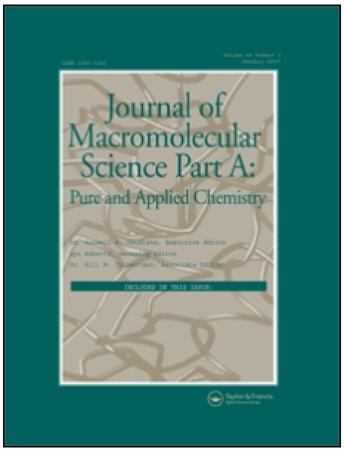

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Magnetic and Spectral Investigations of Some Lanthanide Complexes of 2-Hydroxypropiophenone

Keemti Lal[a]; S. R. Malhotra[a]
[a] Chemical Laboratories, D. N. College, Meerut, India

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Magnetic and Spectral Investigations of Some Lanthanide Complexes of 2-Hydroxypropiophenone

KEEMTI LAL and S. R. MALHOTRA

Chemical Laboratories
D. N. College
Meerut 250002, India

ABSTRACT

Complexes of the monovalent bidentate 2-hydroxypropiophenone with trivalent La, Pr, Nd, Sm, Gd, Dy, Ho, and Er have been synthesized, and their magnetic and spectral characteristics are reported. The values of naphelauxetic ratio (β), percentage covalency parameter (δ), and bonding parameter ($b^{1/2}$) have been calculated.

INTRODUCTION

A survey of the literature reveals that a fair amount of work has been recently published emphasizing the characteristics of transition metal ions complexes of 2-hydroxypropiophenones [1-5]. However, no work appears to have been carried out on the lanthanide complexes of 2-hydroxypropiophenone (HPro). In this article we report the isolation of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), and Er(III) complexes, and their characterization on the basis of elemental analyses, conductance, magnetic moment, and infrared and electronic spectral studies.

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EXPERIMENTAL

The rare earth nitrates were procured from Indian Rare Earths Ltd, Kerala, India, and used as received. Their aqueous solution (0.01 M) was prepared in distilled water. An ethanolic solution (0.05 M) of 2-hydroxypropiophenone (Fluka, AG, Switzerland) was prepared.

The molar conductance measurements were carried out on a Toshniwal conductivity bridge type CL 01. Magnetic measurements were carried out at 300 ± 1 K in powder form by Gouy's method using $Hg[Co(NCS)_4]$ as the calibrant. The IR spectra of the ligand and the complexes were recorded in KBr on a Perkin-Elmer 257 spectrophotometer in the region 4000-600 cm^{-1} and with a Beckman IR 12 spectrophotometer in the region 650-200 cm^{-1}. The electronic spectra of the complexes were recorded on a Beckman DU-2 (manual) spectrophotometer in dimethylformamide (DMF).

The metal contents of the complexes were determined by the oxalate-oxide method. C and H analyses were carried out at the Microanalytical Laboratory, I.I.T., Kanpur, India.

A solution of lanthanon nitrate (0.01 M) was added to a solution of HPro (0.05 M) with constant stirring. A dilute solution of ammonium hydroxide was then added dropwise until a yellowish precipitate separated out. The reaction mixture was stirred for about 2 h. The precipitated complex was filtered and then washed with water, 50% ethanol, and finally with ether, and then dried in vacuo. The purity of the complexes was established by elemental analyses. Analytical data agreed with the composition of the complexes, i.e., 1:3 (metal:ligand) within the limits of experimental error.

RESULTS AND DISCUSSION

Analytical results of the complexes (Table 1) conform to the general formula $Ln(C_9H_9O_2)_3$. The complexes are insoluble in water, but soluble in benzene, ethyl acetate, chloroform, and dimethylformamide.

The molar conductance (2.0-3.0 mho cm^2 mol^{-1}) of these complexes in DMF suggests that these complexes behave as nonelectrolytes. The nonelectrolytic behavior indicates that these complexes are of the inner sphere type.

The magnetic moments (μ_{eff}) of these complexes were determined at 300 ± 1 K and are reported in Table 1. The magnetic moments of all the complexes show little deviation from the values reported earlier [6]. This indicates that the 4f electrons do not participate in bond formation in these complexes [7].

The IR spectra of all the complexes are almost alike, suggesting a similar type of bonding in them. The assignment of some important

TABLE 1. Analytical Data, Effective Magnetic Moment and ν(M–O) Band of HPro Complexes

	Analysis (%) found (calc)				
Compound	C	H	M	μ_{eff} (BM)	ν(M–O) cm^{-1}
HPro[a]	72.10 (72.00)	6.64 (6.66)	- -	-	-
La$(Pro)_3$	55.22 (55.30)	4.57 (4.61)	23.52 (23.71)	-	285,230
Pr$(Pro)_3$	55.00 (55.11)	4.65 (4.59)	24.02 (23.97)	3.60	305,240
Nd$(Pro)_3$	54.64 (54.80)	4.50 (4.57)	24.22 (24.39)	3.50	310,240
Sm$(Pro)_3$	54.12 (54.24)	4.62 (4.52)	25.00 (25.16)	1.48	320,250
Gd$(Pro)_3$	53.73 (53.62)	4.50 (4.47)	25.86 (26.02)	7.80	325,260
Dy$(Pro)_3$	53.02 (53.16)	4.40 (4.43)	26.80 (26.66)	9.52	325,265
Ho$(Pro)_3$	53.02 (52.95)	4.50 (4.41)	27.00 (26.95)	10.50	335,265
Er$(Pro)_3$	52.58 (52.74)	4.40 (4.39)	27.10 (27.23)	9.20	350,260

[a] HPro = $C_9H_{10}O_2$.

