadiene rings in ferrocene. However, in 1,3- and 1,4-phenylenediamines, the two nitrogen atoms are too far away to form a cycle without destroying the intramolecular hydrogen bonds. Consequently, the hydrogen bonding may be the driving force of the formation of the cyclic structure.

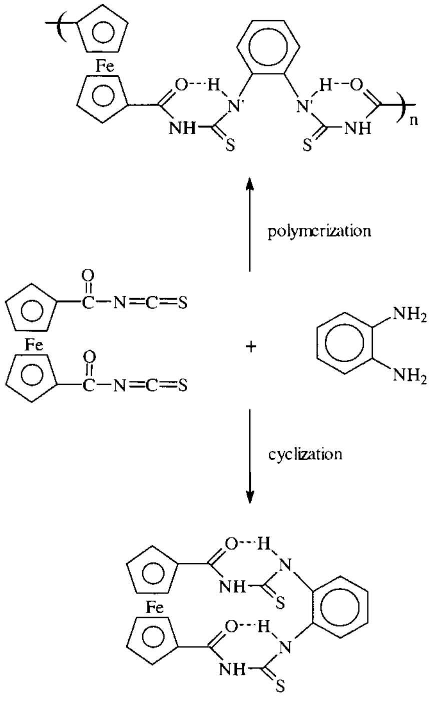


1. monosubstituted **2**. Disubstituted



3. Inter-side-chain hydrogen binding

Scheme 1. Intramolecular hydrogen bonding behavior in ferrocene-containing acyl thiourea derivatives: monosubstituted (**1**), disubstituted (**2**), inter-side-chain hydrogen binding (**3**).



Scheme 2. Contest between polymerization and cyclization.

A strong absorption at 1655.3 cm^{-1} is ascribed to the stretching vibration of the carbonyl groups. The decrease in wavenumber in comparison with normal carbonyl absorptions can be rationalized by both their conjugation with cyclopentadienyl rings and the formation of intramolecular hydrogen bonds. A very strong band at 1511.8 cm^{-1} is allocated as δ(CNH). ν(NCO) is observed at 1278.8 cm^{-1}. It is weaker than both ν(CO) and δ(CNH), due to a mixed vibration involving –N–C=O and N–H modes, which may result from the hydrogen bonding. The medium peak at 3405 cm^{-1} is attributed to the stretching vibration of NH groups adjacent to carbonyl groups. The broad and weak bands in the region 3010–3259 cm^{-1} are classified as the stretching vibration of N′–H as the result of hydrogen bonding. The medium band at 1423.4 cm^{-1} is supposed to be ν(C=S) as reported before [16–18].

Like its acyclic analogs, the chemical shifts of the protons on N′ which forms hydrogen bonds appears at 11.68 ppm while that of the protons on the nitrogen atoms adjacent to carbonyl groups is observed at 8.07 ppm. However, there exists some difference in the cyclopentadienyl proton absorption. In **2**, there are two singlets at 4.72 and 4.92 ppm corresponding to the *meta*- and *ortho*-hydrogens, respectively. The ^{1}H-NMR spectrum of **4** consists of three singlets in this region. The peaks appear at 4.57, 4.86 and 5.36 ppm with a ratio of 2:1:1. This can be explained as such: in acyclic **2**, the single bond between cyclopentadienyls and carbonyls can rotate freely. As a result, the two *ortho*-positions are non-differentiable in ^{1}H-NMR. While in **4**, the formation of the cyclic structure restricted the rotation, thus the two *ortho*-hydrogen atoms have different chemical environments. Owing to the shielding effects of the carbonyl groups, proton *a* should appear a little more upfield than *b*. The protons at *meta*-positions give signals at 4.57 ppm.

