The Chelates of Ferrocenecarbaldehyde Bicyclo[2,2,1]hept-5-en-2-ylcarbonylhydrazone with Lanthanide

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A new organometallic ligand, ferrocenecarbaldehyde bicyclo[2,2,1]hept-5-en-2-ylcarbonylhydrazone (Hbfh) and its lanthanide complexes [Ln(Hbfh)$_3$Cl$_2$]Cl $\cdot$ 4H$_2$O *1* (Ln = Y^{3+}, La^{3+}, Pr^{3+}, Sm^{3+}, and Er^{3+}) and [Ln(bfh)$_3$] $\cdot$ 2H$_2$O *2* (Ln = La^{3+} and Pr^{3+}) have been synthesized and characterized using elemental analyses, IR, ^{1}H NMR, and electronic spectra, molar conductivity, and TGA analyses. The ligand coordinates to the metal ion as a bidentate donor in the keto form or in the enolic form. The complexes coordinating in the enolic form are more thermally stable than in the keto form.

Coordination compounds of the hydrazone of ferrocene derivative with lanthanide and transition metal ions have been described [1—5]. However, the complexes derived from the reaction of hydrazone containing bicyclo[2,2,1]hept-5-en-2-yl moiety with lanthanide have not been reported yet. Recently, we have reported on some derivatives of bicyclo[2,2,1]hept-5-ene and their complexes of some transition elements [6]. In this paper, we will describe a new ligand, which contains ferrocenyl and bicyclo[2,2,1]hept-5-en-2-yl groups, and its lanthanide complexes.

(Hbfh, Fc = C$_5$H$_5$FeC$_5$H$_4$—)
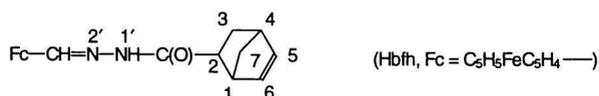
EXPERIMENTAL

Formylferrocene was prepared according to the literature [7]. Bicyclo[2,2,1]hept-5-en-2-ylcarbonylhydrazone was synthesized by the literature method [8]. Lanthanide chloride and other chemicals were reagent grade.

Elemental analyses of C, H, and N were performed with a Perkin—Elmer 240 analyzer. ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer in CDCl$_3$ or DMSO-d_6 solution with TMS as an internal standard. IR spectra were recorded on a FT-170SX spectrometer using KBr discs in the region $\tilde{\nu} = 200$—4000 cm^{-1}. TGA analyses were carried out with a Dupont 1090B thermal analyzer in a nitrogen current. Electronic spectra of compounds ($c = 10^{-5}$ mol dm^{-3}) were recorded on a Shimadzu UV-240 spectrometer in the region $\lambda = 190$—700 nm using DMF as a solvent at room temperature. Molar conductances were measured on a DDS–II conductometer in DMF solutions ($c \approx 10^{-3}$ mol dm^{-3}) at 20 °C. Melting points were determined on a Yanaco MP-500 apparatus, the thermometer was uncorrected.

The lanthanide content, after destroying the organic matter with sulfuric acid—nitric acid ($\varphi_r = 1:3$), was determined volumetrically with EDTA using ascorbic acid as a screening Fe^{3+} agent and xylenol orange as an indicator; chlorine was estimated gravimetrically as AgCl.

Elemental analyses and some physical properties of the ligand and its complexes are listed in Table 1.

Ferrocenecarbaldehyde Bicyclo[2,2,1]hept-5-en-2-ylcarbonylhydrazone (Hbfh)

The solution of bicyclo[2,2,1]hept-5-en-2-ylcarbonylhydrazine (1.5 g; 0.01 mol) and ferrocenecarbaldehyde (2.1 g; 0.01 mol) in 20 cm^3 of anhydrous ethanol was refluxed with stirring for 2 h. The resulting solution was concentrated to about 10 cm^3, the solid that appeared was filtered, washed twice with 95 % ethanol, and recrystallized from anhydrous ethanol. Yield 3.2 g (92 %) of Hbfh was obtained.

