

Synthesis and characterization of lanthanide complexes of N₆ – macrocyclic Schiff base

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Abstract: A new macrocyclic Schiff base complexes were prepared in the presence of lanthanide metal ion [La(III), Ce(III) and Gd(III)] by the reaction of 2,6 – diamino pyridine, benzoyl aceton and metal ion as template effect in the molar ratio of 2: 2: 1 respectively. The lanthanide metal complexes were characterized and investigated by using; ¹HNMR, FTIR, UV/Visible spectroscopy, Elemental analysis (C.H.N.), Magnetic susceptibility and Molar conductivity measurements. The lanthanide metal ions coordinated to six nitrogen atoms of the ligand and three chloride ions to complete geometry of nine coordination complexes.

Keyword: Macrocyclic, Schiff Bases, Lanthanide Complexes, Template Synthesis

1. Introduction

The synthesis of macrocyclic ligands involve several synthetic steps and, sometimes, high dilution techniques to avoid unwanted polymerization, which considerably adds to the cost of the synthesis. In some instances, it is possible to simplify the synthetic procedure by using a templating agent, that is, a metal ion which pre-organizes the reactants in such a way that they do not polymerize and have the right orientation to yield the desired compound.

Macrocyclic complexes of lanthanide ions represent a fairly new field of investigation, since it really started in the mid 1970's, which has sustained considerable development during the last three decades. The receptors synthesized so far have added a new dimension to the coordination chemistry of these ions with potential applications. The complexes of the obtained macrocyclic Schiff bases are studied as magnetic materials, catalysts and models for metalloenzymes [1 – 3]. There are many applications of lanthanide (III) macrocyclic complexes in medicine and biology including their use as fluorescent probes [4, 5] in biological systems, as magnetic resonance imaging (MRI) agents [6 – 8] and as artificial nucleases for the catalytic cleavage of RNA [9 – 14]. All of these applications require that the Ln(III) complexes be resistant to lanthanide ion release under physiological conditions. In aqueous solution, these complexes decompose by hydrolysis of the imine bonds with release of the lanthanide ion. The rate of

decomposition of hexaaza Schiff-base macrocyclic complexes varied for different lanthanide ions and also was dependent on the presence of a competing ligand such as ethylenediamine tetraacetic acid (EDTA) or diethylenetriamine pentaacetic acid (DTPA) [15].

The 2 + 2 condensation of 2,6-diformylphenols with diamines in the presence of metal ions forms a robust and versatile platform for coordination of metal ions. A variety of complex types can be obtained in this procedure, depending on the choice of lateral diamine fragments and metal ions. The mononuclear La(III), Ce(III) and Eu(III) complexes with chloride counter anions [16] as well as La(III), Sm(III) and Gd(III) complexes with nitrate counter anions [17] have been previously reported. In this paper the synthesis of new macrocyclic Schiff base ligand having N₆ donor atoms coordinated to lanthanide metal ion were reported and investigated.

2. Experimental

2.1. Physical Measurements

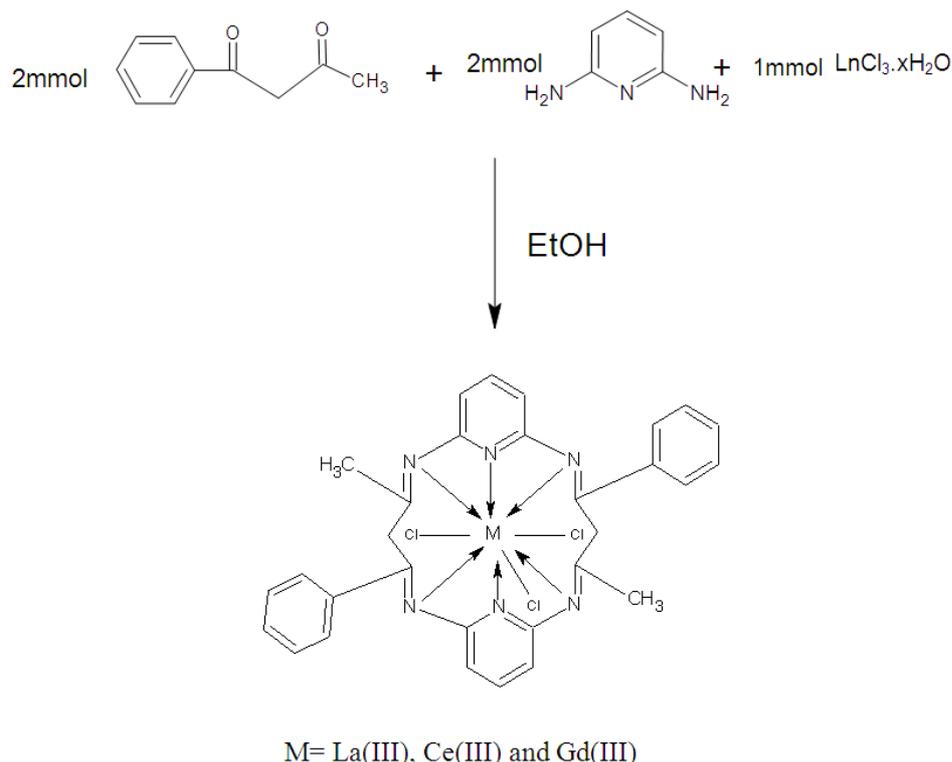
All chemicals were supplied from BDH and Fluka and used without any modification. ¹HNMR spectra were recorded using Bruker 500MHz and d₆ – DMSO as a solvent at Jordanian University. Elemental analysis carried out using CHNS – elemental analyser at University of Al Albait, Jordan. Electronic spectra using Varian UV– visible spectrophotometer, molar conductivity measurements using