The cyclic voltammetric behavior of the macrocyclic product **4** was studied using CH_2Cl_2 as solvent. Attention was essentially centered on the $Fe^{II} \rightarrow Fe^{III}$ oxidation process in the product. The scan rate varied over the 100–200 mV s^{-1} range. The anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, as well as the half wave potential $E_{1/2}$ ($E_{1/2} = 0.5(E_{pa} + E_{pc})$) [19], were determined. For comparison, the parent compound ferrocene was also determined in the measurements. The cyclic voltammograph of **4** consists of one pair of redox

Table 1
Crystal and data collection parameters for compound **4**

Empirical formula	$C_{20}H_{18}O_3S_2N_4Fe$
Formula weight	482.35
Crystal color, habit	Red, prismatic
Crystal dimensions (mm)	0.2 × 0.3 × 0.3
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	10.546(1)
b (Å)	11.098(3)
c (Å)	9.370(2)
α (°)	114.26(2)
β (°)	95.87(2)
γ (°)	91.38(2)
V (Å^3)	992.0(4)
Z	2
D_{calc} (g cm^{-3})	1.615
μ(Mo–K$_\alpha$) (cm^{-1})	10.02
Diffractometer	Rigaku AFC7R
Radiation	Mo – K$_\alpha$ ($\lambda = 0.71069$ Å)
Temperature (K)	293 ± 1
Scan type	ω–2θ
Scan width	($0.89 + 0.30\tan\theta$)
$2\theta_{max}$ (°)	50
Reflections measured	Total 3710, unique 3499
$\Delta\rho$ (e$^-$ Å^{-3})	0.81/−0.53
Goodness-of-fit	2.38
R	0.054
R_ω	0.071

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_\omega = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)]^{1/2}$.

peaks with $E_{1/2}$ at 0.980 V (vs. SCE), which is higher than that of unsubstituted ferrocene (0.428 V), indicating that the side chains exert an electron-withdrawing effect on the ferrocene unit and result in a decrease of its electron density. The experimentally determined anodic and cathodic peak current (i_{pa} and i_{pc}) ratio i_{pc}/i_{pa} reaches 0.24, reflecting its poor redox reversibility.

Single crystal X-ray diffraction reveals that the intramolecular hydrogen bonds still exist in the two acyl thiourea spacers between ferrocenyl and phenyl units in the macrocyclic structure. Table 1 shows crystal and data collection parameters. Selected bond distances and angles are listed in Table 2. In each molecule, there exists two independent intramolecular hydrogen bonds between the carbonyl oxygen and the hydrogen atom on N′ in either –C(O)–NH–C(S)–N′H– moiety, forming two six-membered rings. The planar rings are approximately in the same plane with the cyclopentadienyl rings to which they are attached. The phenyl ring is basically perpendicular to the ferrocenyl unit. The molecular structure of compound **4** is depicted in Fig. 1. Tables 3 and 4 list the least-square planes of relevant groups and the dihedral angles between them.

In comparison with the molecular structure of **2**, we can find in **4** larger dihedral angles between the two cyclopentadiene planes and the hydrogen bonding planes. This cyclic tension may be responsible for its poor reversibility in cyclic voltammetry.

The sandwich structure of ferrocene has attracted much attention from researchers in molecular recognition [3,4,6,14]. The two coplanar cyclopentadienyl rings may rotate with respect to each other about the iron center. As long as there are suitable functional groups for the substrate to bind on the substituents in the 1,1′-disubstituted ferrocene system, the side chains can rotate to the optimal spatial arrangement selectively and organize the correct conformation as a receptor, in spite of steric hindrances, thus providing an element for molecular recognition [1–4]. We determined the crystal structure of the coordination compound of copper chloride and **2**. Copper(II) was reduced to copper(I) during the coordination process. The two sidechains of **2**, instead of enclosing copper(I) within a ball, rotate to the inverse side of ferrocene and form an infinite chain with copper(I). Three sulfur and one chloride coordinate to copper(I) in a tetragonal configuration with a strict C_3 symmetric factor. The entire molecule is an interlocked polymer [7]. As the two sidechains in **4** are fixed by the macrocycle structure, we synthesized its coordinate compounds with bivalent transition metal ions. However, their solubility in common organic solvents is very poor. This hinders further investigation.