IR bands of the complexes has been carried out by comparison with the spectrum of the ligand (HPro). A band due to νOH appears at 2900 cm^{-1} in HPro but disappears in the complexes. This indicates the presence of intramolecular hydrogen bonding in HPro [8]. The absence of this band in the complexes is an indication of the replacement of the hydrogen atom of the phenolic OH group by the lanthanide ion. The lowering of the νC=O frequency from 1630 cm^{-1} in the ligand to 1605-1610 cm^{-1} in the complexes suggests coordination of the oxygen atom of the ketonic group. The strong band at 1230 cm^{-1} in HPro is assigned to the phenolic mode of νC–O [9, 10] which shifts toward the higher frequency side (1240-1255 cm^{-1}) on complexation. This may be due to delocalization of electron density from the oxygen atom to the lanthanide ions. The new bands observed in the region 200-300 cm^{-1} in the spectra of the complexes have been assigned to νM–O (Table 1). These bands are found to be shifted to a higher energy level as the atomic number increases from La to Er. From the position of νM–O it can be inferred that the M–O bond strength increases in the order La < Pr < Nd < Sm < Gd < Dy < Ho < Er.

The electronic spectral data recorded in DMF solution are given in Table 2. The absorption bands of Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), and Er(III) in the visible and the near-IR regions appear to be due to the transition from the ground energy levels $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$, $^8S_{7/2}$, $^6H_{15/2}$, $^5I_8$ and $^4F_{15/2}$, respectively, to higher energy levels [11,12].

The magnitude of red shift (nephelauxetic effect) is dependent on the change in the interelectronic repulsion parameter. The first excited level (^6P) of Gd(III) lies at 32,000 cm^{-1} above the ground state term $^8S_{7/2}$, and hence the spectrum of the ion emerges in the UV region [13]. Because the intense ligand band appears in this region, the electronic spectrum of the Gd(III) complex could not be studied.

The nephelauxetic effect (β), which is regarded as a measure of covalency, has been calculated by using the relation

$$\beta = \frac{\nu_{\text{complex}}}{\nu_{\text{aquo}}}$$

where ν stands for the wavenumber of absorption of the rare earth ions by assuming that each J value of f^n configuration is linearly dependent on the radical integrals [14]. The other two important parameters, percentage covalence parameter (δ) and bonding parameter ($b^{1/2}$), were calculated [15, 16] by using

$$\delta = \frac{(1 - \beta) \times 100}{\beta}$$

$$b^{1/2} = \left[\frac{1 - \beta}{2}\right]^{1/2}$$

The values of δ have been found to be positive in all these complexes, indicating electron delocalization from 4f orbitals. The values of $b^{1/2}$ indicate the extent of 4f participation in the complexation. The greater the magnitude of $b^{1/2}$, the greater is the contribution of the 4f orbital to complex formation. The positive values of δ and $b^{1/2}$ and the less than unity values of β in the present complexes point toward the incidence of covalency in the metal-ligand bond. By comparing the values of these parameters in different lanthanides, we find a gradual increase in the covalency character with an increase of the atomic number of lanthanide. This is in conformity with the lanthanide contraction.

TABLE 2. Electronic Spectral Data and Bonding Parameters of HPro Complexes with Lanthanides

Ion	J-levels	HPro chelates in DMF (cm^{-1})	β	δ	$b^{1/2}$
Pr(III)	$^3H_4 \longrightarrow {}^1D_2$	16,800	0.9882	1.1941	0.0768
	$\longrightarrow {}^3P_0$	20,500	0.9880	1.2148	0.0774
	$\longrightarrow {}^3P_1$	21,100	0.9897	1.0104	0.0714
	$\longrightarrow {}^3P_2$	22,200	0.9880	1.2148	0.0774
Nd(III)	$^4I_{9/2} \longrightarrow {}^5F_{5/2}, {}^4H_{9/2}$	12,280	0.9847	1.5538	0.0872
	$\longrightarrow {}^4F_{7/2}, {}^2S_{3/2}$	13,500	0.9883	1.1838	0.0761
	$\longrightarrow {}^4G_{5/2}, {}^2G_{7/2}$	17,100	0.9850	1.5228	0.0866
	$\longrightarrow {}^4G_{9/2}$	19,300	0.9872	1.2966	0.0800
Sm(III)	$^6H_{5/2} \longrightarrow {}^4I_{13/2}$	21,220	0.9847	1.5534	0.0872
	$\longrightarrow {}^4P_{5/2}$	23,600	0.9833	1.6984	0.0911
	$\longrightarrow {}^4F_{9/2}$	24,400	0.9810	1.9368	0.0975

TABLE 2 (continued)

Ion	J-levels	HPro chelates in DMF (cm^{-1})	β	δ	$b^{1/2}$
Dy(III)	${}^6H_{15/2} \longrightarrow {}^4F_{9/2}$	22,000	-	-	-
	$\longrightarrow {}^4I_{15/2}$	23,020	-	-	-
	$\longrightarrow {}^4G_{11/2}$	23,240	-	-	-
Ho(III)	${}^4I_8 \longrightarrow {}^5F_5$	15,500	0.9748	2.5851	0.1122
	$\longrightarrow {}^4G_4$	18,810	0.9766	2.3961	0.1082
	$\longrightarrow {}^5G_6$	21,900	0.9742	2.6483	0.1136
Er(III)	${}^4F_{15/2} \longrightarrow {}^4I_{11/2}$	10,320	0.9708	3.0078	0.1208
	$\longrightarrow {}^4I_{3/2}$	18,350	0.9728	2.7855	0.1162
	$\longrightarrow {}^4F_{7/2}$	20,480	0.9720	2.8806	0.1183

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