



Microwave assisted synthesis, spectroscopic, electrochemical and DNA cleavage studies of lanthanide(III) complexes with coumarin based imines

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ARTICLE INFO

Article history:

Received 25 January 2011

Received in revised form 13 July 2011

Accepted 15 July 2011

Keywords:

3-Acetylcoumarin thiosemicarbazone

3-Acetylcoumarin semicarbazone

Cyclic voltammetry

Antimicrobial activity

DNA cleavage activity

ABSTRACT

The present work stems from our interest in the synthesis, characterization and biological evaluation of lanthanide(III) complexes of a class of coumarin based imines which have been prepared by the interaction of hydrated lanthanide(III) chloride with the sodium salts of 3-acetylcoumarin thiosemicarbazone (ACTSZH) and 3-acetylcoumarin semicarbazone (ACSHZ) in 1:3 molar ratio using thermal as well as microwave method. Characterization of the ligands as well as the metal complexes have been carried out by elemental analysis, melting point determinations, molecular weight determinations, magnetic moment, molar conductance, IR, ^1H NMR, ^{13}C NMR, electronic, EPR, X-ray powder diffraction and mass spectral studies. Spectral studies confirm ligands to be monofunctional bidentate and octahedral environment around metal ions. The redox behavior of one of the synthesized metal complex was investigated by cyclic voltammetry. Further, free ligands and their metal complexes have been screened for their antimicrobial as well as DNA cleavage activity. The results of these findings have been presented and discussed.

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1. Introduction

Increased environmental deterioration has put a pressing need to develop an alternate synthetic approach for biologically and synthetically important compounds. Microwave irradiation nowadays is an accepted tool for accelerating the organic and inorganic reactions. Chemical reactions brought about by microwave irradiation have gathered momentum in recent years because of their elegance, high yield, and short time span and ecofriendly conditions [1,2]. In addition to providing an ecofriendly “green chemistry” approach to the reaction, it is also free of environmental impacts [3–5]. Coumarin chemistry has become important over the years, which is documented by thousands of papers and patents of coumarin. Coumarin (1,2-benzopyrone) compounds are of a large family of organic compounds having a lactone structure and extensively used in many fields. The biological activities of coumarin and related compounds are multiple and include antimicrobial [6], antioxidant, anti-inflammatory [7], antituberculosis [8], antitumour and antiHIV [9] activities. In particular, coumarin based imines having substituent at position 3 have been reported to have a variety of biological properties viz. antimicrobial

[10] and antitumour [11] activities. Chemistry of lanthanides is a promising research area motivated by the wide range of applications. Coordination chemistry of lanthanides in biological system [12–14] and the development of lanthanide shift reagents have aroused much interest. Our interest in the chemistry of lanthanide complexes with N, O/S donor ligands comes from their structural importance as well as their interesting biological activity. In view of the rapid development and also challenging demands, it has become necessary to synthesize and screen compounds for biological evaluation. Among the different therapeutic strategies to eradicate cancer cells through DNA cleavage, the view of using metal complexes capable of oxidative or hydrolytic DNA cleavage as anticancer drugs is a challenging issue in bioinorganic chemistry. During literature survey, it was revealed that earlier some lanthanide [15,16] complexes have been reported as efficient DNA cleavage agents with or without sequence specificity, moreover the ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate the individual application [17]. An interesting coordination chemistry of lanthanide elements and the important role of their complexes in chemical [18,19], medical [20] and industrial processes are enough to recognize them as worthwhile for the synthesis of complexes. Therefore, an attempt has been made to describe synthesis, characterization and biological evaluation of some lanthanide(III) complexes with the coumarin based imines having substituent at position-3.

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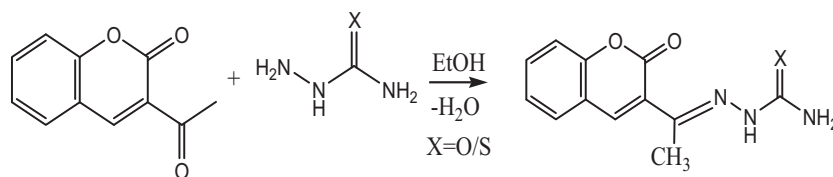


Fig. 1. Synthetic scheme of the ligands.

