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Synthesis and Characterization of Rare Earth Complexes with a *Bis*-Schiff Base from Salicylaldehyde and 1,6-Hexanediamine

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A series of lanthanide(III) complexes of the type $[LnL_2Cl_2]Cl$, where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, L = $C_{20}H_{24}N_2O_2$, a *bis*-Schiff base ligand derived from salicylaldehyde and 1,6-hexanediamine, have been synthesized and characterized by elemental analyses, molar electrical conductivities, infrared and electronic spectra, thermergravimetric analyses. All the complexes were found to be 1:1 electrolytes of the general empirical formula $[LnL_2Cl_2]Cl$. The Schiff base ligand behaves as tetradentate ligand having a N_2O_2 donor sets towards the metal cations. A probable coordination number ten has been assigned in these complexes.

Key Words: Salicyladehyde, 1,6-Hexanediamine, Schiff base, Rare earth complexes.

INTRODUCTION

Schiff base metal complexes have been widely studied subject, because of their industrial and biological applications[1,2]. Various studies have shown that Schiff bases derived from salicylaldehyde and its derivatives have considerable biological importance partly because such ligands have many donor atoms (N, O) and are analogous to biological environment to some extent. They were widely used in the fields of biology, pharmacology, catalysis, organic synthesis, chemical, analysis, *etc.*[3-6]. Studies of new kind of Schiff bases and their complexes are now attracting the attention of biochemists[7,8]. It has been reported that some complexes of Schiff bases with rare earth elements prossess some anticarcinogenic activities[9]. In this work, a *bis*-Schiff base ligand derived from salicylaldehyde and 1,6-hexanediamine (Fig. 1) and its rare earth metal complexes were prepared and characterized.

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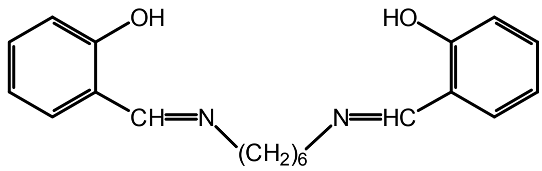

Fig. 1. Structure of Schiff base ligand

EXPERIMENTAL

Lanthanide oxide (99.95 %), salicylaldehyde, 1,6-hexanediamine and other reagents were AR grade. Salicylaldehyde was distilled before use. Methanol was chromatic spectrum pure. $LnCl_3·6H_2O$ was prepared by dissolving lanthanide oxide in concentrated hydrochloric acid and crystallizing the salt by evaporating the solution on a steam bath.

Preparation of the Schiff base ligand: Schiff base ligand L was prepared by mixing salicylaldehyde (10.00 g, 82 mmol) and 1,6-hexanediamine (4.65 g, 40 mmol), respectively, in 100 mL absolute ethanol with constant stirring for 0.5 h.The resulting yellow precipitate was separated by filtration, washed with absolute alcohol five times. The crude ligand were recrystallized from absolute ethanol and stored in a desicator over calcium chloride. The purity of the ligand were established by elemental analysis and IR spectra. Yield 11.23 g (85 %).

Preparation of rare earth complexes: The following detailed synthesis procedure is given as an example, all of the other complexes were prepared similarly.

A solution of $LaCl_3·6H_2O$ (0.35 g, 1 mmol) in 10 mL absolute alcohol was added to the ligand L(0.65 g, 2 mmol) suspended in 30 mL absolute alcohol. The solution was refluxed for 10 min when a yellow precipitate appeared. The solution was stirred 0.5 h and then allowed to cool to room temperature. The precipitate was separated by filtration, washed with absolute alcohol five times and finally air-dried. Yield, 0.71 g (80 %).

