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# Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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# SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 34, No. 3, pp. 479–488, 2004

# Lanthanide Complexes with 1,1'-Diactylferrocene *bis*-2-Furoylhydrazone

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# ABSTRACT

A ligand, 1,1'-diacetylferrocene *bis*-2-furoylhydrazone (H<sub>2</sub>Bafh), and its lanthanide [Ln(III)] complexes,  $[Ln(H_2Bafh)_3] \cdot (ClO_4)_3 \cdot nH_2O$  [complexes **A**: Ln = La(III), Gd(III), Tm(III), Yb(III)], and [Ln(H<sub>2</sub>Bafh)Cl<sub>2</sub>] · Cl · *n*H<sub>2</sub>O [complexes **B**: Ln = Y(III), La(III), Nd(III), Gd(III), Tm(III)] were prepared and characterized by microanalyses, IR, <sup>1</sup>H NMR, and UV-VIS spectra, molar conductivity, and TGA analyses.

Key Words: Lanthanide; Furoylhydrazone; Diactylferrocene.

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# INTRODUCTION

Coordination compounds of acylhydrazones of ferrocene derivatives with lanthanide and transition metals have been prepared and researched as bioactivities inhibitors.<sup>[1–10]</sup> A few reports<sup>[1–4]</sup> have indicated that replacement of aromatic groups by the ferrocenyl moiety in penicillin and cephalosporin has improved their antibacterial activity. Several papers<sup>[5–10]</sup> have indicated that 2-furoylhydrazines and their metal complexes act as superior inhibitors of bacteria and fungi. In the present work, we report the synthesis and characterization of the ligand, 1,1'-diacetylferrocene *bis*-2-furoylhydrazone (H<sub>2</sub>Bafh, Fig. 1), and its complexes with lanthanide.

#### **RESULTS AND DISCUSSION**

The analytical data in Table 1 indicates that two kinds of complexes (complexes **A** and complexes **B**) form with a keto group in each. The ratio of ligand to metal is 3:1 in complexes **A** and 1:1 in complexes **B**. The molar conductivities of complexes **A** is  $205-271 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in DMF, and of complexes **B** is  $76-99 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , which indicates that complexes **A** and complexes **B** are 3:1 and 1:1 electrolytes, respectively.<sup>[11]</sup> A summary of the data for each complex is given in Table 1.

$$3H_2Bafh + Ln(ClO_4)_3 + nH_2O \rightarrow [Ln(H_2Bafh)_3](ClO_4)_3 \cdot nH_2O$$
 (1)  
Complexes A

$$H_2Bafh + LnCl_3 + nH_2O \longrightarrow [Ln(H_2Bafh)Cl_2]Cl \cdot nH_2O$$
Complexes B
(2)

All complexes are soluble in DMF, DMSO, acetone, methanol, ethanol, chloroform, and methylene chloride, and slightly soluble in benzene and



Figure 1. Synthesis of the ligand H<sub>2</sub>Bafh.