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

	Formula	Colour	D.t. °C	w_i(found)/% w_i(calc.)/% C	H	N	Ln	Cl	Λ (Ω^{-1} cm^2 mol^{-1})
Hbfh	$C_{19}H_{20}N_2OFe$	Red	172	65.47	5.72	7.91	–	–	1.87
				65.53	5.79	8.05			
I	La(Hbfh)$_3$Cl$_3$ · 4H$_2$O	Dark	173	49.87	4.86	6.11	10.06	7.67	76.5
	$C_{57}H_{68}Cl_3N_6O_7Fe_3La$	brown		50.26	5.03	6.17	10.20	7.81	
II	Pr(Hbfh)$_3$Cl$_3$ · 4H$_2$O	Brown	176	49.70	4.88	6.06	10.17	7.64	92.2
	$C_{57}H_{68}Cl_3N_6O_7Fe_3Pr$			50.19	5.02	6.16	10.33	7.80	
III	Sm(Hbfh)$_3$Cl$_3$ · 4H$_2$O	Brown	182	49.55	4.83	6.09	10.68	7.58	103.2
	$C_{57}H_{68}Cl_3N_6O_7Fe_3Sm$			49.86	4.99	6.12	10.95	7.74	
IV	Er(Hbfh)$_3$Cl$_3$ · 4H$_2$O	Brown	179	48.93	4.70	5.78	11.89	7.60	87.1
	$C_{57}H_{68}Cl_3N_6O_7Fe_3Er$			49.25	4.93	6.05	12.02	7.65	
V	Y(Hbfh)$_3$Cl$_3$ · 4H$_2$O	Brown	181	51.92	5.19	6.05	6.71	8.05	100.2
	$C_{57}H_{68}Cl_3N_6O_7Fe_3Y$			52.18	5.22	6.14	6.78	8.11	
VI	La(bfh)$_3$ · 2H$_2$O	Brown	176	55.71	4.88	6.67	11.34	–	29.5
	$C_{57}H_{61}N_6O_5Fe_3La$			56.27	5.05	6.90	11.42		
VII	Pr(bfh)$_3$ · 2H$_2$O	Brown	185	55.87	4.79	6.68	11.46	–	41.7
	$C_{57}H_{61}N_6O_5Fe_3Pr$			56.18	5.04	6.90	11.56		

Table 2. Important IR Frequencies of the Ligand and Its Complexes

Compound	$\tilde{\nu}_i$/cm^{-1} ν(C=O)	ν(C=N—N=C)	ν(C=N)	ν(C—O)	ν(N—N)
Hbfh[a]	1660 vs	–	1642 s	–	997 s
I	1640 s (sh)	–	1603 vs, br	–	1002 w
II	1638 s (sh)	–	1607 vs, br	–	1002 m
III	1648 m (sh)	–	1616 vs, br	–	1000 w
IV	1655 vs	–	1606 vs, br	–	1000 w
V	1659 vs	–	1596 vs, br	–	1000 w
VI	–	1610 s, br	1576 s	1252 w	1003 w
VII	–	1599 s	1565 (sh)	1253 w	1002 w

a) The ν(N—H) of Hbfh exhibits at $\tilde{\nu}$ = 3168 cm^{-1}; in complexes I—V, the bands ν(N—H) are overlapped with a broad strong band ν(O—H). vs – very strong, s – strong, m – medium, w – weak, sh – shoulder, br – broad.

Complexes 1 I—V

The solution of Hbfh (0.348 g; 1 mmol) in 20 cm^3 of hot anhydrous ethanol was added dropwise into a solution of lanthanide chloride (0.3 mmol) in 8 cm^3 of anhydrous ethanol with stirring. The mixture was refluxed for 8—12 h, cooled, filtered, and the filtrate was concentrated to 6—10 cm^3, then 20—30 cm^3 of ether was added into the solution under stirring. The resulting precipitate was separated by filtration, washed three times with ethanol—ether (φ_r = 1:4) and twice with ether, and dried under vacuum. Yield was above 50 %.

Complexes 2 VI, VII

The solution of Hbfh (0.348 g; 1 mmol) in 10 cm^3 of anhydrous ethanol was added into a solution of anhy-

drous lanthanide chloride (0.3 mmol) in 20 cm^3 of anhydrous ethanol, then 4 cm^3 of 2.5 × 10^{-4} mol dm^{-3} NaOEt—EtOH were added with stirring. The resulting solution was stirred under reflux for 4—6 h, the precipitate was filtered after cooling, washed successively with water, ethanol, and ether, and dried under vacuum. The brown solid was obtained. Yield was above 50 %.

RESULTS AND DISCUSSION

When the mixture of the ligand and lanthanide chloride in the mole ratio 3:1 was reacted in EtOH, two types of the complexes were obtained.
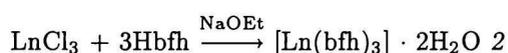
$$LnCl_3 + 3Hbfh \longrightarrow [Ln(Hbfh)_3Cl_2]Cl \cdot 4H_2O \quad 1$$

