

SYNTHESIS AND COMPARATIVE STUDY OF SPECTRAL PROPERTIES OF MIXED LIGAND COMPLEXES OF LANTHANIDES WITH 2,5-DIHYDROXY BUTYROPHENONE THIOSEMICARBAZONES AND 1,10-PHENANTHROLINE

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ABSTRACT:

Synthesis of mixed ligand complexes of Lanthanide (III) metal ion $[LnL_1L_2]Cl$ was carried out [where $Ln = La, Ce, Pr, Nd \text{ \& } Sm$ and $L_1 = 2,5\text{-Dihydroxy butyrophenone thiosemicarbazones}$ as a primary ligand and $L_2 = 1,10\text{-phenanthroline}$ as a co-ligand] and discussion of their physicochemical properties. Analytical results correspond to 1:1:1 (M-L₁-L₂) stoichiometry for the isolated complexes. The complexes are stable and have no tendency of absorbing moisture from the atmosphere. These compounds are fairly soluble in chloroform, ethanol, acetone, DMSO and DMF. The molar conductance in ethanolic solution suggests 1:1 electrolytic behavior of these complexes. The stereochemistry of these complexes has been established on the basis of Electronic and IR spectral studies. The values of β , $\delta\%$, $b^{1/2}$ and η for the isolated complexes have also been calculated. The value of δ has been found to be positive in all the complexes which suggests the electron delocalization from 4f - orbital. The positive values of $b^{1/2}$ show considerable amount of covalency in the metal - ligand bond. The magnitudes of covalency parameter and bonding parameter increases from Pr(III) to Sm(III) indicating that the extent of covalent character of metal-ligand bond increases with the increase in atomic number which is in conformity with the lanthanide contraction.

Keywords: Mixed ligand complexes; Lanthanides; thiosemicarbazones, Electronic structure; Spectral studies

Introduction

The Lanthanones are significant for their resemblance in chemical properties, which is due to the nearly identical configuration of the electrons available for bond formation. Lanthanone chelates of ligands possessing oxygen and nitrogen donor atoms find applications as bactericides and fungicide. Lanthanide mixed ligand complexes have been found to have wide applications as pseudo contact NMR - shift reagents, luminescent and as volatile precursors in the chemical vapor deposition of thin films of electro and magneto ceramic materials. These complexes are known to expand their coordination number by acquiring ligands with lone pairs as a consequence of their coordinate unsaturation. The ligands containing (C=O) group are the largest group of compounds forming complexes with the Lanthanides. In the last four decades an extensive literature, devoted to synthesis, structure and properties of mixed ligand lanthanide complexes has been evolved. The composition and structure of mixed ligand complexes strongly depend on the nature of the central metal ion and electronic features of the ligands⁽¹⁻⁸⁾. The present paper is the description of the synthesis of Lanthanide(III) metal ion complexes using 2,5-Dihydroxy butyrophenone

thiosemicarbazones as a primary ligand and 1,10-phenanthroline as a co-ligand and comparative study of their spectral properties.

Experimental work

Preparation and isolation of ligands:

2,5-Dihydroxy butyrophenone was prepared by the literature method⁽⁹⁾. Its thiosemicarbazone was obtained by refluxing (18g, 0.1M) of 2,5-Dihydroxy butyrophenone dissolved in ethanol(20ml) with thiosemicarbazide(20ml) (9.1g, 0.1M) in conc. HCl for about 3 hours on water bath. On cooling, light yellow compound separated out. It was filtered, washed with ethanol and dry ether and dried well under anhydrous conditions. The compound was recrystallized from acetone - ethanol mixture. Ligand 1,10- phenanthroline was obtained of A. R. quality and used as such.

Preparation and isolation of complexes:

Solution of rare earth salts were prepared by dissolving in water containing ethanol/acetone. A two step procedure was employed for the preparation of the mixed complexes.

