

수용액에서 몇가지 란탄 착화합물의 Hypersensitive Transition에 관한 연구[†]

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A Study on the Hypersensitive Transitions of Nd(III), Ho(III) and Er(III) Complexes in Aqueous Solution[†]

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요 약. 수용액에서 몇가지 란탄 착화합물의 hypersensitive 전이대를 연구하였다. 리간드의 염기도(pK_a)와 란탄 착화합물의 hypersensitive 전이대의 진동자 세기 사이에 정립된 선형 관계에 근거를 두고, 금속-리간드 결합간에 존재하는 공유 결합성을 anthranilate, pyrazine-2-carboxylate 및 pyruvate 착화합물에 대해서 논하였다.

ABSTRACT. The hypersensitive $f \rightarrow f$ transitions of Nd(III), Ho(III), and Er(III) have been studied for some lanthanide complexes in aqueous solution. Based on the linear correlation between the oscillator strength of the transition and the basicity(pK_a) of the ligand, the covalency in the metal-ligand bonding is discussed for lanthanide anthranilate, pyrazine-2-carboxylate, and pyruvate.

INTRODUCTION

The absorption bands of $f \rightarrow f$ transitions in lanthanide ions are sharp and narrow in contrast with those of $d \rightarrow d$ transitions. These bands are also quite insensitive to the environment about the lanthanide ion.¹ However, the certain transitions, so called "hypersensitive transitions", are significantly affected by the environ-

mental change about the ion²⁻⁴.

Judd⁵ proposed that symmetry changes about the lanthanide ion cause the hypersensitivity. The hypersensitivity is observed when symmetries belonging to the groups, C_2 , C_2v or C_{2h} are present. However, it seems like that these symmetries are not always required, since several apparent exceptions have been found.⁶

Henrie and Choppin⁷ have proposed that the covalency in the lanthanide-ligand bonding is directly related to the hypersensitivity, based on

[†]Dedicated to professor Chong Hoe Park on the occasion of his 60th birthday.

the observation of the charge transfer transitions in the lanthanide complexes which are extremely sensitive to the type of ligand and to the metal ion.⁸ They have shown experimentally the linear relationship between the basicity (pK_a) of the ligand and the oscillator strength of the hypersensitive spectral transition in the Nd(III) and Ho(III) complexes.^{9,10}

The lanthanide(III) ions like the alkaline earth metal ions, which belong to the hard acid group, bind strongly with the oxygen atom rather than other type of donor atoms. Their binding is known to be mainly electrostatic but weak covalent. The oscillator strength of the hypersensitive transition could be a measure of the magnitude of the covalency in the lanthanide complexes. We have applied the hypersensitive spectral transitions to discuss the covalent binding effect on the complexation of the furate, anthranilate, and squarate with Nd(III) and Ho(III) ions.¹¹ In the present work, we have investigated the effects of the pyruvate and pyrazine-2-carboxylate ligands on the hypersensitive transitions of Nd(III), Ho(III) and Er(III) complexes.

EXPERIMENTAL

Chemicals. The neodymium, holmium and erbium perchlorate solutions were prepared by dissolving the corresponding lanthanide oxides (American Potash and Chemical, 99.99%) in concentrated perchloric acid. Standardization of the stock solutions was accomplished by EDTA titration with xylenol orange indicator in the acetate buffer ($pH=4.16$). The stock solutions of the ligand acids were prepared and standardized using the acid-base titration method. The total ionic strength of the working solutions was adjusted with $NaClO_4$. Deionized water was used for the preparation of all solutions.

Equipments. pH measurements were made

with a Beckman Model 4500 Digital pH meter and Fisher standard combination electrode. Spectral measurements were made using Pye Unicam SP 1800 spectrophotometer and 4 cm or 10 cm matched fused silica cell.

Procedure. The oscillator strength for each metal complex was calculated with the method described previously.⁹⁻¹¹ In the concentration conditions from which the formation of any significant amounts of complexes greater than ML_3 is prevented, the observed oscillator strength of the solution would be a sum of the oscillator strengths for the metal species as Eq. (1).

