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Synergic Extraction of Lanthanoids(III) with 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione in the Presence of 1,10-Phenanthroline or 2,9-Dimethyl-1,10-phenanthroline

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The synergic extraction of various tervalent lanthanoids (Ln(III)), La, Ce, Nd, Sm, Gd, Tb, Yb, and Lu, with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta) in the presence of a bidentate heterocyclic amine, 1,10-phenanthroline (phen) or 2,9-dimethyl-1,10-phenanthroline (dmp), in benzene was investigated. In the phen system, a synergic enhancement occurred by the formation of the adducts, $\mathrm{Ln(tta)_3phen}$; the higher adduct, $\mathrm{Ln(tta)_3(phen)_2}$, was found for La and Ce. In the dmp system, the formation of only one adduct, $\mathrm{Ln(tta)_3dmp}$, was observed. The values of the adduct formation constants ($\beta_{s,1}$) for phen increase with increasing atomic number of Ln(III); those for dmp, however, decrease with increasing atomic number of Ln(III) and were lower than those for phen.

The synergic extraction of various metal ions including tervalent lanthanoids Ln(III) with an acidic chelating agent and a neutral unidentate organophosphorus ligand, such as tributyl phosphate (tbp), has been widely investigated. From these studies it is concluded that although the extraction efficiency is greatly improved, the separation efficiency becomes poor in the synergic-type extraction, compared with the case of simple chelate extraction using an acidic chelating agent. In these studies only a unidentate neutral ligand involving oxygen, or nitrogen in a few cases, as a coordinating atom was used throughout; only a few systematic studies concerning synergic extraction using the bidentate neutral ligand have been made.

We investigated the synergic extraction of Ln(III) with various β-diketones and neutral bidentate heterocyclic amines, such as 2,2′-bipyridine (bpy).[1—3] A large synergic enhancement was observed. The effect of nonpolar diluents on synergism has also been discussed.[4—6] A new trend regarding synergic extraction was observed: That is, the relation between the synergic enhancement and the atomic number of Ln(III) can be changed inversely by using different combinations of β-diketones and bidentate ligands.[2,3] As a typical case, the synergic extraction of various Ln(III) with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (2-thenoyltrifluoroacetone, Htta) in the presence of bpy or a unidentate heterocyclic amine, pyridine (py), was investigated,[7] as well as the synergic enhancement increase with increasing atomic number of Ln(III) for bpy, contrary to the case of the unidentate ligand.[8]

In the present work, the synergic extraction of various Ln(III) with Htta in the presence of 1,10-phenanthroline (phen) or 2,9-dimethyl-1,10-phenanthroline (dmp) in benzene was investigated. The tendency for a synergic enhancement of Ln(III) for phen and dmp is also compared with that for bpy.

Experimental

Materials. Radioisotopes ^{140}La, ^{141}Ce, ^{147}Nd, ^{153}Sm, ^{153}Gd, ^{160}Tb, ^{169}Yb, and ^{177}Lu were used as tracers; they were produced by the neutron irradiation of each oxide or nitrate in a nuclear reactor (JRR-4) of the Japan Atomic Research Institute at a thermal neutron flux of 5.5×10^{13} n cm^{-2} s^{-1} for 6 h. The irradiated lanthanoid oxides were dissolved in hydrochloric acid, evaporated to dryness and redissolved in a 10^{-3} M (1 M=1 mol dm^{-3}) perchloric acid solution before use. Htta was purified by vacuum sublimation. Benzene was purified by ordinary methods. Unless otherwise stated, the reagents used were of guaranteed reagent grade.

Procedure. An aqueous solution (6 cm^3) containing 10^{-7}—10^{-5} M Ln(III) labeled with its radioisotope and a benzene solution (6 cm^3) containing 10^{-3} M Htta and 10^{-6}—10^{-2} M neutral ligand were agitated for 1—3 h at 25°C. The ionic strength in the aqueous phase was adjusted to 0.1 with sodium perchlorate. In the extraction of Ce(III), 10^{-3} M sodium ascorbate was also present in order to prevent the oxidation of Ce(III) to Ce(IV). After centrifugation, an aliquot was taken from each phase and the γ-activity was measured with a NaI(Tl) well-type scintillation detector connected to a single-channel analyzer. The distribution ratio of Ln(III) was obtained as the radioactivity ratio. The pH of the aqueous phase was adjusted with 10^{-3}—10^{-2} M 1,4-piperazinediethanesulfonic acid and sodium hydroxide solution, and the equilibrium pH was measured with a glass electrode.

