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Chelate Complexes of Formylferrocene *m*-Nitrobenzoylhydrazone with Lanthanide

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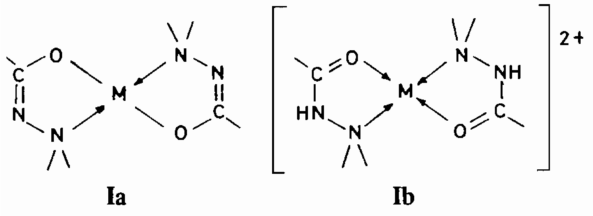
Abstract

A new ligand, formylferrocene *m*-nitrobenzoylhydrazone (HL) and its chelating complexes, $LnL_3 \cdot nH_2O$ (where Ln = lanthanide and Y, n = 1–5) have been prepared by the reaction of HL with the relative metal(III) chloride in acetonitrile. The ligand coordinates to central ions in the enolic form with a molar ratio of 3:1. We discuss the IR, UV, molar conductance and thermogravimetry of the complexes and propose a structure.

Introduction

Due to their biological activities and various bonding, when forming complexes with transition metals, the coordination chemistry of acid hydrazones has attracted the attention of many investigators [1–8]. Edwards and co-workers [9] have shown that the replacement of the aromatic group by the ferrocenyl moiety in the penicillins and cephalosporins improves their antibiotic activity. So, recently a series of ferrocenyl aroylhydrazones and their complexes has been investigated [10–13]. Acid hydrazones can coordinate to transition metals either in the enolic form (**Ia**) or in the keto form (**Ib**). In general, they coordinate to central ions always in the keto form when reacting with metal chlorides, nitrates and sulfates etc., and in the enolic form only with metal acetates in ethanol.

In this communication we wish to report the complexes of formylferrocene *m*-nitrobenzoylhydrazone with Y(III) and lanthanide(III) ions. These complexes, coordinated in the enolic form, can be prepared through the reaction of hydrazone with metal chlorides rather than metal acetates.



Ia **Ib**

Experimental

Physical Measurements

Infrared spectra were recorded using a Nicolet 5DX spectrometer as KBr discs in 400–4000 cm^{-1} region. ^1H NMR spectra were obtained on a FT-80A spectrometer using deutero-dimethyl sulfoxide as solvent and TMS as the internal reference. UV spectra were measured with a DU-7B ultraviolet-visible spectrophotometer in the 190–700 nm region using a solution in DMF. Electrolytic conductance measurements were made with a DDS-IIA molar conductometer and DMF as solvent at 25 °C. Thermal characterization studies were carried out with a Du Pont 1090 thermal analyzer in a nitrogen atmosphere.

Materials

Formylferrocene was prepared according to the literature method [14]. Lanthanide(III) chlorides were prepared from the respective oxides and hydrochloric acid. The other chemicals were analytical reagent grade.

Synthesis of Formylferrocene m-Nitrobenzoylhydrazone(HL)

A solution of formylferrocene (2.14 g, 0.01 mol) in anhydrous ethanol was added dropwise to a solution of *m*-nitrobenzoylhydrazide (1.81 g, 0.01 mol) in anhydrous ethanol refluxing for 1.5 h. The reddish orange crystals formed on cooling were collected on a Büchner funnel, washed several times with cold ethanol, and dried *in vacuo*. Yield 3.6 g (95.5%); melting point (m.p.) 207–208 °C. *Anal.* Found: C, 57.30; H, 4.51; N, 10.30. Calc. for $C_{18}H_{15}FeN_3O_3$: C, 57.30; H, 4.20; N, 11.00%. ^1H NMR: 4.25 (s, 5H) (C_5H_5Fe); 4.47 (t, 2H) (protons on 3,4-positions of C_5H_4Fe); 4.69 (t, 2H) (protons on 2,5-positions of C_5H_4Fe); 7.82–7.92 (m, 4H) (C_6H_4–); 8.76 (s, 1H) (CH=N); 11.83 (s, 1H) (NH which disappears on deuteration) ppm.

