

## Complex formation of rare earths with some bidentate Schiff bases : A thermodynamic study

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Proton-ligand stability constants of 1-(4'-methylphenyl)-2-methyl-2-(2'-hydroxy-5'-bromophenyl)imine ( $R_1$ ), 1-(4'-nitrophenyl)-2-methyl-2-(2'-hydroxy-5'-bromophenyl)imine ( $R_2$ ) and 1-(4'-chloro-5'-nitrophenyl)-2-methyl-2-(2'-hydroxy-5'-bromophenyl)imine ( $R_3$ ) and formation constants of their metal chelates with trivalent La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Yb and Ho have been determined at 25, 35 and 45° and  $\mu = 0.1 M(\text{NaClO}_4)$  in 50 : 50 ethanol-water medium by Irving-Rossotti method. The  $\log K^{\text{H}}$  and  $\log K$  values are used to discuss the effect of substituent and the atomic size of the rare earth elements. The thermodynamic parameters for the formation of 1 : 1 and 1 : 2 complexes have been calculated.

The lanthanide complexes of Schiff bases derived from salicylaldehyde, substituted salicylaldehyde with various primary amines have been reported<sup>1</sup>. No systematic study has been reported so far on the lanthanide complexes of Schiff bases derived from 5-bromoorthohydroxyacetophenones, and mono- and disubstituted anilines. We report here the stability constants and thermodynamic parameters of rare earth complexes of the ligands ( $R_1$ ,  $R_2$  and  $R_3$ ) in 50 : 50 ethanol-water medium at 25° and  $\mu = 0.1 M \text{NaClO}_4$  ionic strength.

### Results and Discussion

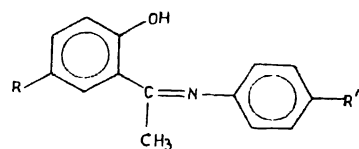
In the present ligands, protonation takes place in the initial stages of titrations because of the presence of azomethine nitrogen. The  $\log K_1^{\text{H}}$  and  $\log K_2^{\text{H}}$  were determined at  $\bar{n}_A = 1.5$  and 0.5, respectively. The values were further checked from the plots of  $\log\{(2-\bar{n}_A)/(\bar{n}_A-1)\}$  vs  $B$  and  $\bar{n}_A/(1-\bar{n}_A)$  vs  $B$  ( $B = \text{pH meter reading}$ ) and are given in Table I

Table I. Values of  $\log K_1^{\text{H}}$  and  $\log K_2^{\text{H}}$  of the ligands at different temperatures

Temp °C	$R_1$		$R_2$	$R_3$
	$\log K_1^{\text{H}}$	$\log K_2^{\text{H}}$	$\log K_2^{\text{H}}$	$\log K_2^{\text{H}}$
25	4.66	9.74	9.76	9.77
35	4.54	9.60	9.63	9.64
45	4.42	9.47	9.64	9.41

Ligand  $R_1$  shows  $\log K_1^{\text{H}}$  which represents the deprotonation of NH group at azomethine nitrogen whereas it is absent in the remaining ligands. Schiff base  $R_2$  bears  $\text{NO}_2$  group at 4-position to azomethine nitrogen and it does not display  $\log K_1^{\text{H}}$  value. The similar observation is noticed in

case of  $R_3$  which has  $\text{NO}_2$  group at 4- and Cl at 2-position with respect to azomethine nitrogen. The absence of  $\log K_1^{\text{H}}$  values in these ligands may be due to strong electron-withdrawing effect of  $\text{NO}_2$  as well as Cl group. The electron density on the azomethine nitrogen is almost totally withdrawn by these groups, resulting in the generation of positive charge on the azomethine nitrogen. Due to this, protonation of azomethine nitrogen does not take place resulting in the absence of  $\log K_1^{\text{H}}$  values. Thus the observed  $\log K_2^{\text{H}}$  values of the Schiff bases are  $R_1 \approx R_2 \approx R_3$ .



