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Coordination Compounds of 1,1′-Diacetylferrocene Benzoylhydrazone with Rare Earth Metals

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Abstract

A new ligand, 1,1′-diacetylferrocene benzoylhydrazone and its 15 rare earth(III) chelates have been synthesized. The IR, UV, TG–DTA and electrolytic conductivity of the ligand and its chelates are discussed. The data show that the ligand coordinates with metal ions in the keto form rather than in the enol form. The chelates are more thermostable than the ligand and are 1:2 electrolytes in dimethyl formamide.

Introduction

Acid hydrazides and their derivatives, RCH=N–NHCOR′ are known to coordinate easily with transition metals and to form stable chelates [1–3]. The hydrazine group may chelate in the enol form [4] or in the keto form [5]. Due to this ability, the aroylhydrazones can be used to inhibit many vital enzymatic reactions catalyzed by transition metal ions [6]. We believe this is the first report on chelates of hydrazone with rare earth metals. In this paper, a new hydrazone, 1,1′-diacetylferrocene benzoylhydrazone and its chelates with rare earth chlorides have been synthesized, characterized, and some of their properties studied.

Experimental

Preparation of Organic Ligand

The 1,1′-diacetylferrocene benzoylhydrazone (**1**, H_2L) was prepared by refluxing a mixture of 1,1′-diacetylferrocene and benzoylhydrazine in a molar ratio of 1:2 in benzene, and water formed was removed simultaneously. The red precipitate produced was filtered and washed with benzene, then the pure product was obtained by recrystallization from ethanol. Yield 81.5%, melting point (m.p.) 199–200 °C, decomposition temperature 211 °C. Elemental analysis of the ligand is listed in Table I.

Preparation of Rare Earth Chelates

The rare earth chelates of the hydrazone ligand were prepared by refluxing a mixture of a rare earth chloride and the ligand in a molar ratio of 1:2 in ethanol–triethyl orthoformate for 9 h. The yellow solid, which formed when the mixture cooled, was collected and washed with anhydrous ethanol. The prepared chelates are listed in Table I together with elemental analysis.

Physical Measurements

IR spectra were taken on a NIC-5DX spectrophotometer. Solid samples were examined as KBr discs. The measurement range was 400–4000 cm^{-1}. The UV spectra in solution were recorded in the 200–500 nm region using a Shimazu 240 spectrophotometer from Japan. Electrolytic conductance measurements were made with a DDS-IIA molar conductometer with dimethyl formamide as solvent at 25 °C.

Thermogravimetry (TG) and differential thermal analysis (DTA)

TG and DTA measurements were carried out by a Thermoflex TG-DTA meter in a nitrogen atmosphere between room temperature and 800 °C.

Results and Discussion

The reaction of 1,1′-diacetylferrocene with benzoylhydrazine in benzene yielded a deep red stable crystalline compound. The elemental analysis of the compound agrees with formula **1**. This compound reacts with lanthanide(III) chlorides to form a series of chelates **2**. These chelates are insoluble in common organic solvents and only sparingly soluble in DMF and DMSO. The elemental analyses (Table I) show that they have a 2:1 metal:ligand stoichiometry, and that the reaction proceeds as shown in the following equation:

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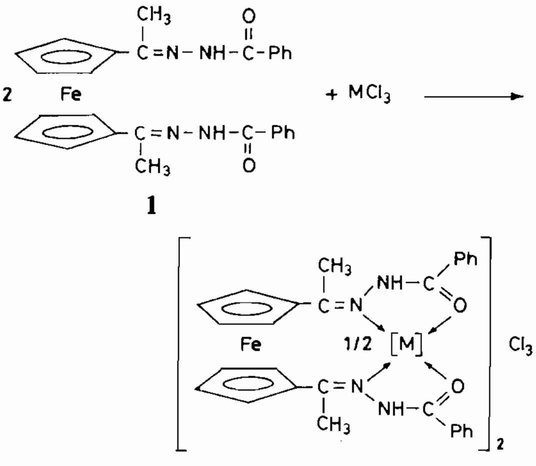

