

# (*E*)-Cinnamoylferrocene *S*-Benzylcarbodithioylhydrazone and its Chelates

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Received 15 December 1997

A new organometallic compound, (*E*)-cinnamoylferrocene *S*-benzylcarbodithioylhydrazone (HCfbc) and its chelates with some metal(II) acetates,  $M(\text{Cfbc})_2 \cdot n\text{H}_2\text{O}$  ( $M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{and } \text{Hg}^{2+}; n = 0-1$ ) were prepared and characterized by elemental analysis, IR, <sup>1</sup>H NMR, and molar conductance. It is shown that HCfbc appears to be a bidentate ligand with *trans* configuration and to coordinate the metal through the azomethine nitrogen and thioenolic sulfur atom.

The Schiff bases from hydrazinecarbodithioate and their complexes have strongly antitumour and antiviral activities [1–5], while the ferrocenyl group can improve medicinal properties [6]. Some ferrocene derivatives are excellent nonlinear optical materials [7], because they are strong electron donors and contain electron-flowing bridge. Due to their interesting structural character and wide-ranging uses, the studies of the Schiff base and ferrocene derivatives attracted many investigators' attention. In the present work, we will report on new organometallic ligand including both the above-mentioned functional groups and their chelates with the *trans* configuration.

## EXPERIMENTAL

### Measurements

The C, H, and N elements were determined with an Erba 1106 elemental analyzer. The IR spectra were recorded on a Nicolet 170 SX spectrophotometer as KBr discs in 200–4000  $\text{cm}^{-1}$   $\tilde{\nu}$ -region. <sup>1</sup>H NMR spectra were measured with an FT-80A or Bruker AM-400FT NMR spectrometer using  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  as a solvent and TMS as an internal standard. Molar conductance was made by a DDS-IIA conductometer in DMF at 20°C.

Acetylferrocene and benzyl hydrazinecarbodithioate were prepared by literature methods [8, 9].

### (*E*)-Cinnamoylferrocene

Acetylferrocene (9.8 g; 0.043 mol) and freshly distilled benzaldehyde (4.6 g; 0.043 mol) were dissolved

in 20  $\text{cm}^3$  of 95 % ethanol, to which the solution of NaOH (2.18 g), 95 % ethanol (10  $\text{cm}^3$ ), and water (20  $\text{cm}^3$ ) was added dropwise under stirring. Then it was stirred for 2 h at room temperature. The mixture was left to stand for several hours and dark red crystals were obtained, which were collected on a Büchner funnel, washed several times with water and recrystallized in 95 % ethanol. Yield 9.4 g (70 %), m.p. = 141–142°C.

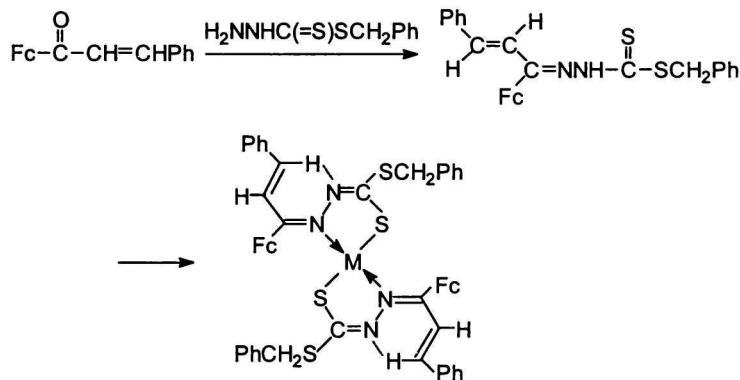
### (*E*)-Cinnamoylferrocene *S*-Benzylcarbodithioylhydrazone (HCfbc)

Two drops of concentrated hydrochloric acid were added into a solution of benzyl hydrazinecarbodithioate (0.674 g; 3.4 mmol) in 95 % ethanol (20  $\text{cm}^3$ ). Then (*E*)-cinnamoylferrocene (1.043 g; 3.3 mmol) in diethyl ether (20  $\text{cm}^3$ ) was added dropwise to this solution under stirring in an argon atmosphere for 0.5 h. The mixture was refluxed for about 24 h until a yellowish precipitate was produced, which was concentrated, cooled, filtered, washed several times with anhydrous ethanol and diethyl ether, and dried *in vacuo*. Yield 1.38 g (84.3 %).

