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The Nephelauxetic Effect in Erbium(III) and Thulium(III) Complexes

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The absorption spectra of erbium(III) and thulium(III) complexes were measured in an aqueous solution with an excess of ligands. The Racah parameter, E^3 and the Landè parameter, ζ_{4f}, were calculated by the least-squares method on the assumption that the energy separation between J-level of the $4f^n$— configuration is a function of F_2 and ζ_{4f}. The nephelauxetic effect in the Tm^{III} and the Er^{III} complexes was then discussed by using the values of E^3 thus obtained.

Introduction

The so-called nephelauxetic effect of metal complex means the expansion of electron cloud and it may be regarded as a measure of the covalency of coordination bonds.[1]

The nephelauxetic effect in lanthanide(III) complexes has been already studied by Jørgensen,[2,3] Sinha,[4] Yatsimirsky[5] and Misumi.[6]

In general, the absorption bands of lanthanide(III) ions, which are attributed to the electronic transitions within the $4f^n$-configuration ($n = 2 \sim 12$), are shifted when the environment of the ion is changed. This is undoubtedly an indication of a change in the radial integrals. 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.[6,7] That is, the separation between J-levels of the $4f^n$-configuration may be expressed in terms of the radial integrals (f)[8] and the spin-orbit coupling parameter. Therefore it is necessary to obtain the radial integrals or Racah parameters, E^k's 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 F_k and ζ_{4f}.

In the previous papers,[6,9] the nephelauxetic effect in the Pr^{III} (f^2) and the Nd^{III} (f^3) complexes was reported. Since the calculation for $4f^n$ and $4f^{14-n}$ are the same except the sign of ζ_{4f}, here, we calculated the Racah parameter E^3 and the Landè parameter ζ_{4f} in the same way as before and discussed the nephelauxetic effect in the Er^{III} (f^{11}) and Tm^{III} (f^{12}) complexes by using the values of E^3 thus obtained and compared with those of the Pr^{III} and Nd^{III} complexes.

Experimental Section

Materials. Erbium(III) and thulium(III) perchlorates were prepared by dissolving pure erbium and thulium oxides (purity: more than 99.9%) in perchloric acid. Since the absorption spectra of the aqueous solutions were completely in accord with the literature,[10] they were not purified further. The ligands used are given in Table I.

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

	Tm^{III}		Er^{III}	
Ligand	M:L	pH	M:L	pH
Aquo		5.12		6.45
Cysteine	1:5	5.41	1:10	5.75
Malate	1:1.5	8.30	1:1.5	10.60
L-serine	1:10	5.95	1:5	10.70
Alanine	1:10	6.39	1:10	7.70
Citrate	1:3	11.61	1:3	10.20
Glycine	1:10	6.21	1:10	7.10
EDTA	1:15	11.00	1:1.5	11.40
DTPA	1:15	10.22	1:1.5	10.20
CyDTA	1:1.5	9.40	1:1.5	12.10
NTA	1:2	7.92	1:3	11.00
IDA	1:3	7.20	1:3	9.61
TPHA	1:1	7.25	1:1	11.99

IDA: iminodiacetic acid. NTA: nitrilotriacetic acid. EDTA: ethylenediaminetetraacetic acid. CyDTA: cyclohexanediaminetetraacetic acid. DTPA: diethylenetriaminepentaacetic acid. TPHA: tetraethylenepentaamineheptaacetic acid.

Measurements. The absorption spectra were measured at room temperature (about 25°C) with Hitachi EPS-2 Spectrophotometer, a 10 mm quartz cell being used.

The concentration of the solution was 0.1 *M* for the lanthanide(III) perchlorate. Enough excess ligand

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

(2) C. K. Jørgensen, *Mat. Fys. Medd. Dan Selk.*, 30 (1956) n. 22.

(3) C. K. Jørgensen, R. Pappalardo, and E. Rittershaus, *Z. Naturforsch.*, *19a*, 424 (1964).

(4) S. P. Sinha, *J. Inorg. Nucl. Chem.*, *27*, 115 (1965).

(5) K. B. Yatsimirsky, N. K. Dauidenke, N. A. Kostromina, and Ternovaya, *Proceed. 8th. I.C.C.C.*, 92 (1965).

