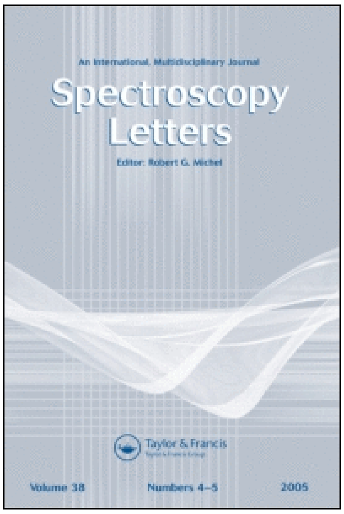

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Structural Study of Lanthanide Complexes Formed with o-Vanillin Salicyloylhydrazone and o-Vanillin Paraanisidine

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STRUCTURAL STUDY OF LANTHANIDE COMPLEXES FORMED WITH o-VANILLIN SALICYLOYLHYDRAZONE AND o-VANILLIN PARAANISIDINE

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ABSTRACT

Ten lanthanide complexes (Ln=La, Ce, Pr, Nd, Sm, Gd, Eu and Dy) with the title ligands have been synthesised and characterised. The structure of these complexes are assigned on the basis of IR spectra, magnetic and thermal analysis data. The IR spectra indicate that o-vanillin paraanisidine (oVPA) is a bidentate ligand coordinating through azomethine N and phenolic O whereas o-vanillin salicyloylhydrazone (oVSH) is tridentate possessing ketonic O as an additional donor site. Involvement of anions (Cl^-, Ac^-) in coordination is explored. Electronic spectra indicate weak covalent nature of metal ligand bond and various parameters β, $b^{1/2}$, η and δ have been evaluated.

INTRODUCTION

There has been considerable interest in the coordination chemistry of lanthanides especially concerning specific features of Ln^{3+} spectra to give information regarding structure and composition of complexes. They find application in colour translating fluorescent screens, surface coating and NMR shift reagents[1,2]. As part of our programme for the synthesis and characterization of solid lanthanide complexes, isolation of ten such complexes, obtained from o-vanillin derivatives, viz. o-vanillin salicyloylhydrazone (oVSH) and o-vanillin paraanisidine (oVPA) are reported. The acetates or chlorides of La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Eu^{III} and Dy^{III} are employed and their complexes studied by IR spectra, magnetic and thermal studies. The nephelauxetic effect(β), bonding parameter ($b^{1/2}$), Sinha's parameter(δ) and angular covalency parameter(η) have been calculated from their electronic spectra. The exchange processes in oVSH and its zinc complexes have also been studied by two dimensional NMR and described elsewhere[3,4].

EXPERIMENTAL

Materials :

o-Vanillin, paraanisidine, hydrazine hydrate, methylsalicylate, DMF (all Sisco Chem.) were employed. Salicylolylhydrazide was synthesised in the laboratory.

Synthesis of o-Vanillin paraanisidine :

Ethanolic solution of o-vanillin (0.05 mol, 7.6 g) and ethanolic solution of paraanisidine (0.05 mol, 6.15 g) was mixed in the 1:1 ratio and refluxed over heating mantle at 90°C for 5h. This brown coloured solution was left overnight at 0°C. The crystalline product was filtered, washed with acetone and dried over calcium chloride in vacuum. oVSH was synthesised as described earlier. Both oVSH and oVPA are characterised from their elemental analysis, IR and NMR spectra[4].