Step-I: A hot saturated solution of the metal chloride(10mM) in aqueous ethanol was mixed with ethanolic solution of 2,5-Dihydroxy butyrophenone thiosemicarbazone(10mM)in the ratio 1:1. The mixture was refluxed for an hour on water bath at about 80°C. The solid complexes separated on cooling were filtered off through suction and washed thoroughly with ethanol, acetone and 2,2'-dimethoxy propane and dried at about 120°C.

Step-II: An ethanolic solution of the above complexes was treated with the hot ethanolic solution (10mM) of 1,10-phenanthroline. An excess of the phenanthroline solution was added to ensure the completion of reaction. After refluxation and on cooling at room temperature, solid complexes separated out. The solid complexes were filtered off, washed properly with ethanol, acetonitrile and dry ether and dried in vacuum over P₄O₁₀. The dry samples were identified by elemental, Electronic and IR spectroscopic analysis. The C, H, N contents were determined by conventional elemental analysis(recorded in Table-1). The lanthanide content was determined titrimetrically with titrant solutions of Na₂EDTA, pH5.5. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer as Nujol and hexachlorobutadiene mulls between KBr plates in the region 4000-400(recorded in Table-2)

Results and discussion:

Analytical results correspond to 1:1:1 (ML₁L₂) stoichiometry for the isolated complexes. The complexes are stable and have no tendency of absorbing moisture from the atmosphere. Their colour does not change even on storage for a pretty long period which shows that they are not decomposed. These compounds are fairly soluble in chloroform, ethanol, acetone, DMSO and DMF. The molar conductance in ethanolic solution suggests the 1:1 electrolytic behaviour of these complexes. By the addition of alcoholic silver nitrate solution to the solution of the complexes, a white curdy precipitate (AgCl) was obtained in each case indicating the presence of at least one chlorine atom in ionic state. Determination of molecular weight of the complexes by cryoscopic method suggests their monomeric nature. Molecular weight data, colour and melting point of the complexes are also recorded in Table-1.

Magnetic Studies:

Lanthanum complex is found to be diamagnetic while all the other complexes show paramagnetic behaviour. The values of magnetic moment for Ce(III), Pr(III), Nd(III) and Sm(III) complexes are 2.42, 3.58, 3.66 and 1.57 B.M. respectively. The magnetic moment values are quite normal for the Lanthanide complexes based on the J-values⁽¹¹⁾.

Electronic Spectral Studies:

Electronic absorption spectra of Lanthanide ion have been subjected to several investigations. The f-f electronic transitions of the Lanthanides are found to be sharp and line like and these can be characterized by the total angular quantum number(J). On complexation, the spectra tend to show the band energy shift as compared to be spectra of Ln(III) aqua ions due to the nephelauxetic effect⁽¹²⁾.

The Ce(III) ion does not show absorption band in the visible region of the spectrum. In the spectra of the Ce(III) complex, five bands i.e. 22,490; 23,670; 32,600; 45,400 and 47,910 cm^{-1} have been noticed. Out of which, first three are assigned to Laporte-allowed i.e. $4f \rightarrow 5d$ transition and the last two bands correspond to the transition: $^2F_{5/2} \rightarrow ^2D_{3/2}$ and $^2F_{5/2} \rightarrow ^2D_{5/2}$ ⁽¹³⁾.

The spectra of Pr(III) complexes in both solid and solution (DMF and DMSO) exhibit bands around 16,680; 20,730; 21,480 and 22,430 cm^{-1} in the visible region which may be due to the hyper-sensitive transitions: $^3H_4 \rightarrow ^1D_2$; $^3H_4 \rightarrow ^3P_0$; $^3H_4 \rightarrow ^3P_1$ and $^3H_4 \rightarrow ^3P_2$ respectively⁽¹⁴⁾.

