Synergistic Extraction of Gallium(III) and Indium(III) with 2,4-Pentanedione and 3,5-Dichlorophenol on the Basis of Outer-Sphere Complexation

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The synergistic extraction of gallium(III) and indium(III) with 2,4-pentanedione (Hacac) in heptane and carbon tetrachloride has been studied using 3,5-dichlorophenol (DCP) as the synergist. A remarkable enhancement of the extraction of both metals(III) with 0.01 mol dm^{-3} Hacac was observed upon the addition of 0.05 mol dm^{-3} DCP, especially in heptane. From an extraction-equilibrium study, the synergistic enhancement was ascribed to the formation of outer-sphere complexes, $M(\text{acac})_3 \cdot n(\text{DCP})$ ($M = \text{Ga}$ or In ; $n = 1 - 3$), in the organic phase. Furthermore, using the synthetic metal(III) chelates hydrogen-bond formation between $M(\text{acac})_3$ and DCP was observed by IR and ^1H NMR in carbon tetrachloride. The effect of DCP on the separation efficiency of gallium(III) and indium(III) from aluminium(III) was discussed by means of the equilibrium constants such as the formation constants of outer-sphere complexes as well as the extraction constants obtained so far. It was concluded that the present synergism caused by outer-sphere complexation improved not only the extraction efficiency, but also the separation efficiency of those metals(III).

Keywords Solvent extraction, synergism, gallium, indium, acetylacetone, dichlorophenol, hydrogen bond

The synergistic effect is one of the important subjects in extraction chemistry, and has been extensively studied in chelate-extraction systems, especially for bivalent transition metals, trivalent lanthanides, and polyvalent actinides.¹ The primary cause for the synergism is an increase in the hydrophobicity of the extracted metal chelate, which is typically due to a replacement of residual water in the inner coordination sphere of the coordinately unsaturated (or hydrated) chelate by organic Lewis bases.

On the other hand, we have proposed a novel synergistic extraction system for coordinately saturated chelates, such as tris(2,4-pentanedionato)-aluminium(III)², -scandium(III)³, and -iron(III)⁴ with 3,5-dichlorophenol (DCP) as a synergist. In those studies, the synergism was explained by the formation of hydrogen-bond complexes or outer-sphere complexation of the metal(III) chelates with DCP in the organic phase; also the magnitude of the synergistic effect of DCP was found to depend on the central metals(III). These findings suggest that the selectivity in the extraction of metals(III) with 2,4-pentanedione (acetylacetone; Hacac) can be enhanced by the addition of hydrogen-bond donors such as DCP.

In the present work, the synergistic extraction of gallium(III) and indium(III) was studied with Hacac and DCP in heptane and carbon tetrachloride. To understand and elucidate the effect of DCP on the distribution of each metal(III), the fundamental equilibrium constants, such as the partition coefficient and the formation constant of gallium(III) and indium(III)

chelates, are determined and used for determining the extraction constants, which have not been reported so far. Thus the synergistic effect of DCP is studied in detail by considering all of the extraction equilibria involving the association reaction of Hacac with DCP in the organic phase. The composition and formation constant of the outer-sphere complexes of the metal(III) chelates with DCP are determined by analyses of the extraction equilibria, being quantitatively evaluated by IR and ^1H -NMR spectrometry using the synthesized gallium(III) and indium(III) chelates. The extraction constants calculated for gallium(III) and indium(III) in the presence or absence of DCP are compared with those for aluminium(III) previously reported, and the effect of DCP on the separation efficiency for those metals(III) is discussed.

Experimental

Reagents

Tris(2,4-pentanedionato)gallium(III) was synthesized with gallium(III) nitrate (99.9% purity) and purified by recrystallization from benzene-diethyl ether and then vacuum sublimation. Tris(2,4-pentanedionato)-indium(III) was purchased from Tokyo Kasei Co. and purified by vacuum sublimation. The purity of those chelates was confirmed by elemental analysis, melting-point measurements, and ^1H NMR.

