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Studies on Some Lanthanide(III) Complexes of 2-N-(*m*-Phenoxybenzylidine)furfurylamine

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Complexes of La(III), Pr(III), Nd(III), Sm(III) and Gd(III) with 2-N-(*m*-phenoxybenzylidine)furfurylamine have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, infrared, NMR and electronic spectral data. It is proposed that the ligand is bidentate ON donor in the complexes.

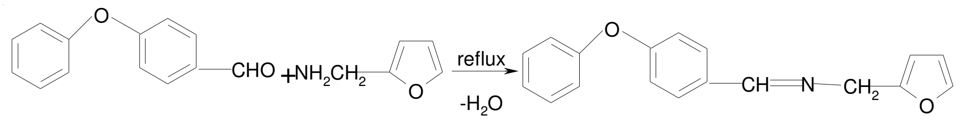
Key Words: Synthesis, Lanthanide(III) complexes, 2-N-(*m*-Phenoxy benzylidine)furfurylamine, Octahedral.

INTRODUCTION

The rare earth form a large number of complexes with a variety of ligands[1,2]. Generally rare earth compounds are used in drugs, radars and steel industry. The increasing biological, analytical, industrial and chemical value of lanthanide(III) complexes of Schiff bases has opened a new field in the chemistry of rare earth ions. The authors report here the complexes of La(III), Pr(III), Nd(III), Sm(III) and Gd(III) with 2-N-(*m*-phenoxybenzylidine)furfurylamine [2-N-(*m*-PBFA)].

EXPERIMENTAL

Synthesis of 2-N-(*m*-phenoxybenzylidine)furfurylamine [2-N-(*m*-PBFA)]: A mixture of furfurylamine (50 mmol) and *m*- phenoxybenzaldehyde (50 mmol) in ethanol was refluxed for 2.5 h over anhydrous sodium sulphate. The solvent was removed in vacuum at 40 ºC giving a yellowish red coloured liquid.



Synthesis of metal complexes: To an ethanolic solution of lanthanide(III) chloride (2.5 mmol) was mixed with ethanolic solution of 2-N-(*m*-PBFA) (7.5 mmol) then stirred for 0.5 h and refluxed for 4 h. The excess of solvent was removed by distillation. A precipitate was obtained by cooling the remaining solution. The separated solid was filtered, washed with ethanol and dried in vacuum at room temperature.

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The synthesized complexes were found very hygroscopic and changed into liquid state on standing in atmosphere. The analytical results of the compounds are presented in Table-1.

TABLE-1
PHYSICAL PROPERTIES AND ANALYTICAL MEASUREMENTS OF LANTHANIDE(III) COMPLEXES

Compounds	m.p. (°C) / (m.w.)	State (colour)	Elemental analysis (%): Found (calcd.)					μ_{eff} (BM)
			C	H	N	M	Cl	
La(2N-*m*-PBFA)$_3$Cl$_3$	235-237	Solid powder	64.40	4.42	4.10	13.72	3.40	Diamag.
	(1077.22)	(Cream)	(64.48)	(4.50)	(4.17)	(13.81)	(3.52)	
Pr(2N-*m*-PBFA)$_3$Cl$_3$	218-220	Solid powder	64.25	4.42	4.00	13.91	3.40	3.62
	(1075.22)	(Brown)	(64.35)	(4.50)	(4.16)	(13.98)	(3.52)	
Nd(2N-*m*-PBFA)$_3$Cl$_3$	260-262	Solid crystalline	64.08	4.34	4.09	14.20	3.40	3.58
	(1078.56)	(Light brown)	(64.14)	(4.48)	(4.15)	(14.26)	(3.51)	
Sm(2N-*m*-PBFA)$_3$Cl$_3$	188-190	Solid powder	63.67	4.38	4.12	14.68	3.48	1.50
	(1084.47)	(Red)	(63.75)	(4.45)	(4.15)	(14.78)	(3.51)	
Gd(2N-*m*-PBFA)$_3$Cl$_3$	215-218	Solid powder	63.25	4.38	4.02	15.30	3.32	7.86
	(1091.57)	(Red)	(63.32)	(4.42)	(4.10)	(15.35)	(3.36)	

RESULTS AND DISCUSSION

The analytical results of all the complexes indicates 1:3 metal ligand stoichiometry. The ligand is bidentate monobasic possessing azomethine (>C=N) nitrogen and furyl oxygen (C-O-C) as the coordinating sites which further get support from the infrared studies of the ligand and the corresponding complexes.

