Ion-size recognition of Group 13 metals (Al³⁺, In³⁺) with modified β-diketones
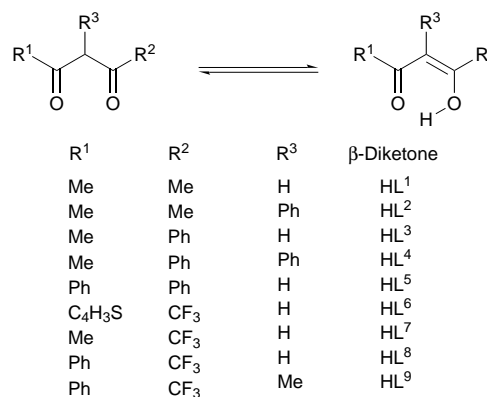
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Ion-size recognition of Group 13 metals (Al³⁺ and In³⁺) with modified β-diketones, 3-phenylpentane-2,4-dione (α-phenylacetylacetone, HL²) and 1,2-diphenylbutane-1,3-dione (α-phenylbenzoylacetone, HL⁴), has been studied by the liquid–liquid extraction method and compared with that of pentane-2,4-dione (acetylacetone, HL¹) and 1-phenylbutane-1,3-dione (benzoylacetone, HL³). While HL¹ and HL³ quantitatively extracted both ions, HL² and HL⁴ greatly discriminated Al³⁺ from In³⁺: Al³⁺ was readily extracted into benzene at a pH below 5, while In³⁺ was entirely unextractable, leading to an effective extraction separation of Al³⁺ from In³⁺. This could be ascribed to the large 'bite size' (O · · · O distance in the chelate ring) in the indium β-diketonates. The steric repulsions between the α-phenyl group and the terminal methyl or phenyl groups prevent HL² and HL⁴ from widening their bite size. In addition, the extraction of Al³⁺ was greatly influenced by the interligand contact due to its remarkably small ionic radius. The extraction order with HL¹ and HL³ is Al³⁺ > In³⁺ obeying the common tendency that the metal ion with a smaller ionic radius is more readily extracted, while that with ligands having bulky terminal groups, such as 1,3-diphenylpropane-1,3-dione (dibenzoylmethane, HL⁵), is the opposite. These steric factors have been evaluated by the investigation of the crystal structures of the complexes of Al³⁺ and In³⁺ and by molecular mechanics calculations. The steric factors have been confirmed through extraction behaviors with various kinds of β-diketones.

β-Diketones have been proven to be versatile ligands for various metal ions. A large number of studies have been done on these chelating reagents, especially in the field of solvent extraction of metal ions for the purpose of separation and concentration.[1–3] Recently, β-diketones have been examined in the disposal of radioactive waste using supercritical fluids,[4–7] in superconducting thin-film manufacturing[8,9] and as metal–organic chemical vapor deposition sources.[10,11] Much attention has also been paid to the structural chemistry of β-diketones involving keto–enol tautomerism and the intramolecular hydrogen bond.[12,13] However, there seems to be a lack of systematic studies on the correlation between the structure of β-diketones and their selectivity for metal ions.

Studies on the solvent extraction of metal ions with acylpyrazolones[14,15] and acylisoxazolones,[16] which are structurally analogous to β-diketones derived from five-membered heterocyclic compounds, revealed that the improved extraction with strongly acidic extractants is usually accompanied by poor selectivity. These compounds were found to have longer distances between the two donating oxygens as compared to the conventional β-diketones, such as acetylacetone and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (thenoyltrifluoroacetone), according to molecular orbital calculations. These facts prompted us to consider that the O · · · O distance plays an important role in complexing metal ions. Recently, on studying the extraction of lanthanides using 2-trifluoroacetylcycloalkanones[17] and acylpyrazolones having bulky substituents at the 4 position,[18] it was found that the separability of lanthanides was clearly improved with those ligands having the shorter O · · · O distance. It could be concluded that the O · · · O distance is one of the most significant factors that govern selectivity in the complexation of β-diketones with lanthanides. If the structure of the β-diketone could be suitably modified by introducing bulky groups at suitable positions to create a steric effect the O · · · O distance could be intentionally controlled, and, consequently, the extractability and/or the separability could be improved. Besides lanthanide ions with very similar ionic radii, we now expand our research to the metal ions of Group 13 having large differences in ionic radii in an attempt to investi-

R¹	R²	R³	β-Diketone
Me	Me	H	HL¹
Me	Me	Ph	HL²
Me	Ph	H	HL³
Me	Ph	Ph	HL⁴
Ph	Ph	H	HL⁵
C₄H₃S	CF₃	H	HL⁶
Me	CF₃	H	HL⁷
Ph	CF₃	H	HL⁸
Ph	CF₃	Me	HL⁹

gate how the O · · · O distance and other factors in the structure of β-diketones affect their complexation reactions.[19]

In the present paper the selectivity of modified β-diketones for Al³⁺ ($r = 0.53$ Å for a co-ordination number of six) and In³⁺ ($r = 0.80$ Å)[20] has been examined *via* the solvent-extraction method, and the stability of β-diketones of Al³⁺ and In³⁺ discussed by means of X-ray crystallographic studies and molecular mechanics calculations.

