



Preparation and Characterization of Lanthanide (III) Chloride Complexes with 2-Aminothiazole (ATZ)

PRAFULL SHARMA

Department of Chemistry,

Ojaswini Institute of Management & Technology, Damoh (India)

ABSTRACT

A new series of complexes of lanthanide (III) complexes with 2-Aminothiazole (ATZ) 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-Aminothiazole (ATZ)

1.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 La^{+3} position and the succeeding 14 ions in the series successively add 14 electrons to the $4f$ sub shell. The lanthanide ions have comparatively large ionic radii and are strongly electropositive. The shrinkage of the ionic radii as the $4f$ 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 $1.061 \text{ \AA}$ to $0.848 \text{ \AA}$ for 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. The coordination numbers exhibited by the tripositive Lanthanide ions usually varies from 6 to 10. Bidentate ligands with smaller bite often yield complexes with higher coordination numbers less than 6 are rare for Lanthanide ions[2-4]. Harman *et al.*[4] have shown that Lanthanum in $\text{La}(\text{C-18-Crown-6})(\text{NO}_3)_3$ attains a coordination number of 12. The coordination sphere around the metal ion may be described in terms of a polyhedron whose vertices represent the positions of the donor atoms. Ideal polyhedra which describe the high coordination number are given in Fig.1. However, it may be noted that a compromise to obtain the maximum shielding for the metal ion and the minimum ligand-ligand repulsions need not always lead to an idealized geometry. Hence, the assignment of ideal polyhedra to describe high coordination number is only an approximation. Thus “non-cartesian” geometry and “partial coordination” are common among the lanthanides. Lanthanide occasionally exhibit mixed coordination number and mixed geometries in their complexes[. In the orthorhombic $\text{Eu}_2(\text{mal})_3 \cdot 8\text{H}_2\text{O}$, there are two inequivalent Eu(III) ions. The coordination polyhedron around are of the Eu(III) ions is a distorted square antiprism. The other Eu(III) ion is non-coordinated with nine examples

have been discussed by Sinha. In certain complexes even though the coordination number is the same, two molecules in the same unit cell exhibit different conformations. Thus, in $\text{Eu}(\epsilon\text{hd})_3\cdot\text{DMSO}$, the gross geometry around Eu(III) is a distorted pentagonal bipyramid with oxygen of the DMSO is occupying one of the apices[9,10], but the structure of the two molecules in the unit cell differs in detail. A similar situation also exists in $\text{Eu}(\text{thd})_3(\text{DMF})_2$ [5,6].

Prior to 1964, nitrogen coordination was well characterized only in association with oxygen donors, as exemplified by polyamine polycarboxylates and 8-quinolates. The observation that cationic complexes derived from N-donors could not be isolated from aqueous media prompted the assumption that $\text{Ln}^{+3}\text{-N}$ interactions were necessarily weaker than $\text{Ln}^{+3}\text{-O}$ interaction. The ability of lanthanide ions to coordinate with neutral N-donors could best be evaluated in non-aqueous media of moderate polarity. Since 1964, a number of cationic or neutral complexes containing N-donor ligands have been isolated utilizing non-aqueous solvent media. The isolation of first lanthanide complexes derived from the weakly basic N-donors 1,10-phenanthroline (Phen) and 2,2'-bipyridyl (Bipy) was reported in 1963[13]. These species are most commonly obtained by treating warm ethanolic solution of a hydrated lanthanide salt with excess ligand. The number of neutral ligands coordinated to the lanthanide ions depends primarily upon the coordinating ability of the anion present. When the anion is a strongly chelating 1,3-diketonate or acetate, only mono substituted complexes are obtained, indicating the inability of the weakly basic amine to displace a strongly coordinated anion from the coordination sphere. However, addition of bidentate phenanthroline or bipyridyl group to the tris-diketone complexes demonstrate expansion of the lanthanide coordination sphere, indicative of significant $\text{Ln}^{+3}\text{-N}$ interaction. Similarly, bipyridyl and 1,10-phenanthroline enter the coordination sphere of the $\text{Ln}(\text{thd})_3$ chelates[7]. Watson *et al.*[8] have reported the complex $[\text{Eu}(\text{acac})_3\text{Phen}]$ in which the Ln^{+3} ion is eight coordinated, with a signally distorted square antiprismatic rearrangement of O- and N-donor atoms. Bisphenanthroline and bipyridyl complexes are obtained when the anion is chloride, nitrate or salicylates[9-12]. Excess ligand does not yield tris species. In each of these species, a coordination number greater than six is achieved by bonding to the anion and solvent molecules. Ten coordination in the species $[\text{La}(\text{bip}_4)_2(\text{NO}_3)_3]$ has been studied by Al-Karaghauili and Wood on the basis of crystal structure determination. Although the weakly basic N- donors donot displace the nitrate and chloride anion from the coordination sphere, 1,10-phenanthroline and bipyridyl ligands are accommodated in the coordination sphere owing to the small steric requirements of the anions. In case of terpyridyl group is accommodated in the coordination sphere owing to the small steric requirements of the anions. In case of terpyridyl group is accommodated in the coordination in the nitrate salt indicate the greater steric requirements of this tridentate ligand.

