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RESEARCH ARTICLE

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STUDIES ON 3-[3-(HYDROXYIMINO) BUTAN-2-YLIDENE] HYDRAZINYLIDENE} METHYL] PHENOL COMPLEXES OF TRIVALENT LANTHANIDES

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ABSTRACT

A new Schiff base 3-[3-(hydroxyimino)butan-2-ylidene]hydrazinylidene}methyl]phenol) has been synthesized by the condensation of m-hydroxybenzaldehyde and diacetylmonoximehydrazone (1:1 molar ratio). Its complexes with trivalent lanthanides (La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+}) have been synthesized. The ligand has two coordination sites, azomethine and oximinonitrogens take part in coordination. The complexes have been assigned the general formula $[Ln(DMHmHB)_2NO_3]$ on the basis of elemental analysis, molar conductance, magnetic moment, PMR, electronic absorption and FT(IR) spectral studies. The electronic spectra of the complexes of La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} have been analyzed and discussed. The spectral parameters show covalent nature of bonding between the metal and the synthesized ligand.

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INTRODUCTION

A number of Schiff base complexes of transition and inner transition metals have been reported in literature[1-4]. The recent reports include complexes of diacetylmonoximehydrazidesalicylidene[5], diacetylmonoximehydrazide[6], benzilmonoxime[7], benzilmonoximehydrazide[8-9] and isonitrosopropiophenonehydrazidesalicyalidene[10]. In this paper we report lanthanide (La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+}) complexes of Schiff base diacetylmonoximehydrazide-m-hydroxybenzalde, IUPAC name of 3-[3-(hydroxyimino)butan-2-ylidene]hydrazinylidene}methyl]phenol (hereafter abbreviated as HDMHmHB) derived from the condensation of equimolar of diacetylmonoximehydrazide and m-hydroxybenzaldehyde.

Experimental: The hydrated lanthanides salts (S.D. Fine Chemicals, LobaChemie and B.D.H., 99.99% pure) were used as such. All the physicochemical methods were similar to that employer earlier[5-7]. The electronic absorption spectra of the complexes were recorded on JASCO V-650 Spectrophotometer. ^1H NMR spectra of the ligand and its metal complexes were obtained on Brucker AV300 NMR spectrometer using TMS as internal standard. The FT(IR) spectrum was recorded in the range 400–4000 cm^{-1} by KBr pellet using a 'Perkin- Elmer spectrum 100' model FT-IR spectrophotometer. Complexes were decomposed by repeated treatment with conc. HNO_3 and H_2SO_4 and finally metal contents were estimated complexometrically by EDTA using xylenol orange at pH-6.

Synthesis of HDMHmHB ligand: The ligand HDMHmHB was synthesized by stirring m-hydroxybenzaldehyde (6.10g, 0.05mol) and diacetylmonoximehydrazide (5.50g, 0.045mol) in 100ml ethanol for about 9h until a red-yellow precipitate separated. It was filtered, washed with ethanol and dried in hot air oven.

Synthesis of complexes: The coordination complexes of the type $[Ln(DMHmHB)_2NO_3]$ were synthesized by refluxing ethanolic solution of the ligand HDMHmHB and the corresponding metal salts in stoichiometric amounts at 70-

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80^0C for 3-15h. The solid complexes were filtered off and washed with aliquots of ethanol and recrystallised from chloroform and finally dried in hot air oven.

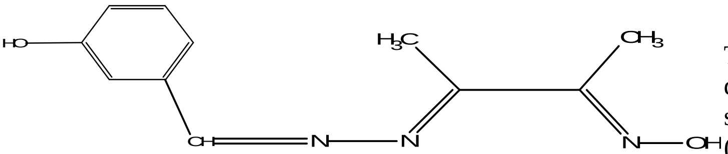

Figure-1. 3-(hydroxyimino)butan-2-ylidene]hydrazinylidene}methyl]phenol)

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Synthesis of complexes: The coordination complexes of the type $[Ln(DMHmHB)_2NO_3]$ were synthesized by refluxing ethanolic solution of the ligand HDMHmHB and the corresponding metal salts in stoichiometric amounts at 70-80^0C for 3-15h. The solid complexes were filtered off and washed with aliquots of ethanol and recrystallised from chloroform and finally dried in hot air oven.

