



Synthesis and Characterization of Some Seven Coordinated Complexes of Lanthanide(III) Perchlorates with 4-[n-(4'-Ethylbenzylideneamino)]- Antipyrine Semicarbazone as Primary Ligand and Pyridine as Secondary Ligand

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ABSTRACT

Mixed ligands complexes of lanthanide(III) perchlorates obtained from 4-[N-(ethylbenzylideneamino)]-antipyrine semicarbazone (*ebaaps*) as primary ligand and pyridine(*py*) as secondary ligand have been synthesized and characterized. The analytical studies on these compounds include elemental analyses, molecular weight determination, molar conductance, and magnetic susceptibility, infrared and electronic spectra. The primary ligand, (*ebaaps*), in these complexes behaves as neutral tridentate (O,N,N) while the secondary ligand pyridine(*py*) acts as unidentate nitrogen donor. The general composition of these complexes may be given as $[Ln(ebaaps)_2(py)](ClO_4)_3$, [Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho]. The values of nephelauxetic effect (β), covalence factor ($b^{1/2}$), Sinha parameter (δ %) and the angular overlap parameter (η) of the complexes have been calculated, and their thermal stabilities worked out by TGA.

Keywords: Lanthanide (III) Complexes, Semicarbazone, Pyridine, Characterization.

INTRODUCTION

Lanthanide ions attach special importance in coordination and bioinorganic chemistry. The study of lanthanide(III) complexes with heterocyclic compounds, bearing nitrogen, oxygen or sulphur, as ligand, has attracted increasing attention¹⁻⁵. Lanthanide ions, in view of their particular electronic configuration and size are often used as a spectroscopic probe, surrogating for calcium(II) ions, in the studies of biological systems, as promoters in the dyeing industry, and as diagnostic

agent in chemicals acting as medicine⁶⁻⁸. Pyrazolone (N-heterocyclic compound) is an active moiety, serving as a pharmaceutical ingredient of many nonsteroidal anti-inflammatory agents used in the treatment of arthritis and other musculoskeletal and joints disorders. Literature reveals that certain drugs showed increased activity when administered in the form of its metal chelates compared to the virgin form. The complexing behavior of 4-aminoantipyrine has been modified into a flexible ligand system by condensing it with a variety of reagents⁹⁻¹³. A number of reports are

available on the coordination abilities of thiosemicarbazones of 4-aminoantipyrine¹⁴⁻¹⁶ with different metal ions but comparatively less is known about the mixed ligand complexes of lanthanide(III) ions with substituted 4-aminoantipyrine. The present study reports the synthesis and characterization of some seven coordinated complexes of lanthanide (III) perchlorates with 4[N-(4'-ethylbenzalidene amino)antipyrine semicarbazone (*ebaaps*) (Fig.1) as primary ligand, and pyridine as secondary ligand.

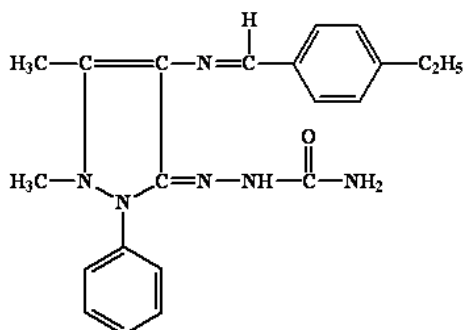


Fig.1.4-[N-(4'-ethylbenzalidene) amino]-antipyrine semicarbazone.

EXPERIMENTAL

The lanthanide(III) oxides were procured from Rare Earth Products Ltd. (India). The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid and then evaporating off the excess of acid¹⁷. The ligand *ebaaps* was synthesized as reported in the literature¹⁸. The commercial pyridine obtained (a C.D.H. product) was used after distillation.

All the complexes were synthesized by a general procedure. A solution of $\text{Ln}(\text{ClO}_4)_3$ (2 mmol), *ebaaps* (4 mmol) and pyridine (2 mmol) in absolute ethanol was refluxed for 2-3 h. The precipitated product collected after concentrating and cooling the hot solution was filtered, washed first with ethanol and then with diethyl-ether, and finally dried in an oven at 100°C to a yield of 70-80%.

