

Coordination Complexes of *S*-Benzyl β -*N*-(Ferrocenyl)methylenedithiocarbazate

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Received 2 January 1996

S-Benzyl β -*N*-(ferrocenyl)methylenedithiocarbazate (HBfm) and its coordination complexes, $M(\text{Bfm})_2 \cdot n\text{H}_2\text{O}$ ($M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{and } \text{Mn}^{2+}$) have been prepared by the reaction of HBfm with the transition metal(II) acetate in ethanol and are characterized by elemental analyses, molar conductivities, IR, NMR, UV spectra, and thermal analyses. The ligand coordinates to central ions in the thio-enolic form with the mole ratio 2:1.

Thio-Schiff bases and their metal complexes have received great attention during recent years [1–5]. A number of these metal chelates have shown anticancer and antitumour activities [6–8]. The bactericidal and fungicidal activities of the thio-Schiff bases may be due to the combination of the active thioketonic sulfur and the azomethine nitrogen with the fungi cells, as well as the inhibition to the fungi growth. Since the ligand is coordinated to the central metal atom through thioketonic sulfur and azomethine nitrogen and forms a chelate, perhaps it would increase fungitoxic action [9]. Many reports have shown that small changes in the ligands may lead to enhanced anticancer and antiviral activities of the metal complexes [10], *e.g.* the replacement of an aromatic group by the ferrocenyl moiety in penicillins and cephalosporins can improve their antibiotic activity [11, 12]. In the profound research of their inhibition effect on some bacteria and fungi, in this paper we report on the preparation and characterization of the *S*-benzyl β -*N*-(ferrocenyl)methylenedithiocarbazate (HBfm) and its complexes with some metal(II) ions.

EXPERIMENTAL

Materials and Measurements

All the solvents were dried by the previously reported method [13]. *S*-Benzyl dithiocarbazate and formylferrocene were prepared according to the literature method [14, 15]. All the solvents and other reagents were anal. grade.

IR spectra were recorded with a Nicolet-5DX spectrometer using KBr discs in the range 200–4000 cm^{-1} . UV spectra were measured with a Shimadzu

UV-240 spectrophotometer in the range 190–600 nm using a solution in DMF and NMR spectra on an FT-80A spectrophotometer using CDCl_3 and $\text{DMSO}-d_6$ as the solvents and TMS as an internal standard. Conductivity measurements were performed with a DDS-IIA conductometer with DMF as the solvent at room temperature. TG analyses were carried out on a DuPont 1090 thermal analyzer between room temperature and 800 °C in a nitrogen atmosphere.

Preparation of *S*-Benzyl β -*N*-(Ferrocenyl)methylenedithiocarbazate (HBfm) and Complexes $M(\text{Bfm})_2 \cdot n\text{H}_2\text{O}$

A solution of formylferrocene (0.02 mol) in ethanol (50 cm^3) was added to a solution of *S*-benzyl dithiocarbazate (0.022 mol) in ethanol (50 cm^3) containing several drops of glacial acetic acid, and refluxed for 4 h. The dark red precipitate was filtered off after cooling, washed with cold ethanol, recrystallized with benzene and dried *in vacuo*. Yield 87 %, m.p. = 160–162 °C.

An anhydrous ethanolic solution (20 cm^3) of $M(\text{OAc})_2 \cdot n\text{H}_2\text{O}$ (0.5 mmol) ($M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{and } \text{Mn}^{2+}$) was added to an anhydrous ethanolic solution (20 cm^3) of HBfm (1 mmol) and refluxed for 6 h. The dark red product was separated, washed with acetone and diethyl ether, and dried *in vacuo*. Yield > 80 %.

RESULTS AND DISCUSSION

The new complexes are dark-coloured solids, stable in the solid state, insoluble in water and non-polar organic solvents, but soluble in polar organic solvents such as DMF, CHCl_3 , and DMSO. The ele-

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Table 1. The Elemental Analyses and Some Physical Properties of the Ligand and Its Complexes

Compound	Formula	Colour	$w_i(\text{found})/\%$ $w_i(\text{calc.})/\%$			Yield %	M.p. °C	Λ^a $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
			C	H	N			
HBfm	$\text{C}_{19}\text{H}_{18}\text{N}_2\text{S}_2\text{Fe}$	Red	57.90 57.87	4.60 4.60	7.31 7.11	87	160—162	4.15
<i>I</i>	$\text{Cu}(\text{Bfm})_2 \cdot \text{H}_2\text{O}$	Dark red	52.79 52.57	4.04 4.18	6.74 6.45	82	174—176	2.35
<i>II</i>	$\text{Ni}(\text{Bfm})_2$	Dark red	54.07 53.99	3.79 4.05	6.63 6.63	82	214—217	5.23
<i>III</i>	$\text{Co}(\text{Bfm})_2 \cdot 3\text{H}_2\text{O}$	Dark red	50.72 50.73	4.01 4.48	6.17 6.23	80	170—172	4.45
<i>IV</i>	$\text{Zn}(\text{Bfm})_2$	Dark red	53.44 53.56	4.32 4.02	6.38 6.58	81	110—112	5.45
<i>V</i>	$\text{Cd}(\text{Bfm})_2$	Red	50.53 50.76	3.71 3.81	6.23 6.23	82	126—128	4.78
<i>VI</i>	$\text{Hg}(\text{Bfm})_2 \cdot \text{H}_2\text{O}$	Brown	45.31 45.40	3.31 3.60	5.56 5.57	80	148—149	4.55
<i>VII</i>	$\text{Mn}(\text{Bfm})_2$	Brown	54.46 54.23	3.88 4.07	6.78 6.66	80	164—168	4.50

a) Molar conductivities.

