

## Tetrad effect in mixed-ligand lanthanide chelates. Part II: Lanthanide. CDTA/DTPA, orcinol/resorcinol/phloroglucinol ternary systems

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**Abstract.** The variation profiles of certain properties of the lanthanide [Ln(III)] series show discontinuities at or around Gd(III) ( $4f^7$  stage), Nd(III)–Pm(III) ( $4f^3 - 4f^4$  stage) and Ho(III)–Er(III) ( $4f^{10} - 4f^{11}$  stage) due to the presence of a tetrad effect. In the present work the occurrence of the tetradic phenomenon has been studied for the formation constants,  $\log K_{MAL}^{MA}$  of the mixed-ligand Ln(III) chelates of the type [Ln(III).A.L], where Ln(III) = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III) or Dy(III); A = CDTA or DTPA; L = orcinol, resorcinol or phloroglucinol. The presence of the tetrad effect in  $\log K_{MAL}^{MA}$  values has been tested with the help of the straight line approximation method, differential plot method and inclined-W hypothesis. The magnitude of the effect has been found to lie in the sequence  $f^7 > f^3 - f^4$ .

**Keywords.** Ln, CDTA/DTPA/phenol/ternary complexes; formation constants; tetrad effect.

### 1. Introduction

The variation profiles of certain properties (Verma and Saxena 1988) of the lanthanide [Ln(III)] series show discontinuities at or around Gd(III) ( $4f^7$  configuration, i.e. half-filled  $4f$ -shell), Nd(III)–Pm(III) ( $4f^3 - 4f^4$  configuration, i.e. one-fourth-filled  $4f$ -shell) and Ho(III)–Er(III) ( $4f^{10} - 4f^{11}$  configuration, i.e. three-fourths-filled  $4f$ -shell) due to the occurrence of the tetrad effect (Peppard *et al* 1969) or double-double effect (Fidelis and Sikierski 1971). It has been suggested (Jorgensen 1970) that the presence of the tetrad effect may be a consequence of changes in the nephelauxetic ratio on complexation. A somewhat similar approach (Nugent 1970) attempts to show that the effect has its origin in the coefficients of the Racah parameters ( $E^1$  and  $E^3$ ) which are related to the angular part of the wavefunctions of the Ln(III) ions. Recently (Sikierski 1981), it has been shown that the effect is present in the Racah parameters ( $E^0$ ,  $E^1$ ,  $E^2$  and  $E^3$ ) also, which are related to the radial part of the wavefunction of the Ln(III) ions. It appears, therefore, that the tetrad effect is an intrinsic property of  $4f$ -orbitals.

The present work aims at studying the presence of the tetrad effect in the solution stabilities ( $\log K_{MAL}^{MA}$ ) of mixed-ligand complexes of the type [Ln(III).A.L], where Ln(III) = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III) or Dy(III); A = 1,2-diaminocyclohexane-N, N, N', N'-tetraacetate (CDTA) or diethylene

\* For correspondence

triamino-N, N, N', N'', N'''-pentaacetate (DTPA); L = orcinol (orc), resorcinol (res) or phloroglucinol (phl). The occurrence of the tetradic phenomenon has been confirmed by using three independent methods viz., straight line approximation method (Siekierski 1981), differential plot method (Verma and Saxena 1987) and inclined-W systematics (Sinha 1975). The magnitude of the effect as a function of  $4f$  configuration of the Ln (III) ions has also been studied in order to find possible experimental evidence in favour of the inter-electronic repulsion theory of the tetrad effect.

## 2. Experimental

The data for the study of the tetrad effect comprise the formation constants,  $\log K_{MAL}^{MA}$  of the mixed-ligand complexes (listed above), determined by potentiometric pH titrations using the Irving-Rossotti approach (Irving and Rossotti 1953, 1954; Chidambaram and Bhattacharya 1970) at 25°C and an ionic strength,  $I = 0.2$  (mol dm<sup>-3</sup>, NaClO<sub>4</sub>).

The Ln(III) nitrates (99.9% purity) were purchased from the Indian Rare Earths Ltd. Their solutions were prepared in double-distilled water and standardised by complexometric EDTA titrations (West 1969). Other chemicals were of standard purity (Sigma/Merck GR grade). Aqueous solutions of ligands were prepared by direct weighing. Final concentrations of the solutions were kept at  $1 \times 10^{-3}$  mol dm<sup>-3</sup> with respect to the Ln(III) ion, A and L. A 0.2 mol dm<sup>-3</sup> carbonate-free NaOH solution was used for pH titrations, which were performed on a digital pH meter (Elico, LI-120) having an accuracy of  $\pm 0.01$  pH unit using a microburette reading upto 0.01 ml. The titrations were repeated to obtain reproducible pH data. The calculated values of formation constants ( $\log K_{ML}^M$  and  $\log K_{MAL}^{MA}$ ) were refined algebraically by the linear plot method (Rossotti and Rossotti 1955) and statistically by the 'Q-test' (Pecsock *et al* 1976). Refined values of the formation constants are recorded in table 1.