$$LnCl_3 + 3Hbfh \xrightarrow{NaOEt} [Ln(bfh)_3] \cdot 2H_2O \quad 2$$

Table 3. The ^{1}H NMR Data of the Ligand and its Complexes

No.	N—H	CH=N	C$_5$H$_5$	C$_5$H$_4$		δ_i					
						H-1	H-2	H-3	H-4	H-5, H-6	H-7
Hbfh	8.87	7.65	4.20	4.38	4.61	3.34	3.67	1.41—1.53	2.95	5.95—6.30	1.70—2.28
	(br, 1H)	(s, 1H)	(s, 5H)	(t, 2H)	(t, 2H)	(m, 1H)	(m, 1H)	(m, 2H)	(m, 1H)	(m, 2H)	(m, 2H)
I	8.84	7.80	4.20	4.37	4.60	3.21	3.50	1.19—1.60	2.70	5.80—6.25	1.70—2.15
	(br, 3H)	(s, 3H)	(s, 15H)	(t, 6H)	(t, 6H)	(m, 3H)	(m, 3H)	(m, 6H)	(m, 3H)	(m, 6H)	(m, 6H)
VI	–	7.84	4.21	4.36	4.60	3.23	3.52	1.16—1.60	2.71	5.82—6.20	1.70—2.09
		(s, 3H)	(s, 15H)	(t, 6H)	(t, 6H)	(m, 3H)	(m, 3H)	(m, 6H)	(m, 3H)	(m, 6H)	(m, 6H)

Table 4. Electronic Spectra of All Compounds

Compound	λ_{max}/nm (log$\{\varepsilon\}$)		
Hbfh	202 (3.41)	266 (4.51)	292 (4.30)
I	202 (2.95)	266 (4.60)	290—300 (4.43)
II	203 (3.68)	267 (4.73)	290—300 (4.40)
III	201	266 (4.69)	290—300 (4.19)
IV	203 (3.72)	267 (4.64)	290—300 (4.35)
V	202 (4.38)	266 (4.97)	290—300 (4.79)
VI	203 (4.24)	266 (4.87)	290—310 (4.69)
VII	202	267 (4.90)	290—310 (4.61)

All complexes are soluble in DMF, DMSO, ethanol, and methanol, sparingly soluble in acetone, and insoluble in petroleum ether. They are photosensitive in solution but stable to air when they are in dry solid. They can absorb the moisture under atmosphere, too. The analytical data indicate that only two kinds of complexes, the keto form *1* and the enolic form *2*, were isolated. In all complexes, the ratio of ligand to metal is equal to 3:1. Dissolving the complexes *1* and *2* in DMF afforded a dark-brown solution. The numerical values $\Lambda/(\Omega^{-1}\ cm^2\ mol^{-1})$ of molar conductivities of Hbfh, complexes *1* and *2*, are 1.9, 76.5—103.2, and 29.5—41.7, respectively, which indicates that in DMF solution Hbfh and complex *2* are nonelectrolytes and complex *1* is 1:1 electrolyte [9].

The important IR frequencies of the ligand and all complexes along with their relative assignments are listed in Table 2. The two kinds of complexes show significant changes as compared with the free ligand. The complex *1* shows that the very strong band at 1660 cm^{-1} assigned to ν(C=O) and the very strong band at 1642 cm^{-1} assigned to ν(C=N) are shifted to lower frequency by 1—22 cm^{-1} and 26—46 cm^{-1}, respectively, whereas the strong band at 997 cm^{-1} assigned to ν(N—N) is shifted to higher frequency by 3—6 cm^{-1}. This indicates that the oxygen atom of the carbonyl group and the nitrogen atom of the azomethine in the ligand coordinate to lanthanide ion in the keto form. Otherwise, the complex *2* shows significant changes as compared with that of the parent ligand. It can be seen that the bands due to N—H and C=O stretching vibrations disappeared in the spec-

tra of these complexes. Two new bands are observed around 1252 cm^{-1} and 1610 cm^{-1}, which can be assigned to ν(C—O) [10] and ν(C=N—N=C) [11], respectively. It is also found that the ν(C=N) band is shifted to a lower frequency by *ca.* 70 cm^{-1} while the ν(N—N) band is shifted to a higher frequency by *ca.* 6 cm^{-1}. Thus, it can be considered that the ligand undergoes enolization and coordinates to lanthanide ions in the enolic form in complex *2*. In addition, the characteristic frequencies of norbornenyl appear around 712 cm^{-1}, 1385 cm^{-1}, 2870 cm^{-1}, 2970 cm^{-1}, and 3050 cm^{-1} in the ligand and complexes.

The ^{1}H NMR chemical shifts [12] of Hbfh, *I* and *VI*, are given in Table 3. It can be seen that the proton signal of N—H disappeared in the complex *VI*. The signal of CH=N shifts downfield, which is due to some deshielding, by $\delta = 0.15$—0.19 compared with that of the parent ligand in the complexes *I* and *VI*. Other signals do not show significant changes as compared with those of the free ligand. It is suggested that the carbonyl group coordinates to central ions through the keto form for complex *I* and the enolic form for complex *VI*, which is consistent with the IR spectra.