Analysis

The lanthanide metal content was estimated as its oxide by direct combustion of the complex in a platinum crucible. Percentage of nitrogen was determined by Kjeldahl method. The perchlorate content was estimated by the Kurz's

method. The molecular weight of the complexes was determined cryoscopically in freezing PhNO_2 system using Beckmann thermometer of $\pm 0.01^\circ\text{C}$ accuracy in. The conductivity measurements were carried on a Toshniwal Conductivity Bridge (Type CL01/01) with a dip-type cell operated at 220 volts AC mains; all the measurements being done at room temperature in PhNO_2 . The magnetic measurements were carried out at room temperature with a Gouy's balance using anhydrous copper sulphate as a calibrant. The infrared spectra of the complexes were recorded on a Perkins Elmer Infrared Spectrophotometer (Model 521) in KBr over a range of 4000-200 cm^{-1} . A Hilger Unispek Spectrophotometer with 1 cm quartz cell was used for recording the visible spectra of Pr^{3+} , Nd^{3+} , Sm^{3+} and Ho^{3+} complexes. Thermogravimetric analysis of the complexes was carried out in static air, using an open sample holder and a small platinum boat, maintaining a heating rate of 6°/minutes.

RESULTS AND DISCUSSION

The analytical data of the complexes (Table.1) agree with the general composition $\text{Ln}(\text{ClO}_4)_3 \cdot 2(\text{ebaaps}) \cdot \text{py}$, (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). That the complexes are anhydrous in nature is evidenced by their analytical, infrared and thermal studies. The complexes are generally soluble in common organic solvents but insoluble in diethyl-ether. The molar conductivity values of the complexes in nitrobenzene (Table.1) reveal that these complexes are 1:3 electrolytes. The effective magnetic moments (Table.1) of the complexes indicate that they are paramagnetic in nature except the La(III) complex which is diamagnetic. The observed magnetic moments of the complexes lie within the range predicted and observed in the complexes of paramagnetic ions as reported earlier¹⁹⁻²⁰.

Infrared spectra

The infrared spectra of *ebaaps*, derived from 4-aminoantipyrine, are somewhat complex so as to designate various bands. Infrared absorptions of the ligand *ebaaps* have been assigned by comparing its spectrum with those of antipyrine and 4-aminoantipyrine,^{12, 21, 22} and some past reports

Table. 1: Analytical, conductivity, molecular weight and magnetic data of lanthanide(III) nitrate complexes of *ebaaps* and pyridine.

Compounds (m.f.)	Elemental analysis (%)			m.w. found (calcd.)	Λ_m (ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} (BM)
	Found (Calcd.)					
	Ln	N	ClO ₄			
La(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·La)	10.88 (10.95)	14.22 (14.34)	23.32 (23.53)	318 (1269)	80.2	Diamag.
Pr(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·Pr)	11.00 (11.09)	14.23 (14.32)	23.28 (23.49)	320 (1271)	82.8	3.5
Nd(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·Nd)	11.22 (11.30)	14.16 (14.29)	23.25 (23.43)	322 (1274)	79.9	3.48
Sm(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·Sm)	11.63 (11.72)	14.14 (14.22)	23.16 (23.32)	323 (1280)	80.8	1.56
Gd(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·Gd)	12.12 (12.20)	14.05 (14.14)	23.04 (23.20)	324 (1287)	83	7.82
Tb(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·Tb)	12.24 (12.33)	14.02 (14.12)	23.02 (23.16)	326 (1289)	82.8	9.82
Dy(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·Dy)	12.46 (12.57)	13.99 (14.08)	22.98 (23.10)	327 (1292)	79.9	10.43
Ho(ClO ₄) ₃ ·(<i>ebaaps</i>) ₂ ·py (C ₄₇ H ₅₃ N ₁₃ O ₁₄ Cl ₃ ·Ho)	12.65 (12.740)	13.96 (14.05)	22.94 (23.05)	329 (1925)	81.3	10.52

