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Synthesis of Macrocyclic complexes and their Spectroscopic and Thermal investigation.

Chemistry

KEYWORDS:

Nidhi Gupta University college of engineering, Punjabi university, Patiala, Punjab, India

ABSTRACT

The lanthanide complexes derived from (3,5,13,15-tetramethyl 2,6,12,16,21-22- hexaazatricyclo[15.3.I1-17I7-11]cosa-1(21),2,5,7,9,11(22),12,15,17,19-decane were synthesized. The complexes were found to have general composition $[Ln(L)X_2{\cdot}H_2O]X$, where Ln = La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} and X= NO_3^- and Cl^-. The ligand was characterized by elemental analyses, IR and Mass spectral studies. All the complexes were characterized by elemental analyses, molar conductance measurements, magnetic susceptibility measurements, IR, Mass, electronic spectral techniques and thermal studies. The ligand acts as a hexadentate and coordinates through four nitrogen atoms of azomethine groups and two nitrogen of pyridine ring. The lanthanum complexes are diamagnetic while the other Ln(III) complexes are paramagnetic. The spectral parameters i.e. nephelauxetic ratio (β), covalency factor ($b^{1/2}$), Sinha parameter (δ%) and covalency angular overlap parameter ( ) have been calculated from absorption spectra of Nd(III) and Sm(III) complexes. These parameters suggest the metal–ligand covalent bonding. In the present study, the complexes were found to have coordination number nine.

1. Introduction

The field of macrocyclic chemistry is developing very rapidly because of its applications and importance in the area of coordination chemistry [1]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and types of donor atoms present in the ligand and their relative positions with the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation [2]. Macrocyclic complexes of lanthanides are currently attracting much attention in the catalytic cleavage of RNA [3], in radioimmunotherapy [4], toward tumor [5] and DNA targeting [6], as contrast enhancing agents in magnetic resonance imaging [7], asNMRshift reagents [8], as radiopharmaceuticals [9], as fluorescent robes in fluroimmunoassay [10] and in laser technology [11]. There is an emerging interest in the application of macrocyclic ligands as effective metal ion chelators and in the separation of lanthanides [12]. Coordination chemistry of lanthanides has become of increasing significant in the last few years due to the wide variety of applications [13] of lanthanides complexes in supramolecular photochemistry [14] and in medicine [15]. Coordination compounds of the lanthanides are frequently used as catalysts, which is demonstrated by the work of Shibasakiet al. [16], Kobayashi and Ishitani [17] and others [18]. The design of macrocycles capable of forming stable lanthanide (III) complexes not only would allow further study of the coordination properties of these metal ions but also would enable chemists to exploit more fully certain important emerging properties of these complexes. The preceding results provide a general guideline for the synthesis and study of a series of lanthanide (III) complexes of macrocyclic ligands. In this paper, we report the synthesis and characterization of lanthanide metal complexes with a hexadentate ligand derived from acetyl acetone and 2,6-diaminopyridine.

2. Experimental

2.1. Materials and methods

All the chemicals used were of AR grade and the solvents were dried and distilled before use according to standard procedures. Lanthanide salts and 2,6-diaminopyridne were purchased from Sigma Aldrich and used as received.

2.2. Synthesis of macrocyclic ligand (L)

The ligand 3,5,13,15-tetramethyl-2,6,12,16,21,22-hexaazatricyclo [15.3.I1-17I7-11]cosa-1(21), 2,5,7,9,11(22),12,15,17,19-decaene[L] was prepared by dropwise addition of a hot ethanolic solution (20 mL) of acetyl acetone (2.0 g, 0.02 mol) to a hot ethanolic solution (20 mL) of 2,6-diaminopyridine (2.1826 g, 0.02 mol) with constant stirring in a 2:2 molar ratio. The solution was refluxed and stirred for 7 h at 75 ◦C in the presence of few drops of conc. HCl. On cooling the reaction mixture a dull white colored crystalline product was precipitated out. It was filtered, washed several times with cold ethanol and dried under vacuum over P_4O_{10} (Fig. 1).

2.3. Synthesis of complexes

The lanthanide complexes of ligand (L) were prepared by the mixing of hot ethanolic solution (20 mL) of corresponding metal salts (0.001 mol), to a hot ethanolic solution (20 mL) of the ligand L (0.001 mol) with constant stirring on a magnetic stirrer. The reaction mixture was continuously stirred and refluxed on a water-bath for 30–35 h at 75–80 ◦C. On cooling the reaction mixture at 0 ◦C for whole night, product was precipitated out, washed with cold EtOH and dried under vacuum over silica gel.

