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Synthesis and structural investigation on tridentate ligands possessing oxygen and nitrogen donor atoms

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Abstract

The dissociation constants of *o*-(N-furan-2-acetylimino) benzoic acid (HFB) and *o*-(N-pyrrole-2-methylimino) benzoic acid (H_2PB) and the stability constants, and thermodynamic parameters 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) have been determined by Calvin-Bjerrum pH-titration technique as modified by Irving and Rossotti. The stability constants of the metal chelates increase with decreasing ionic size of the Ln(III) ions. Solid Ln(III) chelates are characterised by molecular mass measurements, elemental analyses, magnetic moment, conductance, ^1H nmr, electronic and ir spectral data.

Key words: Synthesis and structure, lanthanon(III) chelates, tridentate ligands.

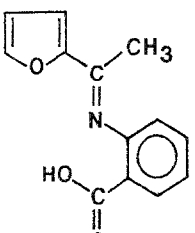
1. Introduction

The complexes formed by Schiff bases containing nitrogen, oxygen and sulphur donor atoms have proved to be promising analytical materials in the determination of some inner transition metals[1–5]. With a view to extend these investigations and to understand more fully the nature of bonds involved in the chelates containing nitrogen and oxygen donor atoms, chelates of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Er(III) with the Schiff bases derived from anthranilic acid and 2-acetyl furan or 2-acetyl pyrrole have been synthesised and characterised by elemental analysis and spectroscopic techniques. The stability constants of the chelates have also been determined.

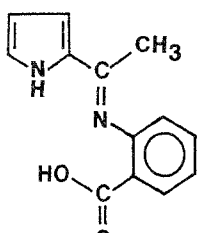
2. Experimental

2.1. *Preparation of HFB and H_2PB*

HFB and H_2PB (fig. 1) were prepared by heating under reflux for 2–3 hours stoichiometric proportions of ethanolic solutions of anthranilic acid and 2-acetyl furan or 2-acetyl pyrrole. On cooling the contents in ice, a solid mass separated out which was crystallised from



O-(N-Furan-2-acetylimino) Benzoic acid (HFB).



O-(N-phrrole-2-methyl-Imino) Benzoic acid (H_2PB).

acetone to obtain HFB and H_2PB (Yield 80–85%). mp 126°C (HFB), 108°C (H_2PB). For HFB found: C, 68.01; H, 4.54; N, 6.01; calcd for ($C_{13}H_{11}NO_3$): C, 68.12; H, 4.80; N, 6.11% and for H_2PB found: C, 68.11; H, 4.93; N, 11.99; calcd for ($C_{13}H_{12}O_2N_2$): C, 68.42; H, 5.26; N, 12.28%. ^1H nmr, $CDCl_3$/TMS, for HFB δ (ppm): ~ 7.40 (Ar–H), ~ 6.29 (furan ring H), ~ 9.72 (–COOH), ~ 1.08 ($H_3C > C{=}N$) and for H_2PB δ(ppm): ~ 7.15(Ar–H), ~ 6.38 (> NH), ~ 10.03(–COOH), ~ 1.32($H_3C > C{=}N$).

2.2. *Preparation of Ln(III) chelates*

The chelates were synthesised by adding an excess of ethanolic solution of HFB or H_2PB to an aqueous solution of Ln(III) nitrate. After adjusting the pH of the solution to the optimum value (7.5–9.0) the solid chelate formed was filtered, washed and dried.

Potentiometric titrations were carried out in accordance with Bjerrum's extension of Irving and Rossotti[6] method in 30% (v/v) dioxan-water medium ($\mu = 0.01$ M, 0.05 M and 0.1 M $NaClO_4$) at 25, 35 and 45°C, and the pH values were corrected for partially aqueous media[7].

The metal in the complexes was determined by complexometric titrations with EDTA[8]. Analysis for carbon, hydrogen and nitrogen were made by microanalytical methods. Molecular mass was determined ebulliometrically in dioxan by Gallenkemp semimicro ebulliometer. Conductance measurements were made on a Toshniwal conductivity bridge and magnetic measurements at room temperature were made on a Gouy magnetic balance[9] using $Hg[Co(CNS)_4]$ as the calibrant. The ir spectra were recorded in nujol on a Perkin-Elmer spectrophotometer using KBr discs. The ^1H nmr spectra were recorded in $CDCl_3$ TMS using Hitachi, nmr spectrometer.

3. Result and discussion

The $\log K_1^H$ of HFB was found to be 5.29 at 25°C, 5.04 at 35°C and 4.81 at 45°C at $\mu = 0.1$ M; for H_2PB the $\log K_1^H$ and $\log K_2^H$ values found were 10.03 and 5.10 at 25°C, 9.76 and 4.96

at 35°C and 9.48 and 4.76 at 45°C, respectively. These values indicate monoprotic nature of the HFB and biprotic nature of the H_2PB. The dissociation constant values decrease with the rise in temperature and increase of ionic strength.

