



## Synthesis, spectral characterization, antimicrobial and cytotoxicity studies of some lanthanide(III) complexes of quinoline derivatives

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### ABSTRACT

The new lanthanide(III) complexes with quinoline derivative (MQAP) obtained by the reaction between 3-formyl-2-mercapto quinoline with 4-amino pyridine have been synthesized and characterized by elemental analysis, molar conductance, magnetic moment measurements, FT-IR, electronic spectra, <sup>1</sup>H-NMR spectra, FAB mass spectra, and thermal analysis studies. The molar conductance studies indicate non-electrolytic behavior of the complexes. The IR and <sup>1</sup>H-NMR studies indicate that MQAP acts as mono basic bidentate ligand of potential donor site of azo methine nitrogen and thiolate sulphur. TG and DTA studies of La(III) and Sm(III) complexes indicate the presence of two coordinated water molecules along with two nitrate and two MQAP moieties. Based on these studies the complexes have been formulated as [Ln(MQAP)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](where Ln = La, Pr, Nd, Sm, Eu, Gd, Yb) with coordination number 8. The cytotoxicity of the ligand and Ln(III) complexes have been screened against cancer cells line HeLa (Cervical cancer cells, Human), which reveals that Ln(III) complexes shows moderate cytotoxicity against tested cell lines.

**Key words:** Lanthanum(III), coordination, cytotoxicity .

### INTRODUCTION

Coordination chemistry of lanthanides is one of the active research fields in inorganic chemistry [1–7]. It seems from the published work that lanthanides are capable of forming stable complexes with quinoline and its derivatives. The work on quinoline Schiff's base complexes have been reported from our laboratory with transition elements [8–9]. As a part of a programme for the synthesis and characterization of solid complexes of lanthanides, presently, complexes of seven lanthanide(III) ions, viz. La(III), Pr(III), Nd(III), Pm(III), Sm(III), Eu(III), Gd(III) and Yb(III) with 3-formyl-2-mercaptoquinoline synthesized. These complexes were characterized by elemental analysis, molar conductance measurements, magnetic moment, infrared, electronic and proton nmr spectra. The TG studies of the lanthanide(III) complexes were carried out in dynamic air, with a heating rate of 10<sup>0</sup>C/min.

### EXPERIMENTAL SECTION

All the chemicals used were of analytical grade purchased from Aldrich, Merck, S.D. Fine, or BDH and the solvents used were purified by standard methods [10]. The complexes were analyzed for their metal content by standard methods [11]. Elemental analyses (C, H and N) were performed on a Perkin- Elmer 2400 CHN elemental Analyzer Model 1106, Carloerba Strumentazione. The IR spectra of the Schiff bases and their La(III) complexes were recorded on a HITACHI-270 IR spectrophotometer in the 4000-250 cm<sup>-1</sup> region using KBr disks. Molar conductivity measurements were recorded on an ELICO-CM-82 T conductivity bridge with a cell having cell constant 0.51. The electronic spectra of the complexes were recorded in DMF on a VARIAN CARY 50-BIO UV-spectrophotometer in the region of 200-1100 nm. The <sup>1</sup>H-NMR spectra of Schiff bases and complexes were

recorded in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  on BRUKER 300 MHz spectrometer at room temperature using TMS as an internal reference. The mass spectrometer was operated in the +ve ion mode. FAB-mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 kV, 10 A) as the FAB gas. The ESR spectra recorded on Variant E-4', X-band ESR Spectrometer using cylindrical quartz sample tube at room temperature. Polycrystalline diphenylpicrylhydrazyl (DPPH) was used as 'g' marker. Thermo gravimetric analysis data were measured from room temperature to 1000 °C at a heating rate of 10 °C/min. The data were obtained by using a PERKIN-ELMER DIAMOND TG/DTA instrument.

#### **Synthesis of 2-chloro-3-formyl quinoline**

This compound was synthesized by the reaction of acetanilide with Vilsmeier-Haack reaction at 80 °C as per the procedure given in the literature [12].

#### **Synthesis of 2-mercapto-3-formyl-quinoline**

One mol of 2-chloro-3-formyl-quinoline was mixed with 1.5 mol of sodium sulfide dissolved in 5 mL of DMF. The mixture was stirred for 1-2 h at room temperature. This mixture was poured in crushed ice followed by acidification with acetic acid to obtain yellow coloured solid melting point 245 °C [13].

