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Structural characterization of newly synthesized Ln (III) nitrate complexes with *o*-vanillin and *p*-toluidine derivatives

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Abstract

The complexes of Ln (III) (Ln = Dy, Ho, Er, Tm and Yb) with Schiff base derived from o-vanillin and p-toluidine have been synthesized. The structures of these newly synthesized complexes were substantiated by elemental analysis, molar conductivities, infrared, and thermal analysis. The general molecular formula of the complexes are $[LnL_2(NO_3)_3]$. The central metal Ln (III) ion in the complexes coordinates with both two ligands through four oxygen atoms of hydroxyl and methoxy groups and with three bidentate nitrates. Thus the coordination number of the metal complexes is ten. Thermal behavior of the complexes has been studied by TG and DTG. The residues after heating in thermal analysis correspond to metal oxide (Ln₂O₃).

Keywords: vanillin, toluidine, IR, TG, DTG

Introduction

The burgeoning growth in lanthanide chemistry within the last 20 years has many reasons, but three areas such as *warm superconductor* ^[1], medicinal applications including *Magnetic Resonance Imaging* ^[2, 3] (MRI) and lanthanide triflates as Lewis acids in synthetic organic chemistry ^[4] are responsible for this.

Various studies showed that Schiff bases derived from salicylaldehyde and its derivatives have considerable biological importance. They were widely used in the fields have in the fields of biology, pharmacology, catalysis, organic synthesis and chemical analysis ^[5, 6]. Many attentions have been focused on these Schiff bases because of the stability of the ligands and various properties of their metal complexes ^[7].

Although lots of work has been done on Ln (III) chelates with tetradentate Schiff bases obtained from salicylaldehyde and ethylenedimine and *o*-phenylenediamine. Ansari *et al.* ^[8] has studied on lanthanide complexes of *bis* vanilline-benidine. But there are little work has been done on Ln (III) complexes of Schiff base about thermal analysis. With this regard, five complexes of Ln (III) nitrates were synthesized and characterized by elemental analysis, molar conductivities, infrared, and thermal analysis.

Experimental

All chemicals such as lanthanide oxide (99.5%) and other reagents were of AR grade. Ln(NO₃)₃.6H₂O were prepared by dissolving lanthanide oxide in concentrated nitric acid and were crystallizing the salt by evaporating the solution on a steam bath. The metal contents were determined by EDTA complex metric titration after decomposition a known amount of the complexes with concentrated nitric acid. Elemental analyses for C, H and N were carried out on an Elementar Vario EL III elemental analyzer. IR spectra on KBr pellets were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer in the range of 4000-400 cm⁻¹. Molar conductivity of the complexes was measured with Shanghai dds-11A conductivity meter in DMF. Thermal analyses were carried out using Mettler-Toludo TGA/SDTA851 thermal analyzer in air atmosphere at a heating rate 10 °C min⁻¹.

Preparation of ligand

Schiff base ligand (L) was prepared by the direct reaction of equimolar quantities of ovanillin (3.46 g) and p-toluidine (3.21 g) in 50 ml absolute alcohol. The reaction mixture was stirred for 0.5 h at room temperature, then the orange solid ligand were isolated by filtration, washed with ehanol and dried in air, yield 86%.

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Preparation of complex

A solution of 0.45 g Ln(NO₃)₃.6H₂O inabsolute ethanol (10 ml) was added drop wise with stirring to a solution of 0.48 g of Schiff base ligand-2-methoxy-6-{[(4-methyl phenyl) imino] methyl} phenol in absolute ethanol (30 ml). The

mixture was stirred at room temperature for 2 hours and the solid formed was separated by filtration, washed with absolute ethanol and dried in air. Yield of the compound was 85%.

$$Ln(NO_3)_3.6H_2O$$
 + HO $Orange solid$ V + $6H_2O$ $complex$

The elemental analysis for C, H and N of the complex was carried out at Central Drug Research Institute (CDRI), Lucknow on an Elementar Vario EL III elemental analyzer.