Formation curves of metal-ligand systems were obtained by plotting $\bar{n}$ *vs* pL. The values of the stability constants thus obtained were further refined by various computational methods; such as interpolation at various $\bar{n}$ values, correction term, convergence formula and successive approximation, and the thermodynamic parameters are shown in Table I. The negative values of ΔG° and ΔH° in all the Ln(III) chelates indicated spontaneity of chelation reaction. The positive values of ΔS° suggested that entropy term was favourable for complexation.

The stability of the metal chelates followed the order La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III) < Er(III) in agreement with the lanthanide contraction.

In terms of Harned's equation[10] the values of θ (the temperature at which pK^H was minimum), pK_m^H (pK^H at $t = 0$) and pK^H were calculated (Table I). The ΔH° values as

Table I

Thermodynamic parameters of lanthanon(III) chelates of o-(N-furan-2-acetylimino) benzoic acid (HFB) and o-(N-pyrrole-2-methylimino) benzoic acid (H_2PB) at 25, 35 and 45 C ($\mu = 0$)

Metal ion	log K°			ΔG° (kJ mole^{-1})			ΔH (kJ mole^{-1})	ΔS (J mole^{-1} K^{-1})
	25°	35°	45°	25°	35°	45°	at 35°C	at 35°C
La(III)	12.74	12.36	12.04	72.69	72.88	73.31	63.51	30 42
	(13.32)	(12.84)	(12.58)	(75.00)	(75.72)	(76.60)	(67.14)	(26.85)
Ce(III)	13.20	12.80	12.47	75.32	75.47	75.93	66.23	30.00
	(13.84)	(13.47)	(13.06)	(78.97)	(79.44)	(79.53)	(70.77)	(28.14)
Pr(III)	13.61	13.31	12.93	77.66	78.48	78.73	61.69	54.51
	(14.40)	(13 94)	(13.57)	(82.17)	(82.21)	(82.63)	(75.30)	(22.43)
Nd(III)	14.02	13.70	13.30	80.00	80.78	80.98	65.32	50.19
	(15.06)	(14.68)	(14.20)	(85.93)	(86 58)	(86.66)	(78.02)	(27.79)
Sm(III)	14.85	14.50	14.14	84.74	85.50	86.10	64.41	68.47
	(15.28)	(14.96)	(14.40)	(87.19)	(88.23)	(88.68)	(79.84)	(27.24)
Gd(III)	15.60	15.14	14.81	89.02	89.27	90.18	71.67	57.14
	(15.52)	(15 16)	(14.63)	(88.55)	(89.41)	(89.68)	(80.75)	(28.11)
Tb(III)	15.94	15.58	15.16	90.96	91.87	92.31	70.77	68.51
	(15.76)	(15.50)	(14.85)	(89.93)	(91.41)	(91.62)	(82.56)	(28.73)
Dy(III)	16.20	15.78	15.48	92.44	93.05	94.26	65.32	90.03
	(16.38)	(16.08)	(15.44)	(93.47)	(94.83)	(94.91)	(85.28)	(31.00)
Ho(III)	16.60	16.19	15.90	94.72	95.47	96.82	63.51	103.77
	(16.76)	(16.58)	(15.77)	(95.63)	(97.78)	(98.02)	(89.82)	(25.84)
Er(III)	17.24	16.85	16.51	98.37	99.37	100.53	66.23	107.60
	(17.32)	(16.92)	(16.31)	(98.83)	(99.79)	(100.31)	(91.63)	(26.49)

Notes: In terms of Harned's equation, pK^H, pK_m^H and θ at 35°C were found to be 5.04 (14.72), 1.43 (3.87) and 268.57 (465.72).

The values in parentheses are those of the H_2PB chelates.

obtained from Harned's equation and the Gibb's–Helmholtz equation, were found in agreement.

3.1. *Solid chelates*

Yield, elemental analysis, molecular mass, magnetic moment and conductance of the metal chelates are given in Tables II and III. The elemental analysis and molecular mass data suggested 1:3 (metal-ligand) stoichiometry of the HFB chelates and 1:2 stoichiometry of the H_2PB chelates. These compounds did not possess sharp melting points but decomposed above 250°C without melting giving their oxides between 290 and 385°C. For HFB chelates, the low conductance values (3.96–8.83 $ohm^{-1} cm^2 mol^{-1}$) obtained indicated their non-electrolytic nature. However, for H_2PB chelates, high conductance values (260–370 $ohm^{-1} cm^2 mol^{-1}$) indicated their ionic nature.

