

Lanthanide (III) Nitrate Complexes with 2,4-dinitro-6 (pyridine-2-ylmethylamino) methylphenolate : Importance, Synthesis, Antimicrobial, Spectral and Thermodynamic studies

Neeraj Sharma

Abstract— Lanthanide (III) Nitrate complexes of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate with rare earth metals have been synthesized and characterized by elemental analysis, thermo gravimetric analysis, conductivity measurements, magnetic susceptibility measurement, UV-visible and infrared spectroscopies. An ethanolic solution of (ligand)2,4-dinitro-6(pyridine-2-ylmethylamino) ethylphenolate was added to an aqueous solution of metal nitrate and followed by adding ethanolic solution of ligand and aqueous solution of potassium thiocyanate to give complexes with general formula $[M L X_3]$ where $M = La(III), Gd(III)$ and $Nd(III)$, $L = 2,4$ -dinitro-6(pyridine-2-ylmethylamino) methylphenolate and $X =$ thiocyanate ion. The results suggested that the complex has octahedral geometry. In thermo gravimetric analysis the TG curve for ligand was broader while the curve of its metal complexes were steeper, suggesting the faster decomposition rate of the metal complexes than that of the ligands, this may be due to catalytic action of metal present in them. The molar conductance of metal complexes suggests their neutral nature. The relative antimicrobial studies of ligand and complexes shows that $Gd(III)$ complex is more effective towards gram positive bacteria like *S. aureus*. The work may be of great utility both for industry and academic research for exploring the ligand metal complexes as antimicrobial and antifungal activity and can be used as chemotherapeutic agent.

Index Terms— 2, 4- dinitro-6 (pyridine-2-ylmethylamino) methylphenolate, Thiocyanate Ion, Lanthanide (III) Nitrate, Thermo gravimetric analysis, ESR, Antimicrobial studies

I. INTRODUCTION

The coordination chemistry of lanthanide is fascinating because they have a tendency to form complexes with coordination number greater than six, even up to twelve[1]. As early as 1979 Thomas et al[2] have reported eleven coordinated lanthanum (III) nitrate complexes with bis (hydrazone) type ligand derived from 2, 6- diacetylpyridine. Some seven and eight coordinated complexes have also been reported [3-5] with similar ligands and various lanthanides. The relaxation rate of surrounding protons to enhance image contrast by large magnetic moment of $Gd(III)$ ion[6]. In all metal ions $Gd(III)$ ion is known to possess the highest paramagnetism. Some representative advantages of employing the $Gd(III)$ ion come from their unique properties

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such as high magnetic moment and long electron spin relaxation time[6]. Despite their wide and successful applications in clinics, however, conventional $Gd(III)$ -based contrast agents (GBCAs) are mostly extracellular fluid (ECF) agents exhibiting rapid renal excretion[7-9]. The salicylaldehyde fragment is well recognized as a good promesogenic unit as the azomethine linkage is stabilized by intermolecular hydrogen bonding in addition to being a good donor site for coordination with metals [10-13]. Chelating ligands containing O and N donor atoms show pronounced biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions[14]. These complexes often possess remarkable and unique spectroscopic, photophysical and electrochemical properties which may be exploited in sensory and diagnostic applications [15-20]. Thus, the aim of this paper is to synthesize and characterize lanthanide(III) complexes as we attempted to throw light on the coordination position for 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate with the lanthanide(III) ion. The structure of ligand is –

