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Rare-earth chelates of o-(N-α-thiophenealdimino)phenol—synthesis and characterization

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Abstract

o-(N-α-thiophenealdimino)phenol (HTP) and its lanthanon chelates have been synthesized and characterized by various physico-chemical methods. Irving-Rossotti method was followed to determine the dissociation constant of the ligand and stability constants of its lanthanon chelates in aqueous medium ($\mu = 0.01$, 0.05 and 0.1M $NaClO_4$) at 25, 35 and 45°C. Solid lanthanon chelates were characterized by molecular mass, magnetic, thermal, spectral, elemental and conductance analysis and are assigned 1:3 (metal-ligand) stoichiometry in which lanthanon showed nine coordination number.

Key words: o-(N-α-Thiophenealdimino)phenol chelates, stability constants, nine coordination

1. Introduction

A variety of lanthanon chelates involving nitrogen- and oxygen-containing ligands have been studied in these laboratories[1-2]. Very little has been reported on sulphur-ligated complexes of the rare-earth metal ion. The present investigation relates to the synthesis and characterization of lanthanon chelates with o-(N-α-thiophenealdimino)phenol (HTP), having a sulphur-ligating site. The structure of the metal chelates can be depicted as shown in fig. 1.

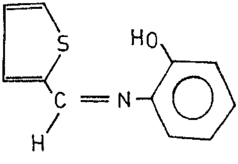

FIG. 1. O-(N-α-Thiophenealdimino) phenol.

2. Experimental

HTP was synthesized by refluxing equimolar ethanolic solutions of o-aminophenol and thiophene-2-aldehyde (Fluka) for an hour in the presence of a drop of piperidene as condensing agent. The reddish-brown mass so obtained was washed and recrystallized from ethanol. The compound was characterized by elemental study (Table I), TLC, physical methods (m.p. 127°C) and IR studies.

The lanthanon chelates were synthesized by stirring magnetically the lanthanon nitrate and ligand ethanolic solutions in stoichiometric proportions; dilute ammonia (1:20) was added dropwise till a flocculant mass obtained. The solid mass was separated, washed, dried and preserved. The composition and purity of the chelates were checked by elemental analysis, molecular mass and TLC.

For potentiometric studies Irving-Rossotti technique[3] was followed. For this purpose the following mixtures (total volume 25 ml) ($\mu = 0.1$, 0.05 and 0.01M $NaClO_4$) were prepared: (i) 5.0 ml 0.01M $HClO_4$ + 2.5 ml 1.0M $NaClO_4$ + 17.5 ml water, (ii) 5.0 ml 0.01M $HClO_4$ + 2.5 ml 1.0M $NaClO_4$ + 10.0 ml 0.01M HTP + 7.5 ml water, (iii) 5.0 ml

Table I
Molecular mass, elemental analysis and magnetic moments of the lanthanon chelates of HTP

Composition	Molecular mass Found (Calcd)	Elemental analysis % Found (calcd)			μ_{eff} B.M. at 308° K
		Sulphur	Nitrogen	Metal	
HTP*	189	15.42	6.75	—	—
	(203)	(15.76)	(6.90)		
[La(TP)$_3$**]	726	12.76	5.49	18.29	Dia
	(745)	(12.88)	(5.64)	(18.67)	
[Pr(TP)$_3$]	735	12.70	5.52	18.52	3.32
	(747)	(12.85)	(5.62)	(18.88)	
[Nd(TP)$_3$]	740	12.82	5.65	18.68	3.55
	(750)	(12.80)	(5.60)	(19.20)	
[Sm(TP)$_3$]	742	12.62	5.42	19.92	1.49
	(756)	(12.70)	(5.56)	(19.84)	
[Gd(TP)$_3$]	749	12.48	5.37	20.66	7.47
	(764)	(12.58)	(5.50)	(20.58)	
[Tb(TP)$_3$]	745	12.44	5.32	20.39	9.52
	(760)	(12.55)	(5.49)	(20.78)	
[Dy(TP)$_3$]	750	12.36	5.49	20.97	10.47
	(769)	(12.47)	(5.46)	(21.20)	
[Ho(TP)$_3$]	752	12.34	5.30	21.52	10.46
	(771)	(12.45)	(5.45)	(21.40)	
[Er(TP)$_3$]	756	12.35	5.28	21.35	9.60
	(773)	(12.42)	(5.43)	(21.60)	

*HTP = $C_{11}H_9NSO$ **TP = $C_{11}H_8NSO$

0.01M $HClO_4$ + 2.5 ml 1.0M $NaClO_4$ + 10 ml 0.01M HTP + 2.0 ml 0.01M metal-ion solution + 5.0 ml water. The titrations, performed in an inert atmosphere, had curves with usual shapes. Calculations of the stability constants were made only up to PH 7.9 beyond which precipitation of the complexes occurred.

3. Results and discussion

The dissociation constant $\log K_H^1$ of HTP ($\mu = 0.1$ M $NaClO_4$) was found: 5.26 at 25°C, 4.97 at 35°C and 4.70 at 45°C, respectively, which suggests it to be a monoprotic ligand. $\mathrm{Log}\, K_H^1$ values were found to fall with the rise of temperature and ionic strength[4] in accordance with Debye-Huckel rule.

