Asian Journal of Chemistry Vol. 22, No. 8 (2010), 5846-5852

Synthesis and Characterization of Lanthanides Mixed Ligand Complexes

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Mixed ligand complexes of La^{3+}, Pr^{3+}, Sm^{3+}, Nd^{3+} and Dy^{3+} with nicotinic acid as primary ligand and thiourea as secondary ligands have been prepared and characterized on the basis of their element analysis, electronic and infrared spectra, thermal analysis and conductivity measurements. It has been observed that electronic and infrared spectra suggest interaction of metal ions with ligands and formation of bonds through nitrogen of pyridine ring in case of nicotinic acid and sulphur of thiourea. The thermal analysis of representative mixed complex shows loss of water around temperatures 170 and 121 °C. Above 154 °C the organic part of complex gets decomposed and complete loss of organic matter takes place at about 400 °C. At 530 °C formation of sesquei oxide of metal takes place. The conductivity measurements of the complex have shown that they are all non-electrolyte type.

Key Words: Mixed ligand complexes, Nicotinic acid, Thiourea.

INTRODUCTION

Several lanthanide complexes with nicotinic acid have been reported[1-3]. Recently, much interest has been shown in the preparation and characterization of mixed ligand and complexes of lanthanide[4-6]. We report here the synthesis and characterization of mixed ligand complexes of La^{3+}, Pr^{3+}, Sm^{3+}, Nd^{3+} and Dy^{3+} ions using nicotinic acid as a primary ligand and thiourea as secondary ligand.

EXPERIMENTAL

Spectroscopically pure rare earth oxides obtained from Indian Rare Earths, Kerala were used after ascertaining the purity by measuring the absorbance of the samples as chlorides in aqueous solutions. Nicotinic acid (m.p. 234 °C, B.D.H.) was used after recrystallization. Thiourea (m.p. 180 °C E. Merc.) was also used after recrystallzation.

The ultraviolet and visible spectra were recorded on Shimadzu UV-vis spectrometer model UV-240. The infrared spectra were recorded on Beckmann spectrometer. Conductance measurements were made on Systronics digital conductometer type-303. Thermal analysis was carried out at CFC Shivaji University, Kolhapur, by using Universal V2.4F-TA instrument.

Lanthanide nicotinic acid complexes were prepared by the method described earlier[1-3]. The mixed complexes were prepared adopting the following procedure. A weighed amount of lanthanide(III) nicotinic acid was dissolved in ethanol and mixed with calculated amount (mole ratio 1:3.5) of thiourea 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 the solid complex separated. The solid complex was 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 mixed complexes were analyzed for metal, nitrogen and sulphur. Sulphur was estimated gravimetrically as barium sulphate. Carbon and hydrogen estimation were carried out in few respective cases at RSIC, CDRI, Lucknow. The analytical data of these mixed lanthanide complexes are given in Table-1.

TABLE-1
ANALYTICAL DATA OF MIXED COMPLEXES

Compound	Elemental analysis (%): Found (Calcd.)				
	C	H	N_2	S	M
$[La(NA)_3(TU)_3 \cdot 2H_2O]$	33.47 (32.77)	3.20 (3.64)	17.54 (16.97)	13.01 (12.93)	18.70 (18.59)
$[Pr(NA)_3(TU)_3 \cdot 2H_2O]$	33.74 (32.68)	3.01 (3.63)	16.90 (16.88)	13.75 (12.86)	18.95 (18.88)
$[Nd(NA)_3(TU)_3 \cdot 2H_2O]$	33.79 (32.58	3.01 (3.63)	17.09 (16.79)	13.25 (12.79)	19.30 (19.22)
$[Sm(NA)_3(TU)_3 \cdot 2H_2O]$	33.68 (32.69)	3.32 (3.58)	17.31 (16.65)	12.95 (12.69)	19.90 (19.87)
$[Dy(NA)_3(TU)_3 \cdot 2H_2O]$	32.42 (31.79)	3.15 (3.52)	17.08 (16.39)	12.85 (12.49)	21.14 (21.24)

1. NA-nicotinic acid ($C_6H_5NO_2$, TU-thiourea (CH_4N_2S).

RESULTS AND DISCUSSION

In the ultraviolet region band shifts and intensity alterations of the ligands indicate the involvement of the ligands in the complexation with lanthanide ions. The primary ligand nicotinic acid exhibit two bands at 204 nm (log ε = 4.180) and 240 nm (log ε = 4.25). In the mixed complexes, band is observed around 240-250 nm (log ε = 4.85-5.14). These bands shifts and intensity alternations of the ligands in the ultraviolet region indicate involvement of ligands in the complexation with lanthanide ions.