**Table 1.** Formation constants ( $\log K_{ML}^M$  and  $\log K_{MAL}^{MA}$ ) along with their  $\Delta \log K$  ( $\log K_{MAL}^{MA} - \log K_{ML}^M$ ) values for mixed-ligand lanthanide chelates. (Temperature = 25°C; ionic strength,  $I = 0.2$  (mol dm<sup>-3</sup> NaClO<sub>4</sub>))

Formation constant	L	La <sup>3+</sup>	Ce <sup>3+</sup>	Pr <sup>3+</sup>	Nd <sup>3+</sup>	Sm <sup>3+</sup>	Eu <sup>3+</sup>	Gd <sup>3+</sup>	Tb <sup>3+</sup>	Dy <sup>3+</sup>
$\log K_{ML}^M$	orc	7.08	7.24	7.54	7.64	7.92	8.00	7.76	8.19	8.29
	res	7.17	7.20	7.44	7.58	7.75	7.85	7.73	7.90	7.98
	phl	6.61	6.83	6.91	7.12	7.22	7.37	7.17	7.49	7.59
$\log K_{MAL}^{MA}$ (A = CDTA)	orc	5.79	5.89	6.02	6.12	6.24	6.37	6.29	6.54	6.67
	$\Delta \log K$	-1.29	-1.35	-1.52	-1.52	-1.68	-1.63	-1.47	-1.65	-1.62
	res	5.45	5.52	5.60	5.83	5.98	6.08	6.03	6.23	6.33
	$\Delta \log K$	-1.72	-1.68	-1.84	-1.75	-1.77	-1.77	-1.70	-1.67	-1.65
	phl	5.25	5.36	5.55	5.60	5.67	5.82	5.76	5.92	6.07
$\Delta \log K$	-1.36	-1.47	-1.36	-1.52	-1.55	-1.55	-1.41	-1.57	-1.52	
$\log K_{MAL}^{MA}$ (A = DTPA)	orc	5.64	5.74	5.92	6.03	6.06	6.16	6.14	6.24	6.36
	$\Delta \log K$	-1.44	-1.50	-1.62	-1.61	-1.86	-1.84	-1.62	-1.95	-1.93
	res	5.35	5.37	5.57	5.69	5.80	5.93	5.90	5.96	6.11
	$\Delta \log K$	-1.82	-1.83	-1.87	-1.89	-1.95	-1.92	-1.83	-1.94	-1.87
	phl	4.78	4.87	5.00	5.12	5.25	5.53	5.31	5.77	5.83
$\Delta \log K$	-1.83	-1.96	-1.90	-2.00	-1.97	-1.84	-1.86	-1.72	-1.76	

### 3. Results and discussion

The present series of mixed-ligand complexes are formed in two distinct steps  $M + A \rightleftharpoons MA$ ;  $MA + L \rightleftharpoons MAL$  as indicated by the nature of titration curves (not shown). The formation of the hydroxo species is not observed in these ternary systems even upto pH 10 or 11. Three observed trends about the solution stabilities of the mixed ligand complexes deserve comments. (i) The  $\Delta \log K$  values are negative due mainly to electrostatic repulsion accompanying the formation of MAL complexes; both MA as well as L species are negatively charged. The values are more negative with DTPA than with CDTA because the former yields a more negative  $A^{n-}$  species on deprotonation and this would enhance the magnitude of electrostatic repulsion. (ii) The driving force of the electrostatic effect leads to the stability sequence  $CDTA > DTPA$  for the MAL complexes as against the known order  $DTPA > CDTA$  for the MA chelates. The order  $DTPA > CDTA$  for the  $[Ln(III) \cdot A]^{n-}$  chelates is a consequence of the difference in the denticities of the two ligands (DTPA:octadentate, CDTA:hexadentate). The MA species formed with CDTA and DTPA are  $[Ln(III) \cdot CDTA]^-$  and  $[Ln(III) \cdot DTPA]^{2-}$ , A greater negative charge on the latter leads to the sequence  $\log K_{Ln(III) \cdot CDTA \cdot L}^{Ln(III) \cdot CDTA} > \log K_{Ln(III) \cdot DTPA \cdot L}^{Ln(III) \cdot DTPA}$  due to the greater coulombic repulsion involved in its case in the formation of MAL ternary complexes as  $MA + L \rightleftharpoons MAL$ . (iii) The stability sequence with respect to the secondary ligands has been observed as  $orc > res > phl$ , which is the order of ligand basicity.