3. Experimental

3.1. General procedures

All the reagents were of analytical grade. Elemental analysis for C, H, N was performed on a CHN-CORDERM7-3 autoanalyzer. Melting points were determined on a PHMK melting point apparatus (made in Germany) and uncorrected. ^{1}H-NMR spectra were recorded on a JEOLFX-90QNMR, using $CDCl_3$ as solvent, TMS as internal standard. IR spectra were carried out with a Nicolet-FT-IR5-DX infrared spectrophotometer using KBr pellets. Cyclic voltammetric experiments were performed on a BAS-100B electrochemical analyzer equipped with a three-electrode assembly with 0.1 mol l^{-1} n-Bu_4NPF_6 as support electrolyte and CH_2Cl_2 as solvent. The working electrode was a platinum disk 1.5 mm in diameter embedded in a cobalt glass seal and was polished consecutively with polishing alumina and diamond suspensions between runs. The reference electrode was a KCl saturated calomel electrode. A platinum filament was used as an auxiliary electrode. The solutions were saturated and blanketed with N_2 before the first scan. Measurements were made at room temperature.

3.2. Synthesis of 1,1′-bis(formylisothiocyanate)-ferrocene

KSCN (0.213 g, 2.2 mmol) was dissolved in 15 ml acetone and added dropwise to the 20 ml acetone solution of 0.311 g (1 mmol) Fc$(COCl)_2$ and refluxed for 30 min. A red solution obtained on filtration of KCl and Fc$(CONCS)_2$ was purified on silica thin layer chromatogaphy.

3.3. Synthesis of **4**

1,2-Phenylenediamine (0.0864 g, 0.8 mmol) dissolved in 20 ml acetone was added dropwise to the acetone

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

Atom	Atom	Distance	Atom	Atom	Distance		
Fe	C(3)	2.041(5)	N(4)	C(14)	1.410(7)		
Fe	C(4)	2.055(5)	N(4)	C(15)	1.378(7)		
Fe	C(5)	2.057(5)	C(2)	C(3)	1.466(7)		
Fe	C(6)	2.058(6)	C(15)	C(16)	1.479(7)		
Fe	C(7)	2.036(6)	O(1)	C(2)	1.213(6)		
Fe	C(16)	2.042(5)	O(2)	C(15)	1.228(6)		
Fe	C(17)	2.048(5)	N(1)	C(1)	1.393(7)		
Fe	C(18)	2.045(6)	N(1)	C(2)	1.382(7)		
Fe	C(19)	2.048(6)	N(2)	C(1)	1.340(7)		
Fe	C(20)	2.035(6)	N(2)	C(8)	1.445(7)		
S(1)	C(1)	1.662(5)	N(3)	C(13)	1.437(7)		
S(2)	C(14)	1.656(6)	N(3)	C(14)	1.336(7)		
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(1)	C(2)	N(1)	122.6(5)	C(1)	N(1)	C(2)	127.3(4)
O(1)	C(2)	C(3)	121.4(5)	C(1)	N(2)	C(8)	120.0(4)
N(1)	C(2)	C(3)	116.0(5)	C(13)	N(3)	C(14)	120.6(4)
Fe	C(3)	C(2)	123.2(3)	C(14)	N(4)	C(15)	127.2(4)
C(2)	C(3)	C(4)	128.3(5)	S(1)	C(1)	N(1)	119.9(4)
C(2)	C(3)	C(7)	124.4(5)	S(1)	C(1)	N(2)	125.0(4)
N(3)	C(14)	N(4)	116.4(5)	N(1)	C(1)	N(2)	115.2(5)
O(2)	C(15)	N(4)	122.6(5)	N(3)	C(13)	C(8)	117.4(4)
O(2)	C(15)	C(16)	122.0(5)	N(3)	C(13)	C(12)	121.3(5)
N(4)	C(15)	C(16)	115.4(5)	S(2)	C(14)	N(3)	125.2(4)
Fe	C(16)	C(15)	124.1(3)	S(2)	C(14)	N(4)	118.4(4)
C(15)	C(16)	C(17)	129.1(5)	N(2)	C(8)	C(9)	121.8(5)
N(2)	C(8)	C(13)	118.4(5)	C(15)	C(16)	C(20)	123.4(5)

