

## The Synergistic Effect in Solvent Extraction\* — Rare Earth $\beta$ -Diketonate System —

Tsunenobu SHIGEMATSU and Takaharu HONJO\*\*

Received November 5, 1969

The synergistic effects of some organic Lewis bases on the extraction of rare earth  $\beta$ -diketonates have been studied. The stability constants of the adducts were determined by the curve-fitting method. The effect of the temperature on the adduct formation was estimated. The results were discussed in relation to the ionic radius of rare earth elements, the steric effect and the inductive effect of the functional groups of  $\beta$ -diketonates, the dielectric constant of the solvent and the solubility of water in the organic solvent, and summarized as follows:

(1) As the ionic radius increases, the stability of rare earth benzoyltrifluoroacetate decreases but that of the adducts increases. Although the overall stability constant of the adduct increases in the following order; lutetium < terbium < europium < lanthanum, the first stability constant does not show such a distinct sequence. Therefore the contribution of the second stability constant seems to be an important factor.

(2) The maximum number of the base bonding to one molecule of rare earth benzoyltrifluoroacetate is 2, except that in the case of lutetium adduct with TOPO, where the formation of secondary adducts is not observed. The adduct formation is carried out successively. Organic bases studied form stable adducts with rare earth benzoyltrifluoroacetates in the following order; *n*-hexyl alcohol < TBP < TOPO. This order corresponds to the donating power of lone pair electrons of the oxygen atoms in these compounds.

(3) The stability of the adduct increases, and larger synergism appears, as aliphatic groups, aromatic groups, and fluoromethyl groups are successively substituted for the functional groups of  $\beta$ -diketonates. This effect may be due to the electron withdrawing effect of the fluoromethyl group and conjugation effect (with a metal chelate ring) of the phenyl group. The steric hindrance of the terminal groups is hardly recognized.

(4) The extraction constant of the chelates increases, while the stability constant of the adducts decreases, with a rise in the temperature. The apparent enthalpy change ( $-\Delta H$  Kcal/mole) by the adduct formation increases in the order: DPM (5.5) < BzA (5.9) < BFA (8.6) chelates. The binding energy between lutetium  $\beta$ -diketonates and TOPO is nearly equivalent to that of hydrogen bonding.

(5) The first stability of lutetium benzoyltrifluoroacetate adduct with TOPO is higher when the solvent has a smaller dielectric constant and a lower solubility of water. However, the stability constant of the second adduct of lutetium chelate is independent of such properties of the solvents. The change in the solvation energy of inert solvent which is attributed to the interaction of the solvent molecules with the reaction chemical species may play an important role in the adduct formation.

### INTRODUCTION

The solvent extraction method, in which metal ions react with a suitable chelating reagent to form extractable metal chelate compounds, is very useful not only for the chemical separation of the metal but also for the qualitative investigation of the metal

\* This article is the summary of the papers published in the Bulletin of the Chemical Society of Japan.<sup>2,3)</sup>

\*\* 重松恒信, 本浄高治: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

chelates in the solution. Some metal chelates can often be extracted at a lower pH region by adding oxygen- or nitrogen-containing Lewis bases to the extraction system.

Such phenomena have generally been called "synergistic effect" and may be caused by the adduct formation of the metal chelates with the active oxygen- or nitrogen-containing compounds. The synergistic enhancement of metal chelate extraction has been found in various systems and the theoretical considerations of the reactions are also made by many investigators.<sup>1)</sup>

However, the mechanism of the adduct formation and the nature of the metal chelate adducts are not yet completely understood.

The authors have mainly investigated these problems to analyse the extraction equilibrium in the synergistic extraction of rare earth  $\beta$ -diketonate adducts with some oxygen containing compounds.<sup>2,3)</sup>

### EXPERIMENTAL

**Apparatus.**—Radioactivity countings were made with a Kobe Kogyo NaI(Tl) (4.45 cm  $\times$  5.08 cm) well-type scintillation counter, model PS-300, connected to a transistorized scaler, model SA-230. A Hitachi-Horiba glass electrode pH meter, model M-3, was used for the pH measurements.

**Materials.**—The radioisotopes, europium-152,154 and lutetium-177 were supplied from The Radiochemical Centre, Amersham, England; lanthanum-140 (<sup>140</sup>Ba-<sup>140</sup>La) was obtained from the Japan Atomic Energy Research Institute, and separated from barium-140 by solvent extraction; and neodymium-147, terbium-160 and some part of lutetium-177 were produced in the Research Reactor of Kyoto University. Specific activities of these isotopes were sufficiently high for this investigation. The sodium perchlorate was prepared from perchloric acid and sodium carbonate and purified by recrystallization from water.

Some substituted  $\beta$ -diketones were synthesized by the acylation of methylketone with aromatic- or aliphatic-ethylester in the presence of sodium amide as the base catalyser.<sup>4)</sup> The boiling points and the melting point of these  $\beta$ -diketones were as follows:

#### Prepared $\beta$ -diketones

$\beta$ -Diketone	BP (°C/mmHg)	MP (°C)
DPM (dipropionylmethane)	77-78/30	—
DIBM (diisobutyrylmethane)	80.5-81.5/17	—
PvA (pivaroylacetone)	66-67/17	—
NtA (naphthoylacetone)	—	79

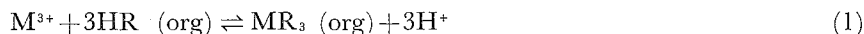
The other  $\beta$ -diketones, AA (acetylacetone), BzA (benzoylacetone), DBM (dibenzoylmethane), TFA (trifluoroacetylacetone), BFA (benzoyltrifluoroacetone), TTA (thenoyltrifluoroacetone), FTA (furoyltrifluoroacetone), HFA (hexafluoroacetylacetone) and DPvA (dipivaroylmethane), and TOPO (tri-n-octylphosphine oxide), were obtained from the Dojindo Co. or the Tokyo Kasei Kogyo Co. TBP (tributylphosphate) was purified by washing with a diluted sodium hydroxide solution,

a diluted hydrochloric acid and a saturated sodium chloride solution, and by centrifugation. All the other reagents were G.R. grade materials and used without further purification.