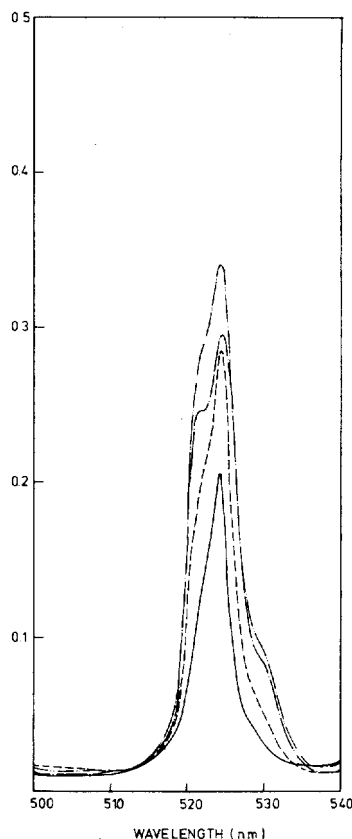


Fig. 1. The absorption bands for the hypersensitive transition in $Er(III)^4I_{15/2} \rightarrow ^2I_{11/2}$; $Er^{3+}(aq)$ —, $ErPy^{2+}$ ·····, $Er\alpha-P^{2+}$ — · — ·, $ErPC^{2+}$ — — —. (Py; Pyruvate, α -P; α -Picolinate, PC; Pyrazine-2-carboxylate).

Table 1. Typical experimental results of Er(III)-pyrazine-2-carboxylate solutions. $I=1.0M$, $T=25^{\circ}C$, $M_T=0.0096M$, $L_T=0.0150M$

| pH | Concentration (M) | | | | | $P_{obs.}$ ($\times 10^6$) | f_M | f_{ML} | f_{ML_1} | f_{ML_2} | f_L |
|-------|-------------------|--------|--------------------|--------------------|--------|---------------------------------|--------|----------|------------|------------|--------|
| | (M) | (ML) | (ML ₂) | (ML ₃) | (L) | | | | | | |
| 1.361 | 0.0096 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.634 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 1.458 | 0.0068 | 0.0027 | 0.0002 | 0.0000 | 0.0006 | 2.376 | 0.7032 | 0.2761 | 0.0202 | 0.0006 | 0.0378 |
| 1.617 | 0.0061 | 0.0032 | 0.0003 | 0.0000 | 0.0008 | 2.588 | 0.6365 | 0.3303 | 0.0319 | 0.0012 | 0.0500 |
| 1.824 | 0.0053 | 0.0038 | 0.0005 | 0.0000 | 0.0011 | 2.722 | 0.5473 | 0.3964 | 0.0535 | 0.0029 | 0.0698 |
| 2.253 | 0.0037 | 0.0047 | 0.0011 | 0.0001 | 0.0018 | 2.782 | 0.3840 | 0.4891 | 0.1160 | 0.0110 | 0.1227 |
| 2.419 | 0.0032 | 0.0049 | 0.0014 | 0.0002 | 0.0022 | 2.890 | 0.3361 | 0.5061 | 0.1420 | 0.0159 | 0.1451 |
| 3.059 | 0.0022 | 0.0050 | 0.0021 | 0.0003 | 0.0032 | 3.021 | 0.2314 | 0.5174 | 0.2155 | 0.0357 | 0.2155 |
| 3.223 | 0.0021 | 0.0050 | 0.0022 | 0.0004 | 0.0034 | 3.230 | 0.2192 | 0.5156 | 0.2258 | 0.0394 | 0.2266 |
| 3.477 | 0.0020 | 0.0049 | 0.0023 | 0.0004 | 0.0036 | 3.473 | 0.2070 | 0.5129 | 0.2367 | 0.0435 | 0.2388 |

Table 2. Oscillator strengths($\times 10^6$) of the complexes in aqueous solution for the hypersensitive transitions. ($^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ for Nd(III), $^5I_8 \rightarrow ^5G_6$, 5F_1 for Ho(III) and $^4I_{15/2} \rightarrow ^2H_{11/2}$ for Er(III))

| | Anthranilate Er(III) | Pyruvate | | | Pyrazine-2-carboxylate | | |
|----------|-------------------------|----------------------|--------------------|------------------------|------------------------|-----------------------|--------------------------|
| | | Nd(III) | Ho(III) | Er(III) | Nd(III) | Ho(III) | Er(III) |
| P_M | 1.63 | 7.86 | 5.97 | 1.61 | 7.70 | 5.61 | 1.89 |
| P_{ML} | 2.91 ± 0.15 | 18.31 ± 2.14 | 13.62 ± 0.72 | 4.40 ± 0.25 | 12.19 ± 0.84 | 8.70 ± 0.39 | 3.47 ± 0.21 |
| pK_a | 2.00 | 2.00 | 2.00 | 2.00 | 2.76 | 2.76 | 2.76 |
| | Furoate Er(III) | Glycolate Er(III) | Acetate Er(III) | Isobutyrate Er(III) | Propionate Er(III) | Picolinate Er(III) | Acetylacetate Er(III) |
| | | | | | | | |
| P_M | 1.78 | 1.52 | 1.92 | 1.90 | 1.99 | 1.50 | 1.99 |
| P_{ML} | 3.17 ± 0.39 | 3.35 ± 0.18 | 3.94 ± 0.19 | 3.91 ± 0.42 | 3.91 ± 0.52 | 4.06 ± 0.31 | 7.03 ± 0.46 |
| pK_a | 3.11 | 3.57 | 4.55 | 4.64 | 4.66 | 5.18 | 8.88 |

$$P_{obs.} = \sum_{i=0}^3 f_i P_{ML_i} \quad (1)$$

The f_i values, the mole fraction of ML_i complex, could be calculated from the stability constants of the species reported in the literature.¹²⁻¹⁵ The P parameters were fit using a linear regression program (SPSS version H Release 8.1) to compute.

