

Studies on trivalent lanthanide complexes of bis-(acetylacetonate) o-dianisidine

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ABSTRACT

The characteristic functional group of schiff bases in the azomethine group ($-\text{RC}=\text{N}$)₁. The coordination interaction of lanthanide (III) chloride with different schiff bases was studied²⁻⁴. It was concluded that bis-acetylacetonate o-dianisidine behaves as a tetradentate bifunctional ligand. The lanthanide metal ions coordinate at the two nitrogen and two oxygen atoms with the chloride and water molecule remaining out of the coordination sphere.

Key words: Trivalent lanthanide complexes, bis (acetylacetonate) o-dianisidine.

INTRODUCTION

Schiff base complexes form a vast and fruitful area of research in coordination chemistry. The characteristic functional group of schiff bases in the azomethine group ($-\text{RC}=\text{N}$)₁. Just about one hundred fifty years ago, H.Schiff¹ discovered salicylaldehyde complexes by reacting metal salicylaldehyde compound with primary amines. The coordination interaction of lanthanide (III) chloride with different schiff bases was studied²⁻⁴. The interaction of Ti(IV), Mn(II) with schiff bases derived from acetylacetonate and ethylenediamine was studied^{5,6}. It was therefore thought interesting to ascertain the mode of interaction of bis (acetylacetonate) o-dianisidine with trivalent lanthanide chlorides. The newly synthesized complexes were subjected to elemental, thermogravimetric and differential thermal analyses. The melting points, magnetic susceptibilities and molar conductances were determined and infra red and electronic spectra were taken.

EXPERIMENTAL

The schiff bases, bis (acetylacetonate) o-dianisidine was prepared in the molar ratio of 2:1 in benzene. The mixture was concentrated on water bath & left for crystallization. The product, thus

obtained was recrystallized from chloroform and dried in vacuo at ambient temperature.

The complexes were prepared by mixing lanthanide metal chloride and ligand in ethanol and benzene respectively in molar ratio of 1:1, The reaction mixture was stirred for about six hours at room temperature when a dirty white precipitate was obtained. The precipitate was washed with ethanol and benzene several times and dried in vacuo.

The complexes were subjected to elemental analyses for carbon, hydrogen and nitrogen at instrumentation center, A.M.U. Aligarh. The chlorine was estimated on AgCl gravimetrically. The melting point and decomposition temperature of the complexes were taken. The thermogram of few complexes was carried out between ambient and 800° C and DTA was recorded for the same temperature. The magnetic susceptibility of the complexes was determined with Faraday balance at room temperature at B.H.U. Varanasi.

The molar conductance of the complexes was determined in DMSO and DMF at 10⁻³ M concentration, using Philip's conductivity bridge. The i.r. spectra of the ligand and the complexes were taken in nujol mull in the range of 4000-400 cm⁻¹ on

Perkin Elmer spectrophotometer at A.M.U. Aligarh. The electronic spectra of few complexes were recorded at room temperature at G.N.D. University, Amritsar.

RESULTS AND DISCUSSION

The elemental analysis for carbon, hydrogen, nitrogen and chlorine show that the lanthanide (III) ions interact with bis (acetylacetonate) o-dianisidine in 1:1 molar ratio with a general formula $[Ln(ac.ac.)_2 o-dian.-2H] Cl.H_2O$, where Ln stands for La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm & Yb in +3 oxidation states and $(ac.ac.)_2 o-dian.$, for the ligand, bis-acetylacetonate o-di-anisidine.

The molar conductances for these complexes in dimethyl- sulphoxide at 10^{-3} M concentration ranges between 58.9 to 78.9. $ohm^{-1} cm^2 mole^{-1}$. This shows that the complexes are 1:1 electrolytes since the established range for such electrolytes is 55-90 $ohm^{-1} cm^2 mole^{-1}$. This is further corroborated by their molar conductances in dimethyl formamide which lie in the range, 82.7 to 95 $ohm^{-1} cm^2 mole^{-1}$. Thus the lone chloride present in the molecule is outside the coordination sphere.

The i.r. spectrum of the ligand shows a medium intensity band⁷ at $1600 cm^{-1}$ which is the carbonyl stretching frequency in the keto form of the ligand. The $1560 cm^{-1}$ band is due to C=C & C=N stretchings and a very strong band at $1220 cm^{-1}$ is

due to the hydroxyl group in hydrogen bonding in enol form at the ligand. The two strong and medium bands at 810 & $765 cm^{-1}$ are due to the CH deformation of the double bonded carbon in hydrogen bonded ring. On complexation with trivalent lanthanide ions, there occurs a perturbation of both carbonyl frequency and the C=N frequency. It thus evinces that the coordination of metal must have occurred at both the nitrogen and the two oxygen atoms. The two aromatic rings of dianisidine can arrange themselves so that one lie flat & the other vertical over it, bringing the two nitrogen atoms closer & facilitating their coordination with metal ions.

The thermograms of the complexes of Pr, Eu, Gd & Tb show that the weight loss greater than that required for one water molecule occurs at a temperature, below $100^\circ C$. It is therefore, quite logical to conclude that the lone water molecule, present in the complexes is not coordinated and is only lattice water. The pattern of weight losses in the thermograms of the above mentioned four complexes lead to conclude that after the elimination of water molecule, there is a removal of acetylacetonate part.