Synthesis of lanthanide complexes

Complexes of oVSH and oVPA were synthesised by refluxing 0.005 mol solution of oVSH (in DMF) or oVPA (in EtOH) together with an ethanolic solution of the different 0.005 mol of lanthanide salt in 1:1 molar ratio on a heating mantle (at 40°C) for 6h. After cooling this solution few drops of ammonia was added to increase the pH. The insoluble complexes thus prepared were filtered off, washed with ethanol and dried over anhydrous $CaCl_2$. [0.005 mol of lanthanide salt solution contains (1.71g of $La(CH_3COO)_3 \cdot 1\frac{1}{2}H_2O$, 1.58 g or $Ce(CH_3COO)_3 \cdot 4H_2O$, 1.28g of $SmCl_3$ 2.03g of $Gd(CH_3COO)_3 \cdot 4H_2O$, 1.69g of $Eu(CH_3COO)_3 \cdot H_2O$, 1.34g of $DyCl_3$ or 1.87g of $LaCl_3 \cdot 7H_2O$, 1.23 g of $CeCl_3$, 1.23 g of $PrCl_3$ and 1.25 g of $NdCl_3$ employing 1.43 g of oVSH or 1.28 g of oVPA].

All the complexes are air stable, have different colours and are insoluble in water, ethanol and other common organic solvents. The yield was found to be 50-55% in all the complexes.

Analytical and spectral measurements

The lanthanide content of the complexes was determined by oxalate-oxide method[5] and C,H,N by microanalysis. The IR spectra were recorded on an Acculab 10 spectrophotometer in the range 4000-200 cm^{-1} using CsI pellets. The room temperature magnetic data were obtained by Gouy's method using $Hg[Co(SCN)_4]$ as a calibrant. The TG studies were carried on a Perkin-Elmer Thermal Analyser (heating rate = 10-15°C/min in nitrogen atmosphere). The solid state electronic spectra were recorded on a Perkin-Elmer 2300 spectrophotometer using MgO pellets in the range 200-1000nm.

RESULTS AND DISCUSSION

Composition

The analytical data of the complexes (Table-I) reveal that the complexes have 1:1 stoichiometry having the general formulae (i) $[M(L)X.2H_2O]$ where H_2L = o-Vanillin salicyloylhydrazone, M(III) = La, Ce, Sm, Gd, Dy or Eu and X = CH_3COO^- or Cl^-. (ii) $[M(L')Cl_2.2H_2O]$. Where HL' = o-Vanillinparanisidine, M(III) = La, Ce, Pr, or Nd.

TABLE-I : Physical Characterstic, Analytical and Magnetic Data of o-Vanillin Salicyloylhydrazone, o-Vanillin-paraanisidine and their Complexes.

No.	Compound	Colour	M.P. (°C)	Elemental analysis(%)				μ (B.M.)
				Carbon found (Calcd)	Hydrogen found (Calcd)	Nitrogen found (Calcd)	Metal found (Calcd)	
I.	H_2L	White	280°	62.35 (62.96)	4.75 (4.89)	9.71 (9.78)	-	-
II.	$[La(L)CH_3COO.2H_2O]$	Yellow	360°	39.40 (39.41)	3.57 (3.66)	6.58 (6.40)	27.20 (26.81)	Diam.
III.	$[Ce(L)CH_3COO.2H_2O]$	Brown	320°	39.60 (39.31)	3.51 (3.69)	6.00 (5.39)	26.90 (26.98)	2.8
IV.	$[Sm(L)Cl.2H_2O]$	Yellow	360°	35.06 (35.61)	3.24 (3.16)	5.50 (5.53)	30.27 (29.74)	3.9
V.	$[Eu(L)CH_3COO.2H_2O]$	Yellow	360°	38.00 (38.44)	3.42 (3.57)	5.66 (5.27)	29.70 (28.61)	4.1
VI.	$[Gd(L)CH_3COO.2H_2O]$	Yellow	360°	38.26 (38.06)	3.00 (3.54)	5.12 (5.22)	29.53 (29.31)	8.3
VII.	$[Dy(L)Cl.2H_2O]$	Brown	360°	33.64 (34.77)	3.14 (3.08)	5.20 (5.40)	31.78 (31.36)	9.8
VIII.	HL'	Brown	230°	69.72 (70.06)	6.04 (5.83)	6.82 (5.44)	-	-
IX.	$[La(L')Cl_2.2H_2O]$	Yellow	250°	35.76 (35.89)	3.24 (3.58)	2.68 (2.78)	28.52 (27.67)	Diam.
X.	$[Ce(L')Cl_2.2H_2O]$	Brown	260°	35.00 (35.00)	3.54 (3.57)	2.60 (2.70)	25.86 (27.84)	4.2
XI.	$[Pr(L')Cl_2.2H_2O]$	Yellow	265°	35.64 (35.75)	3.48 (3.57)	2.44 (2.77)	28.34 (27.96)	4.2
XII.	$[Nd(L')Cl_2.2H_2O]$	Yellow	360°	35.15 (35.51)	3.33 (3.54)	2.50 (2.70)	26.62 (28.43)	5.1

