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Synthesis and Characterisation of Lanthanide Mixed Complexes Using *Ortho*-vanillinmonoxime and Phenylureas as Ligands

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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 primary ligand and N-phenylurea and N,N′-diphenylurea as secondary ligands have been prepared and characterised on the basis of their elemental analysis, electronic and infrared spectra, thermal analysis and conductivity measurements.

INTRODUCTION

Several lanthanide complexes with various oximes have been reported[1–4]. Recently much interest has been shown in the preparation and characterisation of lanthanide mixed complexes[5–8]. We report here the preparation and characterisation of mixed ligand complexes of lanthanides using *ortho*-vanillinmonoxime (*o*-VMO) as the primary ligand and N-phenylurea (NPU) and N,N′-diphenylurea (DPU) as the secondary ligands.

EXPERIMENTAL

Spectroscopically pure rare earth oxides obtained from Indian Rare Earths Ltd., Kerala, were used after ascertaining purity by measuring the absorbance of the samples as chlorides in aqueous solution. *Ortho*-vanillinmonoxime was prepared in the laboratory from *o*-vanillin by oximation[9]. The secondry ligands used in this investigation, *i.e.*, N-phenylurea and N,N′-diphenylurea were synthesised adopting the procedure described by Vogel[10]. The ultraviolet and visible spectra were recorded on Shimadzu UV and visible spectrophotometer model UV240. The IR spectra were recorded on Beckmann spectrophotometer in KBr disc at RSIC, CDRI, Lucknow. All conductance measurements were carried out on systronics conductivity meter type 303. Thermal analysis was carried out at RSIC, Nagpur, using Perkin-Elmer TGS-2 thermogravimetric system.

The complexes were synthesised by the method of Rao *et al.*[2]. To a weighed amount of $LnCl_3 \cdot 6H_2O$ in ethanol, a calculated amount of *o*-vanillinmonoxime in ethanolic solution was added (keeping the metal to ligand ratio *ca.* 1 : 3). The

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pH of the solution was adjusted to 5.8 by the addition of alcoholic ammonia. The solution was concentrated on steam bath, when the desired solid complex separated. The complexes were washed with ether to remove excess ligand. The complexes were further purified from ethanol and vacuum dried over fused calcium chloride for 48 h. The composition of the complexes was found to be Ln(*o*-VMO)$_2$Cl·2H$_2$O. These lanthanide *ortho*-vanillinmonoximates were used in the preparation of mixed complexes.

The mixed complexes were prepared by mixing a weighed amount of lanthanide *ortho*-vanillimonoximate in ethanol with a calculated amount of the secondary ligand in an ethanolic solution keeping the metal: ligand ratio 1 : 3 : 5. The mixture was stirred and alcoholic ammonia was added dropwise to short of neutralisation point. The pH of the solution was found to be 5.8. The resulting solution was concentrated on a steam bath, when the solid complex separated. The excess of ligand was washed with ether. The complexes were further purified from ethanol and vacuum dried over fused calcium chloride for 48 h.

The elemental analysis of the complexes corresponds to 1 : 2 : 3 (metal : *o*-vanillinmonoxime : either N-phenylurea or N,N′-diphenylurea) stoichiometry. Two water molecules are present per lanthanide ion. The analytical data of the two representative complexes of each series is given in Table 1.

TABLE-1
ANALYTICAL DATA OF MIXED COMPLEXES

Compound	% Analysis, Found (Calcd)				
	C	H	M	N	Cl
Pr(*o*-VMO)$_2$(NPU)$_3$Cl·2H$_2$O	45.50 (46.52)	4.75 (4.81)	14.63 (14.77)	11.20 (11.73)	3.30 (3.71)
Sm(*o*-VMO)$_2$(NPU)$_3$Cl·2H$_2$O	45.12 (46.06)	4.72 (4.77)	15.23 (15.53)	11.40 (11.60)	3.35 (3.69)
Pr(*o*-VMO)$_2$(DPU)$_3$Cl·2H$_2$O	55.30 (55.81)	4.94 (4.90)	11.31 (11.91)	9.22 (9.47)	2.78 (3.00)
Sm(*o*-VMO)$_2$(DPU)$_3$Cl·2H$_2$O	55.30 (55.37)	4.70 (4.86)	12.61 (12.61)	9.09 (9.39)	2.69 (2.97)

RESULTS AND DISCUSSION

Ultraviolet spectra: In this region band shifts and intensity alterations of the ligands alone indicate the involvement of ligands in complexation with the lanthanide ions. The primary ligand *ortho*-vanillinmonoxime exhibits three bands at 220, 260 and 310 nm (log ε 4.66, 4.19 and 3.50 respectively). The secondary ligand N-phenylurea exhibits two bands at 204 nm (log ε 4.38) and 236 nm (log ε 4.39). In the *o*-VMO-NPU mixed complexes four bands are observed at 205, 235, 265 and 320 nm (log ε 4.77, 4.71, 4.30 and 3.63 respectively). The secondary ligand $N'N_i$-diphenylurea exhibits two bands at 208 nm (log ε 4.27) and 253 nm (log ε 4.65). In the *o*-VMO-DPU mixed complexes three bands are observed around 210, 253 and 315 nm with log ε values 4.93, 5.23 and 3.70 respectively.

