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Research Paper

Preparation and Characterization of Lanthanide (III) Chloride Complexes with 5-Methylbenzotriazole (MBTAZ)

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Abstract: *A new series of complexes of lanthanide (III) complexes with 5-Methylbenzotriazole (MBTAZ) 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. . The primary purpose of the paper is synthesizing new complexes of lanthanides (Ln= La, Nd, Tb, Dy or Ho) chlorides, with 5- aminothiazole ligand. Studying their properties by various physicochemical techniques. Attempting to understand their bonding and structural characteristics A comprehensive study on their synthasis, 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.*

Keywords: lanthanide complexes, 5-Methylbenzotriazole (MBTAZ), physico-chemical studies.

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 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 $1.061 A^o$ to $0.848\ A^o$ for La^{+3} to La^{+3} ion[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 change 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 $La(C\text{-}18\text{-}Crown\text{-}6\text{-})(NO_3)_3$ 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 Figure 1. However, it may be noted that a compromise to obtain the maximum shielding for the metal ion and the minimum ligand-ligand repulsions heed 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 $Eu_2(mal)_3.8H_2O$, there are two inequivalentEu(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 $Eu(\varepsilon hd)_3.DMSO$, 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 $Eu(thd)_3(DMF)_2$ [5,6].

Prior to 1964, nitrogen coordination was well characterized only in association with oxygen donors, as exemplified by polyamine polycarboxylates and 8-quinolinates. The observation that cationic complexes derived from N-donors could not be isolated from aqueous media prompted the assumption that Ln^{+3}-N interactions were necessarily weaker than Ln^{+3}-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-phenonthrolin (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 bidentatephenanthroline or bipyridyl group to the tris-diketone complexes demonstrate expension of the lanthanide coordination sphere, indicative of significant Ln^{+3}-N interaction. Similarly, bipyridyl and 1,10-phenanthroline enter the coordination sphere of the $Ln(thd)_3$ chelates[7]. Watson *et al.*[8] have reported the complex $[Eu(acae)_3Phen]$ in which the Ln^{+3} ion is eight coordinated, with a signally distorted square antiprismatic rearrangement of O- and N-donor atoms. Bisphenonthroline 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 $[La(bip_4)_2(NO_3)_3]$ has been studied by Al-Karaghauli 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 $Ln(Phen)_3(NCX)_3$ and $Ln(ByPy)_3(NCX)_3$ (n = 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], $Ln(Phen)_4(ClO_4)_3$ and nine coordinate $Ln(terpy)_3(ClO_4)_3$ 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, $[Ln(TPT)(NO_3)_3.H_2O]$. 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 assign 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) holomium(III), $Ho(thd)_3(4\text{-}Pic)_2$, 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 A° with Ho-N bond distance of 2.53 A°.

Preparation and Isolation of the ComplexChloro complexes

$[LnCl_3(MBTAZ)_5]$ (where, Ln = La, Nd, Tb, Dy or Ho)

1 mole of lanthanide chloride was dissolved in 15 ml of methanol mixed with 5mmole of ligand in 30 ml of methanol and heated on the steam bath with stirring, a solid compound was formed which was Stirred with about 10 ml of benzene, filtered, washed with benzene and anhydrous diethyl ether, dried and preserved over P_4O_{10} in vacuum desicator.

Identification of Complex

Analytic, Conductivity and Molecular Weight Data

The analytical data of newly prepared complexes clearly indicate the general composition of the complexes, $LnCl_3$.5MBTAZ (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. The similar behavior is also supported by molecular weight data (Table 1).