The stability constants of lanthanon chelates were read from the formation curves drawn by plotting $\bar{n}$ *vs* pL. The formation curves attained maxima around $\bar{n} = 3$, indicating the stepwise formation of ML_1, ML_2 and ML_3 species. As HTP is a tridentate ligand, it leads to a solution number nine in Ln-HTP chelates having 1:3 (metal-ligand) stoichiometry. The refinement was done by various computational methods[5] and their average values are summarised in Table II. The $\log \beta_3$ values of the metal chelates follow the order La(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) < Er(III), in agreement with Stagg and Powell's rule[6]. The stability of the chelates decreased with increasing ionic strength of the medium, in accordance with the Huckel equation[4,7].

Thermodynamic parameters like changes of free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the lanthanon chelates were evaluated (Table II). More negative values of ΔG° at higher temperature suggested the endothermic nature of the reactions. Positive enthalpy values suggested the existence of steric strain around the metal ion in the chelates due to fused rings. The entropy term seems to be favourable for chelation, as is evident from its positive values.

Table II
Thermodynamic parameters for the lanthanon chelates of HTP ($\mu = 0$)

Metal ion	$\log \beta_3^0$			$-\Delta G^\circ$ KJ mol^{-1}			ΔH° KJ mol^{-1} at 35°C	ΔS° J K^{-1} mol^{-1} at 35°C
	25°	35°	45°	25°	35°	45°		
La(III)	22.14	22.35	22.61	126.33	131.81	137 67	42.64	566.40
Pr(III)	22 60	22.88	23.12	128.96	134.94	140.78	48.08	594.22
Nd(III)	23.05	23.30	23.56	131.53	137.41	143.45	46.27	596.36
Sm(III)	23.53	23.71	23.95	134.26	139.83	145.83	38.10	577.69
Gd(III)	23.88	24.23	24.51	136.26	142.90	149.24	57.16	649.54
Tb(III)	24.33	24.52	24.70	138 83	144.61	150.40	33.57	578.51
Dy(III)	24.91	25.34	25.53	142 14	149 44	155.45	56.25	667.82
Ho(III)	25.42	25.75	26.07	145.05	151.86	158.74	58.97	684.51
Er(III)	26.05	26.37	26.60	148.64	155.52	161.97	49.90	666.95

3.1. *Solid chelates*

Elemental analyses and molecular mass data suggested 1:3 (metal-ligand) stoichiometry of the lanthanon chelates (Table II). The thermal studies (TGA and DTA) proved them to be anhydrous.

The magnetic moment values (Table I) of the lanthanon chelates, as determined by Guoy method and corresponding to the formula $\mu_{eff} = 2[J(J+1)]^{1/2}$, confirmed the tripositive state of the metal in these complexes. The magnetic moments of the complexes (except the lanthanum complex which is diamagnetic) fall in the usual range expected for tripositive lanthanides.

The molecular mass determined by Gallenkemp semimicro ebulliometer (solvent:dioxane) also revealed the monomeric nature of the Ln(III) chelates. Further in the IR spectra of the solid Ln(III) chelates under study, the presence of M-M bondings was not indicated. Thus magnetic moments, molecular mass and IR spectra clearly indicate the monomeric nature of the metal chelates. Negligibly small conductance values (4.16–10.24 ohm^{-1} cm^2 mol^{-1}) of the compounds suggest them to be non-electrolytes.

3.2. *IR spectra*

Comparison of the IR spectra of the ligand with those of its lanthanon chelates indicated coordination of the ligand through azomethine nitrogen, phenolic oxygen and sulphur of the thiophene ring.

In the case of the ligand (HTP), the band observed at 3460 cm^{-1} corresponds to $^{\nu}$CH···N (hydrogen-bonded–OH). This band disappeared in the lanthanon chelates indicating its rupturing and subsequent deprotonation due to chelation. $^{\nu}$C=O shift of the phenolic group (1310 cm^{-1}) towards the higher region (~25 cm^{-1}) suggested bonding between metal and phenolic oxygen atoms.

The band observed around 1625 cm^{-1} due to $^{\nu}$C=N of HTP was shifted towards the lower region 1590–1620 cm^{-1} indicating coordination of the azomethine nitrogen.

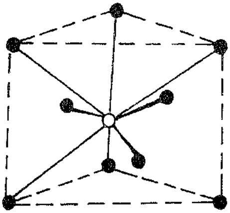

FIG. 2. Tricapped trigonal prismatic geometry.

The lanthanon chelates showed sharp bands in the region 520–550, 400–440 and 300--285 cm^{-1} assignable to M–O M–N and M–S stretching vibrations, respectively[8,9]. M–S-stretching vibration shows the involvement of thiophene ring sulphur in chelation. No band was observed in the range 250–100 cm^{-1} indicating the absence of M–M bonding[10–12].

Based on the above evidence, it is suggested that the lanthanon chelates under study possess a tricapped trigonal prismatic (D_{3h}) stereochemistry[12–14] as shown in fig. 2.

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