### Preparation of Chelates

HCfbc (0.298 g; 0.6 mmol) in ethanol and diethyl ether ( $\psi_s = 1-3$ ) (30  $\text{cm}^3$ ) was added dropwise to a solution of  $M(\text{OAc})_2 \cdot n\text{H}_2\text{O}$  ( $M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{and } \text{Hg}^{2+}; n = 0-1$ ) (0.3 mmol) in anhydrous ethanol (8  $\text{cm}^3$ ), and refluxed for 16–30 h in a dark vessel. The reaction mixture was concentrated under reduced pressure, cooled, filtered, washed sev-

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Scheme 1. Proposed structure for the HCfbc and its chelates (Fc =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>).

Table 1. Elemental Analysis and Some Physical Properties of the Ligand and its Chelates

Chelate	Formula	$w_i$ (calc.)/%			Yield	D.p.	Colour
		$w_i$ (found)/%					
		C	H	N	%	°C	
HCfbc	C <sub>27</sub> H <sub>24</sub> N <sub>2</sub> S <sub>2</sub> Fe	65.3 65.0	4.9 4.8	5.8 6.0	84.3	110—112 (M.p.)	Yellowish
I	Co(Cfbc) <sub>2</sub>	61.9 61.4	4.4 4.4	5.4 5.2	88.7	168	Brown
II	Ni(Cfbc) <sub>2</sub>	61.9 61.4	4.4 4.4	5.4 5.4	93.5	124	Dark-Red
III	Cu(Cfbc) <sub>2</sub> · H <sub>2</sub> O	54.81 54.60	4.28 4.16	6.09 6.06	92.0	160	Brown
IV	Zn(Cfbc) <sub>2</sub>	61.5 61.2	4.4 4.3	5.3 5.3	94.3	165	Dark-Red
V	Cd(Cfbc) <sub>2</sub>	58.9 58.9	4.2 4.2	5.1 5.1	93.2	200	Brown
VI	Hg(Cfbc) <sub>2</sub>	54.5 54.4	3.9 3.9	4.7 4.7	98.0	170	Red-Brown

eral times with anhydrous EtOH and Et<sub>2</sub>O, and dried *in vacuo*. Yield 88—98 %.

## RESULTS AND DISCUSSION

The ligand (*E*)-HCfbc and its chelates are formed as shown in Scheme 1.

HCfbc and its chelates with transition metals are all coloured solids, stable in air, but photosensitive. Their solutions in organic solvent decompose easily either in atmosphere or when exposed to sunlight. HCfbc and its chelates are sparingly soluble in MeOH, EtOH, Et<sub>2</sub>O, Me<sub>2</sub>CO, insoluble in petroleum ether, benzene, CCl<sub>4</sub>, *etc.*, and soluble in CHCl<sub>3</sub>, DMF, DMSO, *etc.* Their elemental analyses and physical properties are shown in Table 1. The data of elemental analyses show that the ligand coordinates to central ions with double mole ratio. The formulae of the chelates agree with M(Cfbc)<sub>2</sub> · nH<sub>2</sub>O (*n* = 0—1).

