BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 25—33 (1968)

The Nephelauxetic Effect in Praseodymium(III) and Neodymium(III) Complexes

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(Received May 19, 1967)

The absorption spectra of praseodymium(III) and neodymium(III) complexes were measured in an aqueous alkaline solution with an excess of ligands. The experimental data being used, the Racah parameter, E^3, and the Landè parameter, ζ_{4f}, werc ealculated by the least-squares method on the assumption that the energy separation between J-levels of the $4f^n$-configuration is a function of E^3 and ζ_{4f}. The nephelauxetic effect in the Pr(III) and the Nd(III) complexes was then discussed by using the values of E^3 thus obtained.

It has been known that the radial integrals of the valence orbitals of a metal ion decrease when the free metal ion combines with ligands to form a metal complex.[1] This phenomenon is called the nephelauxetic effect, which means the expansion of electron clouds; it may be regarded as a measure of the covalency of coordination bands.[1] Although the nephelauxetic effect has been extensively investigated in d-transition metal complexes, the study of f-transition metal complexes has been rather limited because of the theoretical and experimental difficulties.

The absorption bands of lanthanide(III) ions, which are attributed to the electronic transitions within the $4f^n$-configuration (n=2—12), are shifted when the environment of the ion is changed. This is undoubtedly an indication of a change in the radical integrals.[2] However, in lanthanide(III) ions the spin-orbit interaction can not be neglected and the radial integrals should be treated by an intermediate coupling scheme.[3] The separation between J-levels of the $4f^n$-configuration may be expressed in terms of the radial integrals (f)[4] and the spin-orbit coupling parameter.

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[1] C. K. Jørgensen, *Prog. Inorg. Chem.*, **4**, 73 (1962).

[2] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York (1962), p. 143.

[3] B. G. Wybourne, "Spectroscopic Properties of Rare Earth," Interscience, New York (1965), pp. 42—49.

[4] The radial integral of the $4f$-orbital is usually expressed in terms of Slater-Condon Parameters, F^k's (k=0, 2, 4, and 6) or Racah parameters, E^k's (k=0, 1, 2, and 3). In this paper we used E^k for convenience.

Jørgensen and others[5-9] took the value of $1-\beta=\Delta\tilde{\nu}/\tilde{\nu}_{\mathrm{aquo}}=(\tilde{\nu}_{\mathrm{aquo}}-\tilde{\nu}_{\mathrm{complex}})/\nu_{\mathrm{aquo}}$ (where ν stands for the wave number of an absorption band of a lanthanide(III) ion) as a measure of the nephelauxetic effect, assuming that each *J*-level of a $4f^n$-configuration is linearly dependent only on the radial integrals. On this assumption, the $\Delta\tilde{\nu}/\tilde{\nu}_{\mathrm{aquo}}$ of all bands of the same lanthanide(III) complex should be identical; however, an inspection of the experimental data[9] has revealed that the $\Delta\nu/\nu_{\mathrm{aquo}}$ values for different *J*-bands of a lanthanide complex differ from each other considerably. Therefore, it is necessary to obtain the radial integrals or Racah parameters, E^k's (interelectronic repulsion parameters), and the spin-orbit coupling constant or Landè parameter, ζ_{4f}, simultaneously on the assumption that the energy of the *J*-levels is a function of E^k's and ζ_{4f}.

Calculation

In the intermediate coupling scheme, the energy separations between *J*-levels of an f^n configuration ($n=2-12$) are expressed approximately in terms of radial integrals, F_2, F_4 and F_6 (Slater-Condon parameter), or E^1, E^2, and E^3 (Racah parameter), and the spin-orbit coupling parameter, ζ_{nf} (Lande parameter).*2

According to Wybourne, if a hydrogenic wave function is assumed,[6] the ratios of the radial integrals are given by:

$$E^1:E^2:E^3=14.6817:0.0768463:1.48447 \tag{1}$$

This relation being used, the energy of a *J*-level can be expressed as a function of the two variables, E^3 and ζ_{4f}.

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

$$g_i(E^3,\ \zeta)=g_i(E_0^3,\ \zeta_0)+\left(\frac{\partial g_i}{\partial E^3}\right)_{E^3=E_0^3}\chi+\left(\frac{\partial g_i}{\partial \zeta_0}\right)_{\zeta=\zeta_0}y \tag{2}$$

where $g_i(E^3,\ \zeta)$ denotes the energy of the *i*th *J*-level from the ground state, $E^3=E_0^3+\chi$, $\zeta=\zeta_0+y$, $E_0^3\gg\chi$ 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,[10] 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 χ and y, assuming that

$$(\Delta g_i/\Delta E^3)_\zeta=\partial g_i/\partial E^3=a_i:$$

$$(\Delta g_i/\Delta\zeta)_{E^3}=\partial g_i/\partial\zeta=b_i\,.$$

$$g_i(E^3,\ \zeta)=k_i+a_i\chi+b_iy \tag{2'}$$

where $k_i=g_i(E_0^3,\ \zeta_0)$.

