

Periodicity in the formation constant values of lanthanide(III). aminopolycarboxylate. resorcinol/orcinol/phloroglucinol mixed ligand complexes

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Abstract. Formation constants ($\log K_{MAL}^{MA}$) of mixed ligand complexes [Ln(III).A.L], where Ln(III) = La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} or Dy^{3+} ; A = NTA, HEDTA or EDTA and L = resorcinol (res), orcinol (orc) or phloroglucinol (phl), have been determined pH-metrically using the Irving-Rossotti approach at 25°C and at an ionic strength, $I = 0.2$ (mole dm^{-3} , $NaClO_4$). The $\log K_{MAL}^{MA}$ values lie in the sequence: (i) NTA > HEDTA > EDTA and (ii) $orc > res > phl$ with respect to primary (A) and secondary (L) ligands, respectively.

Periodicity has been observed in the formation constant values, which lie in the sequence $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+} < Eu^{3+} > Gd^{3+} < Tb^{3+} < Dy^{3+}$ with respect to Ln(III) ions. The evaluated extrastabilization and nephelauxetic ratio values lend support to inter-electronic repulsion theory; these values and the magnitude of the tetrad effect lie in the sequence $f^7 > f^3 - f^4 \approx f^{10} - f^{11}$. Hydration numbers (HN) of Ln(III) ions have been calculated; tetrad effect is present in HN.

Keywords Periodicity in formation constants; Ln(III).aminopolycarboxylate resorcinol; orcinol; phloroglucinol; ternary complexes.

1. Introduction

Discontinuities are known to occur (Sinha 1983; Verma and Saxena 1988) in the variation profiles of several properties of lanthanides (and actinides). These discontinuities occur prominently at the $4f^7$ (Gd(III)) stage and less markedly at the $4f^3 - 4f^4$ (Nd(III)-Pm(III)) and $4f^{10} - 4f^{11}$ (Ho(III)-Er(III)) stages dividing Ln(III) series into four segments or tetrads. This tetradic phenomenon has been called the tetrad effect (Peppard *et al* 1969) or the double-double effect (Fidelis and Siekierski 1971). The periodicity observed in the properties has been termed variously as microperiodicity (Tishchenko *et al* 1981), regularities (Fidelis 1970), symmetry or systematics (Sinha 1975, 1978, 1983). Attempts have been made to predict the properties of lanthanides using inclined-W systematics (Sinha 1975), semi-empirical equations (Jorgensen 1971, 1979; Poluektov 1982) and quantum chemical calculations (Spitsyn *et al* 1984, 1990; Limaye and Saxena 1992). It is believed that changes in inter-electronic repulsions alter the nephelauxetic ratio leading to extrastabilization (Nugent 1970; Jorgensen 1970, 1971, 1979, 1988) of specific configurations ($f^3 - f^4, f^7, f^{10} - f^{11}$). The possibility

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of ligand field splitting (Yatsimirskii and Kostromina 1964), L-S coupling (Dzhurinskii 1980) and hydration (Williams 1982) contributing to the occurrence of periodicity has also been suggested.

The present work attempts to investigate the occurrence of periodicity in the formation constant values, i.e. free energy of complexation of the mixed ligand complexes of the type $[\text{Ln(III).A.L}]$, where $\text{Ln(III)} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$ or Dy^{3+} ; A = nitrilotriacetate (NTA), 2-hydroxy-ethylethylenediaminetriacetate (HEDTA) or ethylenediaminetetraacetate (EDTA), and L = resorcinol (res), orcinol (orc) or phloroglucinol (phl). Attempts have also been made to examine the systematics in the hydration numbers of Ln(III) ions.

2. Experimental

Chemicals of standard purity were used. Ln(III) nitrates of 99.99% purity were supplied by the Indian Rare Earths Limited. Other chemicals were of Merck GR and Sigma/Fluka make. The solutions were prepared in double distilled water. The Ln(III) solutions were standardized by complexometric titrations (West 1969). The formation constants $\log K_{\text{ML}}^{\text{M}}$ and $\log K_{\text{MAL}}^{\text{MA}}$ were determined pH-metrically using the Irving-Rossotti approach (Irving and Rossotti 1953, 1954; Chidambaram and Bhattacharya 1970) at 25°C and at an ionic strength, $I = 0.2$ (mole dm^{-3} , NaClO_4). An Elico digital (model LI-120) pH-meter with an accuracy of ± 0.01 pH unit and a 1.0 ml microburette reading up to 0.01 ml were used. The final metal and ligand concentrations were maintained at $[\text{Ln(III)}] = [\text{A}] = [\text{L}] = 1.0 \times 10^{-3}$ mole dm^{-3} . A 0.2 mole dm^{-3} carbonate-free sodium hydroxide solution was used for pH titrations, which were always repeated to ascertain reproducibility. The formation constant values were refined statistically by the linear plot method (Rossotti and Rossotti 1955; Pecsok *et al* 1976). Refined values of the formation constants are presented in table 1.

