

Synthesis and Characterisation of Lanthanide Mixed Complexes Using Benzoin- α -Oxime Thiourea and Phenylthioureas as Ligands

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Mixed ligand complexes of rare earth ions La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺ and Dy³⁺ with benzoin- α -oxime (cupron) as primary ligand and thiourea, N-phenylthiourea and N,N'-diphenylthiourea as secondary ligands have been synthesised and characterised on the basis of their elemental analysis, electronic and IR spectral data, thermal analysis and conductivity measurements. These studies indicate that there is a strong interaction between lanthanides and the ligands.

INTRODUCTION

Several lanthanide complexes with various oximes have been reported¹⁻⁴. Recently much interest has been shown in the preparation and characterisation of lanthanide mixed ligand complexes⁵⁻⁸. We report here the preparation and characterisation of mixed ligand complexes of lanthanides using benzoin- α -oxime as the primary ligand and thiourea, N-phenylthiourea and N,N-diphenylthiourea as the secondary ligands.

EXPERIMENTAL

Spectroscopically pure rare earth oxides were obtained from Indian Rare Earth Ltd., Kerala. Benzoin- α -oxime (m.pt. 152°C) (E. Merck) and thiourea (m.pt.) 179-80°C) (E. Merck) were used after recrystallisation. N-phenylthiourea (m.pt. 153-54°C) was synthesised adopting the procedure of Davis and Underwood⁹. N,N'-diphenylthiourea (m.pt. 152-53°C) was synthesised adopting the procedure described by Vogel¹⁰.

Lanthanide (III) benzoin- α -oximates were prepared by the method of Rao *et al.*² The mixed complexes were prepared adopting the following procedure. A weighed amount of lanthanide (III) benzoin- α -oximate was dissolved in ethanol and mixed with calculated amount (mole ratio 1 : 3.5) of thiourea or (mole ratio 1 : 3.5) of either N-phenyl or N,N'-diphenylthiourea in ethanolic solution. The mixture was stirred and pH of the solution was adjusted to 5.8 by addition of alcoholic ammonia. The resulting solution was concentrated on steam bath when solid complex

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separated. The excess of ligand was washed with ether-acetone mixture. The complexes were further purified from ethanol and vacuum dried over fused calcium chloride for 48 hrs. The elemental analysis of the complexes shows that the complexes have 1 : 2 : 5 (metal : benzoin- α -oxime : thiourea) and 1 : 2 : 3 (metal : benzoin- α -oxime : either N-phenyl or N,N'-diphenylthiourea) stoichiometry. Per lanthanide ion one water molecule is present in benzoin- α -oxime-thiourea complexes while three water molecules are present in benzoin- α -oxime-substituted thiourea complexes. The analytical data of two representative complexes of each series is given in Table 1.

TABLE 1

ANALYTICAL DATA OF MIXED COMPLEXES						
Compound	%C	%H	%M	%N	%Cl	%S
La(cupron) ₂ (TU) ₃ .Cl.H ₂ O	37.92 (38.52)	4.04 (4.48)	13.35 (13.53)	14.99 (16.36)	3.40 (3.46)	14.80 (15.59)
Nd(cupron) ₂ (TU) ₃ .Cl.H ₂ O	38.46 (38.38)	5.02 (4.46)	13.92 (13.98)	15.66 (16.28)	3.22 (3.44)	14.73 (15.50)
La(cupron) ₂ (NPTU) ₃ .Cl.3H ₂ O	51.53 (51.65)	4.68 (4.92)	12.09 (12.20)	9.52 (9.84)	3.02 (3.12)	8.31 (8.43)
Nd(cupron) ₂ (NPTU) ₃ .Cl.3H ₂ O	51.27 (51.41)	4.82 (4.90)	12.55 (12.61)	9.65 (9.79)	2.98 (3.10)	8.25 (8.39)
La(cupron) ₂ (DPTU) ₃ .Cl.3H ₂ O	57.50 (58.40)	4.77 (4.98)	10.01 (10.17)	7.77 (8.20)	2.48 (2.60)	7.01 (7.02)
Nd(cupron) ₂ (DPTU) ₃ .Cl.3H ₂ O	58.21 (58.61)	4.76 (4.96)	10.29 (10.52)	8.03 (8.16)	2.32 (2.58)	7.09 (6.99)

Note: 1. Cupron = Benzoin- α -oxime, TU = Thiourea, NPTU = N-phenylthiourea, DPTU = N,N' diphenylthiourea.