Experimental

Syntheses

α-Phenylbenzoylacetone (HL⁴). This compound was synthesized according to the literature[21] through the catalysed acylation of deoxybenzoin with acetic anhydride in the presence of boron trifluoride, followed by treatment with aqueous sodium acetate. To a rapidly stirred dichloromethane solution (200 cm³) of deoxybenzoin (2-phenylacetophenone) (0.3 mol) and acetic anhydride (0.6 mol) kept cold in an ice-bath, BF₃ (0.6 mol) was slowly added and the mixture rapidly stirred for around 20 h. An aqueous solution (500 cm³) of sodium acetate (1.2 mol) was then poured in, and the mixture was refluxed for 3 h. The crude HL⁴ was twice extracted with diethyl ether and accumulated by evaporation. The pale yellow solid obtained

was purified by the copper salt method,[22] twice recrystallized with hexane and dried *in vacuo* at 50 °C (22.4% yield), m.p. 87.6 °C. ^{1}H NMR (CDCl$_3$): δ 2.06 (s, 3 H, CH$_3$), 7.08–7.32 (m, 10 H, C$_6$H$_5$) and 17.39 (s, 1 H, OH) (Found: C, 80.59; H, 5.90; O, 13.47. Calc. for C$_{16}$H$_{14}$O$_2$: C, 80.65; H, 5.92; O, 13.43%); *m/z* 238 (*M*$^+$).

Aluminium dibenzoylmethanate [AlL$^5_3$] 1. This compound was synthesized according to a previously reported general procedure.[23,24] An ethanol solution of dibenzoylmethane was added while stirring to a 5% aqueous solution of a stoichiometric quantity of AlCl$_3$ buffered by sodium acetate. The chelate immediately appeared, and the mixture was stored overnight in a refrigerator for complete precipitation. The precipitate was filtered off, twice recrystallized in a chloroform–heptane mixture and dried at 37 °C *in vacuo*. A single crystal suitable for X-ray analysis was grown in acetone, m.p. 298.5 °C. ^{1}H NMR (CDCl$_3$): δ 6.94 (s, 1 H, CH) and 8.05–7.32 (m, 10 H, C$_6$H$_5$) (Found: C, 77.81; H, 4.76. Calc. for C$_{45}$H$_{33}$AlO$_6$: C, 77.58; H, 4.77%).

Indium dibenzoylmethanate [InL$^5_3$] 2. This compound was synthesized and a single crystal suitable for X-ray analysis obtained in a manner similar to that of [AlL$^5_3$]; the solvent for recrystallization was acetone. M.p. 255.6 °C. ^{1}H NMR (CDCl$_3$): δ 6.81 (s, 1 H, CH) and 7.31–8.02 (m, 10 H, C$_6$H$_5$) (Found: C, 68.88; H, 4.15. Calc. for C$_{45}$H$_{33}$InO$_6$: C, 68.89; H, 4.24%).

Chemicals

4,4,4-Trifluoro-2-methyl-1-phenylbutane-1,3-dione (α-methylbenzoyltrifluoroacetylacetone, HL^9) was synthesized according to the method of Barkley and Levine[25] through the condensation of methyl trifluoroacetate and propiophenone in the presence of sodium methoxide.[26] The compounds HL^2, HL^3, 4,4,4-trifluoro-1-phenylbutane-1,3-dione (benzoyltrifluoroacetone, HL^8) and 1,1,1-trifluoropentane-2,4-dione (trifluoroacetylacetone, HL^7) were from Dojindo and used without further purification. Aqueous solutions of Al^{3+} and In^{3+} were prepared from standard solutions of Wako Chemicals and stocked in 0.02 mol dm^{-3} hydrochloric acid solution. Other chemicals were of analytical reagent grade. Water was demineralized and distilled.

Apparatus

Metal-ion concentrations were measured with a Japan Jarrell Ash Model ICAP-500 inductively coupled argon-plasma atomic emission spectrophotometer. pH Measurements were made with a Hitachi-Horiba F-8L pH meter equipped with a Horiba 6028 glass combination pH electrode. Proton NMR spectra were recorded with a Varian VXR-200 spectrometer (200 MHz) at 25 °C in CDCl$_3$.

Measurements of acid dissociation constants of the ligands (pK_a)

The pK_a values of compounds HL^1, HL^2, HL^3 and HL^4 were determined by a potentiometric titration method: a solution (20 cm^3) of 0.02 mol dm^{-3} diketone in water–1,4 dioxane (25:75 v/v) containing 0.1 mol dm^{-3} tetramethylammonium perchlorate kept at 25 °C was rapidly stirred and titrated by 0.1 mol dm^{-3} tetramethylammonium hydroxide.

