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SPECTRAL AND POTENTIOMETRIC STUDIES OF SOME LANTHANIDE(III) COMPLEXES

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A. INTRODUCTION

The chemical bonds in lanthanide(III) complexes are considered for the most part to be ionic, partly because of their well-shielded 4f orbitals, and partly because of their inert gas electronic configurations. Recently however, partial covalency in the metal ligand bonds has been noticed both theoretically and experimentally. We describe here the results of our recent work on lanthanide(III) complexes, dealing with the nephelauxetic effect in praseodymium(III) and neodymium(III) complexes with various organic ligands[1] and the stability constants of lanthanide(III) complexes with a new ligand tetraethylenepentaamineheptaacetic acid.

Absorption spectra of praseodymium(III) and neodymium(III) complexes were measured in aqueous alkaline solution with excess of the various ligands. The Racah parameter, E^3, and the Landé parameter, ζ_{4f}, were calculated by the least squares method on the basis that the energy separation between J-levels of $4f^n$-configuration is a function of E^3 and ζ_{4f}. By using the values of E^3 obtained, the nephelauxetic effect in the Pr^{III} and the Nd^{III} complexes were compared to that in the d-transition metal complexes.

Potentiometric studies of the interaction between a novel dodecadentate ligand, tetraethylenepentaamineheptaacetic acid (TPHA, H_7L) and lanthanide-(III) (Ln^{III}) ions, were carried out to discover the affinity of the ligand for lanthanide(III) ions. Evidence is given for the formation of lanthanide(III) complexes, having 1 : 1 and 2 : 1 molar ratios of Ln^{III} to ligand. Formation of the monoprotonated complex $LnHL^{3-}$ and of the complex ML^{4-} was noted in the lower pH range and formation constants were calculated graphically.

B. THE NEPHELAUXETIC EFFECT IN Pr^{III} AND Nd^{III} COMPLEXES

It is well known that the radial integrals of the valence orbitals of a metal ion

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decrease when the free metal ion combines with ligands to form a metal complex[2]. This phenomenon is called the nephelauxetic effect and may be regarded as some measure of the covalency in the coordination bond[2].

Although the nephelauxetic effect has been extensively investigated in d-transition metal complexes, the study of f-transition metal complexes has been rather limited.

The absorption bands of a lanthanide(III) ion, which are attributed to electronic transitions within the $4f^n$-configuration ($n = 2 \sim 12$), are shifted when the environment of the ion is changed. This is considered to be an indication of a change in the value of the radial integrals[3]. However, in lanthanide(III) ions the spin-orbit interaction can not be neglected and the radial integrals should be treated by the intermediate coupling scheme[4]. Therefore, the separation between J-levels of $4f^n$-configuration is to be expressed in terms of the radial integrals(f) and the spin-orbit coupling constant. It is necessary to calculate the radial integrals or Racah parameters E^k ($k = 0,1,2$ and 3) and the spin-orbit coupling constant or Landé parameter ζ_{4f} on the basis that the energy of a J-level is an approximate function of E^k and ζ_{4f}.

Calculation—In the intermediate coupling scheme, the energy separation between J-levels of $4f^n$-configuration ($n = 2 \sim 12$) is expressed approximately in terms of the radial integrals, F_2, F_4 and F_6 (Slater-Condon parameters) or E^1, E^2 and E^3 (Racah parameters), and the spin-orbit coupling parameter ζ_{4f} (Landé parameter).

According to Wybourne, if a hydrogenic wave function is assumed[5], the ratios of the radial integrals are given by

$$E^1 : E^2 : E^3 = 14.6817 : 0.0768463 : 1.48447 \qquad (1)$$

This relation being used, the energy of a J-level may be expressed as a function of the two variables, E^3 and ζ_{4f}. If the variations of the parameters are small enough, the energy levels can be calculated through a Taylor's series expansion.

