

Pentadentate N_2O_3 Schiff base complexes of rare earth metals

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Abstract: Acyclic Schiff base ligand containing N_2O_3 donor atoms was synthesized by the reaction of 2,6 – diformyl – 4 – ter-butylphenol and 4 – aminoantipyrine in 1:2 molar ratio. The synthesized ligand (H_1L) and $Ln(III)$ complexes [$Ln = La(III), Ce(III)$ and $Gd(III)$] were characterized by 1H N.M.R., ^{13}C N.M.R., mass spectrometry, UV /Visible, FTIR, Elemental analysis (C.H.N.), Magnetic susceptibility and Molar conductivity measurements. A seven coordinated complex obtained through N_2O_3 and two chloride atoms coordinated to metal ions.

Keyword: Lanthanides, Schiff Bases, 2, 6-Diformyl Phenol, Pentadentate Acyclic Ligand

1. Introduction

Schiff bases can be considered as a very important class of organic compounds due to their ability to form stable complexes with wide range of transition and rare-earth metal ions in different oxidation states via N and O atoms. They have the potential to be used in many areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes, and environmental chemistry. They are becoming important materials in the pharmacological, dye, plastic industries as well as in the field of liquid crystal technology¹⁻⁵.

Transition and lanthanide metal complexes derived from Schiff-base ligands play a major role in the development of modern coordination chemistry providing examples of acyclic and macrocyclic ligand systems and the effects of steric interactions on coordination geometries. The chemistry of metal complexes with heterocyclic compounds containing nitrogen, sulfur, and/or oxygen as ligand atoms has attracted increasing attention. Compounds showing photoactivated cytotoxicity are of considerable importance for their selectivity in killing cancerous cells over the normal cells. When compared to the 3d–5d metal complexes, there are only few reports on the lanthanide complexes showing photoinduced biological activity and there is considerable scope to expand the chemistry of photocytotoxic lanthanide complexes⁶.

It is well known that the heterocyclic compounds exhibit bactericidal, fungicidal, herbicidal, and insecticidal

activities in addition to their application as potential drugs. Such heterocyclic ligands, when complexes with metal ions, exhibit enhanced microbiological activities. As an example, the activity of nickel is known because it is a component of a hydrolase (urease) and activates the genes of hydrogenases. Cerium is industrially important, used in nuclear reactors and in alloys with nickel and chromium in microwave devices. Cerium is also used in agriculture, forestry, and animal husbandry^{7,8}.

The chemistry of lanthanide complexes with Schiff bases has received little attention compared with the d block metal complexes. Recently, there has been a growing interest in the lanthanide–Schiff base complexes owing to the important applications of both metals and ligands. It can be used for the determination of some trace metals by liquid chromatography⁹.

The ability of the lanthanide cations to promote Schiff base condensation of the appropriate diamine and dicarbonyl precursors, giving access to acyclic and macrocyclic complexes of otherwise inaccessible ligands in combination with the applications of lanthanide complexes emerging from biology and medicine have boosted research on these areas^{10, 11}. In this regard Schiff base metal complexes have played a key role to the gradual development of the $Ln(III)$ coordination chemistry, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes^{12, 13}.

Schiff-base ligands with N, O donor sets have often been used since the Schiff-base ligands may assemble coordination architectures directed by the lanthanide (III) ions^{14, 15}.

Since we had found that transition metal complexes with the ligands derived from 2,6 – diformyl-4-substituted phenols were dinuclear, as the ligand has five potential donor atoms (two carbonyl oxygens, two azomethine nitrogens and one phenolic oxygen)¹⁶. Binuclear complex obtained through phenolic oxygen acting as a bridge between two metal ions, as the ligand behaves as hexadentate type.

This study deals with synthesis and characterization, of lanthanide (III) complexes of this ligand. In this study a mono nuclear lanthanide complexes with seven coordination number as the ligand behaves as pentadentate donor atom (N₂O₃) with two chloride ion coordinated to lanthanide ion.