#### **Synthesis of Schiff bases (MQAP)**

A mixture of 0.004 mol of 2-mercapto-3-formyl quinoline and 0.004 mol of 4-aminopyridine in the 1:1 ratio in 20 mL ethanol-acetic acid mixture was stirred at room temperature for 6 h. After the completion of the reaction (monitored by TLC), the solid separated was filtered, washed with excess of cold ethanol, dried and crystallized from ethanol.

#### **Synthesis of Lanthanide(III) complexes (1-7)**

The ethanolic solutions of the respective metal nitrate (0.01 mol) and the Schiff base L (0.01 mol) were refluxed for about 6-7 h on a water bath and the pH of the reaction mixture was adjusted *ca.* 7.0- 7.5. During the refluxation the metal chelates were separated out. The metal chelates thus separated were filtered, washed successively with ethanol and ether and finally dried over fused  $\text{CaCl}_2$  in vacuum. Yield of all the metal complexes lie in the range of 63-68 % (Scheme 1).

## **RESULTS AND DISCUSSION**

#### **Elemental Analysis**

The analytical and physicochemical data of the complexes are summarized in table 1. The values obtained are in good agreement with the theoretical values calculated for the suggested general formula of the complexes such as  $[\text{Ln}(\text{MQAP})(\text{NO}_3)_2(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ .

#### **Molar conductance**

Molar conductance values of lanthanide(III) complexes were measured in dimethylformamide(DMF), dimethylsulfoxide(DMSO), Table.1. These conductance values are much lower than the values reported for 1:1 electrolytes in these solvents [14]. Therefore, the conductance values suggest that all the seven complexes are nonelectrolytes, and hence, they are neutral complexes.

#### **Magnetic behaviour**

Magnetic moments of the lanthanide(III) complexes are given in Table 1. The measured values complexes are very close to the theoretical values calculated for the free lanthanide(III) ions [15]. The observed magnetic moment values suggest that the La(III) and Y(III) complexes are diamagnetic and the remaining complexes are paramagnetic, as expected. As the magnetic moment values of the complexes are almost the same as those for the respective free lanthanide ions, it is presumed that the 4f electrons are not at all disturbed by the ligand field, and hence, it is unlikely that the 4f orbitals of the lanthanide(III) ions are involved in coordination in the present complexes.

#### **Infrared spectra**

In the ligands, a broad band at  $3454\text{ cm}^{-1}$  corresponds to the tautomeric forms of  $\nu(\text{NH})$  and  $\nu(\text{SH})$  of quinoline ring moiety. This confirms the subsequent substitutions by removing the chlorine present at the second position of the quinoline nucleus. A high intensity band observed in the region  $1687\text{ cm}^{-1}$  is attributed to the  $\nu(\text{C}=\text{N})$  vibration [16], which confirms the formation of Schiff base. The sharp intensity band arrived in the region of  $750\text{-}600\text{ cm}^{-1}$  is assignable to the formation of C-S bond. [17].

In the complexes the band in the region 1624-1664  $\text{cm}^{-1}$  assigned to  $\nu_{(\text{C}=\text{N})}$  vibration and this lower shift from 1687  $\text{cm}^{-1}$  in the ligand supports the coordination of metal ion with azomethine nitrogen. The disappearance of the band at 3454  $\text{cm}^{-1}$  and appearance of new medium to high intensity bands in the region 450-510  $\text{cm}^{-1}$  for  $\nu_{(\text{M}-\text{S})}$  supports the coordination of thiolate sulphur to the metal ions via deprotonation [18]. The complexes show six absorption bands near 1470, 1290, 1067, 843, 750 and 611 which are assigned to  $\nu_4, \nu_1, \nu_2, \nu_6, \nu_3$  and  $\nu_5$  vibration of coordinated( $\text{C}_{2v}$ ) nitrate group. These are indicating the coordination of nitrate group. The magnitude of  $\nu_4, \nu_1$  and  $\nu_3, \nu_5$  lies range 185-200 and 55-65  $\text{cm}^{-1}$  respectively, indication the coordination of nitrate group in bidentate fashion and 1380-1384  $\text{cm}^{-1}$  which are assigned to nitrate group. A broad band at 3454-3388  $\text{cm}^{-1}$  attributes to the antisymmetric and symmetric -OH stretching modes of water and a peak in the region 858 - 821  $\text{cm}^{-1}$  in the complexes indicates the presence of coordinated water molecules [19]. The presence of water bound in different ways is supported by the results of the TG analysis.

