

## Synthesis & Characterisation of the Lanthanon Complexes of *o*-(2-pyrrolidinimino)benzoic Acid

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Potentiometric studies on the lanthanon chelates of *o*-(2-pyrrolidinimino) benzoic acid ( $H_2PB$ ) have been carried out by Irving-Rossotti technique in aqueous medium ( $\mu=0.1, 0.05$  and  $0.01 M NaClO_4$ ) at 25, 35 and 45°C. Magnetic, conductance and spectral data of the solid lanthanon chelates suggest an octahedral stereochemistry.

A survey<sup>1-3</sup> of the literature 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) and Ho(III) chelates of *o*-(2-pyrrolidinimino) benzoic acid ( $H_2PB$ ), a schiff base derived from 2-pyrrolidinone and anthranilic acid. Hence, physicochemical investigation on these chelates was undertaken and the findings are presented in the present note.

*o*-(2-Pyrrolidinimino) benzoic acid ( $H_2PB$ ) was synthesized by the general procedure reported earlier<sup>4</sup>; m.p. 180°C [Found: C, 64.74; H, 5.92; N, 13.78. Calc. for  $C_{11}H_{12}O_2N_2$ : C, 64.70; H, 5.88; N, 13.72%]. The ligand solution (0.01 *M*) was prepared in water. Potentiometric studies were carried out by Irving-Rossotti technique<sup>5</sup> in aqueous solution ( $\mu=0.1, 0.05$  and  $0.01 M NaClO_4$ ) at 25, 35 and 45°C. The C, H and N contents in the complexes were determined micro-analytically and the metal contents were estimated by standard methods, after destroying the organic part first with aqua regia and then with concentrated  $H_2SO_4$ .

Conductance measurements were made on a Toshniwal conductivity bridge. A precision pH-meter type OP: 205 equipped with a glass calomel electrode assembly (least count 0.01) was used for pH determination. Molecular weights were determined ebulliometrically in dioxan by a Gallen Kamp ebulliometer. Magnetic measurements at room temperatures were made on a Gouy magnetic balance using  $Hg[Co(CNS)_4]$  as a calibrant. The IR spectra were recorded in nujol on a Perkin-Elmer spectrophotometer using NaCl prisms.

The following solutions (total volume 25.0 ml) were titrated against standard carbonate-free sodium hydroxide (0.01 *M*): (1) 5.0 ml 0.01 *M*  $HClO_4$  + 2.5 ml

1.0 *M*  $NaClO_4$  + 17.5 ml  $H_2O$ ; (2) 5.0 ml 0.01 *M*  $HClO_4$  + 2.5 ml 1.0 *M*  $NaClO_4$  + 10.0 ml 0.01 *M*  $H_2PB$  + 7.5 ml  $H_2O$ ; and (3) 5.0 ml 0.01 *M*  $HClO_4$  + 2.5 ml 1.0 *M*  $NaClO_4$  + 10.0 ml 0.01 *M*  $H_2PB$  + 2.0 ml metal ion solution + 5.5 ml  $H_2O$ .

The titration curves had the usual shapes.

The dissociation constants of  $H_2PB$  and stability constants of its lanthanon chelates were determined at different ionic strengths and at 25, 35 and 45°C. The formation curves of the metal chelates suggest the formation of 1:2 complexes. The stabilities of metal chelates follow the order: La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Gd(III) < Tb(III) < Dy(III) < Ho(III), which is in accordance with the lanthanide contraction.

The thermodynamic stabilities (Table 1) have been obtained by extrapolation of measured formation constants to zero ionic strength in the plot between log of stability and  $\sqrt{\mu}$ , where  $\mu$  is the ionic strength.

### Thermodynamic parameters

The  $\Delta G$  of all the chelates have more negative values at 45° than at 35° and 25°C (accuracy  $\pm 0.01$ ). Also, the  $\Delta H$  is positive in all the cases which suggests that some steric strain exists in the chelates due to the presence of fused rings. The positive values of  $\Delta S$  suggest that entropy term is favourable for the formation of the chelates.

Harned *et al.*<sup>6</sup> gave the relation between  $\log K_1^H$  and temperature as  $(pK^H - ct^2) = -2c\theta t + pK_m^H + c\theta^2$ , where  $pK^H = -\log K^H$  at  $t^\circ C$ ;  $pK_m^H$  is minimum  $pK^H$  value at  $\theta^\circ C$  and  $c$  is a constant having the values  $5.0 \times 10^{-5} \text{ deg}^{-2}$ . A plot of  $(pK^H - ct^2)$  versus  $t$  must be linear having a slope of  $-2c\theta$  and an intercept equal to  $pK_m^H + c\theta^2$  at  $t=0$ ; this was found to be true in the present case. The values of  $\theta^\circ$ ,  $pK^H$  and  $pK_m^H$  are given in Table 1.