**Procedure.**—The extractions are performed by shaking 5 ml. or 10 ml. of the aqueous sample solution with the same volume of the organic solution. The aqueous sample solution, adjusted to a desired pH, contains rare earth ions (in the concentration of a few ppm), sodium perchlorate (0.1 M) and acetic acid (0.001 M). The organic solution is composed of  $\beta$ -diketone (0.05 M or 0.1 M) and various amounts of an organic base such as n-hexylalcohol, TBP and TOPO. Both phases are placed in a 50 ml. separating funnel or a 30 ml. glass-stoppered centrifuge tube and then shaken by a mechanical shaker for one to three hours in a thermostatted room at  $20 \pm 1^\circ\text{C}$ . When the effect of the temperature on the adduct formation is investigated, an electric thermostat ( $-5 \sim 30 \pm 0.05^\circ\text{C}$ ) is used. After organic and aqueous layers are separated, 2 ml. of each of the two phases is pipetted into a test tube (14 mm in diameter) and the radioactivity is counted with the NaI (TI) scintillation counter. The pH value of the aqueous layers is checked after the extraction.

### THEORETICAL

When trivalent rare earth ions,  $\text{M}^{3+}$ , react with  $\beta$ -diketone, HR, and are extracted as neutral chelate,  $\text{MR}_3$ , the overall extraction equilibrium can be written as follows:



The extraction constant is given by,

$$K = \frac{[\text{MR}_3]_{(\text{O})} [\text{H}^+]^3}{[\text{M}^{3+}] [\text{HR}]_{(\text{O})}} \quad (2)$$

The net distribution ratio is generally described as:

$$D = \frac{[\text{MR}_3]_{(\text{O})}}{\sum_{m=0} [\text{MR}_m^{(3-m)+}] + \sum_{i=1} [\text{M}(\text{OH})_i^{(3-i)+}] + \sum_{j=1} [\text{MX}_j^{(3-jN)+}] \quad (3)$$

where  $[\quad]$  and  $[\quad]_{(\text{O})}$  designate the concentration in aqueous phase and in organic phase, respectively; and  $\text{M}(\text{OH})_i^{(3-i)+}$  and  $\text{MX}_j^{(3-jN)+}$  indicate the metal hydroxocomplexes and water soluble complexes formed with masking agents, *etc.*

The equation can be reduced to Eqs. (4) and (4'), if the following assumptions are made: 1) The metal concentration can be neglected in comparison with the total concentration of the  $\beta$ -diketone,  $C_{\text{HR}}$ ; 2) The distribution coefficient of the  $\beta$ -diketone is fairly high, while the acid dissociation is considerably low in the pH region investigated; 3) The formation of hydroxocomplexes can be neglected in the pH region studied and the contribution of complexes to the total metal concentration can also be neglected.

$$D = \frac{PK}{1 + \sum_{m=1} K_m [\text{R}^-]^m} \cdot \left[ \frac{K_A C_{\text{HR}}}{K_D [\text{H}^+]} \right]^3 \quad (4)$$

or

$$\log D = 3(pK_D - pK_A + \log C_{HR} + pH) + \log \frac{PK}{1 + \sum_{m=1} K_m [R^-]^m} \quad (4')$$

where  $K_A$  and  $K_D$  are the acid dissociation constant and the distribution coefficient of the  $\beta$ -diketone;  $K_m$ , the stability constant of the metal  $\beta$ -diketonate; and  $P$ , the distribution constant of the neutral chelate. The pH value at half extraction,  $pH_{1/2}$ , can be given by

$$pH_{1/2} = pK_A - pK_D - \log C_{HR} - \frac{1}{3} \log \frac{PK}{1 + \sum_{m=1} K_m [R^-]^m} \quad (5)$$

If a Lewis base,  $L$ , added in the organic phase reacts with the metal  $\beta$ -diketonate to form the adduct compounds, which are almost insoluble in the aqueous phase, and the Lewis base does not give any change in the acid dissociation and the distribution of  $\beta$ -diketone, then the equilibrium is described as follows:



The stability constant of the metal chelate adduct is given by

$$\beta_n = [MR_3Ln]_{(o)} / [MR_3]_{(o)} [L]_{(o)}^n \quad (7)$$

The distribution ratio in Eq. (4) and  $pH_{1/2}$  value are then:

$$D^* = \frac{PK \left( 1 + \sum_{n=1} \beta_n [L]_{(o)}^n \right)}{1 + \sum_{m=1} K_m [R^-]^m} \left[ \frac{K_A C_{HR}}{K_D [H^+]} \right]^3 \quad (8)$$

or

$$\log D^* = 3(pK_D - pK_A + \log C_{HR} + pH) + \log \frac{PK \left( 1 + \sum_{n=1} \beta_n [L]_{(o)}^n \right)}{1 + \sum_{m=1} K_m [R^-]^m} \quad (8')$$

$$pH_{1/2}^* = pK_A - pK_D - \log C_{HR} - \frac{1}{3} \log \frac{PK \left( 1 + \sum_{n=1} \beta_n [L]_{(o)}^n \right)}{1 + \sum_{m=1} K_m [R^-]^m} \quad (9)$$

Here, if it can be assumed that trivalent metal ions,  $M^{3+}$  are dominant species in the aqueous phase, the  $pH_{1/2}$  shift,  $\Delta pH_{1/2}$ , which serves as a measure of the synergistic effect, can now be derived from Eqs. (5) and (9):

$$\Delta pH_{1/2} = pH_{1/2}^* - pH_{1/2} = -\frac{1}{3} \log \left( 1 + \sum_{n=1} \beta_n [L]_{(o)}^n \right) \quad (10)$$

On the other hand, from Eqs. (4) and (8) the fundamental equations of the curve-fitting method<sup>5-7)</sup> are given by,

$$D^*/D = 1 + \sum_{n=1} \beta_n [L]_{(o)}^n \quad (11)$$

or

$$\log D^*/D = \log \left( 1 + \sum_{n=1}^{\infty} \beta_n [L]^{n_{(0)}} \right) \quad (12)$$

## RESULTS AND DISCUSSION

**Effect of Metal Ions and Organic Bases.**—Figure 1 shows the  $\log D$  vs. pH plot for the extraction of rare earth benzoyltrifluoroacetates, which was obtained in the absence of any adduct forming organic bases. The logarithm of the distribution ratio is linearly related with pH when the concentration of benzoyltrifluoroacetone is kept at constant. The slope of the straight lines is nearly 3, the theoretical value. The extraction constants obtained from these data are given in Table 1.

