Asian Journal of Chemistry Vol. 16, No. 1 (2004), 117–121

Studies on Complexes of Rare Earths with Furohydroxamic Acid

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The complexes of Pr(III), Eu(III), Gd(III), Dy(III) and Yb(III) with furohydroxamic acid (FHA) have been characterised by elemental analysis, magnetic susceptibility measurements, IR and electronic spectral studies. The IR spectra suggest bidentate behaviour of the furohydroxamic acid. A coordination number seven is proposed around the metal ions with capped octahedron geometry of the complexes.

Key Words: **Rare earths, Furohydroxamic acid, Complexes.**

INTRODUCTION

The hydroxamic acids which find extensive uses in analytical chemistry, pharmaceutical and biological activities[1–3] are potential bidentate ligands having complexing sites at hydroxyl and carbonyl groups and thus can give rise to complexes of varied coordination number depending upon the amount of acid used[4]. The chemistry of coordination number of the rare earth ions makes it interesting to study the nature of the rare earth-hydroxamate bond in the complexes with different types of simple and substituted hydroxamic acids[5–7]. Thus in the present work, we report the synthesis and physico-chemical properties of rare earth complexes of furohydroxamic acid .

EXPERIMENTAL

Furohydroxamic acid (FHA) was prepared by the reported method[8]. All reagents used were of AR grade.

Preparation of Metal Complexes

10 mL alcoholic solution of FHA (0.01 M, 25 mL) was added to 10 mL aqueous solution of metal acetate (0.005 M, 25 mL) in a round bottom flask. The solution was stirred for 10 min and refluxed on a water bath for *ca.* 3 h, 2 mL ammonia solution was slowly added to this solution and again refluxed for 1 h. After this the hot solution was filtered and the filtrate was kept at room temperature for crystallization. The crystals were obtained after 24 h, which were washed with water,

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alcohol and followed by ether. Finally the crystals were dried over P_2O_5 in a vacuum desiccator.

Lanthanides(III) were determined gravimetrically or volumetrically by adopting standard methods[9]. The rare earth metal complexes were estimated by igniting them so that their oxides were formed. After dissolving the oxides in 50% HCl, titrated with EDTA using xylenol as indicator. The elemental analyses of carbon, hydrogen and nitrogen were done on CHN microanalyzer. Infrared spectra of metal complexes were recorded in KBr on Perkin-Elmer 577 spectrophotometer in the region *ca.*4000–200 cm^{-1}, were recorded at the RSIC, CDRI, Lucknow. Magnetic susceptibility measuremnts of the synthesized complexes were carried out at room temperature on EG&G Model 155 VSM (vibrating sample magnetometer) at RSIC, IIT, Chennai. The electronic spectra of the complexes in solution (H_2O/DMF) were recorded on Systronics-106 at room temperture at the Department of Chemistry, R.B.S. College, Agra.

RESULTS AND DISCUSSION

The analytical results, melting points, colour and magnetic moments of the complexes are presented in Table-1.

The magnetic moments of the new complexes are found to be indicative of paramagnetic nature. The magnetic moment data of lanthanide(III) complexes are given in Table-1.

In electronic spectra of lanthanide(III) complexes, the value of nephelauxetic parameter (β) has been determined by the method of Jorgenson *et al.*[10, 11] using the relation.

$$(1 - \beta) = \frac{\nu_{aquo} - \nu_{complex}}{\nu_{aquo}}$$

Honrie and Choppin[12] bonding parameter ($b^{1/2}$), the nephelauxetic ratio (β)[13], angular covalency and Sinha's covalency parameter (η) and (δ%) have been calculated by using the following equations:

$$b^{1/2} = \frac{1}{2}\,[(1 - \beta)^{i/2}]$$

$$\beta = \frac{\nu\ (\text{complex})}{\nu\ (\text{free ion})}$$

$$\eta = \frac{(1 - \beta^{1/2})}{\beta^{1/2}}$$

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

The electronic spectra have been recorded in DMF. In the present study of complexes, the value of β is found to be less than unity while the values of δ% and $b^{1/2}$ are found to be positive, thus indicating that the nature of metal-ligand bond is purely covalent. The values of different parameters such as β, δ%, $b^{1/2}$ and η are presented in Table-2. The spectra of Pr(III), Dy(III) and Eu(III) show red shift in the electronic spectral bands in comparison to the aqua metal ions. The complexes of Gd(III) and Yb(III) have no significant absorption.