(6) S. Misumi, S. Kida, T. Isobe and A. Inazumi, *Bll. Chem. Soc. Japan*, *41*, 25 (1968).

(7) E. H. Carlson and H. M. Crosswhite, *Johns HopNins Univ. Spectroscopic Report*, 19 (1960).

(8) 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 in discussion.

(9) S. Misumi, S. Kida, and M. Aihara, *Coordin. Chem. Rev.*, *3*, 189 (1968).

(10) C. V. Banks and P. W. Klingman, *Anal. Chim. Acta*, *15*, 356 (1956).

was added to cause complex formation. The absorption spectra may be affected by the pH of the solution under some conditions, so that dilute ammonia was added carefully to the solution until the increase in pH did not affect the absorption bands any more before precipitation, because of the low basicity of erbium(III) and thulium(III). The pH values and the ratio of metal to ligand in the solution are listed in Table I.

Calculations. Calculations were carried out for erbium(III) and thulium(III) complexes in the same way as those for praseodymium(III) and neodymium(III) complexes in the previous papers.[6,9]. In the intermediate coupling scheme, the energy separations between J-levels of an f^n configuration ($n = 2 \sim 12$) are expressed approximately in terms of radial integrals, F_k (Slater-Condon parameter) and the spin-orbit coupling parameter, ζ_{nf}[11] (Landè parameter).

According to Wybourne,[7,12] if hydrogenic wave function is assumed, the ratios of the radial integrals are given by.

$$F_2 : F_4 : F_6 = 1 : 0.138047 : 0.0151083 \tag{1}$$

Table II. The observed wave numbers (M_i) of Tm^{III}, used for calculation (cm^{-1}).

	J-level			
Ligand	$^1D_2$	$^1G_4$	$^3F_3$	$^3F_4$
Aquo	27902	21209	14457	12650
Cysteine	27878	21209	14445	12607
Malate	27878	21227	14453	12663
L-serine	27863	21213	14453	12633
Alanine	27855	21204	14457	12633
Citrate	27863	21213	14457	12666
Clycine	27847	21200	14453	12617
EDTA	27847	21204	14457	12658
DTPA	27793	21133	14391	12550
CyDTA	27809	21209	14457	12650
NTA	27755	21119	14403	12571
IDA	27739	21093	14355	12566
TPHA	27732	21213	14378	12500

This relation being used, the energy of a J-level can be expressed as a function of two variables, F_2 and ζ_{4f}. ($E^3 = 1.48447\ F_2$).

If $f_i(F_2, \zeta)$ denotes the energy of the ith J-level from the ground state, one may obtain

$$f_i(F_2,\zeta)=f_i(F_{20},\zeta_0)+\left(\frac{\partial f_i}{\partial F_2}\right)_{F_2=F_{20}} x + \left(\frac{\partial f_i}{\partial \zeta}\right)_{\zeta=\zeta_0} y \tag{2}$$

by appling Taylor's theorem and neglecting the higher order terms, where $F_2 = F_{20}+x$, $\zeta = \zeta_0+y$, $F_{20} \gg x$, $\zeta_0 \gg y$ and F_{20} and ζ_0 are constants. The numerical values of the parameters of the trivalent lanthanide complexes, F_{20} and ζ_0 may be taken from the literature,[13,7,14] then $f_i(F_{20}, \zeta_0)$, $(\Delta f_i/\Delta F_2)_\zeta$ and $(\Delta f_i/\Delta\zeta)_{F_2}$ can be calculated by solving the secular equation derived from the spin-orbit matrix and LS term energies, as a function of $\chi(\zeta/F_2 = \chi)$. Accordingly, $f_i(F_2, \zeta)$ is simplified to a linear function of x and y, assuming approximately that

$$\begin{aligned}(\Delta f_i/\Delta F_2)_\zeta &= \partial f_i/\Delta F_2 = a_i\\ (\Delta f_i/\Delta\zeta)_{F_2} &= \partial f_i/\partial\zeta = b_i\\ f_i(F_2,\ \zeta) &= K_i + a_i x + b_i y \end{aligned} \tag{3}$$

where

$$K_i = f_i(F_{20},\ \partial_0)$$

Based on equation (3), x and y can be obtained by the least-squares method using the experimental values. The value of F_2 thus obtained is then converted to E^3.

