

An Europium(III) Hydrolytic Catalyst Favoring Anionic Phosphate Esters over Phosphate Triester

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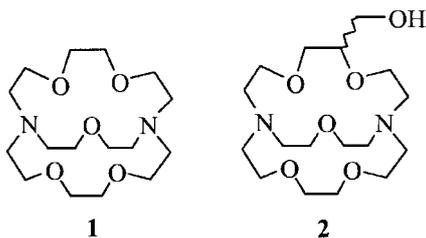
Received October 17, 2000

A Cryptate (221) having a short alcohol pendant (**2**) was metallated with europium(III) in anhydrous condition, and its hydrolytic activity for phosphate esters at neutral pH was examined. While the activity for the phosphate diester and monoester is comparable to that of the parent metal complex [**1**Eu]³⁺, its hydrolytic activity towards a phosphate triester is significantly suppressed. Potentiometric titration and luminescence spectroscopic studies for the equilibrium behavior of the complex in solution suggest that a dimer formation through the metal hydroxides as well as the pendant alcohol is likely to happen. The low hydrolytic activity for the triester seems to be associated with the dimer formation.

Keywords : Europium hydrolytic catalyst, Phosphate esters, Luminescence spectra.

Introduction

Lanthanide ions and their complexes have been shown to be reactive for hydrolyzing various kinds of the substrate such as phosphate diesters, monoesters, and triesters.¹⁻⁴ While the catalysts enhance the rate of the hydrolysis in a similar degree for the various phosphate esters, overall rate constant of the triesters is still higher than that of the corresponding anionic phosphates, reflecting the higher reactivity of the phosphate triesters. Here we report that an europium complex of which activity towards phosphate triesters is so suppressed that the overall rate constants are comparable to each other. It is believed that the suppression is associated with the characteristic equilibrium behavior of [**2**Eu³⁺] complex.



Experimental Section

All chemicals were purchased from Aldrich Chemical Co. and Strem Chemical Co. otherwise mentioned. ¹H- and ³¹P-NMR spectra were recorded on a Bruker AM300 and DPX300 spectrophotometers operating at 300 and 121 MHz, respectively. Melting point was measured in a sealed glass tube and was not corrected. Elemental analysis was performed at Galbraith Laboratories, Inc.

Preparation of the Europium(III) Catalysts. The modified Cryptate (221) having an alcohol pendant (1,4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]trico-5-yl-methan-1-

ol) was prepared as described by Babb *et al.*⁵ Europium trichloride hexahydrate (400 mg, 1.09 mmol) was stirred in triethylorthoformate at room temperature for an hour. After evacuation in vacuum, 1.2 equiv. of Cryptate (221) (**1**, 435 mg, 1.31 mmol) or the modified one (**2**, 475 mg, 1.31 mmol) dissolved in anhydrous methanol were added for the metallation. After the resulting solution was heated at 60 °C for 30 min, diethyl ether was added dropwise at room temperature in order to precipitate the metal complex. The process, the dissolution in methanol and the precipitation, was repeated three times for the purification. These moisture-sensitive europium complexes were handled and weighed in an N₂-filled glove box.

[**2**Eu]Cl₃ (370 mg, 50.7%). mp 218 °C (decomp.). Found: C, 32.52; H, 5.68; N, 4.13. Calc. for C₁₇H₃₄N₂O₆EuCl₃: C, 32.89; H, 5.52; N, 4.51%

Kinetic Measurement. Kinetic traces were recorded on a Hewlett-Packard 8453 diode-array UV-vis spectrophotometer equipped with a temperature-controlled cell holder. Buffers were made up from sodium hydrogen phosphate and standardized HCl and NaOH in deionized water (18 MΩcm⁻¹). The buffer concentration and ionic strength were fixed at 0.20 M and 0.50 M (NaCl), respectively, for the kinetics.

For dissociation kinetic studies, the purified europium(III) Cryptate chlorides were dissolved in a buffer solution at room temperature. The pH of the reaction medium was finely adjusted by titrating with a dilute NaOH solution. The temperature of the stirred reaction mixture was kept at 25 °C by using a constant-temperature water-bath. Typically, the concentration of the europium complex was 5.0 mM. At particular stages of the reaction, an aliquot of the solution was withdrawn, and the UV-vis spectrum was recorded. White precipitate of europium hydroxide was formed as the dissociation proceeded, and was filtered off prior to the spectroscopic measurement. The absorbance was recorded until more than 80% of the complex had dissociated to the metal

ion and the free macrocycle.