Table 1. Formation constants of binary $\text{ML}(\log K_{\text{ML}}^{\text{M}})$ and ternary $\text{MAL}(\log K_{\text{MAL}}^{\text{MA}})$ complexes of Ln(III) ions with NTA, HEDTA, EDTA (A) and res, orc, phl (L).

| Formation constant | A | L | La^{3+} | Ce^{3+} | Pr^{3+} | Nd^{3+} | Sm^{3+} | Eu^{3+} | Gd^{3+} | Tb^{3+} | Dy^{3+} |
|-----------------------------------|-------|-----|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\log K_{\text{ML}}^{\text{M}}$ | — | res | 7.18 | 7.21 | 7.46 | 7.58 | 7.75 | 7.85 | 7.73 | 7.90 | 7.98 |
| | — | orc | 7.08 | 7.24 | 7.54 | 7.64 | 7.89 | 8.00 | 7.76 | 8.19 | 8.29 |
| | — | phl | 6.61 | 6.83 | 6.91 | 7.12 | 7.22 | 7.37 | 7.17 | 7.49 | 7.59 |
| $\log K_{\text{MAL}}^{\text{MA}}$ | NTA | res | 5.94 | 6.03 | 6.13 | 6.33 | 6.40 | 6.55 | 6.40 | 6.65 | 6.73 |
| | HEDTA | res | 5.91 | 5.98 | 6.03 | 6.12 | 6.28 | 6.40 | 6.23 | 6.48 | 6.58 |
| | EDTA | res | 5.40 | 5.50 | 5.60 | 5.80 | 5.90 | 6.04 | 5.93 | 6.21 | 6.29 |
| $\log K_{\text{MAL}}^{\text{MA}}$ | NTA | orc | 6.20 | 6.34 | 6.444 | 6.54 | 6.72 | 6.79 | 6.64 | 6.92 | 7.00 |
| | HEDTA | orc | 6.08 | 6.17 | 6.22 | 6.37 | 6.49 | 6.61 | 6.57 | 6.67 | 6.79 |
| | EDTA | orc | 5.70 | 5.85 | 5.95 | 6.02 | 6.09 | 6.24 | 6.13 | 6.42 | 6.50 |
| $\log K_{\text{MAL}}^{\text{MA}}$ | NTA | phl | 5.57 | 5.72 | 5.85 | 6.02 | 6.19 | 6.32 | 6.22 | 6.53 | 6.74 |
| | HEDTA | phl | 5.52 | 5.71 | 5.85 | 5.92 | 6.08 | 6.25 | 6.15 | 6.22 | 6.32 |
| | EDTA | phl | 4.90 | 5.02 | 5.17 | 5.28 | 5.42 | 5.68 | 5.40 | 5.80 | 5.98 |

Standard deviation: ± 0.005 to 0.03

Temp.: 25°C; Ionic strength, $I = 0.2$ (mol dm^{-3} , NaClO_4)

3. Results and discussion

The formation constant values evidently show a dependence on ligand characteristics. The $\log K_{ML}^M$ values lie in the order $\text{orc} > \text{res} > \text{phl}$, which is the sequence of ligand basicity. The $\log K_{MAL}^{MA}$ values increase in the sequence $\text{EDTA} < \text{HEDTA} < \text{NTA}$ with respect to aminopolycarboxylates. This order appears to be a consequence of electrostatic effect accompanying ternary complexation as $\text{MA} + \text{L} = \text{MAL}$ (charges omitted) although the steric and statistical effects are also expected to contribute to the observed order. The calculated values of the stability quantifying parameter $\Delta \log K (= \log K_{MAL}^{MA} - \log K_{ML}^M)$ are all negative, increasing numerically in the sequence $\text{NTA} < \text{HEDTA} < \text{EDTA}$; e.g. $\Delta \log K$ with res lies in the range NTA : -1.24 to -1.25 , HEDTA : -1.27 to -1.40 , EDTA : -1.69 to -1.78 . Such larger negative values of $\Delta \log K$ with greater negative charge on A^{n-} species have been observed earlier too (Bhattacharya 1981; Singh and Saxena 1990, 1991) with charged ligands.