on semicarbazones²⁰. In the *ebaaps*-Ln (III) complexes, the n(NH₂) of the hydrazinic nitrogen of semicarbazide (ca. 1622 cm⁻¹) is absent in the infrared spectra of *ebaaps*, as expected. The amide-II band is shifted towards the lower energy side as compared to that of the semicarbazone; this is due to a drift in the electron density from the hydrazinic nitrogen²³. The characteristic absorption of the carbonyl group in *ebaaps* is observed at 1701 cm⁻¹²⁴ while in the complexes, this band is shifted towards lower energy in the 1650-1640 cm⁻¹ region (Table.2). The amide-II band in the free *ebaaps* is observed at 1566 cm⁻¹ while in all the complexes, this band is also shifted towards lower wave numbers by ca. 30 cm⁻¹. These observations suggest coordination through the carbonyl oxygen atom. The strong band at 1602 cm⁻¹ in *ebaaps* apparently has a large contribution from the n(C=N) mode of the semicarbazone moiety²⁵. This is found to suffer a blue shift in all the complexes. Another strong band observed at 1615 cm⁻¹ is due to azomethine (C=N) absorption. On complexation, this band is found to shift towards the lower frequency region, clearly indicating the coordination through the azomethine

-N atom²⁶⁻²⁸. This discussion clearly indicates that *ebaaps* serves as a tridentate ligand, coordinating through the carbonyl-O, and the hydrazinic-N and azomethinic-N atoms.

Four strong absorptions occur in the infrared spectra of pyridine in the range 1650-1400 cm⁻¹ which are attributed to C=C, C=N stretchings and ring vibrations^{29,30}. Out of these, the absorptions associated with the cyclic structure apparently remain unaffected on complexation while those arising from heterocyclic ring get shifted to higher frequencies due to tightening of the ring on coordination with Ln³⁺ ions. This suggest that pyridine is bonded to the Ln³⁺ ion through the hetero-N atom^{31,32}. The bands due to n(Ln-O)/n(Ln-N) are also observed in the far infrared region¹⁸. (Table.2).

In all the perchlorate complexes [Ln(*ebaaps*)₂·py](ClO₄)₃, only two strong n₃ and n₄ bands are observed in the 1098-1080 and 635-620 cm⁻¹ regions respectively, due to ClO₄⁻. The presence of these bands indicate that the tetrahedral symmetry of the ClO₄⁻ ion has not been disturbed on

Table. 2: Key infrared spectral bands (cm^{-1}) of lanthanide(III) perchlorato complexes of *ebaaps* and pyridine.

Compounds	$\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})$ and ring vibrations of pyridine	$\nu(\text{C}=\text{N})$ azomethinic hydrazinic	$\nu(\text{C}=\text{O})$			$\nu(\text{Ln}-\text{O})/ n(\text{Ln}-\text{N})$
			I	II	III	
Pyridine	1595sh, 1582s, 1576s, 1485s, 1440s	-	-	-	-	-
<i>ebaaps</i>	-	1616s	1701s	1566m	-	-
$\text{La}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1602sh, 1584s, 1573s, 1472s	1598s	1640s	1532m	444m, 332w	
$\text{Pr}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1632s, 1610vs, 1510vs, 1466vs	1593s	1626s	1532m	436m, 342w	
$\text{Nd}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1645s, 1605s, 1492s, 1480vs	1594s	1632s	1536m	430m, 326w	
$\text{Sm}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1634s, 1605vs, 1525vs, 1472s	1590s	1628s	1526m	436m, 336w	
$\text{Gd}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1643s, 1613vs, 1532s, 1470s	1595s	1626s	1535m	425m, 326w	
$\text{Tb}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1632s, 1610vs, 1523s, 1472vs	1590s	1634s	1532m	435m, 335w	
$\text{Dy}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1643s, 1608s, 1498s, 1484s	1591s	1625s	1528m	435m, 342m	
$\text{Ho}(\text{ClO}_4)_3 \cdot (\text{ebaaps})_2 \cdot \text{py}$	1635s, 1608s, 1514s, 1470s	1588s	1622s	1526m	432m, 335w	

complexation and that these ions are not bonded to Ln^{3+} ions^{33,34}. This conclusion is also supported by the conductance and molecular weight data.

