

## Stability constants of some lanthanide mixed ligand complexes

Rajesh Nagar\*, P C Dwivedi & R C Sharma

Department of Chemistry, Institute of Basic Sciences,  
Agra University, Khandari  
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Stability constants of the mixed ligand complexes of some lanthanides, viz., La(III), Pr(III), Nd(III), Gd(III) and Dy(III) with oxydiacetic acid (ODA), tartaric acid (TRA), malic acid (MEA), iminodiacetic acid (IDA) and glycine (GLY) as ligands have been determined *pH*-metrically at  $25 \pm 1^\circ\text{C}$  and at an ionic strength of  $0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ). A comparison of the values of stability constants of the complexes reveals the order, La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) in terms of metal ions, binary < ternary < quaternary in terms of complex species, TRA < MEA in terms of hydroxy acids and IDA < GLY in terms of amino acids. The  $\Delta \log K$  values are negative for all the ternary and quaternary systems; however,  $\Delta \Delta \log K$  values are significantly positive. These have been explained in terms of intramolecular hydrophobic ligand-ligand interactions. The stability constant data have been used to study the electrostatic factors involved in the formation of these mixed complexes.

A considerable amount of work on ternary complexes of transition metals<sup>1-3</sup> and rare earths<sup>4,5</sup> has been reported, but work on metal complexes having three different ligands is rather scanty.

Statistical aspects of mixed-ligand complexes have been discussed at length<sup>6,7</sup>. The term "total effect" has been proposed<sup>8</sup> for various factors, viz., statistical, electrostatic and others, operative during the formation of complexes. The present work aims at introducing two stability parameters for comparing the stabilities of mixed-ligand complexes at a given temperature. The quaternary systems chosen for study are of the type (M-A-B/C-L/L'), where M = La(III), Pr(III), Nd(III), Gd(III) and Dy(III); A = oxydiacetic acid, B = tartaric acid, C = malic acid, L = iminodiacetic acid and L' = glycine.

### Experimental

The solutions of all the chemicals (AR, BDH or GR, E. Merck) used, were prepared in doubly distilled water. Solutions of rare earth nitrates were prepared and standardized by the oxalate method<sup>9</sup>. The amino acids were used in their monoprotonated form. The solutions of ODA, TRA, MEA, potassium nitrate and

potassium hydrogen phthalate were prepared by direct weighing.

### Method of calculations

*pH* measurements were carried out with a Toshniwal digital *pH*-meter (accuracy  $\pm 0.01$ ). The instrument was standardized against potassium hydrogen phthalate solution ( $0.05 \text{ M}$ ) for *pH* 4 at  $25^\circ\text{C}$  in the beginning of each titration. Each titration was repeated at least twice against ( $0.1 \text{ M}$ ) potassium hydroxide solution at  $25 \pm 1^\circ\text{C}$  to ensure the reproducibility of results, keeping the ionic strength at  $0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ) and total volume constant ( $50 \text{ dm}^3$ ) in the beginning of each titration.

The dissociation constant of ODA ( $pK_1 = 3.10$ ,  $pK_2 = 4.18$ ), TRA ( $pK_1 = 2.71$ ,  $pK_2 = 4.09$ ), MEA ( $pK_1 = 3.22$ ,  $pK_2 = 4.72$ ), KIDA ( $pK_1 = 9.05$ ) and GLY ( $pK_1 = 9.77$ ) were calculated by the method of Chaberek and Martell<sup>10</sup>. Metal-ligand stability constants ( $\log K_{MA}^M$ ,  $\log K_{MAB}^M$ ,  $\log K_{MAC}^M$ ,  $\log K_{MAL}^{MA}$ ,  $\log K_{MAL}^{MA}$ ,  $\log K_{MABL}^{MAB}$ ,  $\log K_{MACL}^{MAC}$ ,  $\log K_{MABL}^{MAB}$ , and  $\log K_{MACL}^{MAC}$ ) were calculated by the modified method<sup>11</sup> of Ramamoorthy and Santappa<sup>12</sup> for the simultaneous chelation of ligands to the metal ion; however, in the case of stepwise addition of the ligand to metal ions, the method of Thompson and Loraas<sup>13</sup> was applied.

### Results and discussion

Potentiometric titrations have been carried out to study the formation of binary, ternary and quaternary complexes. From the nature of resultant curves, it is seen that the ternary systems are of the type  $M + A \rightleftharpoons MA$  ( $pH < 6.35$ );  $MA + L \rightleftharpoons MAL$  ( $pH < 5.65$ );  $M + A + B \rightleftharpoons MAB$  ( $pH < 6.75$ ), and quaternary systems are of the type  $MAB + L \rightleftharpoons MABL$  ( $pH < 7.63$ ) where A = ODA, L = IDA or GLY, B = TRA or MEA. In the formation of ternary and quaternary complexes, IDA and GLY behave as secondary and tertiary ligands. The stability constants (Tables 1 and 2) lie in the order: La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III), which is the order of increasing occupancy of the 4*f* orbitals of these lanthanides accompanied by a gradual decrease in their ionic radii. The stability order has been found to be TRA < MEA in terms of hydroxy acids and IDA < GLY in terms of amino acids. Free energy of formation (Table 1) has been calculated and found to be negative in all the cases, indicating complex formation to be almost spontaneous in nature.