Solvent-extraction procedure

A 10 cm^3 aliquot of an aqueous phase containing 1 × 10^{-4} mol dm^{-3} Al^{3+} or In^{3+}, 0.1 mol dm^{-3} sodium perchlorate and 0.01 mol dm^{-3} sodium acetate as buffering component was adjusted to the desired pH with hydrochloric acid or sodium hydroxide solution. The aqueous phase was shaken with an equal volume of benzene containing the required amount of diketone in a centrifuge tube (30 cm^3) at 25 °C for the appropriate time. After

centrifugation, the pH of the aqueous phase was measured and taken as the equilibrium value. The metal concentration in the aqueous phase was determined by inductively coupled argon-plasma atomic emission spectrometry. That in the organic phase was measured in the same way after back-extraction by stripping with hydrochloric acid solution. The sum of the metal concentrations in the two phases agreed well with the initial concentration.

Calculations

Semiempirical MNDO/H[27] calculation was performed on fully optimized molecular geometries on a Cray Y-MP2E/264 computer using MNDO 93 (Cray Research Inc.).

Molecular mechanics calculations were carried out using the CACHE system[28] on a Macintosh Quadra 800 computer. The program is based on Allinger's MM2 force field[29,30] and computes the net force acting on a molecule as the sum of the energy terms of bond stretch, bond angle, dihedral angle, improper torsion, van der Waals, electrostatics, and hydrogen bond. The augmented force-field parameters obtained by CACHE were used without modification. A charge of 3+ was assigned to Al and In and M–O bonds were described as coordinate bonds. The crystal structure was used as an initial conformation for the calculation of the ligands and complexes.

X-Ray crystallography

Crystallographic data for compounds **1** and **2** are summarized in Table 3. Crystals were mounted on a fine glass fiber with epoxy cement. The lattice parameters and intensity data were measured on a Rigaku AFC7R four-circle diffractometer equipped with Ni-filtered Cu-Kα radiation (λ = 1.54178 Å) at 20 ± 1 °C. The ω–2θ scan technique was used to a maximum 2θ value of 120°. An empirical absorption correction using the program DIFABS[31] was applied to the data sets. The data were corrected for Lorentz and polarisation effects. A correction for secondary extinction was applied. The structures were solved by direct[32] or heavy-atom Patterson methods,[33] expanded using the Fourier technique[33] and refined by full-matrix least squares for 3758 and 4497 reflections, respectively, with |F_o|> 3σ(F_o). The non-hydrogen atoms were anisotropically refined. Hydrogens were fixed at calculated positions. All calculations were performed using the TEXSAN crystallographic software package.[34] The complexes have a distorted octahedral geometry. Their mean dimensions are displayed together for comparison in Table 4.

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Results and Discussion

Molecular orbital calculations

The distances between the two donating oxygens were estimated by semiempirical MNDO/H[27] calculation which takes hydrogen bonding into consideration. Our examination of the semiempirical molecular orbital calculations including AM1[35] and PM3[36] shows that MNDO/H is most suitable to evaluate the structure of β-diketones.[26] The O···O distances found by MNDO/H for various β-diketones are shown in Table 1.

The distances between the two donating oxygens of HL^1 and HL^3 calculated by MNDO/H are 2.50 and 2.51 Å, respectively, whereas those for HL^2 and HL^4 are reduced to 2.44 Å. A shortening of this distance was made by introducing a phenyl group at the α position of HL^1 and HL^3. The steric repulsion between the phenyl group and the two terminal groups in the structure of HL^1 and HL^3 results in a narrowing of this distance. This structural change is also supported by ^{1}H NMR data. The very broad peaks assigned to the enolic proton (OH) for HL^1 and HL^3 appear at δ 15.44 and 16.15, respectively, while those for HL^2 and HL^4 are very sharp and shift downfield to δ 16.67 and

Table 1 Comparison of properties of HL^1, HL^2, HL^3 and HL^4

	HL^1	HL^2	HL^3	HL^4
$O \cdots O$ distance (Å)[a]				
HA	2.50	2.44	2.51	2.44
A^{-}[b]	3.09	2.83	3.10	2.84
E_{OH}[a]/kJ mol^{-1}	65.56	77.53	63.51	75.69
^{1}H NMR, δ(OH)	15.44	16.67	16.15	17.39
pK_a[c]	12.65	12.85	12.66	12.90

[a] From MNDO/H. [b] Fixed at planar. [c] Measured in 1,4-dioxane–water (75 : 25 v/v), $[NMe_4ClO_4] = 0.1$ mol dm^{-3}.

Fig. 1 Extraction of Al^{3+} and In^{3+} with HL^3. $[HL^3]_o = 0.1$ mol dm^{-3} in benzene, $[NaClO_4] = 0.1$ mol dm^{-3}

17.39, respectively. It was reported that the hydrogen-bonded enolic proton signal appears at that low magnetic field.[37] These signals did not move on changing the concentration (0.01–0.1 mol dm^{-3}) but disappeared after adding D_2O. The sharp and downfield signal of the enolic proton is caused by the strong intramolecular hydrogen bonding due to the narrow $O \cdots O$ separation. The intramolecular hydrogen-bond energy (E_{OH}) can be estimated as the energy difference between the hydrogen-bonded structure and the open structure in which the O–H is rotated by 180° in order to minimize the hydrogen-bond energy; these values are shown in Table 1.