For kinetic measurement for the hydrolytic activity, a solution of the metal complex was syringed into a thermostated cell containing an aqueous solution dissolving the substrates (NPP, BNPP, or PNPDP). Addition of aqueous sodium hydroxide solution was followed if necessary. The final concentration of the substrate and the metal complex were fixed at 5.0×10^{-5} M and 5.0×10^{-4} M, respectively. In particular, 10 % (v/v) aqueous acetonitrile solution was employed to dissolve PNPDP. The solution was mixed rapidly, and the absorbance at 400 nm was recorded automatically at intervals of a preset time.

Potentiometric Titration. The pH-meter (Orion 720A) and electrode system (Orion 81-02 Ross combination electrode and Orion ACT-probe 917005) were used. The potentiometric pH titrations were carried out at 25.0 ± 0.1 °C. The deprotonation constants of $[1\text{Eu}]^{3+}$ and $[2\text{Eu}]^{3+}$ complexes were calculated using the computer program PKAS.⁶

Luminescence Spectroscopy. For the luminescence studies, a solution of $[2\text{Eu}]\text{Cl}_3$ was prepared by dissolving appropriate amounts of the sample in deionized H_2O or D_2O (99.9 atom %). The pH of the solution was adjusted by adding aqueous NaOH or NaOD solution, and was measured by using a glass electrode coupled to a digital pH meter (Orion model 720A).

Nd:YAG (Quantel YG681) pumped dye laser (Quantel TDL 50) operating at 10 Hz was employed as the light source. A dye mixture (R590+R610) was used to obtain appropriate laser wavelengths in the 570-585 nm region. The band width of the dye laser was 0.05 cm^{-1} and the laser pulse width was 8 ns. The pulse energy of the laser was kept constant, and about 3.5 mJ pulse was used to avoid the sample decomposition. The laser beam was passed through a 1-cm quartz fluorescence cell containing the sample solution. The Eu(III) $^5\text{D}_0 \leftarrow ^7\text{F}_0$ excitation spectra were obtained by monitoring the luminescence from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ centered at about 619 nm, while scanning the laser wavelength in the 575.5-581.5 nm region. The luminescence signal was collected at 90° from the laser beam direction using a 0.5 m monochromator (Spex 500M) equipped with a cooled PMT (Hamamatsu R928). The signal from the PMT was amplified using a Keithly 428 current amplifier, then fed to a digital oscilloscope (Tektronix TDS520). The output from the digital oscilloscope was transferred to a laboratory computer for the signal averaging and the processing.

Results and Discussion

Preparation of the Europium(III) Catalysts. The modified Cryptate (221) (2) was metallated by the same method used for the preparation of the parent Cryptate (221) complex (1). In order to drive the metallation complete, anhydrous methanol was employed as the reaction solvent. Also, the hexahydrated metal salt was pretreated with triethylorthoformate for the dehydration. A slight excess of the ligands was used to consume the metal salt completely, because the unreacted ligand is easy to eliminate due to its

high solubility in organic solvents. It is assumed that the modified Cryptate (221) (2) binds the europium ion as the same way as the parent Cryptate (221) does,⁷ although there is an ambiguity whether the pendant alcohol coordinates the metallic center or not. The observed spectroscopic properties and the chemical reactivity support the assumption (*vide infra*).

Hydrolytic Activity towards Phosphate Esters. Hydrolytic activity of $[2\text{Eu}]^{3+}$ towards various kinds of substrates has been tested, and was compared with that of $[1\text{Eu}]^{3+}$. The examined substrates include sodium (4-nitrophenyl) phosphate (NPP), sodium bis(4-nitrophenyl) phosphate (BNPP), and (4-nitrophenyl)diphenyl phosphate (PNPDPP). The rates were measured at pH 8.0, in which the observed activity for BNPP is the highest. Being guided by the previous results, use of buffers was avoided in order to suppress the dissociation of the europium complexes.⁸ The pH of the solution was adjusted to 8.0 by adding aqueous NaOH or diluted hydrochloric acid. Only the initial kinetic traces (within one half-life) were analyzed in order to minimize the erroneous effect of the drifted pH.

