



'THERMOGRAVIMATRIC AND DIFFERENTIAL THERMAL ANALYSIS OF QUINONE DERIVATIVES WITH LANTHANIDE COMPLEX'

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ABSTRACT

The design and development of thermodynamically stable lanthanide complexes with an encapsulating ligand is currently a key area of vital importance in the field of luminescence as it offers the possibility to obtain luminescent materials possessing better sensitivity and specificity. The Gd(III), Dy(III) and Sm(III) complexes of Schiff base as a ligand have been developed with acetoacetanilide and 1,3-diaminopropane, [Ln(LH₂) X₃], where X= Cl, NO₃⁻, NCS⁻, have been synthesized in ethyl alcohol as a solvent. Ligand LH 2 acts as a tetradentate ligand bonded through two azomethine nitrogen atoms and the two enolizable carbonyl group of acetoacetanilide organic moiety. TG & DTA study exhibits the thermal behavior in tune with the expected one for the synthesized complexes.

KEYWORDS : Analytical tools, TG, DTA.

INTRODUCTION

Synthesis of tetradentate Schiff base ligands from diamines and corresponding salicylaldehyde derivative is a reaction of importance in organic chemistry,

due to the thermodynamic stability of these tetradentate ligands with different lanthanide cations. The earlier literature reveals that Schiff base ligands are excellent coordinating ligands in terms of the high thermodynamic stability of the coordination compounds they form, excellent solubility in common conventional solvents and provides for flexibility in the chemical environment about the C=N group. The conjugated p system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. The work presented here is the study of physico-chemical and antimicrobial activity of selected lanthanide ions like Gd(III), Dy(III) and Sm(III) with the Schiff base ligand. Structure for the identified lanthanide complexes is as shown in Fig. 1.

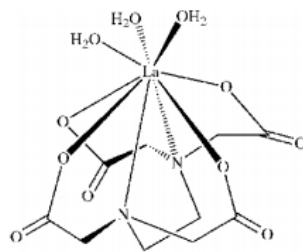


Fig. 1 The structure of La(EDTA)(H₂O)³⁻

Characteristics of the Lanthanides:

The lanthanides exhibit a number of features in their chemistry that differentiate them from the d-block metals. The reactivity of the elements is greater than that of the transition metals, akin to the Group II metals:

1. A very wide range of coordination numbers (generally 6–12, but numbers of 2, 3 or 4 are known).
2. Coordination geometries are determined by ligand steric factors rather than crystal field effects.
3. They form labile 'ionic' complexes that undergo facile exchange of ligand.
4. The 4f orbitals in the Ln³⁺ ion do not participate directly in bonding, being well shielded by the 5s² and 5p⁶ orbitals. Their spectroscopic and magnetic properties are thus largely uninfluenced by the ligand.
5. Small crystal-field splittings and very sharp electronic spectra in comparison with the d-block metals.
6. They prefer anionic ligands with donor atoms of rather high electronegativity (e.g. O, F).
7. They readily form hydrated complexes (on account of the high hydration energy of the small Ln³⁺ ion) and this can cause uncertainty in assigning coordination numbers.
8. Insoluble hydroxides precipitate

at neutral pH unless complexing agents are present.

9. The chemistry is largely that of one (3+) oxidation state (certainly in aqueous solution).

10. They do not form $\text{Ln}=\text{O}$ or $\text{Ln}\equiv\text{N}$ multiple bonds of the type known for many transition metals and certain actinides.

11. Unlike the transition metals, they do not form stable carbonyls and have (virtually) no chemistry in the 0 oxidation state.

MATERIALS AND METHODS:

Metal salts, acetoacetanilide, 1,3-diaminopropane and other reagents were AR grade. Solvents such as ethanol, methanol and acetone were subjected to purification. Thermal Gravimetric and Differential Thermal analysis too was also undertaken in a inert atmosphere with a heating rate of 100C/min.