The electronic spectra of Nd(III) complexes in DMF and DMSO are identical but slightly different from the solid state spectra. The bands corresponding to the energy level $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ shows a significant red shift. For other important bands around 12200, 12750, 13000, 18500, corresponding to $^4I_{9/2} \rightarrow ^2H_{9/2}$, $^4F_{5/2}$; $^4I_{9/2} \rightarrow ^4S_{3/2}$, $^4F_{7/2}$; $^4I_{9/2} \rightarrow ^4G_{7/2}$, the red shift is much less. Sm(III) complex show bands around 7320, 8150, 9300, 21,540, 23,600 and 24,720 corresponding to energy level, $^6H_{5/2} \rightarrow ^6F_{5/2}$; $^6H_{5/2} \rightarrow ^6F_{7/2}$; $^6H_{5/2} \rightarrow ^6F_{9/2}$; $^6H_{5/2} \rightarrow ^6I_{13/2}$; $^6H_{5/2} \rightarrow ^6P_{5/2}$; $^6H_{5/2} \rightarrow ^6F_{11/2}$ ⁽¹⁵⁾.

The values of β , $\delta\%$, $b^{1/2}$ and η for the complexes have also been calculated. The value of δ has been found to be positive in all the complexes which suggest the electron delocalization from 4f - orbital. The positive values of $b^{1/2}$ show considerable amount of covalency in the metal - ligand bond. The magnitudes of covalency parameter and bonding parameter increases from Pr(III) to Sm(III) indicating that the extent of covalent character of metal-ligand bond increases with the increase in atomic number which is in conformity with the lanthanide contraction⁽¹⁶⁾.

IR Studies:

The main IR spectral data has been recorded in Table -2. The broadness of $\nu(\text{NH})$ of the free ligand at 3150 cm^{-1} suggested hydrogen bonding in the solid state. In the spectra of complexes, this band shifted towards lower wave number and appeared around 3060 cm^{-1} , suggesting increased electronegativity of the ring and the absence of deprotonation in the complexes. The spectra of the ligand as well as those of the complexes did not exhibit any band in the 2600 - 2000 cm^{-1} region, indicating that the ligand was present in the thione form⁽¹⁷⁾.

The four ligand bands in the region 1600-1300 cm^{-1} (1460, 1410, 1370 and 1350 cm^{-1}) have been assigned to the thioamide bands I and II arising due to the coupled vibrations of $\delta(\text{NH})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$. In the spectra of the complexes, these bands shifted towards higher wave numbers. Further the blue shift in the band positions suggested the bonding of the metal ions through thiocarbonyl sulphur atom. Two broad bands at 1040 and 820 cm^{-1} of the free ligand shifted towards lower wave

numbers ($\sim 20\text{cm}^{-1}$) in the complexes further confirmed the bonding of metal ion through thiocarbonyl sulphur. One new band which appeared around 300cm^{-1} in the spectra of all the complexes have been assigned to the coupled vibrations of $\nu(\text{M-S})$ ⁽¹⁸⁾.

The free ligand shows a band around $1020 - 1040\text{cm}^{-1}$ due to $\nu(\text{C=S})$. This band disappears in the spectra of complexes and a new band in the range $660-680\text{cm}^{-1}$ appears in the complexes due to $\nu(\text{C-S})$ mode. This data is indicative of sulphur coordination. A medium intensity band observed around 3200cm^{-1} is assigned to the $\nu(\text{OH})$ and $\nu(\text{NH})$ modes. The ligand exhibits the $\nu(\text{C=N})$ in the region $1605-1630\text{cm}^{-1}$ and this band shifts to lower energy side in complexes indicating nitrogen coordination. A shift of the $\nu(\text{C-O})$ phenolic of the ligand ($\sim 1540\text{cm}^{-1}$) to higher energy side by $\sim 20\text{cm}^{-1}$ on coordination constitutes an unambiguous evidence for the formation of phenolic oxygen bond. In the present complexes, the $\nu(\text{C-O})$ phenolic mode shifts to higher energy side by $15-30\text{cm}^{-1}$ in comparison to its position in the ligand spectrum ($1500 - 1520\text{cm}^{-1}$). This indicates the presence of phenolic oxygen atom in metal ligand bond. IR - data are indicative of O, N, and S - donor tridentate mono basic behaviour of the ligand⁽¹⁹⁾.