Based on Eq. (2'), χ and y are obtainable by the least-squares method using the experimental values.

Pr(III). The LS term energies and the spin-orbit matrices were obtained by Condon and Shortley[11] and by Satten and Margolis[12] 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 (*Cf.* Table 2).

Nd(III). Instead of doing laborious calculations, we have made use of the results of the detailed calculation of Carlson and Crosswhite.[13] Putting $E_0^3=492.00\ \mathrm{cm}^{-1}$ and $\zeta=861.72\ \mathrm{cm}^{-1}$, we obtained the numerical values of $g_i(E_0^3,\ \zeta_0)$, $(\partial g_i/\partial E^3)_{E^3=E_0^3}$ and $(\partial g_i/\partial\zeta)_{\zeta=\zeta_0}$ for each J_i-level; then we carried out the least-squares cal-

Table 1. The ratios of metal to ligand and pH of the solutions used for the measurements

Ligand	Pr(III)		Nd(III)	
	metal/ligand	pH	metal/ligand	pH
Aquo	—	—	—	—
Glycine	1 : 10	10.45	1 : 10	10.05
Alanine	1 : 10	10.45	1 : 10	10.25
Malate	1 : 1.5	11.15	1 : 1.5	10.55
Tartarate	1 : 1.5	11.35	1 : 1.5	10.55
NTA	1 : 3	12.05	1 : 3	12.05
Serine	1 : 10	10.75	1 : 10	10.60
EDTA	1 : 1.5	12.85	1 : 1.5	12.85
TPHA	1 : 1.1	10.50	1 : 1	10.50
Citrate	1 : 3	13.50	1 : 3	13.35
Cysteine	1 : 10	10.80	1 : 10	10.55

NTA: nitorilotriacetic acid.
EDTA: ethylendiaminetetraacetic acid.
TPHA: tetraetylenepentaamineheptaacetic acid.

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[9] S. P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).

*2 According to Carnell and Wybourne, it has been a trandition of theoretical spectroscopy to treat the Slater radial integrals and a spin-orbit coupling integral, ζ_{4f}, as parameters to be determined from the available data, usually deriving their magnitudes by a least-squares adjustment to known energy levels. W. T. Carnell and B. G. Wybourne, *J. Chem. Phys.*, **40**, 3428 (1964); B. G. Wybourne, *ibid.*, **36**, 2295, 2301 (1962); E. Y. Wong, *ibid.*, **35**, 544 (1961).

[10] C. K. Jørgensen, "Orbitals in Atoms and Molecules", Academic Press, New York (1962), p. 148; B. G. Wybourne, "Spectroscopic Properties of Rare Earth," Interscience, New York (1965), p. 191.

[11] E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridg University Press, Cambridg (1951), p. 207.

[12] R. A. Satten and J. S. Margolis, *J. Chem. Phys.*, **32**, 573 (1960).

[13] E. H. Carlson and H. M. Crosswhite, *Johns Hopkins Univ. Spectroscopic Report,*" 19 (1960).

TABLE 2. THE OBSERVED WAVE NUMBERS OF *J*-BANDS AND AN EXAMPLE OF CALCULATED WAVE NUMBER OF *J*-LEVELS OBTAINED FROM THE RESULTS OF LEAST SQUARE METHOD (cm^{-1})

	J-Level	Cald for aquo ion	Aquo	Glycine	Alanine	Malate	Tartrate
Pr(III)	$^3P_2$	22473	22523	22351	22346	22386	22331
	$^3P_1$	21309	21413	21204	21155	21177	21209
	$^3P_0$	20729	20725	20572	20576	20619	20534
	$^1D_2$	17123	16935	16869	16846	16906	16835
Nd(III)	$^4D_{1/2}$	29134	28893	28662	28662	28629	28637
	$^4D_{3/2}$	28420	28257	28011	28003	28011	27980
	$^2P_{1/2}$	22793	23397	23256	23245	23245	23234
	$^4G_{11/2}$	21823	21650	21524	21505	21542	21505
	$^2G_{9/2}$	19578	19554	19444	19467	19482	19444
	$^4G_{7/2}$	19045	19171	19048	19004	19044	19019
	$^4G_{5/2}$	17259	17271	17241	17229	17241	17221
	$^4F_{9/2}$	14590	14663	14620	14599	14663	14620
	$^4F_{7/2}$	13570	13550	13495	13459	13477	13477
	$^4F_{5/2}$	12583	12563	12500	12484	12500	12484
	$^4F_{3/2}$	11458	11468	11468	11442	11468	11442