2. Materials and Methods

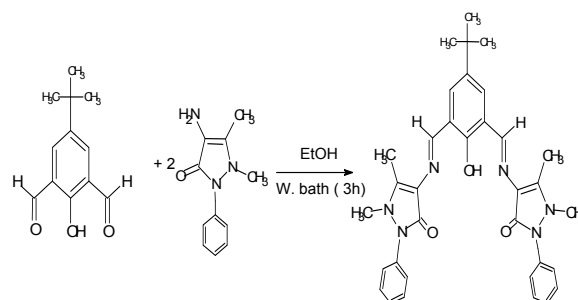
All chemicals were analytical grade supplied from BDH and Fluka and used without any modification. Elemental analysis for the ligand and metal complexes were carried out using CHNS – elemental analyser at University of Al Albait, Amman, Jordan. ¹H and ¹³CNMR spectra using Bruker 500MHz and DMSO as a solvent. Mass spectra using Electro Spray Ionization Mass Spectrometry at Jordanian University. Electronic spectra using Varian UV–visible spectrophotometer, Molar conductivity measurements using WTW56 apparatus and DMSO as a solvent at Mustanseriyah University, Magnetic susceptibility measurements were carried out using Faraday method with balance magnetic susceptibility model MSB – MKI at Al – Nahrain University and FTIR using Shimadzu spectrophotometer and IR uses Pye – Unicam with CsI disc in Ibn – Sina Company, Baghdad, Iraq.

3. Experimental

3 – 1 Preparation of ligand: 4 – tert-But-2,6-diformylphenolbis(4-aminoantipyrine)(H₁L): The ligand was prepared according to our previous paper¹⁷; (0.4g, 2 mmol) of 2,6 – diformyl – 4 – ter-butylphenol dissolved in ethanol (10 ml) was added slowly with stirring to (0.80g, 4 mmol) of 4 – amino antipyrine dissolved in ethanol (20 ml). The resulting mixture was stirred under reflux on water bath for 3 hrs and the yellow precipitate was filtered, dried and then recrystallized from ethanol to afford bright yellow crystals with 90% yield (scheme 1). Elemental analysis data; Found (calculated); %C, 70.73 (70.51); %H, 6.25 (6.16) %N 14.56 (14.39).

3 – 2 Preparation of complexes: The metal complexes of [LaIII, CeIII and GdIII] were prepared by reaction of metal chloride dissolved in ethanol (20 ml) and H₁L dissolved in ethanol (20 ml) with 1:1 molar ratio, by stirring under reflux for 7 hrs then reduced the volume by evaporation,

cooled and left aside for overnight. Fine powder obtained, filtered and recrystallized from ethanol to afford the appropriate precipitate (table 1).



Scheme 1. synthesis of the ligand L¹H

Table 1. some physical properties of ligand(L₁H) and lanthanide complexes

Chemical formula	Color	m.p.(°C)	Yield%
C ₃₄ H ₃₆ N ₆ O ₃	Light orange	265-263	90
[LaL ¹ Cl ₂]	Off white	>300	60
[CeL ¹ Cl ₂]	Pale yellow	>300	53
[GdL ¹ Cl ₂]	Orange	>300	45

4. Results and Discussion

4 – 1 ¹HN.M.R. and ¹³CN.M.R. spectroscopy: Using d₆ – DMSO, only one compound recorded in ¹HNMR spectroscopy belonging to the ligand, ¹³CN.M.R. spectroscopy showed the exact numbers and locations of the carbon atoms. The locations and assignment of each peak as follows (values in δppm): for ¹HN.M.R.; 1.328 (–CH₃)₃, 2.453 [2(CH₃–C)], 3.205 [2(CH₃–N)], 7.382–7.835(Ar–H), 9.866[2(H–C=N)], 13.866 OH; for ¹³CN.M.R.; 10.34 C (5,5'), 31.63 C (1,2,3), 34.82 C (4), 35.74 C (6,6'), 115.79–134.62 C (Ar), 141.62 C (7,7'), 151.56 C (8,8'), 154.48 C (9), 157.82 C (10,10'), 159.80 C (11,11'). Due to the paramagnetic properties of CeIII and GdIII, only ¹HN.M.R. spectra for LaIII complex was recorded using d₆ – dmso as a solvent, which recorded the disappearance of phenolic peak, while the other signals of the ligand were slightly shifted towards low field when compared to those of the free ion ligand, probably due to coordination effects of the metal ion (see figure 1).

4 – 2 *Infra – red spectra*: For the prepared ligand (H₁L) a new band for C=N with the disappearance of two band for NH₂ of the 4 – aminoantipyrine were recorded due to the condensation reaction between 2,6 – diformylphenol and 4 – aminoantipyrine in 1 : 2 molar ratio. A slightly broad band for phenolic OH at 3431 cm⁻¹ indicates forming of hydrogen bonding¹⁸. In metal complexes, the locations of C=N and C=O bands were slightly shifted downwards (5 – 10 cm⁻¹) attributed to the coordination bonds formed between lanthanide ion and N, O atoms. New bands were obtained in the region 600 – 200cm⁻¹ for Ln – N, Ln – O and Ln – Cl (see table 2). The location of phenoxide C – O

suffered a great downfield shift (20 – 25 cm⁻¹) suggest the coordination of phenolic oxygen with metal ions^{19–21}.

