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Steric Effect of 3,5-Bis(trifluoromethyl)phenol as Hydrogen-Bond Donor on Outer-Sphere Complexation in the Synergistic Extraction of Aluminium(III) and Gallium(III) with 2,4-Pentanedione

Hisanori Imura,* Tatsunori Namai, Ken-ichiro Ishimori, Sumiko Hayashi,
Akira Ohashi, and Kousaburo Ohashi

Department of Environmental Sciences, Faculty of Science, Ibaraki University, Mito 310-8512

Received May 13, 2005; E-mail: imura@mx.ibaraki.ac.jp

The synergistic extraction of aluminium(III) and gallium(III) with 2,4-pentanedione (Hacac) in heptane from a weakly acidic solution was investigated in the presence of 3,5-bis(trifluoromethyl)phenol (BTMP). A large enhancement of the extraction of metal(III) was ascribed to the formation of outer-sphere complexes between metal(III) chelates and BTMP in the organic phase. Furthermore, an IR study demonstrated that the outer-sphere complexes were formed by the hydrogen bond between the hydroxy hydrogen atom of BTMP and the oxygen atoms of metal(III) chelates. The formation constants of the outer-sphere complexes with BTMP were determined and compared with those with 3,5-dichlorophenol (DCP) to understand the steric effect of the phenol derivative in this synergistic extraction. The bulky trifluoromethyl-group of BTMP and the short oxygen–oxygen nonbonded distance of $Al(acac)_3$ resulted in a steric repulsion between two BTMP molecules to prevent the formation of $Al(acac)_3 \cdot 3BTMP$, although $Al(acac)_3 \cdot 3DCP$, $Ga(acac)_3 \cdot 3BTMP$, and $Ga(acac)_3 \cdot 3DCP$ could be formed. Such a steric effect on outer-sphere complexation improves the separation efficiency between aluminium(III) and gallium(III) in the present synergistic extraction.

Extensive studies on the synergistic extraction of metal ions have been carried out using various acidic chelating extractants and neutral organic ligands as the synergist.[1] The conventional synergism is mostly explained by a replacement of water molecules of the coordinately unsaturated metal chelates with neutral organic ligands, such as pyridine, 1,10-phenanthroline, trioctylphosphine oxide, tributyl phosphate, and so on.[2]

On the other hand, we found a novel synergism for coordinately saturated chelates with chlorinated phenols as the synergist.[3–7] This synergism was explained by the formation of outer-sphere complexes through hydrogen bonding between metal chelates and chlorinated phenols in the organic phase. It was also shown that the magnitude of the synergistic effect of the chlorinated phenols depends on the central metals[8,9] and the acidity of the hydroxy group of the phenols.[5,10]

In our previous studies on the outer-sphere complexation of tris(2,4-pentanedionato)-aluminium(III) ($Al(acac)_3$)[8] and -gallium(III) ($Ga(acac)_3$)[9] with 3,5-dichlorophenol (DCP), the formation constant of the outer-sphere complex, $Al(acac)_3 \cdot 3DCP$, was lower than that of $Ga(acac)_3 \cdot 3DCP$, although each formation constant of $Al(acac)_3 \cdot DCP$ and $Al(acac)_3 \cdot 2DCP$ was almost the same as that of $Ga(acac)_3 \cdot DCP$ and $Ga(acac)_3 \cdot 2DCP$. This result suggests a steric effect of DCP on the formation of the higher outer-sphere complexes.

In the present study, the synergistic extraction of aluminium(III) and gallium(III) with 2,4-pentanedione (Hacac) in the presence of 3,5-bis(trifluoromethyl)phenol (BTMP) in heptane was investigated to obtain a detailed understanding of the synergism with phenols. BTMP was selected to understand the effect of both the acidity and the steric hindrance of phenols on synergistic extraction, since BTMP has two bulky trifluoromethyl groups with a strong electron-withdrawing property. The composition and formation constant of the outer-sphere complexes of the metal(III) chelates with BTMP were determined by an extraction equilibrium analysis. Furthermore, IR spectroscopy was applied to ascertain that the formation of outer-sphere complexes is due to hydrogen bonding between the metal(III) chelate and BTMP. The steric effect of BTMP on outer-sphere complexation as well as on the separation of the metals(III) was discussed, compared with that of DCP.

