

# Preparation and Characterization of Lanthanide (III) Nitrate Complexes with 2-Amino-4-Methylbenzothiazole (AMBTZ)

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## ABSTRACT

*A new series of complexes of lanthanide (III) complexes with 2-Amino 4-Methylbenzothiazole have been prepared in non-aqueous media and characterized by various physico-chemical studies, viz- elemental analysis, molecular weight, electrolyte conductance and I.R. Spectra etc. And their thermal properties have also been studied.*

**Key words:** *lanthanide (III) chloride complexes and 2-Amino- 4-Methylbenzothiazole*

## INTRODUCTION

Lanthanide elements form the longest continuous services of chemically similar elements in periodic table. The normal oxidation state of Lanthanide ion is +3. Lanthanum has the electronic configuration of the closed Le shell in  $\text{La}^{+3}$  position and the succeeding 14 ions in the series successively add 14 electrons to the uf sub shell. The lanthanide ions have comparatively large ionic radii and are strongly electropositive. The shrinkage of the ionic radii as the uf sub shell is filled is popularly known as “Lanthanide contraction”, although a similar shrinkage in ionic radii occurs as d sub shell is filled. The Lanthanide series has a 22% change in ionic radii from  $1.061\text{Å}$  to  $0.848\text{Å}$  for  $\text{La}^{+3}$  to  $\text{La}^{+3}$ [1]. The influence of the shrinking ion size on coordination number and coordination geometry is the unifying concept in coordination chemistry of the Lanthanide ions. Since the high coordination compounds of the metal ions depends on the effective size of the metal ion and a high positive charge on the central metal atom. Lanthanide ions fulfill both the conditions for high coordination compounds. Lanthanides form a longest series of the periodic table. It is 4f-inner transition series. Lanthanide (III) ions, because of their size and charge are the best ions to form stable complexes with high coordination number[1-5]. Coordination compounds of lanthanide in which lanthanide ions exhibit coordination number 6 to 10 are reported [ 6-7]. Metal complexes with nitrogen containing organic bases have played a major role in the development of coordination chemistry8-11. In this work, we wish to report lanthanide (III) nitrate complexes with 2-Amino 4-Methylbenzothiazole.

## II. PREPARATION AND ISOLATION OF THE COMPLEX

A mixture of metal salts and ligand (AMBTZ) was dissolved in ethanol (molar ratio 1:5) and 2,2-dimethoxy propane was added as dehydrating agent and the reaction mixture was refluxed for half an hour on a water bath. On cooling a solid mass was obtained, which was washed, filtered and dried over anhydrous  $P_2O_5$ .

## III. IDENTIFICATION OF COMPLEX

3.1 Analytic, Conductivity and Molecular Weight Data The analytical data of newly prepared complexes clearly indicate the general composition of the complexes,  $Ln(NO_3)_4 \cdot 4AMBTZ$  (where  $Ln=La, Nd, Tb, Dy, Ho$ ). The monomeric nature and low values of molecular conductance data measured at room temperature in nitrobenzene, clearly indicates that all the three chloride ions are within the coordination sphere (Table 1). The similar behavior is also supported by molecular weight data (Table 1).

### 3.2 MAGNETIC MOMENT

The magnetic moment values observed in the present investigations are summarized in (Tables 2) show that the lanthanum complexes are diamagnetic in nature, as expected from its closed shell electronic configuration and absence of unpaired electrons. All other tripositive lanthanide ions are paramagnetic due to presence of 4f electrons, which are effectively shielded by  $5s^2 5p^6$  electrons. The comparison of these observed values with those observed for 8-hydrated sulphate and those calculated for uncomplexed ions, indicate that the 4f electrons do not participate in any bond formation in these complexes.

The compounds discussed herein show a little deviation from the Van Vleck values although the simple Curie equation has been used. This was to be expected as the crystal field splitting of the f-orbitals was of the order of  $100\text{cm}^{-1}$ , a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to thermal population of excited states whose degenerate levels have been split by the crystal field. It was just possible that the splitting of the lowest excited state of  $Sm(^6H_{7/2})$  might have given an altered value of the magnetic moment but this effect was not observed. Thus, the magnetic moments of the new complexes reported herein are within the range predicted and observed in compounds of paramagnetic ions as reported earlier [12-14]

### 3.3 INFRARED SPECTRA

The ligand 2-amino-4-methyl benzothiazole (AMBTZ) also possesses three possible donor sites, amino nitrogen, tertiary cyclic nitrogen and sulphur of thiazole ring. Further the amino group of thiazole ring is involved in coordination which is shown by a negative shift of  $\nu_{NH_2}$  upto  $60\text{cm}^{-1}$  from its original position in free ligand ( $3110\text{cm}^{-1}$ ). Tertiary cyclic nitrogen and sulphur atoms of thiazole ring do not participate in coordination which is further attributed by the appearance of these frequencies of the almost same position as in free ligand (Table 3). Several absorptions associated with C-H out of plane deformation modes depending on the number of adjacent hydrogen atoms in the aromatic ring appear in the range of  $1000 - 650\text{cm}^{-1}$ . These

absorptions are supposed to undergo a slight positive shift on complexation due to decrease of electron density of aromatic ring[15-16].

A new bond in far IR region  $370-410\text{ cm}^{-1}$  has been assigned to  $\nu\text{M-N}$ . The spectra of free ligand are transparent in this region.