In addition, the facts that the enolic proton signals correspond to one proton and no methyne protons were observed for HL^2 and HL^4 indicate that both compounds exist quantitatively in the enol form in CDCl$_3$. It has been reported that the presence of an α-substituent usually favors the keto tautomer,[12] and our previous results[26] are in agreement with this tendency. The results obtained here agree with reports[38,39] demonstrating that an α-aryl group markedly increases the enol content unlike other α-substituents, such as the methyl or bromo groups. The increase in the keto content diminishes the applicability as an organic ligand.

Acid dissociation constants (pK_a)

All the pH measurements for determining pK_a were made in aqueous 1,4-dioxane, so the reading of the pH meter was calibrated. In this work the pH measurements were carried out at 25 °C with an ionic strength of 0.1 mol dm^{-3} (tetramethylammonium perchlorate) in water–1,4-dioxane (25 : 75 v/v), and the pH reading correction proposed by Irving and Mannot[40] has been adopted; equation (1), where B is the actual pH-meter reading.

$$-\log[H^+] = B + 0.28 \qquad (1)$$

The pK_a values of HL^1, HL^2, HL^3 and HL^4 were found to be 12.65, 12.85, 12.66 and 12.90, respectively. The difference between the pK_a values of a compound and its α-phenyl derivative could be attributed to the fact that the shorter $O \cdots O$ distances of the latter strengthen the intramolecular hydrogen bond and thus restrain the release of the proton, resulting in a decrease in acidity.

Equilibrium analysis

For the extraction of In^{3+} a shaking time of 3 h was found to be long enough to reach equilibrium with all the β-diketones. It is reported that the rate of exchange of co-ordinated water for Al^{3+} is very slow.[41] Consequently, quite a long shaking time was required for the extraction of Al^{3+}. For example, the extraction with HL^2 reached equilibrium at 26 h of shaking.

The complexation of the extractants HL^2 and HL^4 with Al^{3+} and In^{3+}, compared to that of HL^1 and HL^3, has been investigated *via* the solvent-extraction method. Fig. 1 shows plots of the extraction percentages of Al^{3+} and In^{3+} *vs.* the pH of the aqueous phase in the extraction with 0.1 mol dm^{-3} HL^3 in benzene from 0.1 mol dm^{-3} sodium perchlorate aqueous media.
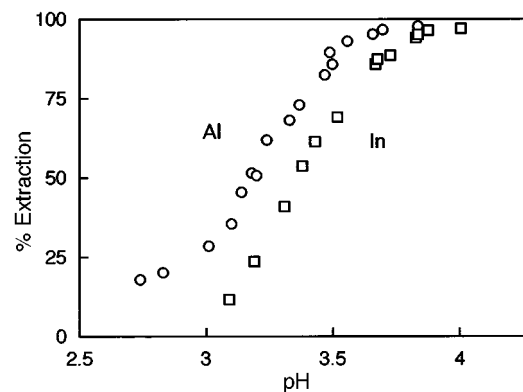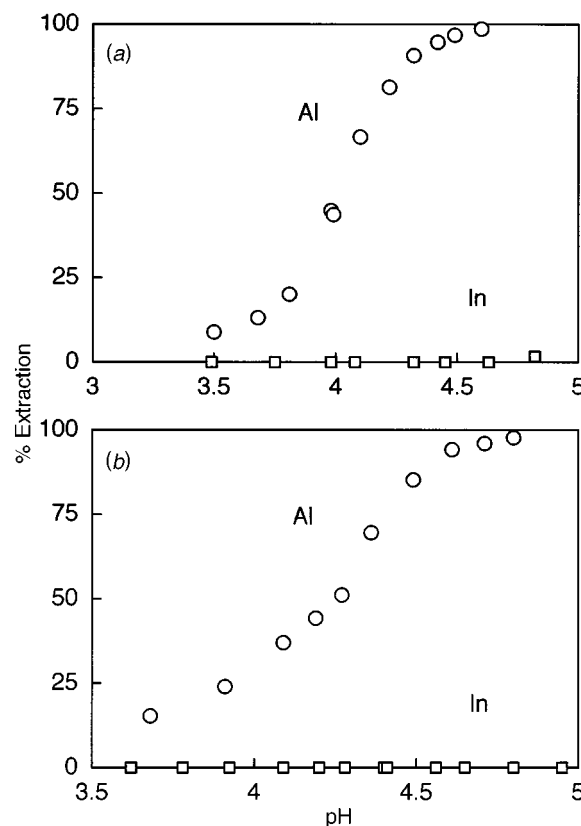
Fig. 2 Extraction of Al^{3+} and In^{3+} into benzene with (*a*) HL^2 and (*b*) HL^4. $[HL^2]_o = [HL^4]_o = 0.1$ mol dm^{-3} in benzene, $[NaClO_4] = 0.1$ mol dm^{-3}