Electronic spectra

Typical spectral data for the solutions of the mixed ligand complexes of lanthanide(III) perchlorates with *ebaaps* and pyridine are presented in Table. 4. The data for the aqueous salt solution are also given for comparison. Lanthanide (III) ion has no significant absorption bands in the visible region. However, the absorption bands for Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) ions appear in the visible and near infrared regions; this is due to the transitions from the ground levels of $^3\text{H}_4$, $^4\text{I}_{9/2}$, $^6\text{H}_{5/2}$, $^5\text{S}_{7/2}$ and $^6\text{H}_{15/2}$ to the respective excited J-levels of the 4f-configurations. Some red shift or nephelauxetic effect is observed in the methylcyanide solutions of these complexes. This red shift is usually accepted as an evidence of a higher degree of covalency³⁵. A marked enhancement in the intensity of the bands has been observed in all the complexes. This red shift of the hypersensitive bands has been utilized to calculate the nephelaxetic effect (b) in the complexes. The covalence factors, $b^{1/2}$ (values varies from 0.0340-0.0469), Sinha parameters (d %) (0.05247-0.8898) (metal-ligand covalency per cent), and the covalency angular overlap parameter (h) (0.0023-0.0044) of the complexes have been calculated from the respective b value, (0.09912-0.9954)^{36,37}. The positive values of (1-b) and (d %) in the complexes suggest that the bonding between the metal and the ligand is covalent compared to the bonding between the metal and an aqua ion. The positive values of bonding ($b^{1/2}$) and angular overlap parameter (h) again indicate covalent bonding.

Thermal studies

The pyrolysis curves of some representative complexes $[\text{Ln}(\text{ebaaps})_2\text{py}](\text{ClO}_4)_3$ (Ln = La, Pr, Sm, Dy) show that the complexes are anhydrous in nature. The thermal curves indicate that there is mass loss (6.02-6.18 %) in the 125-155 °C temperature range due to the removal of pyridine. In the temperature range 240-280°C, the mass loss (34.92-35.58 %) corresponds to one mole of *ebaaps*. At about 355°C, the remaining *ebaaps*

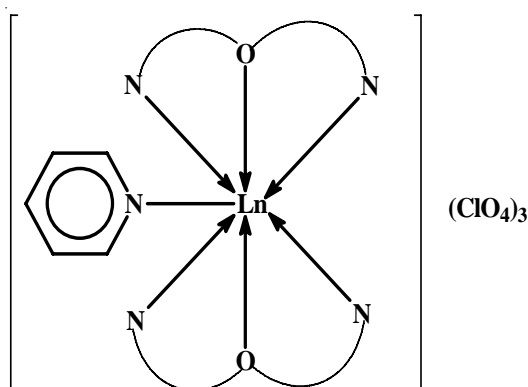


Fig. 2. General structure of $[\text{Ln}(\text{ebaaps})_2\text{py}](\text{ClO}_4)_3$, [Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho].

is also lost. The residue obtained after heating at about 835°C to a constant weight is very close to that expected for the lanthanide oxide^{38,39}.

Stereochemistry

The molar conductance of the complexes observed in nitrobenzene indicates that they behave as 1:3 electrolytes. Hence, none of the three ClO₄⁻ ions is bonded to the Ln³⁺ ion, and all are present outside the coordination sphere. ebaaps is a neutral tridentate (O, N, N) ligand, and pyridine is coordinating to the central metal ion through its hetero -N atom. Thus, a coordination number of 7 is assigned to these complexes as shown below in a general structure of the complexes⁴⁰ (Figure. 2).

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