Where HL' = oVPA and H_2L = oVSH.

Infrared spectral studies

Definite IR spectral data (Table-II) has shown that oVSH exists in keto form in the solid state as the characteristic bands appear at 1602 cm^{-1} due to C=O stretching in the ligand [6,7], which is not observed in oVPA, obviously due to absence of C=O group. Characteristic phenolic (OH) stretching frequency due to presence of hydroxy group at ortho position are observed in oVSH and oVPA at 3200-3400 cm^{-1} respectively. oVSH exhibit ν(N-H) band at 3240 cm^{-1}[8]. Both the ligands oVSH and oVPA show characteristic band at 1565, 1600 due to ν(C=N)[9] indicating the formation of Schiff base[10,11]. Bands appearing at 1455, 1450 cm^{-1} are due to ν(C-O) phenolic and at 1070 cm^{-1} due to ν(N-N) in oVSH[12]. A broad band is observed at 3200-2800 cm^{-1} in oVSH due to intramolecular hydrogen bonding between C=O and OH of salicyloylhydrazide. The disappearance of ν(OH) from the spectra of complexes II, III, IV, V, VI, VII, IX, X, XI, and XII indicates the involvement of phenolic oxygen in coordination through deprotonation[13]. ν(C=N) band is shifted to higher frequencies in complexes II, III, IV, V, VI, VII, IX, X, XI and XII by 30-40 cm^{-1} suggesting the involvement of azomethine nitrogen in coordination[14-16]. This fact is further evidenced by the presence of new band in the spectra of oVSH complexes at 1530-40 cm^{-1} due to ν(>C=N-N-C<)[17,18]; band of oVSH ν(NH) is not observed in its complexes II, III, IV, V, VI and VII whereas a negative shift is observed by 80-100 cm^{-1} due to ν(C-O) phenolic in complexes II, III, IV, V, VI, IX, X, XI and XII. Nonparticipation of methoxy group during coordination is indicated by its negligible shift in $\nu(OCH_3)$ at ~2720 cm^{-1}.

New bands are observed at 3400 cm^{-1} due to coordinated water molecule ($H_2O \longrightarrow M \longleftarrow OH_2$) in all complexes of oVSH and oVPA[19,20]. The corresponding OH bending vibrations have been observed at 1600 and rocking vibrations between 730-750 cm^{-1}.

TABLE II: IR Spectral bands(cm^{-1}) of oVSH, oVPA and their metal complexes.