A perusal of $\log K_{ML}^M$ and $\log K_{MAL}^{MA}$ values, as recorded in table 1, reveals the stability sequence of $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} > \text{Gd}^{3+} < \text{Tb}^{3+} < \text{Dy}^{3+}$ with respect to Ln(III) ions. A clearly visible depression at Gd^{3+} indicates the presence of tetrad effect in the formation constant values. The periodicity in $\log K$ (i.e. formation constant in general) values has been examined by: (i) $\log K$ vs $4f^q$ (q is the number of $4f$ electrons in Ln(III) ions) plots, which show (figure not included) in the present case, as usual, a single prominent break at the $4f^7$ (Gd(III)) stage; (ii) straight line approximation method (Siekierski 1981) in accordance with which the values of deviations $\Delta (= P_{\text{exptl}} - P_{\text{int}})$, where P_{exptl} = experimental value of a property and P_{int} = interpolated value) have been found to be, in general, negative ($\Delta < 0$) for $q = 1, 2, 5, 6, 8, 9, 12, 13$ and positive ($\Delta > 0$) for $q = 3, 4, 7, 10, 11$. This shows the existence of minor discontinuities at the $f^3 - f^4$ and $f^{10} - f^{11}$ stages also besides a major break at f^7 . The periodicity in $\log K$ values is clearly demonstrated; and (iii) differential plot method (Verma and Saxena 1987, 1988) in compliance with which plots (figure 1) of $\Delta \log K / \Delta r$ vs $4f^q$ (where $\Delta \log K$ and Δr represent the differences in the values of $\log K$ and ionic radius, r , of Ln(III) ion, respectively, between two successive Ln(III) ions), i.e. rate of change in $\log K$ with ionic radius vs $4f^q$, show

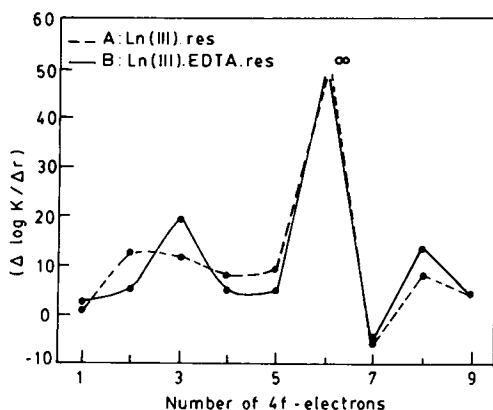


Figure 1. Representative differential plots showing the variation profiles of $\Delta \log K / \Delta r$ with $4f^q$.

well-marked depression at the three stages: 1/4th-filled shell: $f^3 - f^4$, 1/2-filled shell: f^7 and 3/4th-filled shell: $f^{10} - f^{11}$. The superiority of this method lies in the fact that it not only shows the presence of periodicity, but also indicates that the magnitude of tetrad effect lies in the sequence $f^7 > f^3 - f^4 \approx f^{10} - f^{11}$. The same conclusions have been arrived at with the help of the straight line approximation method by calculating the magnitude of tetrad effect at different $4f^q$ configurations. These results offer experimental evidence in favour of the inter-electronic repulsion theory of Jorgensen (1990) and Nugent (1970).

Extrastabilisation of various $4f^q$ configurations may be evaluated using a semi-empirical equation (Spitsyn *et al* 1984, 1990), the reduced form of which may be written as,

$$\Delta G_{ML}^M \text{ (or } \Delta G_{MAL}^{MA}) = E_B - \delta E_{st}, \quad (1)$$

where ΔG_{ML}^M or ΔG_{MAL}^{MA} stands for free energy change accompanying complexation, E_B = energy of the baricentre of $4f^q$ configuration and δE_{st} = extrastabilization energy. The parameters E_B and δE_{st} may be correlated by the expressions,

$$E_B = C + qV + [q(q-1)/2] \cdot E^0 \quad (2)$$

$$\delta E_{st} = K_1 \cdot \delta E^1 + K_3 \delta E^3. \quad (3)$$

In (2) and (3), C and V are constants, q , the number of f -electrons in Ln(III) ion, E^0 , E^1 and E^3 , the inter-electronic repulsion Racah parameters. K_1 and K_3 , the S - and L -dependent coefficients given by,

$$K_1 = 18/13[S(1/2 - S)], \quad (4)$$

$$K_3 = L/180[L(222 - 48L) - 234], \quad (5)$$

where S and L stand for the spin- and total orbital angular momentum-quantum number, respectively.

