

## The Synergistic Effect in Solvent Extraction. The Effect of the Chelating Ligands on the Stability Constant of Lutetium $\beta$ -Diketonate Adducts with TOPO

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The steric effect and the inductive effect of the functional groups of  $\beta$ -diketones on the adduct formation between lutetium chelates and TOPO in benzene was studied by using various  $\beta$ -diketones with aliphatic groups (acetylacetone, dipropionylmethane, pivaloylacetone, diisobutyrylmethane and dipivaloylmethane), aromatic groups (benzoylacetone, naphthoylacetone and dibenzoylmethane) and fluoromethyl groups (trifluoroacetylacetone, furoyltrifluoroacetone, thenoyltrifluoroacetone, benzoyltrifluoroacetone and hexafluoroacetylacetone). The effect of the temperature on the adduct formation was then estimated. These results may be summarized as follows: (1) The stability of the adduct increases, and the larger synergism appears, as 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 chelates increases, while the stability of the adducts decreases, with a rise in the temperature. The apparent enthalpy change ( $-\Delta H$  kcal/mol) upon the adduct formation increases in the order: DPM (5.5) < BzA (5.9) < BFA (8.6) chelates.

During the course of the solvent extraction of metal chelates, an extremely enhanced extraction is often observed in the presence of some neutral Lewis bases. This phenomenon is generally called the synergistic effect and explained by the adduct formation between the metal chelates and the Lewis bases.

The synergism in the extraction of rare earth  $\beta$ -diketonate has been widely investigated;<sup>1-4</sup> solid adducts have been prepared and their properties studied.<sup>5,6</sup> However, the mechanism of the adduct formation and the nature of the metal chelate adducts are not yet completely understood.

Shigematsu and his co-workers have carried out a systematic study of the synergistic extraction of rare earth metals,<sup>7,8</sup> and the following results have been obtained.

(1) In rare earth-benzoyltrifluoroacetone (BFA)-

-TOPO, TBP and *n*-hexanol systems, the extraction constant of the chelates increases, while the stability of the adducts decreases, with a decrease in the ionic size of the metal. The tendency has also been reported for lanthanum, europium, lutetium-TTA-dimethylsulfoxide, TBP, and hexone systems.<sup>9</sup>

(2) Oxygen-containing Lewis bases, having a stronger donating power of lone-pair electrons, form more stable adducts and therefore show a larger synergism; esters and ketones < alcohols < TBP < TOPO. Organic phosphate and phosphine oxide especially give rise to a large synergism.

(3) Nitrogen-containing Lewis bases, such as amines and heterocyclic compounds, also produce the synergism. The synergistic enhancement of the extraction is of almost the same magnitude as that of oxygen-containing Lewis bases: The effect of the amines is similar to that of alcohols. However, the solid adducts of the former are thermally more stable than the adducts of the latter.

1) H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **21**, 169 (1961).

2) T. V. Healy, *ibid.*, **19**, 314 (1961); *ibid.*, **19**, 328 (1961).

3) T. Sekine and M. Ono, *This Bulletin*, **38**, 2087 (1965).

4) H. Yoshida, *ibid.*, **39**, 1810 (1966).

5) T. V. Healy and J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **24**, 1449 (1962).

6) J. R. Ferraro and T. V. Healy, *ibid.*, **24**, 1463 (1962).

7) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *This Bulletin*, **39**, 165 (1966); *ibid.*, **40**, 2807 (1967).

8) T. Shigematsu and T. Honjyo, *Bull. Inst. Chem. Res., Kyoto Univ.*, **25**, 282 (1967).

9) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **29**, 1481 (1967).

(4) The maximum number of base molecules bound to one molecule of the metal chelate is 2 except in the case of lutetium  $\beta$ -diketonates-TOPO in benzene, where only one molecule of TOPO binds one molecule of the chelates.