Electronic absorption spectra of the ligand and its chelates in DMF are shown in Table 4. The spectra of the two kinds of complexes *1* and *2* are similar to that of the ligand. A shoulder peak at $\lambda_{max} = 290$—310 nm is attributed to the K band of the azomethine for complexes *I—V*, and for complexes *VI* and *VII* it is attributed to the band of the π—π^* transition of the conjugation system O—C=N—N=C [13]. The very

Table 5. Thermal Analysis Data

Compound	d.t./°C	Leaving group	Mass loss/% found (calc.)
Hbfh	172—248	C_5H_6	18.7 (19.0)
	248—416	$CH_2=CH-C$	10.1 (11.2)
	416—510	C_5H_5, $C_5H_4CH=NNH$	48.5 (49.2)
	> 510	FeO	22.9 (20.6)
I	25—70	$4H_2O$	6.1 (5.3)
	173—262	$3C_5H_6$	14.5 (14.6)
	262—355	$3CH_2=CH-C$, 3HCl	15.9 (16.6)
	355—708	$3C_5H_5$, $3C_5H_4CH=NNH$	38.4 (37.7)
	> 708	3FeO, $1/2La_2O_3$	26.1 (27.8)
VI	25—90	$2H_2O$	3.3 (3.0)
	176—345	$3C_5H_6$	16.2 (16.3)
	345—460	$3CH_2=CH-C$	8.9 (9.6)
	460—1050	$3C_5H_5$, $3C_5H_4CH=NN$	40.5 (42.1)
	> 1050	3FeO, $1/2La_2O_3$	31.1 (31.1)

strong peak at $\lambda_{max} = 266-267$ nm is due to the B band of the cyclopentadienyl ring [14] in all complexes. There is a very weak band around $\lambda_{max} = 202$ nm, which can be attributed to the $\pi-\pi^*$ transition on norbornenyl.

The thermal analysis data of Hbfh and its two kinds of chelates are listed in Table 5. The temperature of water loss is below 90°C, thus it is obvious that the water is crystallized rather than coordinated [15, 16] in the chelates. The chelates are somewhat more thermally stable than Hbfh due to formation of the chelate rings, furthermore, the complex *VI* is more stable than complex *I*, *i.e.* the coordination of the enolic form is more thermally stable than the coordination of the keto form. All complexes decompose at 170—350°C and release cyclopentadienes by the retro Diels—Alder reaction. The ferrocenyl moiety decomposes at very higher temperature, so we can say that this group is the most stable one in these complexes. The residue is metal oxide.

Based on the chemical composition of all complexes and their physical measurements discussed above, Hbfh acts as a bidentate ligand, it coordinates to the metal ion in the enolic form or in the keto form, through the azomethine nitrogen and the enolic oxygen or the carbonyl oxygen (in the keto form). In complexes, all water is crystallized water. The coordination numbers are equal to eight for complex *1* and to six for complex *2*. Therefore, we suggest the proposed structures for the two kinds of complexes in Formula 1.

complexes 1 I—V

complexes 2 VI, VII
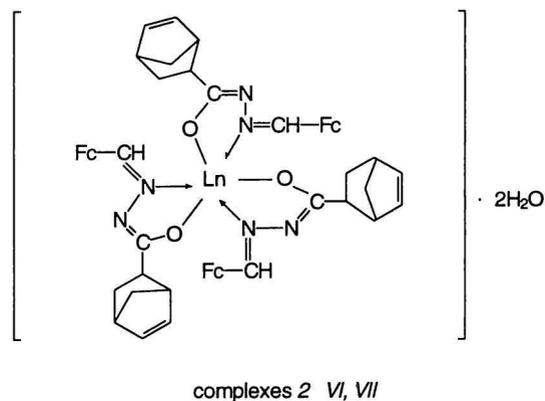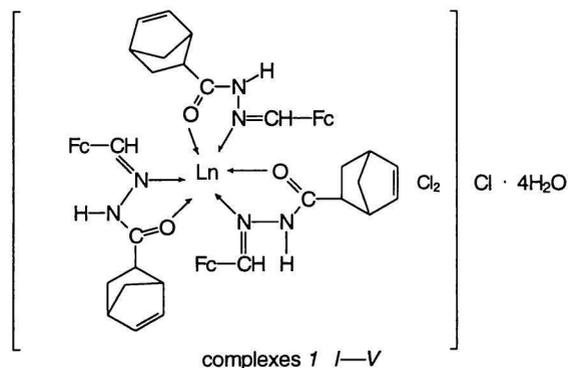
Formula 1

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