The shielding of the  $4f$ -electrons is exhibited in the stability constants of the present rare earth complexes, which shows very little difference in these values with the increase in atomic number. In these complexes the rare earth metal ions bind predominantly to oxygen and weakly to nitrogen in the Schiff bases<sup>2</sup>. These complexes show a regular increase of stability constants from  $\text{La}^{\text{III}}$  to  $\text{Eu}^{\text{III}}$  with a discontinuity of  $\text{Gd}^{\text{III}}$  which is commonly known as gadolinium break. After  $\text{Gd}^{\text{III}}$ , stability constant increases up to  $\text{Dy}^{\text{III}}$  and then decreases for  $\text{Ho}^{\text{III}}$ . This shows occasional maxima and minima after gadolinium break.

In all cases, the  $\text{Gd}^{\text{III}}$  chelates have lower value of  $\log K_1$  in relation to those of  $\text{Eu}^{\text{III}}$  to  $\text{Tb}^{\text{III}}$  chelates. The change

**Table 2.** Stability constants of thermodynamic parameters of rare earth metal complex of Schiff bases (R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>)<sup>a</sup>Temp = 25 ± 0.1°, μ = 0.1 M (NaClO<sub>4</sub>)

Compd	log K <sub>1</sub>	log K <sub>2</sub>	-ΔG		-ΔH		ΔS	
			kJ mol <sup>-1</sup>		kJ mol <sup>-1</sup>		J K <sup>-1</sup> mol <sup>-1</sup>	
La <sup>III</sup> R <sub>1</sub>	5.99	4.46	34.18	25.45	18.73	16.41	51.8	30.3
La <sup>III</sup> R <sub>2</sub>	6.07	4.46	34.64	26.59	13.06	12.22	72.4	48.2
La <sup>III</sup> R <sub>3</sub>	6.10	5.00	34.81	28.53	15.04	14.36	66.3	47.6
Ce <sup>III</sup> R <sub>1</sub>	6.13	4.66	34.98	26.59	13.79	17.55	71.1	30.3
Ce <sup>III</sup> R <sub>2</sub>	6.30	4.71	35.95	26.88	15.49	14.47	68.7	41.6
Ce <sup>III</sup> R <sub>3</sub>	6.15	5.04	35.09	28.76	15.12	14.86	67.0	46.7
Pr <sup>III</sup> R <sub>1</sub>	6.33	5.14	36.12	29.33	15.23	12.77	70.1	55.6
Pr <sup>III</sup> R <sub>2</sub>	6.43	4.86	36.69	27.73	13.79	11.54	76.8	54.4
Pr <sup>III</sup> R <sub>3</sub>	6.19	5.10	35.32	39.10	17.41	14.63	60.1	48.6
Nd <sup>III</sup> R <sub>1</sub>	6.39	5.23	36.46	29.84	15.41	17.04	70.6	43.0
Nd <sup>III</sup> R <sub>2</sub>	6.61	5.20	37.72	29.67	16.38	12.57	71.6	57.4
Nd <sup>III</sup> R <sub>3</sub>	6.29	5.28	35.89	30.13	13.76	16.75	74.3	44.9
Sm <sup>III</sup> R <sub>1</sub>	6.45	5.32	36.80	30.36	16.46	13.68	68.3	56.0
Sm <sup>III</sup> R <sub>2</sub>	6.68	5.28	38.12	30.13	13.85	13.40	81.4	56.1
Sm <sup>III</sup> R <sub>3</sub>	6.47	5.65	36.92	32.24	11.40	13.16	85.6	64.0
Eu <sup>III</sup> R <sub>1</sub>	6.58	5.59	37.55	31.90	11.58	17.68	87.1	47.7
Eu <sup>III</sup> R <sub>2</sub>	6.71	5.40	38.29	30.81	12.27	16.99	87.3	46.4
Eu <sup>III</sup> R <sub>3</sub>	6.65	5.77	37.95	32.92	16.29	11.40	70.3	72.2
Gd <sup>III</sup> R <sub>1</sub>	6.17	5.26	35.21	30.01	14.91	19.97	68.1	33.7
Gd <sup>III</sup> R <sub>2</sub>	6.28	5.22	35.83	29.79	14.36	10.81	72.1	63.7
Gd <sup>III</sup> R <sub>3</sub>	6.41	5.32	36.58	30.36	15.33	13.77	70.6	56.0
Tb <sup>III</sup> R <sub>1</sub>	6.28	5.38	35.83	30.70	12.07	15.01	79.8	52.6
Tb <sup>III</sup> R <sub>2</sub>	6.49	5.31	37.03	30.30	12.35	10.49	82.8	66.5
Tb <sup>III</sup> R <sub>3</sub>	6.46	5.42	36.86	30.93	10.64	9.12	88.0	73.2
Dy <sup>III</sup> R <sub>1</sub>	6.62	5.87	37.77	33.50	15.96	12.64	73.2	70.0
Dy <sup>III</sup> R <sub>2</sub>	6.60	5.64	37.66	32.18	12.60	16.65	84.1	52.1
Dy <sup>III</sup> R <sub>3</sub>	6.53	5.51	37.26	31.44	15.96	10.90	71.5	68.9
Ho <sup>III</sup> R <sub>1</sub>	6.25	5.36	35.66	30.58	13.96	18.53	72.8	40.5
Ho <sup>III</sup> R <sub>2</sub>	6.50	5.51	37.09	31.44	12.57	12.49	82.3	63.6
Ho <sup>III</sup> R <sub>3</sub>	6.40	5.44	36.52	31.04	16.51	10.26	67.2	69.7