Table 1: Analytic, Conductivity and Molecular weight data of Lanthanide(III) chloride Complexes of 5-methylbenzotriazole

Complex	Found(Calculated) %					Ω m (ohm^{-1} cm^2 mole^{-1})	Electrolytic Nature	Ave. Mol. Wt.	Formula Wt.
	M	C	H	N	Anion				
$LaCl_3(MBTAZ)_5$	15.50 (15.35)	46.49 (46.38)	3.97 (3.86)	23.28 (23.19)	11.85 (11.76)	4.3	Non electrolyte	900	905.5
$NdCl_3(MBTAZ)_5$	15.94 (15.81)	46.23 (46.12)	3.95 (3.84)	23.19 (23.06)	11.82 (11.70)	3.9	-do-	901	910.5
$TbCl_3(MBTAZ)_5$	17.29 (17.18)	45.51 (45.38)	3.79 (3.78)	22.78 (22.69)	11.63 (11.51)	3.7	-do-	913	925.5
$DyCl_3(MBTAZ)_5$	17.61 (1749)	45.32 (45.21)	3.77 (3.76)	22.774 (22.60)	11.60 (11.46)	4.4	-do-	918	929.0
$HoCl_3(MBTAZ)_5$	17.84 (17.71)	45.19 (45.09)	3.76 (3.75)	22.67 (22.55)	11.59 (11.43)	4.8	-do-	922	931.5

Magnetic Moment

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

Table 2: Permanent magnetic moment (BM) of lanthanide chloride ions and their complexes with 5-methybenzotriazole at room temperature

R_3	Theoretical			Measured
	Hund	VanVleck	$R_2(SO_4)_3.8H_2O$	
La	0.00	0.00	0.00	Diamag.
Nd	3.62	3.68	3.52	3.51
Tb	9.70	9.70	9.40	9.89
Dy	10.60	10.60	10.30	10.20
Ho	10.60	10.60	10.40	10.40

Infrared Spectra

The ligand 5-methylbenzotriazole (MBTAZ) also possesses three possible cyclic donor sites, one cyclic secondary nitrogen (-NH-) and other two cyclic tertiary nitrogen (=N-). Further the secondary nitrogen atom is involved in coordination which is conferred by the negative shift of this frequency from its original position (1350 cm^{-1}) on complexation. The formation of coordinate bond between the ligand and metal ion results in lowering the frequency than the free ligand.

This lowering in frequency has been attributed to the weakening of N-H bond, resulting from the drainage of electron density from nitrogen on its coordination to the metal ion (Table 3), while the absorption associated with tertiary nitrogen do not show any markable shift from its original position (1375 cm^{-1}) which precludes the possibility of coordination from tertiary nitrogen[17]. In addition all the metal complexes show non-ligand bands in far IR region at 390-410 cm^{-1} [19,20].

Table 3: IR absorption frequencies of lanthanide (III) chloride complexes of 5-methyl benzotriazole

S. No.	Assignment	ATZ	La Cl_3 $(MBTAZ)_5$	Nd	Tb	Dy	Ho
1.	ν -NH- cyclic	1350	1280	1278	1285	1290	1288
2.	ν =N- cyclic	1375	1370	1370	1375	1378	1375
3.	ν M-N	-	402	400	390	390	400

Stereo Chemistry and Structure of the Complexes

All these complexes are non-ionic in nature and IR reveals that MBTAZ is coordinated to lanthanide via its secondary nitrogen atom. From these observations it can be concluded that the coordination number of lanthanide ion is eight in 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.

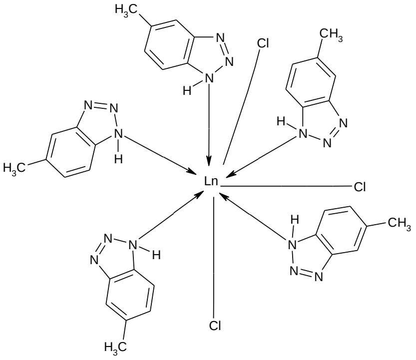

Figure 1: Probable Structure of Lanthanide III Chloride Complexes of 5-Methyl Benzotriazole

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 5- aminothiazole ligand. Studying their properties by various physicochemical techniques. Attempting to understand their bonding and structural characteristics.