In $\text{Ln}(\text{Phen})_3(\text{NCX})_3$ and $\text{Ln}(\text{ByPy})_3(\text{NCX})_3$ ($n = \text{S or Se}$)[12] complexes, the IR data suggest that all NCX^- ions are coordinated through the nitrogen. A coordination number 9 has tentatively assigned for lanthanide ions in these complexes. Maximum coordination by the amines is obtained when the anion is the weakly coordinating perchlorate. Thus both the eight coordinate[13], $\text{Ln}(\text{Phen})_4(\text{ClO}_4)_3$ and nine coordinate $\text{Ln}(\text{terpy})_3(\text{ClO}_4)_3$ species have been isolated. The crystal structure of this terpyridyl complex verifies the formation of nine metal-nitrogen bonds. Infra red data indicate that all the nitrate groups are coordinated[14] in the 2,4,6-tri- α -pyridyl 1,3,5 triazine (TPT) chelates, $[\text{Ln}(\text{TPT})(\text{NO}_3)_3\cdot\text{H}_2\text{O}]$. All the three nitrate ions are present in the coordination sphere

and IR reveals the bidentate nature of nitrate ions. A sever coordination number has been assigne in this complex. A nine coordinated complex $[Ln(TPT)_3](ClO_4)_3$ has also been studied by some workers[14].

The structure of tri(2,2,6,6-tetra-methyl heptane-3,5-dinato) bis (4-picoline) holmium(III), $Ho(thd)_3(4-Pic)_2$, contains an eight coordinate metal ion with a coordination polyhedron closely resembling a square antiprism[15]. The picoline ligands are situated at apices of opposite square face as far removed as possible. The crystal symmetry is C_2 with one chelate ring spanning a lateral[1] edge and the other two spinning S-edges. The Ho-O bond distance averages $2.27 \text{ \AA}$ with Ho-N bond distance of $2.53 \text{ \AA}$.

II.PREPARATION AND ISOLATION OF THE COMPLEX

A mixture of metal salts and ligand (ATZ) 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, $LnCl_3 \cdot 6ATZ$ (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

Due to closed shell electronic configuration lanthanum is found to be diamagnetic while all other tripositive lanthanide ions are paramagnetic. On complexation, the magnetic moment values of lanthanide ions remain almost unchanged (Table 2) indicating thereby that 4f-electrons do not participate in bond formation[16].

3.3 Infrared Spectra

The IR spectra of 2-Aminothiazole (ATZ) and its complexes with lanthanide (III) salts have been recorded in the range $4000-200 \text{ cm}^{-1}$ and absorption frequencies associated with various fundamental modes of vibrations alongwith their possible assignment are listed in Table 3. The ligand ATZ possesses three possible donor sites, tertiary cyclic nitrogen, amino nitrogen and sulphur of the thiazole ring. The amino group of thiazole ring is involved in coordination through Nitrogen atom. Coordination through N of the amino group invariably results in negative shift in ν_{NH_2} (3105 cm^{-1}) by atleast 50 cm^{-1} . The IR frequency of tertiary cyclic nitrogen of thiazole ring appears at 1375 cm^{-1} and remains almost unchanged on complexation[17-19].