	J-Level	NTA*	Serine	EDTA*	TPHA*	Citrate	Cysteine
Pr(III)	$^3P_2$	22356	22326	22311	22262	22371	22277
	$^3P_1$	21268	21182	21186	21200	21254	21137
	$^3P_0$	20636	20568	20525	20462	20576	20492
	$^1D_2$	16943	16863	16807	16779	16892	16807
Nd(III)	$^4D_{1/2}$	28629	28637	28604	28571	28637	28547
	$^4D_{3/2}$	28027	27996	27988	27980	27956	27956
	$^2P_{1/2}$	23256	23234	23229	23229	23207	23202
	$^4G_{11/2}$	21552	21505	21551	21552	21529	21496
	$^2G_{9/2}$	19436	19451	19444	19444	19399	19417
	$^4G_{7/2}$	19011	18990	18997	19015	18997	18997
	$^4G_{5/2}$	17147	17182	17227	17200	17197	17173
	$^4F_{9/2}$	14641	14620	14641	14665	14577	14620
	$^4F_{7/2}$	13477	13441	13459	13441	13405	13441
	$^4F_{5/2}$	12469	12469	12484	12453	12453	12438
	$^4F_{3/2}$	11468	11429	11390	11442	11377	11390

* *Cf.* the footnote of Table 1.

culation using eleven experimental values for each neodymium(III) complex (*Cf.* Table 2).

Experimental

Measurements. The absorption spectra were measured at room temperature (about 20°C) with a Hitachi EPS-2 spectrophotometer, a 10 mm quartz cell being used.

The concentration of the solution was 0.1 mol/*l* for the lanthanide(III) perchlorate. Enough excess ligand was used as to cause complex formation. Since the absorption spectra may be affected by the pH of the solution under some conditions, ammonia was added to the solution until the increase in pH did not affect the absorption bands any more. The pH values and the ratio of metal to ligand in the solution are listed in Table 1.

Materials. The lanthanide(III) perchlorate solutions were prepared by dissolving pure lanthanide

TABLE 3. E^3 AND ζ (cm^{-1})

Ligand	Nd(III)		Pr(III)	
	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
Cystein	484.7	930.2	454.0	708.1

* *Cf.* the footnote of Table 1.

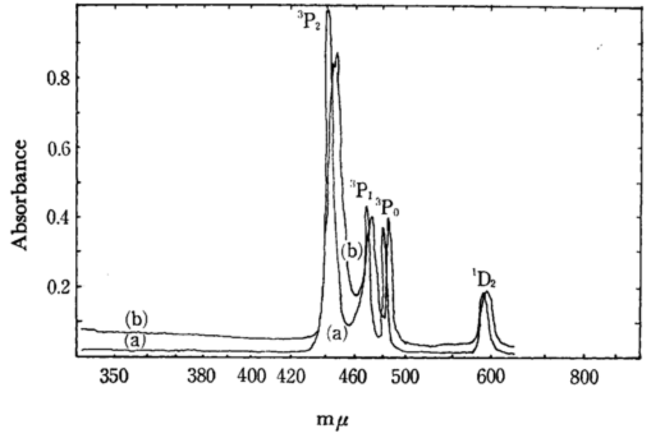

Fig. 1. Absorption spectra of glycinate and aquo complexes of Pr(III) in aqueous solutions. pH=10.45, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + glycine (1 : 10)

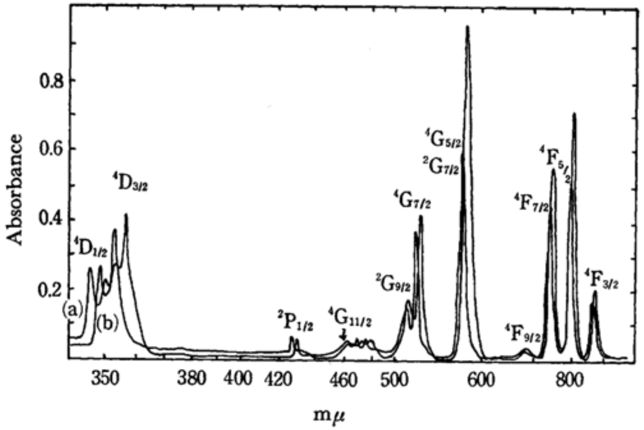

Fig. 2. Absorption spectra of glycinate and aquo complexes of Nd(III) in aqueous solutions. pH=10.05, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + glycine (1 : 10)