In order to obtain more detailed information on this interesting phenomenon, the present research studied the steric effect and the inductive effect of the functional groups of various  $\beta$ -diketones on the adduct formation between lutetium chelates and TOPO.

### Experimental

**Materials.** The radioisotope of lutetium-177 was produced by irradiating pure lutetium oxide in a thermal neutron flux of about  $5 \times 10^{12}$  n/cm<sup>2</sup>sec in the Research Reactor of Kyoto University. After the irradiated sample had been dissolved in hot hydrochloric acid, the lutetium was extracted at pH 5 with 0.05 M BFA in benzene and stripped into 0.1 M perchloric acid. The resulting solution was evaporated to fumes, and then the residue was dissolved in an appropriate amount of perchloric acid to make a stock solution. The specific activity of the tracer was 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 catalyzer.<sup>10</sup> The boiling points and the melting point of these  $\beta$ -diketones were as follows:

Prepared  $\beta$ -diketones

$\beta$ -Diketones	Bp(°C/mmHg)	Mp(°C)
DPM (dipropionylmethane)	77 — 78/30	—
DIBM (diisobutylmethane)	80.5—81.5/17	—
PvA (pivaroylacetone)	66 — 67/17	—
NtA (naphthoylacetone)	—	79

The other  $\beta$ -diketones, AA (acetylacetone), BzA (benzoylacetone), DBM (dibenzoylmethane), TAA (trifluoroacetylacetone), BFA (benzoyltrifluoroacetone), TTA (thenoyltrifluoroacetone), FTA (furoyltrifluoroacetone), HFA (hexafluoroacetylacetone), DPvM (dipivaroylmethane), and TOPO (tri-*n*-octylphosphine oxide), were obtained from the Dojindo Co. and the Tokyo Kasei Kogyo Co.

**Procedure.** The experimental procedure was almost the same as has previously been described.<sup>7</sup> To 5 ml of an aqueous solution containing lutetium (a few ppm), sodium perchlorate (0.1 M) and acetic acid (0.01 M) and having a desirable pH, 5 ml of benzene containing  $\beta$ -diketone (0.05 M or 0.1 M) and various amounts of TOPO were added. Both phases were placed in a 30 ml glass-stoppered centrifuge tube and agitated by a mechanical shaker for from one to three hours at a constant temperature in an electric thermostat ( $-5$ — $30 \pm 0.05^\circ\text{C}$ ). After centrifugation, 2 ml of each phase were pipetted into test tubes (14 mm in diameter),

and the  $\gamma$ -radioactivities were measured with a NaI(Tl) well-type scintillation counter. The pH value of the aqueous layers was checked after the extraction.

The extraction constants of the metal chelates,  $K$ , and the stability constants of the metal chelate adducts,  $\beta_n$ , can be calculated by the following equations\*<sup>1</sup>:

$$K = [\text{MR}_3]_0[\text{H}^+]^3/[\text{M}^{3+}][\text{HR}]_0^3 \quad (1)$$

$$\log K = \log D - 3 \log [\text{HR}]_0 - 3\text{pH} \quad (2)$$

$$\beta_n = [\text{MR}_3\text{L}_n]_0/[\text{MR}_3]_0[\text{L}]_0^n \quad (3)$$

$$\log D^*/D = \log(1 + \sum_{n=1}^n \beta_n [\text{L}]_0^n) \quad (4)$$

where  $D$  and  $D^*$  are the distribution ratio in the absence and in the presence of TOPO; M stand for metal, HR for  $\beta$ -diketone, and L for TOPO, and  $[ ]$  and  $[ ]_0$  designate the concentration of the chemical species in the aqueous and organic phases respectively.