The magnetic moment values of the Ln(III) chelates as determined by Gouy method, corresponded to the formula $\mu_{eff} = g[J(J+1)]^{\frac{1}{2}}$ and confirmed the tripositive state of the lanthanon ion in the chelates. The La(III) chelate was found to be diamagnetic. The observed magnetic moments for the remaining lanthanon(III) chelates were in good agreement with those of the lanthanide sulphates[11] and indicated the presence of 1, 2, 3, 5, 7, 6, 5, 4 and 3 unpaired electrons in Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) and Er(III) chelates, respectively. Magnetic moments of the chelates when plotted against atomic numbers of the lanthanons gave an unequal double-humped curve as usual[12].

3.2. *Electronic spectra*

The electronic spectra of the H_2PB chelates were recorded in dioxane. The bands observed in the case of Pr(III) chelates were at 22334, 20601 and 17017 cm^{-1} assignable to $^3H_4 \rightarrow {}^3I_2$, $^3P_0$ and $^1D_2$, respectively. For Nd (III) chelates, the bands observed were at 13467, 14479, 17128, 18900 and 22620 cm^{-1} that corresponded to the transitions $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4F_{9/2}$, $^4G_{5/2}$ and $^4G_{7/2}$, $^4G_{7/2}$ and $^2P_{1/2}$, respectively. For Sm (III) chelates the bands observed were at 17751, 21321, 23800 and 24346 cm^{-1} assignable to $^6H_{5/2} \rightarrow {}^4G_{5/2}$, $^4I_{9/2}$, $^6P_{5/2}$ and $^6P_{3/2}$, respectively. For Tb (III) chelates, the bands observed were at 4877 and 26020 cm^{-1} which corresponded to the transition $^7F_6 \rightarrow {}^7F_2$ and $^5D_3$, respectively. The bands observed in the case of Dy (III) chelates were at 10156, 12964, 20736 and 23071 cm^{-1} assignable to $^6H_{15/2} \rightarrow {}^6H_{5/2}$, $^6F_{3/2}$, $^4F_{9/2}$ and $^4G_{11/2}$, respectively. For Ho (III) chelates the bands observed were at 15095, 18138, 21063 and 23662 cm^{-1} which corresponded to the transitions $^5I_8 \rightarrow {}^5F_5$, $^5F_4$, $^3K_3$ and $^3G_5$, respectively. The bands observed in the case of Er (III) chelates were at 15087, 18818, 26016 and 27404 cm^{-1} assignable to $^4I_{15/2} \rightarrow {}^4F_{9/2}$, $^4S_{3/2}$, $^4G_{11/2}$ and $^2G_{7/2}$, respectively.

3.3. *Ir spectra*

Comparison of the ir spectra of the ligands (HFB and H_2PB) with those of their lanthanon(III) chelates indicated coordination of the ligands through azomethine nitrogen, carboxylate oxygen besides furan ring oxygen or pyrrole ring nitrogen in HFB and H_2PB, respectively.

Table II
Yield, molecular mass, elemental analysis and magnetic moment of lanthanon(III) chelates of HFB

Composition	Yield (%)	Molecular mass		Elemental analyses (%)								μ_{eff} B.M. at 308°C
				C		H		N		Metal		
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	
$[C_{13}H_{11}NO_3]$	80	226	229	68.01	68.12	4.54	4.80	6.01	6.11	—	—	—
$[La(C_{13}H_{10}NO_3)_3]$	65	820	823	56.42	56.87	3.36	3.64	5.00	5.10	16.55	16.89	Dia
$[Ce(C_{13}H_{10}NO_3)_3]$	62	821	824.12	56.35	56.79	3.25	3.64	4.97	5.09	16.61	17.00	2.32
$[Pr(C_{13}H_{10}NO_3)_3]$	58	822	825	56.31	56.73	3.21	3.63	4.96	5.09	16.78	17.09	3.19
$[Nd(C_{13}H_{10}NO_3)_3]$	71	825	828.2	56.11	56.51	3.19	3.62	4.93	5.07	16.98	17.41	3.50
$[Sm(C_{13}H_{10}NO_3)_3]$	55	832	834.4	55.82	56.09	3.15	3.60	4.90	5.03	17.43	18.03	1.47
$[Gd(C_{13}H_{10}NO_3)_3]$	63	838	841.2	55.50	55.63	3.12	3.57	4.85	4.99	17.95	18.63	7.83
$[Tb(C_{13}H_{10}NO_3)_3]$	58	840	843	55.36	55.52	3.10	3.56	4.83	4.98	18.15	18.85	9.55
$[Dy(C_{13}H_{10}NO_3)_3]$	60	843	946.5	55.06	55.29	3.08	3.54	4.81	4.96	18.36	19.19	10.46
$[Ho(C_{13}H_{10}NO_3)_3]$	55	845	849	54.89	55.13	3.05	3.53	4.80	4.95	18.64	19.42	10.51
$[Er(C_{13}H_{10}NO_3)_3]$	68	848	851.3	54.63	54.97	3.04	3.52	4.77	4.93	18.87	19.65	9.70