Applying Taylor's theorem and neglecting the higher order terms, one may obtain

$$g_i(E^3, \zeta) = g_i(E_0{}^3, \zeta_0) + \left(\frac{\partial g_i}{\partial E^3}\right)_{E^3 = E_0{}^3} X + \left(\frac{\partial g_i}{\partial \zeta_0}\right)_{\zeta = \zeta_0} Y \qquad (2)$$

where $g_i(E^3, \zeta)$ denotes the energy of the i-th J-level from the ground state, $E^3 = E_0{}^3 + X$, $\zeta = \zeta_0 + y$, $E_0{}^3 \gg X$ and $\zeta_0 \gg y$. The numerical values of the parameters of the trivalent lanthanide compounds, $E_0{}^3$ and ζ_0 may be taken from the literature[6] and then $g_i(E_0{}^3, \zeta_0)$, $(\Delta g_i/\Delta E^3)\zeta$ and $(\Delta g_i/\Delta\zeta)_{E^3}$ can be calculated by solving the secular equation derived from the spin-orbit matrix and the LS term energies. Accordingly, $g_i(E^3, \zeta)$ is simplified to a linear function of X and y, assuming $(\Delta g_i/\Delta E^3)\zeta = \partial g_i/\partial E^3 = a_i$,

$$(\Delta g_i/\Delta\zeta)_{E^3} = \partial g_i/\partial\zeta = b_i \cdot g_i(E^3, \zeta) = k_i + a_i X + b_i y \qquad (3)$$

where $k_i = g_i(E_0{}^3, \zeta_0)$. Based on equation (3), X and y can be obtained by the least squares method using experimental values.

Pr^{III} complex: The LS term energies and the spin-orbit matrices were obtained from Condon and Shortley[7], and Satten and Margolis[8], respectively. The calculation was carried out by putting $E_0{}^3 = 451.36\ \mathrm{cm}^{-1}$ and $\zeta = 729.5\ \mathrm{cm}^{-1}$. Four experimental values were used for the least squares calculation for each praseodymium(III) complex.

Nd^{III} complex: We have made use of the result of the detailed calculation of Carlson and Crosswhite[9]. Putting $E_0{}^3 = 492.00\ \mathrm{cm}^{-1}$ and $\zeta = 861.72\ \mathrm{cm}^{-1}$, we have obtained the numerical values of

$$g_i(E_0{}^3, \zeta_0), \quad \left(\frac{\partial g_i}{\partial E^3}\right)_{E^3 = E_0{}^3} \quad \text{and} \quad \left(\frac{\partial g_i}{\partial \zeta}\right)_{\zeta = \zeta_0}$$

for each J_i-level, and then carried out the least square calculation, using eleven experimental values for each neodymium(III) complex.

Experimental—The absorption spectra were measured at room temperature (about 20°C) with a Hitachi EPS-2 spectrophotometer, a 10 mm quartz cell being used. Excess of the ligand was used to ensure complex formation. Since the absorption spectra may be affected by the pH of the solution, ammonia was added to the solution until the increase of pH did not affect the absorption bands any more. Some examples of the pH values and the ratio of metal to ligand in the solution are shown in Table I.

Since the absorption spectra of aqueous solutions were completely in accord with the literature,[10] further purification of the lanthanide(III) perchlorate (purity: more than 99.99%) used was not necessary.

Results and discussion—Since it was difficult to obtain the baricenter of the J-band experimentally, we had to be satisfied with taking the center of the band (not the peak).

TABLE I

THE RATIOS OF METAL TO LIGAND AND pH OF THE SOLUTIONS USED FOR THE MEASUREMENTS

	Pr^{III}		Nd^{III}	
ligand	*metal/ligand*	*pH*	*metal/ligand*	*pH*
glycine	1 : 10	10.45	1 : 10	10.05
alanine	1 : 10	10.45	1 : 10	10.25
serine	1 : 10	10.75	1 : 10	10.60
malate	1 : 1.5	11.15	1 : 1.5	10.55
tartarate	1 : 1.5	11.35	1 : 1.5	10.55
citrate	1 : 3	13.50	1 : 3	13.35
NTA*	1 : 3	12.05	1 : 3	12.05
EDTA	1 : 1.5	12.85	1 : 1.5	12.85
TPHA	1 : 1.1	10.50	1 : 1	10.50
cysteine	1 : 10	10.80	1 : 10	10.55