As shown in the figure, the extraction of rare earth benzoyltrifluoroacetates is enhanced in the following order; lanthanum < neodymium < europium < terbium < lutetium.

The sequence of  $\text{pH}_{1/2}$  is, therefore, of the same; in other words, the value of  $\text{pH}_{1/2}$  rises as the ionic radius of the central rare earth metal increases, and this can be seen more evidently in Fig. 2. Equation (5) indicates that the  $\text{pH}_{1/2}$  value is a measure of the stability of metal chelates.

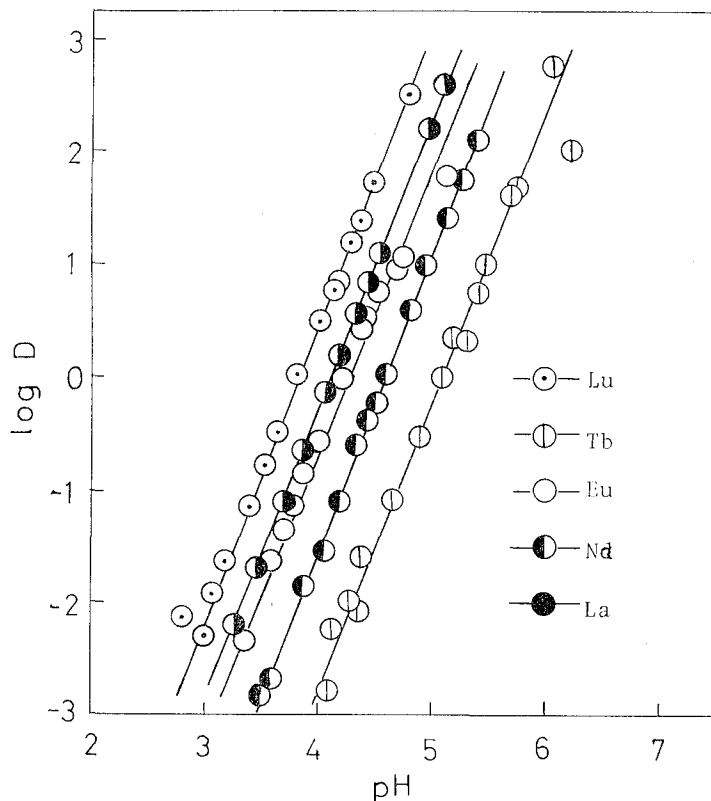


Fig. 1. Logarithm of the distribution ratio of rare earth elements as a function of the pH value.

Organic phase:  $5 \times 10^{-2}$  M BFA in benzene

Aqueous phase:  $10^{-1}$  M  $\text{NaClO}_4$

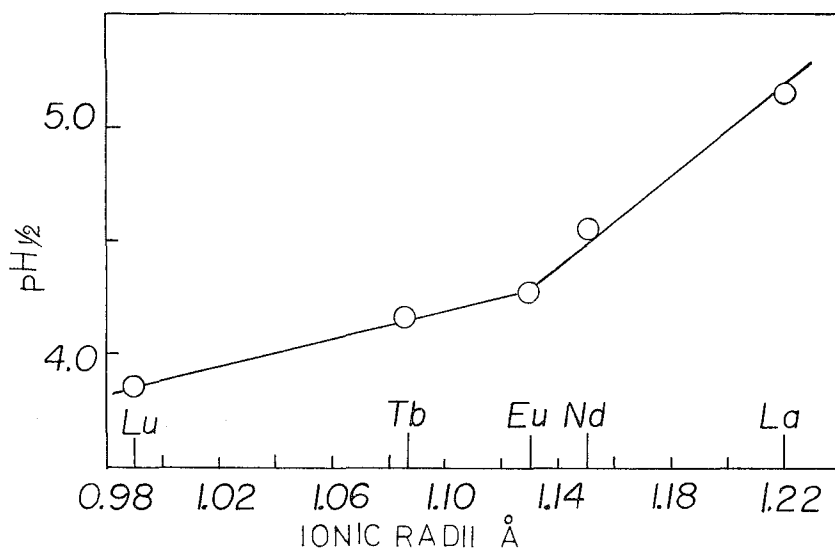


Fig. 2.  $pH_{1/2}$  in the extraction of rare earth benzoyltrifluoroacetate as a function of the ionic radius.