2. Values in brackets are calculated values and without brackets are observed values in%.

RESULTS AND DISCUSSION

In the ultraviolet region band shifts and intensity alterations of the ligands alone indicate the involvement of ligands in complexation with lanthanide ions. The primary ligand benzoin- α -oxime exhibits a band at 208 nm ($\log \epsilon$ 4.30). The secondary ligands thiourea exhibits two bands at 204 nm ($\log \epsilon$ 4.18), 240 nm ($\log \epsilon$ 4.25), NPTU exhibits two bands at 204 nm ($\log \epsilon$ 4.38), 260–262 nm ($\log \epsilon$ 4.21) and DPTU exhibits two bands at 208 nm ($\log \epsilon$ 4.39), 270 nm ($\log \epsilon$ 4.23). In mixed complexes only two bands are observed around 204 nm ($\log \epsilon$ 4.85–5.04), 240 nm

($\log \epsilon$ 4.95–5.21) in thiourea complexes, 204 nm ($\log \epsilon$ 5.16–5.00), 262 nm ($\log \epsilon$ 5.02–4.83) in NPTU complexes and 205 nm ($\log \epsilon$ 5.22–4.84) 270 nm ($\log \epsilon$ 4.90–4.66) in NN'DPTU complexes. The merging of 208 nm band of primary ligand with that of secondary ligands and also the intensification of absorption indicates that there is strong interaction between the lanthanide ions and the ligands.

The electronic visible spectra of the complexes in visible region were recorded in DMSO. Nephelauxetic effect was observed on complexation. Covalency parameter $b^{1/2}$ and Sinha's parameter δ were calculated. The Pr(III) complexes show two bands with red shift at 445 and 470 nm, the $b^{1/2}$ and $\delta\%$ values are 0.0583, 0.0655 and 0.6846, 0.8674 respectively. In lanthanide-benzoin- α -oxime-thiourea complex one more band is observed with red shift at 595 nm, the $b^{1/2}$ and $\delta\%$ values are 0.0652 and 0.8572 respectively. The Nd(III) complexes show characteristic λ_{\max} with red shift at 580, 735, 805 and 865 nm, the $b^{1/2}$ and $\delta\%$ values are 0.0777, 0.0583, 0.05612, 0.02449 and 1.2248, 0.6846, 0.0600 respectively. Lanthanide-benzoin- α -oxime-thiourea complex shows a band with red shift at 750 nm ($b^{1/2}$ 0.08948, $\delta\%$ 1.6261) and lanthanide-benzoin- α -oxime-substituted thiourea complexes show a band at 745 nm ($b^{1/2}$ 0.06855, $\delta\%$ 0.9489).

The primary ligand benzoin- α -oxime exhibits a band at 3200–3380 cm^{-1} assignable to OH stretch of oxime and secondary ligands thiourea, NPTU and N,N' DPTU exhibit bands at 3381, 3275, 3177 cm^{-1} , 3460, 3220–3200 cm^{-1} and 3230 cm^{-1} respectively due to NH stretch. These bands are merged in all the mixed complexes. Close comparison of the bands observed in this region indicate slight lowering of the OH stretch suggesting the involvement of nitrogen of the oxime group in complexation without the elimination of oxime proton. NH stretch bands are either observed unaffected or shifted to higher frequencies in some of the complexes indicating non-involvement of nitrogen of the secondary ligands in bonding. The bands at 3550–3600 cm^{-1} in mixed complexes confirm the presence of water in complexes which is supported by thermal data.

The primary ligand benzoin- α -oxime exhibits a band at 1600 cm^{-1} due to C=N stretch. The secondary ligands thiourea (1614 cm^{-1}) and NPTU (1625 cm^{-1}) exhibit bands due to NH_2 bending and NN' DPTU (1610 cm^{-1}) due to NH bending. These bands are almost unaffected in all the mixed complexes indicating non-involvement of nitrogen of secondary ligands in bond formation and an indirect evidence of S \rightarrow M bond in the complexes. The C=N stretch band of primary ligand gave a composite picture with that of secondary ligand bands in this region.

