

Synthesis and Characterization of Mixed Ligand Complexes of Lanthanides(III)

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Mixed ligand complexes of rare earth ions La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} and Dy^{3+} with *ortho*-vanillinmonoxime as the primary ligand and 8-hydroxyquinoline(oxine), thiourea as the secondary ligands have been prepared and characterized on the basis of their elemental analysis, electronic, infrared and NMR spectra, thermal analysis and conductivity measurements. A study of ultraviolet spectra gave an evidence about complexation. Visible spectra of Pr^{3+} , Nd^{3+} and Sm^{3+} complexes indicated nephelauxetic effect in these complexes. The covalency parameter and $\delta\%$ covalency indicate strong interaction of lanthanide ions and the ligands. The shift in the characteristic infrared frequencies of free ligand band confirms the centres of coordination. Thermal analysis indicated the presence of coordinated water molecules. The molar conductance in DMF and DMSO indicated that the 8-hydroxyquinoline complexes behaved as non-electrolyte while the thiourea complexes behaved as 1 : 1 electrolyte system.

Key Words: Lanthanide mixed ligand complexes, Thiourea, Vanillinmonoxime, 8-Hydroxyquinoline.

INTRODUCTION

Lanthanide ions are known to pose interesting bonding possibilities with various types of ligands. Rare earths have acquired significant applications both in diagnostic and remedial purposes¹⁻³. Recently extensive investigations have been carried out in the synthesis and biological activity of heterocyclic compounds and their complexes⁴. In this investigation studies of lanthanide complexes using *o*-vanillinmonoxime (*o*-VMO) as the primary ligand and 8-hydroxyquinoline (oxine) and thiourea (TU) as the secondary ligands are reported.

EXPERIMENTAL

Materials and the experimental details were essentially the same as described earlier⁵.

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RESULTS AND DISCUSSION

The elemental analysis of the complexes shows that the complexes have 1 : 2 : 1 (metal : *o*-VMO : 8-hydroxyquinoline) and 1 : 2 : 5 (metal : *o*-VMO : thiourea) stoichiometry. Two and one water molecules are present respectively in these complexes. Analytical data of the two representative complexes are given in Table-1.

TABLE-1
ANALYTICAL DATA OF MIXED LIGAND COMPLEXES OF LANTHANIDES(III)

Compound	% Found (Calculated)					
	C	H	M	N	S	Cl
[Pr(<i>o</i> -VMO) ₂ (Oxine) ₁ ·2H ₂ O]	45.22 (45.96)	3.82 (4.01)	20.92 (21.57)	5.69 (6.43)	—	—
[Sm(<i>o</i> -VMO) ₂ (Oxine) ₁ ·2H ₂ O]	44.98 (45.30)	3.73 (3.95)	22.42 (22.69)	5.80 (6.34)	—	—
[Pr(<i>o</i> -VMO) ₂ (TU) ₅ H ₂ O]Cl	27.09 (27.80)	3.97 (4.22)	14.96 (15.33)	18.02 (18.53)	17.56 (17.67)	3.24 (3.91)
[Sm(<i>o</i> -VMO) ₂ (TU) ₅ H ₂ O]Cl	27.02 (27.51)	3.94 (4.18)	16.20 (16.41)	18.07 (18.33)	16.92 (17.49)	3.56 (3.87)

o-VMO = *ortho*-vanillinmonoxime, oxine = 8-hydroxyquinoline, TU = thiourea.

Ultraviolet spectra were recorded in methanol. The primary ligand *ortho*-vanillinmonoxime exhibits three bands at 220, 260 and 310 nm (log ϵ 4.63, 4.36, 3.72 respectively). The secondary ligand 8-hydroxyquinoline exhibits three bands at 206, 240 and 310 nm (log ϵ 4.33, 4.63, 3.46 respectively) and thiourea exhibits two bands at 204, 240 nm (log ϵ 4.18, 4.25 respectively). In the 8-hydroxyquinoline mixed complexes 5 bands are observed at 208, 220, 240, 255 and 320 nm. In the thiourea mixed complexes three bands are observed at 205, 240 and 330 nm. Merging of bands and intensification of absorption indicate a strong interaction between ligands and lanthanide ions.

The electronic spectra of the complexes in the visible region were recorded in DMSO. Nephelauxetic effect was observed on complexation. Covalency parameter $b^{1/2}$ and Sinha's parameter $\delta\%$ were calculated^{6,7}. For Pr(III) mixed ligand complexes the covalency $b^{1/2}$ and $\delta\%$ values are in the range 0.041–0.071 and 0.034–1.02 respectively, while for Nd(III) complexes the values are in the range 0.036–0.087 and 0.271–1.571 respectively. Only one band could be located in Sm(III) 8-hydroxyquinoline mixed ligand complex with $b^{1/2}$ and $\delta\%$ values as 0.103 and 2.15 respectively. In the thiourea mixed complexes characteristic Sm(III) bands could not be located. The positive values of $b^{1/2}$ and $\delta\%$ strongly support the covalent nature of bond between the ligand and lanthanide ions and also indicate involvement of *f*-orbital in the bond formation.