*NTA: nitorilotriacetic acid

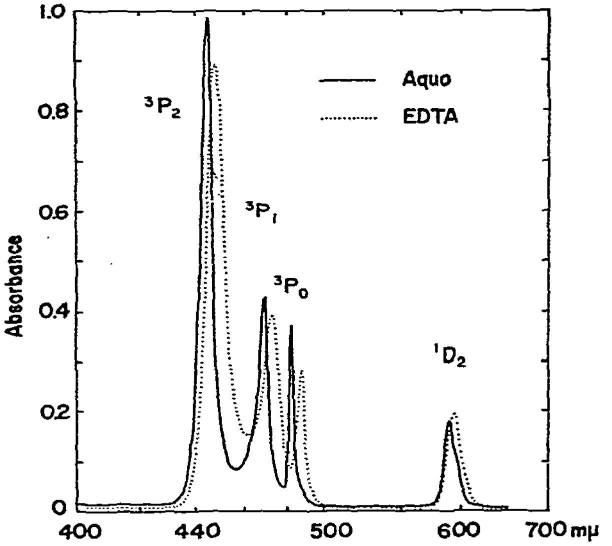


Fig. 1. Absorption Spectra of Aquo and EDTA Complexes of Pr^{III} in Aqueous Solutions.

For example, Fig. 1 shows the absorption spectra of aquo and ethylenediaminetetraacetato complexes of Pr^{III} in aqueous solutions at pH = 12.85 and a temp. of 25.0 + 0.1°C. The red shift of the absorption spectra of the EDTA complex can be seen clearly. Fig. 2 also shows the absorption spectra of aquo and EDTA complexes of Nd^{III} in aqueous solution under the same conditions. The red shift can be similarly observed.

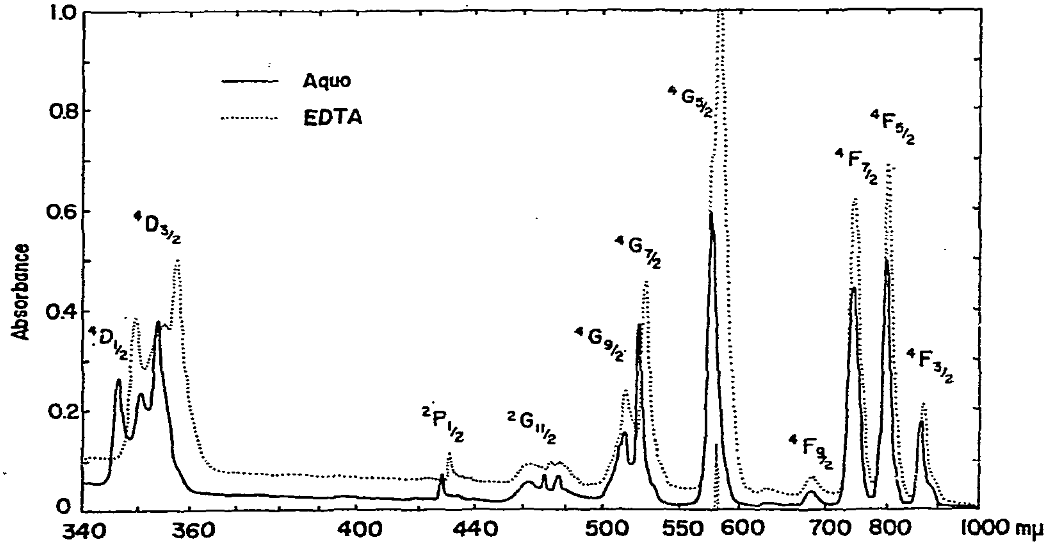


Fig. 2. Absorption Spectra of Aquo and EDTA Complexes of Nd^{III} in Aqueous Solutions.

The energies of the J-levels of each lanthanide(III) complex were obtained using the least squares calculation. The accordance of the calculated values with the observed values was satisfactory. The calculated values of the aquo complexex, for example, are shown in Table II.