As shown in Table 1, the phosphate diester (BNPP) has the lowest uncatalyzed rate constant, and the phosphate triester (PNPDPP) the highest. In the above particular condition, the parent complex $[1\text{Eu}^{3+}]$ enhances the hydrolysis of the phosphate esters by a factor of 10^4 to 10^6 . While the enhancement factor is the highest for BNPP, those for NPP and PNPDP are similar to each other. It is worthwhile to notice that the overall rate constant for PNPDP is the largest, reflecting the fastest uncatalyzed reaction of the triester.

At the same condition, the rate constant of $[2\text{Eu}]^{3+}$ for NPP is $4.6 \times 10^{-3} \text{ s}^{-1}$, which is 8.5 times larger than that of the parent europium catalyst. The activity of $[2\text{Eu}]^{3+}$ for BNPP is comparable to that of $[1\text{Eu}]^{3+}$ as shown in Table 1. The striking difference is observed for PNPDP: The hydrolytic activity of $[2\text{Eu}]^{3+}$ is significantly suppressed for the particular substrate. The rate constant for PNPDP is 45 times smaller than that of the parent europium Cryptate complex. As a result, the overall rate constant for the various phosphate esters are comparable to each other in the presence of the modified europium complex. The modified catalyst promotes the anionic substrates by a factor of 10^4 to 10^6 , but it promotes the neutral substrates only marginally. The 6th column of the table clearly shows that the two catalysts behave very differently. The activity of $[2\text{Eu}^{3+}]$ is slightly enhanced or constant for the anionic substrates, but that is

Table 1. Pseudo-first-order rate constants of $[1\text{Eu}]^{3+}$ and $[2\text{Eu}]^{3+}$ towards the various substrates at pH 8.0 and 50 °C

Substrate	$k_o[\text{s}^{-1}]^a$	$k(1)[\text{s}^{-1}]^b$	$k(2)[\text{s}^{-1}]^c$	$k(2)/k_o$	$k(2)/k(1)$
NPP	6.0×10^{-8}	5.4×10^{-4}	4.6×10^{-3}	7.7×10^4	8.5
BNPP	3.0×10^{-10}	6.1×10^{-4}	5.7×10^{-4}	1.9×10^6	0.93
PNPDPP	2.6×10^{-6}	8.5×10^{-2}	1.9×10^{-3}	7.3×10^2	0.022

^aRate constant for the uncatalyzed reaction at pH 7.0 and 50 °C (J. Chin and X. J. Zou, *J. Am. Chem. Soc.*, 1988, 110, 223). For PNPDP the rate was recorded at pH 9.0 and 25 °C (Ref. 3). ^bRate constant for $[1\text{Eu}]^{3+}$. ^cRate constant for $[2\text{Eu}]^{3+}$.

reduced for the neutral substrate by a factor of 0.022.

It is known that an alcohol pendant in the proximity of the reaction center is sometimes so activated that the pendant alcohol behaves as a nucleophile and catalyzes the transesterification.⁹ In order to find out whether a transesterification is involved in the system, the reactions were followed by ³¹P-NMR spectrometer. The NMR spectra showed that only inorganic phosphate was produced during the catalytic hydrolysis of NPP with [2Eu]³⁺. Also, the phosphate was the major product for the hydrolysis of PNPDP in the presence of the catalyst. The NMR analysis clearly showed that truly hydrolysis is operative in this particular catalytic system.

Dissociation Kinetics. Kinetic stability of the [2Eu]³⁺ complex against the demetallation will give a clue to a question whether the methylenehydroxyl group coordinates the europium(III) center or not. It is expected that the stability will increase significantly if the extra alcohol coordinates the metallic center in an intramolecular manner. The dissociation kinetics was studied by the same method applied for the Cryptate (221) europium complex.⁸ The linearity obtained on plotting log A (absorbance) against the reaction time indicates that the dissociation rate exhibits a first-order dependence on the concentration of the metal complex. In phosphate buffer (c = 0.20 M), the dissociation rate constant for [2Eu]³⁺ is $2.1 \times 10^{-5} \text{ s}^{-1}$ at pH 7.0 and 25 °C, while the one for the parent europium(III) complex is $2.4 \times 10^{-5} \text{ s}^{-1}$ at the particular condition. Even though there is an ambiguity on the mechanism of the dissociation, the observed increase of the stability is too marginal to suppose the intramolecular coordination of methylenehydroxyl group to the metal center. The experimental observation is in accordance with a molecular modeling result showing that the methylenehydroxyl group is too short to coordinate the metal center intramolecularly.