oVSH	Complex						oVPA	Complexes				
I	La(III) II	Ce(III) III	Sm(III) IV	Eu(III) V	Gd(III) VI	Dy(III) VII	VIII	La(III) IX	Ce(III) X	Pr(III) XI	Nd(III) XII	Assignments
3200	3220	3200	3210	3400	3400	3400	3400	3400	3400	3400	3400	ν(OH)phenolic or Water
3240	-	-	-	-	-	-	-	-	-	-	-	ν(NH)
3100	3100	3100	3100	3120	3100	3100	2900	2900	2900	2900	2900	ν(CH)
2720	2720	2730	2720	2720	2720	2720	2800	2800	2800	2800	2800	$\nu(OCH_3)$
1602	-	-	-	-	-	-	-	-	-	-	-	ν(C=O)
1565	1585	1595	1585	1595	1585	1585	1600	1640	1630	1620	1610	ν(C=N)
-	1530	1540	1540	1530	1540	1540	-	-	-	-	-	ν(>C=N-N=C<)
1540	-	-	-	-	-	-	-	-	-	-	-	Amide II
1455	1430	1430	1430	1430	1440	1450	1450	1440	1440	1440	1440	ν(C-O)phenolic
-	1480	1460	1470	1480	1490	-	-	-	-	-	-	ν_{asy}(OCO)
-	1360	1370	1370	1380	1370	1390	-	-	-	-	-	ν_{sy}(OCO)
1075	1020	960	1020	1030	960	1020	-	-	-	-	-	ν(N-N)
-	750	740	740	750	740	730	-	740	740	730	730	γ H_2O(rocking)
629	-	-	-	-	-	-	-	-	-	-	-	Amide IV
535	-	-	-	-	-	-	-	-	-	-	-	Amide VI
-	420	450	500	500	520	480	-	520	450	500	480	ν(M-N)
-	380	375	370	380	450	400	-	400	350	380	400	ν(M-O)
-	-	-	250	-	-	240	-	250	250	280	240	ν(M-Cl)

Coordination of acetate ion in complexes II, III, V and VI is supported by the appearance of two bands at 1490–1460, 1390–1360 cm^{-1} due to $\nu_{as}(COO^-)$ and $\nu_{sy}(COO^-)$ modes respectively[21]. In complexes IV, VII, IX, X, XI and XII a medium intensity band is observed at 280–250 cm^{-1} due to the coordinated chloride ion. The non-ligand bands appearing at 520–420 and 450–350 cm^{-1} are assigned to ν(M–N) and ν(M–O) modes respectively[22,23].

Electronic spectral and magnetic studies

Most of the absorption bands due to f-f transitions of the lanthanide ions in the visible region are obscured due to the broad charge transfer bands. However in the Pr(III), Nd(III), Sm(III) and Eu(III) complexes f-f band are observed. The electronic absorption bands of Pr(III), Nd(III) and Sm(III) appear due to the transitions arising from the ground level $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$ to excited J-levels of $4f^n$ configuration respectively. Pr(III) complexes of oVPA show bands around 25000 and 16891 cm^{-1} corresponding to transition from $^3H_4$ to $^3P_2$ and $^4D_2$ energy levels. Nd(III) complex of oVPA shows bands around 25510, 20833, 17241, 15822 and 12820 cm^{-1} assignable to transitions from $^4I_{9/2}$ level to $^2P_{1/2}$, $^4G_{9/2}$, $^4G_{4/2}$, $^4F_{9/2}$ and $^4F_{5/2}$ energy level respectively. Samarium (III) complex of oVSH shows band around 25000, 20833 and 17857 cm^{-1} corresponding to energy levels $^4F_{9/2}$, $^4G_{7/2}$ and $^4G_{5/2}$ respectively.

The nephelauxetic effect $(\beta)^{24}$, bonding parameter ($b^{1/2}$), Sinha's parameter(δ) and angular covalency parameter (η) have also been calculated. The bonding parameter reflects the extent of participation of 4f-orbitals in the complexation. The positive values of $b^{1/2}$ for the present complexes show covalent nature of metal ligand bond. It is also supported by the calculated values of β in complexes Sm-oVSH (0.996), Pr-oVPA (0.993) and Nd-oVPA (0.990). Here the values of δ(%) in Sm-oVSH (0.400), Pr-oVPA