The formation constants  $\log K_{MAL}^{MA}$  as well as  $\log K_{ML}^M$  vary across the Ln(III) series (cf. table 1) in the sequence  $La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Eu(III) > Gd(III) < Tb(III) < Dy(III)$ . This gradual increase in the solution stability with the number of  $4f^n$ -electrons ( $4f^n$ ) along with a depression at Gd(III) shows the occurrence of the tetrad effect. The variation profile may be seen in figure 1 which contains representative plots of  $\log K_{MAL}^{MA}$  vs.  $4f^n$ . In all these plots a prominent dip at Gd(III) ( $4f^7$  configuration) is observed due to the tetrad effect. The general stability enhancement with  $4f^n$  is a consequence of decrease in ionic radii and increase in

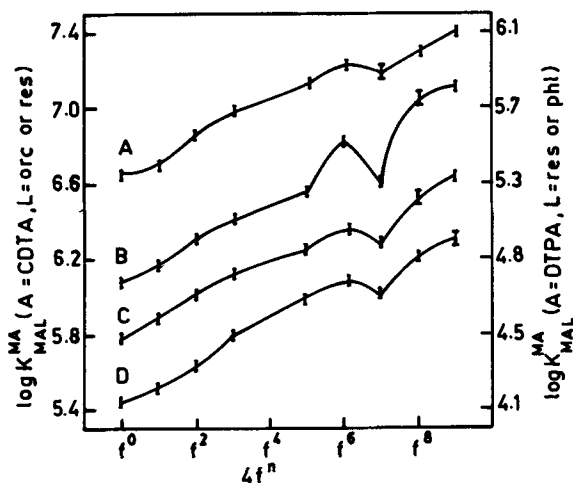


Figure 1. Variation in formation constants ( $\log K_{MAL}^{MA}$ ) with  $4f^n$ . Curves A:  $\log K_{Ln(III) \cdot DTPA \cdot res}^{Ln(III) \cdot DTPA}$ ; B:  $\log K_{Ln(III) \cdot DTPA \cdot phl}^{Ln(III) \cdot DTPA}$ ; C:  $\log K_{Ln(III) \cdot CDTA \cdot orc}^{Ln(III) \cdot CDTA}$ ; D:  $\log K_{Ln(III) \cdot CDTA \cdot res}^{Ln(III) \cdot CDTA}$ .

ionic potential of the Ln(III) ions. The plots do not, however, show a clearly visible discontinuity at the  $4f^3-4f^4$  stage.

The presence of the tetrad effect may be examined with the help of the straight line approximation method (Siekierski 1981), which is a statistical tool. Dividing the entire Ln(III) series ( $4f^0-4f^{14}$ ) into four segments  $f^0-f^3$ ,  $f^4-f^7$ ,  $f^7-f^{10}$  and  $f^{11}-f^{14}$  we may determine the deviations  $\Delta$  between the experimental and interpolated values ( $\Delta = P_{\text{exp}} - P_{\text{int}}$ , where  $P_{\text{exp}}$  = experimental value of property,  $P_{\text{int}}$  = interpolated value of property at the same  $4f^n$  configuration) of  $\log K_{\text{MAL}}^{\text{MA}}$  or  $\Delta G (= -2.303RT \log K_{\text{MAL}}^{\text{MA}})$ . In the presence of the tetrad effect  $\Delta < 0$  for  $f^1, f^2, f^5, f^6, f^8, f^9, f^{12}$  and  $f^{13}$  and  $\Delta > 0$  for  $f^3, f^4, f^7, f^{10}$  and  $f^{11}$  configurations. In the present case the deviations are observed as above, in general, (figure not shown) but some disagreements with the method are also noted.

The authors have found the use of the differential plot method (Verma and Saxena 1987) to be more satisfactory. Differential plots of  $\Delta \log K_{\text{MAL}}^{\text{MA}}/\Delta r$  vs.  $4f^n$  (where  $\Delta \log K_{\text{MAL}}^{\text{MA}}$  and  $\Delta r$  represent, respectively, the differences between the formation constants and ionic radii for the Ln(III) ions of  $4f^{n-1}$  and  $4f^n$  configurations) for two representative mixed-ligand complexes are reproduced in figure 2. The plots show well-marked minima at the end of the first tetrad ( $f^3-f^4$  configuration) also besides more prominent depressions at the end of the second tetrad ( $f^7$  configuration). The advantage of the differential plots is that the first derivative becomes more prominent than the value of the change on a linear scale.