RESULTS AND DISCUSSION

The hypersensitive transitions studied are $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ for Nd^{3+} , $^5I_8 \rightarrow ^5G_6$, 5F_1 for Ho^{3+} , and $^4I_{15/2} \rightarrow ^2H_{11/2}$ for Er^{3+} . The absorption bands which are due to the hypersensitive transitions of Nd^{3+} , Ho^{3+} , and Er^{3+} ions occur at 5450~

6100Å, 4350~4367Å, and 5030~5350Å, respectively. Fig. 1 shows the hypersensitivity of the absorption spectra of the Er^{3+} in various environments. A typical set of the experimental data for Er(III)-pyrazine-2-carboxylate is Table 1. The oscillator strengths for individual complexes calculated from Eq. (1) are given in Table 2 along with the values of pK_a of the ligands. The data in Table 2 show that the oscillator strengths are varied with the variation of the ligands. The calculated P_M values should be equal to the $P_{obs.}$ ($=1.36 \times 10^{-6}$) observed in the aqueous perchlorate solution. The satisfactory agreement between the values of P_M calculated for the complex solutions and those

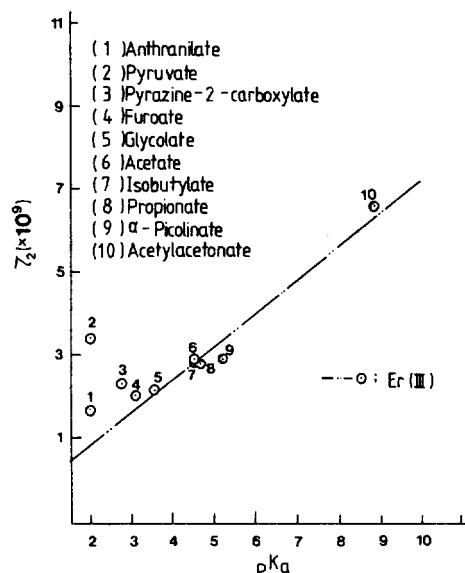


Fig. 2. The correlation diagram of pK_a vs τ_2 for the monobasic ligands.

of the aqueous ion is a good evidence for the validity of the data analysis.

The oscillator strength of an induced electric-dipole transition would be written as¹⁶

$$P = \sum_{\lambda=2,4,6} \tau_{\lambda} \bar{\nu} (f^{N\Phi J} \| U^{(\lambda)} \| f^{N\Phi' J'}) / (2J+1) \quad (2)$$

where $\bar{\nu}$ is the transition energy, $(f^{N\Phi J} \| U^{(\lambda)} \| f^{N\Phi' J'})$ are the square of the matrix elements of the unit tensor operator $U^{(\lambda)}$ connecting the initial and final states $(\Phi J$ and $\Phi' J')$ and $2J+1$ is the ground state multiplicity. τ_{λ} ($\lambda=2, 4$, and 6) are the phenomenological parameters which are related to the radial wavefunctions of the states, the refractive index of the medium, and the ligand field parameters. The τ_4 and τ_6 parameters are small, compared with τ_2 parameter. It has been assumed that the τ_4 and τ_6 parameters are constant and equal to the aqueous values for all the complexes in the calculation of the values of τ_2 . τ_2 parameter is consequently assumed to be directly proportional to the oscillator strength of the hypersensitive band. The values

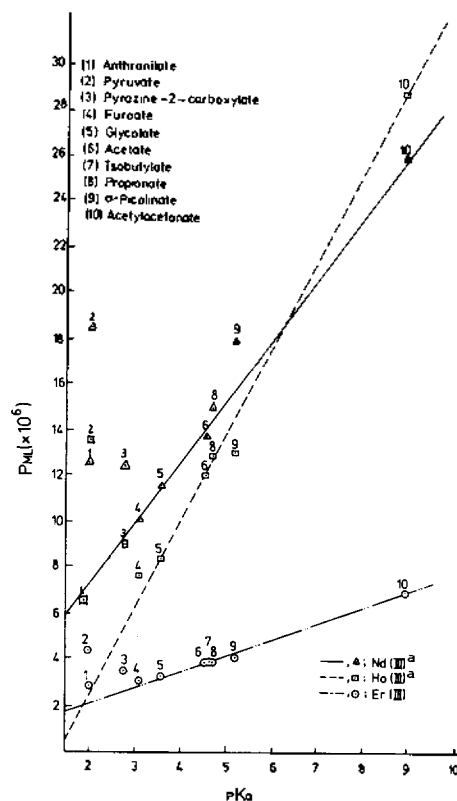


Fig. 3. The correlation diagram of pK_a vs P_{ML} for the monobasic ligands (*Data from reference 9, 11 beside those of the pyruvate and the pyrazine-2-carboxylate).