The values of E^3 and ζ_{4f} obtained are listed in Table III. By using these data, the degree of the nephelauxetic effect of 4f-transition metal complexes can be compared with that of d-transition metal complexes in terms of $1-\beta'$ (where $\beta' = F_k(\text{complex})/F_k(\text{aquo})$ as exemplified in Table IV.

TABLE 2

EXAMPLES OF CALCULATED AND OBSERVED WAVE NUMBERS OF J-LEVELS OF THE AQUO COMPLEXES, OBTAINED FROM THE RESULTS OF LEAST SQUARE METHOD. (cm^{-1})

	Pr^{III}			
J-level	$^3P_2$	$^3P_1$	$^3P_0$	$^1D_2$
calc.	22473	21309	20729	17123
obs.	22523	21413	20725	16935

Nd^{III}

J-level	$^4D_{1/2}$	$^4D_{3/2}$	$^2P_{1/2}$	$^4G_{11/2}$	$^2G_{9/2}$	$^4G_{7/2}$	$^4G_{5/2}$	$^4F_{9/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$
calc.	29134	28420	22793	21823	19578	19045	17259	14590	13570	12583	11458
obs.	28893	28257	23397	21650	19554	19171	17271	14663	13550	12563	11468

TABLE 3

E^3 AND ζ (cm^{-1})

	Nd^{III}		Pr^{III}	
ligand	E^3	ζ	E^3	ζ
aquo	489.8	930.1	459.8	708.6
glycine	486.5	928.3	455.9	707.9
alanine	486.2	928.4	455.5	707.6
malate	486.1	932.1	456.3	709.8
tartarate	485.9	928.9	455.2	709.8
NTA*	485.8	931.1	457.4	703.3
serine	485.8	927.8	455.9	703.0
EDTA	485.4	932.5	455.0	706.4
TPHA	485.3	932.8	454.3	705.8
citrate	485.2	928.3	456.3	710.5
cysteine	484.7	930.2	454.0	708.1

**cf.* the footnote of Table I.

TABLE 4

THE NEPHELAUXETIC EFFECT OF 4f- AND 3d-TRANSITION METAL COMPLEXES

Metal ion	*Co^{III}*	*Ni^{II}*	*Mn^{II}*	*Pr^{III}*	*Nd^{III}*
ligand	3 (oxalate)	EDTA	EDTA	EDTA	EDTA
β'	0.88	0.91	0.96	0.990	0.991
$1-\beta'$	0.12	0.09	0.04	0.010	0.009

The values of $1-\beta'$ for lanthanide(III) complexes are only about one tenth of those for 3d-transition metal complexes.

Jørgensen[11] reported a similar comparison by regarding $(\nu_{aquo}-\nu_{comp.})/\nu_{aquo} = 1-\beta'$, assuming that the separation between the J-levels are linearly dependent only on E^3.

It should be noted that the absorption spectrum of a lanthanide(III) complex in an aqueous solution depends not only on the species of the metal ion and the ligand, but also on the metal–ligand ratio and the pH of the solution. Some examples of the experimental conditions for the nephelauxetic effect obtained in this study are shown in Table I. In spite of this limitation, however, the results of the present study are still useful for estimating the covalent character of the 4f electrons of the lanthanide(III) ion. Furthermore, in some cases, the present data may serve to give some information about the configuration of the complex.

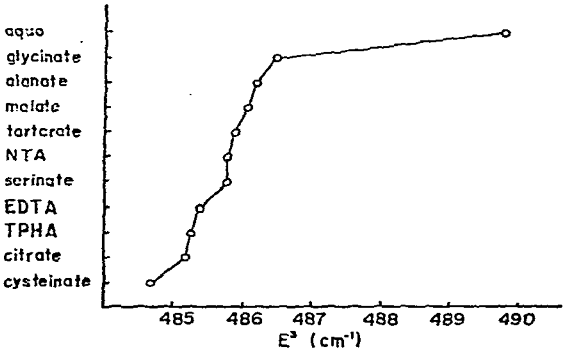
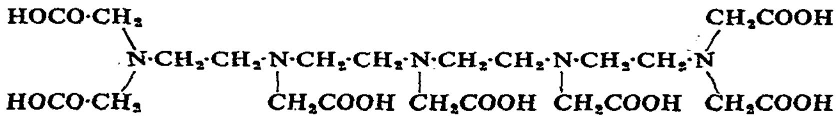


Fig. 3. E^3 of Nd^{III} Complexes.

