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Acylpyrazolone derivatives of high selectivity for lanthanide metal ions: effect of the distance between the two donating oxygens

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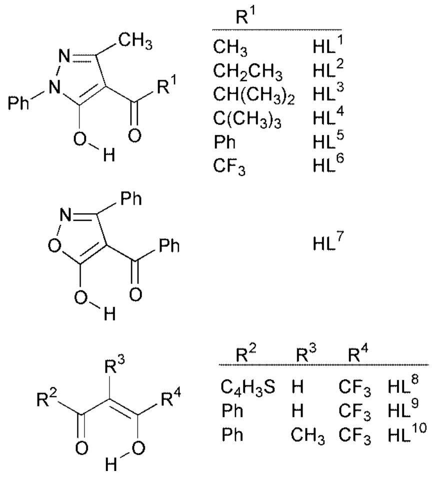
Four 4-acyl-3-methyl-1-phenyl-5-pyrazolone derivatives [4-acyl = acetyl (HL^1), propionyl (HL^2), isobutyryl (HL^3) and pivaloyl (HL^4)] have been synthesized. Their distribution behaviors between cyclohexane and aqueous 0.1 mol dm^{-3} sodium perchlorate solution were examined, and the partition constants and the acid dissociation constants obtained. The structures of the acylpyrazolone derivatives were evaluated by semi-empirical MNDO/H molecular orbital calculation and ^1H NMR. The solvent extraction of lanthanide metal ions (La^{3+}, Pr^{3+}, Eu^{3+}, Ho^{3+} and Yb^{3+}) into chloroform was examined, and it was found that the selectivity improves as the 4-acyl groups become bulkier. This improvement could be attributed to the narrowed distance between the two donating oxygens ("bite size"), which is caused by the steric repulsion between the 3-methyl and bulky 4-acyl groups. The extraction selectivity for lanthanide metal ions including 4-benzoyl-(HL^5) and 4-trifluoroacetyl-pyrazolone (HL^6), 4-benzoyl-3-phenyl-5-isoxazolone (HL^7), and other β-diketones could be elucidated by considering the effect of the bite size, suggesting that this is one of the most significant factors that govern the selectivity in the extraction of lanthanide metal ions. The separability of the 4-pivaloyl derivative (HL^4) is comparable to that of bis(2-ethylhexyl) hydrogenphosphate, one of the most selective extractants for lanthanides.

Introduction

The solvent extraction method has been proven to be a powerful means for the concentration and separation of various metal ions.[1–3] The extraction mechanism has been investigated in terms of the nature of the metal ions, the role of the solvents and the chelation and distribution behavior of the extractants. Studies on the solvent extraction of metal ions with acylpyrazolones[4–6] and acylisoxazolones,[7] which are structurally analogous to β-diketones derived from 5-membered heterocyclic compounds, revealed that the improved extraction with strongly acidic extractants is usually accompanied by poor selectivity. These ligands were found to have longer distances between the two donating oxygens as compared to the conventional β-diketones, such as acetylacetone and thenoyltrifluoroacetone, according to estimation by 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,[8] it has been found that the separability of lanthanides was clearly improved with those ligands having shorter O···O distances. Besides lanthanide ions with ionic radii very similar to each other, we have expanded our research to the metal ions of Group 13 with large differences in ionic radii in an attempt to investigate how the O···O distance and other factors in the structure of β-diketones would affect their complexation reactions.[9] 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 metal ions. If the structure of the β-diketone could suitably be modified by introducing bulky groups at suitable positions to create a steric effect, this distance could intentionally be controlled, and consequently the extractability and/or the separability could be improved.

In the present paper, four 4-acyl-3-methyl-1-phenyl-5-pyrazolone derivatives were synthesized, and the solvent extraction of lanthanide metal ions was examined. The separability is discussed in terms of the effect of the bite size. It was found that the separability with other β-diketones could also be explained by taking this effect into consideration.



Experimental

Materials

Acylpyrazolone derivative (HL^1–HL^3) were prepared by referring to the literature.[10] The crude compound was recrystallized from methanol–water and dried under reduced pressure. For HL^1, white powder, 48% yield, mp 65–66 °C. Calc. for C_6H_6NO: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.50; H, 5.57; N, 12.87%. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.43 (s, 3 H), 2.44 (s, 3 H), 7.21–7.30 (m, 1 H), 7.36–7.47 (m, 2 H) and 7.77–7.85 (m, 2 H). For HL^2, white powder, 45% yield, mp 59–60 °C. Calc. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.80; H, 6.08; N, 12.12%. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.15 (t, 3 H), 2.45 (s, 3 H), 2.70 (q, 3 H), 7.22–7.32 (m, 1 H), 7.38–7.49 (m, 2 H) and 7.78–7.86 (m, 2 H). For HL^3, white powder, 34% yield, mp 59–60 °C. Calc. for C_7H_8NO: C, 68.83; H, 6.60; N, 11.47.