Experimental

Reagents. Gallium(III) and aluminium(III) perchlorate solutions were prepared by evaporating the respective standard solutions (AAS grade, Wako Pure Chem.) in the presence of perchloric acid and dissolving in dilute perchloric acid solutions. Hacac (>99%, Aldrich), BTMP (>96%, Tokyo Kasei Co.), and heptane (HPLC grade, Kishida Chemical) were used as obtained. Carbon tetrachloride (HPLC grade, Wako Pure Chem.) used for IR measurements was dried with molecular sieves (A-3, Wako Pure Chem.).

$Ga(acac)_3$ was synthesized from gallium(III) nitrate (99.9%, Wako Pure Chem.) and purified by recrystallization from benzene–diethyl ether and vacuum sublimation at 403 K. $Al(acac)_3$ was obtained from Dojindo Laboratories and purified by vacuum sublimation at 403 K.

Water was distilled, demineralized with a Mega-Pure system (Corning), and further purified with a Milli-Q equipment (Millipore) just before use. All other chemicals were of analytical reagent grade and were used without further purification.

Apparatus. The metal concentration in an aqueous phase was determined by an inductively coupled plasma atomic-emission spectrophotometer (ICP-AES, Nippon Jarrell-Ash ICAP-575).

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The concentration of Hacac in heptane in the presence of BTMP was determined by a capillary gas chromatograph (GC, Hewlett-Packard HP-6890) equipped with a fused-silica capillary column (J&W Scientific DB-1, 0.53 mm i.d. × 15 m, 1.5 µm thickness) and an FID detector. The IR spectrum of BTMP in the presence or absence of metal(III) chelates was measured by an FT-IR spectrophotometer (Shimadzu FTIR-8200A) with a demountable cell having calcium fluoride windows, of which the path length was adjusted to 1 mm. The UV–vis spectrum was measured with a JASCO 560 spectrophotometer. The pH measurements were performed by a Radiometer PHM93 pH meter equipped with a combination glass electrode. All of the experiments were carried out in a thermostated room at 298 K.

Determination of the Distribution Constant of BTMP. A heptane solution of 3.5×10^{-4} mol dm^{-3} BTMP was shaken with a 0.10 mol dm^{-3} sodium perchlorate solution at pH 1.0 to 9.7 for 1 h. After centrifugation, the pH value was measured with a pH meter, and the absorbance of the heptane phase was measured at 278.2 nm to obtain the distribution ratio of BTMP.

Determination of the Association Constant of Hacac with BTMP. A heptane solution containing $(1.00\text{–}2.37) \times 10^{-3}$ mol dm^{-3} Hacac and $(0.51\text{–}8.97) \times 10^{-2}$ mol dm^{-3} BTMP was shaken with a 0.10 mol dm^{-3} sodium perchlorate solution at pH 2.7 for 1 h. After phase separation, 2×10^{-3} mol dm^{-3} *o*-dichlorobenzene as an internal standard was added to the heptane phase, and then the equilibrium concentration of Hacac in heptane was determined with a GC. The equilibrium concentration of Hacac in the aqueous phase was calculated from the Hacac concentration in the organic phase and the initial one. The distribution ratio of Hacac in the presence or absence of BTMP was calculated from the Hacac concentrations in both organic and aqueous phases.

Extraction of Metals(III). An aqueous solution of 5.0×10^{-5} mol dm^{-3} metal(III) and a heptane solution containing $(0.98\text{–}5.1) \times 10^{-3}$ mol dm^{-3} Hacac and $2.0 \times 10^{-4}\text{–}8.2 \times 10^{-2}$ mol dm^{-3} BTMP were placed in an extraction vial with a screw cap, and then shaken for 3–6 h. After phase separation, the pH and the metal concentration in the aqueous phase were determined. For determining the metal(III) concentration in the organic phase, the obtained organic phase was shaken with 0.5 mol dm^{-3} perchloric acid for 1 h to back-extract metal(III) extracted, and then the resulting aqueous solution was analyzed with an ICP-AES. The distribution ratio of metal(III) was calculated as the ratio of the metal(III) concentrations in both phases. The ionic strength was kept at 0.10 mol dm^{-3} with sodium perchlorate.

IR Measurement. The IR spectra of $(1.2\text{–}3.1) \times 10^{-2}$ mol dm^{-3} BTMP in the absence and presence of $2.8 \times 10^{-4}\text{–}5.1 \times 10^{-2}$ mol dm^{-3} metal(III) chelates in carbon tetrachloride were measured. To avoid moisture contamination, samples were prepared in a glove box using diphosphorus pentaoxide as a desiccant.