For example, Fig. 3 shows a plot of the values of E^3 against the various ligands for Nd^{III} complexes. The cysteinato complex shows the smallest E^3 and is located at the bottom of the nephelauxetic series, on the other hand, the other α-amino acids such as glycinato, alaninato, and serinato complexes are placed on the upper positions of the series. This fact suggests that the sulfur atom of cysteine is taking part in the formation of the cysteinato complex in solution. The nephelauxetic effect of sulfur coordinated to a metal ion[12] is much larger than that of oxygen or nitrogen coordination.

C. LANTHANIDE(III) COMPLEXES OF TPHA

A new dodecadentate ligand tetraethylenepentaamineheptaacetic acid (TPHA) was used as the ligand for lanthanide(III) complexes.



$$(HOCO\cdot CH_2)_2N\cdot CH_2\cdot CH_2\cdot \underset{CH_2COOH}{N}\cdot CH_2\cdot CH_2\cdot \underset{CH_2COOH}{N}\cdot CH_2\cdot CH_2\cdot \underset{CH_2COOH}{N}\cdot CH_2\cdot CH_2\cdot N(CH_2COOH)_2$$

The interaction between TPHA and the lanthanide(III) ions was investigated by a potentiometric titration method using the glass electrode and the stability constants of the lanthanide(III)-TPHA complexes were calculated.

Experimental—TPHA was synthesized by I. Murase[13] and its chemical formula was given by $C_{33}H_{27}N_5O_{14}.4HCl.2H_2O$. Elemental analyses were in accord with the formule given. Found %. C = 40.32, H: 6.33, N: 11.05. Calcd %. C = 40.70, H: 6.62, N: 10.75.

The experimental method consisted of potentiometric titration of the hepta basic acid TPHA with CO_2-free KOH solution in the absence and presence of the lanthanide(III) ion. All lanthanide(III) ions were titrated in both 1 : 1 and 2 : 1 molar ratios of metal ion to ligand. A Hitachi-Horiba P-type pH meter fitted with glass and saturated calomel electrodes was used. Measurements were made in nitrogen gas at a temperature of 25.0 ± 0.1°C and at a constant ionic strength μ of 0.1 in KNO_3.

Results and discussion—The neutralization of the free ligand TPHA occurs in two steps as shown by titration curve (1) in Fig. 4, which has a strong inflection at a = 5 (where a is the number of moles of base added per mole of ligand present in the experimental solution) and a weaker inflection at a = 6. This curve is in good agreement with the predicted titration curve from the dissociation constants of TPHA obtained by N. M. Dyatlova.[14]

The potentiometric titration curve (2), for example, for the 1 : 1 lanthanum-(III)-TPHA complex has a very sharp inflection at a = 7. This indicates the formation of a stable 1 : 1 complex.

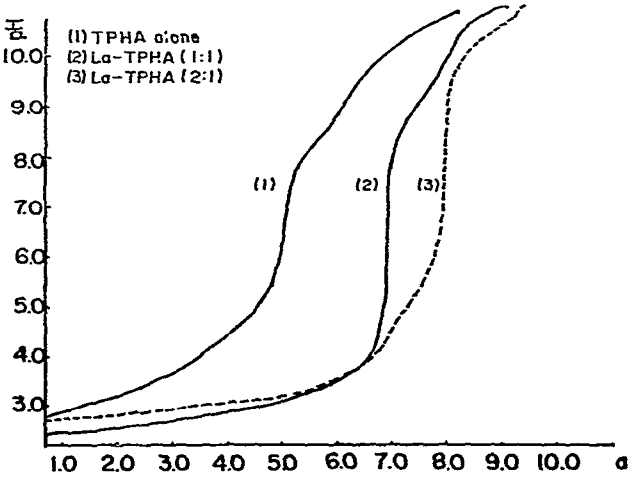


Fig. 4. Potentiometric titration of TPHA at 25°.