Physical properties and elemental analysis of the complexes is given as:

Elemental analysis

| | % of Ln found/(Cal) | % of C found/(Cal) | % of H found/(Cal) | % of N found/(Cal) |
|---|---------------------|--------------------|--------------------|--------------------|
| $[DyL_2(NO_3)_3]$ | 19.45/(19.45) | 43.38/(43.18) | 3.69/(3.64) | 8.41/(8.47) |
| [HoL ₂ (NO ₃) ₃] | 19.85/(19.85) | 43.21/(43.05) | 3.68/(3.63) | 8.38/(8.45) |
| $[ErL_2(NO_3)_3]$ | 19.90/(20.01) | 43.15/(42.95) | 3.60/(3.62) | 8.35/(8.44) |
| [TmL2(NO3)3] | 20.07/(20.17) | 43.00/(42.89) | 3.58/(3.61) | 8.37/(8.44) |
| [YbL ₂ (NO ₃) ₃] | 20.47/(20.56) | 42.21/(42.15) | 3.54/(3.59) | 8.29/(8.39) |

Results and discussion

All Ln (III) complexes are stable in air and have no sharp melting point. They are soluble in polar organic solvents and little soluble in non-polar solvents. The molar conductance values are too low to account for any dissociation. Thus complexes are non-electrolytes; it indicates that anions are coordinated with the metal atom. The molar conductance of these complexes in DMF is given in following table.

| Complexes | Soluble | Conductance (A _m Scm ² mol ⁻¹) | Colour |
|---|-----------------------------------|--|--------|
| $[DyL_2(NO_3)_3]$ | MeOH, EtOH, Acetone, DMF and DMSO | 17 | Orange |
| $[HoL_2(NO_3)_3]$ | MeOH EtOH, Acetone, DMF and DMSO | 19 | Orange |
| $[ErL_2(NO_3)_3]$ | MeOH, EtOH, Acetone, DMF and DMSO | 18 | Orange |
| [TmL2(NO3)3] | MeOH, EtOH, Acetone, DMF and DMSO | 19 | Orange |
| [YbL ₂ (NO ₃) ₃] | MeOH, EtOH, Acetone, DMF and DMSO | 21 | Orange |

Spectral Studies Ln³⁺ Complexes

The infrared, ¹H NMR and electronic spectra of the complexes were obtained from external agency C.D.R.I., Lucknow. The infrared spectra of the solid Ln³⁺ complexes

with Schiff base ligand-2-methoxy-6-{[(4-methyl phenyl)imino]methyl}phenol in absolute ethanol are given below.

| Compound | v _{CN} Str. | v_{OH} | $v_{ m Ln-O}$ | v_{CO} |
|---|----------------------|-------------------|---------------|----------|
| Ligand | 1616 s | 3451 | | 1261s |
| [DyL ₂ (NO ₃) ₃] | 1642s | 3426 | 489 | 1240s |
| [HoL ₂ (NO ₃) ₃] | 1640s | 3427 | 488 | 1241s |
| [ErL ₂ (NO ₃) ₃] | 1641s | 3427 | 489 | 1241s |
| $[TmL_2(NO_3)_3]$ | 1642s | 3426 | 489 | 1243s |
| [YbL2(NO3)3] | 1641s | 3419 | 492 | 1241s |

The broad absorption band at 3451 cm⁻¹ due to the hydroxyl group in IR spectra of the free ligand appears at lower frequency in the corresponding complexes in between 3427 to 3419 cm⁻¹. It indicates that coordination of oxygen atom of the phenolic hydroxyl with the central metal ion. The shift of the C-O_{str} vibration of the phenolic part of o-vanillin from 1261 cm⁻¹ to 1243-1240 cm⁻¹ also supports the coordination of oxygen atoms. However, a strong band in the free Schiff base ligand occurring at 1617 cm⁻¹ due to C=N stretching is found shifted higher frequency say 1642-1635 cm⁻¹ but the nitrogen atom of azomethine was regarded as non- coordination with Ln (III) metal ions [9]. A new band at 492-488 cm⁻¹ was present due to (Ln-O) stretching vibration¹¹. Five absorption peaks at 1505-1500 cm⁻¹, 1298-1294 cm⁻¹, 1029-1023 cm⁻¹, 819-818 cm⁻¹and 743-742 cm⁻¹ in the spectra of complexes are coordinated nitrates which behaves as bidentate ligand [10, 11].

Thus Schiff base ligand-2-methoxy-6-{[(4-methyl phenyl) imino] methyl} phenol behaves as bidentate ligand. Therefore, it is concluded that every Ln (III) ion in the complexes coordinates with two Schiff base ligands via four oxygen atoms of phenol hydroxyl groups and methoxy groups and three nitrates via oxygen atoms. Thus their coordination numbers are ten. The proposed general structures of complexes are shown as:

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