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Preparation of Complexes

Yttrium(III) or lanthanide(III) chloride (0.20 mmol) was dissolved in 50 cm^3 of acetonitrile under heating. Twenty cm^3 of solution of formylferrocene *m*-nitrobenzoylhydrazone (0.80 mmol) in acetonitrile containing 2 cm^3 of triethyl orthoformate were added dropwise into the above solution. The mixture was maintained under refluxing for 10 h. The precipitate was separated, filtered on cooling and washed several times with cold acetonitrile and ether. Then the crude product was purified through recrystallization in DMF. The physical properties and elemental analyses of these complexes are listed in Table 1 along with their formulae.

Results and Discussion

These lanthanide complexes are amorphous and brown solids. They are insoluble in petroleum ether and water, sparingly soluble in diethyl ether and benzene, but soluble in methanol, ethanol, DMSO and DMF. Their elemental analyses show that $LnCl_3 \cdot nH_2O$ forms complexes with loss of chloride ions and they conform to the formula $LnL_3 \cdot nH_2O$ (n = 1–5).

IR Spectra

The important IR frequencies of the ligand and its complexes along with their relative assignments are given in Table 2. The IR spectra of these complexes

TABLE 1. Some physical properties and elemental analyses of the complexes

Complex	Formula	Color	Decomposition point (°C)	Elemental analysis: found (calc.) (%)		
				C	H	N
I	$YL_3 \cdot 5H_2O$ [a]	brown	280	49.52 (49.60)	3.34 (3.23)	9.28 (9.64)
II	$LaL_3 \cdot 5H_2O$	deep brown	280	46.95 (47.77)	3.79 (3.86)	8.72 (9.29)
III	$CeL_3 \cdot 3H_2O$	deep brown	280	48.94 (49.02)	3.37 (3.63)	9.38 (9.53)
IV	$PrL_3 \cdot 3H_2O$	deep brown	280	49.55 (49.71)	3.44 (3.55)	9.21 (9.65)
V	$NdL_3 \cdot 3H_2O$	deep brown	280	49.13 (48.86)	3.22 (3.17)	9.02 (9.49)
VI	$SmL_3 \cdot H_2O$	deep brown	280	50.24 (50.01)	3.50 (3.42)	9.77 (9.72)
VII	$EuL_3 \cdot H_2O$	deep brown	280	50.46 (49.95)	3.49 (3.42)	9.65 (9.71)
VIII	$GdL_3 \cdot 3H_2O$	deep brown	280	48.45 (48.41)	3.40 (3.61)	9.25 (9.41)
IX	$TbL_3 \cdot 2H_2O$	deep brown	280	49.66 (49.02)	3.51 (3.50)	9.26 (9.52)
X	$DyL_3 \cdot 2H_2O$	deep brown	280	48.60 (48.87)	3.71 (3.50)	9.98 (9.50)
XI	$HoL_3 \cdot H_2O$	deep brown	280	50.18 (50.12)	3.39 (3.38)	10.14 (9.61)
XII	$ErL_3 \cdot H_2O$	deep brown	280	48.79 (49.35)	3.28 (3.38)	9.49 (9.60)
XIII	$TmL_3 \cdot H_2O$	deep brown	285	50.02 (49.32)	3.53 (3.37)	9.88 (9.58)
XIV	$YbL_3 \cdot H_2O$	deep brown	285	50.06 (49.17)	3.55 (3.34)	9.17 (9.55)
XV	$LuL_3 \cdot H_2O$	deep brown	285	49.07 (49.08)	3.55 (3.34)	9.26 (9.53)

[a] $C_5H_5FeC_5H_4{=}NN{=}C(O^-){-}C_6H_4{-}NO_2$-m.

TABLE 2. Important IR absorption bands (in cm^{-1}) of the ligand and its complexes