The DTA curves for the complexes of Pr, Eu, Gd, & Tb show four ditches at 350° , 310° , 300° and 290° ; 480° , 400° , 380° and 430° ; and 550° , 510° , 480° and 450° respectively. It is probably due to the removal of water and acetylacetonate part of the ligand.

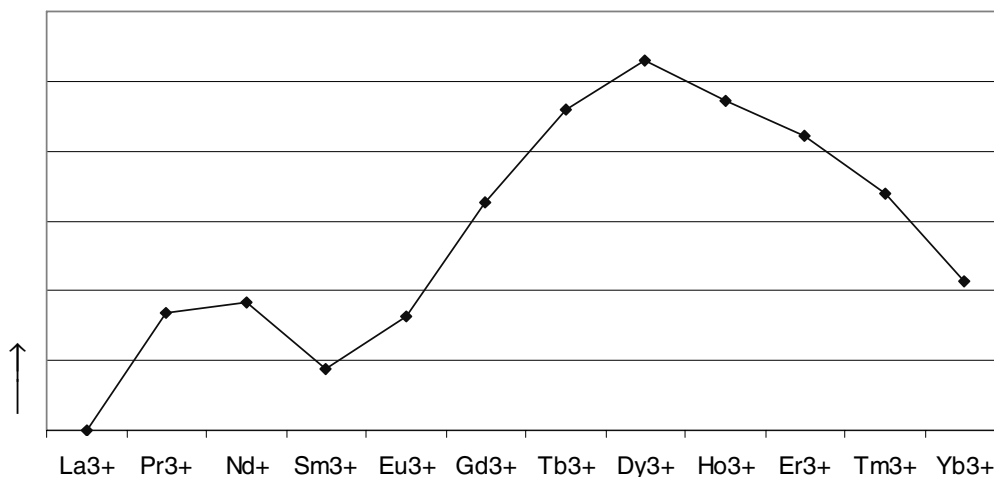


Fig. 1: $[Ln(ac.ac.)_2 Dian-2H] Cl.H_2O$

Table 1: Result of analyses & some characterizing data (Bis (acetylacetonate) o-dianisidine complexes)

S. No.	Compounds	Colour	Decomp. Temp.C	%C	%H	%N	%Cl	** ΔM in DMF	** ΔM in DMSO	μ eff. in BM
1.	La(ac.ac) ₂ Dian-2H.Cl.H ₂ O	Dirty white	195	48.10 (48.13)	4.78 (4.61)	4.61 (4.68)	5.59 (5.93)	62.7	90.3	diamag.
2.	La.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	205	48.00 (47.97)	5.0 (4.66)	4.65 (4.66)	-	67.5	86.5	3.37
3.	Nd.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	200	47.18 (47.70)	4.80 (4.64)	4.60 (4.64)	5.18 (5.88)	58.9	-	3.68
4.	Sm.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	220	47.11 (47.22)	4.69 (4.59)	4.60 (4.59)	-	58.9	82.7	1.74
5.	Eu.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	204	46.20 (47.10)	4.78 (4.58)	4.53 (4.58)	5.60 (5.81)	62.7	-	3.28
6.	Gd.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	210	46.15 (46.69)	4.69 (4.54)	4.63 (4.54)	-	67.5	-	6.55
7.	Tb.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	210	46.36 (46.57)	4.81 (4.53)	4.60 (4.53)	5.14 (5.74)	78.9	-	9.21
8.	Dy.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	207	46.00 (46.30)	4.62 (4.50)	4.38 (4.50)	-	62.7	-	10.58
9.	Ho.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	228	46.02 (46.12)	4.68 (4.48)	4.57 (4.48)	5.39 (5.69)	62.7	-	9.42
10.	Er.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	204	45.74 (45.95)	4.58 (4.47)	4.37 (4.47)	-	65.6	95.0	8.42
11.	Tm.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	230	45.20 (45.83)	4.66 (4.46)	4.55 (4.46)	-	67.5	-	6.79
12.	Yb.C ₂₄ H ₂₆ O ₄ N ₂ .Cl.H ₂ O	Dirty white	210	45.12 (45.33)	4.56 (4.43)	4.47 (4.43)	5.80 (5.61)	67.5	95.3	4.25

* Calculated values are given in parenthesis.

** Molar conductances are given in ohm⁻¹ cm² mole⁻¹

The magnetic moments of the complexes were calculated from the magnetic susceptibility values of the complexes. A double humped curve was obtained when the magnetic moment values of the complexes were plotted against the atomic number of the lanthanides. (Fig. 1)

The electronic spectra of the complexes of Pr, Nd, & Sm show the following bands with their assignments.

1. Paraseodymium complex:
31745 cm⁻¹ charge transfer
2. Neodymium complex:
34480 cm⁻¹ charge transfer
32260 cm⁻¹ charge transfer

- | | | |
|------------------------------|-------------------------------------|-------------------------------|
| 19230 cm ⁻¹ | ⁴ I _{9/2} | ² G _{9/2} |
| 17240 cm ⁻¹ | ⁴ I _{9/2} | ⁴ G _{5/2} |
| 13515 cm ⁻¹ | ⁴ I _{9/2} | ² S _{3/2} |
3. Samarium complex:
34480 cm⁻¹ charge transfer
32260 cm⁻¹ charge transfer

On the basis of above discussion, it can be concluded that the bis-acetylacetonate dianisidine behaves as a tetradentate bifunctional ligand. The lanthanide metal ions coordinate at the two nitrogen and two oxygen atoms with the chloride and water molecule remaining out of the coordination sphere.

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