TABLE-1

PHYSICAL PROPERTIES AND ANALYTICAL DATA AND MAGNETIC MOMENT VALUES OF LANTHANIDE COMPLEXES

S. No.	Complexes	Physical properities				Analytical Data, % Found (Calcd.)					μ_{eff} (B.M.)
		m.p. (°C)	Colour	m.w.	State	C	H	N	O	Ln	
1.	$Pr(C_5H_5NO_3)_2\ (CH_3COO)_3$	200	Brown	620.15	Solid (Powder)	33.42 33.58	3.23 3.34	4.80 4.89	33.40 33.55	24.55 24.62	3.62
2.	$Eu(C_5H_5NO_3)_2\ (CH_3COO)_3$	210	Light brown	568.35	Solid (Crystalline)	32.80 32.94	3.20 3.28	4.72 4.80	32.81 32.91	26.01 26.05	3.77
3.	$Gd(C_5H_5NO_3)_2\ (CH_3COO)_3$	215	Red	668.12	Solid (Crystalline)	32.58 32.65	3.12 3.25	4.63 4.75	32.72 32.61	20.68 26.71	7.86
4.	$Dy(C_5H_5NO_3)_2\ (CH_3COO)_3$	195	Brown	611.54	Solid (Powder)	32.31 32.36	3.10 3.22	4.60 4.71	32.20 32.33	27.28 27.36	8.39
5.	$Yb(C_5H_5NO_3)_2\ (CH_3COO)_3$	245	Light yellow	615.54	Solid (Crystalline)	31.64 31.79	3.12 3.16	4.58 4.63	31.64 31.76	28.50 28.63	4.47

TABLE-2

ELECTRONIC SPECTRAL DATA AND VARIOUS LIGAND FIELD PARAMETERS FOR THE Pr(III), Eu(III) AND Dy(III) COMPLEXES

Band position (standard)	Band position (in complex)	Assignments	β	$b^{1/2}$	δ%	η
		$Pr(C_5H_5NO_3)_2(CH_3COO)_3$				
16949	16129	$^3H_4 \rightarrow {}^1D_2$	0.9516	0.1550	5.086	0.025
20833	20000	$\rightarrow {}^3P_0$	0.9600	0.1414	4.166	0.020
22472	21739	$\rightarrow {}^3P_2$	0.9695	0.1234	3.145	0.016
		$Eu(C_5H_5NO_3)_2(CH_3COO)_3$				
21500	20833	$^5F_0 \rightarrow {}^5D_2$	0.9690	0.1245	3.1992	0.0158
		$Dy(C_5H_5NO_3)_2(CH_3COO)_3$				
12345	12391	$^6H_{15/2} \rightarrow {}^6F_{5/2}$	0.9925	0.0612	0.7549	0.0037
—	26810	$\rightarrow 4M_{19/2}$	—	—	—	—
27855	—	$\rightarrow 4I_{11/2}$	—	—	—	—
3344	—	$\rightarrow 4H_{13/2}$	—	—	—	—

TABLE-3

INFRARED SPECTRAL DATA (cm^{-1}) OF LANTHANIDE COMPLEXES

Complexes	Bands assignments				
	ν(N—OH)	ν(C=O)	ν(C—N)	ν(N—O)	ν(Ln—O)
$Pr(C_5H_5NO)_2(CH_3COO)_3$	—	1593b	1402b	1017m	480w
$Eu(C_5H_5NO_3)_2(CH_3COO)_3$	—	1594s	1366s	1076b	465w
$Gd(C_5H_5NO_3)_2(CH_3COO)_3$	—	1592s	1369s	1016m	470m
$Dy(C_5H_5NO_3)_2(CH_3COO)_3$	—	1589b	1410b	1016s	455s
$Yb(C_5H_5NO_3)_2(CH_3COO)_3$	—	1599b	1408b	1017s	480s

Important IR frequencies are given in Table-3. Band observed at *ca.* 3155 cm^{-1} may be assigned to ν(N—OH)[14] group in the ligand. These frequencies in the spectra of complexes disappear. The strong band at *ca.* 1595 cm^{-1} in the ligand is attributed to ν(C=O) shifted to lower frequencies in the complex at 1560 cm^{-1}, suggesting coordination through keto group[15]. The strong band at *ca.* 1361 cm^{-1} in the ligand is attributed to ν(C—N) shifted to higher frequencies *ca.* 1420 cm^{-1} on complexation, indicating that coordination of hydroxamic acid occurs through oxygen of C=O group. A medium band due to N—O stretching vibration *ca.* 904 cm^{-1} in the ligand gets shifted to higher frequencies *ca.* 1020 cm^{-1} on complexation. The new band which appeared in the spectra of complex at 480–450 cm^{-1} indicates the presence of ν(Ln—O) bonds. The IR spectra of complexes confirm that FHA acts as a bidentate ligand coordinating through two hydroxyl and two carbonyl oxygen. Based on the results a tentative structure may be proposed for these seven coordinated complexes of lanthanides.

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(*Received*: 13 March 2003; *Accepted*: 20 August 2003) AJC-3152