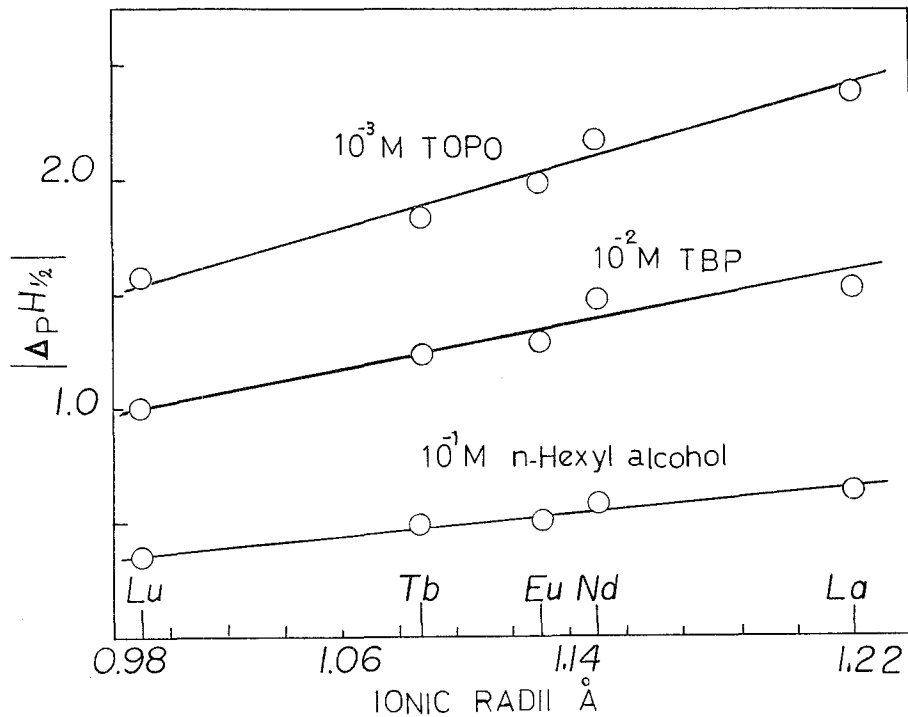


Fig. 3. Shift of  $pH_{1/2}$  ( $-\Delta pH_{1/2}$ ) in the synergistic extraction as a function of the ionic radius of rare earth elements.

## Synergistic Effect in Solvent Extraction

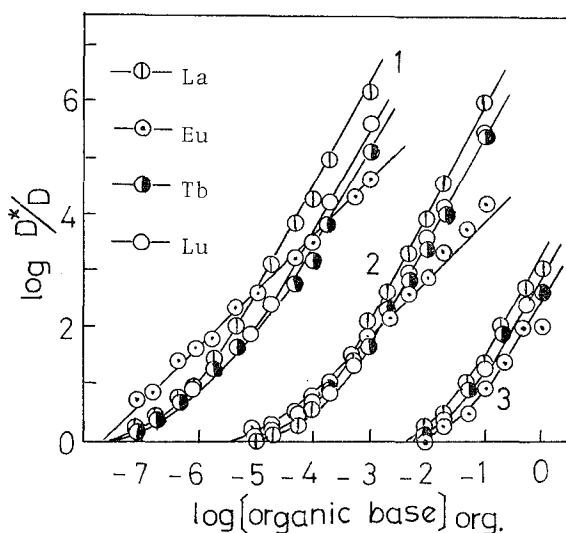


Fig. 4. Variation of the distribution ratio as a function of the organic base concentration.

1: TOPO, 2: TBP, 3: *n*-hexyl alcohol

The lower the  $pH_{1/2}$  value, the more stable the chelate. Accordingly, the stability of rare earth benzoyltrifluoroacetate decreases with the increase of the ionic radius of rare earth element.

As described above, the  $pH_{1/2}$  value must shift to lower, when Lewis bases were added to the extraction system to form the metal chelate adducts. In Fig. 3, are plotted as a function of the ionic radius, the absolute values of the  $pH_{1/2}$  shift,  $|\Delta pH_{1/2}|$ , which was obtained in the presence of 0.1 M *n*-hexylalcohol, 0.01 M TBP and 0.001 M TOPO, respectively.

The  $|\Delta pH_{1/2}|$  value rises linearly with the increase in the ionic radius of rare earth element. Equation (10) suggests that the  $\Delta pH_{1/2}$  value correlates directly with the logarithm of the overall stability constants of metal chelate adducts,  $\log \beta_n$ , under the constant concentration of adduct-forming materials. Therefore, it can be expected that the stability of rare earth chelate adducts increases with the increases in the ionic

Table 1. Stability Constants of Rare Earth Benzoyltrifluoroacetates and their Adducts

	La		Eu		Tb		Lu	
$\log K_3$	-11.6		-8.9		-8.8		-7.7	
$\log \beta_n$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$
<i>n</i> -Hexyl alcohol	1.95 (1.90)	3.30 (3.80)	1.85 (1.75)	3.10 (3.50)	1.85 (1.75)	3.10 (3.50)	1.65 (1.55)	2.70 (3.10)
TBP	4.38 (4.55)	7.80 (8.50)	4.55 (4.60)	7.40 (7.80)	4.50 (4.58)	7.30 (7.76)	4.70 (4.90)	6.00 (6.40)
TOPO	7.00 (6.80)	12.30 (13.00)	6.85 (6.93)	11.70 (11.86)	6.90 (7.18)	11.20 (11.76)	7.50 (7.83)	*

\* Formation of the second adduct,  $MR_3L_2$  was not observed. The values in the bracket were determined by analysing the curves of  $-\Delta pH_{1/2}$  vs.  $\log: [\text{organic base}]_{\text{org}}$  plots.

radius of rare earth element, just in contrast with the stability of the chelates. In order to make the phenomena clearer and to obtain the stability constants of the chelate adducts, the data were analysed by the curve-fitting method. The analysed curves are shown in Fig. 4, and the stability constants are summarized in Table 1.

The results draw the following conclusions:

(1) Both the stabilities of rare earth benzoyltrifluoroacetates and of the adducts formed between the chelates and some organic Lewis bases are related with the ionic radii of rare earth elements. However, the relation appears quite reversely; that is, the stability of the former decreases but that of the latter increases, as the ionic radius increases.

(2) The maximum number of base molecules bonded to one molecule of the metal chelate is 2, except in the case of lutetium adduct with TOPO, where the formation of secondary adducts is not observed. The adduct formation is carried out successively.

(3) Although the overall stability constant of the adducts increases in the following order; lutetium < terbium < europium < lanthanum, the first stability constant does not show such a distinct sequence. Therefore the contribution of the second stability constant seems to be an important factor, even when lutetium chelate-TOPO adduct is considered.