Table III
Yield, molecular mass, elemental analysis and magnetic moment of lanthanon(III) chelates of H_2PB

Composition	Yield (%)	Molecular mass		Elemental analyses (%)								μ_{eff} B.M. at 308°C
				C		H		N		Metal		
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	
$[C_{13}H_{12}N_2O_2]$	85	225	228	68.21	68.42	4.93	5.26	11.99	12.28	—	—	—
$[La(C_{26}H_{20}N_4O_4)]^-H^+$	72	589	591	52.65	52.79	3.31	3.38	9.21	9.47	23.13	23.52	Dia
$[Ce(C_{26}H_{20}N_4O_4)]^-H^+$	66	588	592	52.57	52.70	3.29	3.38	9.28	9.46	23.38	23.65	2.26
$[Pr(C_{26}H_{20}N_4O_4)]^-H^+$	68	590	593	52.39	52.61	3.26	3.37	9.13	9.44	23.49	23.78	3.36
$[Nd(C_{26}H_{20}N_4O_4)]^-H^+$	74	595	596	52.01	52.35	3.24	3.36	9.12	9.40	24.00	24.16	3.61
$[Sm(C_{26}H_{20}N_4O_4)]^-H^+$	58	600	602	51.63	51.83	3.19	3.32	9.09	9.30	24.79	25.08	1.57
$[Gd(C_{26}H_{20}N_4O_4)]^-H^+$	69	606	609	50.98	51.23	3.26	3.28	8.91	9.20	25.64	25.78	7.87
$[Tb(C_{26}H_{20}N_4O_4)]^-H^+$	63	608	611	50.88	51.06	3.13	3.27	8.87	9.17	25.87	26.02	9.49
$[Dy(C_{26}H_{20}N_4O_4)]^-H^+$	56	613	615	50.49	50.73	3.10	3.25	8.85	9.11	26.21	26.50	10.41
$[Ho(C_{26}H_{20}N_4O_4)]^-H^+$	59	613	617	50.26	50.57	3.09	3.24	8.82	9.08	26.51	26.74	10.40
$[Er(C_{26}H_{20}N_4O_4)]^-H^+$	72	618	619	50.18	50.40	3.04	3.23	8.89	9.05	26.69	26.98	9.69

The ir spectra of HFB showed two strong absorption bands at 2590 and 1615 cm^{-1} assignable to ν–COOH and $\nu > C{=}N$, respectively, whereas H_2PB showed three absorption bands at 2605, 1600 and 3315 cm^{-1} assignable to ν–COOH, $\nu > C{=}N$ and $\nu > NH$, respectively. In the metal chelates, the $\nu > C{=}N$ was found lowered ($\sim 15-20\,cm^{-1}$) indicating its participation in coordination.

The bands at 2590 cm^{-1}, 2605 cm^{-1} and 3315 cm^{-1} as observed in the ligands disappeared in the Ln(III) chelates suggesting complexation through the carboxylate oxygen and pyrrole ring nitrogen. $\nu_{as}(COO^-)$ (at 1605 and 1620 cm^{-1}) and $\nu_{sym}(COO^-)$ (at 1445–1460 cm^{-1}) as compared to 1475 cm^{-1} and 1485 cm^{-1} in the free ligands were observed in the spectra of the Ln(III) chelates indicating the involvement of carboxylate group in coordination.

In the spectra of Ln(III) chelates, three new bands in the far-infrared region at 525, 490 and 400 or 385 cm^{-1} were observed, which may be assigned to νM–O (furan ring oxygen), νM–N (pyrrole ring nitrogen) and νM–O (carboxylate oxygen), respectively.

3.4. ^1H *nmr spectra*

To substantiate further the bonding in these chelates, ^1H nmr spectra of the ligands and their Ln(III) chelates were recorded in $CDCL_3$/TMS. The chemical shift values (δ, ppm) of different protons are given here.

The signals due to –COOH proton of the ligands HFB and H_2PB appeared at δ 9.72 and 9.95 ppm but disappeared in the spectra of the corresponding Ln(III) chelates. The multiplets due to aromatic protons at 7.40–7.48 ppm remain unchanged in the chelates showing non-involvement of these protons in coordination. In metal chelates, the coordination of C=N deshields the $-CH_3$ protons and hence they shift downfield (.10–.20 ppm). The multiplet due to furan ring protons at δ6.29 ppm remain unchanged. Further, in H_2PB the singlet observed at δ6.38 ppm due to $>NH$ disappeared in the spectra of its Ln(III) chelates.

From the above data, the lanthanon (III) HFB and H_2PB chelates are tentatively assigned nine and six coordinated structures, respectively.

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