Potentiometric Titration. Potentiometric titration is an important method to retrieve valuable information on the behavior of metal complexes in solution. On top of pK_a value of the coordinated water molecules, the associative nature of metal centers can be monitored if any. It is particularly true for the lanthanide ions, of which strong associative nature to form multinuclear species is indicated by the low slope of the titration curves.

Potentiometric titration curve for [2Eu]³⁺ is compared with those for free europium(III) ion as well as for the parent europium complex. As in Figure 1, the curve for [2Eu]³⁺ resembles that of europium trichloride. At present, it is not clear why pH increases sharply around 2.5 equiv. of NaOH rather than 3.0 equiv. One possible explanation is that the europium hydroxide aggregates formed at pH over 8.0 segregate from the solution, even though it is well below the pH giving the particles observable with bare eyes. The formation of the aggregates invisible to eyes will result in the early break point.

Another resemblance is a rather slow increase of pH up to 2 equiv. of NaOH. The behavior of [2Eu]³⁺ is strikingly different from the parent europium complex [1Eu]³⁺, of which pH increase is more than three pH units in the range. Small

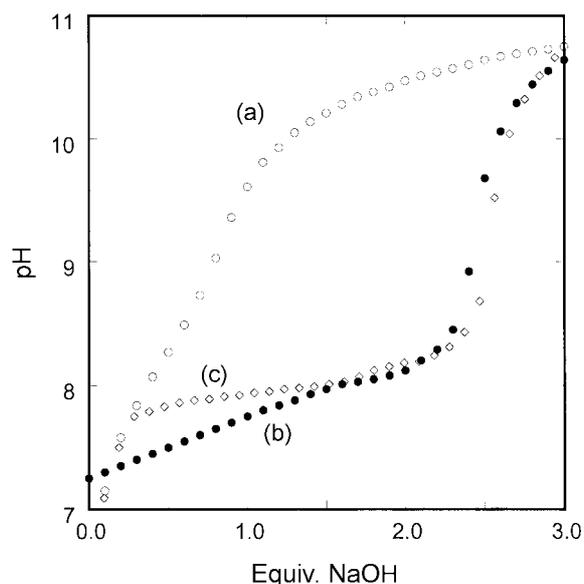
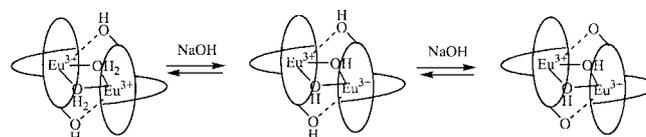


Figure 1. Potentiometric titration curves (c = 0.40 mM): (a) [1Eu]Cl₃. (b) [2Eu]Cl₃. (c) EuCl₃·6H₂O.

increase of pH upon addition of NaOH results from the fact that pK₂ is very close to pK₁, being invoked by the formation of the multinuclear species.¹⁰ Indeed, analysis of the recorded curve for [2Eu]³⁺ with a program (PKAS)⁶ shows that pK₁ and pK₂ are 7.1 and 8.2, respectively. Thus, the methylenehydroxyl group of [2Eu]³⁺ complex is believed to induce the intermolecular association in solution. Taken the shape of the Cryptate complex into consideration,⁷ the bimolecular association is most likely to happen (Scheme 1). Upon the addition of base, the association must be fortified by the formation of the hydroxide bridges.¹¹

It is believed that the water molecule bound to the europium center is further activated by the neighboring metallic center. In other words, the bridged water is expected to be more acidic than the terminal water bound to the metallic center. The observed first pK of the complex (7.1) would be associated with the deprotonation of the bridged water. As expected, the value is lower than the one (7.8) observed for the monomeric [1Eu]³⁺ complex.² Upon the dimer formation the alcohol pendant is also activated as well. The pK₂ value (8.2) appears to be associated with the alcoholic proton. It has been known that the alcohol can be so acidic upon the coordination to the acidic metal center, and the examples are well characterized by Kimura *et al.*⁹ However, an alternative, the former deprotonation is associated with the pendant alcohol, can not be excluded.