The rare earth content was determined by conversion into the corresponding oxide. Micro-analysis for carbon, hydrogen and nitrogen were performed by a Cario Erba EA1100 elemental analyses instrument. Conductance measurements were made with a Shanghai Model DDB-6200 conductometer. IR spectra were recorded on a Perkin-Elmer PK-6000 (4000-400 cm^{-1}) using KBr discs. Electronic spectra of the rare earth metal complexes were recorded on a Japan HITACHI U-3400 spectrophotometer (200-400 nm). TG-DTG measurements were carried out on a Mettler-Toledo TGA/SDTA 851^e thermal balance in static air from room temperature to 900 ºC with a heating rate of 10 ºC/min.

RESULTS AND DISCUSSION

The elemental analyses and some physical properties of the complexes are listed in Table-1. All the complexes are yellow solids. The elemental analyses indicate that the complexes have the general formula LnL_2Cl_3. All these complexes are soluble in DMSO, DMF, pyridine and a part of soluble in methanol, ethanol, but are insoluble in water, ether, benzene. The molar electrical conductivities of the complexes in methanol (0.001 M) are in the range of 79-85 S cm^2 mol^{-1}, indicating that the complexes are 1:1 electrolytes[10]. It is, therefore, concluded that two of three chloride ions are present in inside and one in outside. The formulation of the complexes may be represented by the general equation:

$$LnCl_3{\cdot}nH_2O + 2L \longrightarrow [LnL_2Cl_2]Cl\downarrow \text{ (yellow)} + nH_2O$$

The important infrared frequencies of the free ligand and its complexes, along with their assignments are given in Table-2. In the spectra of the *bis*-Schiff base ligand, a strong band occurring at 1633 cm^{-1} (s) due to C=N stretching is found shifted to higher frequency. 1650-1649 cm^{-1} (s) for its complexes, indicating coordination through the two azomethine nitrogens. The broad absorption bond at 3450 cm^{-1} (w), due to the hydroxy group of phenolic in the IR spectra of the ligand appears at lower frequency in the corresponding complexes, *viz*., 3432-3409 cm^{-1}, showing coordination of oxygen atoms of the phenolic hydroxyl with the central Ln(III) ion. The shift of the C-O stretching vibration of the phenolic part of salicylaldehyde from 1281 cm^{-1} (s) to 1295-1291 cm^{-1} (s) also supports the coordination of oxygen atoms. A band at 581-571 and 412-408 cm^{-1} attributed to ν(Ln-N), ν(Ln-O) are observed in the spectra of all the complexes, which are not found in the spectrum of the free ligand. It however, confirms that the nitrogens of azomethine and oxygens of phenolic are involved in the complexes formation.

The UV-Vis of ligand and complexes are summarized in Table-3. At 200-400 nm ligand have strong absorbption (max absorbption peak: 252.5 nm, 314.1 nm, 397.3 nm). The absorbption of complexes are similar with ligand. At the absorption 252.5 nm little change in the UV-Vis absorption bands of the complexes are observed. This is the feature absorbption about benzene ring. The band of 397.3 nm are the C=N bond absorbption which are the n-π^* transition. Whereas at 314.1 nm the absorbption are red shifted 2~4 nm., probability the Schiff base ligand and Ln(III) formed a coordination bond through oxygen atoms of phenol-hydroxy group.

The TG-DTG figures of the complexes are very similar. The Gd complex is discussed here as an example. The complexes are stable upto 200 ºC. The decomposition pattern of Gd(III) complex shows a three-step decomposition. The first (222.5-347.8 ºC) weight loss 11.85 % (calc. 12.00 %),

