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# Synergistic Effect in Solvent Extraction—Effect of the Chelating Ligands on the Stability of Lutetium Mixed Chelates with β-Diketones and Their Adducts with TOPO—

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The effect of the chelating ligands on the stability of mixed chelates of lutetium with β-diketones and the stability of their adducts with TOPO in benzene was studied by extracting lutetium with mixtures of two β-diketones, benzoylacetone (BzA) and dibenzoylmethane (DBM), and benzoylacetone and benzoyltrifluoroacetone (BFA), in the absence or in the presence of TOPO. The results are summarized as follows. (1) The extraction constants of Lu-BzA-DBM mixed chelates are almost the same as statistically calculated, while those of Lu-BzA-BFA mixed chelates are somewhat lower than the theoretical values. (2) The stability of the TOPO adducts of the mixed chelates increases in the order, $M(BzA)_2(DBM) \approx M(BzA)(DBM)_2 < M(BzA)_2(BFA) < M(BzA)(BFA)_2$, which is almost the same as that found among the extraction constants of the mixed chelates. The fluoromethyl group stabilizes the adduct more than phenyl group. (3) All the mixed chelates of lutetium β-diketonates bind one molecule of TOPO per metal chelate.

In the solvent extraction of rare earth β-diketonates, the presence of TOPO brings about the considerably enhancement of the extractability, which results from the adduct formation between the metal chelates and TOPO. The authors investigated the

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effects of the size of central rare earth metal ions and of the terminal group of $\beta$-diketones on the synergistic extraction, and concluded that the stability of the adducts increased as the ionic radius of rare earth metal ions increased[1] or the terminal groups of $\beta$-diketones were substituted with aliphatic, aromatic and fluoromethyl groups.[2]

Recently, Sekine and Dyrssen[3,4] described the extraction of copper, zinc, indium and europium with mixtures of TTA and $\beta$-isopropyltropolone, and presented the extraction constants of the mixed chelates of these metals and the stability constants of the adducts of europium chelates with undissociated chelating agent, $\beta$-isopropyltropolone. However, the stability of the adducts formed between mixed chelates and neutral Lewis bases such as TOPO was reported neither by them nor by other investigators.

As it seems interesting to know how the stability of such adducts depends upon the successive formation of various mixed chelates, and it is also important to obtain more detailed information about the effect of the chelating ligands on the stability of the adducts, the authors attemped to deal with this subject. In the present research, the extraction behaviors of lutetium with mixtures of two $\beta$-diketones, benzoylacetone and dibenzoylmethane, and benzoylacetone and benzoyltrifluoroacetone in benzene were studied in the absence or in the presence of TOPO, and the extraction constant of the mixed chelates and the stability constants of their adducts with TOPO were obtained.

## Experimental

**Materials.** The radio-isotope, lutetium-177 was produced by irradiating pure lutetium oxide in a thermal neutron flux of about $5\times10^{12}$ n/cm$^2$·sec in the Research Reactor of Kyoto University. After the irradiated sample was dissolved in hot hydrochloric acid, lutetium was extracted at pH 5 with 0.05M BFA in benzene and stripped into 0.1M perchloric acid. The resulting solution was evaporated to fume and the residue was dissolved with an appropriate amount of perchloric acid to make a stock solution. Specific activity of the tracer was sufficiently high for this investigation. Sodium perchlorate was prepared by dissolving sodium carbonate in perchloric acid and purified by recrystallization. Benzoylacetone (BzA), dibenzoylmethane (DBM), benzoyltrifluoroacetone (BFA) and tri-*n*-octylphosphine oxide (TOPO) were obtained from the Dojindo Co.

**Procedure.** Experimental procedure was almost the same as previously described.[1,2] Five milliliters of an aqueous solution containing lutetium (a few ppm), sodium perchlorate (0.1M) and acetic acid (0.01M), and having a desirable pH, were shaken with 5 m*l* of a benzene solution including $\beta$-diketones and various amount of TOPO, for one to three hours at 20±1°C. After separating both phases, 2 m*l* of each phase were pipetted into test tubes (14 mm in diameter), and the radioactivities were measured with a NaI(Tl) well-type scintillation counter. The pH value of the aqueous layers after extraction was again measured with a glass electrode pH meter.

