

# Polymeric complexes of 2,5-Dihydroxy-1,4-benzoquinone with some Lanthanides

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**Abstract-** Polymeric solid complexes having distorted square antiprismatic geometries of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) with 2,5-Dihydroxy-1,4-benzoquinone are reported. Their compositions and geometries are supported by elemental analysis, IR spectroscopy, magnetic susceptibility measurements and electronic absorption spectroscopic studies.

## I. INTRODUCTION

Lanthanide(III) ions, because of their size and charge are the best ions to form stable complexes with high coordination number<sup>[1]</sup>. Lanthanide(III) complexes have biological<sup>[2-5]</sup> and light emitting<sup>[6-7]</sup> applications. Keeping in view the applications of Lanthanide complexes, we described the synthesis and spectroscopic characterization of some lanthanide(III) complexes with 2,5-Dihydroxy-1,4-benzoquinone.

## II. EXPERIMENTAL

2,5-Dihydroxy-1,4-benzoquinone was prepared by reported method M.P. 212.5 °C (Lit. 213 °C)<sup>[8]</sup>. Purity was checked by simple spot test. The solid complexes were prepared by mixing the aqueous solutions of respective lanthanide chloride (taken in large excess) and ligand (taken as sodium salt). The precipitated complexes were separated by filtration and excess metal chlorides were removed by washings with water. The complexes were finally dried under vacuum over anhydrous calcium chloride.

Estimation of C and H was carried out by combustion method using microanalytical technique. The metal (M) content was estimated by the ignition of the complexes to their respective oxides.

IR spectra of the ligand and the complexes were recorded in 4000-200 cm<sup>-1</sup> region using KBr pellets.

The electronic absorption spectra of the complexes were recorded as diffuse reflectance spectra of VSU2P (Carl Ziess) spectrophotometer from 50,000 and 12500 cm<sup>-1</sup>. Magnetic susceptibility measurements were carried out by Guoy method.

## III. RESULTS AND DISCUSSION

The elemental analysis results given in Table suggest molecular formula [M(C<sub>6</sub>H<sub>2</sub>O<sub>4</sub>)<sub>1.5</sub>2H<sub>2</sub>O]<sub>n</sub> where M = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III).

The bonding of the metal to the ligand is studied by comparing the IR spectrum of the ligand with those of the complexes<sup>[9-10]</sup>. In the ligand spectrum, bands at 3300 cm<sup>-1</sup>, 1610 cm<sup>-1</sup> and 1210 cm<sup>-1</sup> are due to intramolecular hydrogen bonded of hydroxyl groups at position 2 and 5, the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{O}-\text{C})$  respectively. The spectra of the complexes in comparison show significant shifts in the above mentioned bands due to coordination to metal ions. The band due to intramolecular hydrogen bonded hydroxyl groups disappears in the spectra of the complexes as a result of the coordination to the metal ion through the oxygens of the hydroxyl and abstraction of protons. In the complexes of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) bands at 3500, 3400, 3200, 3450, 3300, 3400, 3500 cm<sup>-1</sup> respectively are assigned to the stretching modes of coordinated water molecules. The bands in the range of 500 to 710 cm<sup>-1</sup> are due  $\nu(\text{M}-\text{O})$  stretching modes.

The qualitative assignments of bands of absorption spectra are made by comparing with reported data (table)<sup>[11-15]</sup>. The other bands, are assigned as 5d←4f type transitions, metal to ligand, ligand to metal and electronic transitions within the ligand. Absorption band shifts to higher frequency in the complexes due to chelation. The  $\mu_{\text{eff}}$  values (Table) suggest that La(III) complex is diamagnetic whereas all other complexes are paramagnetic due to presence of 4f-electrons. The 4f electrons shielded by 5s<sup>2</sup>2p<sup>2</sup> electrons<sup>[16]</sup> and hence not involved in bonding. The magnetic moment values of these complexes slightly deviate from the values reported for free ions<sup>[17]</sup>. The proposed geometry of the complexes is distorted square antiprismatic<sup>[18]</sup> with eight coordination.