TABLE-1
ELEMETAL ANALYSIS AND OTHER DATA OF THE LIGAND AND ITS COMPLEXES

Compound	m.w.	Yield (%)	Colour	m.p. (ºC)	Elemental analysis (%)				Λ_M (S cm^2 mol^{-1})
					C	H	N	Ln	
L	324.424	85	Yellow	73	74.08(74.05)	7.42(7.46)	8.67(8.63)	---	---
[LaL_2Cl_2]Cl	894.098	80	Yellow	267-269	53.80(53.73)	5.48(5.41)	6.32(6.27)	15.51(15.54)	81
[CeL_2Cl_2]Cl	895.298	82	Yellow	234	53.70(53.66)	5.45(5.26)	6.35(6.26)	15.62(15.65)	83
[PrL_2Cl_2]Cl	896.098	85	Yellow	267.1-267.9	53.60(53.61)	5.42(5.40)	6.31(6.25)	15.74(15.72)	82
[NdL_2Cl_2]Cl	899.398	80	Yellow	258.1-258.3	53.45(53.41)	5.39(5.38)	6.25(6.23)	16.00(16.03)	80
[SmL_2Cl_2]Cl	905.598	81	Yellow	242.2-244	53.11(53.05)	5.37(5.34)	6.21(6.19)	16.58(16.61)	83
[EuL_2Cl_2]Cl	907.198	80	Yellow	207.6-208	53.06(52.95)	5.37(5.33)	6.22(6.18)	16.70(16.75)	81
[GdL_2Cl_2]Cl	912.498	83	Yellow	202-204	52.72(52.65	5.34(5.30)	6.19(6.14)	17.20(17.24)	79
[TbL_2Cl_2]Cl	914.098	82	Yellow	195.2-195.7	52.63(52.55)	5.33(5.29)	6.15(6.13)	17.35(17.39)	84
[DyL_2Cl_2]Cl	917.698	81	Yellow	207	52.43(52.35)	5.32(5.27)	6.15(6.11)	17.65(17.71)	82
[HoL_2Cl_2]Cl	920.098	80	Yellow	180	52.29(52.21)	5.31(5.26)	6.13(6.09)	17.89(17.92)	83
[ErL_2Cl_2]Cl	922.498	82	Yellow	>300	52.15(52.08)	5.29(5.25)	6.13(6.07)	18.10(18.14)	85
[TmL_2Cl_2]Cl	924.098	79	Yellow	>300	52.08(51.99)	5.29(5.24)	6.12(6.06)	18.22(18.28)	80
[YbL_2Cl_2]Cl	928.198	80	Yellow	>300	51.90(51.96)	5.26(5.27)	6.10(6.04)	18.61(18.64)	81
[LuL_2Cl_2]Cl	930.698	82	Yellow	183	51.78(51.64)	5.25(5.20)	6.08(6.92)	18.77(18.83)	82

TABLE-2
IR SPECTRAL DATA OF THE LIGAND AND ITS Ln(III) COMPLEXES (cm^{-1})

Compound	ν(C=N)	ν(OH)	ν(C–O)	ν(Ln–N)	ν(Ln–O)
L	1633 s	3450 w	1281 s	–	–
$[LaL_2Cl_2]Cl$	1649 s	3434 w	1291 s	571 w	409 w
$[CeL_2Cl_2]Cl$	1649 s	3431 w	1291 s	571 w	409 w
$[PrL_2Cl_2]Cl$	1650 s	3432 w	1292 s	572 w	410 w
$[NdL_2Cl_2]Cl$	1650 s	3429 w	1291 s	573 w	410 w
$[SmL_2Cl_2]Cl$	1649 s	3429 w	1293 s	573 w	410 w
$[EuL_2Cl_2]Cl$	1650 s	3428 w	1293 s	573 w	410 w
$[GdL_2Cl_2]Cl$	1650 s	3429 w	1291 s	573 w	410 w
$[TbL_2Cl_2]Cl$	1650 s	3430 w	1293 s	575 w	408 w
$[DyL_2Cl_2]Cl$	1650 s	3429 w	1294 s	575 w	412 w
$[HoL_2Cl_2]Cl$	1650 s	3431 w	1294 s	575 w	412 w
$[ErL_2Cl_2]Cl$	1650 s	3412 w	1294 s	581 w	412 w
$[TmL_2Cl_2]Cl$	1650 s	3428 w	1294 s	576 w	412 w
$[YbL_2Cl_2]Cl$	1650 s	3430 w	1294 s	575 w	411 w
$[LuL_2Cl_2]Cl$	1650 s	3427 w	1295 s	576 w	412 w

