

Short Communication

Synthesis and characterisation of lanthanon (III) chelates of O-(N- α -oxindolimino) benzoic acid and O-(N- α -oxindolimino) propanoic acid possessing N-N-O moiety

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Received on April 6, 1992; Revised on October 27, 1992.

Abstract

Schiff bases derived from the condensation of oxindole with anthranilic acid and β -alanine and their lanthanon (III) chelates have been synthesized and characterized by physicochemical techniques. Potentiometric studies have been carried out by Irving-Rossotti method in 30% (v/v) dioxane-water media ($\mu = 0.01M$, and $0.05M$, and $0.10M NaClO_4$) at 25, 35 and $45^\circ C$. ΔG° , ΔH° and ΔS° of the metal chelates have also been evaluated.

Key words: O-(N- α -oxindolimino) benzoic acid and O-(N- α -oxindolimino) propanoic acid chelates, stability constants, dissociation constants.

1. Introduction

Several reactions of lanthanon (III) ions with polydentates were reported¹⁻³ earlier in these laboratories. A survey of the literature has revealed that no work has been done so far on the lanthanon (III) chelates of the Schiff bases derived by the condensation of oxindole with anthranilic acid (H_2OB) and β -alanine (H_2OP), respectively. Hence, physicochemical investigation on these chelates was undertaken and its findings are reported in the present communication.

2. Experimental

All the chemicals used were of Anal-R grade and used without further purification. The instruments employed were the same as reported earlier⁴.

2.1. Synthesis of H_2OB and H_2OP

H_2OB and H_2OP were synthesized by the condensation of oxindole with anthranilic acid or β -alanine in the presence of piperidine as the condensing agent. After refluxing equimolar ethanolic solutions of these compounds for 2-3 h, the light brownish yellow and pale yellow solutions obtained were filtered hot, concentrated and cooled when brownish yellow (H_2OB) and pale yellow (H_2OP) crystals were obtained. These were recrystallised from ethanol (Fig. 1).

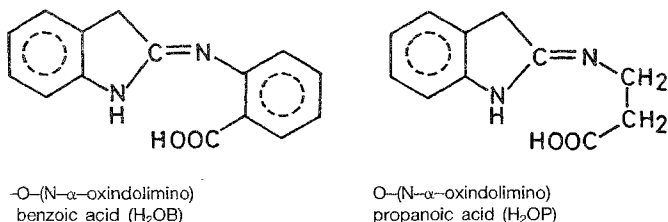


FIG. 1.

The authenticity and purity of the ligands were established by elemental analysis, molecular weight, ¹H nmr and ir spectra. H₂OB (m.p., 78°C) Found: C, 71.10; H, 4.22; N, 10.68; Calc for (C₁₅H₁₂N₂O₂): C, 71.42; H, 4.76; N, 11.11%. H₂OP (m.p., 118°C) Found: C, 70.31; H, 5.50; N, 13.24; Calc for (C₁₁H₁₂N₂O₂): C, 70.58; H, 5.88; N, 13.72%.

2.2. Synthesis of lanthanon (III) chelates

To an ethanolic solution of H₂OB or H₂OP (0.04 M) a solution of lanthanon (III) nitrate (0.02 M) in 80% ethanol was added gradually and the mixture was 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 h. The mass was then filtered under suction, washed with hot ethanol and preserved in a vacuum desiccator.

The ligand solution was prepared in 30% (v/v) dioxane–water media. Potentiometric studies were carried out by Irving–Rossotti technique in 30% (v/v) dioxane–water solution ($\mu = 0.1$ M, 0.05 M and 0.01 M NaClO₄) at 25°, 35° and 45°C and PH values were corrected for partially aqueous media². The C, H and N contents in the complexes were determined by standard methods after destroying the organic part first with aqua regia and then with conc. sulphuric acid. The experimental results obtained were found satisfactory. The metal nitrates (BDH) and the solvents were reagent-grade chemicals.

3. Results and discussion

The pK₁ and pK₂ values of H₂OB were found to be 9.45 and 4.98 at 25°C, 9.08 and 4.59 at 35°C, 8.68 and 4.28 at 45°C, the corresponding values for H₂OP were found to be 9.52 and 5.19 at 25°C, 9.23 and 4.675 at 35°C, 8.61 and 4.38 at 45°C, respectively ($\mu = 0.1$ M NaClO₄).

