

Gadolinium Metal Complex with 2,4-dinitro-6 (pyridine-2-ylmethylamino) methylphenolate : Synthesis, characterization and Antimicrobial Activities

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ABSTRACT

An ethanolic solution of (ligand)2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate was added to an aqueous solution of gadolinium chloride and followed by adding ethanolic solution of ligand and aqueous solution of potassium thiocyanate to give complex with general formula [M L X₃] where M= Gd(III), L = 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate and X = thiocyanate ion. The resulting product was characterized using elemental analyses, UV-visible and infrared spectroscopies, magnetic susceptibility measurement and TGA. The results suggested that the complex has octahedral geometry. The TGA curves of the Gd(III) complex showed the decomposition follows the zero order kinetics. The molar conductance of Gd(III) metal complex suggests their neutral nature. The relative antimicrobial studies of ligand and complex shows that Gd(III) complex is more effective towards gram positive bacteria like S. aureus.

Keywords: 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate, Thiocyanate Ion, Gadolinium metal, Thermo gravimetric analysis, ESR

1. INTRODUCTION

Because of the useful magnetic and optical behaviour of lanthanide ions, the coordination chemistry of these ions has been widely investigated in recent years and it could exhibit coordination numbers 6–12, with 8 or 9 being omnipresent [1]. The relaxation rate of surrounding protons to enhance image contrast by large magnetic moment of Gd (III) ion[2]. 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 such as high magnetic moment and long electron spin relaxation time[2]. 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[3-5]. The salicylaldimine 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 [6-9]. *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[10]. These complexes often possess remarkable and unique spectroscopic, photophysical and electrochemical properties which may be exploited in sensory and diagnostic applications [11-16]. Thus, the aim of this paper is to synthesize and characterize Gd(III) complex as we attempted to throw light on the coordination position for 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate with the Gd(III) ion. The structure of ligand is –

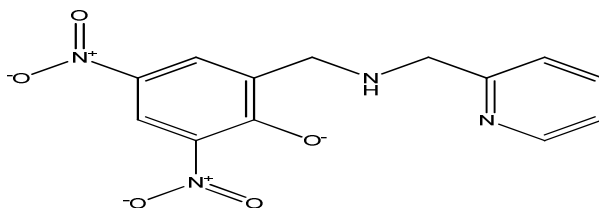


Fig. 1-2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate

Experimental

2. MATERIALS AND SPECTRAL MEASUREMENTS

All the chemicals used were of analytical grade and procured from standard firm like Merk 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 complex was made on Goy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as standard. Electronic spectrum of complex was recorded on Elico SL-171 spectrophotometer at 25°C using ethanol/acetone as solvent. Thermo gravimetric analysis of complex was done at a constant heating rate of $10^\circ\text{C}/\text{min}$ up to 1000°C temperature on a TGA instrument model Perkins Elmer (Pyris Diamond) and FTIR spectrum of complex was recorded on Perkin Elmer-842 spectrophotometer. Metal content and water percentage were determined by thermo gravimetric techniques [17]. The ligand and Gd(III) complex 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 triticena* and *Fusarium species* by serial dilution method[18] using Mueller-Hinton agar (MHA) medium and Sabouraud's dextrose agar (SDA) medium, for bacteria and fungi respectively.

Synthesis of Gd(III) Complex

Gd(III) complex was prepared by the general procedure with stoichiometric amount of ligands and metal chloride in a 1:1:1 mole ratio. Metal ligand complex was prepared by refluxing the equimolar solutions of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate, metal chloride solution and potassium thiocyanate solution at $50-60^\circ\text{C}$ for 3hrs. The pH of the reaction mixture was maintained between 6.5-7.0. The colored precipitate obtained was 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 was recrystallized with benzene:methanol (9.5:0.5) solution.

3. RESULT AND DISCUSSION

The coloured microcrystalline complex was found to be stable at room temperature. In complex, 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 [19]. The molar conductivity (Λ_m) in DMSO at 25^oC is 12 Ohm⁻¹ cm² mol⁻¹, which indicates that the Gd (III) complex is neutral [20].

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 Gd(III) complex by 20 cm⁻¹ and 11 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 at 475 cm⁻¹ in the spectrum of the complex which, may be assigned to ν (M-N)[21]. The presence of new weak bands around at 450 cm⁻¹ and at 568 cm⁻¹ in complex was attributed to δ (M-SCN) [22] and ν (M-O) linkage[23].

Magnetic susceptibility and Electronic Spectrum

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 spectrum of the Gd(III) complex exhibits weak broad bands at 279, 408 and 981nm which is attributed to the electronic transitions of 4T₁g(F) \rightarrow 4A₂g(F), 4T₁g(F) \rightarrow 4T₁g(P) and 4T₁g(F) \rightarrow 4T₂g(F) respectively. These transitions correspond for Gd(III) as a octahedral complex. The magnetic moment for Gd³⁺ complex should be around 3.872 B.M while the measured value of μ_{eff} was shown to be higher than the expected value.

Thermo gravimetric analysis

To confirm the proposed structure for the complex, thermogravimetric analyses TGA and DTG are measured under nitrogen. The decomposition reaction of [C₁₃H₁₁N₄O₅Gd(SCN)₃] occur in four steps from 144 °C to 800 °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 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 [24]. 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 Gd (III) complex showed the decomposition of metal complex follows the zero order kinetics. The value of energy of activation were calculated by using Freeman Carrolls [25], Horowitz Metzger's [26] and Coats Redfern's [27] equations .

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 complex shows that Gd(III) complex is more effective towards gram positive bacteria like *S. aureus*.