The extractions are enhanced with increase in pH and Al^{3+} is extracted better than In^{3+}; however, their extraction behaviors are fairly similar. The extraction behavior with HL^1 was analogous to that with HL^3. The extraction behaviors significantly changed through the introduction of a phenyl group at the α position. The solvent extractions of Al^{3+} and In^{3+} from a 0.1 mol dm^{-3} sodium perchlorate aqueous phase to a 0.1 mol dm^{-3} HL^2 or HL^4 benzene phase are shown in Fig. 2. Almost 100% of Al^{3+} is extracted around pH 4.6 with HL^2, while In^{3+} is totally unextracted below pH 5. A similar result was obtained for HL^4. The extraction of In^{3+} over pH 5 was also null, while the concentration of In^{3+} in the aqueous phase decreased, probably due to hydrolysis.

To clarify the composition of the extracted species, the effects of pH and $\log[HA]_o$ on $\log D$ ($D = [M^{3+}]_o/[M^{3+}]$) was also examined. Here, HA stands for the diketone and the subscript o denotes the species in the organic phase. Plots of $\log D$ *vs.* pH and *vs.* $\log[HA]_o$ are straight lines with a slope of 3, indicating that the extracted species is AlA_3 and no self-adducts, such as

Table 2 Extraction data for Al and In

| | $pH_{1/2}{}^a$ | | $\log K_{ex}$ | |
Diketone	Al	In	Al	In
HL^1	3.30	3.95	−6.90	−8.85
HL^2	4.01	—	−9.03	—
HL^3	3.20	3.39	−6.60	−7.17
HL^4	4.24	—	−9.72	—
HL^7	2.12	2.63	−3.36	−4.89
HL^8	3.00	2.51	−6.00	−4.53
HL^9	3.47	4.98	−7.41	−11.97

^{a} [HA]$_o$ = 0.1 mol dm^{-3} in benzene, [NaClO$_4$] = 0.1 mol dm^{-3}. ^{b} Data taken from ref. 42. ^{c} Data taken from ref. 19.

AlA$_3$(HA)$_s$ (s = 1,2 ...) are observed. Based on these slope analyses, the extraction equilibrium can be expressed as in equation (2). The extraction constant, K_{ex}, is defined in

$$Al^{3+} + 3HA_o \rightleftharpoons AlA_{3,o} + 3H^+ \qquad (2)$$

equations (3) and (4). The log K_{ex} values are obtained by substi-

$$K_{ex} = \frac{[AlA_3]_o[H^+]^3}{[Al^{3+}][HA]_o^3} = D\frac{[H^+]^3}{[HA]_o^3} \qquad (3)$$

$$\log K_{ex} = \log D - 3pH - 3\log[HA]_o \qquad (4)$$

tuting the pH$_{1/2}$ values, *i.e.* the pH read from plots of log *D vs.* pH at which half of the metal ion is extracted (log *D* = 0), in equation (4) and are summarized in Table 2. Since the concentration of the metal ions is much smaller than that of the extractant, extractant concentration in the organic phase {[HA]$_o$ in equation (4)} can be considered equal to the initial concentration.

As previously mentioned, Al^{3+} and In^{3+} are extracted with HL^1 and HL^3 with similar extraction constants. On the contrary, In^{3+} is not extracted at all with HL^2 and HL^4, while Al^{3+} is extracted with smaller extraction constants compared to those for HL^1 and HL^3. Considering that the substituents at the α position of the β-diketones should essentially not affect their complexation with the metal ions, the present results are surprising.

An X-ray crystallographic consideration of β-diketones of Al and In was made to confirm the role of the substituent at the α position. The O···O distances of the β-diketones in AlL$^1_3$ **3**,^{43} InL$^1_3$ **4**^{44} and InL$^6_3$^{45} were reported to be 2.726, 2.905 and 2.905 Å, respectively. A survey of X-ray data for β-diketones of Al and In shows that the O···O distances in aluminium β-diketones are among the shortest ones, while those in indium β-diketones are among the longest. According to MNDO/H calculations (Table 1), the O···O distances in the anionic form of HL^2 and HL^4 are 2.83 and 2.84 Å, while those for HL^1 and HL^3 are 3.09 and 3.10 Å. The non-extractability of In^{3+} with HL^2 and HL^4 could be ascribed to the phenyl group at the α position which prevents the O···O separation of the anionic form from widening to fit to the desired configuration in the indium complex owing to the steric repulsion between the α-phenyl group and the terminal groups.