As shown by titration curve (3), in the presence of two moles of La^{III} per mole of the ligand TPHA there is a strong inflection at $a = 8$. Both La ions are bound up to a pH of 8, indicating that a binuclear complex, $La_2(OH)TPHA^{2-}$ is formed above pH 8. Though the complex formed is unstable, the hydroxide does not precipitate because of the high stability of the lanthanum(III)-TPHA complex.

Calculations—The values of the dissociation constants of TPHA obtained by Dyatlova[14] were used in this work, namely,

pk_1	pk_2	pk_3	pk_4	pk_5
9.95	8.85	5.56	3.82	2.79

As the sixth and seventh dissociation constants are not reported, the calculations were carried out in the range of $a = 4.5 \sim 6.1$ (above pH 2.9), where no influence of K_6 and K_7 was observed at all.

For the 1 : 1 lanthanide(III)-TPHA system, where a monoprotonated lanthanide(III) complex $LnHL^{3-}$ and the complex LnL^{4-} are presumed to exist in the region of $a = 4.5 \sim 6.1$, the equilibria involved are

$$Ln^{3-} + HL^{6-} \rightleftharpoons LnHL^{3-} \qquad K_{LnHL} = \frac{[LnHL^{3-}]}{[Ln^{3+}][HL^{6-}]} \tag{4}$$

$$LnHL^{3-} \rightleftharpoons LnL^{4-} + H^+ \qquad K^{H}_{LnHL} = \frac{[LnL^{4-}][H^+]}{[LnHL^{3-}]} \tag{5}$$

$$Ln^{3+} + L^{7-} \rightleftharpoons LnL^{4-} \qquad K_{LnL} = \frac{[LnL^{4-}]}{[Ln^{3-}][L^{7-}]} \tag{6}$$

From the usual mass balance and electroneutrality relationships, the following equations may be obtained.

$$T_L = \sum_{j=1}^{7} [H_jL^{(7-j)}] + [L^{7-}] + [LnL^{4-}] + [LnHL^{3-}] \tag{7}$$

$$T_{Ln} = [Ln^{3+}] + [LnL^{4-}] + [LnHL^{3-}] \tag{8}$$

$$T_L(7-a) = [H^+] - [OH^-] + \sum_{j=1}^{7} j[H_jL^{(7-j)-}] + [LnHL^{3-}] \tag{9}$$

where T_{Ln} is the total concentration of lanthanide(III) species and T_L is the total concentration of ligand TPHA added. From equations (4), (5), (7), (8) and (9), equations (10) and (11) are obtained.

$$[HL^{6-}] = \frac{[H^+]\{T_L(6-a) - [H^+] + [OH^-]\}}{[H^+](Y-X) + Y K^{H}_{LnHL}} + \frac{\{T_L(7-a) - [H^+] + [OH^-]\} K^{H}_{LnHL}}{[H^+](Y-X) + Y K^{H}_{LnHL}} \qquad 10)$$

$$K_{\mathrm{LnHL}} = \frac{\mathrm{T_L}(7-\mathrm{a})-[\mathrm{H}^+]+[\mathrm{OH}^-]-[\mathrm{HL}^{6-}]\mathrm{Y}}{[\mathrm{HL}^{6-}]^2\mathrm{X}} \tag{11}$$

Also

$$\mathrm{X} = \frac{k_1}{[\mathrm{H}^+{}_3} + 1 + \sum_{\mathrm{i}=1}^{6} \frac{[\mathrm{H}^+]^{\mathrm{i}}}{\prod\limits_{\mathrm{z}=2}^{\mathrm{i}+1} k_{\mathrm{z}}} \quad \text{and} \quad \mathrm{Y} = 1 + \sum_{\mathrm{i}=1}^{6} \frac{(\mathrm{i}+1)\,[\mathrm{H}^+]^{\mathrm{i}}}{\prod\limits_{\mathrm{z}=2}^{\mathrm{i}+1} k_{\mathrm{z}}}$$

where

$$k_{\mathrm{z}} = \frac{[\mathrm{H_{z-1}L}^{(6-\mathrm{z})-}]\,[\mathrm{H}^+]}{[\mathrm{H_zL}^{(7-\mathrm{z})-}]}, \quad \mathrm{z} = 1, 2 \ldots .7.$$

and k_{z} represents the corresponding dissociation constant of the ligand.