Results and Discussion

Distribution Constant of BTMP between Heptane and Water. The distribution ratio of BTMP, D_{BTMP}, was obtained from the following equations:

$$D_{\mathrm{BTMP}} = \frac{[\mathrm{BTMP}]_{\mathrm{org}}}{[\mathrm{BTMP}]_{\mathrm{aq}} + [\mathrm{BTMP}^-]_{\mathrm{aq}}} = \frac{A_{\mathrm{org,f}}}{A_{\mathrm{org,init}} - A_{\mathrm{org,f}}} \cdot \frac{V_{\mathrm{aq}}}{V_{\mathrm{org}}}, \tag{1}$$

Table 1. Distribution and Acid-Dissociation Constant of BTMP and Association Constant of Hacac with BTMP in the Heptane–Water System

Hydrogen-bond donor	$\log K_{\mathrm{d,s}}$	$\mathrm{p}K_{\mathrm{a,s}}$	$\log \beta_{\mathrm{ass,R,1}}$	$\log \beta_{\mathrm{ass,R,2}}$
BTMP	0.93 ± 0.01	7.65 ± 0.03	1.80 ± 0.07	2.68 ± 0.21
DCP	0.42[b]	8.18[a]	1.42[b]	2.66[b]

a) Ref. 11. b) Ref. 12.

where BTMP^- denotes the anionic (phenolate) form of BTMP, *A* and *V* denote the absorbance and volume, respectively, and the subscripts org, aq, init, and f refer to the organic phase, aqueous phase, initial, and final, respectively. The D_{BTMP} value is expressed by the distribution constant of BTMP ($K_{\mathrm{d,s}}$), defined as $K_{\mathrm{d,s}} = [\mathrm{BTMP}]_{\mathrm{org}}/[\mathrm{BTMP}]_{\mathrm{aq}}$, and the acid-dissociation constant of BTMP ($K_{\mathrm{a,s}}$) as follows:

$$\log D_{\mathrm{BTMP}} = \log K_{\mathrm{d,s}} - \log\left(1 + \frac{K_{\mathrm{a,s}}}{[\mathrm{H}^+]}\right), \tag{2}$$

where the hydrogen-ion concentration in the aqueous phase was calculated from the pH value measured and the activity coefficient, which was calculated by the Debye–Hückel equation as 0.83 at $I = 0.10$. The values of $K_{\mathrm{d,s}}$ and $K_{\mathrm{a,s}}$ were obtained by analyzing plots of $\log D_{\mathrm{BTMP}}$ vs $-\log[\mathrm{H}^+]$ based on Eq. 2, and are listed in Table 1 together with those of DCP for a comparison.[11,12] The $K_{\mathrm{d,s}}$ and $K_{\mathrm{a,s}}$ values of BTMP are larger than those of DCP because of the more hydrophobic and stronger electron-withdrawing properties of trifluoromethyl groups of BTMP.

Association Constant of Hacac with BTMP. Since Hacac and BTMP have a property of proton-accepter and proton-donor, respectively, the association between Hacac and BTMP should occur in the organic phase. This results in a decrease in the equilibrium concentration of free Hacac and BTMP in both phases. Therefore, the association equilibrium of those reagents must be clarified in order to carry out an equilibrium analysis of the synergistic extraction of metal(III). The association between Hacac and BTMP in an organic phase can be expressed as follows:

$$\mathrm{Hacac_{org}} + x\mathrm{BTMP_{org}} \rightleftharpoons \mathrm{Hacac}\cdot x\mathrm{BTMP_{org}}, \tag{3}$$

$$\beta_{\mathrm{ass,R},x} = \frac{[\mathrm{Hacac}\cdot x\mathrm{BTMP}]_{\mathrm{org}}}{[\mathrm{Hacac}]_{\mathrm{org}}[\mathrm{BTMP}]^x_{\mathrm{org}}}, \tag{4}$$

where $\mathrm{Hacac}\cdot x\mathrm{BTMP_{org}}$ denotes the association complex formed in the organic phase. The enhancement of distribution ratio of Hacac with BTMP is related to the association constant and the equilibrium concentration of BTMP in the organic phase,

$$D_{\mathrm{HA}}/D_{\mathrm{HA,0}} = 1 + \Sigma\beta_{\mathrm{ass,R},x}[\mathrm{BTMP}]^x_{\mathrm{org}}, \tag{5}$$

where D_{HA} and $D_{\mathrm{HA,0}}$ denote the distribution ratio of Hacac in the presence and absence of BTMP, respectively. Figure 1 shows plots of $\log(D_{\mathrm{HA}}/D_{\mathrm{HA,0}})$ vs $\log[\mathrm{BTMP}]_{\mathrm{org}}$. The slope of the plot tends to be over unity in the higher BTMP concentration region. This suggests that Hacac formed not only a 1:1, but a 1:2 association-complex with BTMP in heptane, as observed in the Hacac-DCP case. The $\beta_{\mathrm{ass,R},x}$ values were calculated by a nonlinear least-squares fitting based on Eq. 5, and are listed in Table 1 together with those of DCP.[12]