Interligand contact in β-diketonates of Al and In

The intracomplex interligand contacts should have great influence on the stability of aluminium β-diketonates, which could be deduced from the extraction order of Al^{3+} and In^{3+} with β-diketones.^{1,3,42} In general, organic ligands including β-diketones form more stable complexes with metal ions having smaller ionic radii when the valency is the same. Consequently, the extraction constants for the smaller metal ions are usually higher than those for the larger ones. However, in the extraction of

Table 3 Crystallographic data * for AlL$^5_3$ **1** and InL$^5_3$ **2**

	1	2
Formula	C$_{45}$H$_{33}$AlO$_6$	C$_{45}$H$_{33}$InO$_6$
M	696.73	784.57
a/Å	10.7308(8)	11.497(2)
b/Å	17.939(2)	16.339(1)
c/Å	9.8365(9)	10.5361(4)
α/°	94.784(9)	97.319(8)
β/°	107.184(6)	102.079(9)
γ/°	93.213(9)	107.474(8)
U/Å^3	1796.0(3)	1087.3(4)
Crystal size/mm	0.20 × 0.15 × 0.60	0.40 × 0.20 × 0.40
D_c/g cm^{-3}	1.288	1.442
μ/cm^{-1}	9.05	56.32
Reflections collected	5082	5111
Independent reflections	4793	4835
Observed reflections	3758	4497
R	0.044	0.034
R'	0.058	0.047
Goodness of fit	1.75	1.66

* Details in common: triclinic, space group $P\bar{1}$ (no. 2); *Z* = 2; $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R' = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Al^{3+} and In^{3+}, the opposite extraction order is frequently seen depending on the bulkiness of the ligands. Aluminium is extracted better than In^{3+} with HL^1 and HL^3. In the case of bulky β-diketones, such as HL^5 and HL^6, the steric crowding of the ligands around Al^{3+} greatly destabilizes complexation because of its very small ionic radius, while this is not so serious in the case of In^{3+}. As a result, In^{3+} is better extracted than Al^{3+} with these bulky β-diketones. It should be noted here that the O···O distances of HL^1, HL^3, HL^6 and HL^5 are similar according to the molecular orbital calculations.

It is seen from the extraction constants (Table 2) that although Al^{3+} is completely isolated from In^{3+} by HL^2 and HL^4, the extractions were disturbed compared to those for HL^1 and HL^3, *i.e.*, the distribution curves log *D vs.* pH of Al^{3+} for HL^2 and HL^4 shifted more to the alkaline region than those of HL^1 and HL^3. The poor extractions of Al^{3+} with HL^2 and HL^4 are partly ascribed to the lower acidity, though this is not so important because the differences in the pK_a values are very small. It could be also attributed to the interligand contact in the aluminium complex. The steric crowding of the ligands is enhanced by the α-phenyl group which disturbs the free rotation of the terminal methyl or phenyl groups. The free rotation is expected to diminish the interligand contact.

Crystal structures of β-diketonates of Al and In

The steric factors were evaluated by examining the crystal structures of AlL$^5_3$ **1** and InL$^5_3$ **2** in addition to those of AlL$^1_3$ **3**^{43} and InL$^1_3$ **4**.^{44}

The M–O distances for compounds **1** and **3** are much shorter than those for **2** and **4** due to the remarkably small ionic radius of Al^{3+}. The M–O distance in AlL$^1_3$ is one of the shortest among the tervalent metal acetylacetonates, while that in InL$^1_3$ is one of the longest.^{46} Consequently, the mean distance of diagonal O···O for aluminium complexes is significantly short, meaning that three ligands are forced to be packed into a small space. As seen in Table 4, the M–O distances for **1** and **2** are shorter than those for **3** and **4**, respectively. The shorter M–O is brought about by the terminal phenyl group. This corresponds with the fact that metal ions are usually better extracted in the order HL^5 > HL^3 > HL^1,^{45} except for Al^{3+} where the effect of the interligand contact is significant. The shorter M–O in **1** than in **3** would enhance the interligand contact.

Indium β-diketonates are characterized by their long O···O distances. The O···O distance in InL$^1_3$ is the longest among the tervalent metal acetylacetonates, while that in AlL$^1_3$ is one of the shortest.^{46} Such long O···O distances would be intrinsic

Table 4 Mean dimensions (Å or °) in AlL^5_3 **1**, InL^5_3 **2**, AlL^1_3 **3** and InL^1_3 **4**

	1	**2**	**3**[a]	**4**[b]
M–O	1.874(1)	2.122(1)	1.892(6)	2.132(2)
Bite size (O⋯O)	2.658(2)	2.872(2)	2.726(4)	2.904(1)
Bite angle	90.30(4)	85.2(1)	90.30(2)	85.53(1)
Diagonal O⋯O	3.747	4.234	3.783	4.255

[a] Data taken from ref. 43. [b] Data taken from ref. 44.

Table 5 Steric energy change (kJ mol⁻¹) for complex formation

	$\Delta U(ML^5_3)$	$\Delta U(ML^1_3)$	$\Delta(\Delta U)$
Al^{3+}	−372.0	−277.0	−95.0
In^{3+}	−368.4	−214.1	−154.3

for indium complexes. The enlargement of the O⋯O distance could be disturbed by the α-substituent.