Table 2. Some Characteristic IR Data for the Ligand and Its Complexes

Compound	$\tilde{\nu}_i/\text{cm}^{-1}$							
	$\nu(\text{O—H})$	$\nu(\text{N—H})$	$\nu(\text{C=S})$	$\nu(\text{C=N})$	$\nu(\text{N—N})$	$\nu(\text{C—S})$	$g(\text{Fe—ring})$	$\nu(\text{M—S})$
HBfm	—	3081 w	1229 m	1597 vs	1084 m	—	487 vs	378 w
<i>I</i>	3310 w, sh	—	—	1592 vs	1106 w	568 w	482 vs	378 w
<i>II</i>	—	—	—	1584 vs	1105 w	564 w	484 vs	380 w
<i>III</i>	3400 w, sh	—	—	1583 vs	1106 w	565 w	492 vs	381 w
<i>IV</i>	—	—	—	1585 vs	1106 w	563 w	478 vs	372 w
<i>V</i>	—	—	—	1591 vs	1106 w	561 w	480 vs	386 w
<i>VI</i>	3415 w, sh	—	—	1590 vs	1106 w	564 w	485 vs	373 w
<i>VII</i>	—	—	—	1590 vs	1106 w	563 w	480 vs	369 w

vs - very strong, s - strong, m - medium, w - weak, sh - shoulder.

mental analyses and some physical properties of the ligand and its complexes are given in Table 1. The suggested structures of the complexes are shown in Fig. 1. The elemental analyses show the complexes have a 1:2 (metal:ligand) stoichiometry and the ligand HBfm coordinates to the metal ions in the thioenolic form as a bidentate donor. Their molar conductivity data, 2.35—5.45 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, show that all the complexes are nonelectrolytes [16], which is consistent with the suggested structures of complexes.

The important IR frequencies of the ligand and its complexes along with their relative assignments are given in Table 2. The bands of the ligand appearing at 3081 cm^{-1} , 1597 cm^{-1} , 1515 cm^{-1} , 1229 cm^{-1} , and 1084 cm^{-1} may be assigned to the vibrations of $\nu(\text{N—H})$, $\nu(\text{C=N})$, $\delta(\text{N—H})$, $\nu(\text{C=S})$, and $\nu(\text{N—N})$, respectively [17]. The ligand does not show any band of the $\nu(\text{S—H})$ at about 2500 cm^{-1} , which implies that the ligand maintains the thione form in the solid state [18]. The IR spectra of the chelates show significant changes as compared with that of the ligand.

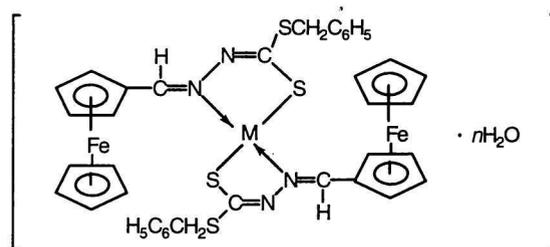


Fig. 1. Suggested structure of the complexes. $M = \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{and Mn}^{2+}$, $n = 0-3$.

The bands $\nu(\text{C=S})$, $\nu(\text{N—H})$, and $\delta(\text{N—H})$ disappear, which indicates that the ligand enolizes in solution and forms a bond between sulfur and metal(II) ions through replacing the proton in the mercapto group. The $\nu(\text{N—N})$ is shifted to higher frequency and $\nu(\text{C=N})$ to lower frequency. This information suggests that the azomethine nitrogen and thio-enolic sulfur

after deprotonation coordinate to the metal ion as a bidentate ligand. In addition, the characteristic frequencies of the ferrocenyl moiety appear at *ca.* 3073 cm^{-1} , 1469 cm^{-1} , 1068 cm^{-1} , 823 cm^{-1} , and 482 cm^{-1} . The appearance of $\nu(\text{O—H})$ of water in complexes *I*, *III*, and *VI* shows that these results are in accord with their elemental analyses.

The UV spectral data of the ligand and its complexes are given in Table 3. The K band ($\pi\text{—}\pi^*$ transition) and the R band ($n\text{—}\pi^*$ transition) of the ligand are observed at 284 nm and 333 nm, respectively, but in the complexes, a significant bathochromic shift occurred, resulting from chelation of the ligand to metal ion and forming a conjugate system which made $\pi\text{—}\pi^*$ and $n\text{—}\pi^*$ transitions easier. A broad and weak absorption of band III arises from transition of 3*d* electron on iron to nonbonding or antibonding orbitals of the cyclopentadienyl ring.