A series of values was assumed for K_{LhHL} and corresponding values for K_{LnHL} were calculated from equation (11)[15]. The resulting values of K_{LnHL} were plotted against the assumed values of $K^{\mathrm{H}}_{\mathrm{LnHL}}$ to give the intersecting lines shown in Fig. 5.

The different lines obtained from different points on one titration curve all intersect at one point as shown in Fig. 5 for the 1 : 1 La-TPHA system. This indicates the existence of a set of unique values for K_{LnHL} and K_{LnHL} which will satisfy the assumed reactions at any point along the titration curve between $\mathrm{a} = 4.5 \sim 6.1$. The values for K_{LnL} are obtained from equation (12) where K^{H}_1 is the 1st formation constant of the ligand TPHA.

$$K_{\mathrm{LnL}} = K^{\mathrm{H}}_{\mathrm{LnHL}} \cdot K_{\mathrm{LnHL}} \cdot K^{\mathrm{H}}_1 \tag{12}$$

Stability constants, $\log K_{\mathrm{LnHL}}$ and $\log K_{\mathrm{LnL}}$ are given in Table V.

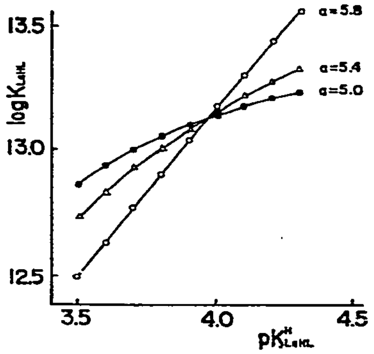
TABLE 5

STABILITY CONSTANTS OF LANTHANIDE(III)–TPHA COMPLEXES

Temperature 25.0±0.1 °C. Ionic strength $\mu = 0.1$.

	La	*Pr*	*Nd*	*Sm*	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	*Tm*	*Yb*	*Lu*
$\log K_{\mathrm{LnHL}}$	13.12	13.46	14.10	14.13	14.51	14.11	14.47	14.13	13.97	13.98	13.80	13.26
$\log L_{\mathrm{LnL}}$	19.10	19.64	20.18	20.50	20.72	20.41	20.68	20.42	20.35	20.11	19.75	19.14

The plot of $\log K_{\mathrm{LnL}}$ *vs.* atomic number is shown in Fig. 6. By a close inspection of this curve, we find that there is a regular increase in the stability constants of the lanthanide(III)-TPHA complexes with decreasing ionic radius from lanthanum(III) to europium(III), according to the lanthanide(III) contraction, then the usual gadolinium break and beyond terbium (III) a slight decrease in the stability constants of the complexes to lutetium(III) probably due to the steric hindrance of the ligand and the decrease of the coordination number of the central lanthanide(III) ion. Concerning this trend in the stabiliiy constants of these complexes, the behaviour of TPHA as a ligand seems to be very similar to that of diethylene-



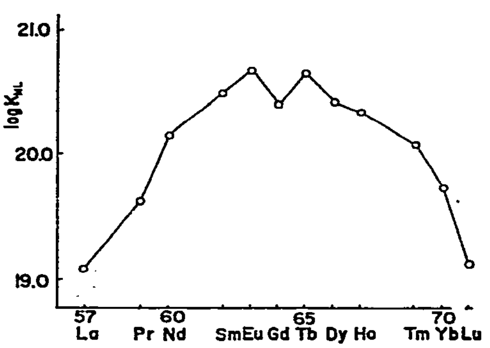


Fig. 5. Graphical solution for K_{LaHL} and $K^{\mathrm{H}}{}_{\mathrm{LaHL}}$ (La: TPHA (1 : 1).

