

Physicochemical Studies of La(III), Ce(III), Pr(III), Nd(III), Sm(III) & Gd(III) Chelates of *o*-(2-Pyrrolideneimino)benzoic Acid & 3-(2-Pyrrolideneimino)propionic Acid

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The stability constants of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) complexes with *o*-(2-pyrrolideneimino)benzoic acid have been determined using Calvin-Bjerrum pH-titration technique in aqueous media ($\mu=0.1, 0.05$ and $0.01M$) at $25^\circ, 30^\circ$ and 35° . The order of the stability constants has been found to be: La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III). Changes in free energy, enthalpy and entropy and pK_m^H have been calculated for the ligand. Complexes of the analogous ligand 3-(2-pyrrolideneimino)propionic acid with the same metal ions have also been isolated in solid state and characterised on the basis of magnetic, conductance and IR studies.

IN continuation of our earlier work on the *o*-(2-pyrrolideneimino)benzoic acid¹ (H_2PB) and 3-(2-pyrrolideneimino)propionic acid (H_2PP), we now report the results of our studies on the chelates

of La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Gd(III) with these ligands.

H_2PB and H_2PP were synthesized by the method reported earlier². For stability constant measurements an aqueous solution ($0.01M$) of H_2PB was prepared and for the evaluation of thermodynamic constants, experiments were carried out in media of different low ionic strengths ($0.1, 0.05$ and $0.01M$). From these an extrapolation to zero ionic strength was possible. The following solutions (total vol. 40.0 ml) were titrated against standard carbonate-free sodium hydroxide ($0.1M$) when titration curves of usual shapes were obtained. (i) 10.0 ml of $0.01M$ H_2PB + 4.0 ml of $NaClO_4$ ($1.0M$) + 26.0 ml of water; (ii) 10.0 ml of $0.01M$ H_2PB + 4.0 ml of $NaClO_4$ ($1.0M$) + 10.0 ml of $0.01M$ metal ion solution + 16.0 ml of water; (iii) 20.0 ml of $0.01M$ H_2PB + 4.0 ml of $NaClO_4$ ($1.0M$) + 10.0 ml of $0.01M$ metal ion solution + 6.0 ml of water.

The dissociation constants of H_2PB and the stability constants of its chelates with trivalent metal ions obtained at different ionic strengths and temperatures are shown in Table 1. The formation curves of the metal chelates suggest the formation of 1:2 complexes. The stabilities of the metal chelates follow the order: La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III), which is in accordance with the lanthanide contraction.

TABLE 1 — DISSOCIATION CONSTANTS OF H_2PB AND STABILITY CONSTANTS OF ITS TRIVALENT METAL CHELATES AT DIFFERENT IONIC STRENGTHS

Dissociation/ stability constants	μ at 25°			μ at 30°			μ at 35°		
	$0.1M$	$0.05M$	$0.01M$	$0.1M$	$0.05M$	$0.01M$	$0.1M$	$0.05M$	$0.01M$
H_2PB									
pK_1^H	3.89	3.93	4.01	3.86	4.89	3.96	3.84	3.87	3.93
pK_2^H	9.10	9.12	9.18	9.07	9.09	9.14	9.02	9.05	9.11
La(III)									
$\log K_1$	3.42	3.55	3.75	3.63	3.75	3.88	3.74	3.90	4.16
$\log K_2$	3.15	3.25	3.37	3.41	3.45	3.57	3.45	3.55	3.64
Ce(III)									
$\log K_1$	3.72	3.86	4.03	3.99	4.06	4.14	4.03	4.16	4.37
$\log K_2$	3.42	3.51	3.63	3.60	3.66	3.73	3.90	3.99	4.08
Pr(III)									
$\log K_1$	3.98	4.10	4.24	4.14	4.19	4.25	4.24	4.37	4.56
$\log K_2$	3.71	3.80	3.91	3.84	3.88	3.94	4.05	4.14	4.24
Nd(III)									
$\log K_1$	4.36	4.49	4.67	4.59	4.66	4.75	4.64	4.76	4.90
$\log K_2$	4.03	4.12	4.21	4.15	4.22	4.32	4.45	4.53	4.65
Sm(III)									
$\log K_1$	4.55	4.67	4.84	4.81	4.91	5.01	4.91	5.01	5.17
$\log K_2$	4.27	4.34	4.43	4.40	4.49	4.57	4.72	4.81	4.90
Gd(III)									
$\log K_1$	4.92	5.03	5.21	5.16	5.26	5.37	5.28	5.39	5.58
$\log K_2$	4.57	4.62	4.69	4.65	4.73	4.82	4.95	5.02	5.10

The thermodynamic formation constants (Table 2) were obtained by extrapolation of the experimentally obtained constants to zero ionic strength in the plots between log of stability constants against $\sqrt{\mu}$, where μ is the ionic strength.