Several strong absorptions in the spectra of free ligand L2 have been found to exist in $1600-1400\text{cm}^{-1}$ which has been attributed to C-C, C-N and ring stretchings. Bands observed at $420-430$ and $250-260\text{cm}^{-1}$ in the complexes are assigned as $\nu(\text{M-N})$ and $\nu(\text{C1})$. Two weak bands observed are ~ 3420 and 3210cm^{-1} in the thiosemicarbazone spectrum assignable to $\nu_{\text{as}}\text{NH}_2$ and $\nu_{\text{s}}\text{NH}_2$, remain unchanged indicating that NH_2 group is not involved in complex formation⁽²⁰⁻²¹⁾.

Table : 1

Analytical Data of Mixed Ligand Complexes of Lanthanides(III) with 2, 5-Dihydroxy Butyrophenone Thiosemicarbazone(L1) as Primary Ligand and 1,10-Phenanthroline(L2) as Co-ligand

S. No	Complex	% Chemical Analysis ; Found (Calculated)						Mole. Weight Found (Calcd.)	Colour	M.pt. (°C)	Molar Conductance $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
		C	H	N	S	Halogen	Metal				
1	[La L1L2 Cl]Cl	42.90 (42.99)	3.35 (3.42)	10.82 (10.90)	4.90 (4.98)	10.95 (11.06)	21.50 (21.64)	316.00 (641.91)	Green	142	93.86
2	[Ce L1L2Cl]Cl	42.85 (42.91)	3.35 (3.42)	10.78 (10.88)	4.88 (4.97)	10.90 (11.03)	21.65 (21.78)	318.00 (643.12)	Brown	208	79.30
3	[Pr L1L2Cl]Cl	42.78 (42.86)	3.34 (3.41)	10.75 (10.87)	4.88 (4.96)	10.90 (11.02)	21.70 (21.88)	320.00 (643.91)	Brown	162	74.12
4	[Nd L1L2Cl]Cl	42.58 (42.64)	3.30 (3.39)	10.74 (10.81)	4.88 (4.94)	10.85 (10.96)	21.20 (22.28)	319.00 (647.24)	Cream	210	71.10
5	[Sm L1L2Cl]Cl	42.18 (42.24)	3.27 (3.36)	10.60 (10.71)	4.78 (4.89)	10.80 (10.86)	22.90 (23.01)	322.00 (653.35)	Yellow	152	88.45

Table : 2
Main IR Absorption Bands (cm⁻¹) of Mixed Ligand Complexes of Lanthanides(III) with 2, 5-Dihydroxy Butyrophenone Thiosemicarbazone(L1) as Primary Ligand and 1,10-Phenanthroline(L2) as Co-ligand

S. No	Complex	v(C=N)	v(C=S)	v(C-C)	v(C-O)	v(C-N)	v(M-O)	v(M-S)	v(C-S)	v(M-N)	v(Cl)
1	[La L1L2 Cl]Cl	1610sh	1040	1600s	1520m	1490	500m	280w	660m	425w	250w
2	[Ce L1L2Cl]Cl	1620sh	1010	1605s	1510m	1480	515m	285w	670m	420m	255w
3	[Pr L1L2Cl]Cl	1610sh	1020	1600 m	1510m	1470	510m	290w	660m	430w	255w
4	[Nd L1L2Cl]Cl	1620sh	1030	1615w	1500m	1480	515m	288w	680m	425m	260w
5	[Sm L1L2Cl]Cl	1620sh	1020	1610sh	1500m	1470	510m	285w	665m	420w	250w

sh – sharp w – weak m – medium s – strong

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