The important features of the infrared spectra of all the complexes are the appearance of two strong bands at 354-360  $\text{cm}^{-1}$  region are assignable  $\nu(\text{M}-\text{N})$  and those in the region 500-510  $\text{cm}^{-1}$  to  $\nu(\text{M}-\text{S})$  vibrations, supporting the coordination through thiolate sulphur via deprotonation and azomethine nitrogen in the ligand MQAP [20]. The infrared spectral data of the L and its Ln(III) complexes are listed in Table-2.

### Electronic spectra

The electronic spectra of the ligand and the complexes were taken, and are given in Table 4. The electronic spectra of the ligand shows two absorption maxima at 29660  $\text{cm}^{-1}$  and 38240  $\text{cm}^{-1}$ , which are attributed to the n-p and p-p\* transitions, respectively [21]. In the lanthanide(III) complexes, a bathochromic shift is observed for the n-p at 26560-27800  $\text{cm}^{-1}$ , and p-p\* at 36950-37230  $\text{cm}^{-1}$ . Some f-f transitions are also observed in the case of Nd(III) complex, and further lanthanide(III) complexes these bands could not be identified as they are masked by the ligand charge transitions [22]. The charge transfer transition bands are observed in 18400 to 21300  $\text{cm}^{-1}$  range Table 3.

### $^1\text{H-NMR}$ spectral studies

The Schiff base exhibits the resonance at 8.37 ppm due to the azomethine proton. A singlet corresponding to one proton observed at 14 ppm is probably due to SH group. Hydrogen bonding leads to deshielding and to an increase in the frequency of the  $^1\text{H}$  NMR signal of the hydrogen bonded proton. This may explain the observed increase in the chemical shift. The sharp multiplet signals of the phenyl protons are found in the region 7.44-8.37 ppm. The peak due to SH group appeared at 14 ppm in the ligand is not observed in the La(III) complex. This confirmed the involvement of thiolate sulphur in coordination with the metal via deprotonation. The downfield shift of the methine proton from 8.37 ppm in the ligand spectrum to 9.5 ppm in the complexes indicate the participation of azomethine nitrogen in the coordination [23].

### FAB-MASS

In the spectrum of one of the representative complex  $[\text{Ln}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  molecular ion peak at  $m/z$  581 is equivalent to its molecular weight. This molecular ion undergoes fragmentation with the loss of one lattice water molecule giving a species *i.e.*  $[\text{Ln}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  at  $m/z$  563. Further, this fragment ion by the loss of two nitrate molecules and two coordinated water molecules gave a fragment ion at  $m/z$  403. Finally it undergoes demetallation to form the species  $[\text{L} + \text{H}]^+$  at a fragment ion at  $m/z$  248.

### Thermal Studies

The thermal decomposition of representative complexes  $[\text{Ln}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  and  $[\text{Yb}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  were carried out for TGA proceeds with an endothermic peak in the temperature range 70-100  $^\circ\text{C}$  for the decomposition of one lattice water molecule. Further in the temperature range 270-275  $^\circ\text{C}$  the decomposition of two coordinated water molecules take place. In the third stage of decomposition in the temperature range of 350-360  $^\circ\text{C}$  decomposes two coordinated nitrate molecules. The temperature range of 425-460  $^\circ\text{C}$  decomposes the ligand moiety. Finally the most stable metal oxide forms were obtained. The percentage weight loss, nature of decomposed chemical change with the temperature range and percentage of metal oxide obtained which are in good agreement with calculated values are given in the Table 4.

### In-vitro cytotoxicity Studies [24, 25]

#### Cell line and growth media

HeLa (Cervical cancer cells, Human) were cultured in MEM (minimum essential medium). The medium also contains 10% fetal calf serum, penicillin (100 U) and streptomycin (100  $\mu\text{g}$ ).