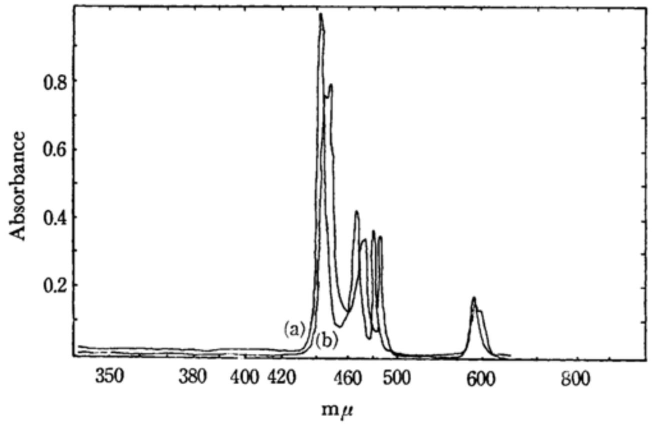

Fig. 3. Absorption spectra of alaninate and aquo complexes of Pr(III) in aqueous solutions. pH=10.45, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + alanine (1 : 10)

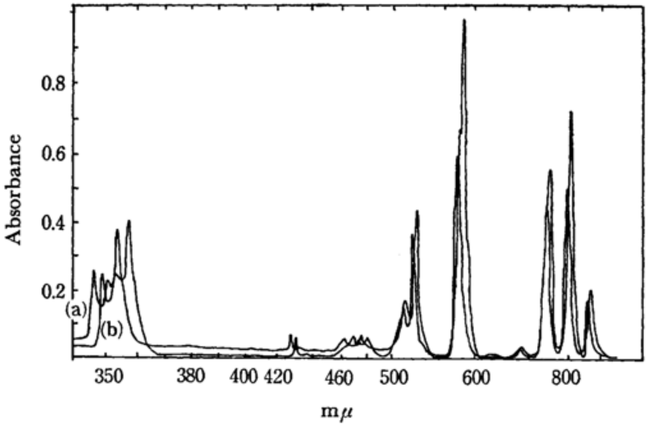

Fig. 4. Absorption spectra of alaninate and aquo complex of Nd(III) in aqueous solutions. pH=10.25, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + alanine (1 : 10)

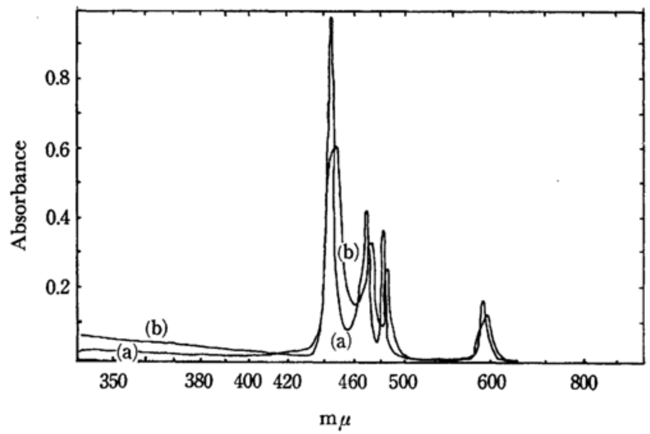

Fig. 5. Absorption spectra of malate and aquo complexes of Pr(III) in aqueous solutions. pH=11.15, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + malate (1 : 1.5)

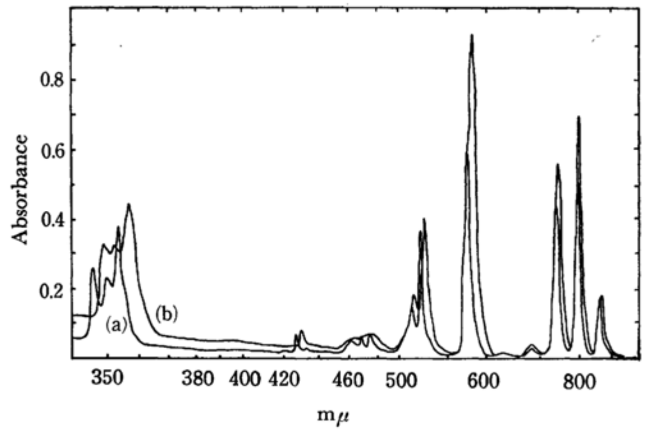

Fig. 6. Absorption spectra of malate and aquo complexes of Nd(III) in aqueous solutions. pH=10.55, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + malate (1 : 1.5)