The general orders of stabilities for the complexes have been found to be  $\log K_{MA}^M > \log K_{MAL}^{MA}$  and

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$\log K_{MA}^M > \log K_{MAL}^{MA}$ . But the overall stability of quaternary complexes is greater than that of the ternary complexes and the overall stability of ternary complexes (Table 2) is greater than that of the binary complexes, i.e.,  $\log K_{MA}^M < \log K_{MAB}^M < \log K_{MAC}^M$  &  $\log \beta_1 < \log \beta_2 < \log \beta_3 < \log \beta_4 < \log \beta_5 < \log \beta_6$ .

A comparison of the stability constants of the binary (ML) and ternary complexes (MAL) gives a measure of the relative ease (or difficulty) experienced by

the secondary ligand (L) in combining with MA to form the mixed complexes. Hence, the use of  $\Delta \log K$  (Table 1) has been preferred for comparing the stabilities of the quaternary and ternary complexes in relation to those of the corresponding binary complexes. The  $\Delta \log K$  values are negative in all the cases, which should be primarily due to the electrostatic repulsion induced by the secondary or tertiary ligands. The greater stabilization of the ternary and quaternary complexes may be explained on the basis of a

Table 1—Metal-ligand stability constants of 1:1 binary, 1:1:1 ternary and 1:1:1:1 quaternary complexes and other related properties

$[\mu = 0.1 \text{ mol dm}^{-3}(\text{KNO}_3); \text{Temp.} = 25 \pm 1^\circ\text{C}; T_M: T_A: T_B: T_L = 1:1:1:1]$

System	Property	Value for metal ion				
		La(III)	Pr(III)	Nd(III)	Gd(III)	Dy(III)
1:1, M(III)-ODA	$\log K_{MA}^M$	2.41	2.53	2.67	2.76	2.86
	$-\Delta G$	3.29	3.45	3.64	3.76	3.90
1:1:1, M(III)-ODA-IDA	$\log K_{MAL}^{MA}$	2.12	2.30	2.39	2.48	2.59
	$-\Delta G$	2.89	3.14	3.26	3.38	3.53
	$-\Delta \log K$	0.29	0.23	0.28	0.28	0.27
	-(%)R.S.	62.67	61.92	62.36	61.73	60.81
	$\log K_S$	4.04	4.28	4.51	4.62	4.73
1:1:1, M(III)-ODA-GLY	(%)R.A.	47.52	46.26	47.00	46.32	45.24
	$\log K_{MAL}^{MA}$	2.29	2.41	2.52	2.61	2.74
	$-\Delta G$	3.12	3.29	3.44	3.56	3.74
	$-\Delta \log K$	0.12	0.12	0.15	0.15	0.12
	-(%)R.S.	59.18	57.64	56.70	56.13	54.93
1:1:1:1, M(III)-ODA-TRA-IDA	$\log K_S$	3.69	3.79	3.93	4.04	4.15
	(%)R.A.	37.94	36.41	35.88	35.39	33.97
	$\log K_{MABL}^{MAB}$	5.33	5.44	5.48	5.53	5.67
	$-\Delta G$	7.27	7.42	7.47	7.54	7.73
	$-\Delta \log K$	0.71	0.62	0.51	0.48	0.33
1:1:1:1, M(III)-ODA-TRA-GLY	-(%)R.S.	6.16	9.93	13.70	14.66	14.22
	$\log K_S$	7.41	7.63	7.79	7.91	8.02
	(%)R.A.	28.07	28.70	29.65	30.09	29.30
	$\log K_{MABL}^{MAB}$	5.44	5.56	5.61	5.70	5.76
	$-\Delta G$	7.41	7.58	7.65	7.77	7.85
1:1:1:1, M(III)-ODA-MEA-IDA	$-\Delta \log K$	1.50	1.38	1.27	1.19	1.12
	-(%)R.S.	3.03	4.47	5.71	4.20	5.26
	$\log K_S$	6.68	6.79	6.86	6.97	7.06
	(%)R.A.	18.56	18.11	18.22	18.23	18.41
	$\log K_{MACL}^{MAC}$	5.50	5.55	5.60	5.65	5.70
1:1:1:1, M(III)-ODA-MEA-GLY	$-\Delta G$	7.50	7.57	7.64	7.70	7.77
	$-\Delta \log K$	1.44	1.39	1.28	1.24	1.18
	-(%)R.S.	3.17	8.11	11.81	12.80	13.76
	$\log K_S$	7.97	8.18	8.35	8.46	8.56
	(%)R.A.	30.99	32.15	32.93	33.21	33.41
1:1:1:1, M(III)-ODA-MEA-GLY	$\log K_{MACL}^{MAC}$	5.53	5.64	5.71	5.79	5.87
	$-\Delta G$	7.54	7.69	7.79	7.89	8.01
	$-\Delta \log K$	1.41	1.30	1.17	1.10	1.01
	-(%)R.S.	1.43	3.09	4.03	2.69	3.45
	$\log K_S$	7.25	7.34	7.42	7.52	7.61
(%)R.A.	23.72	23.16	23.04	23.00	22.86	

