Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 124 (2014) 564–570

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectroscopic characterization of Lanthanoid derived from a hexadentate macrocyclic ligand: Study on antifungal capacity of complexes

Sulekh Chandra [a,*], Swati Agrawal [b]

[a] Department of Chemistry, Zakir Husain Delhi College (University of Delhi), JLN-Marg, New Delhi 110 002, India
[b] Department of Chemistry, Motilal Nehru College (University of Delhi), Benito Juarez Road, New Delhi 110 021, India

HIGHLIGHTS

- A hexadentate macrocyclic ligand i.e. 3,5,13,15,21,22-hexaaza-2,6,12,16-tetramethyl-4,14-dithia-tricyclo[15.3.1.1(7-11)]docosane-1(21),2,5,7,9,11(22),12,15,17,19-decaene was synthesized and characterized.
- Lanthanoid complexes were synthesized and characterized using various spectral techniques.
- Spectral parameters suggested formation of metal ligand covalent bonding.
- The complexes were found to have coordination number nine.
- *In vitro* antifungal capacity was determined of the synthesized compounds.

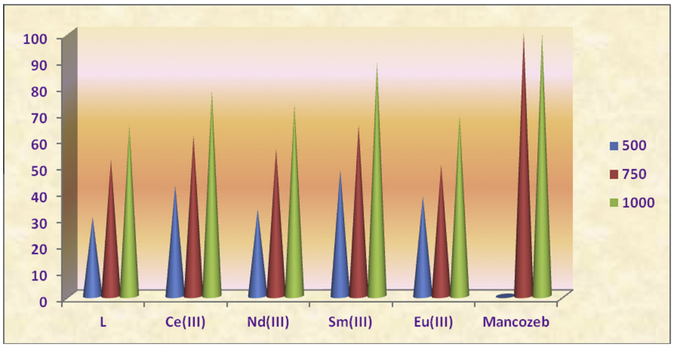
ARTICLE INFO

Article history:
Received 19 September 2013
Received in revised form 21 December 2013
Accepted 8 January 2014
Available online 21 January 2014

Keywords:
Hexadentate ligand
Lanthanoid
Spectroscopic characterization
Antifungal capacity

GRAPHICAL ABSTRACT

Growth inhibition of synthesized compounds against *Fusarium oxysporum*.



ABSTRACT

Complexes of Ce(III), Nd(III), Sm(III) and Eu(III) were synthesized with NO-donor macrocyclic ligand, i.e. 3,5,13,15,21,22-hexaaza-2,6,12,16-tetramethyl-4,14-dithia-tricyclo[15.3.1.1(7-11)]docosane-1(21),2,5,-7,9,11(22),12,15,17,19-decaene. The ligand was obtained by the condensation of 2,6-diacetylpyridine with thiourea and characterized by elemental analysis, mass, IR and ^{1}H NMR 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 coordinated through four nitrogen atoms of azomethine groups and two nitrogen atoms of pyridine ring. The value of spectral parameters i.e. nephelauxetic effect (b), covalency factor ($b^{1/2}$), Sinha parameter (δ%) and covalency angular overlap parameter (η) account for the covalent nature of the complexes. The macrocyclic ligand and its Lanthanoid were tested *in vitro* against two plant pathogenic fungi in order to assess their antifungal capacity.

Introduction

The design and synthesis of complexes of lanthanide metal ions with macrocyclic ligands constitute a fascinating area of research because of their importance in basic and applied chemistry [1–3]. They are also useful in industrial and synthetic processes such as catalysis, photochemistry and in biological systems [4]. Macrocyclic ligands are able to recognize the presence of lanthanide metal ions. Therefore they are widely used in the selective extraction of metals [5] and as NMR shift reagents [6]. Lanthanide complexes

---

* Corresponding author. Tel.: +91 1122911267; fax: +91 1123215906.
E-mail address: schandra_00@yahoo.com (S. Chandra).

1386-1425/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2014.01.042

have an increasingly important role in medicine, where they are employed as diagnostic as well as therapeutic agents [7]. A larger number of Lanthanoid complexes with Schiff-base macrocyclic ligands derived from 2,6 diacetylpyridine have already been published [8–11]. The stability of macrocyclic complexes depends upon a number of factors, including the number and types of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate ring formed on complexation [12]. Schiff bases also play an important role in the development of coordination chemistry related to catalysis, enzymatic reactions, magnetism, and molecular architectures [13]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [14–16].

In view of these facts, reaction of the Lanthanoid metal ion and macrocyclic ligand has been carried out and structure of the resulting complexes were investigated using spectroscopic techniques. All the synthesized compounds were evaluated against plant pathogenic fungi in order to assess their antimicrobial properties.