### Synthesis of solid chelates

To an ethanolic solution of  $H_2PB$  (0.023 *M*), a solution of rare earth metal nitrate (0.02 *M*) in 80% ethanol was added gradually and the mixture was stirred magnetically. Dilute ammonia (1:20) was then added dropwise to the mixture until a flocculent mass was obtained which was stirred continuously for 4-5 hr. The mass was filtered under suction, washed with hot ethanol, dried and preserved *in vacuo*. The yields and elemental analyses data are summarised in Table 2. The chelates possess 1:2 (metal-ligand) stoichiometry. The complexes are non-electrolytes  $\Lambda_m = 5-10 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

NOTES

Table 1—Thermodynamic Parameters of *o*-(2-Pyrrolidinimino)benzoic Acid (H<sub>2</sub>PB) and Its Lanthanone Chelates

Ligand/ metal chelates	log β <sub>2</sub>			Thermodynamic parameters at 35°C		
	25°	35°	45°	−ΔG (kJ mol <sup>−1</sup> )	ΔH (kJ mol <sup>−1</sup> )	ΔS (J deg <sup>−1</sup> mol <sup>−1</sup> )
H <sub>2</sub> PB	16.17	16.58	17.42	97.98	90.74	23.50
La(III)	12.40	12.50	12.80	73.71	36.29	121.46
Ce(III)	12.45	12.72	13.00	75.01	49.89	81.55
Pr(III)	12.57	12.95	13.10	76.37	48.08	91.85
Nd(III)	12.58	13.12	13.20	77.37	47.73	98.05
Sm(III)	12.86	13.24	13.35	78.08	40.73	121.20
Gd(III)	13.20	13.80	13.90	81.38	63.50	58.05
Tb(III)	13.78	13.95	14.00	82.27	19.95	202.30
Dy(III)	13.92	14.05	14.17	82.86	22.68	195.37
Ho(III)	14.10	14.17	14.82	83.56	65.32	59.28

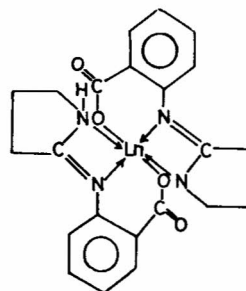
In terms of Harned's equation:  $pK^H$  at 35° is 16.58;  $pK_m^H = 2.17$  and  $\theta(^{\circ}C) = 583.93$ .

Table 2—Characterisation Data of *o*-(2-Pyrrolidinimino)benzoic Acid (H<sub>2</sub>PB) and Its Lanthanone Chelates

Ligand/chelate	Yield (%)	Molec. wt Found (Calc.)	Found (Calc.), %				Metal	$\mu_{eff}$ (B.M.) at 308°K
			C	H	N			
(C <sub>11</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub> )	100	204 (209)	64.74 (64.70)	5.92 (5.88)	13.72 (13.78)	—	—	
[La(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	80	544 (548)	48.51 (48.52)	3.76 (3.86)	10.29 (10.33)	25.55 (25.68)	Diamag.	
[Ce(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	67	545 (549)	48.39 (48.44)	3.81 (3.85)	10.27 (10.29)	25.68 (25.69)	2.23	
[Pr(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	64	545 (550)	48.40 (48.44)	3.73 (3.85)	10.27 (10.28)	25.68 (25.72)	3.33	
[Nd(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	59	549 (558)	48.01 (48.08)	3.80 (3.82)	10.20 (10.28)	26.22 (26.24)	3.62	
[Sm(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	76	555 (561)	47.42 (47.56)	3.69 (3.78)	10.29 (10.29)	27.02 (27.04)	1.58	
[Cd(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	73	562 (563)	46.89 (46.97)	3.63 (3.73)	9.96 (9.99)	27.93 (27.99)	7.79	
[Tb(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	69	564 (565)	46.72 (46.80)	3.68 (3.72)	9.92 (9.96)	28.19 (28.27)	9.64	
[Dy(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	72	567 (569)	46.53 (46.56)	3.59 (3.70)	9.87 (9.98)	28.57 (28.83)	10.38	
[Ho(C <sub>22</sub> H <sub>21</sub> O <sub>4</sub> N <sub>4</sub> )]	68	570 (576)	46.21 (46.31)	3.51 (3.68)	9.82 (9.96)	28.94 (29.00)	10.44	

The La(III) chelate was found to be diamagnetic. The observed magnetic moments (Table 2) for the remaining rare earth chelates are in good agreement with the typical values for lanthanide sulphates<sup>7</sup>.

The IR spectrum of H<sub>2</sub>PB shows three bands at 3150, 2570 and 1610 cm<sup>−1</sup>, assignable to νNH, νOH(carboxylate) and νC=N, respectively. In all metal chelates the weak band at 2570 cm<sup>−1</sup> could not be located which indicated deprotonation of carboxylate group due to chelation. In the spectra of the metal chelates (having 1:2 metal ligand stoichiometry) the appearance of only one band at 2250 cm<sup>−1</sup> indicates the presence of bonded NH group. The NH appears to be coordinated to the central metal atom giving rise to six-coordinated



(I)

complexes. In the spectra of the metal chelates νC=N mode was lowered to 1580-1590 cm<sup>−1</sup> suggesting participation of azomethine group in complexation.

Based on the above evidences the metal chelates may be represented by the structure (I).

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