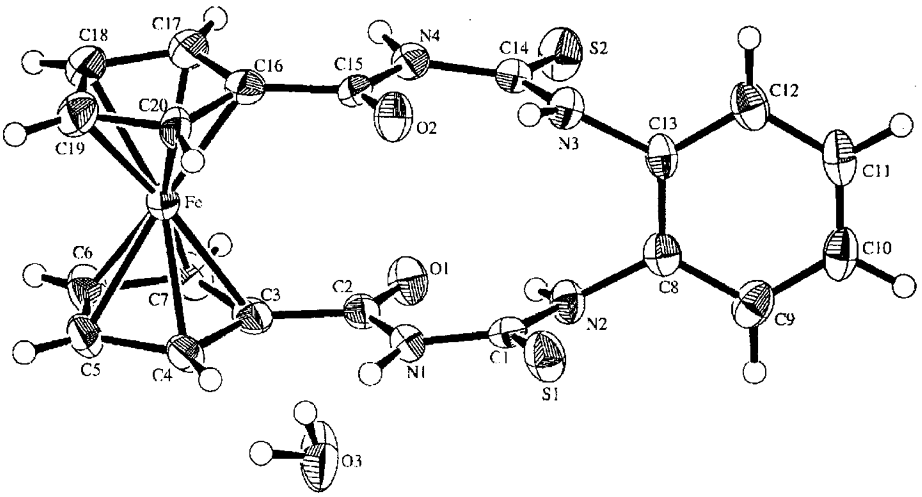


Fig. 1. Molecular structure of the title compound showing the atomic labeling scheme.

Table 3
Least-square planes between planes

Atoms of plane	Average deviation of an atom from the plane (Å)
1. C(8), C(9), C(10), C(11), C(12), C(13)	0.008(6)
2. S(2), O(2), N(3), N(4), C(14), C(15)	0.045(4)
3. S(1), O(1), N(1), N(2), C(1), C(2)	0.056(4)
4. C(3), C(4), C(5),C(6),C(7)	0.003(5)
5. C((16), C(17), C(18), C(19), C(20)	0.003(6)

Table 4
Dihedral angles between planes (°) between planes

Plane	1	2	3	4
2	94.93			
3	93.97	14.74		
4	85.07	11.92	12.00	
5	84.41	14.78	10.51	3.74

solution of 0.285 g (0.8 mmol) $Fc(CONCS)_2$. After filtration of the polymer, red crystals were obtained on concentration and cooling of the filtrate. Yield 41%, melting point 287–288 °C. Anal. Found: C, 51.92; H, 3.67; N, 12.45. Anal. Calc. for $C_{20}H_{18}FeN_4O_2S_2$: C, 51.72; H, 3.45; N, 12.07%. IR (cm^{-1}): ν_{N-H} 3405(m), $\nu_{N'-H}$ 3010–3259(w), $\nu_{C=O}$ 1655.3(s), $\nu_{C=S}$ 1323.4(m), δ_{CNH} 1511.8(vs), $\nu_{C(O)-N}$ 1278.8(m), and $\nu_{C(S)-N}$ 1161.3(vs). ^1H-NMR (δ, ppm): 4.57 (s, 4H, C_5H_4), 4.86 (s, 2H, C_5H_4), 5.36 4.86 (s, 2H, C_5H_4), 8.07 (s, 2H, N–H), 11.68 (s, 2H, N′–H), 7.9 (s, 4H, $2C_6H_4$).

4. Supplementary material

Crystallographic data for the structural analysis for compound **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157491. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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