It is believed that further deprotonation of another water ligand happens upon the increase of pH of the solution. (The



Scheme 1. Intermolecular association and deprotonation of [2Eu]³⁺ in solution.

second water ligand is omitted at the schematic drawing for the simplicity.) However, the reduced hydrolytic activity at high pH indicates that the latter species is not significant in terms of the reactivity.

Luminescence Spectroscopy. Luminescence spectroscopy is a valuable tool to understand the behavior of europium (III) complexes in solutions.¹² For identification of the Eu(III) species in aqueous media, ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra were obtained as a function of pH. When 1.5 mM of $[2Eu]^{3+}$ complex was dissolved, one major peak as well as two minor ones were observed in the neutral environment as in Figure 2(a). The minor peaks at 578.4 and 580.0 nm are very similar to that observed for $[1Eu]^{3+}$ complex in terms of the peak position (578.6 and 579.9 nm). For $[1Eu]^{3+}$ case, it

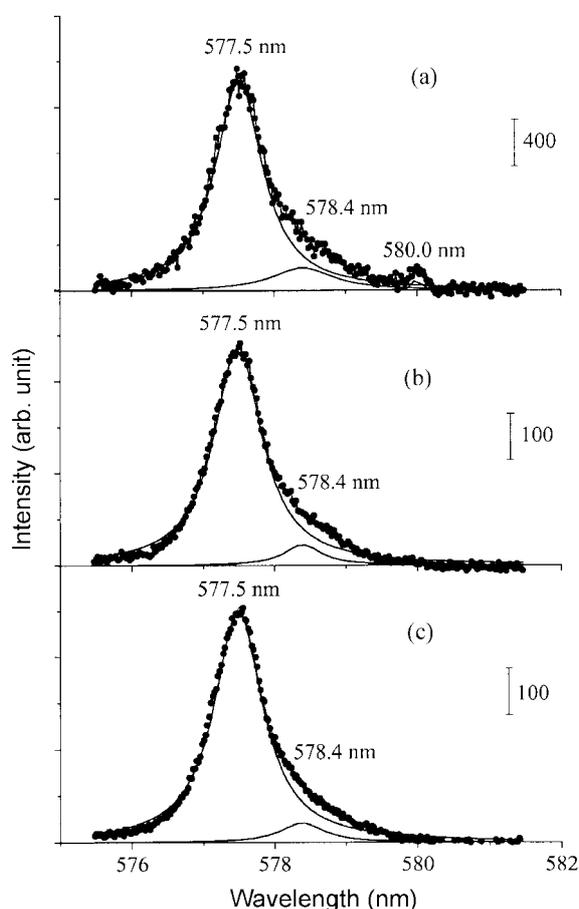
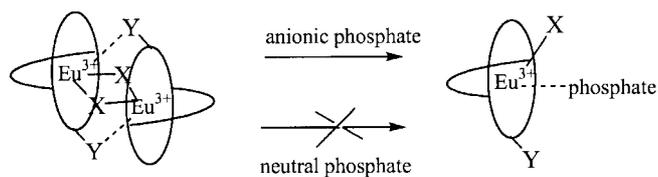


Figure 2. Excitation spectra: (a) $[2Eu]^{3+}$ ($c=1.5$ mM; $pH=6.8$); (b) $[2Eu]^{3+}$ ($c=0.40$ mM; $pH=7.2$); (c) $[2Eu]^{3+}$ ($c=0.40$ mM; $pH=8.3$).



X = OH₂ or OH
Y = OH⁻ or O

Scheme 2. Dissociation into the mononuclear species upon addition of the anionic phosphates.

was observed that the relative ratio of two peaks is sensitive to pH. While both peaks were observable at neutral pH, only the former peak was recorded at basic condition such as pH 8.8. Because the peaks have been identified as arising from $[1Eu(OH)(OH_2)_{n-1}]^{2+}$ and $[1Eu(OH_2)_n]^{3+}$ species, respectively,⁷ we can assign the minor peaks as arising from $[2Eu(OH)(OH_2)_{n-1}]^{2+}$ and $[2Eu(OH_2)_n]^{3+}$.