RESULTS AND DISCUSSION

The ligand HDMHmHB interacts with the trivalent lanthanide ions and yields complexes which on the basis of elemental analyses and molar conductance (Table-1) have been given the general formula $[Ln(DMHmHB)_2NO_3]$ i.e. $(LnC_{33}H_{36}N_{10}O_9)$.

The formation of the complexes may be represented by the general equation:

$$Ln(NO_3)_3.6H_2O + 3HDMHmHB \xrightarrow[\text{(Ethanol)}]{\text{Stirring + Heating}} [Ln(DMHmHB)_3.NO_3]$$

The complexes were well-defined solids with high decomposition points. They are air-and moisture-stable and soluble in common organic solvents. The stoichiometric data (Table-1) show the presence of three nitrates ions per lanthanide metal; this is quite understandable since the ligand is neutral and lanthanide is originally trivalent. The molar conductance of the complexes at 10^{-3}M dilution in nitrobenzene is in the range 20.63-26.13$\Omega^{-1}cm^2mol^{-1}$, expected for 1:1 electrolytes[11]. It is therefore, concluded that one out the three nitrates is present inside the coordination sphere.

Electronic Absorption spectra: The electronic spectra of all complexes were recorded in chloroform and presented in **Table-2**. The electronic spectra of the inner transition metal complexes show a red shift of the bands as compared to those of respective aqua-ions which is known as nephelauxetic effect[12]. The shift is a measure of covalency in a given complex. The nephelauxetic ($\bar{\beta}$), bonding ($b^{1/2}$) and covalency (δ) parameters have been calculated by the same method as reported elsewhere[13]. The parameter $\bar{\beta}$ is less than one, and $b^{1/2}$ and δ are positive for these complexes showing covalent nature of bonding between the metal and the ligand. It is evident from the **Table-2** that the present complexes can be arranged in the following decreasing order of covalency: La>Nd>Sm>Gd>Tb>Dy.

FT(IR) Spectra: The FT(IR) of all prepared complexes absence any band between 3300-3400cm^{-1} due to oximino –OH,which is reported at 3316cm^{-1} in ligand HDMHmHB, indicated that hydroxyl group deprotonated during complexation. The IR band characteristic of phenolic –OH, appearing at 3192cm^{-1} in the spectrum of ligand, remains almost unchanged in the spectra of the complexes. The lack of a change in the phenolic band indicates that this group does not take part in coordination. In the spectrum of the HDMHmHB, a band occurring at 1617cm^{-1} has been assigned to the azomethine>C=NN- stretching[14]. This band in the complexes appears at lower frequency (1597-1603cm^{-1}) for metal complexes, indicating coordination through azomethine nitrogen. The absorption band at 1571cm^{-1} assigned as oximino (>C=NOH) group and is shifted in the complexes to lower site (1505-1540cm^{-1}), has been assigned to the metal-nitrogen stretching[15-16].

Table 1. Physical and Analytical data of HDMHmHB ligand and its Ln(III) complexes

Compound	Colour	% Yield	MP/DP in ºC	% Element Content, Expected (Observed)					Molar Cond	Magntic Moments
				C	H	N	O	M		
HDMHmHB	Yellow	66.47	201	60.26 (60.23)	5.98 (5.97)	19.17 (19.15)	14.60 (14.58)	-	-	-
$[La(DMHmHB)_3]NO_3$	Yellow	67.59	276	47.39 (47.33)	4.31 (4.27)	15.08 (15.00)	11.49 (11.41)	16.62 (16.59)	23.47	Dia
$[Nd(DMHmHB)_3]NO_3$	Yellow Brown	70.59	281	47.09 (46.99)	4.28 (4.27)	14.98 (14.93)	11.41 (11.39)	17.15 (17.12)	26.13	3.60
$[Sm(DMHmHB)_3]NO_3$	Brown	64.17	289	46.67 (46.58)	4.25 (4.22)	14.87 (14.82)	11.33 (11.31)	17.75 (17.69)	21.74	1.65
$[Gd(DMHmHB)_3]NO_3$	Brown	66.49	273	48.81 (48.70)	4.44 (4.39)	15.53 (15.44)	11.83 (11.78)	19.38 (19.37)	20.68	7.92
$[Tb(DMHmHB)_3]NO_3$	Red Brown	69.28	267	46.28 (46.23)	4.21 (4.19)	14.72 (14.41)	11.22 (11.03)	18.57 (18.39)	20.64	9.76
$[Dy(DMHmHB)_3]NO_3$	Brown	73.33	289	48.50 (48.49)	4.41 (4.33)	15.43 (15.38)	11.75 (11.70)	19.90 (19.87)	22.92	10.58