Table I
Thermodynamic parameters of the lanthanon (III) chelates of H₂OB and H₂OP at $\mu = 0$

Metal ion	log β_0			$-\Delta G^\circ$ (KJ mol ⁻¹)			$-\Delta H^\circ$ (KJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)
	25°	35°	45°	25°	35°	45°	at 35°C	at 35°C
La(III)	13.46 (12.97)	13.26 (12.72)	12.85 (12.31)	76.80 (74.01)	78.20 (75.02)	78.24 (74.96)	55.34 (59.88)	74.22 (49.15)
Ce(III)	14.27 (13.36)	14.00 (13.06)	13.61 (12.64)	81.42 (76.23)	82.56 (77.02)	82.87 (76.96)	59.88 (65.32)	73.64 (37.98)
Pr(III)	14.40 (13.68)	14.10 (13.41)	13.72 (13.09)	82.17 (78.06)	83.15 (79.09)	83.54 (79.70)	61.69 (53.53)	69.67 (82.98)
Nd(III)	15.21 (14.09)	14.85 (13.83)	14.52 (13.50)	86.79 (80.40)	87.58 (81.56)	88.41 (82.20)	62.60 (53.53)	81.10 (91.00)
Sm(III)	15.78 (14.66)	15.42 (14.38)	15.07 (13.98)	90.04 (83.65)	90.94 (84.81)	91.76 (85.12)	64.41 (61.69)	86.13 (75.06)
Gd(III)	16.30 (15.27)	15.87 (14.84)	15.57 (14.57)	93.01 (87.13)	93.59 (87.52)	94.80 (88.72)	66.23 (63.51)	88.83 (77.95)
Tb(III)	16.56 (15.62)	16.21 (15.31)	15.83 (14.92)	94.49 (89.13)	95.60 (90.29)	96.39 (90.85)	66.23 (63.51)	95.35 (86.95)
Dy(III)	16.66 (16.05)	16.24 (15.00)	15.94 (15.43)	95.06 (91.58)	95.78 (93.18)	97.06 (93.95)	65.32 (56.25)	98.90 (119.90)
Ho(III)	17.25 (16.27)	16.80 (15.97)	16.50 (15.62)	98.43 (92.84)	99.08 (94.18)	100.47 (95.11)	68.04 (58.97)	100.78 (114.32)
Er(III)	17.94 (16.88)	17.50 (16.58)	17.16 (16.18)	102.37 (96.32)	103.21 (97.78)	104.49 (98.52)	70.77 (63.50)	105.32 (111.30)

In terms of Harned's equation, pK^H , pK_m^H and θ at 35°C were found to be 13.67 (13.90), -12.97 (24.92), and 750 (848), respectively.

The values given in parentheses are those of the H₂OP chelates.

These values suggest the biprotic nature of the ligands. The pK_1 and pK_2 values of H₂OB and H₂OP decreased with increasing temperature. By plotting \bar{n} vs pL , the formation curves of the metal-ligand systems were obtained. The values of stability constants derived from the formation curves were refined by different computational methods⁶. The stabilities of these metal 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) which is in accordance with the lanthanide contraction.

Thermodynamic stabilities were obtained by extrapolation of measured formation constants to zero ionic strength in the plot between log of stability and $\sqrt{\mu}$ where $\sqrt{\mu}$ is the ionic strength.

3.1. Thermodynamic parameters

The ΔG° , ΔH° and ΔS° values (Table I) were evaluated using Gibbs-Helmholtz equation. Log β_0 values decreased with increase in ionic strength of the medium, in agreement with Huckel equation. The stabilities decreased with increase in temperature.

The ΔG° values of all the chelates have more negative values at 45°C than at 35 and 25°C. The negative values of ΔH° suggest the exothermic nature of the reaction and positive values of ΔS° suggest favourable chelation reactions. The data were also analysed in terms of Harned equation⁷ and the values of θ , pK^H and pK_m^H were evaluated. The ΔH values obtained by Harned's equation and Gibbs-Helmholtz equation were found to be in agreement.

3.2. Solid chelates

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

La(III) chelates were found to be diamagnetic. The observed magnetic moments for the remaining rare-earth chelates were in good agreement with the typical values for lanthanide sulphates and indicated 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, Er complexes, respectively.

The bands observed in the case of Pr(III), Nd(III), Sm(III), Tb(III), Dy(III), Ho(III) and Er(III) chelates were attributed to the transition from ground levels 3H_4 , $^4I_{9/2}$, $^6H_{5/2}$, 7F_6 , $^6H_{15/2}$, 3I_8 , $^4I_{15/2}$, respectively, to the excited J levels of $4f^n$ configuration, thereby exhibiting six coordination number. But intra-ligand charge transfer bands were observed in La(III) and Gd(III) chelates.

In the lanthanon(III) chelates of H_2OB and H_2OP , $\nu C = N$ and νNH were found to be lowered ($\sim 15-20\text{ cm}^{-1}$) indicating coordination of the ligands through the $>C = N$ and $>NH$ groups. In the ir spectra of metal chelates, new bands in the far-infrared region at 520-550 and 400-440 cm^{-1} were observed which were assigned to $\nu(M-O)$ and $\nu(M-N)$ modes, respectively.

In the 1H nmr spectra of the H_2OB and H_2OP , signals due to COOH and -NH protons appeared at $\delta 11.7$ and 11.5 and 6.66 and 6.62 ppm, respectively. The position of signals due to $-CH_2$ ($\delta 3.05-3.12$) (multiplet) in H_2OP and aromatic protons ($\delta 7.13$) (multiplet) in H_2OB were found unchanged in the metal chelates.

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

Acknowledgement

LJ thanks the UGC, New Delhi, for the award of a fellowship.

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