TABLE III: Electronic Spectral Data (cm^{-1}) and Parameters

Compound	band maxima (cm^{-1})	Assignment	Spectral parameter			
			β	$b^{1/2}$	δ	η
$[Sm(L)Cl.2H_2O]$	25000	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.996	0.044	0.400	0.003
	20833	$\rightarrow {}^4G_{7/2}$				
	17857	$\rightarrow {}^4G_{5/2}$				
$[Gd(L)CH_3COO.2H_2O]$	Intra-ligand transition	-	-	-	-	-
$[Pr(L')Cl_2.2H_2O]$	25000	$^3H_4 \rightarrow {}^3P_2$	0.993	0.654	0.059	0.004
	16891	$\rightarrow {}^4D_2$				
	15625					
	12195					
$[Nd(L')Cl_2.2H_2O]$	25510	$^4I_{9/2} \rightarrow {}^2P_{1/2}$	0.990	0.069	0.96	0.006
	20833	$\rightarrow {}^4G_{9/2}$				
	17241	$\rightarrow {}^4G_{4/2}$				
	15822	$\rightarrow {}^4F_{9/2}$				
	12820	$\rightarrow {}^4F_{5/2}$				

(0.059) and Nd-oVPA (0.960) are found much below 1.5, which also suggest weak covalent bonding as well as weak metal-ligand interaction.

Lanthanum acetate and lanthanum chloride complexes of oVSH and oVPA are diamagnetic whereas the other lanthanide complexes are paramagnetic. The experimental magnetic moment (Table-I) of the complexes agree well with the theoretical values calculated by Van-Vleck formula in most of the cases indicating the non-participation of 4f electrons in bonding.

Thermogravimetric analysis

The composition of the complexes and IR spectral studies indicate the association of two molecules of water within coordination sphere of the metal which is further supported by TG data. The thermogram of the metal complexes exhibit loss of water at high temperature suggesting that water molecules are present in the coordination sphere. The nature of decomposition of individual complexes is stated below.

La(III)-oVSH complex in its thermogram indicates that the complex is stable upto 120°C then it starts losing water gradually and the loss continues upto 250°C. The total loss of water is equivalent to two moles. The complex undergoes decomposition at temperature 285°C, this sharp decomposition continues upto 355°C as shown by steep fall in curve. The decomposition continues upto 600°C corresponding to the formation of La_2O_3. The presence of two water molecules in Ce(III), Sm(III), Eu(III) and Dy(III) complexes of oVSH is further confirmed by the observed percentage weight loss of 6.0, 6.5, 6.2 and 6.5 which is approximately equal to the calculated values of 6.9, 7.7, 6.7 and 6.9 respectively. The temperature range of water loss is 100–290°C for oVSH complex. These molecules are coordinated to the complex and are not lattice

