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Physicochemical Investigation on Lanthanon(III) Chelates of Multidentates Possessing N, O, O Donors

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The dissociation constants of O-(N-O-hydroxy benzophenimino) benzoic acid (H_2 BB) and O-(N-O-hydroxy benzo-phenimino) propanoic acid (H_2BP') and thermodynamic stability constants of their chelates with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III). Dy(III) Ho(III) and Er(III) were determined by Calvin-Bjerrum pH titration technique as modified by Irving. Rossotti method in 30% (v/v) dioxane-water media (μ = 0.01 N. 0.05 M and 0.1 M $NaClO_4$). The solid Ln(III)-chelates were characterised by physico-chemical techniques and stereochemistry established.

INTRODUCTION

A survey of the literature[1–3] has indicated that no work has been done on La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Er(III)-chelates of the polydentate ligands obtained by the condensation of 2-hydroxy benzophenone with anthranilic acid (H_2BB) or β-alanine (H_2BP') hence the same was undertaken and its finding are reported in the present communication.

EXPERIMENTAL

Synthesis of H_2BB and H_2BP'

H_2BB and H_2BP' were synthesised in an inert atmoshere of nitrogen gas by the condensation of 3-hydroxy benzophenone with anthranilic acid or β-alanine in presence of a drop of piperidine. After refluxing equimolar ethanolic solutions of these compounds for 2–3 hrs., the light brown and light yellow solutions obtained were filtered hot, concentrated and cooled when brown (H_2BB) and yellow (H_2BP') crystals were obtained. These were recrystalized from ethanol. The authenticity and purity of the ligands were established by elemental analysis, molecular mass, electronic, IR and ^1H NMR spectral data. (m. pt. 182°C) Found: C, 75.36; H, 4.41; N, 4.17 calc. for ($C_{20}H_{15}NO_3$): C, 75.71; H, 4.73; N, 4.41%. H_2BP' (m. pt, 213°C). Found: C, 71.11; H, 5.26; N, 4.91; Calc. for ($C_{16}H_{15}NO_3$): C, 71.38; H, 5.58; N, 5.20%.

Synthesis of Ln(III) Chelates

In an ethanolic solution of H_2BB or H_2BP' (0.04 M), a solution of lanthanon(III)-nitrates (0.02 M) in 80% ethanol was added gradually and the mixture stirred magnetically. Dilute ammonia (1 : 20) was added dropwise to the mixture until a flocculent mass was obtained which was stirred continuously for 4–5 hrs. The mass was filtered under suction, washed with hot ethanol, dried and preserved in vacuum desiccator.

The C, H and N were determined microanalytically using Carlo Erba-Strumentazione elemental analyser–MOD 1106 in an inert atmosphere of helium gas, and the metal contents were estimated by standard methods. All the chemicals and solvent used were of AnalaR grade. The physicochemical measurements were carried out as reported earlier[4,5]. The potentiometric studies were carried out by Irving-Rossotti method[6] at 25°, 35° and 45°C in 30% (v/v) dioxane-water media (μ = 0.05, 0.01 M & 0.1 M $NaClO_4$) and the values were corrected for partially aqueous media[7].

RESULTS AND DISCUSSION

The pK_1 and pK_2 values of H_2BB were found to be 9.62 and 5.30 at 25°, 9.38 and 4.84 at 35°, 9.15 and 4.62 at 45°C; the corresponding values for H_2BP' were found to be 9.88 and 5.73 at 25°, 9.72 and 5.53 at 35°, 9.33 and 5.18 at 45°C respectively (μ = 0.1 M $NaClO_4$). These values suggest biprotic nature of the ligands. The pK_1 and pK_2 values of H_2BB and H_2BP' decreased with increasing temperature. By plotting $\bar{n}$ vs pL, the formation curves of metal-ligand systems were obtained. The values of stability constants derived from the formation curves were refined by different computational methods[8].

The stabilities of the Ln(III)-chelates were found to follow the order: La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) < Er(III) in accordance to the Stagg and Powell rule[9].

Thermodynamic Parameters

$\Delta G°$, $\Delta H°$ and $\Delta S°$ values (Table 1) were evaluated using Gibbs-Helmholtz equation. log β_0 values decreased with increase in ionic strength of the medium, in agreement with Huckel equation[10]. The stabilities decreased with increase in temperature.