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Table 1 Comparison of the ligands

	HL^1	HL^2	HL^3	HL^4	HL^5	HL^6	HL^7
O···O distance/Å							
HA	2.60	2.56	2.54	2.48	2.65	2.66	2.90
A^-	3.05	3.00	2.98	2.84	3.06	2.98	3.13
E_{OH}/kcal mol^{-1}	13.93	14.95	15.41	18.38	12.43	10.74	5.71
^{1}H NMR (OH, δ)	—	—	—	14.9	—	—	—
log P_{HA}	1.11	1.77	2.43	2.64	2.33[a]	1.67[a]	1.23[b]
pK_a	3.94	4.15	4.18	4.26	3.92[a]	2.56[a]	1.24[b]

[a] Taken from ref. 5. [b] Taken from ref. 7.

Found: C, 68.79; H, 6.56; N, 11.46%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.25 (d, 6 H), 2.48 (s, 3 H), 3.15 (septet, 1 H), 7.22–7.32 (m, 1 H), 7.38–7.49 (m, 2 H) and 7.78–7.86 (m, 2 H).

It was reported that synthesis of HL^4 by the similar method resulted in failure.[10] It was synthesized as follows: 35 g (0.2 mol) of 3-methyl-1-phenyl-5-pyrazolone were dissolved in 150 cm^3 1,4-dioxane by the application of heat, and 30 g (0.4 mol) of calcium hydroxide were added. The solution was stirred and 24 g (0.2 mol) of pivaloyl chloride were added dropwise. Addition should be made carefully for the temperature increased very rapidly. The mixture was heated to reflux for 1 hour. An oily phase was precipitated after the mixture was acidified with a hydrochloric acid solution. It was collected and the solvent removed as much as possible by evaporation under reduced pressure. Recrystallization from methanol–water gave 9.5 g of bright yellow powder, 19% yield, mp 93–94 °C. Calc. for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.65; H, 6.82; N, 10.96%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.38 (s, 9 H), 2.61 (s, 3 H), 7.22–7.32 (m, 1 H), 7.38–7.48 (m, 2 H) and 7.77–7.87 (m, 2 H).

2-Morpholinoethanesulfonic acid monohydrate (MES) was purchased commercially from Dojindo Laboratories and used without further purification. Other chemicals were all reagent-grade materials. 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 glass electrode. ^{1}H NMR spectra were measured with a Varian VXR-200 spectrometer (200 MHz) at 25 °C in $CDCl_3$. The extractions were performed in 30 cm^3 centrifuge tubes with the aid of a Taitek Bio-shaker type BR-30L thermostatted at 25 °C. Semi-empirical MNDO/H[11] calculations were performed on fully optimized molecular geometries on a Cray T94/4128 computer using MNDO 94 (Cray Research, Inc.).

Distribution of the ligands

The experiments were performed in a 30 cm^3 glass-stoppered centrifuge tube. A 10 cm^3 aliquot of an aqueous phase containing 0.1 mol dm^{-3} sodium perchlorate and 0.01 mol dm^{-3} sodium acetate or MES 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 cyclohexane containing 0.01 mol dm^{-3} acylpyrazolone at 25 °C for one hour. After centrifugation the pH of the aqueous phase was measured and taken as the equilibrium value. The ligand concentration in the organic phase was measured spectrophotometrically. The ligand concentration in the aqueous phase was measured after dilution with a sodium hydroxide solution to complete the dissociation of the ligand. This anionic form which is stable enough for a few days exhibits strong absorption at 250–300 nm. The sum of the ligand concentrations determined in each phase coincided well with the initial concentration.

Extraction of lanthanide metal ions

A 10 cm^3 aliquot of an aqueous phase containing 1×10^{-4} mol dm^{-3} of lanthanide metal ion, 0.1 mol dm^{-3} sodium perchlorate and 0.01 mol dm^{-3} sodium acetate or MES 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 chloroform containing the required amount of ligand at 25 °C for one hour. The shaking time of 1 h was found to be long enough to reach equilibrium. 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 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.

Results and discussion

Molecular structure of the ligands

The molecular structure of the ligands was evaluated by semi-empirical MNDO/H[11] calculation which takes the hydrogen bond into consideration. Our examination of the semi-empirical molecular orbital calculations including AM1[12] and PM3[13] shows that MNDO/H is most suitable to evaluate the structure of β-diketones.[14] The O···O distances found by MNDO/H for various β-diketones are shown in Table 1.