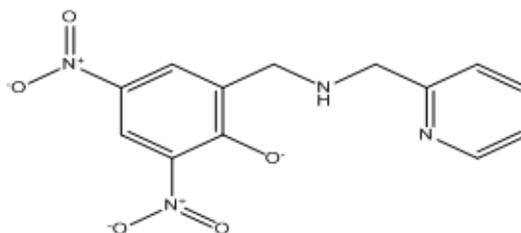


Fig. 1-2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate

II. EXPERIMENTAL

Materials and spectral measurements

All the chemicals used were of analytical grade and procured from standard firm like Merck and Aldrich. The molar conductivity in DMSO ($10^{-3}M$) at room temperature was measured using an Equiptronics digital conductivity meter. The magnetic susceptibility measurements of the complexes were made on Goy balance using $Hg[Co(SCN)_4]$ as standard. Electronic spectra of complexes were recorded on Elico SL-171 spectrophotometer at $25^{\circ}C$ using ethanol/acetone as solvent. Thermo gravimetric analysis of complexes were done at a constant heating rate of $10^{\circ}C /min$ up to $1000^{\circ}C$ temperature on a TGA instrument model Perkins Elmer (Pyris Diamond) and FTIR spectra of complexes were recorded on Perkin Elmer–842 spectrophotometer. Metal

content and water percentage were determined by thermo gravimetric techniques [21]. The ligand and metal complexes were evaluated for their in-vitro antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi* and antifungal activity against *Aspergillus flavous*, *Aspergillus niger*, *Penicillium triticeana* and *Fusarium species* by serial dilution method[22] using Mueller-Hinton agar (MHA) medium and Sabouraud's dextrose agar (SDA) medium, for bacteria and fungi respectively.

III. SYNTHESIS OF Gd(III) COMPLEX

Lanthanide (III) Nitrate complexes were prepared by the general procedure with stoichiometric amount of ligands and metal nitrate in a 1:1:1 mole ratio. Metal ligand complexes were prepared by refluxing the equimolar solutions of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate, metal nitrate solution and potassium thiocyanate solution at 50-60°C for 3hrs. The pH of the reaction mixture was maintained between 6.5-7.0. The colored precipitate obtained were filtered washed several times with hot water followed by ethanol to remove the soluble impurities and dried in an oven at 100 °C for 1hr and finally kept in desiccator over anhydrous CaCl₂. The dried solid were recrystallized with benzene: methanol (9.5:0.5) solution.

IV. RESULT AND DISCUSSION

The coloured Lanthanide (III) nitrate complexes were found to be stable at room temperature. In complexes, ligands and metal are in 1:1:1 molar ratio possessing general formula [M L X₃] it was confirmed by elemental analysis and mass estimation by Fenger's method [23]. The molar conductivity (Λ_m) in DMSO at 25°C is 12 Ohm⁻¹ cm² mol⁻¹, which indicates that the metal complexes are neutral [24].

A. Infrared Spectra

The infrared spectrum of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate exhibited a strong band at 1658 cm⁻¹ and 1356 cm⁻¹ which is attributed to ν (C=O) and C=N stretching frequencies respectively. This band shifted to lower wave number in the metal complexes by 20-25 cm⁻¹ and 11-20 cm⁻¹, indicating that the (C=O) and (C=N) group is involved in complex formation respectively. The coordination through the nitrogen atom in (C=N) groups are further supported by the occurrences of new band around at 475 cm⁻¹ in the spectra of the complexes which, may be assigned to ν (M-N)[25]. The presence of new weak bands around at 450 cm⁻¹ and at 568 cm⁻¹ in complexes were attributed to δ (M-SCN) [26] and ν (M-O) linkage[27].

B. Magnetic susceptibility and Electronic Spectrum

The electronic spectra of ligand and their corresponding lanthanide (III) complexes are recorded in DMF in the region 200-900 nm. The ligands show bands in the ranges 255-300, 350-370 and 380-400 nm and in the corresponding

lanthanide (III) nitrate complexes, bands around 280 and 410 nm are observed. In the region from 210-490 nm the bands are quite intensive both for the ligands and corresponding complexes. Thus the weak f-f transitions occurring in this region due to the metal ion in the complexes are obscured in the intense ligand bands. Also the ligand band remains largely unaffected on the complexation. No absorption band due to f-f transition of Lanthanide (III) ions could be located in the visible region in the spectra of all these complexes. This is probably due to the fact that the f-f bands are weak and are obscured by the intense charge transfer bands. The electronic spectra of free ligand and SCN⁻ ion showed that the absorption bands in the UV region can be annotated as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectra of the metal complexes exhibits weak broad bands at 279, 408 and 981nm which is attributed to the electronic transitions of 4T_{1g}(F) \rightarrow 4A_{2g}(F), 4T_{1g}(F) \rightarrow 4T_{1g}(P) and 4T_{1g}(F) \rightarrow 4T_{2g}(F) respectively. These transitions correspond for octahedral complexes.