## Theoretical

When tervalent ions, $M^{3+}$, are extracted with a mixture of two chelating acids, HA and HB, the ideal extraction equilibrium may be written as

$$M^{3+} + m\mathrm{HA(org)} + (3-m)\mathrm{HB(org)} \rightleftharpoons \mathrm{MA}_m\mathrm{B}_{3-m}\mathrm{(org)} + 3\mathrm{H}^+ \qquad (1)$$

The extraction constants of the reaction, $K_{m,3-m}$ and the distribution ratio of the metal, $D$, can be given by

$$K_{m,3-m} = [\mathrm{MA}_m\mathrm{B}_{3-m}]_o[\mathrm{H}^+]^3[\mathrm{M}^{3+}]^{-1}[\mathrm{HA}]_o^{-m} \times [\mathrm{HB}]_o^{-(3-m)} \quad (m=0,1,2,3) \qquad (2)$$

$$D = \sum_{m=0}^{3}[\mathrm{MA}_m\mathrm{B}_{3-m}]_o[\mathrm{M}^{3+}]^{-1} \qquad (3)$$

where [ ] and [ ]$_o$ designate the concentration of chemical species in the aqueous and organic phase, respectively.

From Eqs. (2) and (3), a fundamental equation of the curve fitting method is obtained as follows:

$$\begin{aligned}\log D[\mathrm{H}^+]^3[\mathrm{HB}]_o^{-3} - \log K_{0,3} &= \log\{1+K_{0,3}^{-1}K_{1,2}([\mathrm{HA}]_o/[\mathrm{HB}]_o) \\ &\quad + K_{0,3}^{-1}K_{2,1}([\mathrm{HA}]_o/[\mathrm{HB}]_o)^2 \\ &\quad + K_{0,3}^{-1}K_{3,0}([\mathrm{HA}]_o/[\mathrm{HB}]_o)\}\end{aligned} \qquad (4)$$

Comparing the experimental curves, $Y=\log D\cdot[\mathrm{H}^+]^3[\mathrm{HB}]_o^{-3}-\log K_{0,3}$, $X=\log([\mathrm{HA}]_o/[\mathrm{HB}]_o)-\frac{1}{3}\log K_{0,3}K_{3,0}^{-1}$, with the normalized curves, $Y=\log(1+pv+qv^2+v^3)$, $X=\log v$, the following relations can be obtained.

$$K_{1,2} = p(K_{0,3}^2K_{3,0})^{1/3} \qquad (5)$$

$$K_{2,1} = q(K_{0,3}K_{3,0}^2)^{1/3} \qquad (6)$$

The statistical relation between these equilibrium constants can be given as, $K_{1,2}=3(K_{0,3}^2\,K_{3,0})^{1/3}$ and $K_{2,1}=3\,(K_{0,3}\,K_{3,0}^2)^{1/3}$ (*cf.* Ref. 4).

When metal chelates, $\mathrm{MA}_m\mathrm{B}_{3-m}$ form the adducts with a neutral Lewis base, L, in the organic phase, the equilibrium may be expressed as

$$\mathrm{MA}_m\mathrm{B}_{3-m}\mathrm{(org)} + n\mathrm{L(org)} \rightleftharpoons \mathrm{MA}_m\mathrm{B}_{3-m}\mathrm{L}_n\mathrm{(org)} \qquad (7)$$

The stability constants of the adducts, $\beta_n$, and the distribution ratio, $D^*$, are given by

$$\beta_n = [\mathrm{MA}_m\mathrm{B}_{3-m}\mathrm{L}_n]_o/[\mathrm{MA}_m\mathrm{B}_{3-m}]_o[\mathrm{L}]_o^n \qquad (8)$$

$$D^* = \{[\mathrm{MA}_m\mathrm{B}_{3-m}]_o + \sum_{n=1}^{n}[\mathrm{MA}_m\mathrm{B}_{3-m}\mathrm{L}_n]_o\}/[\mathrm{M}^{3+}] \qquad (9)$$

From Eqs. (3) and (9), the following equations can be obtained,

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[1] T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, This Bulletin, **40**, 2807 (1967).

[2] T. Honjyo, *ibid.*, **42**, 995 (1969).

[3] T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 2013 (1964).