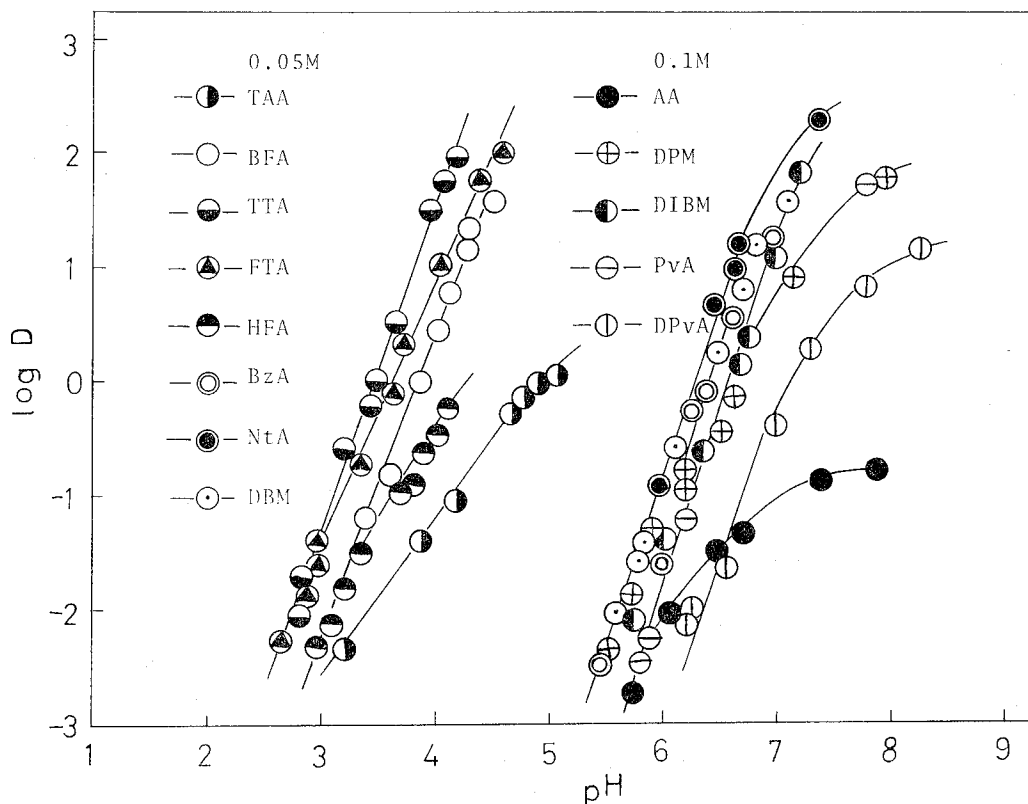


Fig. 5. The distribution ratio of lutetium  $\beta$ -diketonates as a function of pH.  
Organic phase: 0.1 or 0.05 M  $\beta$ -diketone in benzene  
Aqueous phase: 0.1 M  $\text{NaClO}_4$



(4) Organic bases studied form stable adducts with rare earth benzoyltrifluoroacetates in the following order; n-hexyl alcohol < TBP < TOPO. This order corresponds to the donating power of lone pair electrons of the oxygen atoms in these compounds.

**Effect of Chelating Ligands.**—Figure 5 shows the  $\log D$  vs. pH plots in the extraction of lutetium ions with various  $\beta$ -diketones in benzene. With  $\beta$ -diketones having a fluoromethyl group, lutetium can be extracted in the lower pH region. This fact is caused by the inductive effect of the fluoromethyl group, which raises the acidity of the enol form. The high extractability can be attained with  $\beta$ -diketones possessing bulky groups, such as benzoyl-, thenoyl- and pivaroyl groups (*e.g.*, BFA, TTA, and DPvm); this may be due to the hydrophobic structure of the molecule, which prevents the formation of water-soluble complexes and minimizes the solubility of the metal chelates in water. In the extraction with  $\beta$ -diketones which are comparatively soluble in water (*e.g.*, AA, TAA and HFA), the slopes of the  $\log D$ —pH curves deviate from 3, the theoretical value, because of the formation of water soluble complexes.

Figure 5 confirms the general concept that  $pH_{1/2}$  value for the extraction of metal  $\beta$ -diketonates is directly correlative with the  $pK_D$  value of the  $\beta$ -diketone.

The effects of the functional groups of various  $\beta$ -diketones on the adduct formation are shown in Fig. 6 as  $\log D^*/D$  vs.  $\log [TOPO]_{(0)}$  plots. The straight lines with a slope of 1 indicate that one molecule of TOPO binds one molecule of the metal chelate.

The HFA chelate adduct contains two molecules of TOPO. The extraction constants of lutetium  $\beta$ -diketonates,  $\log K$ , and the stability constants of their TOPO adducts,  $\log \beta_n$  are summarized in Table 2. The stability of the TOPO adduct with

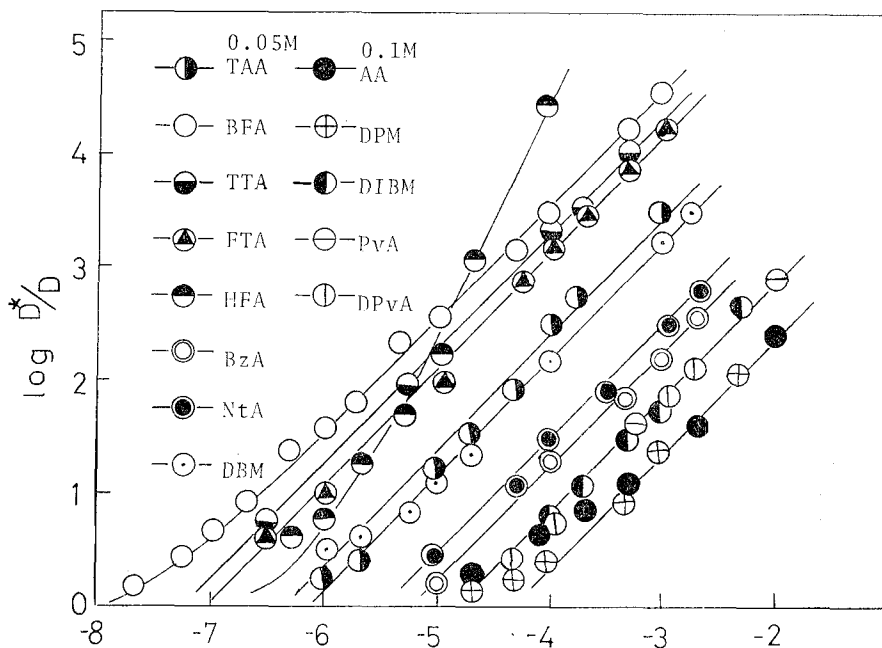









Fig. 6. The distribution ratio of lutetium  $\beta$ -diketonates as a function of TOPO concentration,  $\log [TOPO]_{(0)}$ .