The $\nu_{\text{C}=\text{S}}$ band appears at 770 cm^{-1} in free ligand, does not show any significant shift on complexation which includes the possibility of coordination from tertiary N and S of the ligand. The absorptions attributed to C-H in plane deformation and ring breathing mode has also been identified and their positions in the free ligand and in the corresponding complexes are very close to each other.

The author has assigned a new band in the far IR region $375\text{--}410\text{ cm}^{-1}$ to $\nu(\text{M-N})$ and assume it to be indicative of N bonding to central metal atom i.e. lanthanide ions. The spectra of the free ligand is relatively transparent in this region and these frequencies are in good agreement with M-N stretching modes observed for several lanthanide complexes reported by earlier workers[20-21].

3.4 Stereo Chemistry and Structure of the Complexes

The non electrolytic behavior of these complexes suggests that all the chloride ions are coordinated to the metal. Hence, a coordination number nine can be postulated. 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 complex is shown below (fig.1)

IV. FIGURE

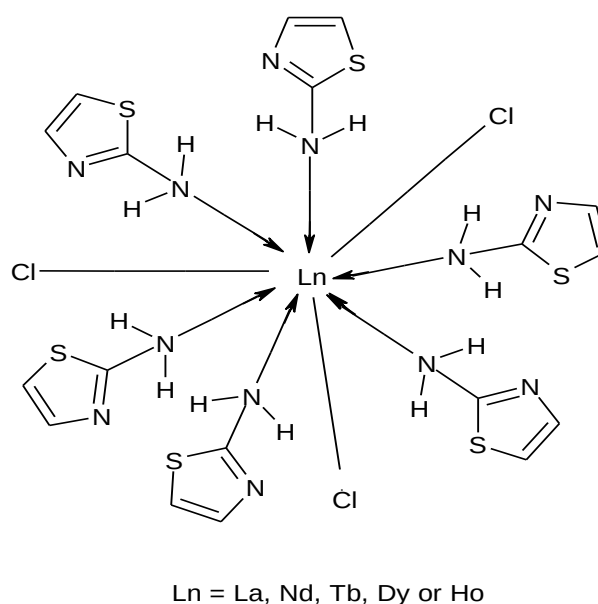


Fig.1: Probable Structure of Lanthanide III chloride complexes of 2-Aminothiazole

V.TABLES

Table - 1 Analytic, Conductivity and Molecular weight data of Lanthanide (III) chloride Complexes of 2-aminothiazole

Complex	Found(Calculated) %					$\Omega\ m$ (ohm ⁻¹ cm ² mole ⁻¹)	Electrolyti c Nature	Ave. Mol. Wt.	Formula Wt.
	M	C	H	N	Anion				
LaCl ₃ (ATZ) ₆	16.59 (16.44)	25.66 (25.54)	2.98 (2.84)	19.99 (19.87)	12.76 (12.60)	4.2	Non- electrolyte	839	845.5
NdCl ₃ (ATZ) ₆	17.05 (16.93)	25.56 (25.40)	2.95 (2.82)	19.93 (19.75)	12.69 (12.52)	3.7	Non- electrolyte	837	850.5
TbCl ₃ (ATZ) ₆	18.50 (18.37)	25.10 (24.96)	2.92 (2.77)	19.56 (19.41)	12.48 (12.30)	5.1	Non- electrolyte	850	865.5
DyCl ₃ (ATZ) ₆	18.82 (18.70)	25.02 (24.86)	2.91 (2.76)	19.49 (19.33)	12.40 (12.25)	4.9	Non- electrolyte	852	869
HoCl ₃ (ATZ) ₆	19.10 (18.93)	24.91 (24.78)	2.88 (2.75)	19.42 (19.28)	12.39 (12.22)	4.8	Non- electrolyte	860	871.5

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

R ₃	Theoretical			Measured
	Hund	VanVleck	R ₂ (SO ₄) ₃ .8H ₂ O	Cl
La	0.00	0.00	0.00	Diamag.
Nd	3.62	3.68	3.52	3.58