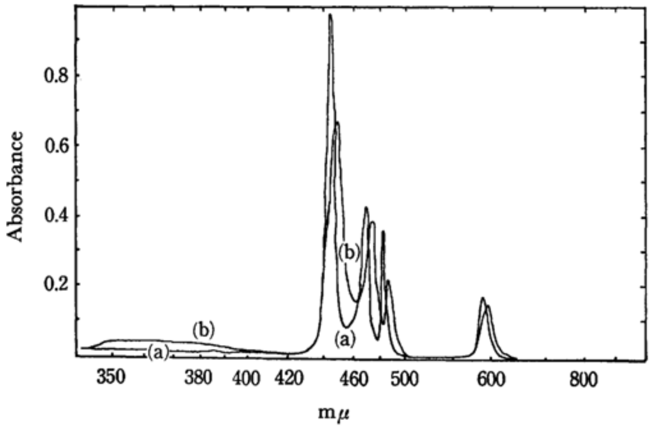

Fig. 7. Absorption spectra of tartarate and aquo complexes of Pr(III) in aqueous solution. pH=11.35, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + tertarate (1 : 1.5)

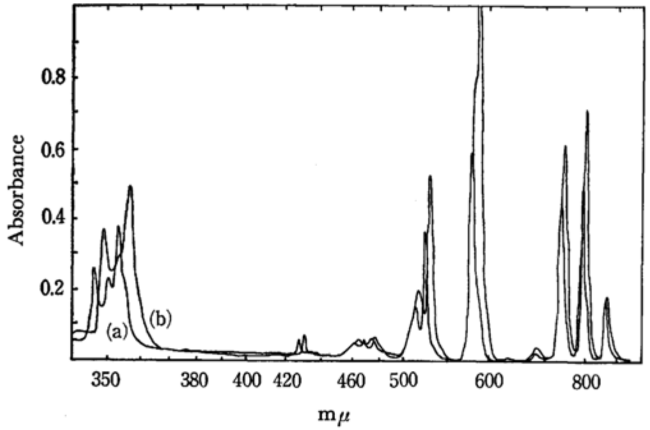

Fig. 8. Absorption spectra of tartarate and aquo complexes of Nd(III) in aqueous solutions. pH=10.55, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + tartarate (1 : 1.5)

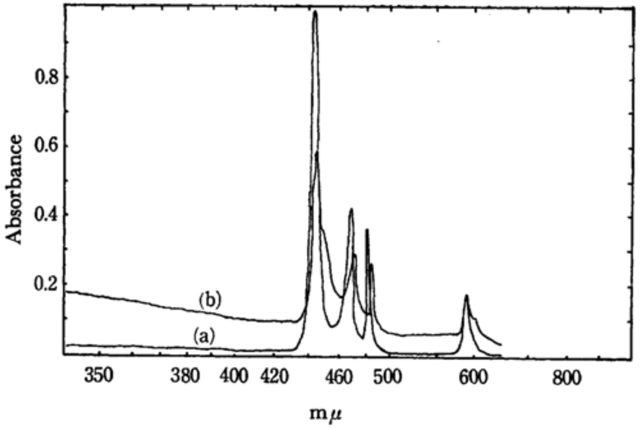

Fig. 9. Absorption spectra of NTA and aquo complexes of Pr(III) in aqueous solutions. pH=12.05, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + NTA (1 : 3)

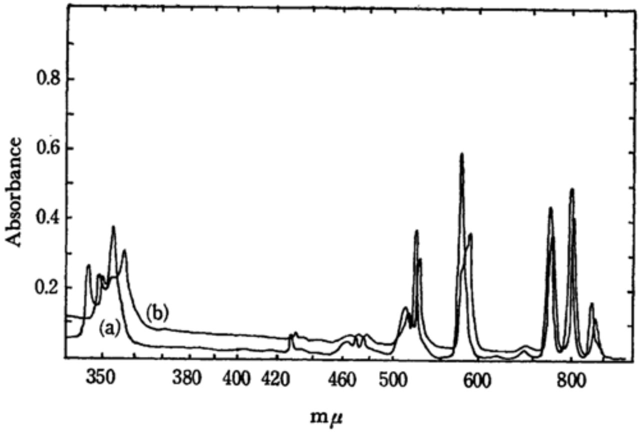

Fig. 10. Absorption spectra of NTA and aquo complexes of Nd(III) in aqueous solutions. pH=12.05, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + NTA (1 : 3)