A gallium(III) and an indium(III) stock solution were prepared by dissolving their high purity (99.99%)

metals with dilute hydrochloric acid, evaporating to dryness, heating after the addition of a small amount of perchloric acid, and then dissolving with dilute perchloric acid. A phthalate pH standard solution and a phosphate pH standard equimolar solution were obtained from Wako Pure Chemical Industries, Ltd. All other reagents were the same as those used previously.²

Procedure

An aqueous solution of 5×10^{-5} – 2×10^{-4} M (1 M = 1 mol dm⁻³) metal(III) was shaken with an equal volume of an organic solution of 1×10^{-2} – 2×10^{-1} M Hacac or a mixture of 1×10^{-2} M Hacac and 3×10^{-4} – 1×10^{-1} M DCP for 3 – 22 h at $25 \pm 0.5^\circ\text{C}$. After centrifugation, the equilibrium concentration of metal(III) in the aqueous phase was determined by ICP-AES. To determine the metal(III) concentration in the organic phase, an aliquot of it was separated and shaken with 0.5 M perchloric acid. The metal(III) stripped was determined by ICP-AES. The distribution ratio of metal(III) was calculated as the ratio of the metal(III) concentration in the organic phase to that in the aqueous phase. The pH of the aqueous phase was measured with a glass electrode just after phase separation. The ionic strength was maintained at 0.10 M with sodium perchlorate.

IR and ¹H NMR spectra of 1×10^{-2} M DCP in the presence (4×10^{-3} – 1×10^{-1} M) or absence of the metal(III) chelates in carbon tetrachloride were measured with an FT-IR spectrophotometer (Shimadzu FTIR-8200A) with a demountable cell having CaF₂ windows and an FT-NMR spectrometer (JEOL GSX-400) respectively.

Equations

The distribution ratio (D_0) of M^{3+} in extraction with a chelating reagent (HA) can be expressed as follows:

$$D_0 = \frac{[MA_3]_{\text{org}}}{[M^{3+}] + \sum [MA_n^{3-n}]} = \frac{P_M \beta_3 [A^-]^3}{1 + \sum \beta_n [A^-]^n}, \quad (1)$$

where the subscript org denotes the organic phase, MA_3 the extractable metal(III) chelate, P_M the partition coefficient of MA_3 , and β_n the overall formation constant of MA_n^{3-n} in the aqueous phase. The equilibrium concentration of the anionic species, $[A^-]$, was calculated using

$$[A^-] = \frac{C_{\text{HA}}}{1 + [H^+](P_{\text{HA}} + 1)/K_{\text{HA}}}, \quad (2)$$

where C_{HA} , P_{HA} , and K_{HA} denote the total concentration, the partition coefficient, and the acid-dissociation constant for HA, respectively.

The extraction equilibrium of M^{3+} with HA is simply expressed as

The extraction constant (K_{ex}) is given by

$$K_{\text{ex}} = \frac{[MA_3]_{\text{org}}[H^+]^3}{[M^{3+}][HA]_{\text{org}}^3} = \frac{P_M \beta_3 K_{\text{HA}}^3}{P_{\text{HA}}^3}. \quad (4)$$

In the synergistic extraction of M^{3+} with HA and a hydrogen-bond donor (HD) the distribution ratio (D) can be given as

$$D = \frac{[MA_3]_{\text{org}} + \sum [MA_3 \cdot m(\text{HD})]_{\text{org}}}{[M^{3+}] + \sum [MA_n^{3-n}]} = \frac{P_M \beta_3 [A^-]^3 (1 + \sum \beta_{\text{ass},m} [\text{HD}]_{\text{org}}^m)}{1 + \sum \beta_n [A^-]^n}, \quad (5)$$

where $\beta_{\text{ass},m}$ is the overall formation constant of the outer-sphere complex, $MA_3 \cdot m(\text{HD})$, given in the following equilibrium:

Equations (1) and (5) provide the following equation:

$$D/D_0 = 1 + \sum \beta_{\text{ass},m} [\text{HD}]_{\text{org}}^m. \quad (7)$$

The synergistic extraction equilibrium and extraction constant are given as follows:

$$K_{\text{ex},s,m} = \frac{[MA_3 \cdot m(\text{HD})]_{\text{org}} [H^+]^3}{[M^{3+}] [HA]_{\text{org}}^3 [\text{HD}]_{\text{org}}^m} = K_{\text{ex}} \beta_{\text{ass},m}. \quad (9)$$