The broad major peak centered at 577.5 nm is totally new. Taking the results from the potentiometric titration as well as its molecular geometry into consideration, the new peak is most likely coming from the binuclear species. Figure 2(b) and 2(c) show spectra obtained from a solution of lower concentration ($c=0.4$ mM), and they clearly indicate that the species is dominant even at the low concentration. Because the broad peak at 577.5 nm is the major one at pH 7.2 and 8.3, the peak appears to represent all kinds of the binuclear species including the hydroxide-bridged and alkoxide-bridged ones. The peak at 580.0 nm representing $[2Eu(OH_2)_n]^{3+}$ is almost invisible presumably due to the low concentration as well the influence of the high pHs.

Because the anionic substrates such as diphenyl phosphate, phenyl phosphate, inorganic phosphate, and carbonate show the strong binding affinity towards the hard metallic centers including the europium (III), the addition of substrate could disrupt the binuclear association (Scheme 2). Indeed, it was observed that the addition of the anionic phosphates such as phenyl phosphate and diphenyl phosphate ($c=4.0$ mM) reduced the intensity of the 577.5 nm peak (Fig-

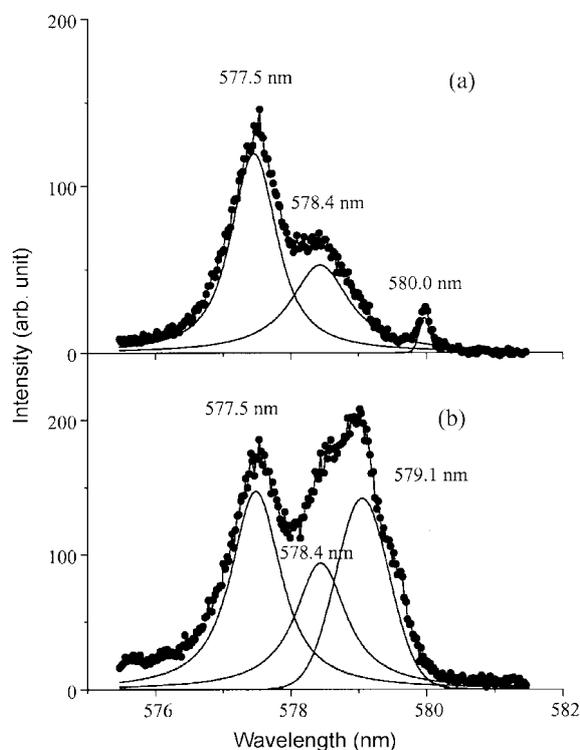


Figure 3. Excitation spectra: (a) $[2Eu]^{3+}$ ($c=0.40$ mM) in the presence of diphenyl phosphate ($c=4.0$ mM; $pH=7.0$); (b) $[2Eu]^{3+}$ ($c=0.40$ mM) in the presence of phenyl phosphate ($c=4.0$ mM; $pH=7.0$).

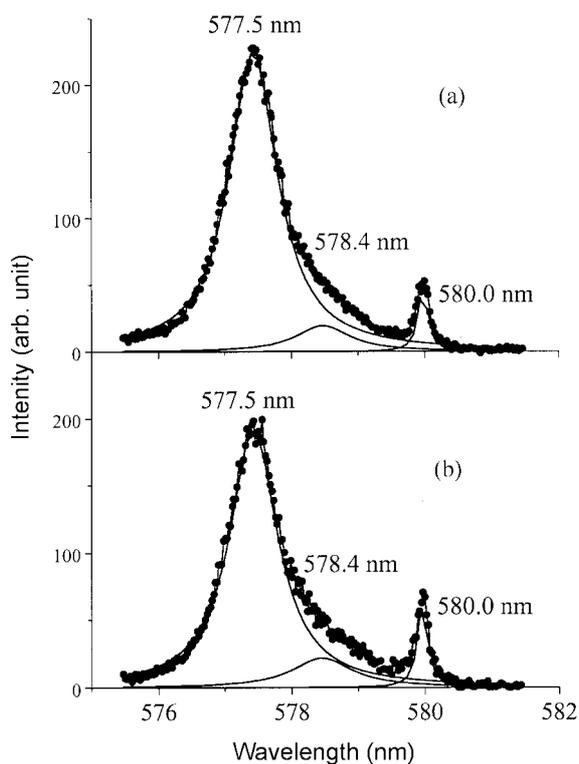
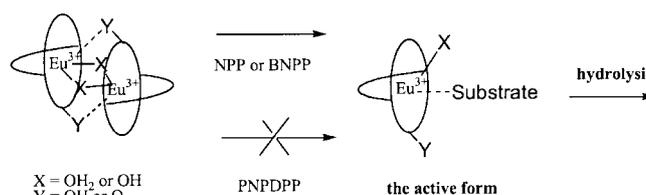