In the mixed complexes three bands are located around 204, 236 and 262 nm giving an indication of presence of both the ligands in the complexes. As compared to free ligand bands reasonable increase in the log ε is observed on complexation. The log ε value of the 262 nm band is lowered in all the mixed complexes except in case Nd mixed complex, where it shows increased value. Thus there are different effects on this band on complexation.

From the large intensification, it is suggested that both the ligands are involved in bond formation with lanthanide ions. The spectral data is summarized in Table-2.

TABLE-2
ULTRAVIOLET ABSORPTOION BANDS OF LANTHANIDE-
NICOTINIC ACID-THIOUREA MIXED COMPLEXES

Solvent-Methanol		
Compound	Wavelength (nm) λ_{max}	log ε_{max}
Nicotinic acid	204	4.58
	262	4.08
Thiourea	204	4.18
	240	4.25
La-Complex	204	4.84
	236	4.82
	262	4.02
Pr-Complex	205	4.85
	236	4.88
	262	4.00
Nd-Complex	204	5.14
	236	5.05
	262	4.31
Sm-Complex	205	4.84
	236	4.81
	262	4.08
Dy-Complex	205	4.88
	236	4.78
	262	4.03

La(III), Pr(III), Nd(III), Sm(III), Dy(III) nicotinic acid-thiourea mixed complexes					
Solvent methanol, log ε_{max}					
Wavelength (nm)	La(III) Complex	Pr(III) Complex	Nd(III) Complex	Sm(III) Complex	Dy(III) Complex
190	4.12	4.28	4.15	4.16	4.36
200	4.59	4.51	4.45	4.52	4.62
208	4.89	4.96	4.86	4.86	5.03
210	4.87	4.89	4.85	4.77	5.00
220	4.66	4.62	4.70	4.99	4.80
230	4.49	4.24	4.41	4.32	4.68

The electronic spectra of mixed complexes of Pr (III) and Nd(III) were recorded in methanol. Nephelauxetic effect was observed on complexation. Covalancy parameter $b^{1/2}$ and Sinha's parameter δ % were calculated[7,8]. The Pr(III) mixed complex exhibits four bands at 444, 468, 480 and 590 nm. The δ % values 0.462 and 0.430 for the first two bands. The Nd(III) mixed complexes show four bands at 522, 580, 740 and 797 nm. The $b^{1/2}$ and δ % values have been found to be 0.048, 0.077, 0.037, 0.049, 0.381, 1.22, 0.28 and 0.51, respectively. The +ve values $b^{1/2}$ and δ % in these

complexes suggest that the bonding between metal and ligand is covalent as compared to that in metal aqua ion[9,10]. The spectral data is given in Table-3.

TABLE-3

$[Pr(NA)_3(TU)_3 2H_2O]$				$[Nd(NA)_3(TU)_3 2H_2O]$			
Wavelength (nm)	Optical density	MEC	log ε	Wavelength (nm)	Optical density	MEC	log ε
350	0.0720	58.73	1.7674	428	0.028	15.640	1.1942
360	0.0580	47.15	1.6735	440	0.024	13.400	1.1271
380	0.0430	34.95	1.5434	460	0.022	12.290	1.0896
400	0.0360	29.26	1.4661	480	0.021	11.730	1.0693
420	0.0320	26.01	1.4152	800	0.020	11.717	1.0480
438	0.0300	24.39	1.3872	510	0.024	13.400	1.1271
444	0.0340	27.64	1.4415	516	0.022	12.290	1.0896
450	0.0360	24.39	1.3872	522	0.029	16.200	1.2095
460	0.0800	22.76	1.3572	530	0.020	11.700	1.0480
468	0.0290	23.57	1.3724	540	0.019	10.610	1.0257
476	0.0270	21.95	1.3414	560	0.018	10.050	1.0021
480	0.0280	22.76	1.3572	564	0.018	10.050	1.0021
500	0.0230	18.69	1.2713	580	0.045	25.130	1.4002
520	0.0220	17.88	1.2524	590	0.021	11.730	1.0693
540	0.0210	17.07	1.2322	600	0.015	8.370	0.9221
560	0.0200	16.26	1.2111	620	0.014	7.820	0.8982
580	0.2000	16.26	1.2111	640	0.013	7.260	0.8609
600	0.0199	16.17	1.0287	660	0.012	6.760	0.8261
620	0.0198	15.85	1.2001	680	0.014	7.820	0.8932
640	0.0196	15.44	1.1886	700	0.012	6.700	0.8261
660	0.0180	14.63	1.1653	720	0.012	6.700	0.8261
680	0.0180	14.63	1.1653	730	0.013	7.260	0.8609
700	0.0175	14.22	1.1529	732	0.014	13.400	1.1271
720	0.0170	13.82	1.1406	736	0.023	12.240	1.1219
740	0.0165	13.41	1.1274	740	0.028	15.640	1.1942
760	0.0165	13.41	1.1274	760	0.013	7.260	0.8609
780	0.0166	13.00	1.1139	770	0.012	6.700	0.8261
800	0.0170	13.82	1.1406	780	0.013	7.260	0.8609
820	0.0150	12.19	1.0860	797	0.033	18.430	1.2655
840	0.0150	12.19	1.0860	810	0.015	8.370	0.9227
860	0.0140	11.38	1.0562	820	0.013	7.260	0.8609
880	0.0130	10.56	1.0236	840	0.011	0.640	0.7884
900	0.0130	10.56	1.0236	860	0.013	7.260	0.8609
380	0.0950	53.07	1.1746	862	0.016	8.930	0.9509
360	0.0600	33.51	1.5251	870	0.017	9.490	0.9773
380	0.0390	21.78	1.3881	880	0.012	6.760	0.8281
400	0.0300	16.75	1.2240	900	0.011	6.140	0.7882
420	0.0270	15.08	1.1784				