The negative values of $\Delta H°$ suggest the exothermic nature of the reaction and positive values of $\Delta S°$ suggest favourable chelation reactions. The data were also analysed in terms of Harned's relation[11] $[(pK^H - Ct^2) = -2COt + (pK_m^H - C\theta^2)]$ and the values of θ, pK^H and

pK_m^H were evaluated (Table 1). The ΔH values obtained by Harned's equation and Gibbs-Helmholtz equation were found to be in agreement.

Solid Chelates

Based on elemental analysis and ebulliometric molecular weight determination the solid lanthanon chelates approached 1 : 2 (metal-ligand) stoichiometry (Table 2).

The room temperature magnetic moment values of the lanthanon chelates correspond to the formula, $\mu_{eff} = 2[J(J + 1)]^{1/2}$ and, as shown in Table 2, the magnetic moments suggest the presence of 0, 1, 2, 3, 5, 7, 6, 5, 4, 3 unpaired electrons in La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er complexes, respectively, indicating the tripositive oxidation state of the Ln(III) ions in them. A double humped curve is obtained on plotting μ_{eff} values versus number of unpaired electrons. However, La(III) chelates were found to be diamagnetic. The μ_{eff} values also indicated the absence of metal-metal bonding. The high conductance values (270–368 $ohm^{-1}\ cm^2\ mol^{-1}$) obtained indicated the ionic-nature of the metal chelates.

Electronic Spectra

The result of the study is shown in Table 3. The energies at which the various bands appeared were lower as compared to their positions in aquo ions. The shift could be ascribed to a nephelauxetic effect,[12] the extent of which is related to the amount of covalence in the metal-ligand bond. Sinha has proposed a scale for this covalency given by the parameter (Sinha's parameter) as $\delta\% = [(1 - \beta)/\beta] \times 100$. The value $(1-\beta)$, being less than unity, in the chelates of both H_2BB and H_2BP', suggests the covalent nature of the metal-ligand bond. The bonding parameter $b^{1/2}$, the magnitude of which suggested the involvement of the 4f-orbital in metal-ligand bond, was correlated to nephelauxetic ratio β by the expression $b^{1/2} = (1 - \beta)^{1/2}/2$. Another parameter called covalency angular (η) was also evaluated using the expression, $\eta = (1 - \beta^{1/2})/\beta^{1/2}$.

Infra-red Spectra

A comparison of the IR spectra of the ligands H_2BB and H_2BP' with those of their Ln(III)–chelates indicated their coordination through azomethine nitrogen, carboxylic oxygen and phenolic oxygen. In the IR spectra of H_2BB and H_2BP' four major peaks were observed in the ranges 1610–1630, 3270–3300, 1740–1770 and 3350–3380 cm^{-1} assignable to ν>C=N, νOH (phenolic), νC=O & νOH (of carboxylic) modes respectively.

In the Ln(III) chelates of H_2BB and H_2BP' the bands in the range, 3350-3380 cm^{-1} disappeared suggesting deprotonation of OH (of carboxylic) and its subsequent chelation. ν (> C=N) and νOH (phenolic) were found to be lowered (*ca* 15–25 cm^{-1}) indicating coordination of the ligands