Theoretical. The distribution ratio (D_0) of a tervalent cation, $\mathrm{M^{3+}}$, with a chelating extractant, HA, can be expressed as follows:

$$D_0=\frac{[\overline{\mathrm{MA_3}}]}{[\mathrm{M^{3+}}]+\Sigma[\mathrm{MA}_n{}^{3-n}]}=\frac{P_\mathrm{M}\beta_3[\mathrm{A^-}]^3}{1+\Sigma\beta_n[\mathrm{A^-}]^n}, \quad (1)$$

where the horizontal line over the species denotes the organic phase, β_n the overall chelate formation constant of $\mathrm{MA}_n{}^{3-n}$ in the aqueous phase, P_M the partition coefficient of $\mathrm{MA_3}$, and $\mathrm{A^-}$ the chelating anion in the aqueous phase. When $\mathrm{MA}_n{}^{3-n}$ chelates can be neglected, the extraction equilibrium of $\mathrm{M^{3+}}$ with HA is given as

$$\mathrm{M^{3+}}+3\overline{\mathrm{HA}}\rightleftarrows\overline{\mathrm{MA_3}}+3\mathrm{H^+}:K_\mathrm{ex} \quad (2)$$

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and the extraction constant (K_{ex}) can be expressed as

$$K_{\mathrm{ex}} = \frac{[\overline{\mathrm{MA_3}}][\mathrm{H^+}]^3}{[\mathrm{M^{3+}}][\overline{\mathrm{HA}}]^3} = \left(\frac{K_{\mathrm{HA}}}{P_{\mathrm{HA}}}\right)^3 \frac{D_0}{[\mathrm{A^-}]^3}. \tag{3}$$

Here, K_{HA} and P_{HA} denote the acid dissociation constant and the partition coefficient of HA, respectively.

In the synergic extraction of $\mathrm{M^{3+}}$ with HA and a neutral ligand, S, the distribution ratio (D) can be expressed as

$$D = \frac{[\overline{\mathrm{MA_3}}] + \Sigma[\overline{\mathrm{MA_3S}_m}]}{[\mathrm{M^{3+}}] + \Sigma[\mathrm{MA}_n{}^{3-n}]} = \frac{P_{\mathrm{M}}\beta_3[\mathrm{A^-}]^3(1+\Sigma\beta_{\mathrm{s},m}[\overline{\mathrm{S}}]^m)}{1+\Sigma\beta_n[\mathrm{A^-}]^n}, \tag{4}$$

where $\beta_{\mathrm{s},m}$ is the adduct-formation constant in the organic phase corresponding to the following equilibrium:

$$\overline{\mathrm{MA_3}} + m\overline{\mathrm{S}} \rightleftarrows \overline{\mathrm{MA_3S}_m} : \beta_{\mathrm{s},m}. \tag{5}$$

From Eqs. 1 and 4, the following equation is obtained:

$$D/D_0 = 1 + \Sigma\beta_{\mathrm{s},m}[\overline{\mathrm{S}}]^m. \tag{6}$$

If $\mathrm{MA_3S}_m$ is the only dominant species in the organic phase, D/D_0 depends on the m' th power of the concentration of S in the organic phase.

The synergic extraction constant ($K_{\mathrm{exs},m}$) is defined by the following equiliblium:

$$\mathrm{M^{3+}} + 3\overline{\mathrm{HA}} + m\overline{\mathrm{S}} \rightleftarrows \overline{\mathrm{MA_3S}_m} + 3\mathrm{H^+}; \tag{7}$$

$$\begin{aligned} K_{\mathrm{exs},m} &= \frac{[\overline{\mathrm{MA_3S}_m}][\mathrm{H^+}]^3}{[\mathrm{M^{3+}}][\overline{\mathrm{HA}}]^3[\overline{\mathrm{S}}]^m} = \left(\frac{K_{\mathrm{HA}}}{P_{\mathrm{HA}}}\right)^3 P_{\mathrm{M}}\beta_3\beta_{\mathrm{s},m} \\ &= K_{\mathrm{ex}}\beta_{\mathrm{s},m}. \end{aligned} \tag{8}$$

