

Synthesis and Characterization of Some Lanthanide(III) Chloro Complexes Derived from 4[N-(4'-Hydroxy-3'-Methoxybenzalidene) Amino] Antipyrine Semicarbazone and 4[N-(3',4',5'-Trimethoxybenzalidene) Amino]Antipyrine Semicarbazone

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ABSTRACT: Lanthanide(III) chloro complexes of 4[N-(4'-hydroxy-3'-methoxybenzalidene) amino] antipyrine semicarbazone (HMBAAPS) (I) and 4[N-(3',4',5'-trimethoxybenzalidene) amino] antipyrine semicarbazone (TMBAAPS) (II) with the general composition $\text{LnCl}_3 \cdot 2\text{L}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}$ or Ho ; $\text{L} = \text{HMBAAPS}$ or TMBAAPS) are reported. All the complexes were synthesized in ethanolic medium and refluxed the reaction mixture (1:2.2, M:L ratio). The yield percentage ranging from 78 – 82%. The complexes are non-ionic in nature. The infrared spectral studies reveal that both of the semicarbazones are tridentate (N,N,O) ligands. Magnetic spectral and thermal properties of the complexes have also been investigated. A coordination number nine is tentatively suggested in these complexes.

KEY WORDS: Lanthanide(III) complexes, Lanthanide(III) chloro complexes, Lanthanide(III) chloro complexes of 4[N-(4'-hydroxy-3' methoxybenzalidene)amino] antipyrine semicarbazone and Lanthanide(III) chloro complexes of 4[N-(3',4',5'-trimethoxybenzalidene)amino]antipyrine semicarbazone.

INTRODUCTION

The cationic size and the charge on the metal atom are important factors in the formation of stable coordination

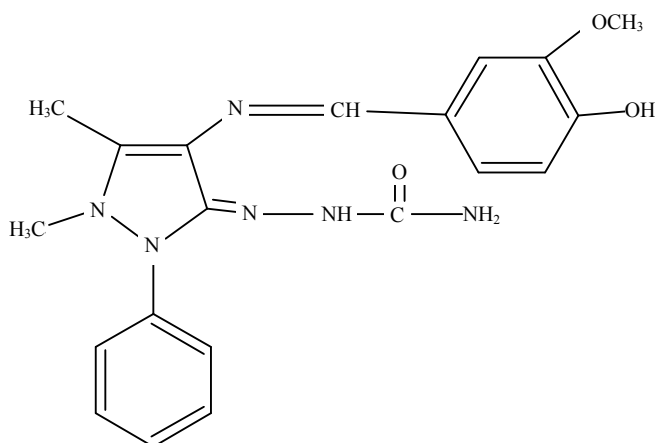
compounds. Pauling rule [1] provide a good correlation between cation-anion radius ratio and the coordination

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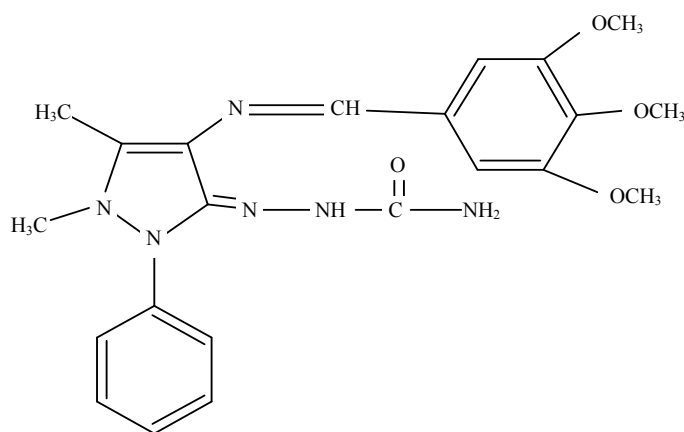
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4[N-(4'-Hydroxy-3'-methoxybenzalidene)amino]antipyrine semicarbazone (TMBAAPS)



4[N-(3',4',5'-Trimethoxybenzalidene)amino]antipyrine semicarbazone (TMBAAPS)

Fig. 1

number of the metal ions for the ionic compounds with the simple AB composition. Because of their large size, the lanthanide ions generally have higher coordination number than transition elements [2], while coordination numbers greater than 6 are rare for transition elements. On the other hand lanthanide(III) ions with their high positive charge and large size are the best candidates to form stable complexes with high coordination numbers and generally coordination numbers of 6 to 10 are observed in lanthanide(III) complexes [2]. The chemistry of lanthanide(III) coordination compounds studied have been derived from strongly chelating, anionic or neutral ligands containing highly electronegative donor atoms [3]. The trivalent lanthanide ions are classified as hard acids according to

Pearson [4]. Thus these metal ions are expected to form stronger complexes with ligands containing O and N-donor atoms.