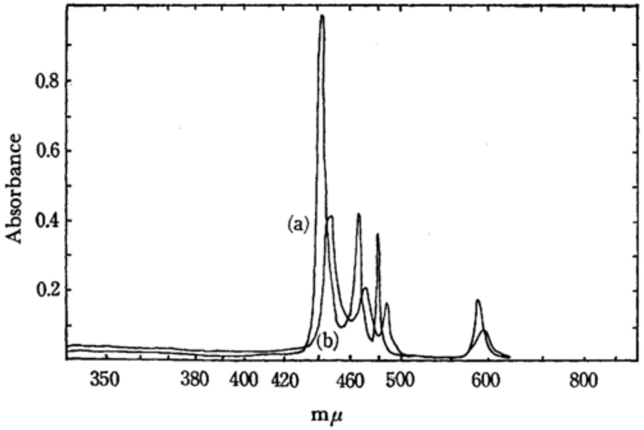

Fig. 11. Absorption spectra of serinate and aquo complexes of Pr(III) in aqueous solutions. pH=10.75, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + serine (1 : 10)

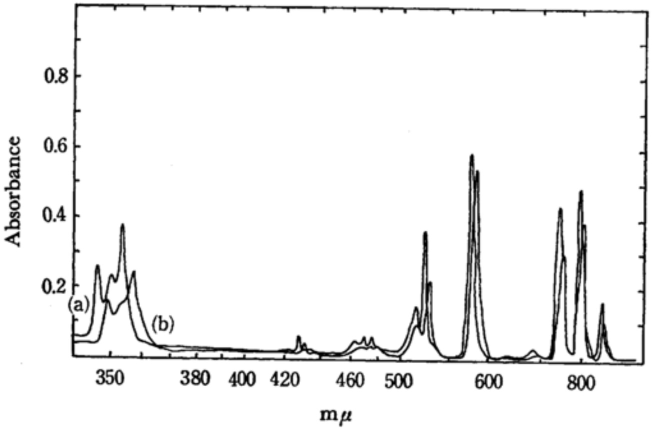

Fig. 12. Absorption spectra of serinate and aquo complexes of Nd(III) in aqueous solutions. pH=10.60, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + serine (1 : 10)

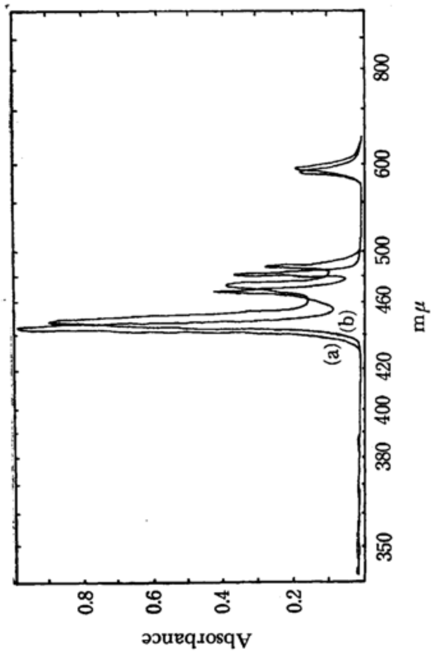

Fig. 13. Absorption spectra of EDTA and aquo complexes of Pr(III) in aqueous solutions. pH=12.85, 25°C.
(a) Pr^{3+} aquo (b) Pr^{3+} + EDTA (1 : 1.5)

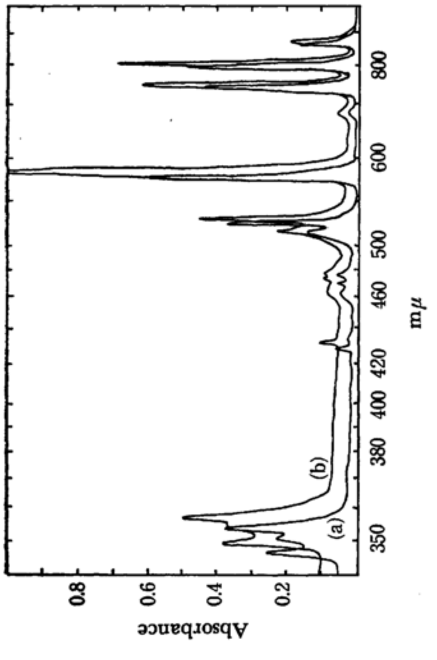

Fig. 14. Absorption spectra of EDTA and aquo complexes of Nd(III) in aqueous solutions. pH=12.85, 25°C.
(a) Nd^{3+} aquo (b) Nd^{3+} + EDTA (1 : 1.5)