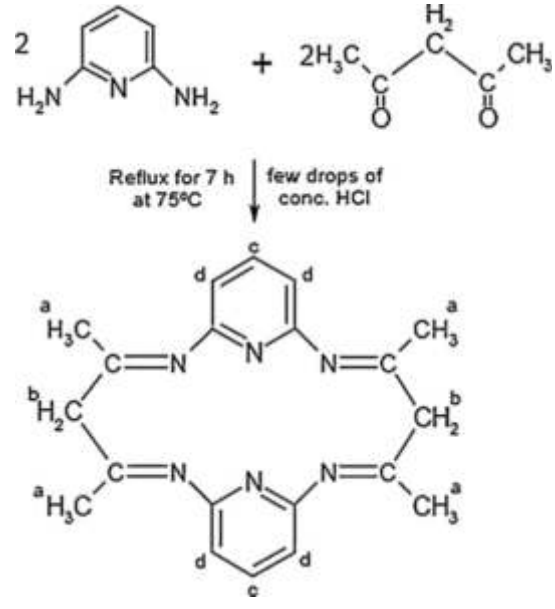

Fig.1 Synthesis of ligands

2.4. Analysis and physical measurements

Carbon, hydrogen and nitrogen analysis were carried out on a Carbo-Erba EA 1106 analyzer. Metal ion in the complexes were determined by volumetric method using EDTA solution [19].Molar conductivity was measured on an ELICO (CM 82T) conductivity bridge with a cell having a cell constant of 0.51cm^{-1}. The magnetic moment was determined at room temperature on a Gouy balance using $Hg[Co(SCN)_4]$ as a callibrant. The electronic spectra of the complexes were recorded on a ShimazduUVmini-1240 spectrophotometer using DMSO as a solvent. IR spectra were recorded as CsI pellets on a FT-IR spectrum BX-II spectrometer in the region 200–4000cm–1.

Electron impact mass spectrum was recorded on JEOL. JMS, DX-303 mass spectrometer. TG measurements of the complexes were carried out in a nitrogen atmosphere on a Rigaku thermoflex instruments using a limiting temperature of 600 ◦C and heating rate 10 ◦C/min.

3. Result and discussion

3.1. Composition and coordination geometry

The analytical data of complexes indicate that all the complexes have the general composition $[Ln(L)X_2{\cdot}H_2O]$ X, where Ln = La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} and X=NO_3^- and Cl^-. All the complexes are sparingly soluble in common organic solvents such as ethanol and methanol but highly soluble in DMF and DMSO. Molar conductance values of all the complexes in DMF fall in the expected range of 1:1 electrolytes [20].

3.2. IR spectra

The IR absorption bands, which provide information about the formation of macrocyclic ligand and the mode of coordination in its complexes are given in Table 2. The spectrum displays a strong band at 1687cm^{-1} [21] corresponding to (C- N) stretching vibration on complex formation, the (C- N) band shows the negative shift [22] which indicates that the nitrogen atom of azomethine group is coordinated to metal ion [23,24]. The spectrum also shows the bands at 1487cm^{-1}, 666cm^{-1} and 429cm^{-1} due to the pyridine ring deformation, in-plane-ring-deformation and out-of plane-ring deformation, respectively. These absorption bands show the positive shift in complexes which indicates that the nitrogen of pyridine ring is involved in coordination [25]. This mode of coordination of ligand is also supported by appearance of band corresponding to (M–N) in the range 421–492cm^{-1} [26]. The appearance of various IR bands in the nitrato complexes clearly reveals the presence of coordinated and uncoordinated NO_3 ions. These bands are found in the range 1410–1461cm^{-1}, 1317–1355cm^{-1} and 1012–1077cm^{-1}. The difference of NO stretching vibration is 93–106cm^{-1} which suggests the monodentate coordination [27] of nitrate groups. The appearance of strong bands in the range 1384–1390cm^{-1} indicate the presence of ionic nitrate [28]. The chloro complexes show the bands corresponding (Ln–Cl) [29] in the region 311–326cm^{-1} (Fig. 2).

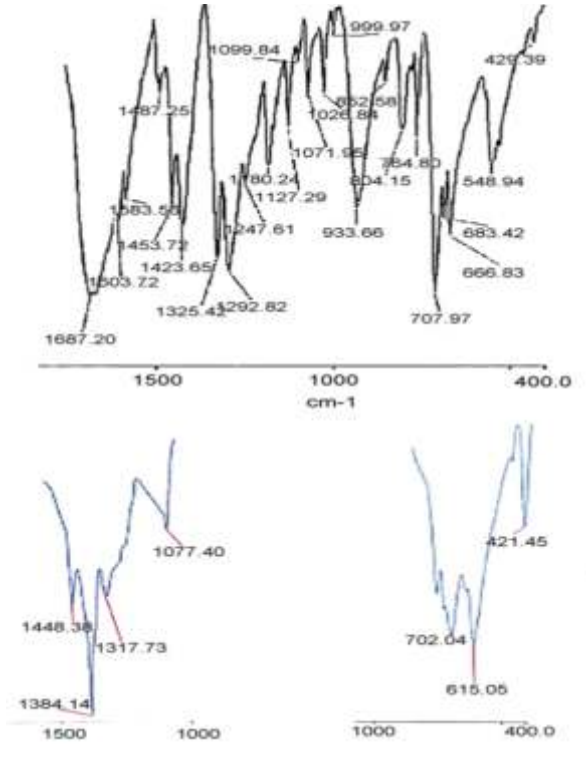

Fig. 2. (a) IR spectrum of ligand (L). (b) IR spectrum of $[Nd(L)(NO_3)_2H_2O]NO_3$. (c) IR spectrum of $[Ce(L)(NO_3)_2{\cdot}H_2O]NO_3$.