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The important IR frequencies of the ligand and its chelates are listed in Table II. It can be seen that the $\nu_{C=O}$ frequency of the amide I shifts from 1669 to 1625 cm^{-1}, and the δ_{N-H} frequency of the amide II moves 9 cm^{-1} towards higher frequency, i.e. from 1529 to 1538 cm^{-1}. The changes of these frequencies suggest that oxygen in the carbonyl group participates in coordination with the metal ion in the keto form. The δ_{C-N} absorption band of the amide III shifts *ca.* 12 cm^{-1}, from 1300 to 1312 cm^{-1}. This may be due to the induction effect resulting from the formation of chelates. In addition, the $\nu_{C=N}$ frequency shifts *ca.* 85 cm^{-1}, from 1651 to 1566 cm^{-1}. It is shown that nitrogen in the imido group (C=N) coordinates to the metal atom. The characteristic bands of the ferrocenyl appear at 3089, 1471, 1136 and 820 cm^{-1}.

TABLE I. Elemental Analysis of H_2L and its Chelates

Compound	Color	Elemental analysis (%)[a]			
		C	H	N	Cl
H_2L (I)	reddish orange	66.67 (66.67)	5.15 (5.16)	10.98 (11.11)	
$La(H_2L)_2Cl_3$ (II)	pale yellow	53.20 (53.46)	3.99 (4.14)	8.39 (8.90)	8.52 (8.41)
$Ce(H_2L)_2Cl_3$ (III)	pale yellow	53.21 (53.38)	3.99 (4.13)	8.53 (8.90)	8.52 (8.41)
$Pr(H_2L)_2Cl_3$ (IV)	pale yellow	53.12 (53.31)	3.78 (4.11)	8.21 (8.89)	8.49 (8.39)
$Nd(H_2L)_2Cl_3$ (V)	orange	53.18 (53.22)	4.11 (4.12)	8.84 (8.87)	8.38 (8.43)
$Sm(H_2L)_2Cl_3$ (VI)	orange	52.68 (52.96)	3.97 (4.10)	8.70 (8.82)	8.52 (8.37)
$Eu(H_2L)_2Cl_3$ (VII)	orange	52.88 (52.89)	3.95 (4.07)	8.56 (8.81)	8.23 (8.39)
$Gd(H_2L)_2Cl_3$ (VIII)	orange	52.79 (52.66)	4.06 (4.08)	8.69 (8.78)	8.30 (8.38)
$Tb(H_2L)_2Cl_3$ (IX)	orange	52.59 (52.62)	4.05 (4.07)	8.52 (8.79)	8.32 (8.34)
$Dy(H_2L)_2Cl_3$ (X)	orange	52.50 (52.46)	4.08 (4.06)	8.76 (8.76)	8.30 (8.31)
$Ho(H_2L)_2Cl_3$ (XI)	golden yellow	52.59 (52.38)	4.03 (4.05)	8.58 (8.73)	8.18 (8.30)
$Er(H_2L)_2Cl_3$ (XII)	golden yellow	53.09 (52.30)	4.04 (4.03)	9.01 (8.72)	8.51 (8.28)
$Tm(H_2L)_2Cl_3$ (XIII)	golden yellow	52.25 (52.21)	3.97 (4.04)	8.78 (8.70)	8.25 (8.27)
$Yb(H_2L)_2Cl_3$ (XIV)	golden yellow	52.62 (52.06)	4.07 (4.03)	8.75 (8.68)	8.34 (8.25)
$Lu(H_2L)_2Cl_3$ (XV)	golden yellow	52.08 (51.95)	3.96 (4.02)	8.65 (8.66)	8.20 (8.25)

[a] Calculated values are given in parentheses.