Table 2—Overall stability of ternary and quaternary complexes

System	Property	Metal ions				
		La(III)	Pr(III)	Nd(III)	Gd(III)	Dy(III)
1:1:1, M(III)-ODA-TRA	$\log K_{MAB}^M$	8.45	8.59	8.66	8.77	8.86
1:1:1, M(III)-ODA-MEA	$\log K_{MAC}^M$	9.35	9.47	9.55	9.65	9.74
1:1:1, M(III)-ODA-IDA	$\log \beta_1$	4.53	4.83	5.06	5.24	5.35
1:1:1, M(III)-ODA-GLY	$\log \beta_2$	4.70	4.94	5.19	5.37	5.50
1:1:1:1, M(III)-ODA-TRA-IDA	$\log \beta_3$	13.78	14.03	14.14	14.30	14.53
1:1:1:1, M(III)-ODA-TRA-GLY	$\log \beta_4$	13.89	14.15	14.27	14.47	14.62
1:1:1:1, M(III)-ODA-MEA-IDA	$\log \beta_5$	14.85	15.02	15.15	15.30	15.44
1:1:1:1, M(III)-ODA-MEA-GLY	$\log \beta_6$	14.88	15.11	15.26	14.44	15.61

cooperative effect<sup>14</sup> between the primary, secondary and tertiary ligands in these cases. The existence of intramolecular hydrophobic interaction may be examined in terms of relation  $\Delta\Delta \log K = \log K_1 - \log K_2$ . Significantly positive values of  $\Delta\Delta \log K$  (Table 3) for ternary and quaternary systems may be regarded as an evidence of hydrophobic interactions responsible for relatively greater stabilization of the mixed complexes.

A comparison of the relative stabilities of different mixed complexes can be more satisfactorily achieved on the basis of a new parameter "% Relative stabilization" (Table 1). In the present work  $\log K_{MAL}^{MA}$  is found to be less than  $\log K_{ML}^M$  due to the electrostatic repulsion involved between the primary and secondary ligands during the formation of ternary complex. Statistically, the tendency of a metal ion to combine with a ligand goes on decreasing with increase in the number of ligands bound to metal ion. This idea would imply that the tendency of metal ion to bind itself to L should decrease after it has already been bound to A in MA. Thus, statistically,  $\log K_{MAL}^{MA}$  should be lower than  $\log K_{ML}^M$ . The statistical value of  $\Delta \log K$  varies depending on the geometry of the complex and denticity of the ligands<sup>15</sup>.

Statistical stability constants ( $\log K_s$ ) of mixed complexes have been calculated<sup>16</sup> (Table 1). It has been found that, in general,  $\log K_s$  values are greater than  $\log K_{MAL}^{MA}$  or  $\log K_{MABL}^{MAB}$ , which clearly indicates the involvement of 'astatistical' factors such as electrostatic effect, steric effect, size of chelate rings, asymmetry of the ligands field, etc., in the formation of mixed-ligand complexes. A quantitative measure of astatistical factors involved in the formation of mixed-ligand complexes may be expressed in terms of another parameter "% Relative Astatisticality". The values are positive and numerically high indicating that the astatistical factors affect the stability of mixed-complexes.

For log-log type of stability correlation<sup>17</sup>, (a)  $\log$

Table 3—Possibility of occurrence of intramolecular hydrophobic ligand-ligand interaction in ternary and quaternary complexes

System	$\Delta\Delta \log K$ for metal ions				
	La(III)	Pr(III)	Nd(III)	Gd(III)	Dy(III)
1:1:1, M(III)-ODA-IDA/GLY	0.17	0.11	0.13	0.13	0.15
1:1:1:1, M(III)-ODA-TRA-IDA/GLY	0.11	0.12	0.13	0.17	0.09
1:1:1:1, M(III)-ODA-MEA-IDA/GLY	0.03	0.09	0.11	0.14	0.17

$K_{MAL}^{MA}$  versus  $\log K_{MA}^M$ , (b)  $\log K_{MAL}^{MA}$  versus  $\log K_{MA}^M$ , (c)  $\log K_{MAB}^M$  versus  $\log K_{MA}^M$ , (d)  $\log K_{MAC}^M$  versus  $\log K_{MA}^M$ , (e)  $\log K_{MAL}^{MA}$  versus  $\log K_{MABL}^{MAB}$ , (f)  $\log K_{MABL}^{MAB}$  versus  $\log K_{MAB}^M$ , (g)  $\log K_{MAC}^M$  versus  $\log K_{MAC}^M$ , (h)  $\log K_{MABL}^{MAB}$  versus  $\log K_{MAB}^M$  and (i)  $\log K_{MAC}^M$  versus  $\log K_{MAC}^M$  have been plotted. All plots are linear, which shows that the affinity of the association of secondary and tertiary ligands in ternary and quaternary systems follows, in general, the same pattern as it does with aqueous metal ion  $M(H_2O)_n$ .

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