Figure 4. Excitation spectra: (a) $[2\text{Eu}]^{3+}$ ($c=0.40$ mM) in 30% aqueous acetonitrile (v/v). (b) $[2\text{Eu}]^{3+}$ ($c=0.40$ mM) in the presence of triphenyl phosphate ($c=4.0$ mM) in aqueous acetonitrile.

ure 3). The particular phosphates were chosen, because they are less activated phosphates for the hydrolysis. It can be easily assumed that their binding affinity towards the metal center should be very close to those of the fully activated phosphates. While 70% of the initial intensity ($I_{\text{initial}}=ca. 500$; $I_{\text{final}}=ca. 150$) was lost upon the addition, another peaks at 578–580 nm were significantly increased. Figure 3(a) shows that the addition of the diphenyl phosphate increases the peaks at 578.4 and 580.0 nm, of which positions are essentially identical to those of monomeric species. Because strong acidic nature of the diphenyl phosphate ($\text{p}K_{\text{a}} < 2$),¹³ it is expected that it forms an outer-sphere complex.¹⁴ The particular property to form an outer-sphere complex can explain why the monomeric peak positions are not shifted in spite of the binding. The addition of the dianionic phosphate decreases the intensity of the broad peak as in the former case, but it generates a new peak at 579.1 nm as well as the peak at 578.4 nm. Given that $\text{p}K_{\text{a}}$ of the dianionic phosphate should be close to that of 4-nitrophenyl phosphate (5.09),¹³ the anion has a high tendency to form an inner-sphere complex. The new peak at 579.1 nm could be explained by a monomeric species that binds phenyl phosphate through the inner-sphere coordination. Disappearance of the peak at 580.0 nm suggests that the acidic form of $[2\text{Eu}]^{3+}$ ($[2\text{Eu}(\text{OH})_n]^{3+}$) forms an inner-sphere complex with phenyl phosphate, rendering a peak at 579.1 nm. The spectrum shows that the two species, the inner-sphere and outer-sphere complexes, coexist at the particular condition coincidentally. The similar spectral change was observed for the inorganic phosphates



Scheme 3. Selective transformation of the inactive binuclear species into the active form.

and the carbonates.

The excitation spectrum taken in 30% acetonitrile and the one obtained in the presence of 10 equiv. of triphenyl phosphate are shown in Figure 4. It is evident that the broad peak is persistent in both cases. Only slight increase of the peak at 580.0 nm was observed. The latter change as well as the decrease of the total emission intensities could be associated with the change of the solvent polarity. From the observation that the broad peak is dominant in the spectra, it can be said that the neutral substrates are not as effective as the anionic substrates for the competitive binding. The binding affinity of the neutral substrates seems so weak that they cannot induce the dissociation effectively (Scheme 2).

Mechanism. Potentiometric titration and luminescence spectroscopic results provided valuable clues for elucidating the mechanism of the hydrolytic selectivity. It is believed that the new europium catalyst $[2\text{Eu}]^{3+}$ forms a dimer through coordinated hydroxides and/or water molecules as well as the pendant alcohols in solution. It can be deduced that the particular anionic phosphates such as (4-nitrophenyl) phosphate and bis(4-nitrophenyl) phosphate disrupt the binuclear association to generate the mononuclear species that are active for the hydrolysis. In the presence of phosphate triester, the association appears to be maintained so that the hydrolytic activity is significantly suppressed (Scheme 3).

Acknowledgment. Student fellowships of the Brain Korea 21 are greatly acknowledged, and also the work is supported by the Korea Science and Engineering Foundation through CIMS. We thank Professor Chin for his helpful discussion.

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