

## Lanthanide (III) complexes with 2-(2'-hydroxyphenyl)-4, 6-dimethylbenzothiazolyl hydrazone

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### ABSTRACT

Lanthanide (III) complexes with the ligand 2-(2'-hydroxyphenyl)-4, 6-dimethylbenzothiazolyl hydrazone (L) have been prepared and characterized by various physico-chemical techniques, viz. elemental analysis, molar conduction measurements, thermogravimetry, uv-visible and IR spectroscopy.

**Keywords:** Lanthanide (III) complexes, hydrazone.

The ligand 2-(2'-hydroxyphenyl)-4, 6-dimethylbenzothiazolyl hydrazone (L) was synthesized in three steps. First 2-amino-4, 6-dimethylbenzothiazole was prepared from 2, 4-xylydine<sup>1</sup>. Then it is converted to 2-hydrazino-4, 6-dimethylbenzothiazole by refluxing with hydrazine hydrate in ethylene glycol at 160°C in oil bath. Equimolar proportions of 2-hydrazino-4, 6-dimethylbenzothiazole and salicylaldehyde in ethanol were refluxed on water bath for one hour and allowed to cool. The solid obtained was filtered and recrystallized from ethanol (m. p. 210°C).

The complexes were prepared by following the method of Rao et. al<sup>2</sup>. To a weighed amount of lanthanide (III) chloride in ethanol, a calculated amount of the ligand (L) (1:1.5 stoichiometric ratio) in ethanol was added. pH of the solution was adjusted by the addition of alcoholic ammonia. The solution was concentrated on steam bath, the complex separated, washed with ether to remove excess of the ligand and dried on anhydrous calcium chloride for 48 hours.

Molar conduction in methanol ranges from 137 – 148.3 suggest that the complexes are 1:1 electrolytes<sup>3</sup>. Analytical data of the complexes clearly

indicates that 1:1 (M:L) complexes are formed having general composition  $[Ln L Cl_2 (H_2O)_3] Cl$  where Ln = La, Pr, Nd, Sm, Gd, Dy.

The ligand exhibited a strong band at 3252  $cm^{-1}$  and a weak sharp band at 3050  $cm^{-1}$  which are assigned to phenolic hydroxy group<sup>4</sup>.

In the complexes, a broad band in the region 3100 – 3500  $cm^{-1}$  is observed (Table -1) which corresponds to the hydroxy group and water molecules coordinated to metal ion<sup>5-7</sup>. Thermogravimetry shows presence of three moles of water per mole of the complex. Co-ordination through phenolic oxygen is further supported by the shift of 1449  $cm^{-1}$  ligand band (C-O phenolic) to lower frequency<sup>8,9</sup>. A sharp strong ligand band at 1613  $cm^{-1}$  assigned to  $\nu$  C=N (azomethine) and found shifted to higher frequency<sup>6,10</sup> indicating co-ordination in IR spectra of the ligand and attributed to  $\nu$  C-N (Thiazole ring)<sup>6,8</sup>. A negative shift of this band in all the complexes indicates the involvement of nitrogen of thiazole moiety in coordination<sup>7</sup>, whereas the band appearing for  $\nu$  C-S (Cyclic) do not show any shift indicating non-involvement of sulphur in co-ordination<sup>11</sup>.

**Table 1: Characteristics IR bands (cm<sup>-1</sup>) of the ligand and its lanthanide complexes**

Ligand (L)	La (III) complex	Pr (III) complex	Nd (III) complex	Sm (III) complex	Gd (III) complex	Dy (III) complex	Assignment
3252 ss	3356 bs	3567 bs					v O – H (water) and
	2300 ss	3264 bs	3254 bs	3154 bs	3260 bs	2362 bs	v O – H (Phenolic)
3050 sw		3100 sh	3050 sh				
1613 ss	1620 ss	1622 ss	1620 ss	1623 ss	1626 ss	1624 ss	v C = N (azomethine)
1564 ss	1540 bs	1542 bs	1543 bs	1545 bs	1543 bs	1544 bs	v C = N (cyclic)
1449 bm	1402 ss	1402 bs	1410 bs	1404 bs	1404 bs	1404 bs	v C – O (phenolic)
754 ss	756 sm	754 ss		754 ss	756 bm	755 ss	v C – S (ring)

**REFERENCES**

- Adams Roger 'Organic Reactions', **3**: 256, Johh Wiley and sons, Inc. New York (1956).
- Ramchandra Roa V., Clarke G. A. and Marinsky J. A., progress report, Dept. of Chem., Suny and Buffalo, N.Y.A.E.C. contract No. at (30-D), 2269 (1964).
- Patil B. K. and Deshpande M. N., *Asian J. Chem.*, **2**: 464 (1990).
- Sharma A. Jain L, Shrama S., Kacchwah G., Jangid S. and Mehta R. K., *Asian J. Chem.*, **5**: 153 (1993).
- Sinha S. P., *Spectrochim. Acta*, **20**: 879 (1964).
- Sinha A. I. P. and Bala Manju, *Asian J. Chem.*, **3(1)**: 45 (1991).
- Revanakr V. K., Arali V. H. and Mahale V. B., *Indian J. Chem.*, **29(A)**: 889, (1990).
- Dash D. C., Behera P. K., (Miss.) Sen M. and Meher F. M., *J. Indian Chem. Soc.*, **68**: 663 (1991).
- Singh R. V. and Tandon J. P., *Indian J. Chem.*, **19(A)**: 602 (1980).
- Garb A. A., *Asian J. Chem.*, **3(2)**: 216 (1991).
- Gupta S. K., Sharma P., Thakur D., Shirngi M. and Takur S., *Oriental J. Chem.*, **24(3)**: 1149 (2008).