[4] T. Sekine and D. Dyrssen, *ibid.*, **29**, 1489 (1967).

$$D^*/D = 1 + \sum_{n=1}^{n} \beta_n[\mathrm{L}]_o{}^n \tag{10}$$

or

$$\log D^*/D = \log\,(1+\sum_{n=1}^{n} \beta_n[\mathrm{L}]_o{}^n) \tag{11}$$

The derivations of the equations are described in previous papers.[1,3,4)]

## Results and Discussion

**Lutetium-β-Diketone System.** Figures 1 and 2 show the extraction of lutetium with BzA, DBM and BFA alone in benzene as a function of pH and the chelating agent concentration, respectively. All the plots give almost a straight line with a slope of 3 indicating that the extraction of lutetium is ideally performed.

Figure 3 indicates the extraction of lutetium with

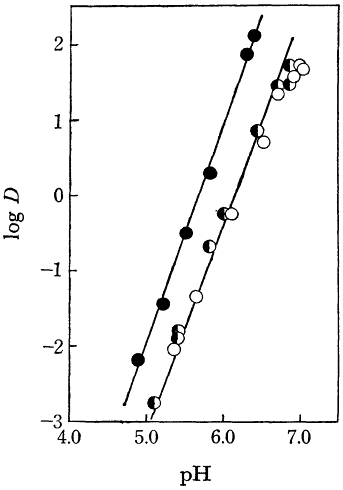

Fig. 1. Variation of the distribution ratio of lutetium as a function of pH.
Organic phase: —●— $10^{-3}$M BFA, —◐— $10^{-1}$M DBM, —○— $10^{-1}$M BzA in benzene
Aqueous phase: $10^{-1}$M $NaClO_4$

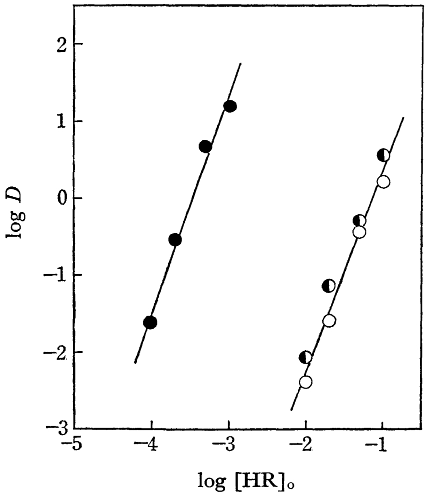

Fig. 2. Variation of the distribution ratio of lutetium as a function of chelate ligand concentration.
Organic phase: —●—BFA, —◐— DBM, —○— BzA in benzene
Aqueous phase: $10^{-1}$M $NaClO_4$, pH=6.25

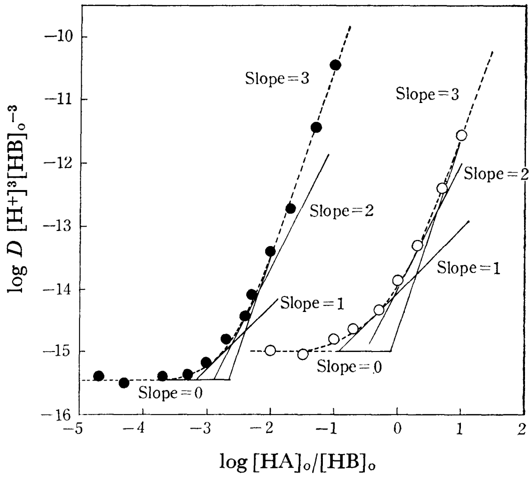

Fig. 3. Extraction of lutetium with mixtures of BFA and BzA (●) or DBM and BzA (○) in benzene at different mixing ratio.
The two dotted curves represent the normalized curves $Y=\log\,(1+pv+qv^2+v^3)$, $X=\log v$ with $p=1$, $q=1$ (mixtures of BFA and BzA) and $p=3$, $q=3$ (mixtures of DBM and BzA).

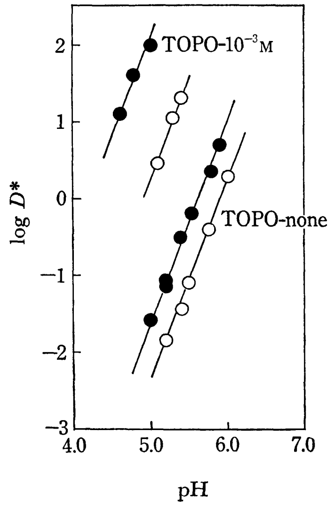

Fig. 4. Variation of the distribution of letetium in the presence or in the absence of TOPO as a function of pH.
Organic phase: —●— mixtures of BFA ($5\times10^{-4}$M) and BzA ($10^{-1}$M) $\log\,[\mathrm{HA}]_o/[\mathrm{HB}]_o=-2.30$, —○— mixtures of DBM ($3.3\times10^{-2}$M) and BzA ($10^{-1}$M) $\log\,[\mathrm{HA}]_o/[\mathrm{HB}]_o=-0.48$
Aqueous phase: $10^{-1}$M $NaClO_4$