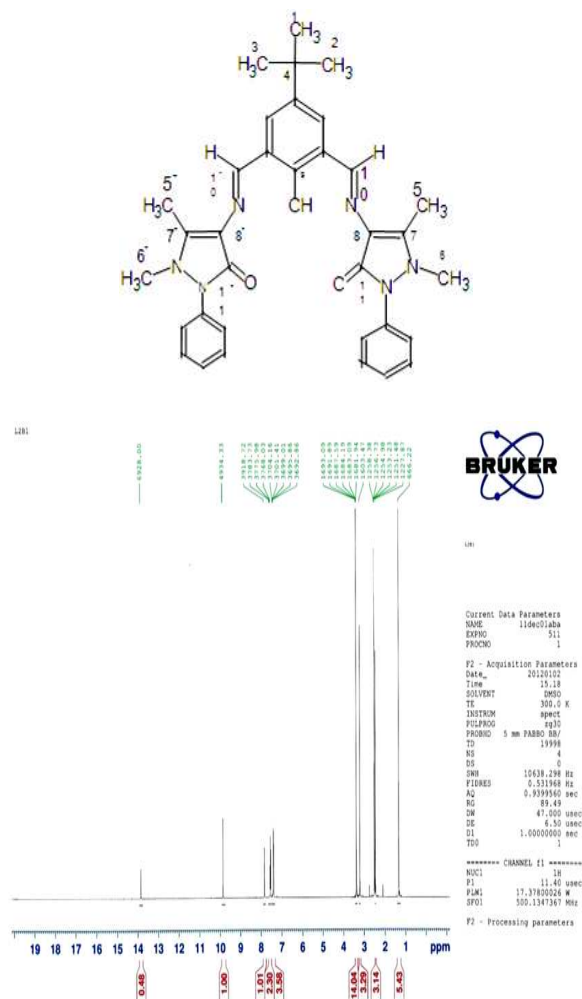


Figure 1. ¹H NMR spectrum of H₁L

Table 2. Major Infra – red spectra of ligand (L¹H) and complexes (cm⁻¹)

Compound	ν(C=O)	ν(C=N)	ν(C-O)	ν(M-N)	ν(M-O)	ν(M-Cl)
C ₃₄ H ₃₆ N ₆ O ₃ (L ¹ H)	1658	1628	1296	-	-	-
[LaL ¹ Cl ₂]	1654	1617	1272	481	447	310
[CeL ¹ Cl ₂]	1649	1623	1276	473	424	328
[GdL ¹ Cl ₂]	1651	1621	1274	477	430	312

4 – 3 Electronic spectra: The electronic spectra of lanthanide complexes were carried out using DMSO as a solvent and concentration of 10⁻³M. The ligand showed two strong bands at 267 and 332nm attributed to π → π* transition of aromatic C = C and C = N, while the inter charge transfer band (INCT) of phenoxide group appeared at 388nm²². Ce(III) compounds are colorless, since the metal-centered f – d transition gives rise to an absorption in the near UV region and it combine with charge transfer band²³. Gd(III) ion had half filled (f⁷) so absorptions are not observed since they are apparently too weak and no bands found in the visible region.

4 – 4 Mass spectra: By using Electro Spray Ionization Mass Spectra (ESIMS) technique, the parent ion P⁺ (576.68) was recorded which agree with the suggested molecule formula (C₃₄H₃₆N₆O₃) ESIMS (+) m/z 615.7[M+K]⁺, 599.8[M+Na]⁺, 577.8 [M+H]⁺ (see figure 2). We were not able to get mass spectra for the lanthanide complexes possibly because they were not volatile even at high temperatures.