Tm^{III}. This LS term energies and the spin-orbit matrices were obtained by Satten and Margolis[15] and Dieke.[14] The calculation was carried out by putting $\chi = 6.00$ ($F_2 = 450\ cm^{-1}$, $\zeta = 2700\ cm^{-1}$).[13] Four experimental values were used for the least-squares method for each thulium(III) complexes.

Er^{III}. We have made use of the results of the calculation of Carlson and Crosswhite.[7] The numerical values of $f_i(F_{20}, \zeta_0)$, $(\partial f_i/\partial F_2)_{\zeta=\zeta_0}$ and $(\partial f_i/\partial\zeta)_{F_2=F_{20}}$ for

Table III. The observed wave numbers of Er^{III} used for calculation (cm^{-1})

	Ligand												
J-level	Aquo	Cysteine	Malate	L-serine	Alanine	Citrate	Clycine	EDTA	DTPA	CyDTA	NTA	IDA	TPHA
$^2G_{7/2}$	28090	28090	28019	28027	28043	28003	28074	28027	28090	28050	28003	28035	28011
$^4G_{11/2}$	26406	26371	26316	26274	26302	26302	26316	26302	26302	26274	26274	26302	26267
$^2H_{9/2}$	24492	24492	24474	24486	24456	24456	24492	24486	24468	24516	24468	24456	24468
$^4F_{3/2}$	22568	22533	22523	22482	22512	22533	22517	22533	22507	22604	22497	22492	22517
$^4F_{5/2}$	22148	22099	22075	22075	22060	22060	22075	22041	22046	22051	22065	22051	22060
$^4F_{7/2}$	20442	20408	20408	20396	20387	20404	20408	20396	20387	20400	20396	20396	20396
$^2H_{11/2}$	19150	19084	19077	19051	19033	19037	19044	19058	19069	19040	19051	19029	19037
$^4S_{3/2}$	18365	18305	18345	18305	18312	18312	18308	18325	18285	18352	18298	18292	18362
$^4F_{9/2}$	15253	15198	15260	15237	15188	15195	15195	15216	15188	15230	15195	15195	15175
$^4I_{9/2}$	12399	12422	12407	12407	12361	12392	12384	12438	12399	12571	12356	12353	12369
$^4I_{11/2}$	10254	10215	10254	10238	10204	10188	10194	10238	10184	10284	10233	10193	10135

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(11) 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).

(12) B. G. Wybourne, « Spectroscopic Properties of Rare Earth », Interscience, New York, (1965).

(13) J. B. Gruber and J. C. Conway, *J. Chem. Phys.*, *32*, 1178 (1960).

(14) G. H. Dieke, « Spectra and Energy Levels of Rare Earth Ions in Crystals », Interscience Publishers, London (1968).

(15) R. A. Satten and J. S. Margolis, J. *Chem. Phys.*, 32 (2), 573 (1960).

each J-level were obtained by putting $\chi = -5.70$ and then the least-squares calculation was carried out by using eleven experimental values for each erbium(III) complexes.

Results and Discussion

Since it was difficult to obtain the barycenter of the J-band experimentally, we had to be satisfied with taking the center of the band (not the peak). For example, Figure 1 and 2 show the absorption spectra of EDTA and aquo complexes of Er^{III} and Tm^{III} in aqueous solution, respectively at 25⁰C. The values of E^3 and ζ_{4f} obtained are listed in Table IV.

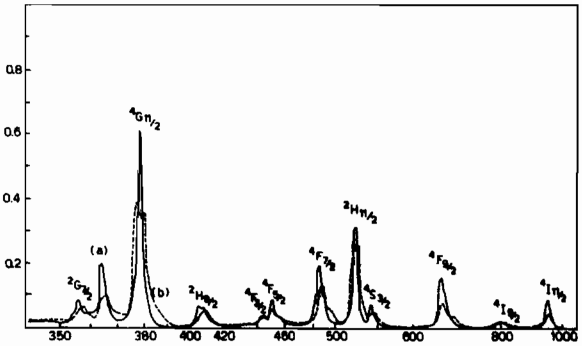

Figure 1. Absorption spectra of EDTA and aquo complexes of Er^{III} in aqueous solution. (a) Er^{3+} aquo (b) Er^{3+}+EDTA (1:1.5). pH = 11.40, 25°C.