Results and Discussion

Synergic Extraction of Ln(III). The synergic extraction of La(III), Ce(III), Nd(III), Sm(III), Gd(III), Tb(III), Yb(III), and Lu(III) with 10^{-3} M Htta and various concentrations of phen in benzene were carried out; plots of log D/D_0 against log $[\overline{\mathrm{phen}}]$ are shown in Fig. 1. It was confirmed that the presence of $\mathrm{MA}_n{}^{3-n}$ chelates in the aqueous phase can be neglected under the experimental conditions. The value of the distribution ratio (D_0) of Ln(III) in extraction with Htta alone in benzene was evaluated using Eq. 3 employing the extraction constant;[7] the equilibrium concentration of $\mathrm{tta^-}$ in the aqueous phase was calculated using

$$[\mathrm{A^-}] = \frac{C_{\mathrm{HA}}}{(P_{\mathrm{HA}}+1)[\mathrm{H^+}]/K_{\mathrm{HA}}+1}, \tag{9}$$

where C_{HA} denotes the initial concentration of Htta. The literature values of K_{HA} and P_{HA} were adopted, i. e. log $K_{\mathrm{HA}}=-6.23$[9] and log $P_{\mathrm{HA}}=1.62$.[10] The equilibrium concentration of phen in the organic phase was calculated using

$$[\overline{\mathrm{S}}] = \frac{C_{\mathrm{S}}}{1+(1+[\mathrm{H^+}]/K_{\mathrm{HS}})/P_{\mathrm{S}}}, \tag{10}$$

where C_{S} denotes the initial concentration of phen; K_{HS} and P_{S} are the acid dissociation constant of the protonated phen and the partition coefficient of phen, respectively. The values of K_{HS} and P_{S} were obtained experimentally:[1] log $K_{\mathrm{HS}}=-5.04$ and log $P_{\mathrm{S}}=0.78$.

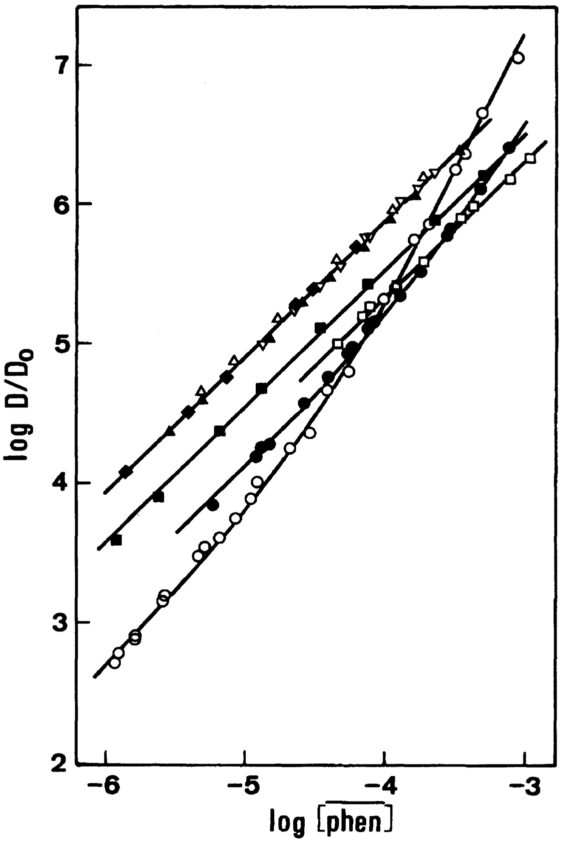

Fig. 1. Effect of the phen concentration in benzene on the synergic extraction of Ln(III) with Htta. $[\mathrm{Htta}]_{\mathrm{init}}=10^{-3}$ M; ○: La, ●: Ce, □: Nd, ■: Sm, ▽: Gd, ▲: Tb, △: Yb, ◆: Lu.