**Method for Passaging the Cells:****Procedure**

All the reagents were brought to 37°C before use. The sufficient amount of Trypsin-phosphate-versene-glucose (TPVG) solution was added to cover the monolayer, rinsed and discarded. Fresh TPVG solution was added and allowed to stand at room temperature for 2-3 minutes. TPVG solution was discarded and the flask containing the monolayer was incubated at 37 °C for 3-5 minutes and slightly tapped to free the cells from the surface. 10 mL of MEM containing 10% serum was added to the flask and pipetted to breakdown the clumps of cells. Total cell count was taken using a haemocytometer. Calculated the total number of cells. The medium was added according to the cell population needed. Required amount of medium containing the required number of cells ( $0.5-1.0 \times 10^5$  cells/ml) was transferred into bottles according to the cell count and the volume was made up with medium and required amount of serum (10% growth medium and 2% maintenance medium) was added. The flasks were incubated at 37°C and the cells were periodically checked for any morphological changes and contamination. After the formation of monolayer, the cells were further utilized.

**Cytotoxicity Screening****Determination of Mitochondrial Synthesis by Microculture Tetrazolium (MTT) Assay**

The ability of the cells to survive a toxic insult has been the basis of most cytotoxicity assays. This assay is based on the assumption that dead cells or their products do not reduce tetrazolium. The assay depends both on the number of cells present and on the mitochondrial activity per cell. The cleavage of MTT to a blue formazan derivative by living cells in clearly a very effective principle on which the assay is based.

The principle involved is the cleavage of tetrazolium salt of 3-(4,5 dimethyl thiazole-2 yl) - 2,5-diphenyl tetrazolium bromide (MTT) into a blue coloured product (formazan) by mitochondrial enzyme succinate dehydrogenase. The number of cells was found to be proportional to the extent of formazan production by the cells used.

**Procedure**

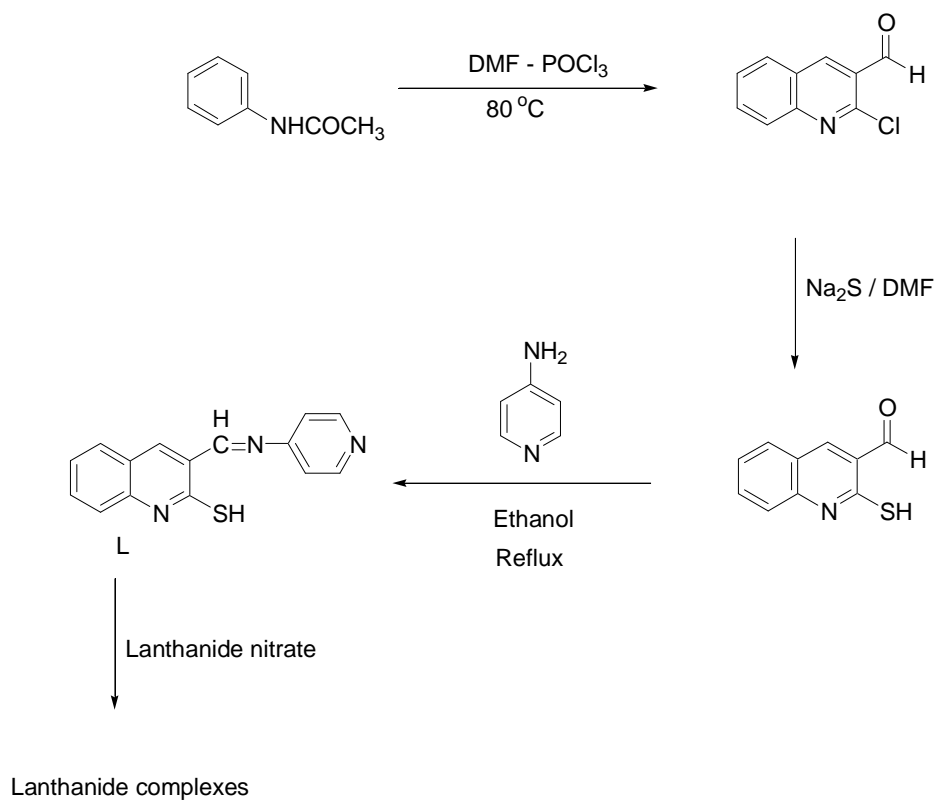
The monolayer cell culture was trypsinized and the cell count was adjusted to  $1.0 \times 10^5$  cells/ml using medium containing 10% new born calf serum. To each well of the 96 well microtitre plate, 0.1 mL of the diluted cell suspension (approximately 10,000 cells) was added. After 24 hours, when a partial monolayer was formed, the supernatant was flicked off, washed the monolayer once and 100 µl of different drug concentrations was added to the cells in microtitre plates. The plates were then incubated at 37 °C for 3 days in 5% CO<sub>2</sub> atmosphere, and microscopic examination was carried out and observations recorded every 24 hours. After 72 hours, the drug solutions in the wells were discarded and 50µl of MTT in MEM was added to each well. The plates were gently shaken and incubated for 3 hours at 37°C in 5% CO<sub>2</sub> atmosphere. The supernatant was removed and 50µl of propanol was added and the plates were gently shaken to solubilize the formed formazan. The absorbance was measured using a microplate reader at a wavelength of 540nm.