Results

Extraction with Hacac alone

The extraction of gallium(III) and indium(III) with Hacac in heptane was carried out to determine the equilibrium constants, such as the partition coefficient and the formation constant of the chelates, which are inevitable to elucidate the synergistic effect of DCP. Figure 1 shows plots for $\log D_0$ vs. the logarithmic value of the acac^- concentration, which was calculated by Eq. (2) using the following constants quoted: $\log P_{\text{HA}} = -0.052$ for heptane⁵ and $\log K_{\text{HA}} = -8.82$.⁶ The distribution ratio of each metal(III) increases with an increase in the acac^- concentration and approaches a limiting value which corresponds to the partition coefficient of $M(\text{acac})_3$. Since the distribution ratio of each metal(III) is a function of only the acac^- concentration which was adjusted by various combinations of different initial concentrations of Hacac and different pHs

Fig. 1 Distribution ratio of gallium(III) and indium(III) between heptane and 0.1 M NaClO₄ as a function of the acac⁻ concentration in the aqueous phase at pH 3–7. Total concentration of gallium(III), 5×10^{-5} – 1×10^{-4} M; total concentration of indium(III), 5×10^{-5} – 2×10^{-4} M. ■, 0.2 M Hacac; ●, 0.1 M Hacac; ◆, 0.03 M Hacac; ▲, 0.01 M Hacac.

(cf. Eq. (2)), it is concluded that the existence of hydroxo complexes of the metals(III) in the aqueous phase can be neglected under the given conditions.

The P_M and β_n values were computed by the least-squares fitting (SALS program, University of Tokyo) for the distribution data in Fig. 1 on the basis of Eq. (1). In this calculation no reliable value of β_1 for each metal(III) was obtained because the fraction of the $M(\text{acac})^{2+}$ species in the aqueous phase was very low under the experimental conditions; in the lower concentration region of acac⁻, the D_0 values were too low to be accurately determined. Regarding gallium(III) the P_M value in carbon tetrachloride was also determined by the least-squares fitting using the formation constants obtained in the heptane system and the partition coefficient of Hacac, $\log P_{\text{HA}} = 0.503$.⁷ The extraction constants were calculated using the P_M and β_3 values by Eq. (4), and are listed in Table 1 together with other equilibrium constants. The solid lines in Fig. 1 indicate the values computed using Eq. (1) and the equilibrium constants obtained, and well agree with the experimental plots. The formation constants in Table 1 are close to the literature values: $\log \beta_2 = 17.0$ and $\log \beta_3 = 22.5$ for gallium(III);⁸ $\log \beta_2 = 14.2$ for indium(III).⁸

Synergistic extraction with Hacac and DCP

The extraction of gallium(III) and indium(III) was

Fig. 2 Synergistic enhancement of the extraction of gallium(III) and indium(III) with 0.01 M Hacac in the presence of 0.05 M DCP in heptane. ● ○, Ga; ▲ △, In; a b, calculated values in 0.01 M Hacac alone; c d, calculated values in 0.01 M Hacac–0.05 M DCP.

carried out with 0.01 M Hacac in the presence or absence of DCP at varying pHs. Figure 2 shows a remarkable enhancement of the extraction of metals (III) by the addition of 0.05 M DCP. Gallium(III) and indium(III) are quantitatively extracted in the lower pH region using a mixture of Hacac and DCP in heptane although the extraction with Hacac alone is greatly depressed, even at relatively higher pH. It can be expected that the present synergism will make it possible to use a simple extractant, like Hacac, and the inert solvent of alkane in practical applications.

A synergistic enhancement of the distribution ratio of metal(III) can be expressed by Eq. (7) as a function of the DCP concentration in the organic phase. According to this equation, the formation constant of outer-sphere complexes can be determined by a least-squares fitting of plots of $\log(D/D_0)$ vs. $\log[\text{DCP}]_{\text{org}}$. The D_0 value is calculated by Eq.(1) using the equilibrium constants determined above, the total Hacac concentration, and the pH. However, since an association between Hacac and DCP also occurs in the organic phase, the equilibrium concentrations of free Hacac and DCP in the organic phase must be calculated by solving the following simultaneous equations derived from the mass balance for Hacac and DCP in both phases:

Table 1 Equilibrium constants in the extraction of gallium(III) and indium(III) with Hacac