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

| | Chelate | log $K$ (found) | log $K$ (calcd)* | log $\beta_1$ |
|---|---|---|---|---|
| BzA-BFA mixed system | $Lu(BzA)_3$ | $-15.21$ | | 5.25 |
| | $Lu(BzA)_2(BFA)$ | $-12.7$ | $-12.2$ | 6.15 |
| | $Lu(BzA)(BFA)_2$ | $-10.2$ | $-9.7$ | 6.65 |
| | $Lu(BFA)_3$ | $-7.69$ | | 7.50 |
| BzA-DBM mixed system | $Lu(BzA)_3$ | $-15.21$ | | 5.25 |
| | $Lu(BzA)_2(DBM)$ | $-14.7$ | $-14.7$ | 5.60 |
| | $Lu(BzA)(DBM)_2$ | $-14.7$ | $-14.7$ | 5.70 |
| | $Lu(DBM)_3$ | $-15.16$ | | 6.15 |

* The values were estimated from Eqs. (5) and (6) by assuming $p=3$ and $q=3$ (theoretical value).

mixtures of BzA and DBM, and BzA and BFA in benzene with different mixing ratios. From the plots, $p$ and $q$ values of the normalized curves were obtained by the curve fitting method, and the extraction constants of mixed chelate, $K_{1,2}$ and $K_{2,1}$ were calculated by Eqs. (5) and (6), using $K_{0,3}$ and $K_{3,0}$ values which were obtained by extraction with each $\beta$-diketone. The results are listed in Table 1. The extraction constants experimentally obtained of the BzA-DBM mixed chelates are almost the same with the value statistically calculated, while those of the BzA-BFA mixed chelates are somewhat lower than the calculated values. Similar results have been observed on europium-TTA-IPT and indium-TTA-IPT mixed chelates.[4]

The $\log D[H^+]^3[HB]_o^{-3}$ *vs.* $\log([HA]_o/[HB]_o)$ plots have two asymptotes with the slope of 0 (for $[HA]_o/[HB]_o \rightarrow 0$) and 3 (for $[HA]_o/[HB]_o \rightarrow \infty$). The slope of the tangent gently changing from 0 to 3, indicates the composition of the metal chelates extracted under the condition. Namely, $MA_3$, $MA_2B$, $MAB_2$ and $MB_3$ may each exist as a predominant species in the region where the slope of the tangent is 0, 1, 2 and 3, respectively.

**Lutetium-$\beta$-Diketone-TOPO System.** Figures 4 and 5 indicate the log $D$ *vs.* pH plots in the extraction of lutetium ions with the mixtures of two $\beta$-diketones in the absence and presence of $10^{-3}$M TOPO in benzene: The mixing ratio of two $\beta$-diketones lies in the region where the predominant species is $MA_2B$ (Fig. 4) and $MAB_2$ (Fig. 5). The large enhancement of the extraction observed in the

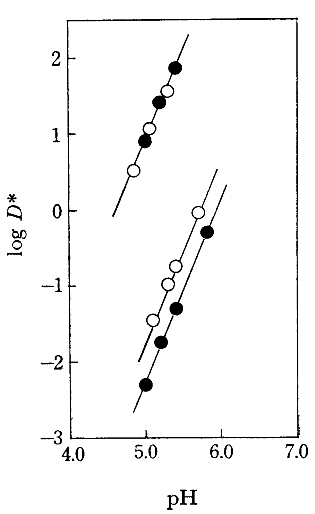

Fig. 5. Variation of the distribution of lutetium in the presence or in the absence of TOPO as a function of pH.
Organic phase: —●— mixtures of BFA ($1.25\times10^{-4}$M) and BzA ($10^{-1}$M), $\log[HA]_o/[HB]_o=-2.90$ —○— mixtures of DBM ($10^{-1}$M) and BzA ($5\times10^{-2}$M), $\log[HA]_o/[HB]_o=0.30$