Molecular mechanics calculations

The interligand contact is quantitatively elucidated by molecular mechanics calculations estimating the change in steric energy (strain energy) that arises from the complexation of one metal trivalent atom with three ligands to yield a tris complex.

The change in steric energy on MA_3 complex formation (ΔU) was assessed on the basis of equations (5) and (6) where U_{MA_3},

$$M^{3+} + 3A^- \rightleftharpoons MA_3 \qquad (5)$$

$$\Delta U = U_{MA_3} - U_{M^{3+}} - 3U_{A^-} \qquad (6)$$

$U_{M^{3+}}$ and U_{A^-} represent the steric energy of the complex, metal ion and ligand, respectively. For simplicity, the value of $U_{M^{3+}}$ was assumed to be zero; U_{MA_3} and U_{A^-} were obtained by optimizing the crystal structures in the MM2 force field.

Table 5 summarizes the increase in the steric energy of MA_3 complex formation, $\Delta U(MA_3)$. Since $U_{M^{3+}}$ is assumed to be 0 for all metals, the comparison of the absolute values of $\Delta U(MA_3)$ is meaningless. Therefore, we noted the difference between $\Delta U(ML^1_3)$ and $\Delta U(ML^5_3)$ for each metal, equation (7).

$$\Delta(\Delta U) = \Delta U(ML^5_3) - \Delta U(ML^1_3) \qquad (7)$$

The term $U_{M^{3+}}$ is cancelled in $\Delta(\Delta U)$, so that it can be compared between metals. As can be seen in Table 5, $\Delta(\Delta U)$ of Al^{3+} is 59.3 kJ mol⁻¹ larger than that for In^{3+}; the steric energy change in complexation from HL^1 to HL^5 is more drastic for Al^{3+} than that for In^{3+} due to the bulkiness of HL^5 and the small size of Al^{3+}. This confirms our postulation that the complexation of Al^{3+} and In^{3+} with HL^1 follows the general conception, while those with HL^5 and other bulky β-diketones do not. In the present calculations solvation was not taken into account and the electron distribution was simplified. Nevertheless, it is very probable that the above steric energy change dominates the stability in the real system.

Simultaneous effects of the bite size and the interligand contact

Finally, the effects of the O⋯O distance and the interligand contact on the solvent extraction of Al^{3+} and In^{3+} have been confirmed again using HL^7, HL^8 and HL^9. The results are shown in Fig. 3 and Table 2. Aluminium was better extracted than In^{3+} with HL^7; the O⋯O distance of HL^7 is 2.50 Å according to MNDO/H, and no significant interligand contact seems to take place among the terminal methyl and trifluoromethyl groups. When the methyl group is replaced by the bulky phenyl group to obtain HL^8, its O⋯O distance (2.52 Å) and pK_a are still similar to those of HL^7. The extraction of Al^{3+}
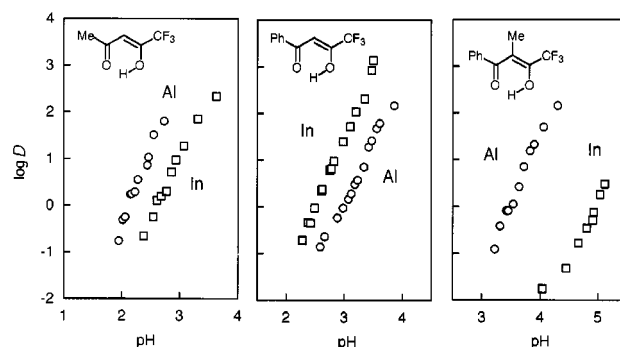
Fig. 3 Extraction of Al^{3+} and In^{3+} with HL^7, HL^8 and HL^9. $[HA]_o =$ 0.1 mol dm⁻³ in benzene, $[NaClO_4] = 0.1$ mol dm⁻³

with HL^8 shifted to the alkaline region, while that of In^{3+} scarcely changed. It can be concluded that the reduced extraction was brought about by the interligand contact which does not work for In^{3+}. When a methyl group was introduced at the α position of HL^8 to get HL^9 the O⋯O distance and pK_a are reduced.[26] Owing to the lower acidity and the enhanced interligand contact caused by the α-methyl group as in the case of HL^2 and HL^4, the extraction constant for Al^{3+} decreased; however, the influence of the narrowed O⋯O distance is marked for the extraction of In^{3+}. The extraction of In^{3+} drastically decreased; the shift of the $pH_{1/2}$ value being 2.47; consequently, Al^{3+} was extracted much better then In^{3+} resulting in a facilitated separation.