<sup>a</sup>Standard deviation for log K<sub>1</sub> and log K<sub>2</sub> are ±0.019 and ±0.035, respectively

in free energy is directly related to the log *K* values. The thermodynamic parameters for lanthanide complexes with Schiff bases were obtained from log *K*<sub>1</sub> and log *K*<sub>2</sub> at different temperatures. From Table 2 it seems that the log *K*<sub>1</sub> and log *K*<sub>2</sub> values decrease with the increase in temperature, indicating that the high temperature does not favour the formation of stable complexes. The Δ*H*<sub>1</sub> and Δ*H*<sub>2</sub> values are all negative, while Δ*S*<sub>1</sub> and Δ*S*<sub>2</sub> are all positive. The resulting Δ*G*<sub>1</sub> and Δ*G*<sub>2</sub> values are all negative. The more negative values of Δ*G*<sub>1</sub> and Δ*G*<sub>2</sub> indicate that the 1 : 1 and 1 : 2 complex formation is thermodynamically favoured. The negative values of Δ*H*<sub>1</sub> and Δ*H*<sub>2</sub> also lead to the same inference. The entropy effect is found to be predominant over the enthalpy effect which is indicated by the high positive values of entropy.

### Experimental

All the chemicals used were of A.R. grade. The Schiff

bases were synthesized by the reported method<sup>3</sup>. Solutions of the rare earth nitrates were prepared in double-distilled water and standardized<sup>4</sup>. The initial ionic strength of all the solutions was maintained at 0.1 *M* by NaClO<sub>4</sub>. An Elico LI-120 pH meter in conjunction with a combined electrode was used. The measurements were made at 25, 35 and 45° (±0.01°) and μ = 0.01 *M* NaClO<sub>4</sub> in 50% aqueous ethanol. The log *K*<sup>H</sup> and log *K* values were computed by half-integral method, pointwise calculations and also by the method of least-squares. The average log *K* values were used to calculate Δ*G* from the van't Hoff's isotherm. The Δ*H* and Δ*S* values were calculated from the van't Hoff's isochore and the equation Δ*G* = Δ*H* - *T*Δ*S*, respectively.

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## Note

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