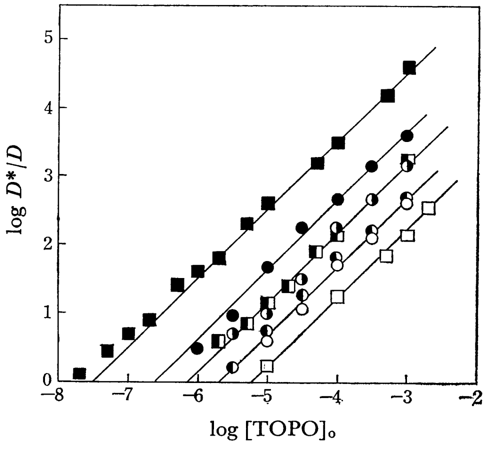

Fig. 6. Variation of the distribution of letetium as a function of TOPO concentration.
Organic phase: —□— BzA ($5\times10^{-2}$M); —○— mixtures of DBM ($3.3\times10^{-2}$M) and BzA ($10^{-1}$M), $\log[HA]_o/[HB]_o=-0.48$; —◐— mixtures of DBM ($10^{-1}$M) and BzA ($5\times10^{-2}$M), $\log[HA]_o/[HB]_o=0.30$; —◧— DBM ($5\times10^{-2}$M); —◑— mixtures of BFA ($1.25\times10^{-4}$M) and BzA ($10^{-1}$M), $\log[HA]_o/[HB]_o=-2.90$; —●— mixtures of BFA ($5\times10^{-4}$M) and BzA ($10^{-1}$M), $\log[HA]_o/[HB]_o=-2.30$; —■— BFA ($5\times10^{-2}$M).

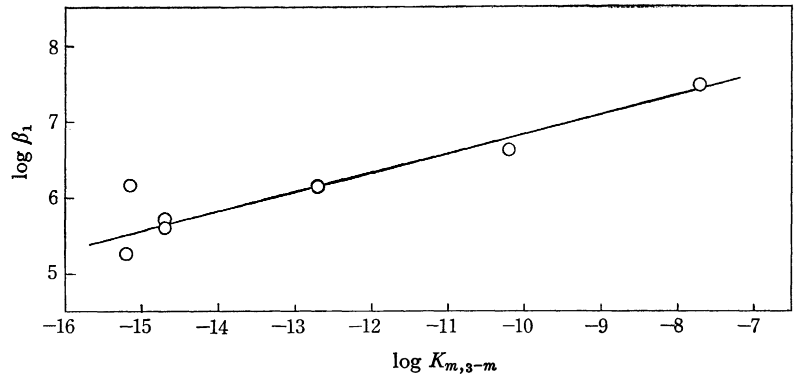

Fig. 7. Stability constant of lutetium $\beta$-diketonate adducts with TOPO as a function of the extraction constant of lutetium $\beta$-diketonates.

presence of TOPO shows that the mixed chelates, $MA_2B$ and $MAB_2$ form adducts with TOPO as the simple chelates $MA_3$ and $MB_3$.

Figure 6 indicates $\log D^*/D$ *vs.* $\log [\mathrm{TOPO}]_o$ plots in the extraction of lutetium with each of three $\beta$-diketones or with mixtures of two $\beta$-diketones. All the plots give the straight line with a slope of 1, showing that one molecule of TOPO binds to one molecule of the metal chelates. The apparent stability constants of the adducts with TOPO are summarized in Table 1. The stability of the adduct of the mixed chelates increases in the order, $\mathrm{Lu(BzA)_2(DBM)} \approx \mathrm{Lu(BzA)(DBM)_2} < \mathrm{Lu(BzA)_2(BFA)} < \mathrm{Lu(BzA)(BFA)_2}$.

Figure 7 shows the relation between $\log K$ and $\log \beta_1$. Both values linearly correlate with each other and in the BzA-BFA mixed system, increase smoothly without showing any irregularity, as BzA is successively replaced by BFA. The fact leads to the following conclusions: (1) The concept that metal chelates having higher $K$ value form more stable adducts is true of the mixed chelates, as well as of the simple chelates. (2) Asymmetry of the structure of mixed chelates does not give a measurable effect on the adduct formation. (3) Fluoromethyl group, irrespective of simple chelates or mixed chelates, makes the chelates form stable adducts. (3) can be explained by the electron withdrawing effect of fluoromethyl group.[2]

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