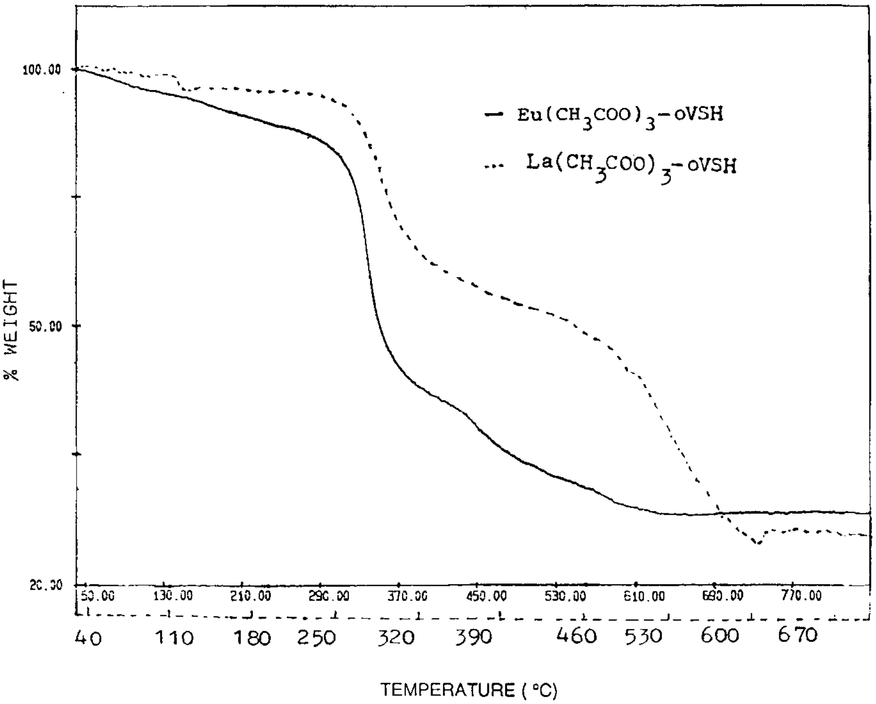

Fig.I TG CURVES OF COMPLEX

water molecule as the loss occurs at quite high temperature (200–340°C). The decomposition product of all the complexes does not exactly match any single oxide which may be a mixture of oxides. The formation of intermediate product is confirmed by the presence of one or two plataeu in their thermograms.

The presence of two water molecules in La(III), Ce(III), Pr(III) and Nd(III) complexes of oVPA is further confirmed by the observed percentage weight loss 7.0, 6.3, 6.8 and 6.8 which is approximately equal to the calculated values of 7.1 in each case respectively. The temperature range of water loss is 100–180°C for oVPA complexes. oVPA complexes decomposed between 120–220°C. Some typical thermograms are also shown in fig I.

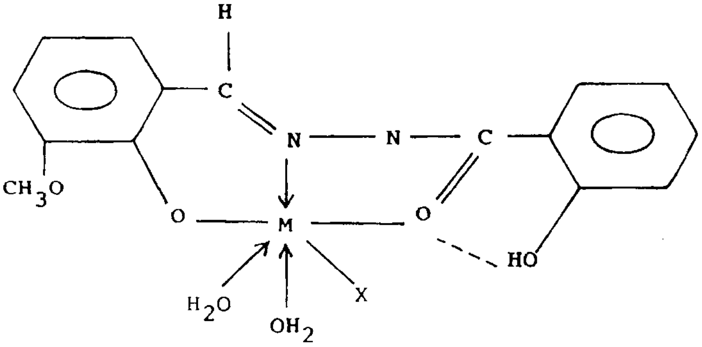

Fig.II [M(L) X $2H_2O$]

M(III) = La, Ce, Sm, Eu, Gd, Dy

H_2L = **oVSH**

X = CH_3COO, Cl

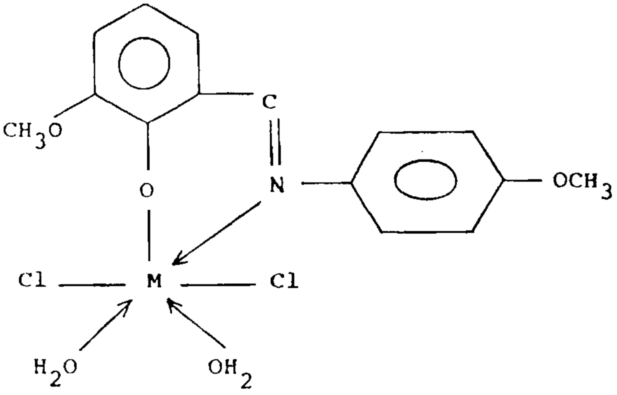

Fig.III [M(L') $Cl_2 \cdot 2H_2O$]

M(III) = La, Ce, Pr, Nd

HL' = **oVPA**

CONCLUSION

The structural studies are discussed largely in the light of elemental, magnetic measurements,diffuse reflectance spectra and IR analysis. The ligand oVSH acts as a tridentate in nature coordinating through azomethine nitrogen and two phenolic groups whereas oVPA behaves as a bidentate ligand coordinating through phenolic oxygen and azomethine N only. The valency of the metal ion is neutralised by these ligand molecules and anions (chloride, acetate) thus leading to the formation of a stable neutralized structure. The other coordination sites are occupied by water molecule. The structures encountered in this paper has been illustrated below showing all the positions of coordination sites. (Fig.II & III).

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