References

1. Templeton D.H. and Daubon C.H., Lattice Parameters of Some Rare Earth Compounds and a Set of Crystal Radii, *J. Am. Chem. Soc.*, **76**, 5237–5239**(1954)**.
2. Gothra J.S., Hursthouse M.P. and Welch A.J., Three-co-ordinatescandium(III) and europium(III); crystal and molecular structures of their trishexamethyldisilylamides, *J. Chem. Soc. Chem. Commun.*, **18**, 669-670**(1973)**.
3. Cotton S.A., Hart F.A., Heusthane M.B. and Welch A.J., Preparation and molecular structure of a σ-bonded lanthanide phenyl, *J. Chem. Soc. Chem. Commun.*, **22,** 1225-1226**(1972)**.
4. Harman M.E., Hart F.A., Hursthouse M.B., Mass G.P. and Raithby P.R., 12-Co-ordinated crown ether complex of lanthanum; X-ray crystal structure, *J. Chem. Soc. Chem. Commun.*, 11, 396 **(1976).**
5. Sievers R.E., Cunningham J.A. and Rhine W.E., Proc. 11th Rare. Earth Cong., Traverse City, Michigan, Oct., 7-11 **(1974).**
6. Dyer D.S., Cunningham J.A., Brooks J.J., Seivers R.E. and Rondeane R.E., Nuclear Magnetic Resonance Shift Reagents, R.E. Sievers (Ed.), 12 **(1973)**, Academic Press (N.Y.).
7. Karayannis N.M., Speca A.N., Chasan D.E. and Pytlewski L.L., Coordination complexes of the n-oxides of aromatic diimines and diazines, *Coord. Chem. Rev.*, **20(1)**, 37 **(1976)**.
8. Linton E.P., “The Nature of the Chemical Bond”, *J. Amer. Chem. Soc.*, **62**, 1945 **(1940)**.
9. Katritzky A.R., Randall E.W. and Sutton L.E., The Electric dipole moments of a series of 4-substituted pyridines and pyridine 1- Oxides, *J. Chem. Soc.*, **334**: 1769 **(1957)**.
10. Sharpe A.N. and Walker S., Electric dipole moments of substituted pyridines, pyridine 1-Oxides and nitrobenzenes, *J. Chem. Soc.*, **891,**4522 **(1961)**.
11. Melby L.R., Rose N.J., Abramson E. and Caris J.E., Synthesis and Fluorescence of Some Trivalent Lanthanide Complexes, *J. Amer. Chem. Soc.*, **86**, 5117 9**(1964)**.
12. Krishnamurthy V.N. and Soundararajan S., Pyridine N-oxide complexes of rare earth perchlorates, *Canad. J. Chem.*, **45**, 189 **(1967)**.
13. Harrison C.H. and Watson W.H., Lanthanide complexes of 4-methylpyridine-1-oxide, *J. Inorg. Nucl. Chem.*, **32(7)**: 2255 **(1970)**.
14. Shivapullah P.V. and Saundararajan S., Heats of Organic Reactions. IX. A New Calorimeter and the Denaturation of Methemoglobin by Alkali *Inorg. Nucl. Chem. Lett.*, **13**, 291 **(1977)**.
15. Ramakrishnan L. and Saundararajan S., Complexes of lanthanide iodides with 3-methylpyridine-1-oxide, *Canad. J. Chem.*, **54**, 3169 **(1976)**.
16. Agarwal R.K. and Gupta S.K., Spectral and thermal properties of some oxocations chelates of 2-ethoxycarbonylaminopyridine, *Polish J. Chem.*, **61**: 341 **(1987)**.
17. Shukla P., Ph.D. Thesis "Synthesis and Structural Investigation of Coordination Compounds" Bundelkhand University Jhansi.

18. Nakamoto K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley **(1978)**.
19. Gupta S.K., Dohare R.S. and Thakur S., Coordination Compounds of Lanthanide (III) Chlorides With 2-Benzoylaminopyridine N-Oxide, *Orient, J. Chem.*, **21(1)**: 145 **(2005)**.
20. Gupta S.K., Sharma P., Thakur D., Shirngi M. and Thakur S., Preparation and Characterization of Lanthanide (III) Chloride Complexes with Benzothiazole, *Orient. J. Chem.*, **24(3)**:1149-1150**(2008)**