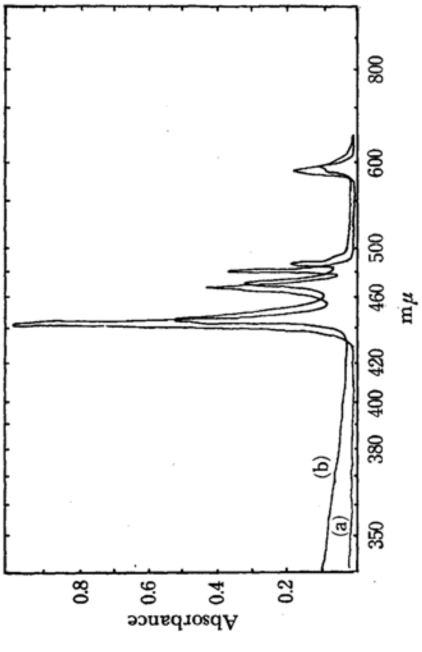

Fig. 15. Absorption spectra of TPHA and aquo complexes of Pr(III) in aqueous solutions. pH=10.50, 25°C.
(a) Pr^{3+} aquo (b) Pr^{3+} + TPHA (1 : 1.1)

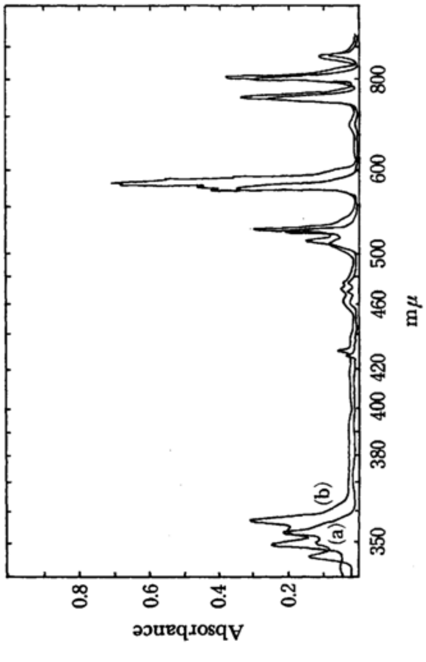

Fig. 16. Absorption spectra of TPHA and aquo complexes of Nd(III) in aqueous solutions. pH=10.50, 25°C.
(a) Nd^{3+} aquo (b) Nd^{3+} + TPHA (1 : 1)

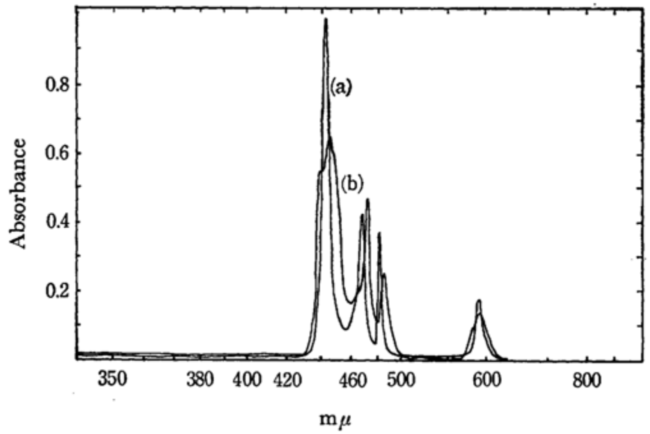

Fig. 17. Absorption spectra of citrate and aquo complexes of Pr(III) in aqueous solutions. pH=13.50, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + citrate (1 : 3)

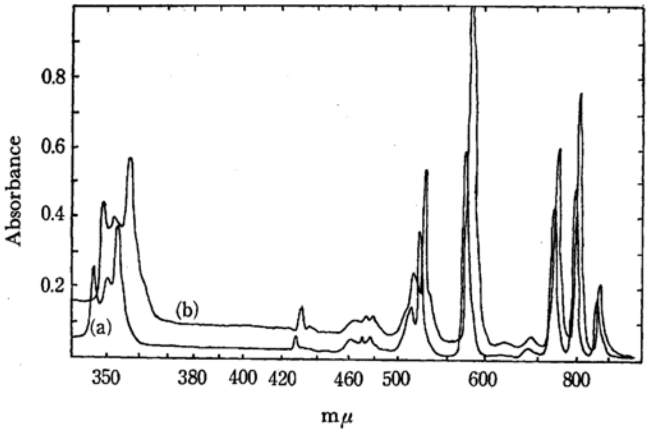

Fig. 18. Absorption spectra of citrate and aquo complexes of Nd(III) in aqueous solutions. pH=13.35, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + citrate (1 : 3)

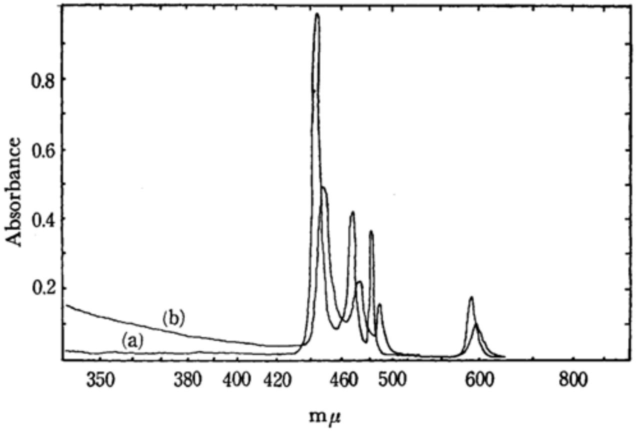

Fig. 19. Absorption spectra of cysteine and aquo complexes of Pr(III) in aqueous solutions. pH=10.80, 25°C.