Table-2. UV-Visible spectral data of HDMHmHB ligand and its Ln (III) metal complexes

Compound	λnm	ε (dm^3/mol/cm)	Transition	
HDMHmHB	366	12664	$\pi^* \leftarrow \pi$	
	298	7980	$\pi^* \leftarrow \pi$	
	225	7198	$\pi^* \leftarrow \pi$	
[Nd(DMHmHB)$_3$]	827	568	$^4F_{9/2} \leftarrow {}^4H_{5/2}$	$\beta_{ave} = 0.9770$ $b^{1/2} = 0.01355$ δ% = 2.1659 η = 1.047
	770	3068	$^4P_{13/2} \leftarrow {}^4H_{5/2}$	
	600	4098	$^4P_{9/2} \leftarrow {}^4H_{5/2}$	
	526	9480	$^4P_{7/2} \leftarrow {}^4H_{5/2}$	
[Tb(DMHmHB)$_3$]	595	1700	$^7F_4 \leftarrow {}^5D_4$	
	531	1600	$^7F_5 \leftarrow {}^5D_4$	
	400	4500	$^7F_6 \leftarrow {}^5D_4$	
	370	5969	MLCT	
[La(DMHmHB)$_3$]	263	15468	MLCT	
[Sm(DMHmHB)$_3$]	748	700	$^4F_{9/2} \leftarrow {}^4H_{5/2}$	$\beta_{ave} = 0.9949$ $b^{1/2} = 0.0053$ δ% = 1.0101
	515	2087	$^4P_{13/2} \leftarrow {}^4H_{5/2}$	
	434	3871	$^6P_{7/2} \leftarrow {}^4H_{5/2}$	
	393	5836	$^4P_{9/2} \leftarrow {}^4H_{5/2}$	
[Gd(DMHmHB)$_3$]	345	12356	$^8S_{1/2} \rightarrow {}^6P_{1/2}$	$\beta_{ave} = 0.9458$, $b^{1/2} = 0.0271$, δ% = 5.42η = 1.1146
	267	19563	MLCT	
[Dy(DMHmHB)$_3$]	429	6530	$^4H_{15/2} \rightarrow {}^4F_{9/2}$	
	348	7458	$^4H_{15/2} \rightarrow {}^4I_{15/2}$	
	302	12670	MLCT	

Table 3. IR spectral bands of the ligand (HDMHmHB) and its metal complexes (cm^{-1})

Assignments	HDMHmHB	Nd(III)	Tb(III)	La(III)	Sm(III)	Gd(III)	Dy(III)
Oximino-OH	3316	-	-	-	-	-	-
Phenolic -OH	3173	3192	3148	3213	3181	3109	3226
νC=C Ar.	3022	3000	2946	3045	3068	3045	3021
νC=NN	1617	1596	1596	1600	1603	1597	1598
νC=NO	1571	1529	1529	1507	1505	1506	1540
$\nu_1(NO_3)$	1450	1449	1452	1454	1469	1463	1477
$\nu_2(NO_3)$	1030	1033	1029	1331	1033	1029	1028
$\nu_3(NO_3)$	1334	1340	1340	1334	1324	1323	1324
$\nu_4(NO_3)$	1387	1387	1385	1384	1384	1387	1386
$\lvert \nu_4(NO_3) - \nu_1(NO_3) \rvert$	63	62	67	70	85	76	91
νN-N	970	1008	1008	1008	1008	1009	1033
νN→O	-	1212	1194	1226	1225	1225	1226
νM-N	-	570	570	566	571	565	582
νM→N	-	522	522	521	523	525	528