SYNTHESIS OF THE LANTHANIDE COMPLEXES

The lanthanide(III) chlorides, nitrates and thiocyanates were synthesized using methanolic solution of the ligand LH 2 (0.001 mol), and was added upon by a methanolic solution of the Ln(III) salt (0.001 mol) in a dropwise manner with constant stirring on a magnetic stirrer. The pH of the reaction mixture was adjusted to 7- 8 by adding 10% liquor ammonia followed by refluxing the reaction mixture for 10 hours. The resulting solution was pre-concentrated to one third of its original volume and kept on standing overnight. The precipitated metal complex was then filtered using Whatmann filter paper no. 41, washed with methanol (3X) and finally dried in a vacuum desiccator.

Simultaneous TG-DTA of the samples were carried out under static air conditions, either on a Stanton Redcroft TR-OI thermobalance or on a Derivatograph (Mom OD-162 model) using 56 or 108 mg of finely powdered samples at a heating rate of 8 C/min. Finely powdered z_3 (—alumina was used as the reference substance.

All the chemicals used are AR grade including Lanthanide chlorides and solvents used are of high purity. The procedure followed in both conventional and microwave assisted synthesis is as follows:

Conventional heating method: A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapson (0.248 g, 0.01 mol.) was added to ethanol (100 mL) and the solution was refluxed for 5 h at 60 C. The resulting solution was cooled and the precipitate was filtered, dried at room temperature and purified.

Ultrasound assisted method: A mixture of 2,3-dichloro-1,4-naphthaquinone (0.227 g, 0.01 mol.) and dapson (0.248 g, 0.01 mol.) was ground together and subjected to ultrasonication in water and acetone separately for 15 minutes. After the completion of the reaction, the product was set aside to cool and then ice cold water (100 mL) was added. The solid product was filtered, dried at room temperature and recrystallized from ethanol.

RESULT AND DISCUSSION:

All the complexes were stable at ambient temperature and non-hygroscopic which was confirmed using TG/DTA tools. They are insoluble in common organic solvents like ether, acetone, benzene, carbon tetrachloride and nitrobenzene but are readily soluble in DMF and DMSO.

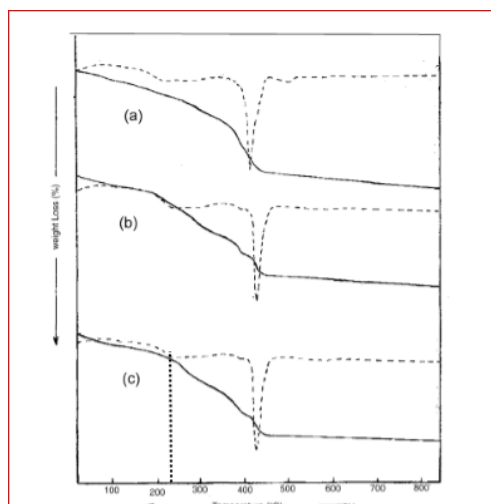


Fig.2 TG Curves for [a] Nd (III) ,[b] Sm (III) , [c] Eu (III) complexes.

All complexes were studied by thermo gravimetric analysis in the temperature range 50°C to 800°C in inert atmosphere. Thermo grams obtained for most of the compounds were similar in character.

All complexes decompose in a gradual manner with two distinct stages and all of them start to lose mass at around 240 °C. Higher temperature indicating the thermal stability of the complex. The stability is due to hydrogen bonding as well as the strong bonding of the tridentate ligand with Ln(III) resulting in the formation of a thermodynamically stable complex.

In first stage decomposition (190-240 °C) indicates the loss of four water molecule.

Second stage decomposition corresponds to the loss of three coordinated ions and ligand molecule resulting in the formation of metal oxide. The weight loss data obtained from TG measurement and the theoretical value confirms the final residue as Ln₂O₃.

CONCLUSION:

The thermodynamically stable complexes of the lanthanide ions like Sm, Gd or Dy have been synthesized and it is corroborated with the analytical data which show that all the complexes have the empirical formula base in its composition as [Ln(LH₂) X₃], where M = Sm(III), Gd(III), Dy(III) and X = Cl, NO₃ - and NCS-.

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