Harned³⁻⁵ found a parabolic relationship between $\log K_1^H$ and temperature (Eq. 1).

$$pK^H - pK_m^H = c(t-0)^2 \quad \dots(1)$$

or $(pK^H - ct^2) = -2c0t + (pK_m^H - c0^2)$ where $pK_H = -\log K^H$ at t° , pK_m^H is the minimum pK^H value at 0°C and c is a constant ($= 5.0 \times 10^{-5} \text{ deg}^{-2}$). A plot of $(pK^H - ct^2)$ versus t must be linear having a slope of $-2c0$ and an intercept equal to $(pK_m^H + c0^2)$ at $t = 0$ and this was found to be true in the present case. The values of 0 and pK_m^H were calculated at 303°K and found to be 164.2° and 12.20 respectively. ΔH values were also calculated (Table 3) using Harned's³⁻⁵ equation:

$$\Delta H = 2.303 \times 10^{-4} RT^2(t-0)$$

Solid rare earth chelates of the analogous ligand H_2PB were synthesized by the method reported⁶ earlier. The yields, molecular weight, magnetic moment, and molar conductance data of the chelates are given in Table 4. These data suggest 1:2 (metal-ligand) stoichiometry for the chelates.

TABLE 2 — THERMODYNAMIC FORMATION CONSTANTS AND FREE ENERGIES OF H_2PB AND ITS METAL CHELATES

Ligand/ chelate	At 25°		At 30°		At 35°	
	$\log K^\circ$	$-\Delta F^\circ$	$\log K^\circ$	$-\Delta F^\circ$	$\log K^\circ$	$-\Delta F^\circ$
H_2PB	13.30	18.13	13.18	18.27	13.12	18.49
La(III)	7.40	10.09	7.65	10.60	8.06	11.36
Ce(III)	7.91	10.78	8.26	11.45	8.70	12.27
Pr(III)	8.39	11.44	8.64	11.98	9.02	12.72
Nd(III)	9.10	12.41	9.38	13.00	9.77	13.77
Sm(III)	9.50	12.95	9.84	13.64	10.26	14.46
Gd(III)	10.10	13.77	10.45	14.49	10.99	15.33

TABLE 3 — THERMODYNAMIC PARAMETERS OF H_2PB at $\mu = 0.1M$

Temp. (°K)	pK^H^*	$-\Delta F$ (kcal mole ⁻¹)	$-\Delta H^*$ (kcal mole ⁻¹)	ΔS^* (cal/deg mole ⁻¹)
298	12.99	17.72	5.66†	41.13
303	12.93	17.93	5.46, 5.64†	41.13
308	12.86	18.12	5.61†	41.13

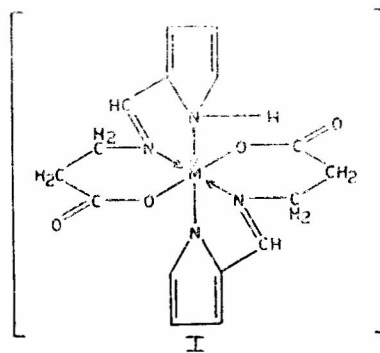
*Average values.

† $-\Delta H$ values obtained using Harned's equation.

TABLE 4 — YIELDS, MOLECULAR WEIGHT, MAGNETIC MOMENT AND CONDUCTANCE VALUE DATA OF METAL CHELATES OF H_2PB

Composition*	Yield (%)	Mol. wt		Magnetic moment (at 303°K)	ΔM (ohm ⁻¹ cm ² mole ⁻¹)
		Found	Calc.		
[La C ₁₆ H ₁₇ N ₄ O ₄]	75	457	468	—	5.8
[Ce C ₁₆ H ₁₇ N ₄ O ₄]	82	459	469	2.27	6.1
[Pr C ₁₆ H ₁₇ N ₄ O ₄]	77	455	470	3.39	5.9
[Nd C ₁₆ H ₁₇ N ₄ O ₄]	78	480	473	3.62	7.6
[Sm C ₁₆ H ₁₇ N ₄ O ₄]	76	465	479	1.59	7.2
[Gd C ₁₆ H ₁₇ N ₄ O ₄]	80	492	486	7.82	6.8

*These compounds gave satisfactory C, H, N and metal analyses.



WHERE M(III) = La, Ce, Pr, Nd, Sm or Gd

H_2PB melts at 172° but its chelates do not display sharp melting points and start decomposing above 210° giving respective metal oxides. These compounds are soluble in water, dioxane, DMF and pyridine.

IR spectrum of H_2PB exhibits four bands at $1655, 1690, 2570$ and 3315 cm^{-1} , assignable to $\nu\text{C}-\text{N}$, $\nu\text{C}-\text{O}$, νCOOH and $\nu\text{N}-\text{H}$ respectively. In the metal chelates the band at 2570 cm^{-1} disappears which indicates deprotonation of the carboxylic group on chelation. In the spectra of the complexes $\nu\text{C}-\text{N}$ and $\nu\text{N}-\text{H}$ are observed in the ranges $1640-1630$ and $3300-3295 \text{ cm}^{-1}$ respectively suggesting that azomethine nitrogen and the imine nitrogen are coordinated to the central metal ion.

Excepting the La(III) chelate which was found to be diamagnetic, all other compounds are paramagnetic (Table 4). The molar conductance values of $10^{-3}M$ solution of metal chelates in dioxane and DMF were found to be very small suggesting them to be neutral in nature.

Based on these data a tentative structure (I) may be assigned to the metal chelates.

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