The percentage growth inhibition was calculated using the formula below:

$$\% \text{ Growth Inhibition} = 100 - \left( \frac{\text{Mean OD of Individual Test Group}}{\text{Mean OD of Control Group}} \right) \times 100$$

**Interpretation:**

The above compounds were tested for cytotoxicity against Cancer cell line HeLa. The compounds showed moderate cytotoxicity against the tested cell lines. La complex is more cytotoxic towards HeLa cells with lowest CTC<sub>50</sub> value of  $145.23 \pm 5.23$  followed by Samarium complex with CTC<sub>50</sub> value of  $147.63 \pm 4.14$ . These compounds merits further investigations.



Scheme 1. Synthesis of Schiff base (L) and lanthanide (III) complexes (1-7)

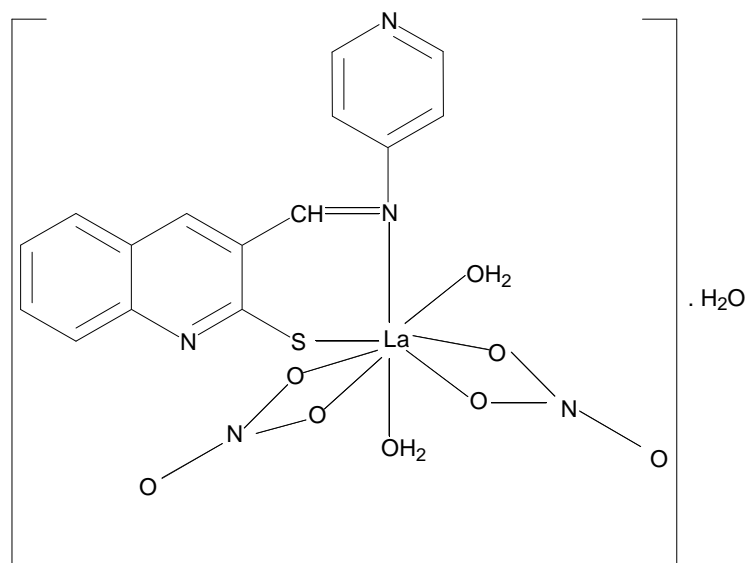


Figure 1. Proposed structure of Lanthanide complexes

**Table 1. Analytical, magnetic and conductance data of the PQT and its Lanthanide(III) complexes**

Complex	C% Calc. (Found)	H% Calc. (Found)	N% Calc. (Found)	S% Calc. (Found)	M% Calc. (Found)	Magnetic	Molar conductance Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
L <sub>1</sub>	67.9 (67.5)	4.15 (4.32)	15.84 (15.75)	12.07 (12.12)	-	-	-
[La(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	30.98 (31.56)	2.75 (2.93)	12.04 (11.9)	5.50 (5.52)	23.92 (23.97)	Dia	22.36
[Pr(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	30.87 (31.99)	2.74 (2.92)	12.0 (11.62)	5.48 (5.50)	24.18 (24.23)	3.47	29.62
[Nd(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	30.71 (30.76)	2.73 (2.90)	11.94 (11.56)	5.46 (5.40)	24.57 (24.74)	3.52	21.25
[Sm(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	30.40 (30.47)	2.70 (2.87)	11.82 (11.47)	5.40 (5.36)	25.33 (25.43)	1.49	23.63
[Eu(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	30.03 (30.37)	2.67 (2.87)	11.78 (11.23)	5.38 (5.40)	25.58 (25.63)	3.36	26.85
[Gd(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	30.05 (30.09)	2.67 (2.84)	11.68 (11.36)	5.34 (5.39)	26.21 (26.48)	7.92	22.52
[Yb(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	29.2 (30.20)	2.60 (2.92)	11.38 (11.11)	5.2 (5.17)	28.29 (28.14)	4.49	23.49