Conclusion

From our results so far there are two factors governing the complexation of Al^{3+} and In^{3+} with β-diketones: the distance between the two donating oxygens and the interligand interaction, and their balance should decide the stability of each complex, that is, the extraction order, as well as the separation of Al^{3+} and In^{3+}. This observation may contribute to the basic knowledge of organic ligands, especially on the concepts of their complexation with metals, and confirms our suggestion for a perspective strategy for designing novel ligands of high selectivity from well known typical ones.[26]

References

1 T. Sekine and Y. Hasegawa, *Solvent Extraction Chemistry*, Marcel Dekker, New York, 1977.
2 D. N. Solokov, *Russ. Chem. Rev.*, 1988, **57**, 956.
3 *Principles and Practices of Solvent Extraction*, eds. J. Rydberg, C. Musikas and G. R. Choppin, Marcel Dekker, New York, 1992.
4 K. E. Laintz, C. M. Wai, C. R. Yonker and R. D. Smith, *J. Supercrit. Fluids*, 1991, **4**, 194.
5 K. E. Laintz, C. M. Wai, C. R. Yonker and R. D. Smith, *Anal. Chem.*, 1992, **64**, 2875.
6 Y. Lin and C. M. Wai, *Anal. Chem.*, 1994, **66**, 1971.
7 J. Wang and W. D. Marshall, *Anal. Chem.*, 1994, **66**, 1658.
8 R. M'Hamdi, J. R. Bocquet, K. Chhor and C. Pommier, *J. Supercrit. Fluids*, 1991, **4**, 55.
9 B. N. Hansen, B. M. Hybertson, R. M. Barkley and R. E. Sievers, *Chem. Mater.*, 1992, **4**, 748.
10 W. Lin, T. H. Warren, R. G. Nuzzo and G. S. Girolami, *J. Am. Chem. Soc.*, 1993, **115**, 1164.
11 I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, J. McAleese, D. J. Otway and J. C. Plakatouras, *Inorg. Chem.*, 1995, **34**, 1384.

12 J. Emsley, *Struct. Bonding* (*Berlin*), 1984, **57**, 147.
13 G. Gilli, F. Bellucci, V. Ferretti and V. Bertolasi, *J. Am. Chem. Soc.*, 1989, **111**, 1023.
14 A. Roy and K. Nag, *J. Inorg. Nucl. Chem.*, 1978, **40**, 331.
15 S. Umetani and H. Freiser, *Inorg. Chem.*, 1987, **26**, 3179.
16 Q. T. H. Le, S. Umetani, H. Takahara and M. Matsui, *Anal. Chim. Acta*, 1993, **272**, 293.
17 S. Umetani, Y. Kawase, H. Takahara, Q. T. H. Le and M. Matsui, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 78.
18 S. Umetani, Y. Kawase, T. H. Q. Le and M. Matsui, unpublished work.
19 T. H. Q. Le, S. Umetani, M. Suzuki and M. Matsui, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2271.
20 R. D. Shannon, *Acta. Crystallogr.*, *Sect. A*, 1976, **32**, 751.
21 C. R. Hauser, F. W. Swamer and J. T. Adams, *Org. React.*, 1954, 59.
22 J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, 1950, **72**, 2948.
23 E. W. Berg and J. T. Truemper, *J. Am. Chem. Soc.*, 1960, **64**, 487.
24 E. G. Zaitseva, I. A. Baidina, P. A. Stabnikov, S. V. Borisov and I. K. Igumenov, *Zh. Strukt. Khim.*, 1990, **31**, 184.
25 L. B. Barkley and R. Levine, *J. Am. Chem. Soc.*, 1953, **75**, 2059.
26 T. H. Q. Le, S. Umetani, M. Suzuki and M. Matsui, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 643.
27 K. Y. Burstein and A. N. Isaev, *Theor. Chim. Acta*, 1984, **64**, 397.
28 CACHE, Version 3.8, CAChe Scientific, Oxford, 1995.
29 N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.
30 U. Burkert and N. L. Allinger, *Molecular Mechanics*, The American Chemical Society, Washington, DC, 1982.
31 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
32 G. M. Sheldrick, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, Oxford, 1985, p. 175.
33 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
34 TEXSAN, Molecular Structure Corporation, Houston, TX, 1985.
35 M. J. S. Dewar, E. G. Zeobisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
36 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
37 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1981.
38 J. Emsley and Y. Y. L. Ma, *J. Mol. Struct.*, 1988, **178**, 297.
39 J. Emsley, J. N. Freeman, A. P. Bates and B. M. Hursthouse, *J. Chem. Soc.*, *Perkin Trans. 1*, 1988, 297.
40 H. M. N. H. Irving and U. S. Mannot, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1215.
41 M. Eigen, *Pure Appl. Chem.*, 1963, **6**, 105.
42 J. Stary, *The Solvent Extraction of Metal Chelates*, Pergamon, London, 1964.
43 P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, 1973, **3**, 67.
44 G. J. Palenik and K. R. Dymock, *Acta. Crystallogr.*, *Sect. B*, 1980, **36**, 2059.
45 H. Soling, *Acta Chem. Scand.*, *Ser. A*, 1976, **30**, 163.
46 E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, 1966, **88**, 2951.