2. Experimental

2.1. Materials and methods

All the chemicals were of reagent grade and solvents of analytical grade were distilled from appropriate drying agents immediately prior to use. 3-Acetylcoumarin, Samarium(III) and Neodymium(III) salts were purchased from Alfa Aesar, Gadolinium(III) salt was procured from Sigma–Aldrich. The metal chlorides used were in hydrated form. Molecular weight determinations were carried out by the Rast Camphor Method [21]. Sulfur and nitrogen were estimated by the Messenger's [22] and Kjeldahl's [23] method, respectively. The metal contents were estimated complexometrically with EDTA using Erichrome Black T as an indicator. Melting point was determined by using capillaries in electrical melting point apparatus. Magnetic moment measurements were recorded at room temperature with the Faraday balance using Hg [Co(NCS)₄] as calibrant. Conductivity measurements were made on century digital conductivity meter model CC 601. Carbon and hydrogen analyses were performed at the Central Drug Research Institute (CDRI), Lucknow. Infrared spectra of the ligands and their complexes were recorded with the help of Nicolet Magna FTIR-550 spectrophotometer on KBr pellets. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL-AL-300 FT NMR spectrometer in DMSO-d₆ using TMS as the internal standard. EPR spectra of the complexes were monitored on Varian make E line century X-band EPR spectrometer (Model E-112). The electronic spectra were recorded on a Varian–Cary/5E spectrophotometer. XRD were measured on Panalytical make Xpert Pro 3040 and mass spectra were recorded on JEOL GCmate spectrometer at SAIF, IIT Madras, Chennai.

2.2. Preparation of the ligands

For comparison purpose, the ligands were prepared by employing following two different routes. The synthetic scheme of both the ligands has been shown in Fig. 1.

2.2.1. Microwave method

In microwave assisted synthesis of the ligands, thiosemicarbazone and semicarbazone of 3-acetylcoumarin were prepared by the condensation of 3-acetylcoumarin (2.520 g, 0.01 mol) with thiosemicarbazide (1.220 g, 0.01 mol) and semicarbazide hydrochloride (1.493 g, 0.01 mol) (in presence of sodium acetate

(1.098 g) in 1:1 molar ratio using a 50 mL beaker through a conventional microwave oven by taking 2–3 mL solvent. The reactions were completed in a short period of 4–7 min.

2.2.2. Thermal method

In this method, conventional heating technique was used. In this method, weighed amount of starting materials for the ligands were dissolved in ~100 mL of ethanol and were refluxed for 3–4 h. The residue formed was separated out, filtered off, recrystallized from the same solvent and finally dried. A comparison between thermal method and microwave method is given in Table 1.

2.3. Synthesis of the sodium salt of the ligands

Sodium metal was taken corresponding to the ligand. Now both the sodium metal and ligand were dissolved in minimum amount of methanol separately. Ultimately these two solutions had been dissolved to prepare sodium salt of the ligand. In this process the sodium metal first reacts with methanol and forms sodium methoxide. This sodium methoxide in the next step reacts with the ligand and replaces acidic proton from the enolic form of the ligand with the sodium metal and forms sodium salt of the particular ligand. We can use the ligand as such but the rate of reaction will be slow as compared to the sodium salt.

2.4. Synthesis of the lanthanide(III) complexes

2.4.1. Microwave method

In microwave assisted synthesis, first the methanolic solution of the hydrated lanthanide(III) chloride (LnCl₃·6H₂O) was mixed with methanolic solution of the sodium salt of the ligand in 1:3 molar ratios and then was irradiated in conventional microwave oven for 5–6 min. The products were recovered from the microwave oven and dissolved in a 4–5 mL of dry methanol, where the precipitate of sodium chloride formed during the course of the reaction was removed by filtration and the filtrate was dried under reduced pressure. The resulting compounds were washed and recrystallized.

2.4.2. Thermal method

In this method, the mixture was heated under reflux for about 13–16 h. On cooling, the sodium chloride which formed in this reaction was separated out by the separating funnel and then filtrate

Table 1

Comparison between conventional and microwave methods.

| Compound | Yield (%) | | Solvent (mL) | | Time | |
|---|-----------|-----------|--------------|-----------|-------------|-----------------|
| | Thermal | Microwave | Thermal | Microwave | Thermal (h) | Microwave (min) |
| ACTSZH | 85 | 92 | 100 | 3 | 3.5 | 5 |
| ACSZH | 84 | 90 | 100 | 2 | 4 | 6 |
| Nd(ACTSZ) ₃ ·3H ₂ O | 70 | 82 | 35 | 3 | 13 | 8 |
| Sm(ACTSZ) ₃ ·3H ₂ O | 72 | 86 | 40 | 4 | 14 | 5 |
| Gd(ACTSZ) ₃ ·3H ₂ O | 74 | 82 | 45 | 2 | 13 | 5 |
| Nd(ACSZ) ₃ ·3H ₂ O | 65 | 80 | 50 | 3 | 15 | 7 |
| Sm(ACSZ) ₃ ·3H ₂ O | 75 | 79 | 45 | 2 | 14 | 6 |
| Gd(ACSZ) ₃ ·3H ₂ O | 72 | 81 | 50 | 4 | 16 | 5 |

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