**Table 2. Infrared spectral data (in cm<sup>-1</sup>) of L<sub>1</sub> and its Lanthanide(III) complexes.**

Compound Code	ν(OH)	ν(SH) ν(NH)	ν(C=N)	ν(CNC)	ν(M-N)	N (M-S)	ν(CS)
L <sub>1</sub>	-	3454s	1687s	956	-	-	-
[La(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	3399b	-	1655s	945m	354m	500m	749
[Pr(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	3388b	-	1655s	999m	356m	500m	749
[Nd(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	3393b	-	1625s	989m	354m	500m	750
[Sm(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	3422b	-	1664s	960m	360m	502m	746
[Eu(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	3404b	-	1647s	960m	358m	502m	754
[Gd(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	3411b	-	1624s	960m	359m	503m	749
[Yb(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	3390b	-	1661s	980m	358m	504m	742

*S=strong; b=broad; m=medium; w=weak.*

**Table 3 Electronic spectral bands of hap and its lanthanide(III) complexes**

complexes		
Complex	Abs. Max./cm <sup>-1</sup>	Tentative assignment
L <sub>1</sub>	29658	n-p
	38235	p-p*
	26546	n-p
	36954	p-p*
[La(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	20670	Charge transfer
	29580	n-p
	38180	p-p*
[Pr(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	19570	Charge transfer
	29400	n-p
	37230	p-p*
	19080	4I9/2 → 4G7/2
[Nd(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	17380	4I9/2 → 2G7/2
	13720	4I9/2 → 4F7/2
	12490	4I9/2 → 4F5/2
	11660	4I9/2 → 4F3/2
[Sm(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	27780	n-p
	37230	p-p*
	20570	Charge transfer
[Eu(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	27800	n-p
	37230	p-p*
	21300	Charge transfer
[Gd(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	27800	n-p
	37250	p-p*
	21256	Charge transfer
[Yb(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	26560	n-p
	36950	p-p*
	19200	Charge transfer

Table 4. Thermal data of representative Lanthanide(III) complexes

Complex	Temp range (°C)	% weight loss Obs.	Nature of decomposition	% of metal
[La(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	71-100	3.09	Loss of one lattice water molecule	23.92
	150-180	6.19	Loss of two coordinated water molecules	
	275-310	21.34	Loss of two nitrate molecule	
	390-410	32.53	Loss of quinoline moiety	
[Yb(L <sub>1</sub> )(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	50-100	3.25	Loss of one lattice water molecule	28.29
	150-180	6.42	Loss of two coordinated water molecules	
	300-320	21.75	Loss of two nitrate molecule	
	370-390	32.33	Loss of quinoline moiety	

Table 5. Results of CTC<sub>50</sub> by using MTT assay

Compound Code	CTC <sub>50</sub> in (µg/ml) by MTT assay
	HeLa cells
L	205.53 ± 5.47
[La(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	145.23 ± 5.23
[Pr(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	192.18 ± 5.28
[Nd(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	179.48 ± 5.17
[Sm(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	147.63 ± 4.14
[Gd(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	155.13 ± 4.54
[Dy(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	171.18 ± 4.56
[Y(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	164.27 ± 5.14

### CONCLUSION

The ligand MQAP formed colored complexes with Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Yb(III) and colorless complex with La(III) ion. The analytical, thermoanalytical and FAB-mass spectral data suggests the general molecular formula of the complex as [Ln(MQAP)(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].H<sub>2</sub>O. The conductance study reveals non-electrolytic nature of the complexes. The IR and <sup>1</sup>H NMR studies reveals bidentate nature of the ligand with coordinating sites of thiolate sulphur via deprotonation and azomethine nitrogen in addition to the coordination of water and the coordination of bidentate fashion of nitrate group to the Ln(III) ion. Based on the above studies, the ligand MQAP, nitrate ion and water coordinates to the Ln(III) ions with the coordination number eight. The following structure may be proposed for the complexes (figure 1).

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