3.3. Mass spectrum of the ligand (L)

The mass spectrum of the ligand (L) shows the peaks at m/z = 346 (50%) and 347. These peaks correspond to the M+ (parental ion) and M+ +1, ^{13}C isotope. The peak at m/z = 331, 316, 301 and 286 (70%) are due to the stepwise removal of the four methyl groups from the macrocyclic ligand. The intensity of the peak at 286 is 70% because it corresponds to the macrocyclic moiety. A peak of very high intensity (100%) is also present at m/z=79 which is the base peak due to the pyridine ring. Some other peaks are also present in the spectrum at 246, 169, 143, 103, 40, 26 and 15 due to the other fragmented ions [31]. The peaks area provides an idea of abundance of these ions.

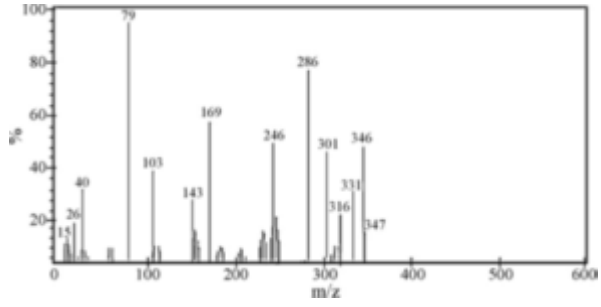

Fig. 3. Mass spectrum of ligand (L).

3.4. Electronic spectra

The electronic spectra of the complexes were recorded in DMSO solution. Nd(III) and Sm(III) complexes display four electronic spectral bands in the range 9112–11507cm^{-1}, 11305–12468cm^{-1}, 13550–18540cm^{-1} and 17182–22331cm^{-1} [33–35], whereas in other complexes bands are appeared only in the ultra violet region. The assignments of these bands are given in Table 3. The complexes exhibit effective enhancement in the intensity of "hypersensitive" bands from which nephelauxetic effect (**β**) is calculated by using the following expression:

$$\beta = 1/n\sum_{\square}^{n-1} \upsilon i complex/\upsilon i aqua$$

β is the measure of the metal–ligand covalent bonding. The value of is utilized to estimate the covalency factor ($b^{1/2}$), Sinha parameter i.e. degree of metal–ligand covalency (β) and the covalency angular overlap parameter (η).

4. Thermal studies

The thermogravimetry (TG) analyses of the complexes were carried in the temperature range 30–60 C in a static nitrogen atmosphere. All the complexes undergo first step decomposition with

weight loss exp. 2.52–2.99% (ca. 2.59–2.95%), between 165 and 225 ◦C due to the loss of the one coordinated water molecule. In the second step decomposition of the complexes show weight loss exp. 17.15–27.04% (ca. 17.09–26.99%) in the temperature range 315–375 ◦C due to the removal of the coordinated and uncoordinated anions. The third step decomposition is due to the loss of the ligand exp. 49.91–56.79% (ca. 49.85–56.72%) in the temperature range 450–540 ◦C .The final residues was analyzed by IR spectra and identified as metal oxide which is corresponding to the calculated value (Fig. 8).

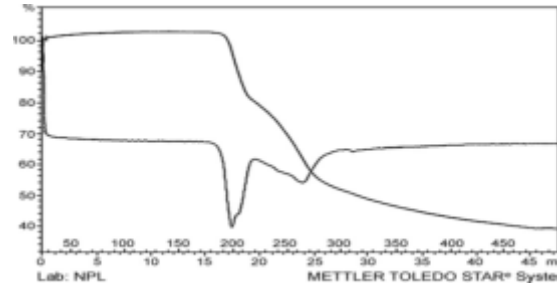

Fig. 4. TGA curve of the complex $[La(L)Cl_2{\cdot}H_2O]Cl$.

5. Structure of the complexes

On the basis of above spectral studies the following structure may be suggested for the complexes (Fig. 9).

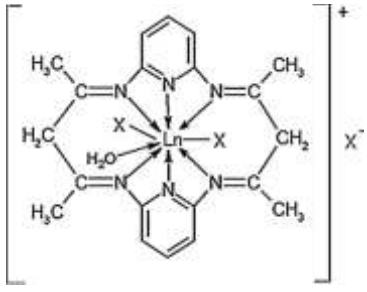

Fig. 5. Structure of complexes with L. Where Ln = La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} and X= Cl^- and No_3–.

6. Conclusion

In this paper, we describe the synthesis and characterization of a hexadentate macrocyclic ligand and its La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} complexes. On the basis of absorption spectra we calculate the different parameters i.e. nephelauxetic ratio (β), covalency factor ($b^{1/2}$), Sinha parameter (δ%) and covalency angular overlap parameter (**η**) for Nd(III) and Sm(III). The values of these parameters suggest the metal–ligand covalent bonding. Except La(III), all the complexes are paramagnetic in nature. The thermal studies reveal the presence of coordinated water molecule. All the complexes were found to have coordination number nine.

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