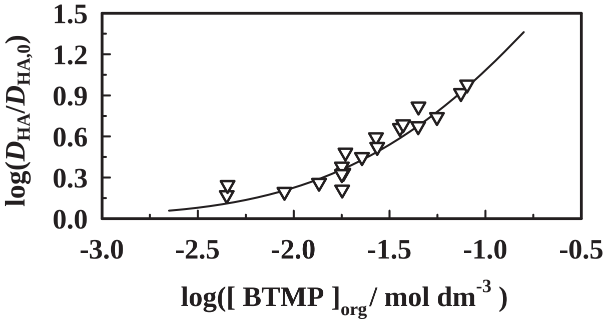

Fig. 1. Enhancement of the distribution ratio of Hacac as a function of the equilibrium concentration of BTMP in heptane. Hacac, (1.0–2.4) × 10^{-3} mol dm^{-3}; BTMP, (0.51–9.0) × 10^{-2} mol dm^{-3}; NaClO$_4$, 0.10 mol dm^{-3}; pH 2.7.

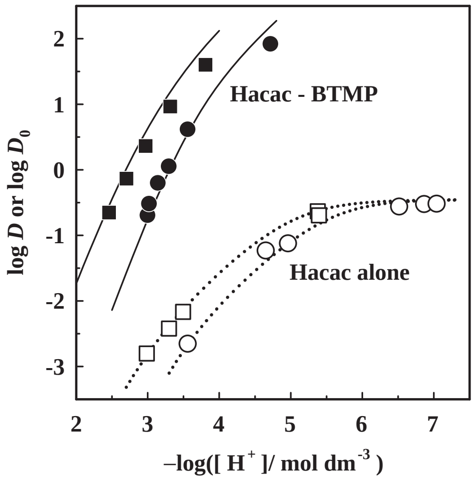

Fig. 2. Extraction of aluminium(III) and gallium(III) with 1.0 × 10^{-2} mol dm^{-3} Hacac in the presence or absence of 5.0 × 10^{-2} mol dm^{-3} BTMP in heptane. Al(III) (○, ●), Ga(III) (□, ■); metal(III) concentration, 5.0 × 10^{-5} mol dm^{-3}; NaClO$_4$, 0.10 mol dm^{-3}.

Synergistic Extraction of Metal(III) with Hacac and BTMP. Figure 2 shows the extraction of aluminium(III) and gallium(III) with Hacac in heptane in the presence and absence of BTMP. The extractability of aluminium(III) and gallium(III) with Hacac alone at even higher pH values is rather low, indicating that the extracted M(acac)$_3$ is less hydrophobic. On the other hand, each metal(III) was quantitatively extracted in the lower pH region after the addition of BTMP. A similar synergistic effect of DCP on the extraction of aluminium(III)[8] and gallium(III)[9] with Hacac was previously found. The remarkably large synergistic effect observed here should be ascribed to the formation of a hydrophobic outer-sphere complex between M(acac)$_3$ and BTMP through a hydrogen bond in heptane. To quantitatively evaluate outer-sphere complexation, the following equilibrium analysis was carried out:

The extraction equilibrium of M^{3+} with Hacac can be expressed as

$$\mathrm{M}^{3+} + 3\mathrm{Hacac}_{\mathrm{org}} \rightleftharpoons \mathrm{M(acac)}_{3,\mathrm{org}} + 3\mathrm{H}^+. \tag{6}$$

The distribution ratio of M^{3+}, D_0, is expressed as

$$D_0 = \frac{[\mathrm{M(acac)_3}]_{\mathrm{org}}}{[\mathrm{M}^{3+}] + \Sigma[\mathrm{M(acac)}_n{}^{3-n}]} = \frac{K_{\mathrm{d,M}}\beta_3[\mathrm{acac}^-]^3}{1 + \Sigma\beta_n[\mathrm{acac}^-]^n}, \tag{7}$$