Tb	9.70	9.70	9.40	9.20
Dy	10.60	10.60	10.30	10.43
Ho	10.60	10.60	10.40	10.48

Table -3 IR absorption frequencies (cm^{-1}) of lanthanide (III) chloride complexes of 2-Amino thiazole

S. No.	Assignment	ATZ	La $\text{Cl}_3(\text{ATZ})_6$	Nd	Tb	Dy	Ho
1.	$\nu \text{ NH}_2$	3105	3060	3855	3048	3052	3055
2.	$\nu \text{N Cyclic}$	1375	1370	1372	1365	1380	1378
3.	$\nu \text{ C=S (Cyclic)}$	770	775	768	765	772	770
4.	$\nu \text{ M-N}$	-	375	390	410	380	380

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 ($\text{Ln} = \text{La, Nd, Tb, Dy or Ho}$) chlorides, with 2- aminothiazole ligand. Studying their properties by various physicochemical techniques. Attempting to understand their bonding and structural characteristics.

REFERENCES

- [1.] D.H. Templeton and C.H. Daubon, *J. Amer. Chem. Soc.*, **76**, 5237 (1954).
- [2.] J.S. Gothra, M.P. Hursthouse and A.J. Welch, *J. Chem. Soc. Chem. Commun.*, 669 (1973).
- [3.] S.A. Cotton, F.A. Hart, M.B. Heusthane and A.J. Welch, *J. Chem. Soc. Chem. Commun.*, 1225 (1972).

- [4.] M.E. Harman, F.A. Hart, M.B. Hursthouse, G.P. Mass and P.R. Raithby, *J. Chem. Soc. Chem. Commun.*, 396 (1976).
- [5.] R.E. Sievers, J.A. Cunningham and W.E. Rhine, Proc. 11th Rare. Earth Cong., Traverse City, Michigan, Oct., 7-11 (1974).
- [6.] D.S. Dyer, J.A. Cunningham, J.J. Brooks, R.E. Seivers and R.E. Rondeane, Nuclear Magnetic Resonance Shift Reagents, R.E. Sievers (Ed.), 12 (1973), Academic Press (N.Y.).
- [7.] N.M. Karayannis, A.N. Specca, D.E. Chasan and L.L. Pytlewski, *Coord. Chem. Rev.*, **20**, 37 (1976).
- [8.] E.P. Linton, *J. Amer. Chem. Soc.*, **62**, 1945 (1940).
- [9.] A.R. Katritzky, E.W. Randall and L.E. Sutton, *J. Chem. Soc.*, 1769 (1957).
- [10.] A.N. Sharpe and S. Walker, *J. Chem. Soc.*, 4522 (1961).
- [11.] L.R. Melby, N.J. Rose, E. Abramson and J.E. Caris, *J. Amer. Chem. Soc.*, **86**, 5117 91964).
- [12.] V.N. Krishnamurthy and S. Soundararajan, *Canad. J. Chem.*, **45**, 189 (1967).
- [13.] C.H. Harrison and W.H. Watson, *J. Inorg. Nucl. Chem.*, **32**, 2255 (1970).53
- [14.] P.V. Shivapullah and S. Saundararajan, *Inorg. Nucl. Chem. Lett.*, **13**, 291 (1977).
- [15.] L. Ramakrishnan and S. Saundararajan, *Canad. J. Chem.*, **54**, 3169 (1976).
- [16.] R.K. Agarwal and S.K. Gupta, *Polish J. Chem.*, **61**: 341 (1987).
- [17.] Pratibha Shukla, Ph.D.Thesis "Synthesis and Structural Investigation of Coordination Compounds" Bundelkhand University Jhansi.
- [18.] N.M. Karayannis, A.N. Specca, D.E. Chasen and L.L. Pytlewski, *Coord. Chem. Rev.* **20**: 37 (1976).
- [19.] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" John Wiley (1978).
- [20.] S.K. Gupta, R.S. Dohare and S. Thakur, *Orient, J. Chem.* 21(1): 145 (2005).
- [21.] S.K. Gupta, P. Sharma, D. Thakur , M. Shirngi and S. Thakur , *Orient, J. Chem.* 24(3):1149-1150(2008)