Table 2. Stability constants of lutetium  $\beta$ -diketonates and their adducts with TOPO

	R	R'	pK <sub>D</sub> *	log K	log $\beta_1$
AA	CH <sub>3</sub>	CH <sub>3</sub>	12.70 (11.27)	—	4.35
DPM	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	—	-16.57	4.35
DIBM	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	(12.48)	-16.57	4.80
PvA	CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	14.20	-16.90	4.80
DPvM	C(CH <sub>3</sub> ) <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	(14.48)	-18.37	4.80
BzA	CH <sub>3</sub>		12.85	-15.21	5.25
NtA	CH <sub>3</sub>		—	-15.06	5.45
DBM			13.75	-15.16	6.15
TAA	CH <sub>3</sub>	CF <sub>3</sub>	8.70	—	6.25
BFA		CF <sub>3</sub>	9.20	-7.69	7.50
TTA		CF <sub>3</sub>	9.10	-6.56	7.25
FTA		CF <sub>3</sub>	8.50	-6.78	7.15
HFA	CF <sub>3</sub>	CF <sub>3</sub>	6.0	—	6.25 ( $\log \beta_2$ =12.50)

\* Negative logarithm of the acid dissociation constant of the  $\beta$ -diketone in 75% (V/V) dioxane. L. G. Van Uitert, W. Conard, Fernelius and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953): The values in bracket were obtained by G. S. Hammond, W. G. Borddein and G. A. Guter, *J. Am. Chem. Soc.*, **81**, 4682 (1959).

various lutetium  $\beta$ -diketonates increases in the following order: aliphatic groups (AA and PPM < PvA, DIBM and DPvM) < aromatic groups (BzA < NtA  $\ll$  DBM) < fluoromethyl groups (TFA < FTA < TTA < BFA  $\ll$  HFA). In general, the log  $\beta_n$  increases with an increase in the log K value, as is indicated in Fig. 7, and no steric hindrance by terminal aliphatic or aromatic groups to the adduct formation is observed.

Figure 8 shows the effect of the temperature on the adduct formation of DPM, BzA, and BFA chelates with TOPO, while Table 3 presents the extraction constants of these chelates and the stability constants of their adducts.

The extraction constants of the chelates increase, while the stability of the TOPO adducts decreases, with a rise in the temperature. This phenomenon supports the empirical fact that the more stable the chelate, the less stable the adduct is, because the extraction constant can be taken as a measure of the stability of the metal chelate in the extraction with the same chelating reagent. The apparent enthalpy changes in the adduct formation have been estimated and are presented in Table 3. The value increases in the sequence of DPM, BzA, and BFA.

The conclusions reached would be expressed as follows:

- (1) The stability of the adduct increases, and the larger synergism appears, as

## Synergistic Effect in Solvent Extraction

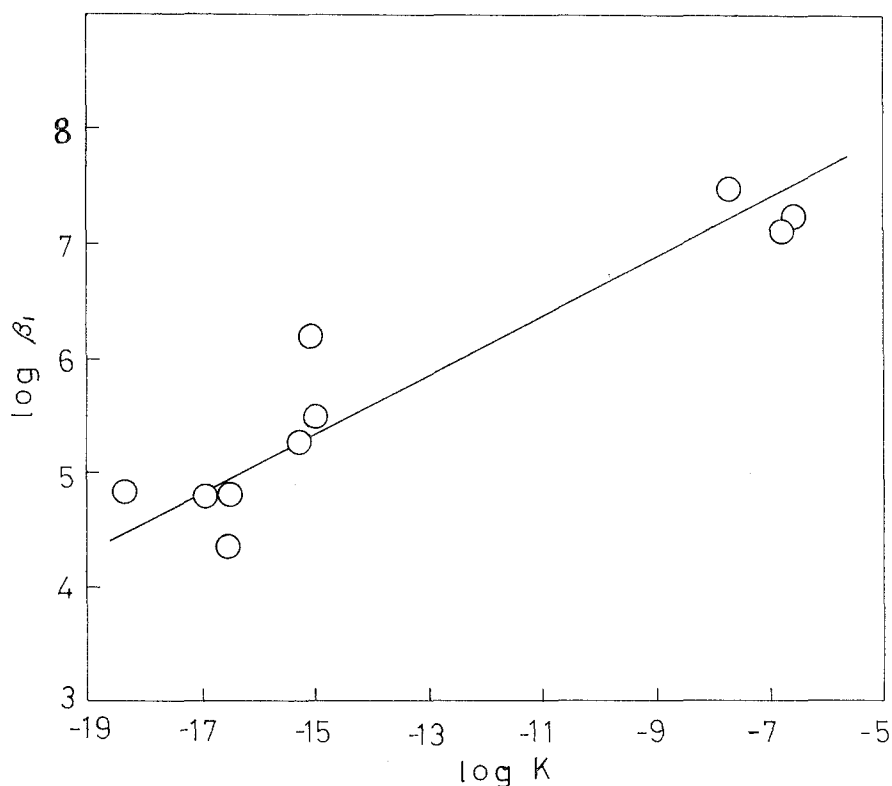


Fig. 7. The stability constant of lutetium  $\beta$ -diketonate TOPO adduct,  $\log \beta_1$  as a function of the extraction constant of the chelate,  $\log K$ .

aliphatic groups, aromatic groups, and fluoromethyl groups are successively substituted for the functional groups of  $\beta$ -diketones. This effect may be due to the electron-withdrawing effect of the fluoromethyl group and the conjugation effect (with a metal chelate ring) of the phenyl group.

(2) The adducts contain one molecule of TOPO per metal chelate except for the HFA adduct, which contains two molecules of TOPO. The steric hindrance of the terminal groups is hardly recognizable.

(3) The extraction constant of the chelate increases, while the stability of the adducts decreases, with a rise in the temperature. The apparent enthalpy change ( $-\Delta H$  Kcal/mole) upon the adduct formation increases in the order: PPM (5.5) < BzA (5.9) < BFA (8.6) chelates.