where $K_{\mathrm{d,M}}$ and β_n denote the distribution constant of M(acac)$_3$ and the overall formation constant of M(acac)$_n{}^{3-n}$ in the aqueous phase, respectively. The values of these constants based on the hydrogen-ion activity had already been obtained for aluminium(III)[8] and gallium(III),[9,13] and were recalculated using the hydrogen-ion concentration at $I = 0.10$ as: $\log K_{\mathrm{d,M}} = -0.45 \pm 0.01$, $\log\beta_1 = 8.10 \pm 0.12$, $\log\beta_2 = 15.85 \pm 0.05$, and $\log\beta_3 = 21.42 \pm 0.06$ for aluminium(III); $\log K_{\mathrm{d,M}} = -0.46 \pm 0.01$, $\log\beta_1 = 9.0$,[13] $\log\beta_2 = 17.15 \pm 0.05$, and $\log\beta_3 = 23.19 \pm 0.04$ for gallium(III). The equilibrium concentration of the anionic species, [acac$^-$], can be calculated using the concentration quotients of the distribution constant, $K_{\mathrm{d,HA}}$ ($10^{-0.052}$ for heptane),[14] and the acid-dissociation constant, $K_{\mathrm{a,HA}}$ ($10^{-8.82}$),[15] of Hacac. The broken lines in Fig. 2 are the calculated values from Eq. 7 using the values of these constants. They agree well with the present experimental plots.

In the synergistic extraction of M^{3+} with Hacac and BTMP, the distribution ratio of M^{3+}, D, is given by

$$D = \frac{[\mathrm{M(acac)_3}]_{\mathrm{org}} + \Sigma[\mathrm{M(acac)_3}\cdot m\mathrm{BTMP}]_{\mathrm{org}}}{[\mathrm{M}^{3+}] + \Sigma[\mathrm{M(acac)}_n{}^{3-n}]} = \frac{K_{\mathrm{d,M}}\beta_3[\mathrm{acac}^-]^3(1 + \Sigma\beta_{\mathrm{ass},m}[\mathrm{BTMP}]^m_{\mathrm{org}})}{1 + \Sigma\beta_n[\mathrm{acac}^-]^n}, \tag{8}$$

where $\beta_{\mathrm{ass},m}$ is the overall formation constant of the outer-sphere complex, M(acac)$_3$$\cdot m$BTMP, given in the following equilibrium:

$$\mathrm{M(acac)}_{3,\mathrm{org}} + m\mathrm{BTMP}_{\mathrm{org}} \rightleftharpoons \mathrm{M(acac)_3}\cdot m\mathrm{BTMP}_{\mathrm{org}}. \tag{9}$$

Dividing Eq. 8 by Eq. 7, the following equation is derived:

$$(D/D_0) = 1 + \Sigma\beta_{\mathrm{ass},m}[\mathrm{BTMP}]^m_{\mathrm{org}}. \tag{10}$$

Therefore, the synergistic enhancement of the distribution ratio of metal(III) is expressed as a function of the BTMP concentration in the heptane phase. According to Eq. 10, the formation constant of outer-sphere complexes can be calculated by a non-linear least-squares method for the plots of log(D/D_0) vs log[BTMP]$_{\mathrm{org}}$. However, since Hacac forms the association complexes with BTMP in heptane, as mentioned above, the equilibrium concentration of free Hacac and BTMP has to be calculated by solving the following simultaneous equations:

$$C_{\mathrm{HA}} = \left\{1 + \frac{1}{K_{\mathrm{d,HA}}}\left(1 + \frac{K_{\mathrm{a,HA}}}{[\mathrm{H}^+]}\right) + \beta_{\mathrm{ass,R,1}}[\mathrm{BTMP}]_{\mathrm{org}} + \beta_{\mathrm{ass,R,2}}[\mathrm{BTMP}]^2_{\mathrm{org}}\right\}[\mathrm{Hacac}]_{\mathrm{org}}, \tag{11}$$

$$C_{\mathrm{BTMP}} = \left\{1 + \frac{1}{K_{\mathrm{d,s}}}\left(1 + \frac{K_{\mathrm{a,s}}}{[\mathrm{H}^+]}\right) + \beta_{\mathrm{ass,R,1}}[\mathrm{Hacac}]_{\mathrm{org}} + 2\beta_{\mathrm{ass,R,2}}[\mathrm{Hacac}]_{\mathrm{org}}[\mathrm{BTMP}]_{\mathrm{org}}\right\}[\mathrm{BTMP}]_{\mathrm{org}}, \tag{12}$$

where C_{HA} and C_{BTMP} are the initial concentration of Hacac and BTMP, respectively.