Solvent methanol					
	Wavelength				
Complex	λ (nm)	cm^{-1}	log ε	$b^{1/2}$	δ (%)
$Pr(NA)_3(TU)_32H_2O$	444.00	22522	1.440	0.0470	0.462
	4.68	21367	1.370	0.0460	0.430
	4.80	20833	1.350	–	–
	590.00	16949	1.220	–	–
	591.00	16920	1.220	0.0290	0.170
$Nd(NA)_3(TU)_32H_2O$	510.00	19607	1.230	–	–
	522.00	19157	1.210	0.0436	0.381
	580.00	17241	1.400	0.0770	1.220
	740.00	13513	1.190	0.0370	0.280
	797.00	12547	1.270	0.0490	0.510
	870.00	11494	0.098	0.0580	0.690

Infrared spectra: The primary ligand nicotine acid exhibits a band around 3600-3500 cm^{-1} which is assigned to the free OH sterch and it can be said that the acid is in the undissociated form according to Bellamy[11]. The presence of these bands can also be attributed to the OH strech arising due to absorption of moisture by potassium bromide window in which medium the spectra was recorded[12]. The second ligand thiourea exhibited a band around 1575 cm^{-1} which has practically remained unchanged in all complexes. The N-C-N asymmetric stretch at 1455 cm^{-1} is slightly lowered in the complexes. The primary ligand nicotinic acid had a band around 1690 cm^{-1} which could be attributed to to free COO^- stretch. In La and Pr mixed complexes a band is observed around 1614 cm^{-1} while in Sm and Dy mixed complexes a band is observed at 1617 and 1592 cm^{-1}.

On comparing the effect of NH_2 bending vibration mode, it can be said that it is almost unaffected but considerable lowering is observed in COO^- asymmetric mode of the primary ligand. Thus lowering is clear indication of the interaction of carboxyl oxygen with the lanthanide ion.

Free ligand nicotine acid exhibits a doublet at 1590-1570 cm^{-1} which is assigned to C=C and C=N stretching mode frequency[13]. Secondary ligand thiourea also exhibits a band at 1575 cm^{-1}. A combined effect of these two bands is observed around 1575 cm^{-1} in La, Pr and Sm complexes. In Pr and Dy complexes no band could be observed at 1590-1570 cm^{-1}. From this observation it is concluded that the band due to aromatic ring vibration and C=C and C=N stretching mode frequency, practically remained unchanged in all the complexes. Such an effect on the C=C and C=N stretching mode is taken as an indication of the involvement of nitrogen of pyridine ring in the bond formation.

The bands around 1420 and 1375 cm^{-1} in free ligand thiourea are due to C=S stretch. In all the complexes the 1420 cm^{-1} band is very much reduced in intensity. The 1375 cm^{-1} band is split into two inflections in La, Pr, Sm and Dy complexes. These observations indicate that the bonding is through sulphur of thiourea. The free ligand thiourea exhibits a low doublet at 735-720 cm^{-1} which could be assigned

to C=S stretch with some contribution from N-C-N stretch. In all the complexes only a single band is observed around 747-731 cm^{-1}.