Recently a good number of coordination compounds of lanthanide(III) with various Schiff bases are described in literature [5-9], but comparatively less is known about the lanthanide(III) coordination compounds of semicarbazones of 4-aminoantipyrine [10,11]. Semicarbazones are the best donor ligands in case of hard acid like lanthanides. In the present work, we report some nona-coordinated complexes of lanthanide(III) chloride derived from 4[N-(4'-hydroxy-3'-methoxybenzalidene)amino]antipyrine semicarbazone (HMBAAPS) and 4[N-(3',4',5'-trimethoxybenzalidene)amino]antipyrine semicarbazone (TMBAAPS) (Fig. 1).

EXPERIMENTAL

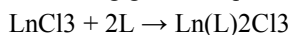
The detail experimental procedure about the synthesis of ligand is given elsewhere [10]. The ligands HMBAAPS and TMBAAPS were synthesized from 4-aminoantipyrine by the reported method [10]. The lanthanide(III) chlorides obtained from Rare Earth Products Ltd., (India) were used without further purification. All the complexes were prepared by following general methods.

The respective lanthanide(III) chloride and the corresponding ligand were taken in (1:2.2) molar ratio both in ethanol and the reaction mixture was refluxed for ~ 2 h on a water bath. The reaction mixture was then concentrated on a water bath to reduce the volume by about 50% until a precipitate was obtained (digested for about 20 min), filtered, washed thoroughly with ethanol and diethyl ether and dried over P4O10 in a vacuum desiccator.

The chemical analysis and physico-chemical studies of the metal-complexes were performed as reported earlier [7-9].

RESULTS AND DISCUSSION

The reactions of lanthanide(III) chloride with HMBAAPS and TMBAAPS result complexes of the general composition $[\text{Ln}(\text{L})_2\text{Cl}_3]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}$ or Ho ; $\text{L} = \text{HMBAAPS}$ or TMBAAPS) according to the following general equation:



The analytical data including yield percentage of the complexes are presented in table 1. The complexes are generally stable and could be stored for a long time. The low molar conductance values (table 1) in nitrobenzene reveal their non-electrolytic nature [12]. The ratio of molecular weight observed to that calculated (~ 0.98) shows that all the complexes are monomeric in nature.

The magnetic moment values observed in the present study are also presented in table 1, which shows that lanthanum complexes are diamagnetic in nature. All other tripositive lanthanide complexes are paramagnetic in nature due to the presence of 4f-electrons, which are effectively shielded by 5s25p6 electron [13, 14].

Infrared Spectra

The partial infrared spectra of HMBAAPS and

TMBAAPS and their lanthanide(III) coordination compounds are presented in table 2. In the present complexes, as expected, the $\nu(\text{NH}_2)$ of the hydrazinic nitrogen of semicarbazide (~ 1622 cm^{-1}) is absent in the infrared spectra of HMBAAPS and TMBAAPS [15]. It has also been observed that the amide-II band is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen [16]. The characteristic absorption of the carbonyl group in HMBAAPS and TMBAAPS is observed at 1702 and 1700 cm^{-1} respectively [17]. In all the complexes, this band is shifted towards lower energy in the 1650-1640 cm^{-1} region (Table 2). The amide-II band in both the ligands has been observed in 1565-1560 cm^{-1} region. In all the present complexes this band is also shifted towards lower wave numbers by ~ 30 cm^{-1} . This observation suggests coordination to the lanthanides through carbonyl oxygen atom. The strong band at ~ 1605 cm^{-1} in these semicarbazones apparently has a large contribution from the $\nu(\text{C}=\text{N})$ mode of semicarbazone moiety [18]. This has been observed as a blue shift in the position of the (C=N) band in all complexes as compared to the free ligands. Another strong band was observed in 1620-1615 cm^{-1} region due to azomethine (C=N) absorption. On complexation, this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethine-N atom [19-21]. In far infrared region the bands due to $\nu(\text{Ln}-\text{O})/\nu(\text{Ln}-\text{N})$ are also observed [22,23]. The above discussion clearly indicates that these ligands serve as tridentate ligands, coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms. In the present studies $\nu(\text{Ln}-\text{Cl})$ has been assigned in the region 290-270 cm^{-1} .