Fig. 6. Relation between $\log K_{\mathrm{ML}}$ and atomic number.

triaminepentaacetic acid (DTPA). This suggests that factors outside the lanthanide(III) contraction influence this trend. It is supposed that the coordination number may decrease with the steric hindrance caused by the large size of the ligand as the lanthanides(III) decrease in size. Stability constants $\log K_{\mathrm{LnOHL}}$ were calculated for the hydroxo-lanthanide(III)-TPHA (1 : 1) complexes. For example, the potentiometric titration curve of the 1 : 1 La-TPHA complex shown in Fig. 4, has a weak inflection above a = 7 inferring the overlap of inflections is due to some hydroxo complexes. At least mono or dihydroxo complexes are presumed to be present; they involve the following equilibria.

$$\begin{aligned} &\mathrm{LnL^{4-} + OH^- \rightleftharpoons Ln(OH)L^{5-}} && K'_1 = \frac{[\mathrm{Ln(OH)L^{5-}}]}{[\mathrm{LnL^{4-}}][\mathrm{OH^-}]} \\ &\mathrm{Ln(OH)L^{5-} + OH^- \rightleftharpoons Ln(OH)_2L^{6-}} && K'_2 = \frac{[\mathrm{Ln(OH)_2L^{6-}}]}{[\mathrm{Ln(OH)L^{5-}}][\mathrm{OH^-}]} \end{aligned} \tag{13}$$

Assuming the degree of dissociation of $\mathrm{LnL^{4-}}$ to be extremely small and $\mathrm{LnL^{4-}}$ as a only species to be formed in solution above a = 7, $\mathrm{Ln(OH)L^{5-}}$ and $\mathrm{Ln(OH)_2L^{6-}}$ should exist in equilibria. Therefore, if a solution of $\mathrm{LnL^{4-}}$ is titrated with standard base, the following equations may be written to describe the stoichiometry.

$$\mathrm{T_L = T_{Ln} = [LnL^{4-}] + [Ln(OH)L^{5-}] + [Ln(OH)_2L^{6-}]} \tag{14}$$

$$\mathrm{T_{OH} - [OH^-] = [Ln(OH)L^{5-}] + 2[Ln(OH)_2L^{6-}]} \tag{15}$$

where $\mathrm{T_L}$ and $\mathrm{T_{Ln}}$ denote the total concentration of ligand and lanthanide(III) ions respectively and $\mathrm{T_{OH}}$ represents the concentration of hydroxyl ions added at any point along the titration curve. The Bjerrum quantity, $\bar{n}_{\mathrm{OH}}$ may be expressed by equation (16), by using equations (13), (14) and (15).

$$n_{OH} = \frac{T_{OH}-[OH^-]}{T_{Ln}} = \frac{[Ln(OH)L^{5-}]+2[Ln(OH)_2L^{6-}]}{[LnL^{4-}]+[Ln(OH)L^{5-}]+[Ln(OH)_2L^{6-}]} = \frac{K'_1[OH^-]+2K'_1 \cdot K'_2[OH^-]^2}{1+K'_1[OH^-]+K'_1 \cdot K'_2[OH^-]^2} \tag{16}$$

It is seen that the relationship between $\bar{n}_{OH}$ and $[OH^-]$ is identical with the usual Bjerrum function, $\bar{n}_A$ relationship with the free ligand concentration (A). Hence, $\log K'_1$ may be determined to a first approximation from a plot of n_{OH} *vs.* pOH, at $\bar{n}_{OH}$ values of 0.5.

Calculated values of $\log K'_1$ are listed in Table VI.

TABLE 6

STABILITY CONSTANTS OF HYDROXOLANTHANIDE(III)-TPHA COMPLEXES

Temperature 25.0+0.1 °C. Ionic strength $\mu = 0.1$.

	La	*Pr*	*Nd*	*Sm*	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	*Tm*	*Yb*	*Lu*
$\log K'_1$	4.75	5.27	5.34	5.29	5.25	5.34	5.25	5.22	5.21	5.15	5.23	5.11

The usual trend for the lanthanide contraction could not be observed, because of the coexistence of other hydroxo complexes in solution.

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