### 3.4 STEREO CHEMISTRY AND STRUCTURE OF THE COMPLEXES

The non electrolytic behaviour of lanthanide nitrate complexes in nitrobenzene, in conjunction with IR data for the nitrate group suggests a coordination number ten for all these complexes. However, the exact coordination geometry of these complexes can be decided only by X-Ray structural data. Unfortunately, the author was not able to perform such investigations. The possible structures of the complexes are shown in the Figure 1.

### IV.FIGURE

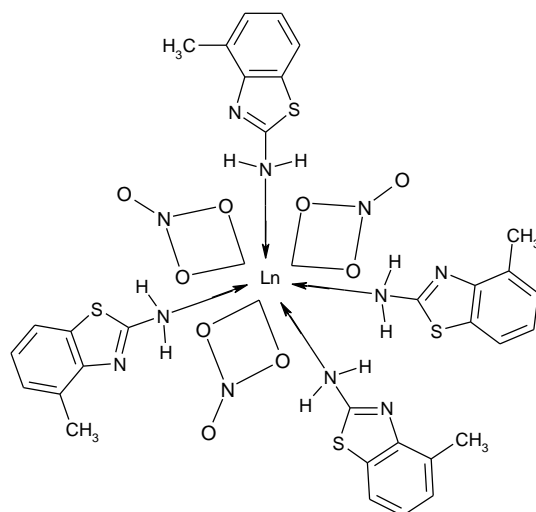


Fig.1: Fig.6.6 : Probable Structure of Lanthanide III Nitrate Complexes of 2-Amino-4-methyl benzothiazole

### V.TABLES

Table - 1 Analytic, Conductivity and Molecular weight data of Lanthanide(III) nitrate Complexes of 2-amino 4-methylbenzothiazole

Complex	Found(Calculated) %				$\Omega\text{ m}$ ( $\text{ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$ )	Electrolytic Nature	Ave. Mol.Wt.	Formula Wt.
	M	C	H	N				
$\text{La}(\text{NO}_3)_3(\text{AMBTZ})_4$	14.62 (14.49)	36.15 (36.01)	3.56 (3.43)	16.63 (16.51)	3.6	Non-Electrolyte	920	933

Nd(NO <sub>3</sub> ) <sub>3</sub> (AMBTZ) <sub>4</sub>	15.51 (15.35)	35.96 (35.82)	3.55 (3.41)	16.57 (16.42)	4.8	Non-Electrolyte	924	938
Tb(NO <sub>3</sub> ) <sub>3</sub> (AMBTZ) <sub>4</sub>	16.80 (16.68)	35.31 (35.26)	3.50 (3.36)	16.31 (16.16)	4.6	Non-Electrolyte	946	953
Dy(NO <sub>3</sub> ) <sub>3</sub> (AMBTZ) <sub>4</sub>	17.12 (16.99)	35.24 (35.13)	3.50 (3.35)	16.24 (16.10)	5.2	Non-Electrolyte	947	956.5
Ho(NO <sub>3</sub> ) <sub>3</sub> (AMBTZ) <sub>4</sub>	17.35 (17.20)	35.21 (35.04)	3.48 (3.34)	16.20 (16.06)	3.9	Non-Electrolyte	943	959

Table -2 Permanent magnetic moment (BM) of lanthanide ions and their complexes with 2-amino4-methylbenzothiazole at room temperature

R <sub>3</sub>	Theoretical			Measured
	Hund	VanVleck	R <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .8H <sub>2</sub> O	NO <sub>3</sub>
La	0.00	0.00	0.00	Diamag.
Nd	3.62	3.68	3.52	3.60
Tb	7.94	7.94	7.81	7.92
Dy	10.60	10.60	10.30	10.51
Ho	10.60	10.60	10.40	10.46

Table -3 IR absorption frequencies of lanthanide (III) nitrate complexes of 2-Amino 4-methyl benzothiazole

S. No.	Assignment	ATZ	La(NO <sub>3</sub> ) <sub>3</sub> (AMBTZ) <sub>4</sub>	Nd	Tb	Dy	Ho
1.	v NH <sub>2</sub>	3110	3060	3065	3162	3055	3052
2.	vN Cyclic	1370	1365	1368	1372	1370	1375
3.	v C=S (Cyclic)	775	772	775	770	765	765
4.	v M-N	-	410	410	405	395	400

## VI. CONCLUSION

The last forty years have witnessed hectic research activity in the chemistry of the lanthanides. No single family of chemical elements has perhaps attracted so much attention as lanthanides.

The fourteen elements after La (57) to Lu (71), with almost similar physical and chemical properties in group third and sixth of the periodic table have been used. Complexation of lanthanides with various kinds of ligands has been the subject of interest for research workers in many diverse disciplines, both experimental and theoretical. The considerable interest on the complexes of lanthanides in the modern times is due to their manifold applications in various fields of chemical, analytical, biological, industrial and agricultural interest. A comprehensive study on their synthesis, physico-chemical properties and structural characteristics is, therefore, worth investing. Coordination chemistry of aromatic amines is of particular interest because of the variation in stoichiometry in which these ligands may be bound to a metal ion. Thus in present investigation new complexes with aromatic amines such as 2-aminothiazole has been synthesized.

The primary purpose of the paper is synthesizing new complexes of lanthanides (Ln= La, Nd, Tb, Dy or Ho) chlorides, with 2- aminothiazole ligand. Studying their properties by various physicochemical techniques. Attempting to understand their bonding and structural characteristics.

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