The inclined-W hypothesis (Sinha 1975) may also be applied. In this case one studies the variation profile of a Ln(III) property with the  $L$ -quantum number, which is a non-linear function of the atomic number of the lanthanides. The correlation of a property (here  $\log K_{\text{MAL}}^{\text{MA}}$ ) with  $L$  may be justified on the basis that the ground state configurations of the Ln(III) ions are all  $4f^n$ ; they are more than 95% pure  $L-S$  states and are only nominally perturbed in complexation due to little or no involvement

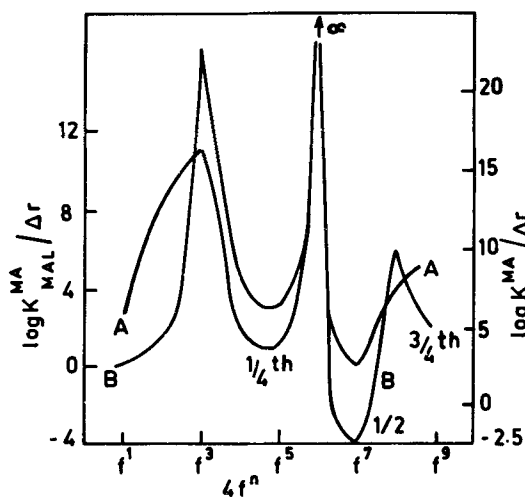


Figure 2. Variation in  $\Delta \log K_{\text{MAL}}^{\text{MA}}/\Delta r$  with  $4f^n$  electrons (differential plots). Curve A: Ln(III)·DTPA·orc; B: Ln(III)·CDTA·res.

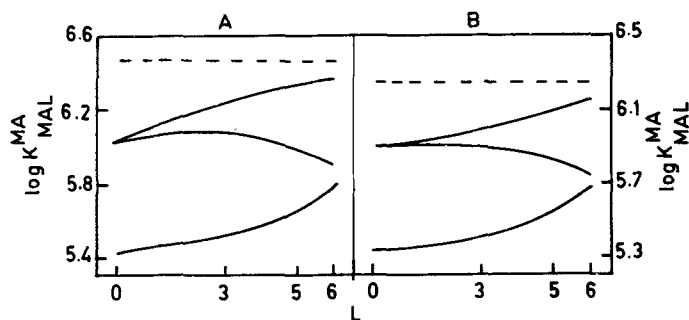


Figure 3. Variation in formation constants ( $\log K_{MAL}^{MA}$ ) with  $L$  of Ln(III) ions. Curve A:  $\log K_{Ln(III)-CDTA}^{Ln(III)-DTPA}$ ; B:  $\log K_{Ln(III)-DTPA}^{Ln(III)-DTPA-res}$ .

of  $4f$ -orbitals in M-L bonding (Sinha 1983). Representative inclined-W plots of  $\log K_{MAL}^{MA}$  vs.  $L$  are presented in figure 3. The fourth segment of the inclined-W has been tentatively shown by a dotted line as lanthanides beyond the  $4f^9$  configuration were not available to us for the present study. These  $L$ -correlation plots are quite satisfactory, but they lack symmetry and linearity within segments. The characteristics of these plots is that the three vertices of the inclined-W coincide with the three configurations  $f^3-f^4$ ,  $f^7$  and  $f^{10}-f^{11}$  where discontinuities due to the tetrad effect occur in the variation profiles.

Jorgensen (1970) and Nugent (1970) have separately proposed that the occurrence of the tetrad effect in a Ln(III) property is related to changes in inter-electronic repulsions on complexation. Jorgensen (1970) has demonstrated that a change in the nephelauxetic ratio causes the appearance of the tetrad effect. Nugent has shown that the effect is present in both the 'spin part' as well as the 'orbital part' of the wave function. Two inferences may be drawn from this work:

- (i) the tetrad effect should have the same direction (dip) at the three stages i.e. half-filled, one-fourth filled and three-fourths filled  $4f$ -shell
- (ii) the magnitude of the effect at the one-fourth and three-fourths filled shell stages should be the same and each much weaker, i.e., about  $1/6$  of the magnitude at the half-filled stage.

In order to test the validity of inter-electronic repulsion theory, the magnitude of the tetrad effect has been calculated at different  $4f^n$  configurations following a published procedure (Siekierski 1981). The magnitude of the effect at the  $4f^7$  stage has been found to lie between about 0.8 and 2.8 for the present mixed-ligand complexes and that at the  $4f^3-4f^4$  stage is much smaller, lying between about 0.1 and 0.4. This sequence  $f^7 > f^3-f^4$  in the magnitude as well as the ratio of the numerical values of the magnitudes for the two configurations are in agreement with the theoretical treatments mentioned above. The same conclusion may be drawn profitably directly from the proposed differential plots (figure 2).

A significant point may be raised here; although the participation of  $4f$ -orbitals in complexation has been doubted (Williams 1982) or regarded as marginal (Sinha 1983), the trends in observed stability data and other facts (references cited above) can be explained on the basis of the properties of  $4f$ -orbitals.

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