Experimental

Materials and methods

All the chemicals used were of Anala R grade and received from Sigma–Aldrich and Fluka. Lanthanoide salts were purchased from E. Merck and were used as received.

Synthesis of ligand

A hot ethanolic solution (20 mL) of 2,6-diacetylpyridine (3.26 g, 0.02 mol) was added to an ethanolic (20 mL) solution of thiourea (1.52 g, 0.02 mol). This mixture was refluxed at 80 °C for 8 h in the presence of few drops of concentrated HCl (pH$\sim$4) over a water condenser. On cooling the reaction mixture, a solid white product was precipitated out. It was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10}. Yield 75%, mp 250 °C. Elemental analyses found (Calcd.) for $C_{20}H_{18}$ N_6S_2: C, 59.0 (59.11); H, 4.47 (4.43); N, 20.50 (20.68)%. Scheme of synthesis of ligand is given in Fig. 1. ^{1}H NMR spectrum of ligand (*L*) was recorded in dueterated acetonitrile (CD_3CN) and is depicted in Fig. 2. The spectrum exhibits a singlet at ca. δ 2.0 ppm (s, 12H, $4CH_3^a$) due to four methyl groups. The spectrum exhibits another multiplet in the range ca. δ 7.16–7.35 ppm which may be due to the protons of aromatic rings [17]. The mass spectrum of the ligand (Fig. 3) shows the peaks at $m/z = 406$ and 407. These peaks correspond to the M^+ (parental ion) and $M^+ + 1$, ^{13}C isotope. The peak at $m/z = 391$, 376, 361 and 346 are due to the stepwise removal of the four methyl groups from the macrocyclic ligand. The intensity of the peak at 346 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 330, 276, 203, 180, 126, 44, 27 and 15 due to the other fragmented ions [18]. The peaks area provides an idea of abundance of these ions. The fragmentation path of the ligand is given in Fig. 4.

Synthesis of complexes

The Lanthanoid of ligand (*L*) were prepared by the mixing of hot ethanolic solution (20 mL) of the 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 24 h, complex was precipitated out, washed with cold EtOH and dried under vacuum over silica gel.

Physical measurements

Carbon, hydrogen and nitrogen were carried out on a Carbo-Erba EA 1106 analyzer. Metal ion in the complexes were determined by volumetric method using EDTA solution. Molar conductivity was measured on an ELICO (CM 82T) conductivity bridge with a cell having a cell constant of 0.51 cm^{-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 200–4000 cm^{-1}. The ^{1}H NMR spectrum of macrocyclic ligand was recorded at room temperature on a model Bruker Advance DPX-300 spectrometer operating at 300 MHz using $CDCl_3$ as solvent and tetramethyl silane as the internal standard. Electron impact mass spectrum was recorded on JEOL. JMS, DX-303 mass spectrometer. Thermogravimetric analysis (TGA) was carried out in dynamic nitrogen atmosphere (30 ml/min) with a heating rate of 10 C/min using a Schimadzu TGA-50H thermal analyzer.

Antifungal screening

The synthesized compounds were assayed against the fungi, i.e. *Aspergillus niger* and *Fusarium oxysporum* for their fungicidal behavior by employing Poison Food Technique [19,20]. The stock solutions of the compounds were prepared in DMSO solvent. The diluted solution was directly added to the PDA (Potato Dextrose Agar) medium and the mixture was poured into the petri plate. The petri plates were kept for a day to check the sterility. A disk

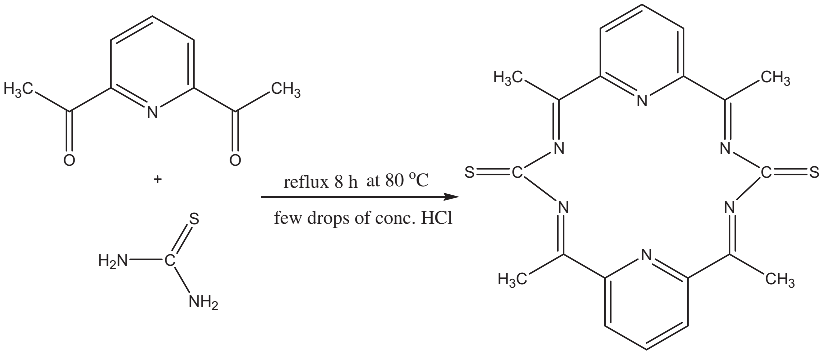


Fig. 1. Synthesis and structure of the ligand.