Table 3. Effect of temperature on Stability Constant of Lu- $\beta$ -diketonate-TOPO Complexes

Abbrev.	10°C		20°C		30°C		$-\Delta H$ Kcal/mole
	log K	log $\beta_1$	log K	log $\beta_1$	log K	log $\beta_1$	
DPM	-16.81	4.75	-16.57	4.35	-15.98	4.25	5.5
BzA	-16.16	5.70	-15.21	5.25	-14.96	5.10	5.9
BFA	-7.99	8.10	-7.69	7.50	-7.37	7.25	8.6

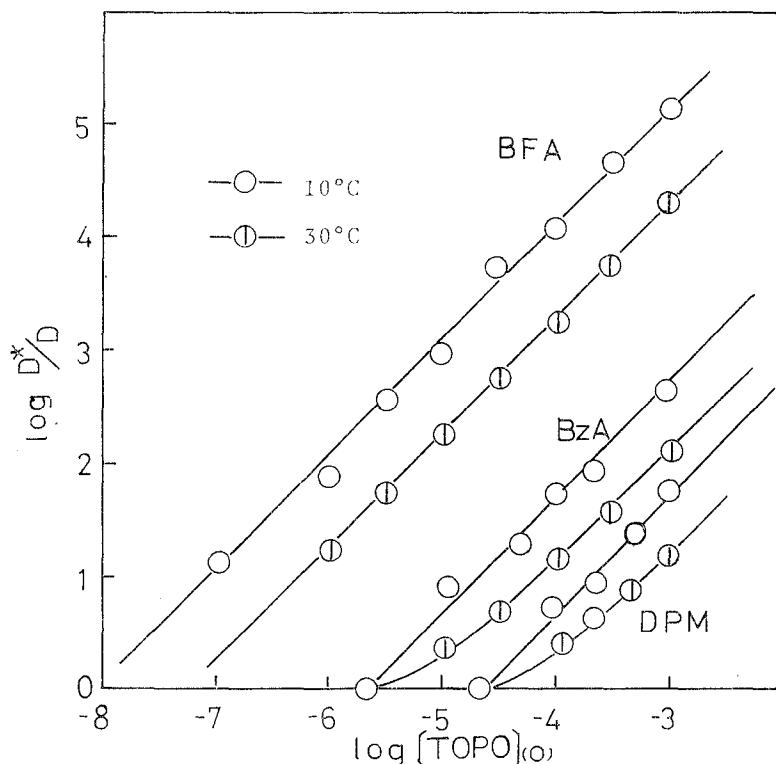


Fig. 8. Variation of the distribution ratio of lutetium complexes as a function of TOPO concentration at 10°C (—○—) and at 30°C (—⊖—).

**Effect of Inert Solvent.**—The  $\log D$  vs. pH plots in the extraction of lutetium benzoyltrifluoroacetate in various inert solvents such as cyclohexane, benzene, monochlorobenzene and nitrobenzene in the presence or absence of TOPO are shown in Fig. 9. All the figures given the straight line with a slope of almost 3, indicating that the extraction behavior is ideally performed. In the presence of TOPO, the extractability of metals is much enhanced by the adduct formation between metal chelates and TOPO. The variation of the distribution ratio of lutetium in the synergistic solvent

Table 4. Extraction constant of lutetium benzoyltrifluoroacetate and the stability constant of its adduct with TOPO.

Solvent	Dielectric constant	Solubility of water (wt %)	Lu		
			log K	log $\beta_1$	log $\beta_2$
Cyclohexane	2.0	0.004 (25°C)	-8.3	8.20	13.00
benzene	2.3	0.06 (25°C)	-7.7	7.50	*
monochlorobenzene	5.6	0.18 (25°C)	-8.2	7.60	*
nitrobenzene	34.8	0.19 (20°C)	-6.5	6.11	10.60

\* Formation of the second adduct,  $MR_3L_2$  was not observed.

Synergistic Effect in Solvent Extraction

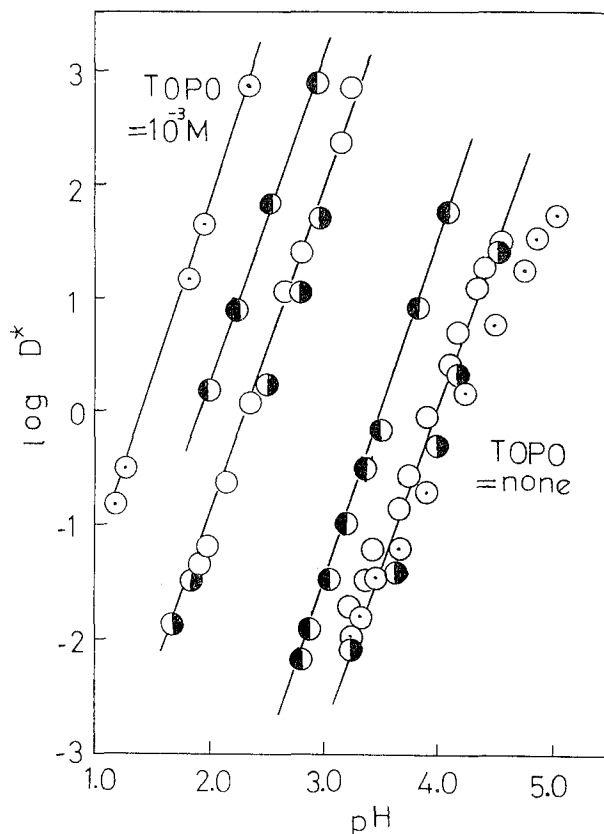


Fig. 9. Logarithm of the distribution ratio of lutetium benzoyltrifluoroacetone as a function of pH in the presence or absence of TOPO.

Organic phase :  $5 \times 10^{-2}$  M BFA

Aqueous phase :  $10^{-1}$  M  $\text{NaClO}_4$

○: Benzene,    ◐: cyclohexane,    ◑: monochlorobenzene,  
 ●: nitrobenzene

extraction is shown in Fig. 10 as a function of TOPO concentration.