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REFERENCE

- [1] Chakraborty J., Ray A., Pilet G., Chastanet G., Luneau D., Ziessel R. F., Charbonni L., Carrella L., Rentschler E., El Fallahe M. S. and Mitra S.” *Syntheses characterisation,, magnetism and photo luminescence of a homodinuclear Ln(III)-Schiff basefamily*”; Dalton Trans., 2009;10263.
- [2] Caravan, P.; Ellison, J. J.; McMurry, T. J.; Lauffer, R. B. Chem. Rev. 1999, 99, 2293.
- [3] Kobayashi, H.; Sato, N.; Hiraga, A.; Saga, T.; Nakamoto, Y.; Ueda, H.; Konishi, J.; Togashi, K.; Brechbiel, M. W. Mag. Reson. Med. 2001, 45, 454.
- [4] Ayyagari, A. L.; Zhang, X.; Ghaghada, K. B.; Annapragada, A.; Hu, X.; Bellamkonda, R. V. Mag. Reson. Med. 2006, 55, 1023.
- [5] Schwickert, H. C.; M., S.; van Dijke, C. F.; Roberts, T. P.; Mann, J. S.; Demsar, F.; Brasch, R. C. Acad. Radiol. 1995, 2, 851.
- [6] A. Dossing “Luminescence from Lanthanide(3+) Ions in Solution” Eur. Journal of Inorg.Chemistry 8 (2005) 1425.
- [7] Bhattacharjee C. R., Das G.,Mondal P, Prasad S. K. and Rao D. S “ *Novel photoluminescent hemidisclike liquid crystalline Zn(II) complexes of [N2O2] donor 4-alkoxy substituted salicyldimine Schiff base with aromatic spacer*” Polyhedron; 2010;29, 3089.
- [8] Bhattacharjee C. R., Das G.,Mondal P, Prasad S. K. and Rao D. S” *Novel Green Light Emitting Nondiscoid Liquid Crystalline Zinc(II) Schiff-Base Complexes*” Eur. Journal of Inorg. Chemistry; 2011;14, 1418.

- [9] Bhattacharjee C. R., Das G., Mondal P, Prasad S. K. and Rao D. S.” *Lamellar columnar mesomorphism in a series of oxovanadium(IV) complexes derived from N, N'-di-(4-nalkoxysalicylidene) diamminobenzene*” *Inorg. Chemical Communication*; 2011; 14, 606.
- [10] Hung W., Lin C., *Inorg. Chem.*, 2009; 48 (2), 728–734.
- [11] Beer P. D.. *Charged guest recognition by redox responsive ligand systems*, *Adv. Mater.* 1994;6, 607-609.
- [12] Van Veggel F. C. J. M., Chiosis G., Cameron B. R. and Reinhoudt D. N.. *Preorganized metalloceptor: Selective receptor for NH₃*, *Supramolecular Chem.*, 1994;4, 177-183.
- [13] Nabeshima T.. *Regulation of ion recognition by utilizing information at the molecular level* . *Coord. Chem. Rev.*, 1996;148, 151-169.
- [14] Canary W. and Gibb B. C., *Selective recognition of organic molecules by metallohosts*. *Prog. Inorg. Chem.*, 1997; 45, 1-81.
- [15] Gray J. M.. *Metallacrown ethers: Unique inorganic ligands. Comments Inorg. Chem.* ,1995; 17, 95.
- [16] Pecoraro V. L., Stemmler A. J., Gibney B. R., Bodwin J. J., H. Wang, Kampf J. W. and Barwinski A., *Metallacrowns: a new class of molecular recognition agents*. *Prog. Inorg. Chem.*, 1997;45, 83-177.
- [17] Vogel A I., *A Text Book of Quantitative Inorganic Analysis*, 3rd Edn, Longmans, London (1964).
- [18] Quasted J H, *J. Gen. Microbial.*, 1996, 45:14.
- [19] Job P,” *Job Plot: A Job plot is used to determine stoichiometry*” *Anm. Chim. (Paris)*, 1928; 9:113-203.
- [20] W J Geary, *Coord. Chem. Rev.*, 7, 85, 1971.
- [21] Cramer Roger, E., Douglas M. Ho, William Van Doorn, James A., Ibers, Ted Norton & Midori K.. *Triphenylmethylphosphoniumtrichloro(caffeine) platinum(II)*. *Inorg. Chem.* 1988;20: 2457-2461.
- [22] Michael Bron & Rudolf Holze. *Cyanate and thiocyanate adsorption at copper and gold electrodes as probed by in situ infrared and surface-enhanced raman spectroscopy*. *Journal of Electroanalytical Chemistry*. 1995; 385: 105-113.
- [23] Nakamoto K, Fujita J, Murata H, “*Infrared Spectra of Metallic Complexes. V. The Infrared Spectra of Nitro and Nitrito Complexes*” *J. Am. Chem. Soc.*, 1958; 80(18): 4817-4823.
- [24] Duan HD, Hou WG, Wu YM , Han SH, Wang LZ, “*Gelation of polyacrylamide by Cr₃₊: analysis of mechanism and thermal stability of the gel*” *J. Ind. Chem. Soc.*, 2002;79: 509-512.
- [25] Freeman ES, Caroll BJ, “*The Application of Thermoanalytical Techniques to Reaction Kinetics: The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate*” *Ohys. Chem.*, 1958; 62(4): 394-397.
- [26] Horowitz HH, Metzger G, “*A New Analysis of Thermogravimetric Traces*” *Anal. Chem.*, 1963;35(10): 1464-1468.
- [27] Coats AW, Redferns JP, “*Kinetic Parameters from Thermogravimetric Data*” *Nature*, 1964; 201: 68-69.