Electronic Spectra

Typical spectral data of some representative complexes are given in table 3. Lanthanum has no significant absorption in the visible region. The absorption bands of Pr(III), Nd(III) and Sm(III) complexes in the visible and near infrared region appear due to transitions from the ground levels $^3\text{H}_4$, $^4\text{I}_{9/2}$ and $^6\text{H}_{5/2}$ respectively to the excited J-levels of 4f configuration. Some red shift or nephelauxetic

Table 1: Analytical, Molecular Weight, Conductivity, and Magnetic susceptibility Data of Lanthanide(III) Chloride Complexes of HMBAAPS and TMBAAPS

Complex	Colour, Yield %	Analysis: Found (calcd.) %			m. w. Found (calcd.)	A_m (ohm ⁻¹ cm ² mole ⁻¹)	μ_{eff} (B.M)
		Ln	N	Cl			
LaCl ₃ ·2(HMBAAPS)	Yellow 79	13.36 (13.42)	16.16 (16.25)	10.22 (10.30)	1030 (1033.5)	2.3	Diamagnetic
PrCl ₃ ·2(HMBAAPS)	Yellow 80	13.49 (13.57)	16.12 (16.22)	10.20 (10.28)	1031 (1035.5)	2.1	3.54
NdCl ₃ ·2(HMBAAPS)	Pale yellow 82	13.69 (13.78)	16.08 (16.17)	10.18 (10.25)	1033 (1038.5)	1.9	3.52
SmCl ₃ ·2(HMBAAPS)	Yellow 82	14.27 (14.36)	15.97 (16.08)	10.12 (10.19)	1039 (1044.5)	2.2	1.73
GdCl ₃ ·2(HMBAAPS)	Dark yellow 80	14.82 (14.93)	15.87 (15.97)	10.07 (10.12)	1047 (1051.5)	2.1	7.82
TbCl ₃ ·2(HMBAAPS)	Yellow 78	14.98 (15.09)	15.83 (15.94)	10.04 (10.10)	1046 (1053.5)	1.8	9.82
DyCl ₃ ·2(HMBAAPS)	Yellow 82	15.26 (15.37)	15.80 (15.89)	10.02 (10.07)	1050 (1057)	1.7	10.26
HoCl ₃ ·2(HMBAAPS)	Yellow 81	15.34 (15.49)	15.77 (15.87)	10.00 (10.06)	1051 (1058.5)	1.5	10.31
LaCl ₃ ·2(TMBAAPS)	Yellow 80	12.28 (12.39)	14.87 (14.97)	9.43 (9.49)	1116 (1121.5)	1.3	Diamagnetic
PrCl ₃ ·2(TMBAAPS)	Yellow 81	12.42 (12.51)	14.87 (14.95)	9.40 (9.47)	1118 (1123.5)	1.9	3.59
NdCl ₃ ·2(TMBAAPS)	Yellow 80	12.66 (12.78)	14.82 (14.91)	9.38 (9.45)	1121 (1126.5)	2.0	3.50
SmCl ₃ ·2(TMBAAPS)	Yellow 81	13.08 (13.16)	14.74 (14.82)	9.34 (9.40)	1126 (1132.5)	2.1	1.67
GdCl ₃ ·2(TMBAAPS)	Yellow 82	13.68 (13.77)	14.64 (14.74)	9.28 (9.34)	1133 (1139.5)	1.9	7.84
TbCl ₃ ·2(TMBAAPS)	Yellow 80	13.82 (13.92)	14.62 (14.71)	9.27 (9.32)	1134 (1141.5)	1.9	9.88
DyCl ₃ ·2(TMBAAPS)	Yellow 82	14.08 (14.19)	14.57 (14.67)	9.23 (9.30)	1138 (1145)	2.0	10.31
HoCl ₃ ·2(TMBAAPS)	Yellow 79	14.20 (14.30)	14.55 (14.65)	9.24 (9.28)	1140 (1146.5)	1.8	10.37

effect is observed in acetonitrile solution of these coordination compounds. This red shift is usually accepted as evidence of a higher degree of covalency than existing in the aquo compounds [24,25]. In all the complexes marked, enhancement in the intensity of the bands has been observed. The red-shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate complexes. From the β -values, the covalence factor ($b^{1/2}$), Sinha's covalency parameters ($\delta\%$) (metal-ligand covalency per cent) and the covalency angular overlap parameter (η) have been calculated [26]. The positive values for $(1-\beta)$ and $\delta\%$ in these coordination compounds suggest that the bonding

between the metal and HMBAAPS is covalent compared with the bonding between the metal and an aquo ion. The values of parameter of bonding ($b^{1/2}$) and angular overlap parameter (η) were found to be positive indicating covalent bonding.