The ^1H NMR spectral data of the ligand and complex *V* are shown in Table 4. The signal of the N—H proton in the free ligand appears at $\delta = 10.43$ as a singlet, which disappears on deuteration of D_2O , however, in the spectra of the complexes it does not exist.

Table 4. ^1H NMR Data of the Ligand and $\text{Cd}(\text{Bfm})_2$

Compound	δ					
	N—H	HC=N	C_5H_4	C_5H_5	CH_2	C_6H_5
HBfm	10.43 (s, 1H)	7.63 (s, 1H)	4.46 (m, 2H) 4.66 (m, 2H) 4.48	4.24 (s, 5H)	4.39 (s, 2H)	7.30—7.42 (m, 5H)
$\text{Cd}(\text{Bfm})_2$	—	7.65 (s, 2H)	(m, 4H) 4.92 (m, 4H)	4.17 (s, 10H)	4.39 (s, 4H)	7.29—7.39 (m, 10H)

s - singlet, m - multiplet.

Table 5. Thermal Analysis Data of the Ligand and Some Complexes

Compound	Temperature interval $^{\circ}\text{C}$	Leaving group	Mass loss/%
			$w(\text{found})/\%$ ($w(\text{calc.})/\%$)
HBfm	170—230	SCH_2Ph	32.0 (31.2)
	230—490	CH=N—NH—C=S	20.0 (21.6)
	490—600	C_{10}H_9	33.0 (32.8)
	up to 800	residual Fe	15.0 (14.2)
<i>III</i> $\text{Co}(\text{Bfm})_2 \cdot 3\text{H}_2\text{O}$	230—260	two CH_2Ph and three H_2O	27.0 (26.3)
	260—490	two CH=N—N=C	12.0 (11.8)
	490—580	two C_{10}H_9	29.0 (28.7)
	580—730	S	4.0 (3.6)
	up to 800	residual CoS and FeS (1:2)	28.0 (29.6)
<i>VI</i> $\text{Hg}(\text{Bfm})_2 \cdot \text{H}_2\text{O}$	180—260	two CH_2Ph , two CH=N—N=C , S, and H_2O	33.0 (33.6)
	260—460	two C_{10}H_9	26.0 (25.7)
	460—700	HgS and two S	29.0 (29.5)
	up to 800	residual 2Fe	13.0 (11.1)

Table 3. UV Data of the Ligand and Its Complexes

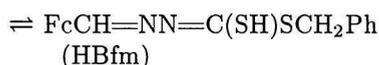
Compound	Characteristic absorption bands $\lambda(\text{DMF})/\text{nm}$		
	I	II	III
HBfm	284	333	461
<i>I</i>	308	349	463
<i>II</i>	314	367	489
<i>III</i>	315	366	486
<i>IV</i>	289	342	480
<i>V</i>	316	355	491
<i>VI</i>	—	330	471
<i>VII</i>	310	345	472

The result indicates that the ligand coordinates to the metal ions in the thio-enolic form.

The thermal properties of the ligand and some complexes were investigated by TG analyses and the data are listed in Table 5. The ligand begins to decompose at 170 $^{\circ}\text{C}$ and loses $\text{SCH}_2\text{C}_6\text{H}_5$, $\text{C}_2\text{H}_2\text{N}_2\text{S}$, and C_{10}H_9 at 170—230 $^{\circ}\text{C}$, 230—490 $^{\circ}\text{C}$, and 490—600 $^{\circ}\text{C}$,

respectively. The residues decompose completely at 800°C leaving Fe. The TG analyses of complex *III* and *VI* show that they lose their water at 180–260°C, which indicates that the water in molecule is coordinated. The thermal decomposition of other group is similar to that of the ligand. The mass loss at 460–700°C of complex *VI* was related to Hg.

Summarizing the above-mentioned results, in IR spectra of these complexes the $\nu(\text{C}=\text{S})$, $\nu(\text{N}-\text{H})$, and $\delta(\text{N}-\text{H})$ disappeared, a new band, $\nu(\text{C}-\text{S})$ exhibited and the $\nu(\text{C}=\text{N})$ was shifted to lower frequency compared with those of their ligand. In the ^1H NMR spectra of the ligand, the proton signal of the N—H disappeared on deuteration with D_2O , and it disappeared too, as expected after forming complexes by the thio-enolic form. So these results indicate that the ligand was thio-enolized firstly, then coordinated to metal cations accompanied by the leave of the active proton on SH and formation of the weak dissociated HOAc as follows



Thus, we propose a plausible structure for the complexes $\text{M}(\text{Bfm})_2 \cdot n\text{H}_2\text{O}$ as shown in Fig. 1.

Acknowledgements. This research has been supported by the National Science Foundation of China.

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