### Results and Discussion

**Lutetium- $\beta$ -diketone System.** Figure 1 shows the  $\log D$  vs. pH plots in the extraction of lutetium ions with various  $\beta$ -diketones in benzene. With  $\beta$ -diketones with 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.<sup>11,12</sup> The high extractability can be

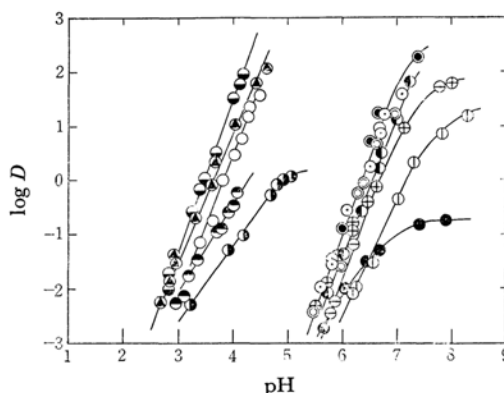


Fig. 1. The distribution ratio of lutetium with various  $\beta$ -diketones as a function of pH. Organic phase: 0.1 M or 0.05 M  $\beta$ -diketone in benzene

Aqueous phase: 0.1 M NaClO<sub>4</sub>  
 0.1 M  $\beta$ -diketone: —●— AA, —○— DPM,  
 —○— DIBM, —○— PvA, —○— DPvM  
 0.05 M  $\beta$ -diketone: —○— BzA, —○— DBM,  
 —○— TAA, —○— BFA,  
 —●— TTA —○— FTA, —○— HFA

\*<sup>1</sup> The treatments of the equations have been interpreted in a previous paper.<sup>7</sup>

<sup>11</sup> G. H. Morisson and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Sons, New York (1957).

<sup>12</sup> J. Stry, "The Solvent Extraction of Metal Chelates," Pergamon Press, Oxford (1964).

<sup>10</sup> J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

attained with  $\beta$ -diketones possessing bulky groups, such as benzoyl-, thenoyl- and pivaloyl 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<sup>13</sup> and minimizes the solubility of the metal chelates into water. In the extraction with  $\beta$ -diketones which are comparatively soluble in water (e.g., AA, TAA and HFA), the slopes of the  $\log D$  vs. pH plots deviate from 3, the theoretical value, because of the formation of water-soluble complexes.

Figure 1 confirms the general concept that the  $\text{pH}_{1/2}$  value for the extraction of metal  $\beta$ -diketonates is directly correlative with the  $\text{p}K_D$  value of the  $\beta$ -diketone.

**Lutetium- $\beta$ -diketone-TOPO System.** Figure 2 indicates the  $\log D^*$  vs. pH plots in the synergistic extraction of lutetium ions with  $10^{-3}\text{M}$  TOPO and various  $\beta$ -diketones in benzene. In the presence

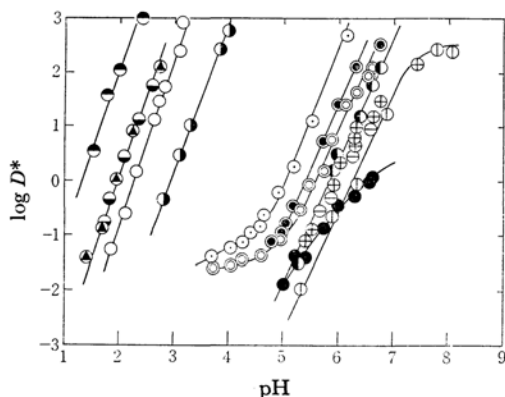


Fig. 2. The distribution ratio of lutetium with various  $\beta$ -diketones in the presence of  $0.001\text{M}$  TOPO as a function of pH. The symbols in the figure are the same as in Fig. 1.