The magnetic moment for lanthanide (III) ions should be around 3.872 B.M while the measured value of μ_{eff} was shown to be higher than the expected value. The observed magnetic moments are compared with the theoretical spin orbital coupling values (the Hunds values) and the values calculated from Van Vleck formula[28] of the respective lanthanide ion. These values agree with each other for all the lanthanide (III) nitrate complexes This indicates the non involvement of 4f-orbitals in the bond formation.

C. Thermo gravimetric analysis

The thermal behaviour of representative lanthanide (III) nitrate complexes including stability ranges, peak temperature, percentage of weight loss and percentage of residue obtained after decomposition process has been studied. To confirm the proposed structure for the complexes, thermogravimetric analyses TGA and DTG are measured under nitrogen. The decomposition reaction of [C₁₃H₁₁N₄O₅La(SCN)₃] occur in four steps from 158 °C to 1000 °C. The first step of decomposition proceeds with a weight loss of 12.40% at 158 °C, associated with the loss of lattice water (calculated 13.94%). The second, third and fourth steps of decomposition proceed at maximum temperatures of 198, 367, and 502 °C, respectively, attributed to the loss of C₁₃H₁₁N₄O₅. The decomposition reaction of [C₁₃H₁₁N₄O₅Gd(SCN)₃] occur in four steps from 144 °C to 1000 °C. The first step of decomposition proceeds with a weight loss of 13.50% at 144 °C, associated with the loss of lattice water (calculated 14.43%). The second, third and fourth steps of decomposition proceed at maximum temperatures of 144, 348, and 489 °C, respectively, attributed to the loss of C₁₃H₁₁N₄O₅. The decomposition reaction of [C₁₃H₁₁N₄O₅Nd(SCN)₃] occur in four steps from 162 °C to 1000 °C. The first step of decomposition proceeds with a weight loss of 15.30% at 144 °C, associated with the loss of lattice water (calculated 16.21%). The second, third and fourth steps of decomposition proceed at maximum temperatures of 144, 348, and 489 °C, respectively, attributed to the loss of C₁₃H₁₁N₄O₅. The total weight loss associated with these steps (38.03%) is in good agreement with the calculated value of 41.79%. The weight of the residue was in

good agreement with the theoretically calculated weight of metal carbide as well as metal oxide [29]. In thermo gravimetric analysis the TG curve for ligand was broader while the curve of its metal complex was steeper, suggesting the faster decomposition rate of the metal complex than that of the ligands, this may be due to catalytic action of metal present in them. The TGA curve of the lanthanide (III) complexes showed the decomposition of metal complex follows the zero order kinetics. The value of energy of activation were calculated by using Freeman Carrolls [30], Horowitz Metzger's [31] and Coats Redfern's [32] equations

D. Antimicrobial Studies

The antimicrobial results show that the best zone of inhibition of all the metal complexes was 500 ppm. The relative antimicrobial studies of ligand and complexes shows that Gd(III) complex is more effective towards gram positive bacteria like *S. aureus*.

ACKNOWLEDGEMENTS

We all thanks CDRI Lucknow and IIT Roorkee, India for the all analytical and elemental analysis. We also thank to Agra College, Agra and GLA University, Mathura India for providing infrastructure. We are highly thankful to Dr. (Mrs.) Kshama Chaturvedi and Prof. G. K. Chaturvedi Ex. Head Dept. of Chemistry, G.B. Pant Nagar University (U.S. Nagar) India for their moral support.

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