WTWF56 and DMSO as a solvent at College of Science, Mustanseriyah University. Magnetic susceptibility measurements were carried out using Faraday method with balance magnetic susceptibility model MSB – MKI in College of Science, Al – Nahrain University. FTIR using Shimadzu spectrophotometer and IR uses Pye – Unicam with CsI disc in Ibn – Sina Company, Baghdad, Iraq

2.2. Synthesis of Complexes

The complexes were prepared according to the following procedure: (0.684g, 0.002 mole) of benzoyl acetone and 1

mmole of $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Ce}$ and Gd) were mixed together in EtOH (20 ml), stirring with heating for 1h then (0.436g, 0.002 mmole) of 2,6 – diamino pyridine dissolved in EtOH (10ml) was slowly added with continuous stirring. Reflux the mixture for 6h, then filtered while it is hot and let the filtrate aside for 24h. The resulting precipitate was filtered and recrystallized from hot EtOH, washed with cold water and cold EtOH then dried under vacuum. The CHN analysis results (see Table 1) were consistent with a stoichiometry with the empirical formula $[\text{LnLCl}_3]$ (Scheme 1).



Scheme 1. Synthesis of lanthanide macrocyclic complexes

Table 1. Some physical properties of lanthanide complexes

Molecular formula	Colour	M.p. °C	Yield %	C	(Found)Calcd. % H	N
[La(C ₃₀ H ₂₆ N ₆)Cl ₃]	Off white	>300	60	(50.34)51.18	(3.63) 3.87	(11.75) 12.10
[Ce(C ₃₀ H ₂₆ N ₆)Cl ₃]	Pale yellow	>300	70	(50.27) 51.43	(3.63) 3.56	(11.73) 11.89
[Gd(C ₃₀ H ₂₆ N ₆)Cl ₃]	White	>300	55	(49.11) 50.98	(3.54) 3.79	(11.46) 11.67

3. Results and Discussion

3.1. ¹H NMR Spectra

Due to the paramagnetic properties of Ce(III) and Gd(III), only ¹H NMR spectra for La(III) complex was recorded using d₆ – DMSO as a solvent. The spectrum gave no signal corresponding to primary amine protons. This suggests the derivatization of carbonyl groups. A multiplet in the range 2.20–2.64 δppm attributed to the imine methyl and methylene protons of benzoyl acetone (6H, CH₃–C=N and 4H, N=C–CH₂–C=N, respectively) [18]. One doublet

and one triplet signals for pyridine ring observed at 8.75 and 8.97δppm. Multiple signals attributed to two aromatic ring protons were recorded at 7.13 – 7.45 δppm.

3.2. Infra – Red Spectra

We were not be able to record the infra – red spectra of the macrocyclic ligand because it is not possible to synthesize it unless in the existence of the metal ions. The infra – red spectra of the complexes show very similar spectra to one another. These spectra indicates the replacement of $\nu(\text{NH}_2)$ and $\nu(\text{C}=\text{O})$ of the starting

materials with $\nu(\text{C}=\text{N})$ which suggest the occurs of the condensation reaction between amine and carbonyl groups[19]. The positions of the $\nu(\text{C}=\text{N})$ was shifted to higher frequency ($1594\text{-}1558\text{cm}^{-1}$) indicate the presence of a coordination bonds with metal ions (Table 2). The presence of an extra donor group (the pyridine nitrogen located between two amine groups, may account for the particular success in obtaining macrocyclic complexes and a reasonable change in the vibration of N – pyridine indicate coordination bonds formed with lanthanide metal ions [20, 21]. New bands recorded at range $556 - 477$ and $394 - 368\text{cm}^{-1}$ attributed for Ln – N and Ln – Cl respectively [22, 23] (see figure 1).

3.3. Electronic Spectra

The electronic spectra of lanthanide complexes were carried out using DMSO as a solvent and concentration of 10^{-3}M . Two intensive absorption bands recorded at 260 and 275nm attributed to $\pi \rightarrow \pi^*$ transition C= C and C= N. Very intensive absorption band was recorded at 360nm with the value of $\epsilon_{\text{max}}=31000\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ attributed to charge transfer transition. Ce(III) compounds are colorless, since the metal-centered f – d transition gives rise to an absorption in the near UV region [24]. Gd(III) ion had half filled (f^7) so absorptions are not observed since they are apparently too weak and no bands found in the visible region.