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	Table 1.	Yields, ele	emental analy	'ses, and ph	iysical prope	rties of th	e complexes.			
		Formula	Four	nd (calcd.,	(%)	Vield		d (I	<b>A</b> a	
No.	Formula	weight	С	Н	Z	(%)	Color	ά C) C	$(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol})$	$^{-1})$
(1)	$La(H_2Bafh)_3(ClO_4)_3 \cdot 5H_2O$	1,986.2	43.5 (43.5)	3.7 (3.9)	8.3 (8.5)	61	Red brown	240	205.9	
(5)	C721176C131 C3L0112C29 Gd(H2Bafh)3(CIO4)3 · 5H2O C H CI E, CAN O	2,004.5	43.2 (43.1)	3.7 (3.8)	8.1 (8.4)	74	Red brown	241	220.3	
(3)	$C_{72}H_{76}C_{13}U_{33}C_{33}C_{29}$ Tm(H <sub>2</sub> Bafh) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	1,980.1	43.4 (43.7)	3.5 (3.7)	8.2 (8.5)	57	Red brown	244	270.3	
(4)	$V_{72}H_{72}U_{3}F_{51}N_{12}U_{27}IIII$ Yb(H <sub>2</sub> Bafh) <sub>3</sub> (ClO <sub>4</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	1,984.2	43.2 (43.6)	3.5 (3.7)	8.2 (8.5)	51	Red brown	244	224.6	
(2)	$C_{72}H_{72}Cl_3Fe_3N_{12}O_{27}Yb$ Y(H_Bafh)Cl_3 · H_2O C II CII T_2N O Y	9.669	41.1 (41.2)	3.4 (3.5)	7.9 (8.0)	65	Brown	248	76.2	
(9)	C24H24CL3FEN4U5 I La(H2Bafh)Cl3·H2O C U CI Ed AN O	749.5	38.2 (38.4)	3.2 (3.2)	7.3 (7.5)	57	Brown	250	84.2	
6	C24H24CL3FCL41V4O5 Nd(H2Bafh)Cl3+2H2O C U CI FON NAO	772.9	37.6 (37.3)	3.3 (3.3)	7.2 (7.2)	60	Brown	250	88.7	
(8)	$C_{24}H_{26}C_{13}H_{21}C_{14}H_{20}C_{6}$ $Gd(H_2Bafh)Cl_3 \cdot H_2O$	767.8	37.3 (37.5)	3.1 (3.2)	7.2 (7.3)	63	Brown	248	98.5	
6)	C24H24U3F600N4U5 Tm(H2Bafh)Cl3 · H2O C24H24Cl3FeN4O5Tm	779.5	36.8 (37.0)	3.1 (3.1)	7.1 (7.2)	55	Brown	245	92.7	
<sup>a</sup> Mola	ar conductance were measured ir	1 a concenti	ration of 1.0	$\times 10^{-4}$ mol	l dm <sup>-3</sup> in DN	AF solutio	n.			

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diethyl ether. Solutions of all the complexes in the above solvents (except for benzene and diethyl ether) are dark-brown in color.

# **IR Spectra**

The important IR frequencies for H<sub>2</sub>Bafh and the nine complexes along with their relative assignment are listed in Table 2. The IR spectra of the complexes show significant changes as compared to the free ligand. The strong broad band at  $3400-3550 \text{ cm}^{-1}$  assigned to  $\nu(O-H)$  is present in each of the complexes, showing that there are some water molecules in the complexes. The very strong absorption band of the ligand at  $1670 \text{ cm}^{-1}$  assigned to  $\nu(C=O)$  is shifted to lower frequency by  $10-40 \text{ cm}^{-1}$  which indicates that the oxygen atom of the carbonyl group has coordinated to the lanthanide ion in the keto-form.<sup>[12]</sup> Two strong bands at 1097-1102 and  $612-620 \text{ cm}^{-1}$  are assigned to the  $\nu_3$  and  $\nu_4$  characteristic absorption bands of  $CIO_4^-$  in complexes **A**.

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

The <sup>1</sup>H NMR chemical shifts of  $H_2Bafh$  and its chelate compounds (1) and (5) are given in Table 3. It can be seen that the signals of all protons in the complexes are shifted upfield as compared to that of the free ligand.

*Table 2.* IR absorption frequencies  $(cm^{-1})$  of the ligand and its complexes.

				ClO <sub>4</sub>	-
Complex	$\nu$ (N–H)	ν(C==0)	$\nu(C=N)$	$\nu_3$	$\nu_4$
H <sub>2</sub> Bafh	3,375 w	1,670 vs	1,591 vs	_	_
(1)	3,371 w(sh)	1,630 s	1,589 vs	1,097 vs,br	612 m
(2)	3,369 w(sh)	1,644 s	1,590 vs	1,102 vs,br	623 s
(3)	3,364 w(sh)	1,657 s	1,597 vs	1,099 vs,br	623 s
(4)	3,379 w	1,647 s	1,589 vs	1,097 vs,br	621 m
(5)	3,358 s(sh)	1,660 vs	1,590 vs	_	
(6)	3,362 s(sh)	1,644 s	1,589 vs	_	
(7)	3,364 s(sh)	1,639 s	1,589 vs	_	
(8)	3,368 s(sh)	1,640 s	1,588 vs	_	_
(9)	3,365 s(sh)	1,649 s	1,589 vs		—

*Notes*: vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder.