of τ_2 for Er(III) have been calculated using the values of oscillator strengths given in Table 2 by the method of Gruen *et al.*¹⁷ and Peacock.¹⁸ Fig. 2 is a plot of τ_2 values of Er³⁺ complexes against the ligand basicity (pK_a). A linear correlation between τ_2 and pK_a with some exceptions is noted from Fig. 2. Choppin *et al.*⁸ have found a similar linear relationship between τ_2 and pK_a for the Nd³⁺ and Ho³⁺ complexes. Thus, they have suggested that the oscillator strength of the complex may be a measure of covalency in the metal-ligand bonding.

Fig. 3 is the plot of the oscillator strength of the complex against the pK_a of the ligand acid for some lanthanide complexes. It is noted

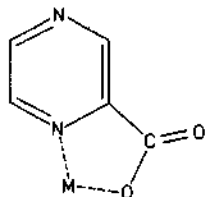


Fig. 4. The structure of lanthanide (III)-pyrazine-2-carboxylate (1:1).

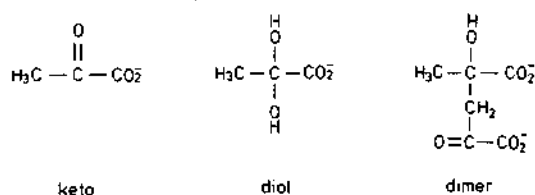


Fig. 5. The structure of various pyruvate species.

that there is a linear correlation between the oscillator strength of the complex and the pK_a of the ligand for the Er(III) complexes as well as for the Nd(III) and Ho(III) complexes already reported by Choppin *et al.*⁹⁻¹⁰ However, the pyruvate, anthranilate, and pyrazine-2-carboxylate deviate well above from the linear line for all of the Nd(III), Ho(III), and Er(III). They seem to require a larger value of pK_a to fit the line. It would mean that the ligands are more basic to the lanthanide ion than to a proton.

We have previously discussed the deviation of the oscillator strength from the value expected from the pK_a of the ligand for the Nd(III) and Ho(III) anthranilate complexes.¹¹ A similar argument is also applied to the Er(III) anthranilate

The deviation of the pyrazine-2-carboxylate is interesting since the analogous α -picolinate has been found to fit on the linear line using the pK_a value for the carboxylate group. It has been reported¹⁵ that the pyrazine-2-carboxylate forms a chelate with a lanthanide ion in the aqueous solution in a fashion of Fig. 4. In this ligand, 4-nitrogen atom of the ring could not

interact with the metal ion by the steric reason. However, 4-nitrogen atom of the ligand may play an important role in the formation of the complex. The basicity of the 4-nitrogen atom would transfer through the π -resonance system of the heterocyclic ring to the 1-nitrogen atom and the carboxylate group. This could enhance the covalency of metal-ligand interaction of the lanthanide pyrazine-2-carboxylate complex.

The pyruvate is a monobasic acid and exists as three forms of the keto, diol, and dimer in the aqueous solution as shown in Fig. 5. The basicities are $pK_a=2.0$ for the keto and $pK_a=3.4$ for the diol.¹⁴ The nmr study of the lanthanide pyruvate in aqueous solution has shown that there are 60% of the keto complex, 20% of the diol complex, and 22% of the dimer complex.¹⁴ The study also has suggested that the diol and dimer of the pyruvate act as a bidentate while the keto form does as a monodentate. As shown in Fig. 3, the oscillator strength of the pyruvate complex is much larger than that expected from the correlation line when the $pK_a=2.0$ of the keto form is used. Even though $pK_a=3.6$ of the diol form is used, the P_{ML} value of the complex solution still deviates above from the linear line. This suggests that the basicity of the dimer would be quite large. Lanthanide-diol pyruvate complexes form chelation as in other α -hydroxy carboxylate ligands.¹⁴ Lanthanide-dimer pyruvate complexes are formed via chelation to the α -hydroxy carboxylate end in others.¹⁴ Thus, the basicity of the α -hydroxy group would also contribute to the oscillator strength of the complex.

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