## IR Spectra

The main features of the IR spectra of free HCfbc and its chelates are shown in Table 2. The bands appearing at 3211 cm<sup>-1</sup>, 1550 cm<sup>-1</sup>, 1459 cm<sup>-1</sup>, 1145 cm<sup>-1</sup>, and 966 cm<sup>-1</sup> are attributed to  $\nu$ (N—H),  $\delta$ (N—H),  $\nu$ (C=N),  $\nu$ (C=S), and  $\nu$ (N—N) [10, 11]. Characteristic bands of ferrocenyl group appear at 3086 cm<sup>-1</sup>, 1410 cm<sup>-1</sup>, 1105 cm<sup>-1</sup>, 824 cm<sup>-1</sup>, and 480 cm<sup>-1</sup> arising from  $\nu$ (C—H),  $\nu$ (C=C),  $\delta$ (C—H),  $\pi$ (C—H),  $g$ (Fe-ring), respectively [12]. The band due to  $\nu$ (S—H) has not been observed at about 2500 cm<sup>-1</sup> [13], which shows that the ligand exists in solid state in thioketo form. In addition, the band of  $\nu$ (C—H) in S—CH<sub>2</sub>— appears at 1257 cm<sup>-1</sup>, and the band at 966 cm<sup>-1</sup> attributed to  $\tau$ (C—H) of *trans*-HC=CH is overlapped with that due to  $\nu$ (N—N).

The IR spectra of the chelates show significant changes when compared with those of the free ligand.

**Table 2.** Some Characteristic IR Wavenumbers of the Ligand and its Chelates ( $\tilde{\nu}_i/\text{cm}^{-1}$ )

Com- pound	$\nu(\text{N—H})$	$\delta(\text{N—H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N—N}=\text{C})$	$\nu(\text{C—H})$ in C—SCH <sub>2</sub>	$\nu(\text{C—S})$	$\nu(\text{N—N})$	$\nu(\text{M—N})$	$\nu(\text{M—S})$	$\nu(\text{O—H})$
HCfbc	3211	1550 m	1459 vs	1483 m	1257 vs	1145 m	966 s	—		
	s, sh			( $\nu_{\text{C}=\text{NNHC}}$ )		( $\nu_{\text{C}=\text{S}}$ )				
<i>I</i>			1450 vs	1494 vs	1281 m	1031 s	964 s	456 w	374 m	
<i>II</i>	—		1450 vs	1494 vs	1284 w	1027 s	976 vs	456 w	377 m	
<i>III</i>		—	1451 vs	1482 vs	1289 vs	1030 s	986 vs	456 w	375 s	3200 br
<i>IV</i>		—	1451 vs	1494 vs	1282 m	1031 s	964 vs	456 m	379 w	
<i>V</i>	—	—	1452 m	1491 vs	1281 w	1048 w	996 vs	458 w	388 m	—
<i>VI</i>	—	—	1451 m	1493 vs	1281 w	1047 m	997 s	457 w	387 m	

s = strong; vs = very strong; m = medium; w = weak; br = broad.

**Table 3.** <sup>1</sup>H NMR Data ( $\delta$ ) and Molar Conductivities ( $\Lambda_m$ ) of the Ligand and its Chelates

Com- pound	N—H	C <sub>6</sub> H <sub>5</sub>	C <sup>α</sup> —H	C <sup>β</sup> —H	C <sub>5</sub> H <sub>4</sub>		C <sub>5</sub> H <sub>5</sub>	S—CH <sub>2</sub>	$\Lambda_m/$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
					2,5-H	3,4-H			
HCfbc	12.62 (s, 1H)	7.38—7.48 (m, 10H)	6.945 (d, 1H, $J = 10.2 \text{ Hz}$ )	7.09 (d, 1H, $J = 10.2 \text{ Hz}$ )	4.70 (s, 2H)	4.47 (d, 2H)	4.24 (s, 5H)	3.34 (s, 2H)	2.5
<i>I</i>									0.89 <sup>r</sup>
<i>II</i>	—	7.44—7.28 (m, 20H)	6.84 (s, 2H)	6.50 (s, 2H)	4.69 (m, 4H)	4.40 (m, 4H)	4.18 (m, 10H)	4.08 (s, 4H)	1.23
<i>III</i>									2.35
<i>IV</i>		7.14—7.43 (m, 20H)	7.10 (s, 2H)	7.04 (s, 2H)	4.22—4.63 (m, 8H)		4.16 (m, 10H)	4.08 (s, 4H)	1.38
<i>V</i>		7.30—7.39 (m, 20H)	6.27 (s, 2H)	6.10 (s, 2H)	4.77 (m, 4H)	4.50—4.57 (m, 4H)	4.10 (m, 10H)	4.10 (s, 4H)	1.07
<i>VI</i>		7.29—7.33 (m, 20H)	6.21 (s, 2H)	6.08 (s, 2H)	4.75 (m, 4H)	4.50—4.57 (m, 4H)	4.08 (m, 10H)	4.08 (s, 4H)	0.96