The plots for Nd, Sm, Gd, Tb, Yb, and Lu give straight lines with slopes of 1.0; those for Gd, Tb, Yb, and Lu are very close to each other. This indicates that the mole ratio of the neutral chelate and phen in the adduct formed in the organic phase is 1 : 1, and provides no evidence for the formation of a higher adduct, $\mathrm{Ln(tta)_3(phen)_2}$, under the present experimental conditions. For Ce, however, although the plots give a parallel line to the plots of heavier lanthanoids in the lower-concentration region of phen, those in the higher-concentration region of phen deviate positively from a straight line. A similar, but more explicit, phenomenon was observed for La: The plots give a curved line having two asymptotes with a slope of 1.0 in the lower-concentration region of phen and a slope of 2.0 in the high-concentration region of phen. This indicates that the higher adduct, $\mathrm{Ln(tta)_3(phen)_2}$, can be formed in the organic phase for La and Ce in the high-concentration region of phen. This type of adduct was also observed in a previous study for a limited combination of Ln(III) and β-diketone.[3] For example, in the 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, Hhfa) system, $\mathrm{La(hfa)_3(phen)_2}$ and $\mathrm{Sm(hfa)_3(phen)_2}$ were formed, and in the 1,1,1-trifluoro-5,5-dimethyl-2, 4-hexanedione (pivaloyltrifluoroacetone, Hpta) system, $La(pta)_3(phen)_2$ was formed. These adduct formations seem to be observed between the mother chelates of the lighter lanthanoids and β-diketones having higher acid dissociation constants. Since the value of K_{HA} of Htta is near to that of Hpta, i. e. $\log K_{HA} = -7.01$,[11] the observation of higher adduct formation for La and Ce supports the above-mentioned tendency. The adduct formation constants, $\beta_{s,1}$ for $Ln(tta)_3phen$ and $\beta_{s,2}$ for $Ln(tta)_3(phen)_2$, are calculated from Eq. 6 using a least-squares method; they are listed in Table 1.

Plots of $\log D/D_0$ against $\log [\overline{\mathrm{dmp}}]$ in the synergic extraction of Ln(III) with 10^{-3} M Htta in benzene are shown in Fig. 2. The equilibrium concentration of dmp in the organic phase was evaluated using Eq. 10 while employing the corresponding values, $\log K_{HS} = -5.81$ and $\log P_S = 1.79$.[1] These plots give straight lines with slopes of 1.0. This suggests that the only one adduct, $Ln(tta)_3dmp$, is formed. In lower concentration region of dmp the plots for Yb and Lu give slightly curved lines because of a contribution of neutral chelate $Ln(tta)_3$ in addition to $Ln(tta)_3dmp$. The values of $\beta_{s,1}$ are also listed in Table 1.

Comparison of the Adduct Formation Constants. The values of $\beta_{s,1}$ are plotted in the order of the atomic number of Ln(III) in Fig. 3. In the phen system, the $\beta_{s,1}$ increase with increasing atomic number of Ln(III). Two nitrogen donor atoms of phen appear to be coordinated to the central metal in the mother chelate and the $\beta_{s,1}$ for phen is compared with the $\beta_{s,2}$ for a unidentate neutral ligand, taking into account the coordination number of the central metal of the adduct. The tendency of $\beta_{s,1}$ for phen is much different from that of $\beta_{s,2}$ for most unidentate neutral ligands, such as Ln(III)-Htta-tbp systems,[12,13] in which the $\beta_{s,2}$ values decrease with increasing atomic number of Ln(III). The peculiar tendency for the adduct formation of phen was also obtained in a synergic extraction of Ln(III)

Table 1. Extraction Constants (K_{ex}), Adduct Formation Constants (β_s) and Synergic Extraction Constants (K_{exs}) in Ln(III)-Htta-Phen or Dmp System

Ln	log K_{ex}[a]	phen		dmp	
		log $\beta_{s,1}$	log $K_{exs,1}$	log $\beta_{s,1}$	log $K_{exs,1}$
La	−10.35	8.65 13.32[c]	−1.70	5.32	−5.03
Ce	−9.47	9.12 12.52[c]	−0.35	5.43	−4.04
Nd	−8.70	9.39	0.69	5.22	−3.48
Sm	−7.93	9.57	1.64	5.07	−2.86
Gd	−7.76	9.82	2.06	4.79	−2.97
Tb	−7.38	9.92	2.54	4.76	−2.62
Tm[b]	−6.84	9.93	3.09	4.06	−2.78
Yb	−6.62	9.99	3.37	3.99	−2.63
Lu	−6.65	9.95	3.30	3.85	−2.80

a) Ref. 7. b) Ref. 1. c) Log $\beta_{s,2}$ see the text.