(a) Pr^{3+} aquo (b) Pr^{3+} + cysteine (1 : 10)

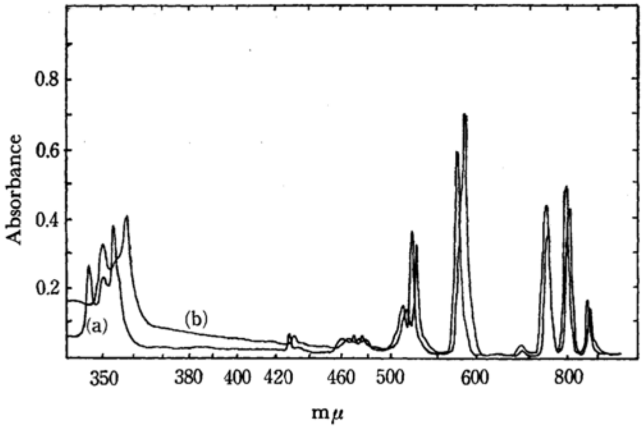

Fig. 20. Absorption spectra of cysteine and aquo complexes of Nd(III) in aqueous solutions. pH=10.55, 25°C.

(a) Nd^{3+} aquo (b) Nd^{3+} + cysteine (1 : 10)

TABLE 4. THE NAPHLAUXETIC EFFECT OF 4*f*- AND 3*d*-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

oxides (purity: more than 99.99%) in perchloric acid. Since the absorption spectra of the aqueous solutions were completely in accord with the literature,[14] they were not purified further.

Results and Discussion

Since it was difficult to obtain the barricenter of the *J*-band experimentally, we had to be satisfied with taking the center of the band (not the peak).

The energies of the *J*-levels of each lanthanide(III) complex were obtained using the results of the least-squares calculations.

The accordance of the calculated values with the observed values was satisfactory. The calculated values of the aquo complexes are shown as examples in the second column of Table 2.

The values of E^3 and ζ_{4f} obtained are listed in Table 3. By using these data, the degree of the nephelauxetic effect of 4*f*-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 illustrated in Table 4.

Jørgensen[5] has made a similar comparison by regarding $(\tilde{\nu}_{\text{aquo}}-\tilde{\nu}_{\text{comp}})/\tilde{\nu}_{\text{aquo}} \fallingdotseq 1-\beta'$, assuming that the separation between *J*-levels is linearly dependent only on E^3. He studied several lanthanide(III) complexes with tartarate, citrate, EDTA, *etc.* in solution and obtained $1-\beta'=0.8$—1.2×10^{-2} for Pr(III) and 0.4—0.7×10^{-2} for Nd(III). In the present study, the values of $1-\beta'$ were 0.8—1.0×10^{-2} for Pr(III) and 0.7—0.9×10^{-2} for Nd(III). Jørgensen's values agree with ours fairly well, considering his simple method and the small differences in materials and conditions.

In connection with the above discussion, 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. The experimental conditions for the nephelauxetic effect, $1-\beta'$, obtained in this study are shown in Table 1. In spite of this limitation, however, the results of the present study are still useful for estimating the covalent character of the 4*f* electrons of the lanthanide(III) ion.

Furthermore, in some cases, the present data may serve to give some information on the configuration of the complex. For example, as may be seen in Table 3, the cysteine complex shows the smallest E^3 and is located on the bottom of the nephelauxetic series in either a praseodymium(III) or a neodymium(III) complex; on the other hand, the other α-amino acids, such as glycine, alanine, and serine, are placed on the upper positions of the series in both praseodymium(III) and neodymium(III) complexes. This fact suggests that the sulfur atom of cysteine takes part in the formation of the cysteine complex in the solution. Jørgensen[15] has already shown that the nephelauxetic effect of sulfur-coordinated metal ions is much stronger in covalency than that of oxygen- or nitrogen-coordinated metal ions.

This study was partly supported by grants from the Ministry of Education and the Japan Society for the Promotion of Science, to both of which organizations the authors wish to express their thanks.

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