Complex	Ln^{3+}	ν(O–H)	ν(N–H)	ν(C=O)	ν(C=N)	δ(N–H)	ν_{as}(N–O)	ν_s(N–O)	ν(C–O)	ν(N–N)
HL			3211m	1642vs	1600m	1540vs	1520vs	1341vs		950w
I	Y	3400br,s			1580m		1520vs	1340vs	1238m	927w
II	La	3400br,s			1580m		1520vs	1344vs	1238m	922w
III	Ce	3400br,s			1580m		1520vs	1344vs	1238m	922w
IV	Pr	3400br,s			1586m		1520vs	1341vs	1238m	921w
V	Nd	3400br,s			1582m		1519vs	1344vs	1240m	920w
VI	Sm	3405br,s			1582m		1520vs	1342vs	1240m	922w
VII	Eu	3405br,s			1580m		1520vs	1340vs	1238m	922w
VIII	Gd	3400br,s			1580m		1520vs	1340vs	1238m	920w
IX	Tb	3400br,s			1582m		1522vs	1342vs	1238m	922w
X	Dy	3400br,s			1580m		1520vs	1343vs	1239m	922w
XI	Ho	3400br,s			1582m		1522vs	1340vs	1240m	922w
XII	Er	3400br,s			1582		1522vs	1342vs	1240m	922w
XIII	Tm	3405br,s			1584m		1520vs	1340vs	1241m	922w
XIV	Yb	3410br,s			1585m		1520vs	1340vs	1240m	922w
XV	Lu	3405br,s			1580m		1520vs	1340vs	1240m	922w

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

show significant changes when compared with those of the parent ligand. The bands due to N–H and C=O (amide I) stretching vibrations, and δ(N–H) disappeared but two new bands were observed around 1580 and 1240 cm^{-1}, which are attributed to ν(C=N–N=C) and ν(C–O). It is shown that the ligand undergoes enolization in acetonitrile and then reacts with the lanthanide ions to form complexes, accompanied by the release of chloride ions. It is also found that the one ν(C=N) band was shifted to a lower frequency by *c.* 10 cm^{-1}, while the ν(N–N) band was shifted to a higher frequency by about 30 cm^{-1}. A shift of ν(C=N) to a lower frequency is due to the conjugation of the p-orbital on the double band with the f-orbital on the metal atom with reduction of the force constant. The shift of ν(N–N) to a higher frequency is attributed to the electro-attracting inductive effect when forming the conjugate system. The result shows clearly that the nitrogen atom in the azomethine participates in coordination to the central ions. The IR spectra of the ligand show a medium and sharp peak of ν(N–H) at 3211 cm^{-1}, whereas those of the complexes exhibit a strong and broad peak of ν(O–H) at about 3400 cm^{-1}. In addition, the characteristic frequencies of the ferrocenyl appear at about 1470, 1150, 820 and 485 cm^{-1} in the ligand and all complexes, and those of the nitro group at *c.* 1520 and 1340 attributed to N$=$O asymmetric and symmetric vibrations.

UV Spectra

The UV spectra of the ligand and its complexes are shown in Table 3 and Fig. 1. It can be seen that the UV spectra of all complexes are similar, but they are different from that of the ligand. The UV spectra of the ligand show characteristic bands at 266 nm arising from the B band of the cyclopentadienyl ring, which occurs as a small bathochromic shift, but changes into a strong and sharp peak as compared with that of the ligand. Band 3 at 450 nm of the ligand is weak and broad due to charge-transfer transition between the cyclopentadienyl ring and iron. This band becomes weaker in the complexes than in the ligand, but its position does not apparently shift. Band 2 at 298 nm in the ligand is attributed to K band (π–π^* transition), but in the complexes a bathochromic shift of about 20 nm is observed. It is possible that the f-orbital of the metal atom and the p-orbital of the ligand overlap each other to form a greater conjugate system after enoliz-

TABLE 3. Important UV spectra of the ligand and its complexes

Complex	Ln^{3+}	Absorption bands (nm, λmax) (1)	(2)	(3)
HL		266	298	450
I	Y	265	320	450
II	La	265	322	450
III	Ce	264	320	450
IV	Pr	265	317	450
V	Nd	265	336	450
VI	Sm	265	320	445
VII	Eu	263	312	450
VIII	Gd	264	330	450
IX	Tb	264	336	445
X	Dy	265	341	450
XI	Ho	266	331	450
XII	Er	266	328	450
XIII	Tm	264	328	445
XIV	Yb	264	314	450
XV	Lu	264	328	450

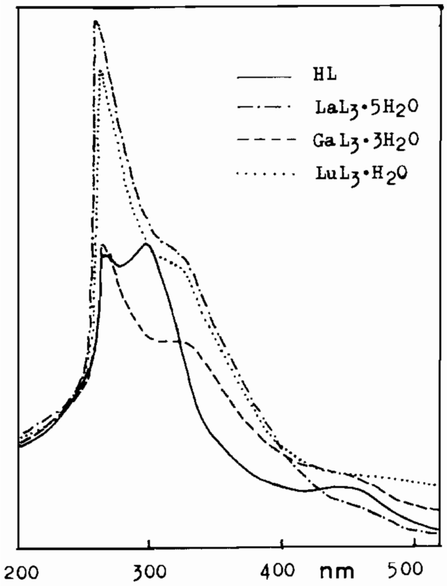

Fig. 1. The UV spectra of the ligand and its complexes.