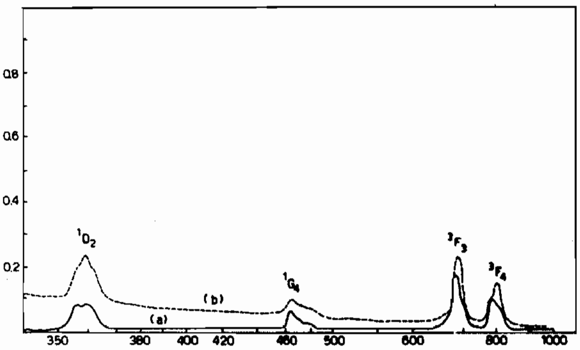

Figure 2. Absorption spectra of EDTA and aquo complexes of Tm^{III} in aqueous solution. (a) Tm^{3+} aquo (b) Tm^{3+}+EDTA (1:1.5). pH = 11.00, 25°C.

Table IV. E^3 and ζ_{4f} (cm^{-1})

Ligand	Tm^{III} E^3	Tm^{III} ζ_{4f}	Er^{III} E^3	Er^{III} ζ_{4f}
Aquo	663.7	2726.2	648.4	2476.6
Cysteine	663.1	2723.8	647.1	2477.2
Malate	662.5	2730.1	646.3	2479.3
L-serine	662.4	2727.1	645.3	2482.7
Alanine	662.2	2726.6	646.4	2470.4
Citrate	662.1	2729.5	646.5	2470.2
Glycine	662.1	2725.2	646.7	2474.1
EDTA	661.7	2728.6	646.0	2479.2
DTPA	661.3	2712.4	646.4	2471.6
CyDTA	660.4	2730.4	646.2	2485.6
NTA	660.0	2714.5	645.2	2479.7
IDA	659.7	2709.7	646.0	2472.6
TPHA	658.6	2720.6	648.0	2455.1

Table V. The nephelauxetic effects of 4f- and 3d-transition metal complexes

Metal ion Ligand	Ni^{II} EDTA	Mn^{II} EDTA	Pr^{III} EDTA	Nd^{III} EDTA	Tm^{III} EDTA	Er^{III} EDTA
$\beta' = \dfrac{F_{k(complex)}}{F_{k(aquo)}}$	0.91	0.96	0.990	0.991	0.997	0.996
1 - B'	0.09	0.04	0.010	0.009	0.003	0.004

The experimental conditions for the nephelauxetic effect 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 as reported in the previous paper.

By using the values of E^3 obtained, the degree of the nephelauxetic effect of 4f-transition metal complexes can be compared with that of d-transition metal complexes in terms of $1\text{-}\beta'$. (where $\beta' = F_{2(complex)}/F_{2(aquo)}$) as illustrated in Table V. The term of $1\text{-}\beta'$ is regarded as a measure of covalency between metal and ligand. It was found that the nephelauxetic effect in Er^{III} and Tm^{III}, the heavy lanthanide(III) complexes was about one third of that in Pr^{III} and Nd^{III}, the light lanthanide(III) complexes and about 1/10 ~ 1/30 of that in Ni^{II} and Mn^{II} (d-transition metal(II)) complexes.

Furthermore, the present data may serve to give some informations on the configuration of the complex. As shown in Table IV, T^{III} and Er^{III} cysteine complexes show the high values of E^3 and are located near the aquo complexes, contrary to the values of E^3 and are located near the aquo complexes, contrary to the values of E^3 for Pr^{III} and Nd^{III} cysteine complexes.

This fact denotes that at pH 5 ~ 6, sulfur atom do not coordinate completely to the heavy lanthanides(III).

It should be noted that among the strong chelating agents such as EDTA and its homologues, the relatively small ligands, NTA and IDA form the complexes of small E^3. The value of E^3 for Er^{III} TPHA complex is next to aquo complex, which is supposed to be due to the anomaly of erbium(III) complex, the decrease of coordination number and the anomalous decrease of stability constant for Er^{III}-TPHA complex.[9]

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