Figure 3 shows plots of $\log(D/D_0)$ vs $\log[\mathrm{BTMP}]_{\mathrm{org}}$. The distribution ratios of aluminium(III) and gallium(III) increase with an increase in the BTMP concentration in both systems. The plots at higher BTMP concentrations in the aluminium(III) and gallium(III) system give straight lines with a slope of two and three, respectively. This suggests that aluminium(III) forms only two types of outer-sphere complexes, i.e., $\mathrm{Al(acac)_3 \cdot BTMP}$ and $\mathrm{Al(acac)_3 \cdot 2BTMP}$, in heptane under the given conditions, while gallium(III) forms three types of outer-sphere complexes from $\mathrm{Ga(acac)_3 \cdot BTMP}$ to $\mathrm{Ga(acac)_3 \cdot 3BTMP}$. The $\beta_{\mathrm{ass},m}$ values were calculated by a non-linear least-squares method based on Eq. 10 for the plots of $\log(D/D_0)$ vs $\log[\mathrm{BTMP}]_{\mathrm{org}}$, and listed in Table 2. The present result, especially for the composition of the outer-sphere complexes of $\mathrm{Al(acac)_3}$, is different from that obtained in the DCP system,[8] suggesting that the bulky substituent group, trifluoromethyl-group, of BTMP results in a steric hindrance upon the formation of outer-sphere hydrogen-bond complexes, as mentioned below. To confirm this result, IR spectroscopy was applied to study of the formation of hydrogen-bond complexes of $\mathrm{M(acac)_3}$ with BTMP.

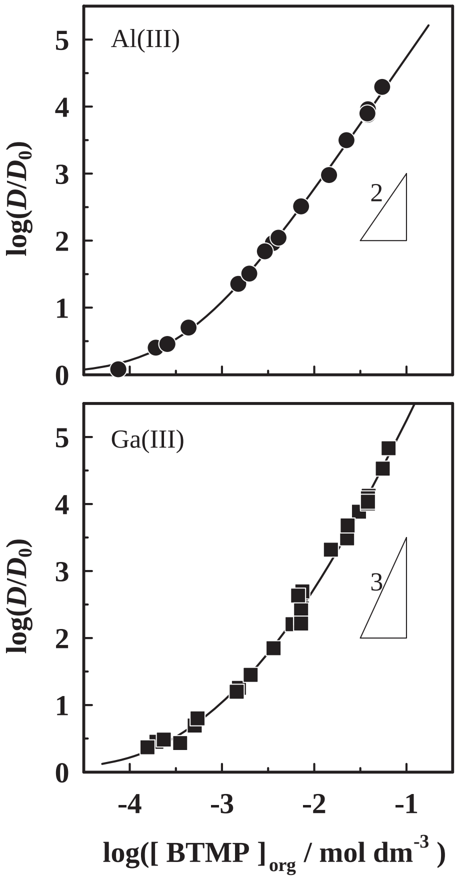

Fig. 3. Enhancement of the distribution ratio of metal(III) as a function of the equilibrium concentration of BTMP in heptane. Metal(III), 5.0×10^{-5} M; Hacac, $(0.98–5.1) \times 10^{-3}$ mol dm^{-3}; BTMP, 2.0×10^{-4}–8.2×10^{-2} mol dm^{-3}; $\mathrm{NaClO_4}$, 0.10 mol dm^{-3}; pH 2.65–4.86.

IR Study of Outer-Sphere Complexes. The IR absorption spectra of BTMP in the absence and presence of $\mathrm{M(acac)_3}$ in carbon tetrachloride were measured without Hacac. Figure 4 shows the spectral changes of BTMP with an increase in the concentration of $\mathrm{M(acac)_3}$. As the concentration of $\mathrm{M(acac)_3}$ becomes higher, the sharp absorption band at 3597 cm^{-1}, due to the O–H stretching vibration of free BTMP, reduced and a broad absorption band that can be assigned to the vibration of the hydrogen-bonded O–H appeared in the lower wavenumber region from 3500 to 3200 cm^{-1}.[16] The dimerization of BTMP was negligible in the concentration range of 0.002–0.032 mol dm^{-3}, since Lambert–Beer's law held well in that range. The molar absorptivity of BTMP at 3597 cm^{-1} was obtained as 2.37×10^2 dm^3 mol^{-1} cm^{-1}. The average binding number of BTMP to $\mathrm{M(acac)_3}$, $\bar{n}$, can be calculated by the following equation:

$$\bar{n} = (C_{\mathrm{BTMP}} - [\mathrm{BTMP}])/C_{\mathrm{MA3}}, \tag{13}$$

where C_{MA3} denotes the initial concentration of $\mathrm{M(acac)_3}$, and [BTMP] the free BTMP concentration at equilibrium. Figure 5 shows the logarithmic plots of $\bar{n}$ vs [BTMP] for different metal(III) chelate-BTMP systems. The concentration of free BTMP is readily determined from the IR spectra by knowing the molar absorptivity of BTMP at 3597 cm^{-1}. The $\bar{n}$ value for aluminium(III) approaches two in the higher equilibrium concentration of BTMP, while that for gallium(III) exceeds two. This result is quite consistent with that obtained in solvent extraction.