The peaks attributed to the  $\nu(\text{N—H})$ ,  $\delta(\text{N—H})$ , and  $\nu(\text{C}=\text{S})$  bands have disappeared and four new bands are observed at 1482—1494  $\text{cm}^{-1}$ , 1027—1048  $\text{cm}^{-1}$ , 456—458  $\text{cm}^{-1}$ , and 375—388  $\text{cm}^{-1}$ , probably due to large conjugate  $\pi$ -bond,  $\nu(\text{C}=\text{N—N}=\text{C})$ , and  $\nu(\text{C—S})$ ,  $\nu(\text{M—N})$ , and  $\nu(\text{M—S})$  [12] of new bonds formed on chelating while the  $\nu(\text{C}=\text{N})$  band at 1459  $\text{cm}^{-1}$  is shifted about 8  $\text{cm}^{-1}$  to a lower wavenumber, which shows that the C=N participates in coordination to metal ions. In addition, all other characteristic bands are practically unchanged both in position and intensity in comparison with those of the free ligand. It can be seen that the sulfur atom in thiocarbonyl (after thioenolization) and the nitrogen atom in C=N are coordinated to the central ions.

### <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR data for free ligand and its chelates are listed in Table 3. The solution of the ligand in DMSO exhibits unsubstituted cyclopentadienyl ring proton signals at  $\delta = 4.24$ , and substituted cyclopentadienyl ring proton signals at  $\delta = 4.70$  (2,5-position) and  $\delta = 4.47$  (3,4-position). The proton signal of the N—H at  $\delta = 12.62$  disappeared upon deuteration, which shows that the ligand exists still in thioketo form in DMSO. The proton signals of the phenyl ring and the S—CH<sub>2</sub> group appeared at  $\delta = 7.38$ —7.48 and  $\delta = 3.34$ , respectively. The signals at  $\delta = 7.77$  ( $J = 10.2 \text{ Hz}$ , 1H) and  $\delta = 7.09$  ( $J = 10.2 \text{ Hz}$ , 1H) attributed to H<sub>α</sub> and H<sub>β</sub> in —N=C—C<sup>α</sup>H=C<sup>β</sup>H, show it is the *trans* isomer [14].

The chelates *I* and *III*, Co(Cfbc)<sub>2</sub> and Cu(Cfbc)<sub>2</sub> H<sub>2</sub>O are paramagnetic, so their data of <sup>1</sup>H NMR have not been obtained. It can be seen from <sup>1</sup>H NMR of other chelates that the N—H proton signals disappeared after forming chelates. It is shown that the ligand undergoes thioenolization upon coordination. In addition, the proton signals of the H<sub>α</sub> and H<sub>β</sub> are shifted upfield. Most of other proton signals are also changed slightly, which is caused perhaps by the *d*-electrons of the central metal ions which donate electrons backing to empty  $\pi$ -orbital to form backing  $\pi$ -bond. Thus, the cloud density becomes more

dense and a stronger magnetic shielding appears. All this shows that the proton magnetic environment has changed forming chelates.

The molar conductivity data in Table 3 approach the values reported in the literature for nonelectrolytes [15].

Summarizing our results, HCfbc is a bidentate ligand with *trans* configuration, two molecules of which coordinate one metal(II) ion in thioenolic form, accompanied by the abstraction of two protons by two acetate ions. Thus we suggest a plausible structure for our chelates as shown in Scheme 1.

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