TABLE 1

THERMODYNAMIC PARAMETERS OF THE LANTHANON(III) CHELATES OF H_2BB AND H_2BP' AT $\mu=0$

Metal Ion	log β°			$-\Delta G°$ (KJ/mole)			$-\Delta H°$ KJ/mole at 35°C	$\Delta S°$ J/K mole at 35°C
	25°C	35°C	45°C	25°C	35°C	45°C		
La(III)	12.52 (11.92)	12.08 (11·61)	11.93 (11.29)	71.44 (66.01)	72.24 (68.47)	72.64 (68.74)	53.53 (57.16)	60·75 (36 72)
Ce(III)	12.77 (12.00)	12.45 (11.69)	12.15 (11.38)	72.87 (68·47)	73·42 (68.94)	73.98 (69.29)	56.25 (56.25)	55.75 (41.20)
Pr(III)	12.86 (12.31)	12.56 (12·08)	12.17 (11.65)	73.38 (70.24)	74.07 (71.24)	74.10 (70.94)	62.60 (59.88)	37.24 (36.88)
Nd(III)	13.22 (12.50)	12.92 (12.20)	12.62 (11.90)	75.43 (71.33)	76.20 (71.95)	76.84 (72.45)	54.44 (54.44)	70.65 (56.85)
Sm(III)	14.00 (13.16)	13.65 (12.97)	13.30 (12.52)	79.89 (75.09)	80.50 (76.49)	80.98 (76.23)	63.50 (58.06)	55.19 (59.84)
Gd(III)	14.35 (13.52)	13.95 (13.23)	13.68 (12.98)	81.88 (77.15)	82.27 (78.02)	83.30 (79.03)	60.79 (48.99)	69.74 (94.25)

TABLE 1. (Contd.)

Metal ion	log β°			$-\Delta G°$ (KJ/mole)			$-\Delta H°$ KJ/mole at 35°C	$\Delta S°$ J/K/mole at 35°C
	25°C	35°C	45°C	25°C	35°C	45°C		
Tb(III)	14.62	14.22	13.89	83.42	83.86	84.58	66.23	57.24
	(13.99)	(13.59)	(13.29)	(79.83)	(80.15)	(80.92)	(63·51)	(54.02)
Dy(III)	14.85	14.50	14.20	84.74	85.51	86.46	58.97	86.17
	(14.45)	(14.24)	(13.80)	(82.45)	(83.98)	(84.03)	(58.96)	(81.20)
Ho(III)	15.26	14.92	14.56	87.07	87.99	88.66	83.51	79.48
	(14.60)	(14·35)	(13.93)	(83.31)	(84.63)	(84.82)	(60.79)	(77.40)
Er(III)	15.68	15.38	14.97	89.47	90.70	91.15	64.43	85.35
	(15.04)	(14.74)	(14.33)	(85.82)	(86.93)	(87.25)	(64.42)	(73.08)

In terms of Harned's equation, pk^H, pK_m^H and θ at 35° were found to be 14.23 (15.25), 5.1700 (1·0160) and 460 (560.25) respectively. The values given in parentheses are those of the H_2BP' chelates.

TABLE 2

MOLECULAR WEIGHT, ELEMENTAL ANALYSIS AND MAGNETIC MOMENT OF THE LANTHANON(III) CHELATES OF H_2BB and H_2BP'

Composition	Molecular weight		Elemental analysis %								μeff B.M. at 308°K
			Carbon		Hydrogen		Nitrogen		Metal		
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	
($C_{20}H_{15}NO_3$)	308 (256)	317 (269)	75.36 (71.11)	75.71 (71.38)	4.49 (5.26)	4.73 (5.58)	4.17 (4.91)	4.41 (5.20)	—	—	—
$H^+[La(C_{40}H_{26}N_2O_6]$	762 (665)	760 (673)	62.09 (56.73)	62.42 (57.10)	3.06 (3.56)	3.38 (3.86)	3·30 (3.85)	3.64 (4.16)	17.80 (20.32)	18.65 (20.65)	Dia.
$H^+[Ce(C_{40}H_{26}N_2O_6)]$	760 (662)	770 (674)	62.00 (56.71)	62.34 (56.97)	3.01 (3.53)	3.38 (3.86)	3.27 (3.88)	3.64 (4.15)	17.84 (20.38)	18.20 (20.77)	2.26 (2.27)
$H^+[Pr(C_{40}H_{26}N_2O_6)]$	763 (667)	771 (675)	61.89 (56.50)	62.26 (56.89)	3.07 (3.52)	3.37 (3.85)	3.32 (3.83)	3.63 (4.15)	17.96 (20.63)	18.27 (20.89)	3.37 (3.36)
$H^+[Nd(C_{40}H_{26}N_2O_6)]$	769 (670)	774 (678)	61.65 (56.31)	62.01 (56.64)	3.02 (3.47)	3.36 (3.83)	3.30 (3.81)	3.62 (4.13)	18.27 (20.92)	18.63 (21.24)	3.62 (3.60)
$H^+[Sm(C_{40}H_{26}N_2O_6)]$	772 (672)	780 (684)	61.11 (55.87)	61.54 (56.14)	3.02 (3.48)	3.33 (3.80)	3.19 (3.82)	3.59 (4.10)	18.91 (21.59)	19.27 (21.93)	1.58 (1.56)
$H^+[Gd(C_{40}H_{26}N_2O_6)]$	781 (680)	787 (691)	60.69 (55.28)	60.99 (55.57)	3.00 (3.36)	3.30 (3.77)	3.28 (3.71)	3.56 (4.05)	19.66 (22.40)	19.98 (22.72)	7.88 (7.89)