The  $\log D^*/D$  vs.  $\log [\text{TOPO}]_{(o)}$  plots using benzene and monochlorobenzene are approximately linear, having a slope of 1 in the range of  $[\text{TOPO}]_{(o)}$  above  $10^{-6}$ , whereas the plots using cyclohexane and nitrobenzene show the maximum slope of 2. This means that the metal chelate adduct exists in the form of  $\text{Lu}(\text{BFA})_3\text{TOPO}$  in the former solvents, but in the latter solvents, the  $\text{Lu}(\text{BFA})_3\cdot 2\text{TOPO}$  type adduct is also successively formed with the increase of  $[\text{TOPO}]_{(o)}$ .

The extraction constants of lutetium chelate,  $\log K$  and the stability constants of the adducts,  $\log \beta_n$  were determined by curve fitting method and the results are listed in Table 4 with the dielectric constant of the solvent and the solubility of water in the organic solvent.

The results can be summarized as follows:

(1) The  $\log \beta_1$  value of lutetium chelate adduct is large when the solvent has a smaller dielectric constant and a lower solubility of water. However, the  $\log \beta_2$  value,

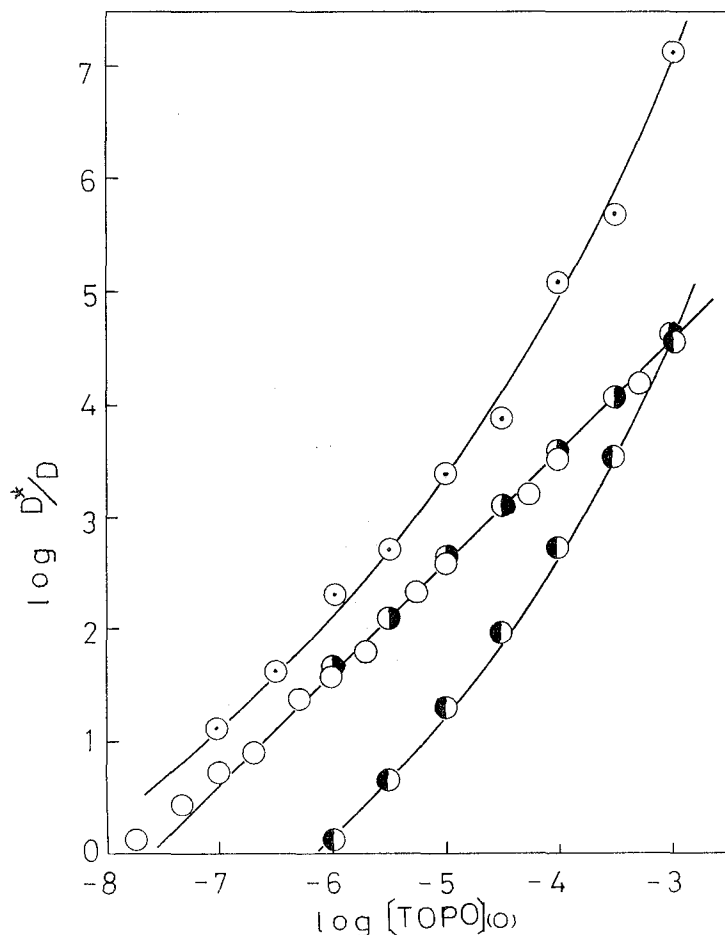


Fig. 10. Variation of the distribution ratio of lutetium as a function of TOPO concentration.

The symbols of solvents are the same as in Fig. 9.

the stability of the second adduct of lutetium chelate is independent of such properties of the solvent.

(2) The second adduct is formed in cyclohexane and nitrobenzene which are the solvents of the lowest and the highest water content investigated, respectively, but not formed in benzene and monochlorobenzene, which give only the first adduct. This fact suggests that the change in the solvation energy of inert solvent which is attributed to the interaction of the solvent molecules with organic bases, chelating ligands, metal chelates and the first metal chelate adducts may play an important role in the adduct formation.

**The Binding in the Adducts.**—The apparent enthalpy change on the adduct formation between lutetium  $\beta$ -diketonates and TOPO is 5.5~8.6 Kcal/mole, which is equivalent to hydrogen bonding.

In europium-2-benzoylcyclohexanone-TOPO extraction system, the synergistic

## Synergistic Effect in Solvent Extraction

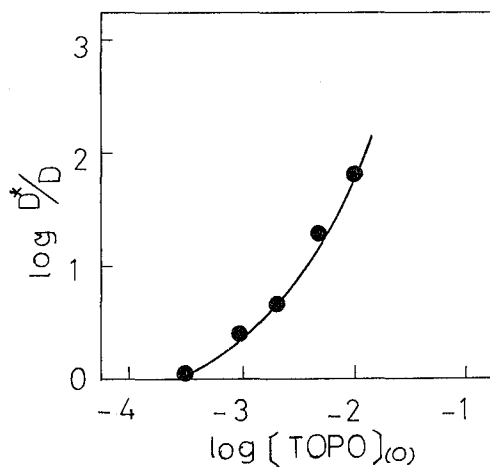


Fig. 11. Variation of the distribution ratio of europium complex with 2-benzoylcyclohexanone as a function of TOPO concentration.

Organic phase: 0.05 M 2-benzoyl cyclohexanone in benzene

Aqueous phase: 0.1 M  $\text{NaClO}_4$

Stability of adducts:  $\log \beta_1=2.90$ ,  $\log \beta_2=5.40$

effect was observed as shown in Fig. 11. This fact suggests that most probably, TOPO bonds directly to the central europium ions.

## REFERENCE

- (1) T. Honjyo and T. Shigematsu, *Kagaku* (Kyoto), **23**, 708 (1968).
- (2) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *Bull. Chem. Soc. Japan*, **39**, 165 (1966); *ibid.*, **40**, 2807 (1967); *ibid.*, **42**, 976 (1969).
- (3) T. Honjyo, *ibid.*, **42**, 995 (1969).
- (4) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).
- (5) D. Dyrssen and L. G. Sillen, *Acta. Chem. Scand.*, **7**, 663 (1953).
- (6) L. G. Sillen, *ibid.*, **10**, 186 (1956).
- (7) T. Sekine and M. Ono, *Bull. Chem. Soc. Japan*, **38**, 2087 (1965).