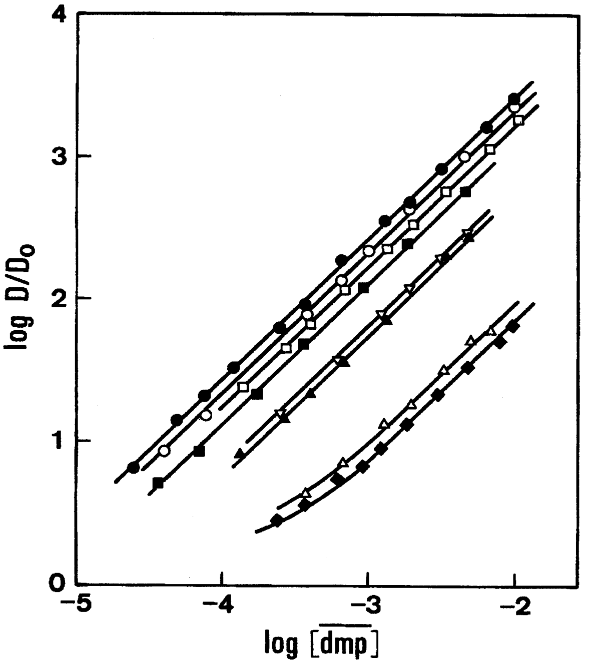

Fig. 2. Effect of the dmp concentration in benzene on the synergic extraction of Ln(III) with Htta. $[Htta]_{init} = 10^{-3}$ M; ○: La, ●: Ce, □: Nd, ■: Sm, ▽: Gd, ▲: Tb, △: Yb, ◆: Lu.

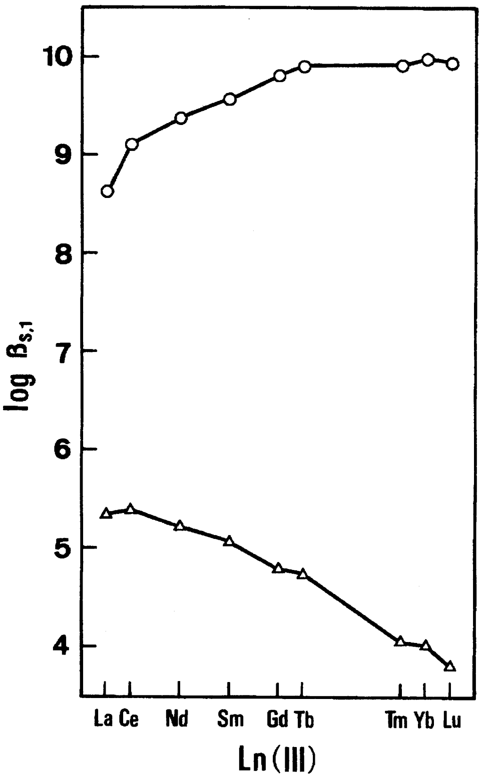

Fig. 3. Plots of $\beta_{s,1}$ in the Ln(III)-Htta-phen or dmp systems in the order of the atomic number of Ln. ○: phen, △: dmp.

with Htta and bpy, having the same functional groups as phen.[7] For a comparison, the difference in the logarithmic values of $\beta_{s,1}$ ($\Delta\log\beta_{s,1}$) between phen and bpy against the reciprocal of the Ahrens' ionic radius of each Ln(III) in a six-fold coordination[14] are plotted in Fig. 4a. The value of $\Delta\log\beta_{s,1}$ is almost constant and the following relationship is obtained:

$$\log\beta_{s,1}(\text{phen}) = \log\beta_{s,1}(\text{bpy}) + 3.42(\pm 0.06). \qquad (11)$$

The constant value of 3.42 seems to reflect mainly the difference in the basicity and in the activity coefficient between phen and bpy;[3] the size effect of the central metal may be compensated between the phen and bpy adducts.

On the other hand, in the dmp system (cf. Fig. 3) the values of $\beta_{s,1}$ decrease with increasing atomic number of Ln(III). In addition, the values of $\beta_{s,1}$ for dmp are about 3 to 6 orders of magnitude lower than those for phen. These may be attributed to a steric hindrance of two methyl groups near to the nitrogen donor atoms of dmp. The value of $\Delta\log\beta_{s,1}$ is also plotted in Fig. 4b. These plots almost fall on a straight line expressed as

$$\Delta\log\beta_{s,1} = 9.33/r - 5.83. \qquad (12)$$

This relationship cannot be explained quantitatively using thermodynamics; any specific intramolecular repulsive force in the dmp adduct seems to increase with decreasing atomic radius of the central metal. The crowding around the central metal may be related to the steric hindrance.