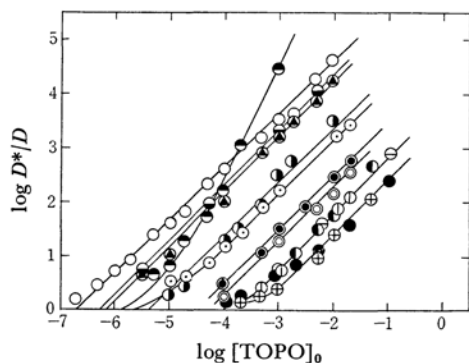


Fig. 3. The distribution ratio of lutetium with  $\beta$ -diketones having various functional groups as a function of TOPO concentration. The symbols in the figure are the same as in Fig. 1.

of TOPO, the extraction of lutetium is very much enhanced by the adduct formation. As may be seen in the figure, the plots of DBM, NtA and BzA curve concavely in the low-distribution region. This curious behavior, however, can not be explained in the present time and was not studied in detail, because it seems not to be very important in this research.

The effects of the functional groups of various  $\beta$ -diketones on the adduct formation are shown in Fig. 3 as  $\log D^*/D$  vs.  $\log [\text{TOPO}]_0$  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 1. The stability of the TOPO adduct with various lutetium  $\beta$ -diketonates increases in the following order: aliphatic groups (AA and DPM < PvA, DIBM and DPvM) < aromatic groups (BzA < NtA < DBM) < fluoromethyl groups (TFA < FTA < TTA < BFA < HFA). In general, the  $\log \beta_n$  increases with an increase in the  $\log K$  value, as is indicated in Fig. 4, and no steric hindrance by terminal aliphatic or aromatic groups upon the adduct formation is observed.

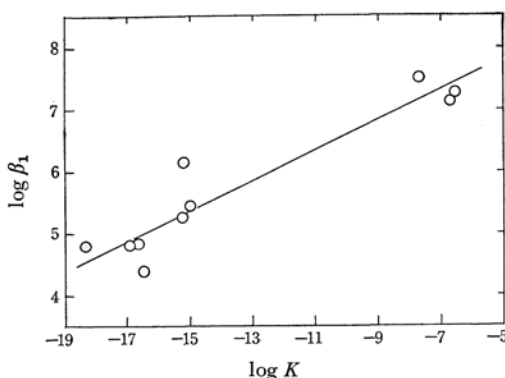


Fig. 4. The stability constant of lutetium  $\beta$ -diketonate TOPO adduct,  $\log \beta_n$  as a function of the extraction constant of metal chelate,  $\log K$ .

As has been described above, the chelates with a fluoromethyl group in the ligand form stable adducts. This may be due to the fact that the electron-withdrawing fluoromethyl group decreases the electron density around the metal ion.<sup>14,15</sup> The fluoromethyl group does not hinder the resonance of the metal chelate ring.<sup>16</sup> The chelates containing the








14) K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962).

15) H. F. Holtzclow, Jr., and W. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).

16) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, N. Y. (1952).

13) J. F. Suttle and T. K. Keenon, *J. Am. Chem. Soc.*, **76**, 2184 (1954).

TABLE 1. STABILITY CONSTANTS OF LUTETIUM  $\beta$ -DIKETONATES AND THEIR ADDUCTS WITH TOPO

	R	R'	$pK_D^*$	$\log K$	$\log \beta_1$		R	R'	$pK_D^*$	$\log K$	$\log \beta_1$
AA	CH <sub>3</sub>	CH <sub>3</sub>	12.70 (11.27)	—	4.35	DBM			13.75	-15.16	6.15
DPM	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	—	-16.57	4.35	TAA	CH <sub>3</sub>	CF <sub>3</sub>	8.70	—	6.25
DIBM	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	(12.48)	-16.57	4.80	BFA		CF <sub>3</sub>	9.20	-7.69	7.50
PvA	CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	14.20	-16.90	4.80	TTA		CF <sub>3</sub>	9.10	-6.56	7.25
DPvM	C(CH <sub>3</sub> ) <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	(14.48)	-18.37	4.80	FTA		CF <sub>3</sub>	8.50	-6.78	7.15
BzA	CH <sub>3</sub>		12.85	-15.21	5.25	HFA	CF <sub>3</sub>	CF <sub>3</sub>	6.0	—	6.25
NtA	CH <sub>3</sub>		—	-15.06	5.45						( $\log \beta_2$ =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, *ibid.*, **81**, 4682 (1959).