TABLE-3
UV SPECTRAL DATA OF THE LIGAND AND ITS Ln(III) COMPLEXES

Compound	λ_{1max}	ε_1	λ_{2max}	ε_2	λ_{3max}	ε_3
L	252.5	23675	314.1	7420	397.3	4000
$[LaL_2Cl_2]Cl$	253.8	51325	317.0	16045	399.7	5875
$[CeL_2Cl_2]Cl$	253.8	55230	317.3	19480	394.2	6315
$[PrL_2Cl_2]Cl$	253.3	57525	316.3	17995	397.6	6590
$[NdL_2Cl_2]Cl$	253.3	54805	318.2	17265	394.1	5460
$[SmL_2Cl_2]Cl$	253.6	63175	317.6	19600	397.8	6855
$[EuL_2Cl_2]Cl$	253.3	52660	317.8	16225	397.6	5430
$[GdL_2Cl_2]Cl$	253.3	51460	316.0	15990	397.0	5420
$[TbL_2Cl_2]Cl$	253.1	56245	318.2	17415	398.2	5680
$[DyL_2Cl_2]Cl$	253.4	62605	317.3	19500	397.8	6620
$[HoL_2Cl_2]Cl$	253.4	56160	316.2	17355	398.4	6440
$[ErL_2Cl_2]Cl$	253.8	51590	318.4	16455	396.5	4600
$[TmL_2Cl_2]Cl$	253.4	52980	316.3	16725	398.3	4936
$[YbL_2Cl_2]Cl$	253.5	54107	318.1	16790	398.9	5218
$[LuL_2Cl_2]Cl$	253.4	55050	318.2	17155	397.0	5435

corresponds to the loss of 3HCl. The second (347.8-386.6 ºC) weight loss 9.11 % (calc. 9.22 %), corresponds to the loss of -$(CH_2)_6$-. The third weight loss 59.88 % (calc. 58.91 %) at 386.6-606.7 ºC, corresponds to the loss of the other part of one ligand and the another ligand. Above 606.7 ºC, no weight loss is observed. The total weight loss with oxidative decomposition of the complex to stable Gd_2O_3 agrees with the analytical data for the metal content.

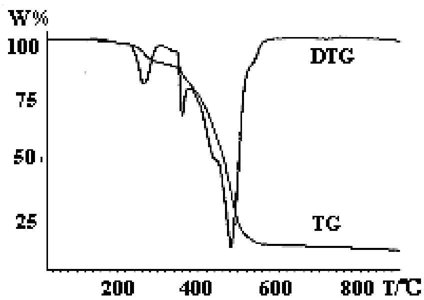

Fig. 2. TG-DTG Curve of $[GdL_2Cl_2]Cl$

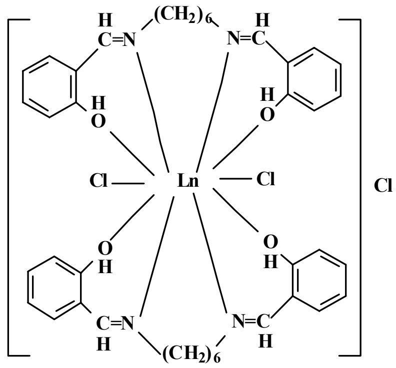

Fig. 3. Structure of the complexes

Conclusion

From measuring of above, it is concluded that every central Ln(III) ion in the complexes coordinates with both two bis-Schiff base ligands *via* four nitrogen atoms of azomethines and four oxygen atoms of phenol hydroxyl groups and two chloride ions. Their coordination numbers are ten. The suggested structure of the complexes are shown in Fig. 3.

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