ing and complexing. The formation of the greater conjugate system makes the energy level difference between the π and π^* orbitals, i.e. π–π^* transition energy required decrease. These factors led to the greater bathochromic shift of the K band of the complexes.

Molar Conductance

Dissolving the lanthanide complexes in DMF afforded a deep brown solution. The molar conductance values (Table 4) of the complexes in DMF lie in the range 13–40 ohm^{-1} cm^2 mol^{-1}. This indicates that the DMF solution of the complexes is non-ionic in nature [15].

TABLE 4. Molar conductances of the complexes in DMF at 25 °C

Complex	Ln^{3+}	Conc. (10^{-3} mol)	λ_m (ohm^{-1} cm^2 mol^{-1})
I	Y	0.99	23
II	La	0.95	37
III	Ce	0.98	39
IV	Pr	1.01	25
V	Nd	0.98	40
VI	Sm	1.02	24
VII	Eu	1.05	22
VIII	Gd	1.06	33
IX	Tb	1.03	30
X	Dy	1.00	21
XI	Ho	1.09	19
XII	Er	1.01	23
XIII	Tm	1.02	18
XIV	Yb	0.99	13
XV	Lu	1.01	20

Thermal Analysis

Thermal analyses of the ligand and its complexes show that an explosive decomposition occurs when heating above 230 °C due to the presence of the nitro group on the phenyl. Hence, the weight loss is difficult to measure accurately, but it is notable that the connecting form of water is variable. The TG and DSC measurements of the ligand indicate melting endothermally at 204.1 °C, then an explosive decomposition at about 230 °C. The complex $LaL_3 \cdot 5H_2O$ loses about 4.0% of its weight at 70 °C accompanied by the release of heat, which corresponds to the loss of three molecules of water (calc. 4%). Then it loses *c.* 2.8% at 123 °C, perhaps indicating that the other two molecules of water break away from the complex (calc. 2.7%). It appears that the former is crystal water and the latter is coordinated. The complex decomposes exothermally and explosively above 303 °C. Similarly, $NdL_3 \cdot 3H_2O$ loses weight gradually; 2.5% (calc. for $2H_2O$, 2.7%) at 70 °C and 1.6% (calc. for H_2O, 1.4%) at 125 °C. It is shown that of the three molecules of water, one is coordinated and two are crystal water. The complex $LuL_3 \cdot H_2O$ loses 1.3% of its weight (calc. for H_2O, 1.4%) at 65 °C, which apparently is crystal water.

It can be seen from the thermal analytic data that the water in these complexes exists in different forms, coordinated or crystal. The number of coordinated water molecules decreases with change of lanthanide from light to heavy, i.e. the coordinate number of central ions decreases progressively due to lanthanide contraction.

Conclusions

Formylferrocene *m*-nitrobenzoylhydrazone is a bidentate ligand, three molecules of which coordinate with one molecule of lanthanide(III) chloride in the enolic form in acetonitrile accompanied by the release of three chloride ions. The coordination number is variable (from 8 to 6). Therefore we suggest a plausible structure for our complexes is as shown in Fig. 2.

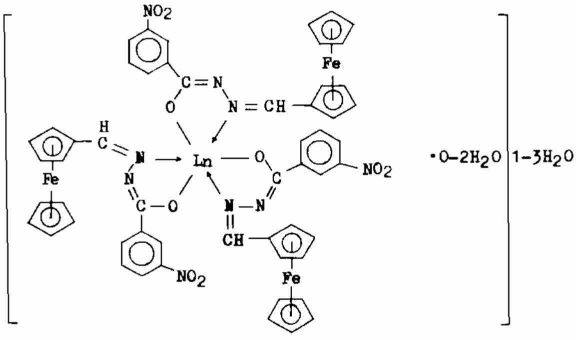

Fig. 2. Proposed structure for the complexes.

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