TABLE II. Important IR Absorption Bands (in cm^{-1}) of the Ligand and its Chelates

Compound	ν_{N-H}	Amide I $\nu_{C=O}$	$\nu_{C=N}$	Amide II δ_{N-H}	Amide III δ_{C-N}	ν_{N-N}
I	3318br, m[a]	1669sh	1651vs	1529vs	1300m	915
II	3385br, m	1624sh	1581vs	1516vs	1297w	917m
III	3236br, m	1625vs	1566s	1538vs	1313s	918m
IV	3169br, m	1624vs	1566s	1537vs	1313s	918m
V	3169br, m	1624vs	1566s	1537vs	1313s	918m
VI	3169br, m	1625vs	1566s	1538vs	1313s	918m
VII	3169br, m	1625s	1566s	1538vs	1313s	917m
VIII	3169br, m	1625s	1566s	1538vs	1312s	917m
IX	3184br, m	1625s	1566s	1538vs	1313s	198m
X	3196br, m	1624vs	1566s	1537vs	1313s	917m
XI	3187br, m	1624vs	1566s	1538vs	1313s	918m
XII	3170br, m	1625vs	1566s	1537vs	1312s	917m
XIII	3178br, m	1624vs	1567s	1538vs	1313s	917w
XIV	3234br, m	1625vs	1567s	1538vs	1313s	917m
XV	3234br, m	1625vs	1566s	1538vs	1313s	917m

[a] vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

The important bands in the UV absorption spectra for the ligand and its chelates are listed in Table III. It can be seen from the Table that the K absorption band (π–π^* transition) of the ligand appears at 318 nm. It is quite possible that the d-orbital from the central ion overlaps with the p-orbital from the coordination atom to cause an increase in conjugation in the complex and a decrease in π–π^* transition energy after chelation. The absorptions (3) of these rare earth chelates, except for La, Ce and Pr, change into a single peak from a shoulder peak at 365 nm, and a new band appears near 353 nm. These changes are all due to the bathochromic shift of band 3. In addition, there is a broad band (4) in the ligand and all of its chelates at 455 nm, which is due to charge-transfer from iron to either the nonbonding or antibonding orbitals on the cyclopentadienyl rings.

Thermal analysis shows that the ligand melts at 200 °C as it is endothermic, then decomposes at 211–250 °C and loses about 21% of its weight as it is now exothermic (Table IV). Since the N–C bond is less stable than the C–C bond, perhaps one PhCO$^+$ group breaks away from the molecule. The other PhCO$^+$ group decomposes at 322–343 °C. The exothermic peak at 421 °C is due to the loss of two molecules of nitrogen. Finally, decomposition is finished and the residue is iron. The TG–DTA diagrams of all the chelates are similar. The diagram of $Pr(H_2L)_2Cl_3$ shows that the first exothermic peak does not appear until 250 °C, while the chelate decomposes and loses four benzene rings (Found 24%, Calc. 22.5%). It is clear that the C–N bond formed in the chelate ring becomes more thermostable than in the ligand. The chelate then decomposes continuously, accompanied by the release of heat in great amounts at 410 °C. Decomposition is finally complete at 600 °C.

TABLE III. UV Spectra of the Ligand and its Chelates

Compound	Characteristic absorption bands λ_{max} (nm)			
	1	2	3	4
I	318		365sh[a]	455
II	330		365sh	455
III	330		365sh	455
IV	330		365sh	455
V	332	354	368	455
VI	332	354	368	455
VII	330	354	368	455
VIII	330	352sh	368	455
IX	328	352sh	368	455
X	330	352	368	455
XI	332	352	368	455
XII	330	352	368	455
XIII	328	352	368	455
XIV	328	352	368	455
XV	328	354	368	455

[a] sh = shoulder.

TABLE IV. Data of Thermal Analysis of H_2L

Decomposition temperature (°C)	Leaving group	Loss of weight (%)
211–250	PhCO$^+$	21(21)[a]
322–343	PhCO$^+$	21(21)
421	$2N_2$	10(11)
692–697	substituted cyclopentadienyl	25(26)
Residual	Fe	13(11)

[a] Calculated values are given in parentheses.

TABLE V. Electrolytic Conductivities of some Chelates of the type $Ln(H_2L)_2Cl_3$ in DMF at 25 °C

Chelate	Λ_m (Ω^{-1} cm^2 mol^{-1})
III	121.8
IV	125.9
V	130.7
VI	105.6
VII	148.3
IX	169.5
XIII	103.0
XIV	109.8

Dissolving the chelates in dimethyl formamide afforded brown solutions. The molar conductances (Table V) of these solutions approach values reported for 1:2 electrolytes [7].

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