Such a merging of the bands, intensification of absorption indicate the involvement of ligands in complexation with lanthanide ions.

Visible Spectra: 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 parameter ($\delta\%$) were calculated[11, 12]. The Pr(III) complexes show two bands with red shift at 470 and 596 nm; the $b^{1/2}$ and $\delta\%$ values are 0.0065, 0.071 and 0.86, 1.02 respectively. The Nd(III) complexes show characteristic λ_{max} with red shift at 524, 582, 738, 750 and 802 nm; the $b^{1/2}$ and $\delta\%$ values are 0.062, 0.085, 0.073, 0.089, 0.035 and 0.77, 1.57, 1.10, 1.62, 0.25 respectively. The positive values of $b^{1/2}$ and $\delta\%$ values strongly support the covalent nature of the band and also indicate involvement of 'f' orbital in bond formation.

Infrared spectra: The primary ligand *o*-VMO exhibits a band around 3330 cm^{-1} due to O—H stretch of oxime and the secondary ligand NPU exhibits two bands at 3400 and 3300 cm^{-1} due to N—H stretch frequency. In the mixed complexes these bands are lowered and observed between 3316 to 3280 cm^{-1} which indicate involvements of nitrogen of oxime group without elimination of oxime proton and nitrogen of NPU in bond formation. The bands 3110 cm^{-1} and 3050 cm^{-1} assignable to intramolecular hydrogen bonding of phenolic —OH in the *o*-VMO could not be observed in any of the complexes which indicate the bonding of the *o*-VMO through phenolic oxygen with the elimination of phenolic proton. The bands at 1615 cm^{-1} and 1655 cm^{-1} in *o*-VMO assignable to C═N stretch and the bands at 1660 cm^{-1} and 1590 cm^{-1} in NPU assignable to C═O and NH_2 bending mixed vibration are observed around 1660 cm^{-1} in the mixed complexes indicating NPU is coordinated through nitrogen. This is also supported by lowering of NH_2 bending frequency of NPU at 1620 cm^{-1} in all the mixed complexes. The N—C—N asymmetric stretch of NPU at 1445 cm^{-1} is split into two inflections and observed around 1450 cm^{-1} and 1402 cm^{-1} in the mixed complexes again supporting involvement of nitrogen of NPU in bonding. The N—O stretch of oxime of *o*-VMO is observed around 956–945 cm^{-1} in the mixed complexes. From these observations it can be concluded that the primary ligand *o*-VMO acts as bidentate ligand and is bonded to the lanthanide ions through nitrogen of oxime and phenolic oxygen. During complexation oxime proton is not eliminated but phenolic proton to eliminated. The secondary ligand NPU has acted as a monodentate ligand and coordinates through nitrogen.

The secondary ligand DPU exhibits two bonds of 3340 cm^{-1} and 3280 cm^{-1} due to N—H stretch frequency. In the mixed complexes this gave a composite picture with 3330 cm^{-1} band of *o*-VMO due to OH stretch of oxime and a broad band around 3290–3240 cm^{-1} is observed in the mixed complexes. The C═O stretch band at 1650 cm^{-1} of DPU has been lowered and observed around 1616 cm^{-1} in the mixed complexes. This lowering of the band confirmed bonding of DPU through oxygen in the complexes. The bonds at 1595 cm^{-1} and 1555 cm^{-1} of DPU assignable to NH deformation and aromatic ring vibration. In the mixed complexes two bands are located around 1580 cm^{-1} and 1545 cm^{-1} indicating lowering of C═N stretch of primary ligand *o*-VMO, while practically there is no change in NH deformation and aromatic ring vibration of DPU. The NH rocking made of DPU at 1155 cm^{-1} remains almost unaffected in all the complexes, further supporting non-involvement of nitrogen in bonding. The N—O stretch of primary ligand *o*-VMO is observed with lowering in frequency between 950–930 cm^{-1}. From these observations it can be concluded that the primary ligand *o*-VMO acts as a bidentate ligand where nitrogen of oxime group and oxygen of phenolic group are the centres of coordination and secondary ligand DPU is bonded through oxygen.

Thermal Analysis: Analytical data indicates the presence of two water molecules which has also been supported by IR spectra of the complexes. A study of thermal analysis of samarium-*ortho*-vanillinmonoxime-NPU/DPU mixed complexes indicated a weight loss at 150°C corresponding to the elimination of one water molecule indicating its presence as lattice water. At 180°C experimental and theoretical weight loss calculations indicate elmination of second water molecule which confirms the presence of one coordinated water molecule. Organic part of the molecule is lost in stages with initial loss of NPU/DPU around 300°C and subsequent loss of *o*-VMO leading to formation of sesquioxide around 600°C.

Conductivity Measurements: The molar conductances of the representative samples measured in DMF are in the range 37–101 ohm^{-1} cm^2 $mole^{-1}$. These values are in the range of the values reported for 1 : 1 electrolyte system[13, 14].

On the basis of above physico-chemical data the present complexes can be assigned 8 coordinated structures, in which *o*-vanillinmonoxime coordinates through oxime nitrogen and phenolic oxygen and the N-phenylurea coordinates through nitrogen while N,N′-diphenylurea coordinates through oxygen. In addition each complex molecule contains one lattice and one coordinated water molecule.

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