The magnetic moment values among the trivalent lanthanide ions is due to the presence of unpaired '4*f*' electrons. The magnetic moment value of La(III), Pr(III), Nd(III), Sm(III) and Gd(III), La(III), Pr(III), Nd(III), Sm(III) and Gd(III) are given in Table-1, which suggested the presence of 0, 3, 2, 5, 9 unpaired electrons in their trivalent state.

NMR spectra: ^{1}H NMR spectra of the ligand was recorded in DMSO. The spectra shows a group chemical shift at δ 7.01-7.32 ppm which may be due to the aromatic protons (5H) present in the first benzene ring. Another multiplet at δ 7.08-7.78 ppm may be assigned as the protons (4H) present in the second benzene ring. A sharp singlet at δ 8.65 ppm is due to azomethine proton (1H). A singlet at δ 4.8 ppm represents the -CH$_2$ protons attached with the furan ring. A doublet at δ 7.20 ppm may be due to heterocyclic proton attached with the hetero atom. Another doublet at δ 6.43 and 6.25 ppm assigned as unsaturated protons (2H).

^{13}C NMR spectra of the ligand were also recorded in DMSO. The spectra shows a chemical shift at δ 156.44 ppm which may be assigned due to unsaturated C atom (-C=) present in the benzene ring. The sharp singlets at δ 117.97,128.30 and 123.50 ppm indicates the presence of saturated and unsaturated carbons (5 CH) present in the benzene ring. Two sharp singlets at δ 130.23 and 130.99 ppm may be due to aliphatic C atoms (2C). A singlet at δ 119.46 and 158.78 ppm assigned as unsaturated

C atoms of aromatic system (2 CH). The C=N atom may be at δ 161.66 ppm. A singlet at δ 57.69 ppm may be due to CH_2 group present in the compound. The singlets at δ 111.06 and 143.12 ppm indicates C=C bonding present in furan ring. The signal at δ 107.93 ppm assigned as -C- present in the heterocyclic ring.

Infrared spectra: The important infrared frequencies of the ligands and their corresponding complexes are given in Table-2. Bands observed at *ca.* 1610 cm^{-1} may be assigned due to $\nu_{C=N}$ group in 2-N (*m*-PBFA).shifting in these bands in the spectra of the complexes indicate the coordination through azomethine nitrogen ν(C=N). The strong and broad band at *ca.* 1230 cm^{-1} in the ligand, is attributed to furyl ν(C-O-C) oxygen, shifted to lower side in all the complexes suggesting the coordination *via* furyl oxygen of the free base[3,4]. The new bands which appeared in the spectra of complexes in the region *ca.* 590 cm^{-1} indicating the ν(Ln-N) bonding and at *ca.* 480 cm^{-1} may be due to Ln-O bonding in the complexes. Some bands at *ca.* 270 cm^{-1} in all the lanthanide(III) complexes may be assigned as Ln-Cl bonding. The broad band in the region *ca.* 3650-3300 cm^{-1} may be expected for water of hydration[5].

TABLE-2
INFRARED SPECTRAL DATA (cm^{-1}) FOR LANTHANIDE(III) COMPLEXES

Compounds	ν(C=N)	ν(C-O-C)	ν(M-N)	ν(M-O)	ν(M-Cl)
2N-*m*-PBFA	1610 s	1230 b	–	–	–
La(2N-*m*-PBFA)$_3$Cl$_3$	1600 s	1215 s	590 m	400 m	290 m
Pr(2N-*m*-PBFA)$_3$Cl$_3$	1595 m	1210 s	580 s	410 s	270 m
Nd(2N-*m*-PBFA)$_3$Cl$_3$	1590 s	1220 m	600 m	425 s	280 m
Sm(2N-*m*-PBFA)$_3$Cl$_3$	1580 s	1200 s	605 w	400 w	290 m
Gd(2N-*m*-PBFA)$_3$Cl$_3$	1600 s	1240 s	615 w	420 w	275 s

Electronic spectra: The electronic spectra of all the complexes were recorded in DMF and results are presented in Table-3. The red shift observed in band position the Pr[2-N(*m*-PBFA)$_3$]Cl$_3$ complexes suggests a small nephelauxetic effect[6] with respect to the free ion[7]. The spectral data of Nd[2-N(*m*-PBFA)$_3$]Cl$_3$ complexes have been compared with those of aquo ion[8] and the calculated values suggesting only a slight shift in band positions, hence a negligible nephelauxetic effect, while the complexe La[2-N(*m*-PBFA)$_3$]Cl$_3$ has no significant absorption. The value of nephalauxetic parameter (β) has been determined by the method of Jorgenson[9] using the relation:

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

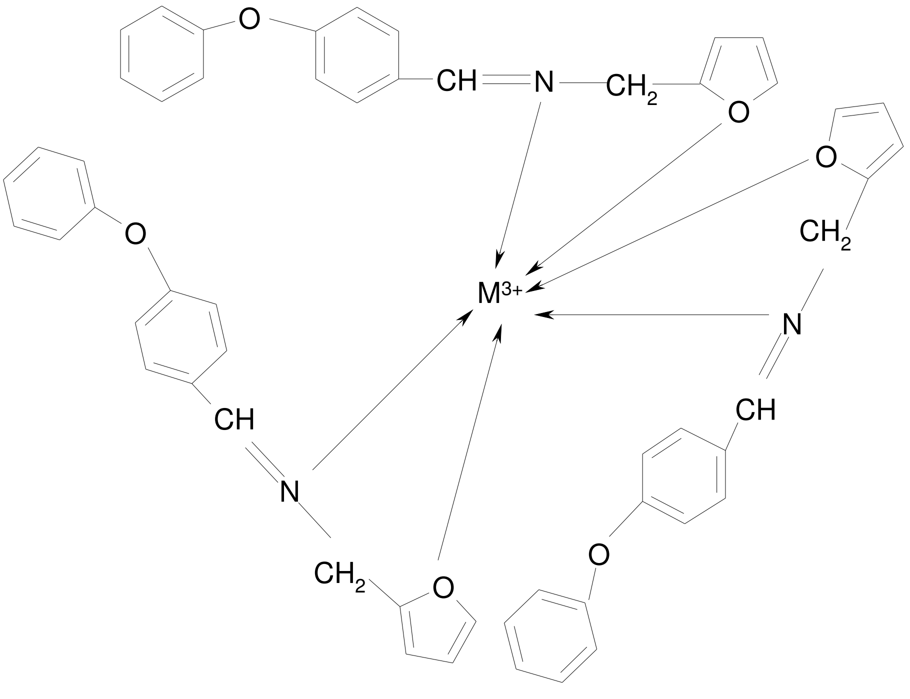
Haneric and Choppin[10] bonding parameter ($\beta^{1/2}$), have also evaluated in terms of nephalaxeutic ratio (1-β). The nephalaxeutic ratio[11], covalency angular and Sinha's covalency (η) and (δ %)[12] have also calculated.

TABLE-3
ELECTRONIC SPECTRSL DATA AND VARIOUS LIGAND FIELD PARAMETERS OF LANTHANIDE (III) COMPLEXES

Compounds	Band position	Assignments	β	b^2	δ%	η
Pr(2N-*m*-PBFA)$_3$Cl$_3$	16790	$H_4 \rightarrow {}^1D_2$	0.98	0.07	1.25	0.0063
	20610	$H_4 \rightarrow {}^3P_0$	0.99	0.05	0.67	0.0034
	22297	$H_4 \rightarrow {}^3P_2$	0.99	0.06	0.77	0.0038
Nd(2N-*m*-PBFA)$_3$Cl$_3$	12015	${}^4I_{9/2} \rightarrow F_{5/2}$	0.96	0.14	4.03	0.0199
	14090	${}^4I_{9/2} \rightarrow F_{11/2}$	0.98	0.08	1,42	0.0070
	15115	${}^4I_{9/2} \rightarrow F_{9/2}$	0.98	0.08	1.29	0.0064
	18385	${}^4I_{9/2} \rightarrow G_{11/2}$	0.99	0.05	0.62	0.0031
Sm(2N-*m*-PBFA)$_3$Cl$_3$	21323	${}^6H_{5/2} \rightarrow G_{5/2}$	0.99	0.06	0.87	0.0044
	23920	${}^6H_{5/2} \rightarrow I_{5/2}$	0.99	0.06	0.75	0.0038
	24910	${}^6H_{5/2} \rightarrow P_{3/2}$	0.99	0.04	0.40	0.0020

The positive values of these parameters suggests that the bonding between metal and ligand is covalent as compared to the metal and aquo ion.

In conclusion, the electrolytic behaviour of these complexes in conjugation with electronic spectral data suggest a coordination number six for these complexes. The proposed structure of the complexes may be



where M^{3+} = La(III), Pr(III), Nd(III), Sm(III) and Gd(III)

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