Primary ligand *o*-VMO exhibits an infrared band at 3330 cm⁻¹ due to OH stretch of oxime. In all the *o*-VMO-oxine mixed ligand complexes a band is located around 3280–3100 cm⁻¹ indicating involvement of nitrogen of N—OH group in bond formation without the elimination of oxime proton. The band due

to phenolic —OH group of secondary ligand oxine is merged with the OH band of the primary ligand and observed with lowering in frequency. The band at 3110 and 3050 cm^{-1} assignable to intermolecular hydrogen bonding of phenolic OH in the *o*-VMO could not be observed in any of the mixed complexes which indicates the bonding of *o*-VMO through elimination of phenolic proton. The bands at 1615 and 1655 cm^{-1} due to (C=N) stretch are observed with lowering in frequency and decrease in intensity indicating the presence of N → M bonding in the mixed complexes. The (N—O) stretch of the primary ligand at 965 cm^{-1} is observed with lowering around 950–940 cm^{-1} in the mixed complexes. From the above observation one can conclude that the primary ligand *o*-VMO is bonded to the lanthanide ions through nitrogen of oxime and phenolic oxygen. During complexation oxime proton is not eliminated but the phenolic proton is eliminated.

The secondary ligand oxine exhibits bands at 1575 and 1495 cm^{-1} due to (C=C) and (C=N) vibrations of pyridine ring. These bands are observed with slight lowering in the mixed complexes. The band around 1090 cm^{-1} in the free ligand oxine due to C—O stretch is shifted to 1100 cm^{-1} with change in intensity indicating (O—M) bond formation.

The secondary ligand thiourea exhibits three bands around 3340, 3225 and 3140 cm^{-1} due to (N—H) stretch frequencies. In the mixed complexes it is observed that the (N—H) stretch frequencies of thiourea remained practically unchanged indicating nitrogen of thiourea is not involved in bond formation. The OH stretch of primary ligand is merged with (N—H) stretch of the secondary ligand. The band at 1575 cm^{-1} due to NH_2 deformation of thiourea remained unchanged in the mixed complexes. The N—C—N asymmetric stretch at 1455 cm^{-1} is slightly lowered in the mixed complexes. The bands around 1420 and 1375 cm^{-1} in the free ligand thiourea due to (C=S) stretch are observed with reduction in intensity and slight shifting of the 1375 cm^{-1} band to higher frequency indicating that the secondary ligand thiourea is bonded through sulphur. The lowering of 735 cm^{-1} band of thiourea due to (C=S) stretch with some contribution from N—C—N stretch supports bonding through sulphur. From the above observations it can be concluded that the primary ligand *o*-VMO acts as bidentate ligand and the secondary ligand thiourea as monodentate ligand bonding through sulphur.

The primary ligand *o*-VMO exhibits three NMR proton signals at δ 3.9 δ 6.75–6.95 (cluster) and δ 8.2 assignable to the proton of methoxy, phenyl and intramolecularly bonded OH groups respectively. In the La(III) and Pr(III) mixed complexes the methoxy and phenyl proton signals are observed without much variation. The NMR signal at δ 8.2 could not be observed in the complexes indicating elimination of phenolic proton during complexation. The downfield shift in H_2 and H_7 proton signal at δ 8.75 and δ 8.15–8.25 respectively in 8-hydroxyquinoline mixed complexes indicates bonding through oxygen and nitrogen. The NH_2 proton signal at δ 7.25 in the free ligand thiourea is observed without much change in the mixed complexes indicating non-involvement of nitrogen in bond formation and indirectly supporting bonding through sulphur.

Thermal analytical data indicate presence of water molecule. Thermal analysis

of samarium *o*-vanillinmonoxime-oxine/thiourea complexes was carried out to study the nature of water molecules. As the water molecules are eliminated above 160°C it can be concluded that the water molecules are present in coordinated sphere. Organic part of the molecule is lost in stages with initial loss of thiourea and oxine in the respective complexes around 350°C and subsequent loss of *o*-VMO leading to the formation of the sesquioxide around 750°C.

The molar conductance of the representative samples is measured in DMF and DMSO. The molar conductance values of *o*-VMO-oxine mixed ligand complexes are in the range 12.27–23.67 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ in the solvent DMF and 10.38–22.02 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ in the solvent DMSO. These values indicate that the mixed complexes behave as non-electrolytes. The molar conductance values of *o*-VMO-thiourea mixed ligand complexes are in the range 84–107 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ in DMF and 62–79 $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ in DMSO solvent. These values being in close agreement with the values reported^{8,9} for 1 : 1 electrolyte system in these solvents, thus it can be concluded that the thiourea mixed ligand complexes behave as 1 : 1 electrolyte system.

Conclusion

From the above observations the, probable structure, electrolyte system and probable coordination number for the complexes studied in this investigation can be summarized as follows:

<i>Complex</i>	Electrolyte system	Probable coordination number
$[\text{Ln}(\textit{o}\text{-VMO})_2(\text{oxine})_1 \cdot 2\text{H}_2\text{O}]$	Non-electrolyte	8
$[\text{Ln}(\textit{o}\text{-VMO})_2(\text{TU})_5 \cdot \text{H}_2\text{O}] \text{Cl}$	1 : 1	10

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