Thermogravimetric studies

Thermoanalytical results of $\text{Ln}(\text{L})_2\text{Cl}_3$ ($\text{Ln} = \text{La, Gd}$ or Dy) are summarized in table 4. The weight loss curves of these complexes suggest that these complexes do not show the presence of water molecule either in or out of the coordination sphere. The analysis of the thermogravimetric curves suggests that above 240°C , the compounds start to lose mass with partial

Table 2: Key Infrared Bands (cm^{-1}) of Lanthanide(III) Chloride Complexes of HMBAAPS and TMBAAPS

Compounds	$\nu(\text{C}=\text{N})$ azomethinic	$\nu(\text{C}=\text{N})$ hydrazinic	$\nu(\text{C}=\text{O})$			$\nu(\text{Ln}-\text{O})/\nu(\text{Ln}-\text{N})$
			I	II	III	
HMBAAPS	1625 s	1605 s	1702 s	1560 m	1355 m	----
$\text{LaCl}_3 \cdot 2(\text{HMBAAPS})$	1600 s	1622 s	1645 s	1535 m	1330 m	470 m, 368 w
$\text{PrCl}_3 \cdot 2(\text{HMBAAPS})$	1595 s	1625 s	1650 s	1530 m	1332 m	472 m, 380 w
$\text{NdCl}_3 \cdot 2(\text{HMBAAPS})$	1602 s	1622 s	1652 s	1532 m	1328 m	470 m, 372 w
$\text{SmCl}_3 \cdot 2(\text{HMBAAPS})$	1598 s	1628 s	1645 s	1530 m	1325 m	480 m, 382 w
$\text{GdCl}_3 \cdot 2(\text{HMBAAPS})$	1595 s	1625 s	1640 s	1535 m	1330 m	475 m, 372 w
$\text{TbCl}_3 \cdot 2(\text{HMBAAPS})$	1592 s	1630 s	1642 s	1530 m	1332 m	470 m, 375 w
$\text{DyCl}_3 \cdot 2(\text{HMBAAPS})$	1593 s	1628 s	1640 s	1532 m	1330 m	465 m, 382 w
$\text{HoCl}_3 \cdot 2(\text{HMBAAPS})$	1592 s	1625 s	1645 s	1535 m	1332 m	472 m, 385 w
TMBAAPS	1615 s	1600 s	1700 s	1565 m	1350 m	----
$\text{LaCl}_3 \cdot 2(\text{TMBAAPS})$	1592 s	1622 s	1645 s	1535 m	1335 m	472 m, 375 w
$\text{PrCl}_3 \cdot 2(\text{TMBAAPS})$	1585 s	1630 s	1650 s	1530 m	1332 m	475 m, 385 w
$\text{NdCl}_3 \cdot 2(\text{TMBAAPS})$	1580 s	1625 s	1652 s	1532 m	1330 m	470 m, 380 w
$\text{SmCl}_3 \cdot 2(\text{TMBAAPS})$	1590 s	1632 s	1645 s	1528 m	1332 m	46 m, 382 w
$\text{GdCl}_3 \cdot 2(\text{TMBAAPS})$	1592 s	1630 s	1640 s	1530 m	1330 m	490 m, 385 w
$\text{TbCl}_3 \cdot 2(\text{TMBAAPS})$	1590 s	1625 s	1642 s	1533 m	1335 m	465 m, 392 w
$\text{DyCl}_3 \cdot 2(\text{TMBAAPS})$	1588 s	1628 s	1640 s	1528 m	1332 m	470 m, 390 w
$\text{HoCl}_3 \cdot 2(\text{TMBAAPS})$	1590 s	1625 s	1643 s	1530 m	1330 m	475 m, 385 w

Table 3: Electronic Spectral Data (cm^{-1}) and Related Bonding Parameters of Lanthanide(III) Chloride Complexes of HMBAAPS