Table 4. PMR spectrum of HDMHmHBand its metal complexes in d_6 DMSO

Compound	Oximino –OH	Phenolic -OH	-CH=	Phenyl Ring	$-CH_3$
HDMHmHB	11.52	11.26	9.00	6.81-7.19	2.51
[La(DMHmHB)$_3$]	-	11.19	9.02	7.08-7.41	2.49

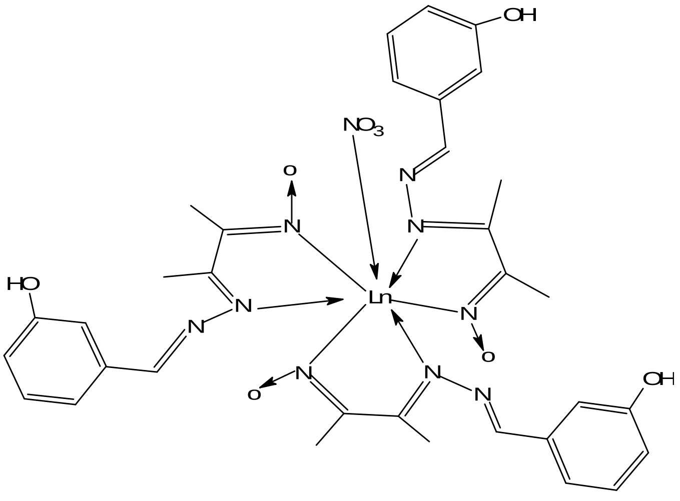

Figure 1. Structure of metal complexes of HDMHmHB ligand

Appearance of new band in all complexes at 1194-1226cm^{-1}corresponds to presence of $N \rightarrow O$ group which indicates oximino group coordinate through nitrogen and not through oxygen[17]. The IR spectra of complexes give a $|\nu_4 - \nu_1|$ separation in the range 62– 91cm^{-1} suggesting monodentate bonding for the nitrate group.Some new medium to weak bands were also observed in the range (521-582cm^{-1}) in case of complexesof HDMHmHB ligand has no absorption. These new medium to weak bands are assigned as; ν(Ln-N) or/and ν(Ln→N) modes observed for various Ln(III) complexes. The partial IR data for HDMHmHB ligand and their corresponding complexes are given in Table-3.

The PMR spectra: PMR spectra were recorded using d_6 DMSO as solvent and TMS was used as an internal standard. Spectral data of HDMHmHB reveals two singlet peaks at 11.52 and 11.26δ. The intensity of the peaks suggests that these are due to single deshielded protons and assigned as oximino and phenolic protons respectively. The peak observed in free ligand HDMHmHB at 11.52δ is absent in prepared La(DMHmHB)$_3$] metal complex, suggested that oximino group deprotonated in complex formation[18-19]. Multiplet observed at in the region 6.81-7.19δ (4H), 1, 3-disubstitted benzene ring and free methyl protons 2.51δ (6H). Another singlet peak reveals at 9.00δ (1H) assigned as methane (-CH=) group of HDMHmHB. All these group unchangeable in La(III) metal complex, indicated that their non-involvement in complex formation and also suggest monobasic character of HDMHmHB ligand[20].

CONCLUSION

The preferred coordination number of Ln(III) metal ion is 7. This coordination number depends upon the nature of the ligand. Conductance and molecular weight data show present of nitrate anion inside the coordination sphere in the complexes. FT(IR) spectral data reveal that ligand is coordinated to metal ions nitrogen atoms of oximino and azomethine linkages in all the complexes studied. Hence, coordination number 7 is suggested for metal ion in this lanthanoid complexes[21-23]. The possible structure of the complexes is given **Figure-1**.

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