To determine the formation constants between $\mathrm{M(acac)_3}$ and BTMP by IR, the following equation was derived from the mass balances for $\mathrm{M(acac)_3}$ and BTMP:

Table 2. Formation Constants of Outer-Sphere Complexes of $\mathrm{M(acac)_3}$ with Phenols Determined by Solvent Extraction in Heptane and IR Spectroscopy in $\mathrm{CCl_4}$

Hydrogen-bond donor	Chelate	Solvent	$\log \beta_{\mathrm{ass},1}$	$\log \beta_{\mathrm{ass},2}$	$\log \beta_{\mathrm{ass},3}$
BTMP	$\mathrm{Al(acac)_3}$	heptane	3.77 ± 0.05	6.73 ± 0.02	n.o.[a]
BTMP	$\mathrm{Ga(acac)_3}$	heptane	3.80 ± 0.08	6.54 ± 0.08	8.15 ± 0.09
DCP[b]	$\mathrm{Al(acac)_3}$	heptane	3.60 ± 0.03	6.06 ± 0.04	7.65 ± 0.04
DCP[c]	$\mathrm{Ga(acac)_3}$	heptane	3.61 ± 0.03	5.95 ± 0.04	7.87 ± 0.02
BTMP	$\mathrm{Al(acac)_3}$	$\mathrm{CCl_4}$	3.11 ± 0.02	5.08 ± 0.02	n.o.[a]
BTMP	$\mathrm{Ga(acac)_3}$	$\mathrm{CCl_4}$	3.05 ± 0.02	4.95 ± 0.06	6.20 ± 0.11
DCP[b]	$\mathrm{Al(acac)_3}$	$\mathrm{CCl_4}$	2.86 ± 0.06	4.52 ± 0.13	5.93 ± 0.29

a) Not observed. b) Ref. 8. c) Ref. 9.

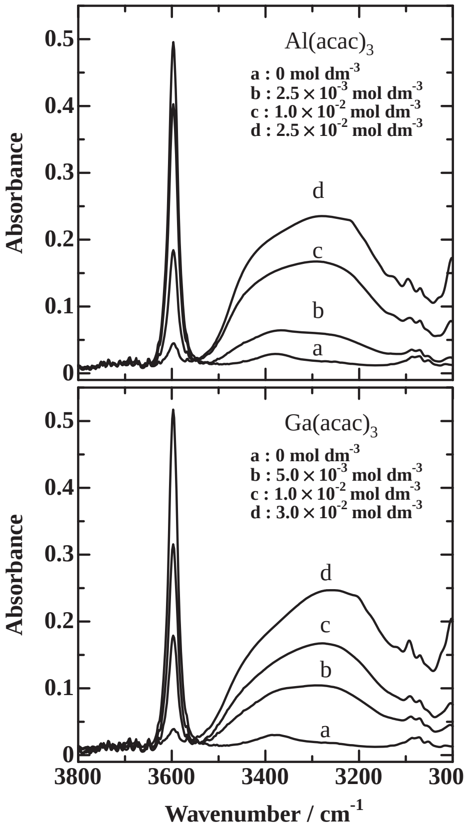

Fig. 4. IR absorption spectra of 0.020 mol dm^{-3} BTMP in the presence of M(acac)$_3$ in carbon tetrachloride.

$$\bar{n} = \frac{\sum_{m=1}^{2\text{ or }3} m\beta_{\text{ass},m}[\text{BTMP}]^m}{1+\sum_{m=1}^{2\text{ or }3}\beta_{\text{ass},m}[\text{BTMP}]^m}. \tag{14}$$

The formation constants, $\beta_{\text{ass},1}$ and $\beta_{\text{ass},2}$ for Al(acac)$_3$ and $\beta_{\text{ass},1}$ to $\beta_{\text{ass},3}$ for Ga(acac)$_3$, were determined by least-squares fittings, as shown in Fig. 5. The obtained values are summarized in Table 2 and compared with those obtained by the extraction method as well as in the DCP system.