$H^+[Tb(C_{40}H_{26}N_2O_6)]$	778 (681)	789 (693)	60.53 (55.09)	60.84 (55.41)	3.03 (3.43)	3.29 (3.75)	3.24 (3.74)	3.55 (4.04)	19.84 (22.85)	20.14 (22.94)	9.91 (9.48)
$H^+[Dy(C_{40}H_{26}N_2O_6)]$	785 (685)	792 (696)	60.24 (54.89)	60.61 (55.17)	2.94 (3.46)	3.28 (3.74)	3.20 (3.68)	3.53 (4.02)	20.88 (23.00)	20.52 (23.28)	10.42 (10.43)
$H^+[Ho(C_{40}H_{26}N_2O_6]$	790 (686)	795 (699)	60.03 (54.63)	60.37 (54.94)	2.94 (3.45)	3.27 (3.72)	3.23 (3.72)	3.52 (4.00)	20.47 (23.27)	28.74 (23.60)	10.39 (10.42)
$H^+[Er(C_{40}H_{26}N_2O_6)]$	788 (691)	797 (701)	59.94 (54.40)	60.22 (54.78)	3.00 (3.35)	3.26 (3.71)	3.25 (3.68)	3.51 (3.99)	20.69 (23.55)	20.99 (23.82)	9.67 (9.68)

The values given in parentheses are those of H_2BP' ($C_{16}H_{15}NO_3$) and its $[Ln(C_{32}H_{26}N_2O_6)]$ chelates.

TABLE 3

ELECTRONIC SPECTRAL DATA OF LANTHANON(III) CHELATES OF H_2BB & H_2BP'

Ion	λ_{max} (cm^{-1})	J-levels	β	δ%	$b^{1/2}$	η
La(III)	31435 (31433)	Infra ligand transition	—	—	—	—
Ce(III)	—	—	—	—	—	—
Pr(III)	22372 (22388)	$^3H_4 \rightarrow {}^3P_2$	0.9957 (0.9960)	0.4319 (0.4016)	0.0328 (0.0316)	0.0022 (0.0020)
	21220 (21229)	$\rightarrow {}^3P_1$				
	20643 (20640)	$\rightarrow {}^3P_0$				
	17050 (17060)	$\rightarrow {}^3D_2$				
Nd(III)	12495 (12493)	$^4I_{9/2} \rightarrow {}^4F_{5/2}$	0.9932 (0.9934)	0.6846 (0.6644)	0.0412 (0.0406)	0.0034 (0.0033)
	13470 (13486)	$\rightarrow {}^4F_{7/2}$				
	14486 (14489)	$\rightarrow F_{9/2}$				
	17148 (17143)	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$				
	18920 (18925)	$\rightarrow {}^4G_{7/2}$				
	21675 (21679)	$\rightarrow {}^4G_{11/2}$				
	22644 (22648)	$\rightarrow {}^2P_{1/2}$				
Sm(III)	17772 (17766)	$^6H_{5/2} \rightarrow {}^4G_{5/2}$	0.9926 (0.9925)	0.7455 (0.7557)	0.0430 (0.0433)	0.0037 (0.0038)
	18755 (18758)	$\rightarrow {}^4F_{3/2}$				
	21343 (21339)	$\rightarrow {}^4I_{9/2}$				
	23822 (23820)	$\rightarrow {}^6P_{5/2}$				
	24370 (24366)	$\rightarrow {}^6P_{3/2}$				

TABLE 3 (Contd.)