The quantities δE_{st} , δE^1 and δE^3 have been calculated using the above equations with a computer program (G5215AP with PL-1) (Limaye *et al* 1990, 1991). These and the evaluated values of nephelauxetic ratio ($\delta E^3/\delta E^1$) (abbreviated as NFE) for the three sets of $4f^q$ configurations, where discontinuities occur due to periodicity, have been recorded in table 2. The observed trends in the values of extrastabilization and nephelauxetic ratio lead to the following conclusions: (i) The δE_{st} values lie in the sequence $f^7 > f^3 - f^4 \approx f^{10} - f^{11}$ showing that these configurations are preferentially extrastabilised in the above sequence giving rise to tetrad effect, (ii) the δE_{st} values reveal a certain dependence on the basicity of secondary ligands, (iii) the observed range, in which the present $\delta E^3/\delta E^1$ values lie, agrees well with the range

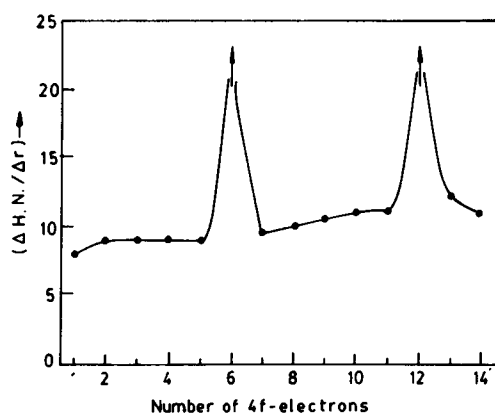
$$-0.194 < \delta E^3/\delta E^1 < 0.214$$

predicted by theoretical quantum chemical calculations (Spitsyn *et al* 1984, 1990; Ionova 1990) and (iv) the plots of δE_{st} vs $4f^q$ (figures not included) exhibit an inverted organ pipe shape for $K_1 \delta E^1$ and inverted tulip for $K_3 \delta E^3$ in agreement with inter-electronic repulsion theory.

In order to examine the role of hydration on the occurrence of periodicity, the values of the first, second, third and total hydration numbers (HN) of Ln(III) ions have been calculated using a recently published method (Sood 1987) assuming that

Table 2. Extrastabilization (δE_{st}) and nephelauxetic effect (NFE) in [Ln(III).L], [Ln(III).A.L] complexes (A = NTA, HEDTA, EDTA; L = res, orc, phl).

| Formation constant | A | L | Extrastabilization energy $\delta E_{st}(\text{cal. deg}^{-1} \text{ mol}^{-1})$ | | | NFE ($\delta E^3/\delta E^1$) | δE^1 | δE^3 |
|---------------------|-------|-----|---|---------------|-------|------------------------------------|--------------|--------------|
| | | | f^9, f^{10} | f^4, f^{11} | f^7 | | | |
| $\log K_{ML}^M$ | — | res | 60 | 98 | 229 | 0.0855 | 0.0157 | 0.00136 |
| | — | orc | 281 | 398 | 818 | 0.1401 | 0.0563 | 0.07897 |
| | — | phl | 175 | 258 | 581 | 0.1112 | 0.0400 | 0.00445 |
| $\log K_{MAL}^{MA}$ | NTA | res | 130 | 192 | 437 | 0.1067 | 0.0302 | 0.0032 |
| | HEDTA | res | 171 | 233 | 436 | 0.1735 | 0.030 | 0.0052 |
| | EDTA | res | 84 | 130 | 314 | 0.0895 | 0.0216 | 0.00193 |
| $\log K_{MAL}^{MA}$ | NTA | orc | 185 | 258 | 519 | 0.147 | 0.0357 | 0.0053 |
| | HEDTA | orc | 22 | 41 | 137 | 0.012 | 0.0095 | 0.0001 |
| | EDTA | orc | 190 | 264 | 511 | 0.1609 | 0.0352 | 0.0056 |
| $\log K_{MAL}^{MA}$ | NTA | phl | 130 | 208 | 527 | 0.0736 | 0.0364 | 0.00268 |
| | HEDTA | phl | 130 | 173 | 306 | 0.1980 | 0.0211 | 0.00419 |
| | EDTA | phl | 235 | 335 | 698 | 0.133 | 0.0480 | 0.00643 |

**Figure 2.** Differential plots showing variations in $\Delta(\text{HN})/\Delta r$ with $4f^n$.

the hydration sphere of Ln(III) ions consists of three concentric zones (Frank and Evans 1945; Gurney 1953). The total HN varies from about 21.91 to 24.22 across Ln(III) series. Application of differential plot method reveals the presence of tetrad effect in HN values (figure 2).

The possibility of contribution from ligand field stabilization and consideration of $L-S$ states are also engaging our attention.

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