TABLE 2. EFFECT OF TEMPERATURE ON STABILITY CONSTANT OF Lu- $\beta$ -DIKETONATE-TOPO COMPLEXES

	10°C		20°C		30°C		$-\Delta H$ kcal/mol
	$\log K$	$\log \beta_1$	$\log K$	$\log \beta_1$	$\log K$	$\log \beta_1$	
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

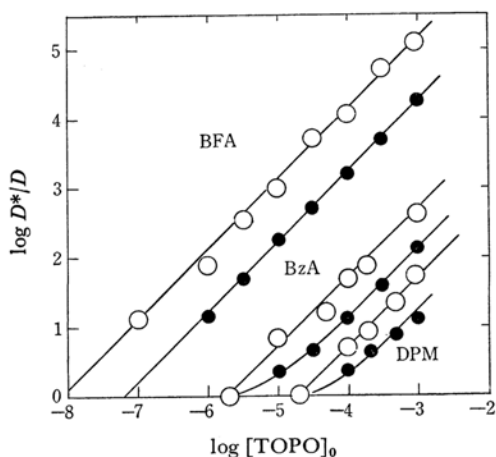


Fig. 5. Variation of the distribution ratio of lutetium as a function of TOPO concentration at 10°C (—○—) and 30°C (—●—).

aromatic group in the ligand also form more stable adducts than those with the aliphatic group do (e.g., TFA < BFA; AA < BvA < DBM). The contribution of the phenyl substitution to the adduct formation may result from the conjugation effect of the groups with the metal chelate rings. Such a conjugation effect may weaken the binding power between the central metals and the coordinated ligand,<sup>17)</sup> thereby enhancing the adduct formation.

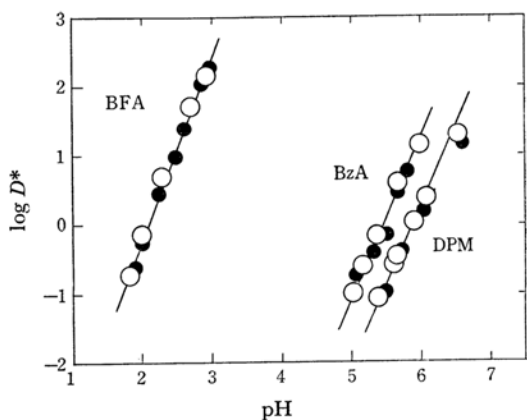


Fig. 6. Logarithm of the distribution ratio of lutetium as a function of pH at 10°C (—●—) and 30°C (—○—).

The conjugation effect was also observed in the NMR measurements of metal TTA chelates.<sup>18)</sup> As a result of the electron-withdrawing effect of the fluoromethyl group and by the conjugation effect of the phenyl-, thenoyl-, and furoyl-groups, BFA, TTA, and FTA form more stable adducts with TOPO than do other  $\beta$ -diketones. A similar ten-

17) R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

18) J. R. Ferraro, *ibid.*, **26**, 225 (1964).

dency has also been found in the adduct formation between uranyl  $\beta$ -diketonates and TBP.<sup>19)</sup>

Figure 5 shows the effect of the temperature on the adduct formation of DPM, BzA, and BFA chelates with TOPO, while Table 2 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 a 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. As may be expected from this fact, the  $\log D^*$  vs. pH plots in the synergistic extraction are little affected by the temperature (in the range from 10°C to 30°C), as is presented in Fig. 6. The apparent enthalpy changes in the adduct formation have been estimated and are presented in Table 2. The value increases in the sequence of DPM, BzA, and BFA.

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19) K. Batzer, D. E. Goldberg, and L. Newman, *ibid.*, **29**, 1511 (1967).