The changes in the region of 1420, 1375 and 740-720 cm^{-1} clearly indicate the involvement of sulphur in bond formation with lanthanide ions. Ligand the results observed in this investigation are in conformity with the observation of Swaminathan *et al.*[14]. It can be definitely said that even in the mixed complexes the thiourea is bonded with the metal through sulphur. The infrared spectral data are detailed in Table-4.

TABLE-4
INFRARED ABSORPTION BANDS OF LANTHANIDE-NICOTINIC ACID-THIOUREA COMPLEXES

NA	TU	La(III) Complex	Pr(III) Complex	Sm(III) Complex	Dy(III) Complex	Assignments
3500 bl	3430 ss	3398 bl	3475 bl	3400 bl	3400	OH- Stretch
3300 bl	3235 ss 3140ss	3220 bl	3400 bl	3200 bl	3200	NH Stretch of TU
1690 bs 1590 sl		1614 ss	1592 ss	1617 ss	1592 ss	COO- asymmetric mode
1570 sl	1575 sh	1575 sh	1575 sh	1575 sh		C=C and C=N stretch of pyridine ring
	1455 ss					C=O, NH_2 mixed vibration
	1420 sm	1400 sh	1400 sh	1400 sh	1400 sh	N-C-N asymmetrical stretch
	1375 sm	1324 Inflex	1370 Inflex	1325 Inflex	1325 Inflex	C=S stretch
		1304 Inflex	1360 Inflex	1300 Inflex	1301 Inflex	
942 sl	1085 san					NH_2 rocking of TU
	735 sl	747 sm	751 sm	748 sm	748 sm	Pyridine ring vibration
	720 doublet					C=S, N-C-N stretch

Thermal analysis: The thermal analysis of Sm-NA-TU mixed ligand complexes has indicated loss of 2.36 % at 170 °C and 4.33 % at 121 °C. This indicates loss of two molecules of coordinated water. The loss of primary ligand (2.5 molecules) takes place at 154 °C which is indicated by calculated loss on heat by 29.72 %. The secondary ligand nicotinic acid starts eliminating at about 200 and 348 °C, the experimental weight loss of 77.24 % corresponds to elimination of 2.5 molecules nicotinic acid. The remaining organic part is eliminated beyond 400 °C leading to the formation of sesquioxide at 530 °C (Table-5).

Conductivity measurements: The molar conductivity of representative samples are measured in methanol. The molar conductance of La-NA-TU mixed complexes are found around 11-32 ohm^{-1} cm^2 mol^{-1} (Table-6). These low values indicate that these complexes behave as non-electrolytes[15,16].

TABLE-5
THERMAL ANALYSIS OF $[Sm(Na)_3(Tu)_3 2H_2O]$

Temperature (ºC)	Wt. loss (%)		Probable composition
	Expt.	Cal	
117	20.02	2.23	$[Sm(NA)_3(TU)_3H_2O]$
121	3.44	4.73	$[Sm(NA)_3(TU)_3]$
154	28.27	29.72	$[Sm(NA)_3(TU)_{1/2}]$
221	53.79	50.77	$[Sm(NA)_2]$
348	77.24	75.15	$[Sm(NA)_{1/2}]$
530	82.75	83.27	Sm_2O_3

TABLE-6
MOLAR CONDUCTIVITES (ohm^{-1} cm^2 mol^{-1}) AT 25 ºC IN METHANOL

Complex	Molarity	Molar condutivity
$[La(NA)_3(TA)_3 \cdot 2H_2O]$	5.34×10^{-4}	20.59
	4.0×10^{-4}	25.00
	3.2×10^{-4}	28.12
	2.6×10^{-4}	31.95
$[Dy(NA)_3(TA)_3 \cdot 2H_2O]$	4.0×10^{-4}	11.25
	3.0×10^{-4}	19.01
	2.4×10^{-4}	22.54
	1.8×10^{-4}	27.12

Conclusion

From all above observations the probable coordination number is 11 for the complexes studied in this investigation.

ACKNOWLEDGEMENTS

The authors is thankful to UGC, New Delhi for financial assistance and Director, CDRI Lucknow, Director, CFC, Shivaji University, Kolhapur and Head, Department of Chemistry, R.T.M. Nagpur University, Nagpur for extending help in carrying out analysis.

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(*Received*: 10 July 2009; *Accepted*: 23 April 2010) AJC-8632