*Table 3.* <sup>1</sup>H NMR spectra of the ligand and its complexes ( $\delta$ , ppm, in DMSO- $d_6$ ).

No.	N=C-CH <sub>3</sub>	C5	$H_4$	$a^{\mathrm{a}}$	b	С	N–H
H <sub>2</sub> Bafh	2.24	4.50	4.78	7.92	7.33	6.72	10.35
	(s, 6H)	(s, 2H)	(s, 4H)	(s, 2H)	(br, 2H)	(br, 2H)	(br, 2H)
(1)	2.18	4.45	4.72	7.87	7.28	6.65	10.34
	(s, 18H)	(s, 12H)	(s, 12H)	(s, 6H)	(br, 6H)	(s, 6H)	(br, 6H)
(5)	2.15	4.35	4.72	7.45	7.05	6.32	10.26
	(s, 6H)	(br, 4H)	(br, 4H)	(s, 2H)	(br, 2H)	(s, 2H)	(br, 2H)

*Notes*: s = singlet, br = broad.

<sup>a</sup>H atoms in  $b = c_0^c a$ .

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The change is greater in compound (5) than in compound (1). The  $\pi$ -electron densities of the cyclopentadienyl rings are lower in compound (5), due to the ligand side chain coordination in the complexes. The results of the <sup>1</sup>H NMR spectra and the IR spectra suggest that the carbonyl group is coordinated with the central metal ion through the keto form.<sup>[12]</sup>

# **UV-VIS Spectra**

The UV–VIS spectra of the ligand and its complexes in DMF are shown in Table 4. The spectra of complexes A are similar to those of complexes B. The

	$C_{\rm ope} \propto 10^5$	Absorption bands $(\log \epsilon)^a$		
No.	$(\text{mol dm}^{-3})$	1	2	
H <sub>2</sub> Bafh	1.08	266.0 (4.39)		
(1)	5.25	266.3 (4.74)	306.2 (4.59)	
(2)	4.99	266.0 (4.88)	308.5 (4.75)	
(3)	5.01	266.2 (4.89)	308.2 (4.72)	
(4)	5.00	266.0 (4.68)	309.8 (4.36)	
(5)	5.03	266.4 (4.94)	306.7 (4.80)	
(6)	5.18	266.3 (4.62)	301.5 (4.45)	
(7)	4.97	266.2 (4.56)	306.4 (4.38)	
(8)	5.32	266.4 (4.85)	305.8 (4.66)	
(9)	4.88	266.5 (4.82)	308.2 (4.63)	

Table 4. UV-VIS spectral data (nm), in DMF.

<sup>a</sup>The units of the  $\varepsilon$  are mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>.



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very strong peak at 301-310 nm is attributed to the K band of the azomethine group in the complexes. Another very strong peak at 266-267 nm is attributed to the B band of the cyclopentadienyl ring in all of the compounds.

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# **TGA Analyses**

Thermal analysis data are listed in Table 5. It can be seen that all of the water molecules in the complexes are lost before 90 °C. Water molecules crystallize in the complexes at lower temperatures. An explosion occurred in complex (1) at 194 °C duo to the perchlorate leaving group.