Metal(III)	Solvent	$\log P_M$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log K_{\text{ex}}$
Ga	heptane	-0.45 ± 0.01	9.0 ^a	17.05 ± 0.04	23.01 ± 0.03	-3.74
	CCl ₄	1.88 ± 0.05	9.0 ^a	17.05^b	23.01^b	-3.08
In	heptane	0.85 ± 0.02	7.5 ^a	13.90 ± 0.04	18.93 ± 0.03	-6.55

a. Ref. 8. b. Used for the calculation of P_M .

$$C_{\text{Hacac}} = \{1 + (1 + K_{\text{HA}}/[\text{H}^+])/P_{\text{HA}} + \beta_{\text{ass,H,1}}[\text{DCP}]_{\text{org}} + \beta_{\text{ass,H,2}}[\text{DCP}]_{\text{org}}^2\}[\text{Hacac}]_{\text{org}}, \quad (10)$$

$$C_{\text{DCP}} = \{1 + (1 + K_{\text{DCP}}/[\text{H}^+])/P_{\text{DCP}} + \beta_{\text{ass,H,1}}[\text{Hacac}]_{\text{org}}\}[\text{DCP}]_{\text{org}} + 2\beta_{\text{ass,H,2}}[\text{Hacac}]_{\text{org}}[\text{DCP}]_{\text{org}}^2, \quad (11)$$

where C_{Hacac} and C_{DCP} stand for the total concentration of Hacac and DCP respectively; $\beta_{\text{ass,H},n}$ ($n=1,2$) is the association constant of $\text{Hacac} \cdot n(\text{DCP})$, and P_{DCP} and K_{DCP} are the partition coefficient and the acid-dissociation constant of DCP respectively. Those values used were as follows: $\log \beta_{\text{ass,H,1}}=1.42$, $\log \beta_{\text{ass,H,2}}=2.66$, and $\log P_{\text{DCP}}=0.42$ for heptane;⁴ $\log \beta_{\text{ass,H,1}}=1.34$, $\log \beta_{\text{ass,H,2}}=2.01$, and $\log P_{\text{DCP}}=1.06$ for carbon tetrachloride;⁹ $\log K_{\text{DCP}}=-8.18$.¹⁰

Figure 3 shows plots of $\log(D/D_0)$ vs. the logarithmic value of free DCP in heptane for both gallium(III) and indium(III). The plots for each metal(III) give a concave line and are asymptotic to a straight line with a slope of 3 in the higher DCP concentration region. This is attributed to the formation of three types of outer-sphere complexes, *i.e.*, $\text{M}(\text{acac})_3 \cdot \text{DCP}$, $\text{M}(\text{acac})_3 \cdot 2(\text{DCP})$, and $\text{M}(\text{acac})_3 \cdot 3(\text{DCP})$, in the organic phase. The formation constants were calculated by applying the least-squares fitting method based on Eq. (7) to the

Fig. 3 Synergistic enhancement of the distribution ratio of gallium(III) and indium(III) as a function of the equilibrium concentration of free DCP in heptane. Total concentration of Hacac, 0.01 M; total concentration of metal(III), 5×10^{-5} M.

plots in Fig. 3. Those equilibrium constants and the overall synergistic extraction constant ($K_{\text{ex,s,3}}$) calculated by Eq. (9) are listed in Table 2. Also, the formation constants for $\text{Ga}(\text{acac})_3 \cdot n(\text{DCP})$ in carbon tetrachloride were determined in the same manner and are tabulated there.

Spectroscopic studies of outer-sphere complexes

The IR absorption spectra of 0.01 M DCP in the presence of 0.01 M $\text{Ga}(\text{acac})_3$ or $\text{In}(\text{acac})_3$ provided experimental proof for hydrogen bonding between the hydroxyl group of DCP and the metal(III) chelates: 1) the sharp absorption at 3600 cm^{-1} due to the O-H stretching vibration of free DCP reduced by the addition of the chelates; 2) a broad absorption band which can be assigned to the vibration of hydrogen-bonded O-H appeared in the lower wavenumber region ($3200 - 3500 \text{ cm}^{-1}$) in the presence of the chelates. Additionally, since the decrease in the absorbance at 3600 cm^{-1} for free DCP caused by the gallium(III) chelate was greater than that by the indium(III) chelate, it was anticipated that the former is a stronger hydrogen-bond acceptor than the latter.