A similar relation was found for the results obtained by the IR and extraction methods. The values of $\beta_{\text{ass},1}$ and $\beta_{\text{ass},2}$ for BTMP are higher than those for DCP, resulting from the higher acidity of the hydroxy group of BTMP as a hydrogen-bond donor. The formation of Al(acac)$_3$•3BTMP in the organic phase was not observed in both IR and extraction experiments. This is associated with the short oxygen–oxygen nonbonded distance of Al(acac)$_3$ as well as the bulky substituent of BTMP, i.e., the van der Waals volume of trifluoromethyl group is 34.0 Å^3 against the chloro group of 19.9 Å^3.[17] If the outer-sphere complex is formed by the hydrogen bond between the hydroxy hydrogen atom of BTMP and the oxygen atoms of acac on an open octahedral face of M(acac)$_3$, perpendicular to the C_3 axis, two molecules of BTMP occupy either of the two faces, respectively. When the third molecule of BTMP forms a hydrogen bond with M(acac)$_3$, however, the two molecules of BTMP have to occupy together either face. Since the oxygen–oxygen nonbonded distance on the open octahedral face of Al(acac)$_3$, 2.646 Å,[18] is shorter than that of Ga(acac)$_3$, 2.733 Å,[19] the outer-sphere coordination of two phenol molecules on one octahedral face of Al(acac)$_3$ is strerically hindered, while that of Ga(acac)$_3$ with a larger open octahedral face is allowed.

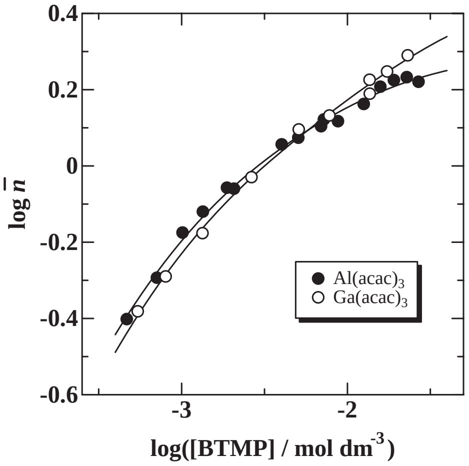

Fig. 5. Average binding number of BTMP to M(acac)$_3$ as a function of the free BTMP concentration at equilibrium. BTMP, (1.2–3.1) × 10^{-2} mol dm^{-3}; Al(acac)$_3$, 2.8 × 10^{-4}–5.1 × 10^{-2} mol dm^{-3}; Ga(acac)$_3$, 2.1 × 10^{-3}–5.0 × 10^{-2} mol dm^{-3}.

Steric Effect of the Hydrogen-Bond Donor on the Separation. The effect of BTMP on the extraction and separation efficiency of aluminium(III) and gallium(III) is demonstrated in Fig. 2. Although the extraction percentage of both metals(III) in Hacac alone was only 26% at the highest, those values of gallium(III) and aluminium(III) became 81 and 15%, respectively, in the presence of BTMP at pH 3.0. The separation factor ($D_{\text{Ga}}/D_{\text{Al}}$) between gallium(III) and aluminium(III) with 0.01 mol dm^{-3} Hacac and 0.1 mol dm^{-3} BTMP at pH 3.0 was calculated by Eq. 8 using the constants determined so far. The obtained value, $10^{1.8}$, is higher than $10^{0.9}$ in 0.01 mol dm^{-3} Hacac alone and $10^{1.4}$ in 0.01 mol dm^{-3} Hacac and 0.1 mol dm^{-3} DCP. The steric effect of the phenol as the synergist is an important factor on outer-sphere complexation, and improves the separation efficiency of metal ions in the present synergistic extraction.

Conclusion

The remarkable synergistic effect of BTMP on the extraction of aluminium(III) and gallium(III) with Hacac in heptane was found and ascribed to the outer-sphere complexation between M(acac)$_3$ and BTMP through a hydrogen bond. The formation constants of outer-sphere complexes of M(acac)$_3$ with BTMP were larger than those with DCP because of a higher acidity of the hydroxy group of BTMP than that of DCP. Moreover, it was found that the formation of a higher outer-sphere complex, Al(acac)$_3$•3BTMP, is prevented by the steric repulsion between two BTMP molecules due to the bulky trifluoromethyl-group of BTMP and the short oxygen–oxygen nonbonded distance of Al(acac)$_3$. Consequently, the present synergistic system improves not only the extractability of both aluminium(III) and gallium(III), but also the separation efficiency between them.

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