Lanthanide possess 4f<sup>n</sup>5d<sup>1</sup>6s<sup>2</sup> configurations, and as a low electronegative of these elements and the increasing stabilization of the 4f, 5d and 6s orbitals (4f>5d>6s), the +3 oxidation state is most stable. The 4f electrons are contracted into the core, they almost do not participate in bonding. As a direct consequence, no  $\pi$ -backbonding is possible. 2,5-Dihydroxy-1,4-benzoquinone has two chelated hydroxyl and carbonyl functional in two vicinal positions 2,5 and 1,4. The hydroxyl groups suffer abstraction of protons thereby giving rise to a divalent C<sub>6</sub>H<sub>2</sub>O<sub>4</sub><sup>2-</sup> anion. The ligand form linear solid polymeric complexes with Lanthanide(III) ions due to two chelating sites at opposite positions. The proposed geometries of the complexes is distorted square antiprismatic<sup>[18]</sup>.

**Table**  
**Elemental Analysis, colour,  $\mu_{\text{eff}}$ (BM), IR spectral and electronic absorption spectra of the complexes**

S. NO	Complex	Colour	$\mu_{\text{eff}}$ B.M	Elemental Analysis (Calc./ Found)			IR spectral bands ( $\text{cm}^{-1}$ )			Electronic Absorption ( $\text{cm}^{-1}$ )	
				C	H	M	$\nu(\text{C}=\text{O})$	$\nu(\text{O}=\text{C})$	$\nu(\text{M}-\text{O})$	Bands	Assignment
1	$[\text{La}(\text{C}_6\text{H}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]_n$	Pink	0.00	28.34/28.00	1.31/1.29	36.45/36.90	1580	1280	570	26512	Intra-ligand Charge transfer
2	$[\text{Ce}(\text{C}_6\text{H}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]_n$	Light Pink	2.50	28.25/28.00	1.31/1.29	36.65/36.56	1540	1270	710	42000 23125	$^2\text{D}_{5/2} \leftarrow ^2\text{F}_{5/2}$ $^2\text{D}_{3/2} \leftarrow ^2\text{F}_{5/2}$
3	$[\text{Pr}(\text{C}_6\text{H}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]_n$	Pink	3.50	28.19/28.89	1.31/1.40	36.39/36.59	1600	1260	550	18818	$^1\text{D}_2 \leftarrow ^3\text{H}_4$
4	$[\text{Nd}(\text{C}_6\text{H}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]_n$	Pink	3.59	27.95/27.85	1.29/1.35	37.33/37.50	1590	1270	680	26122 18915	$^2\text{P}_{1/2} \leftarrow ^4\text{I}_{9/4}$ $^2\text{G}_{9/2} \leftarrow ^4\text{I}_{9/4}$
5	$[\text{Sm}(\text{C}_6\text{H}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]_n$	Pink	---	27.51/26.35	1.27/1.40	38.30/38.12	1600	1260	680	13793	$^6\text{F}_{7/2} \leftarrow ^6\text{H}_{5/2}$
6	$[\text{Gd}(\text{C}_6\text{H}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]_n$	Pink	7.90	27.04/27.35	1.25/1.55	39.37/40.00	1550	1270	550	26122	$^6\text{P}_{7/2} \leftarrow ^8\text{S}_{7/2}$
7	$[\text{Dy}(\text{C}_6\text{H}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_2]_n$	Pink	10.51	26.69/26.59	1.24/1.34	40.15/40.29	1600	1270	500	13793	$^6\text{H}_{3/2} \leftarrow ^6\text{H}_{5/2}$
	$\text{C}_6\text{H}_4\text{O}_4$ (ligand)	Yellow	---	51.58/51.52	2.87/2.84		1610	1210	--	--	-----

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