Since the concentration of free DCP in the presence of the metal(III) chelate can be readily determined from the absorbance at 3600 cm^{-1} , the formation constant of outer-sphere complexes can be calculated by the following equation derived from the mass balance for DCP and the chelate:

$$\frac{C_{\text{DCP}} - [\text{DCP}]}{C_{\text{M}(\text{acac})_3}} = \frac{\beta_{\text{ass,1}}[\text{DCP}] + 2\beta_{\text{ass,2}}[\text{DCP}]^2 + 3\beta_{\text{ass,3}}[\text{DCP}]^3}{1 + \beta_{\text{ass,1}}[\text{DCP}] + \beta_{\text{ass,2}}[\text{DCP}]^2 + \beta_{\text{ass,3}}[\text{DCP}]^3}, \quad (12)$$

where $C_{\text{M}(\text{acac})_3}$ is the total concentration of the chelate. In Fig. 4, the left-hand side of Eq. (12), which gives the average molar ratio of the hydrogen-bonded DCP to the chelate added, is plotted against the concentration of free DCP in carbon tetrachloride. The formation constants of $\beta_{\text{ass,1}}$ and $\beta_{\text{ass,2}}$ were obtained by a least-squares fitting, while the reasonable values for $\beta_{\text{ass,3}}$ were not in the both cases because of the low fraction of the $\text{M}(\text{acac})_3 \cdot 3(\text{DCP})$ species in solutions prepared under the given experimental conditions. The obtained $\beta_{\text{ass,1}}$ and $\beta_{\text{ass,2}}$ values are listed in Table 2 and compared with those obtained by the extraction method in the Ga(III) case. The values obtained by both methods are reasonably close to each other.

The ^1H NMR spectra of 0.01 M DCP in carbon tetra-

Table 2 Formation constants of outer-sphere complexes of $\text{Ga}(\text{acac})_3$ and $\text{In}(\text{acac})_3$ with DCP

Metal(III)	Solvent	$\log \beta_{\text{ass,1}}$	$\log \beta_{\text{ass,2}}$	$\log \beta_{\text{ass,3}}$	$\log K_{\text{ex,s,3}}$
Ga	heptane ^a	3.61 ± 0.03	5.95 ± 0.04	7.87 ± 0.02	4.13
	CCl_4^{a}	2.73 ± 0.02	4.53 ± 0.04	5.92 ± 0.04	2.84
	CCl_4^{b}	2.88 ± 0.04	4.61 ± 0.07	Nd ^c	—
In	heptane ^a	3.09 ± 0.06	5.26 ± 0.13	7.20 ± 0.06	0.65
	CCl_4^{b}	2.45 ± 0.09	4.24 ± 0.12	Nd ^c	—

a. Extraction method. b. IR spectrophotometry. c. Not determined.

Fig. 4 Molar ratio of the hydrogen-bonded DCP to the chelate as a function of the equilibrium concentration of free DCP in carbon tetrachloride.

Fig. 5 Chemical shift of the hydroxyl proton of DCP (0.01 M) as a function of the molar ratio of $\text{Ga}(\text{acac})_3$ or $\text{In}(\text{acac})_3$ to DCP in carbon tetrachloride.

chloride were measured in the presence of varying quantities of the gallium(III) or indium(III) chelate. As shown in Fig. 5, the resonance of the hydroxyl proton of free DCP observed at 4.6 ppm shifts to a lower magnetic field along with an increase in the chelate concentration, and reaches to a limiting value (7.9 ppm). This phenomenon can be ascribed to the formation of hydrogen bonding between the diamagnetic metal(III) chelates and DCP through its hydroxyl hydrogen atom as well as a fast exchange between free DCP and the hydrogen-bonded DCP in the solution on the NMR time scale. If the chemical shift of the hydroxyl proton is given as the weighted averages for the resonance of free and hydrogen-bonded DCP, one can predict the shift by knowing the fraction of the outer-sphere com-

Fig. 6 Correlation between the first formation constant of outer-sphere complexes and the oxygen-oxygen nonbonded distance of $\text{M}(\text{acac})_3$.

plexes, which can be readily calculated from the formation constants obtained by IR and assuming the chemical shift for the hydrogen-bonded DCP to be 7.9 ppm. The solid lines shown in Fig. 5 are the calculated values and well agree with the experimental results for both of the metal(III) chelates.