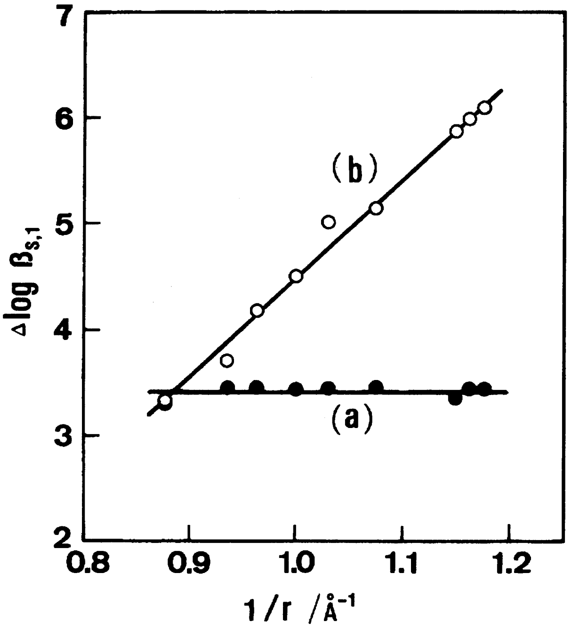

Fig. 4. Correlation between $\Delta\log\beta_{s,1}$ and $1/r$. (a): $\Delta\log\beta_{s,1}=\log\beta_{s,1}(\text{phen})-\log\beta_{s,1}(\text{bpy})$; (b): $\Delta\log\beta_{s,1}=\log\beta_{s,1}(\text{phen})-\log\beta_{s,1}(\text{dmp})$; r: Ahrens' ionic radius.

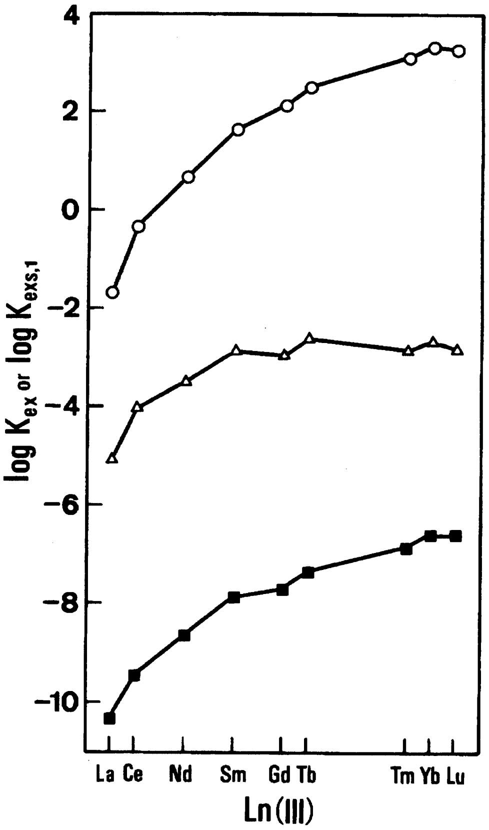

Fig. 5. Plots of $K_{\text{exs},1}$ in the Ln(III)-Htta-phen or dmp systems and K_{ex} in Ln(III)-Htta system in the order of the atomic number of Ln. $K_{\text{exs},1}$; ○: phen, △: dmp. ■: K_{ex}. (Ref. 7)

The synergic extraction constants ($K_{\text{exs},1}$) calculated from the Eq. 8 are listed in Table 1 and are plotted in the order of atomic number of Ln(III) in Fig. 5, together with the extraction constant (K_{ex}) of the mother neutral chelate Ln(tta)$_3$.

The $K_{\text{exs},1}$ for dmp increase with increasing atomic number of Ln(III) and become close to each other for a larger atomic number of the lanthanoids. The separation efficiency is lowered by synergic extraction with dmp. This appears to be a similar behavior to that of a synergic system involving a unidentate neutral ligand; the tendency for dmp, however, may be mainly attributed to the steric effect. On the other hand, it is clearly observed that $K_{\text{exs},1}$ for phen is about 10 orders of magnitude higher than K_{ex} in simple chelate extraction; furthermore, $K_{\text{exs},1}$ for phen increases with an increase in the atomic number of Ln(III). This strongly indicates a new possibility that the separation efficiency can be improved, even in the synergic extraction system.

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