Ln^{3+}	LnCl_3 Electronic Spectral Bands	$\text{LnCl}_3 \cdot 2\text{L}$ Electronic Spectral Bands	J-Levels	$(1-\beta)$	β	$b^{1/2}$	$\delta\%$	η
Pr^{3+}	22,470	22,320	$^3\text{H}_4 \rightarrow ^3\text{P}_2$	0.00667	0.99332	0.04083	0.67148	0.00335
	21,280	21,100	$\rightarrow ^3\text{P}_1$	0.00845	0.99154	0.04596	0.86128	0.00425
	20,830	20,650	$\rightarrow ^3\text{P}_0$	0.00864	0.99135	0.04647	0.87153	0.00435
	16,950	16,750	$\rightarrow ^1\text{D}_2$	0.01179	0.98820	0.05429	1.19307	0.00591
Nd^{3+}	19,420	19,250	$^4\text{I}_{9/4} \rightarrow ^2\text{G}_{9/2}$	0.00875	0.99124	0.04677	0.88273	0.00440
	17,390	17,200	$\rightarrow ^4\text{G}_{5/2}, ^2\text{G}_{7/2}$	0.01092	0.98907	0.05224	1.10406	0.00551
	13,420	13,200	$\rightarrow ^2\text{S}_{3/2}, ^4\text{F}_{7/2}$	0.01639	0.98360	0.06401	1.66632	0.00823
	12,500	12,350	$\rightarrow ^4\text{F}_{5/2}, ^4\text{H}_{9/2}$	0.01200	0.98800	0.05477	1.21457	0.00601
Sm^{3+}	24,850	24,720	$^4\text{H}_{5/2} \rightarrow ^4\text{F}_{9/2}$	0.00523	0.99476	0.03615	0.52575	0.00262
	24,100	23,820	$\rightarrow ^6\text{P}_{5/2}$	0.01161	0.98838	0.05387	1.17464	0.00586
	21,600	21,450	$\rightarrow ^4\text{I}_{13/2}$	0.00694	0.99305	0.04165	0.69885	0.00349

L = HMBAAPS

Table 4: Thermoanalytical Results of Lanthanide(III) Chloride Complexes of TMBAAPS

Complex	Sample weight (mg)	Residual mass (mg)	Ligand mass loss (%)				Residua (%) ~820 °C	
			230-300 °C		350-460 °C		Theor. ^c	Exp.
			Theor. ^a	Exp.	Theor. ^b	Exp.		
LaCl ₃ .2(TMBAAPS)	22.50	3.31	39.05	38.78	78.10	77.82	14.53	14.74
GdCl ₃ .2(TMBAAPS)	25.60	4.12	38.43	38.19	76.87	76.12	15.88	16.10
DyCl ₃ .2(TMBAAPS)	27.90	4.59	38.25	37.94	76.50	76.14	16.28	16.47

a) Calculated for loss of one mole of TMBAAPS

b) Calculated for total loss of TMBAAPS

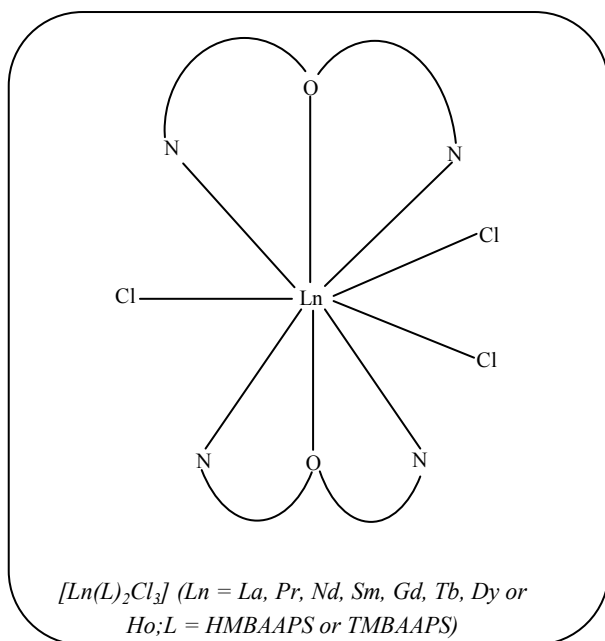
c) Calculated for lanthanide oxides Ln₂O₃ (Ln = La, Gd or Dy)

Fig. 2

evaporation of the organic ligand up to a temperature of 300°C. The mass loss corresponds to one molecule of TMBAAPS. In the temperature range 340-390°C, another molecule of TMBAAPS is also lost. The residues obtained after heating up to ~ 840°C to constant weight, is very close to that expected for the lanthanide oxides [27].

Stereochemistry

The non-electrolytic behaviour of all the present coordination compounds suggests that all three Cl⁻ are coordinated to the metal ion. Since HMBAAPS and TMBAAPS are neutral tridentate organic ligands (N, N, O-donor) a coordination number nine to the lanthanide ion has been suggested in all these coordination

compounds [28]. The possible general structure of these coordination compounds can be shown in Fig. 2.

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