The data above suggest that the ligand,  $H_2Bafh$ , is coordinated to Ln(III) in the neutral keto-form forming two types of complexes, complexes **A** or **B**.<sup>[12]</sup> When using lanthanide perchlorates, complexes **A** are formed, and when using lanthanide chlorides, the complexes **B** are formed. Water molecules crystallize in the lattice. It is suggested that complexes **A** and complexes **B** coordinate in a 3:1 and 1:1 mole ratio, respectively. The proposed structures of the complexes are given in Fig. 2.

## **EXPERIMENTAL**

## **Physical Measurements**

The physical measurements were carried out by literature procedures.<sup>[13]</sup>

No.	Temp. (°C)	Leaving group	Weight loss (%), found (calcd.)
H <sub>2</sub> Bafh	210-335	C <sub>4</sub> H <sub>3</sub> O–CONH	15.5 (16.2)
	335-425	CH <sub>3</sub> CN	7.8 (8.4)
	425-515	C <sub>5</sub> H <sub>4</sub> , C <sub>5</sub> H <sub>4</sub> C(CH <sub>3</sub> )NNHCOC <sub>4</sub> H <sub>3</sub> O	52.4 (57.4)
	Residue	Fe	18.9 (11.5)
(1)	25–90 194	5H <sub>2</sub> O Explosion	4.4 (4.5)
(7)	25-95	2H <sub>2</sub> O	4.5 (4.7)
	178-800	$2C_4H_3O$ –CONH, 2CH <sub>3</sub> CN, 2C <sub>5</sub> H <sub>4</sub>	63.7 (55.7)
	Residue	NdCl <sub>3</sub> , Fe	31.8 (39.7)

Table 5. TGA analysis data.



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Complexes A: Ln = La(III), Gd(III), Tm(III), Yb(III)



Complexes B: Ln = Y(III), La(III), Nd(III), Gd(III), Tm(III)

Figure 2. Proposed structure of the complexes.

# Synthesis of H<sub>2</sub>Bafh

1,1'-Diacetylferrocene was prepared by the method of Graham.<sup>[14]</sup> The ligand, 1,1'-diacetylferrocenyl *bis*-2-furoylhydrazone (H<sub>2</sub>Bafh), was prepared according to an improved method:<sup>[13]</sup> A mixture of 1,1'-diacetylferrocene





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(2.7 g, 0.01 mol) in 10 mL anhydrous ethanol and 2-furoylhydrazide (2.6 g, 0.02 mol) (1:2 molar ratio) in 15 mL anhydrous ethanol was heated at reflux for 10 hr until dark-red crystals appeared. The resulting solution was concentrated to a half its original volume, cooled to ambient temperature for 2 hr, filtered, the crystals washed with 95% ethanol, recrystallized from anhydrous ethanol, and dried in a vacuum to obtain H<sub>2</sub>Bafh; yield 4.4 g (89%); m.p. 210 °C (dec.).

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## **Preparation of Complexes A**

A solution of  $H_2Bafh$  (0.49 g, 1 mmol) in anhydrous ethanol (20 mL) was added drop-wise into a solution of  $Ln(ClO_4)_3$  (0.33 mmol) in anhydrous ethanol (30 mL) with stirring. The mixture was heated at reflux and triethyl orthoformate (5 mL) was added. The reaction mixture was continuously heated for 9 hr under reflux, concentrated to a half its volume, cooled to room temperature for 2 hr, filtered, the solid washed twice with ethanol and diethyl ether, respectively, and dried in a vacuum. A brown solid powder was obtained. The yield and microanalysis results of the complexes are listed in Table 1.

## **Preparation of Complexes B**

A solution of  $H_2Bafh$  (0.49 g, 1 mmol) in anhydrous ethanol (20 mL) was added drop-wise into a solution of  $LnCl_3$  (0.7 mmol) in anhydrous ethanol (40 mL) with stirring. The mixture was heated at 70–75 °C for 8 hr, concentrated to a half of its original volume, cooled to ambient temperature over-night, filtered, the solid washed twice with ethanol and diethyl ether, respectively, and dried in a vacuum. A brown solid was obtained. The yield and analytical data of the complexes are shown in Table 1.

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