Table 2. major infra – red bands of lanthanide complexes (cm^{-1})

Complexes	$\nu(\text{C}=\text{N})_{\text{lib}}$, $\nu(\text{C}=\text{N})$	C-H ν	$\nu\text{M-N}$	$\nu\text{M-Cl}$
[La(C ₃₀ H ₂₆ N ₆)]Cl ₃	1591, 1562	3107, 3058	556, 494	394
[Ce(C ₃₀ H ₂₆ N ₆)]Cl ₃	1588, 1567	3098, 3049	550, 477	371
[Gd(C ₃₀ H ₂₆ N ₆)]Cl ₃	1594, 1558	3095, 3045	544, 484	368

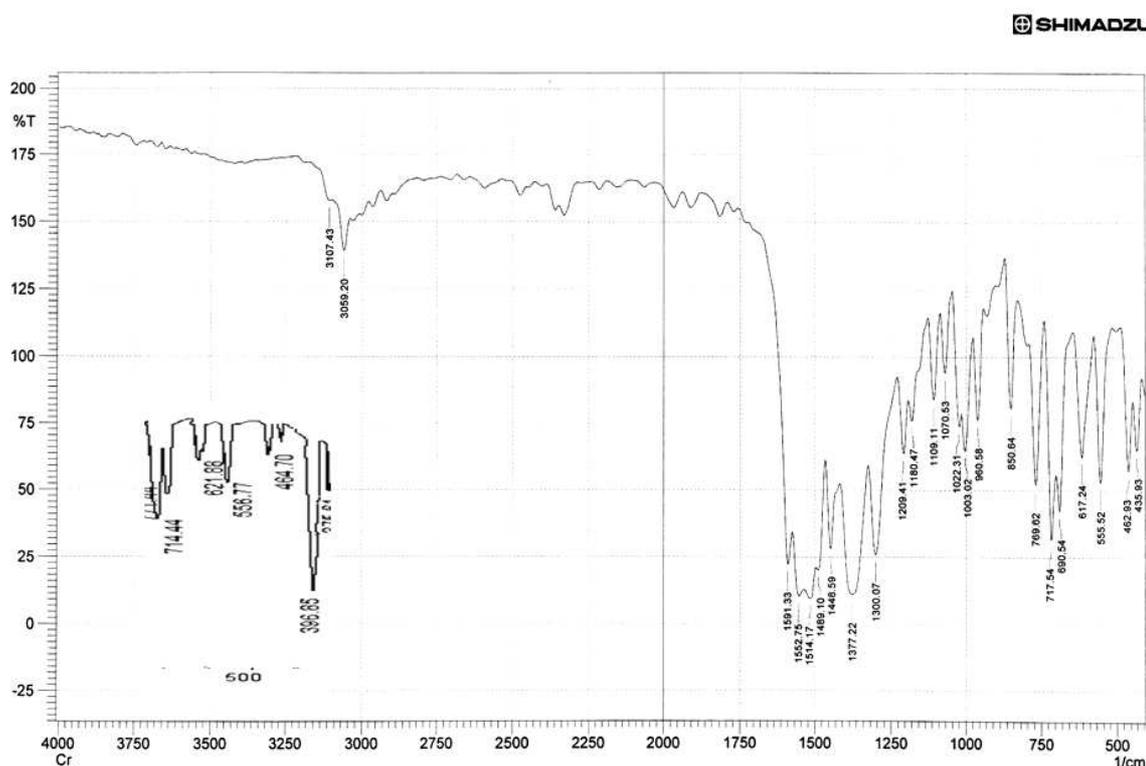


Figure 1. Infra – red spectrum of LnIII complex

3.4. Mass Spectra

It was not possible to get mass spectral data for all the complexes because they were involatile even at high temperatures.

3.5. Magnetic Measurements

Magnetic susceptibility for the complexes was recorded in the solid state at 298 K using Gooney method in

emu/mole units. All the trivalent lanthanide ions, except lutetium, have unpaired f electrons. However the magnetic moments deviate considerably from the spin-only values because of strong spin-orbit coupling. A magnetic moment of 1.92 B.M. was recorded for Ce(III) complex due to the presence of one electron. In Gd(III) complex a magnetic moment of 8.04 B.M was recorded which suggest a maximum number of unpaired electrons is 7, with all the electrons have parallel spin. This property is important for

the use of gadolinium complexes as contrast reagent in MRI scans [25, 26].

3.6. Molar Conductivity Measurements

All the measurements for the complexes were carried out using a concentration of 10⁻³M and DMSO as a solvent. All complexes were non-electrolytes with conductance values of 8–12 S cm² mol⁻¹ indicating the presence of three chloride ions inside the coordination sphere. Thus, these complexes may be formulated as [Ln L Cl₃] and these results agree with the suggested configurations of the lanthanide complexes.

4. Conclusion

New Schiff base macrocyclic complexes were prepared using template effects of some lanthanide metal ions. Physical measurements for metal complexes suggest nine coordination geometry through N₆- macrocyclic ligand and three chloride ions.

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