Thiourea exhibits band at 1470 cm^{-1} due to N–C–N asym. stretch. This band is lowered and split into two inflexations around 1435 cm^{-1} and 1468 cm^{-1} in all the complexes. NPTU exhibits two bands at 1530 cm^{-1} and 1465 cm^{-1} due to N–C–N stretch. The 1530 cm^{-1} band is split into two inflexations around 1520, 1540 cm^{-1} and 1465 cm^{-1} band is

uniformly shifted to higher frequency (1470 cm^{-1}) in all the mixed complexes. NN'DPTU exhibits band due to N-C-N stretch around 1510 cm^{-1} which is observed in all the complexes without much variation. The observations in this region indicate non-involvement of nitrogen of these ligands in bond formation. The band at 1415 cm^{-1} in free ligand thiourea due to C-S stretch is observed with lowering in frequency by 15 cm^{-1} in all the mixed complexes clearly indicating that the bonding is through sulphur. The band at 1455 cm^{-1} due to coupled vibration of NH_2 rocking, N-C-N bending and C-S stretch in NPTU and the band at 1465 cm^{-1} due to coupled vibration of NH rocking, N-C-N bending and C-S stretch in NN'DPTU is observed with lowering in all the mixed complexes indicating involvement of sulphur of both the ligands in bond formation. NH_2 rocking in thiourea at 1084 cm^{-1} is uniformly shifted to higher frequency in all the complexes indicating non-involvement of nitrogen in complexation.

NPTU and NN'DPTU exhibit bands due to coupled vibration of N-C-N-bending and C-S stretch at 1089 , 1070 cm^{-1} and 1085 cm^{-1} respectively. In all the mixed complexes these bands are observed with lowering in frequency. This indicates the involvement of sulphur in bond formation.

The N-O stretch of benzoin- α -oxime at 990 cm^{-1} is unaffected in benzoin- α -oxime-thiourea and benzoin- α -oxime-NPTU mixed complexes. While in benzoin- α -oxime-NN'DPTU mixed complexes it is shifted to higher frequency.

The bands due to coupled effect of 50% or more C-S stretch + C-N stretch are observed around 730 cm^{-1} in thiourea, 820 , 760 and 710 cm^{-1} in NPTU and 870 , 775 and 660 cm^{-1} in NN'DPTU. In all the mixed complexes these bands have been observed with lowering in intensity and frequency. This observations is in conformity with the observations of earlier workers and one can postulate coordination of thiourea, NPTU and NN'DPTU through sulphur.

Thermal analysis of neodymium-benzoin- α -oxime-thiourea complex indicated a weight loss of 1.78% at 183°C which theoretically corresponds to the elimination of one water molecule. As the water molecule is lost above 170°C it is postulated that the complex contains one coordinated water molecule. Study of thermal analysis of neodymium-benzoin- α -oxime-NPTU and neodymium-benzoin- α -oxime NN'DPTU complexes have shown that these complexes contain three water molecules. The water molecules are lost around 150°C in benzoin- α -oxime-NPTU In benzoin- α -oxime-NN'DPTU complex one water molecule is lost around 120°C and remaining two around 145°C . This confirms that in both the complexes water molecules are present as lattice water. Organic part of the molecule is lost in stages with initial loss of thiourea, NPTU and NN'DPTU in respective complexes around 270°C and subsequent loss of benzoin- α -oxime leading to the formation of sesquioxide around 800°C .

The molar conductance of representative neodymium and samarium mixed complexes are in the range 58–88 ohm⁻¹ cm² mole⁻¹ in DMF and 43–87 ohm⁻¹ cm² mol⁻¹ in DMSO. In both the solvents the values are in agreement with those reported for 1 : 1 electrolyte system.

On the basis of above physicochemical data lanthanide-benzoin- α -oxime-thiourea can be assigned 10 coordinated structure [Ln(cupron)₂(TU)₃H₂O]Cl and lanthanide-benzoin- α -oxime-NPTU/DPTU can be assigned 7 coordinated structure [Ln(cupron)₂(NPTU)₃]Cl.3H₂O and [Ln(cupron)₂(DPTU)₃]Cl.3H₂O respectively. Benzoin- α -oxime coordinates through oxime coordinates through oxime nitrogen and alcoholic oxygen and thiourea, NPTU and DPTU through sulphur.

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