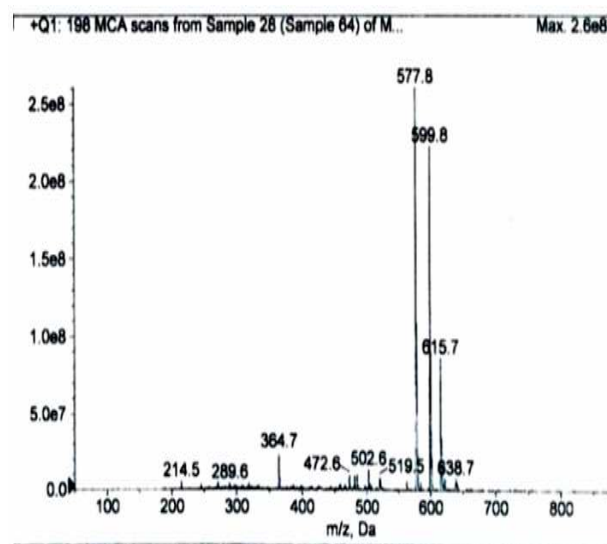


Figure 2. mass spectrum of H₁L

4 – 5 Magnetic measurements: Magnetic susceptibility for the complexes was recorded in the solid state at 298 K using Gouey method in emu/mole units. All the Ln(III) ions, except Lu, have unpaired f electrons .

Landè Calculation for Ln⁺³ ions:

$$1- \text{La}^{+3} = 4f^0, S_0, \mu_J=0 \text{ B.M.} \rightarrow {}^1S_0$$

$$2- \text{Ce}^{+3} = 4f^1, S=\frac{1}{2}, L=3, J=L-S = 3-\frac{1}{2}=\frac{5}{2} \rightarrow {}^2F_{5/2}$$

$$g_J = \frac{3}{2} + \frac{\frac{3}{2}-12}{2 \times 35/4} = 0.857$$

$$P_J = g_J \sqrt{J(J+1)} = 2.53 \text{ B.M.}$$

$$3- \text{Gd}^{+3} = 4f^7, S=\frac{7}{2}, L=0, J=L+S = 0+\frac{7}{2}=\frac{7}{2} \rightarrow {}^8S_{7/2}$$

$$g_J = \frac{3}{2} + \frac{\frac{63}{4}}{2 \times 36/4} = 2P_J = g_J \sqrt{J(J+1)} = 7.94 \text{ B.M.}$$

However the magnetic moments deviate considerably from the spin-only values because of strong spin-orbit coupling (Table 3). Magnetic moment of 2.17B.M. was recorded for Ce(III) complex due to the presence of one electron. In Gd(III) complex a magnetic moment of 8.11 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^{24, 25}.

4 – 6 Molar conductivity measurements: Using dmso as a

solvent and a concentration of 10⁻³M, all complexes showed a behavior of non electrolyte type indicating the presence of two chloride ions inside the coordination

sphere, and these results agree with the suggested configurations of the lanthanide complexes (Table 3).

Table 3. Molar conductivity and magnetic moment data of Ln(III) complexes.

Complexes	μ_{eff} B.M	μ_{eff} Van Vleck B.M.	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Geometry
[LaL ^I Cl ₂]	0.0	X=-0.15×10 ⁻⁶ cm g sec	11.91	Mcoh*. (C.N=7)
[CeL ^I Cl ₂]	2.17	2.54	12.50	Mcoh*. (C.N=7)
[GdL ^I Cl ₂]	8.11	7.94	10.3	Mcoh*. (C.N=7)

* Mcoh=Monocapped octahedron

5. Conclusion

An acyclic Schiff base ligand containing N₂O₃ donor atoms and its mono nuclear lanthanide complexes were prepared. The analytical data observed suggested complexes with seven coordination number as the ligand behaves as pentadentate donor atoms with two chloride ions coordinated to lanthanide ion (figure 3).

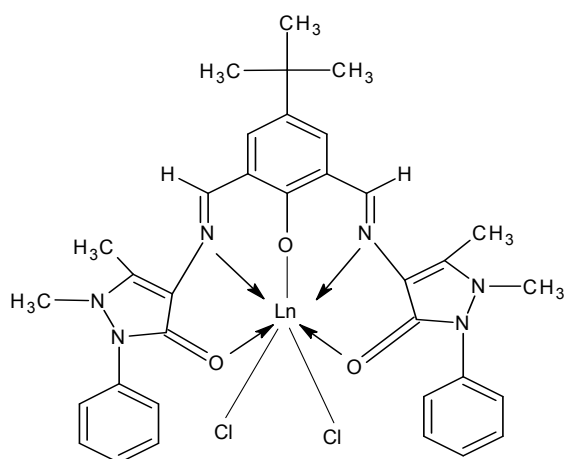


Figure 3. Ln: LaIII, CeIII, GdIII

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