Discussion

Hydrogen-bond accepting power of the metal(III) chelates

The formation constants of the outer-sphere complexes of $\text{M}(\text{acac})_3$ with DCP for gallium(III) and indium(III) were compared with those for aluminium(III)² and other metals(III)^{3,4,11,12} reported so far. The formation constants depend on the central metal ions and are related to the geometry of the chelates; *e.g.*, the ionic radius of the central metal, the metal-oxygen distance, and especially the oxygen-oxygen distance. In Fig. 6, $\log \beta_{\text{ass},1}$ is plotted against the oxygen-oxygen nonbonded distance in the chelates.¹³⁻¹⁷ A good correlation is found for various $\text{M}(\text{acac})_3$ including main-group metals(III) such as aluminium(III), gallium(III), and indium(III) as well as such transition metals(III) as scandium(III), chromium(III), iron(III), and cobalt(III). Therefore, the electron configurations or the electronegativity of the central metals(III) are not a factor governing the hydrogen-bond accepting power of the chelates. If the hydrogen bond between $\text{M}(\text{acac})_3$ and DCP is formed through the coordinated oxygen atoms on an open octahedral face (a plane triangle) perpendicular to the C_3 axis of $\text{M}(\text{acac})_3$, the oxygen-oxygen nonbonded distance among the three oxygen atoms on the face may be associated with the hydrogen-bond accepting power of the chelates. Namely, the proximity of the three nonbonded oxygen

Table 3 Separation factors for aluminium(III), gallium(III), and indium(III)

M ₁ /M ₂	log α_0^a	log α_s^b
Ga/Al	1.84	2.06
Ga/In	2.81	3.48
Al/In	0.97	1.42

a. $\alpha_0 = K_{\text{ex}}(M_1)/K_{\text{ex}}(M_2)$ in Hacac-heptane,

b. $\alpha_s = K_{\text{ex},s,3}(M_1)/K_{\text{ex},s,3}(M_2)$ in Hacac-DCP-heptane.

atoms probably results in an increase in the negative charge density on the face or the shielding of the positive charge on the central metal(III).

The similar correlation was also found for $\beta_{\text{ass},2}$ and $\beta_{\text{ass},3}$ except for the aluminium(III) chelate. The $\beta_{\text{ass},3}$ value of aluminium(III)², $10^{7.65}$, was lower than that of gallium(III), $10^{7.87}$, while the $\beta_{\text{ass},1}$ and $\beta_{\text{ass},2}$ values of the former were almost the same as those of the latter. This difference in $\beta_{\text{ass},3}$ may be ascribed to the structure of the outer-sphere complexes. As described above, if hydrogen bonding occurs between the hydroxyl hydrogen atom of DCP and the oxygen atoms on an open octahedral face of the chelate, two molecules of DCP can occupy either of the two faces, respectively. When the third DCP forms hydrogen bonding, however, the two molecules of DCP must together occupy the either face. In the aluminium(III) chelate having a shorter oxygen-oxygen distance or a narrower face, a steric repulsion may severely occur between the two DCP molecules on one octahedral face. Such a steric effect on outer-sphere complexation is an important factor which affects the selectivity in the present synergistic extraction, as described below.

Improvement of separation efficiency by synergism

The separation factors (α) between two metals(III) of aluminium(III), gallium(III), and indium(III) in the presence or absence of DCP are calculated from the extraction constants ($K_{\text{ex},s,3}$ or K_{ex}) for the corresponding metals(III), and are listed in Table 3. In any combination of metals(III), the separation factors in the presence of DCP are larger than those in its absence. Therefore, the present synergism improves not only the extraction efficiency but also the separation efficiency of those metals(III). This favorable result is derived from the fact that both K_{ex} and $\beta_{\text{ass},3}$ increase in the same order, $\text{In} < \text{Al} < \text{Ga}$, and can be associated with the stability of both metal(III) chelates and outer-sphere complexes. Figure 7 shows the relationship between the formation constant of $\text{M}(\text{acac})_3$ in the aqueous phase and that of $\text{M}(\text{acac})_3 \cdot 3(\text{DCP})$ in the organic phase. A linear free energy relationship is found for aluminium(III), gallium(III), and indium(III). There seems to be a similar correlation for the first transition metals(III), even though only the data for scandium(III) and iron(III) are presently available.

Fig. 7 Relationship between the formation constant of $\text{M}(\text{acac})_3$ and that of the outer-sphere complexes.

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