Ion	λ_{max} (cm^{-1})	J-levels	β	$\delta\%$	$b^{1/2}$	η
Gd(III)	31434 (31438)	Infra ligand transition	—	—	—	—
Tb(III)	4490 (4486)	$^7F_6 \rightarrow {}^7F_3$	0.9865 (0.9863)	1.3685 (1.3890)	0.0581 (0.0585)	0.0068 (0.0069)
	4978 (4983)	$\rightarrow {}^7F_2$				
	5361 (5356)	$\rightarrow {}^7E_1$				
	26041 (26037)	$\rightarrow {}^5D_3$				
Dy(III)	10160 (10155)	$^6H_{15/2} \rightarrow {}^6H_{5/2}$	0.9854 (0.9850)	1.4816 (1.5228)	0.0604 (0.0612)	0.0074 (0.0076
	12964 (12963)	$\rightarrow {}^6F_{3/2}$				
	20745 (20734)	$\rightarrow {}^4F_{9/2}$				
	23082 (23069)	$\rightarrow {}^4G_{11/2}$				
HO(III)	15093 (15084)	$^5I_8 \rightarrow {}^5F_5$	0.9845 (0.9844)	1.5744 (1.5847)	0.0622 (0.0625)	0.0078 (0.0079)
	18134 (18130)	$\rightarrow {}^5F_4$				
	21060 (21067)	$\rightarrow {}^5K_3$				
	23658 (23660)	$\rightarrow {}^5G_3$				
Er(III)	15102 (15107)	$^4I_{15/2} \rightarrow {}^4F_{9/2}$	0.9837 (0.9839)	1.6570 (1.6363)	0.0638 (0.0634)	0.0082 (0.0083)
	18800 (18806)	$\rightarrow {}^4S_{3/2}$				
	20267 (20263)	$\rightarrow {}^4F_{7/2}$				
	25984 (25988)	$\rightarrow {}^4G_{11/2}$				
	27378 (27386)	$\rightarrow {}^4G_{7/2}$				

The values given in parentheses are those of the H_2BP'–Chelates.

through the C = N and —OH groups. νC—O shift of phenolic —OH (1110–1150 cm^{-1}) as obtained towards the higher region *ca* 30 cm^{-1}) suggest bonding between the metal and the phenolic oxygen atom. However, the spectra of the chelates displayed two new bands in the range 1570–1595 and 1370–1385 cm^{-1} assigned to ν_{asym} COO^- and ν_{sym} COO^- cm^{-1} respectively. In addition, the appearance of two new bands in the ranges 490–510 cm^{-1} and 410–430 cm^{-1} were observed, which were assigned to $\nu_{(M-O)}$ and $\nu_{(M-N)}$ modes[13,14] respectively.

^{1}H NMR Spectra

To substantiate further the bonding in these chelates ^{1}H NMR spectra of ligands and their Ln(III)-chelates were recorded in $CDCl_3$/TMS. The chemical shift values (δ, ppm) of different protons are given below. In the ^{1}H NMR spectra of the H_2BB and H_2BP' signals due to —COOH and —OH protons appeared at δ 11.75 and δ 11.50 and δ 8.06 and δ 8.20 ppm respectively. The signals due to —COOH protons disappeared in the spectra of the corresponding metal-chelates. The signals due to —OH proton (of H_2BB and H_2BP') appearing at δ 8.06 & 8.20 ppm were shifted towards higher field in the Ln(III)-chelates (*ca* .10 — .15 ppm). The multiplets, due to aromatic protons and —CH_2—CH_2 appearing at δ 6.90 — 7.16 ppm, δ 3.10 — 3.26 ppm in H_2BB and H_2BP' respectively, were found unchanged in the metal-chelates.

The results obtained conclusively indicate hexa-coordinated octahedral geometry (Fig. 1) for the Ln(III)-chelates under study.

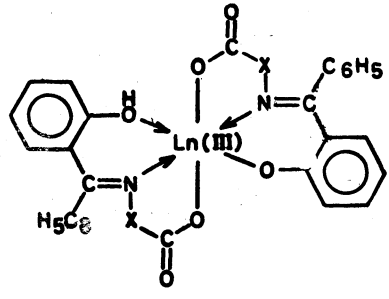

Fig. 1. Structure of Lanthanon (III) Chelates

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