The distance between the two donating oxygens of HL^1 calculated by MNDO/H is 2.60 Å and shortens as the 4-acyl group becomes bulkier. The steric repulsion between the 3-methyl group and the 4-acyl group in the structure of the acylpyrazolone derivatives results in a narrowing of this distance. Such structural change was also seen in 2-trifluoroacetylcycloalkanones[8] and α-substituted β-diketones.[9] It is characterized by ^{1}H NMR data. The O···O distance of representative β-diketones such as acetylacetone or thenoyltrifluoroacetone in their enol form is about 2.5 Å, and a broad peak assigned to the enolic proton (OH) appears at low magnetic field,[15] for example at δ 15.44 for acetylacetone.[9] Deriving from the five-membered heterocycle, acylpyrazolones have a longer O···O distance than conventional β-diketones. No enolic proton peak is usually observed for acylpyrazolones, although they exist quantitatively in the enol form in organic solvents, which can be assured by the lack of a peak for the methyne proton at the 4 position. However, a moderately sharp peak was observed at δ 14.9 only for HL^4, whose O···O distance is the shortest among the acylpyrazolones examined in the present work. This signal did not move on changing the concentration (0.01–0.1

Table 2 Extraction constants for lanthanide metal ions with acylpyrazolones

	HL^1		HL^2		HL^3		HL^4	
	$pH_{1/2}$[a]	log K_{ex}	$pH_{1/2}$[a]	log K_{ex}	$pH_{1/2}$[a]	log K_{ex}	$pH_{1/2}$[a]	log K_{ex}
La^{3+}	5.28	−9.82 ± 0.04	5.33	−9.97 ± 0.07	5.41	−10.19 ± 0.06	6.74	−14.22 ± 0.07
Pr^{3+}	4.76	−8.22 ± 0.05	4.83	−8.46 ± 0.03	4.93	−8.72 ± 0.06	6.16	−12.49 ± 0.03
Eu^{3+}	4.35	−7.13 ± 0.10	4.40	−7.26 ± 0.08	4.44	−7.43 ± 0.11	5.71	−11.13 ± 0.02
Ho^{3+}	4.08	−6.24 ± 0.02	4.15	−6.39 ± 0.06	4.15	−6.46 ± 0.04	5.44	−10.28 ± 0.04
Yb^{3+}	3.78	−5.35 ± 0.02	3.86	−5.56 ± 0.06	3.83	−5.54 ± 0.07	5.10	−9.25 ± 0.08
SF (Yb–La)		4.47 ± 0.06		4.41 ± 0.13		4.65 ± 0.13		4.97 ± 0.15

[a] $[HA]_o = 0.01$ mol dm^{-3} in chloroform.

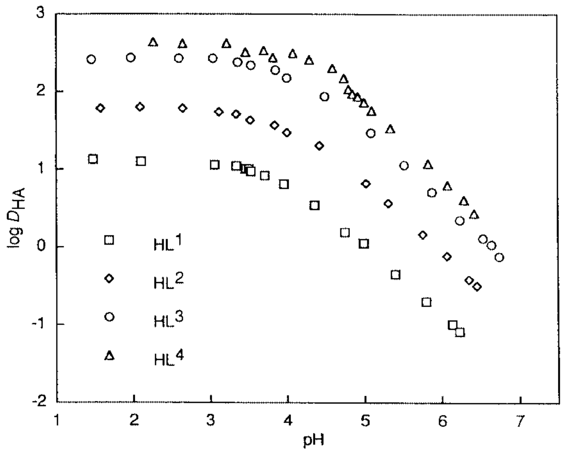

Fig. 1 Distribution of acylpyrazolones between cyclohexane and water as a function of pH. $[HA]_o = 0.01$ mol dm^{-3} in cyclohexane, $[NaClO_4] = 0.1$ mol dm^{-3}.

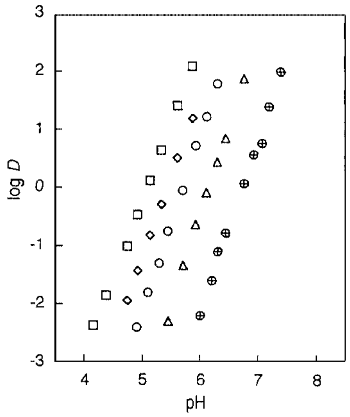

Fig. 2 Extraction of lanthanide metal ions into chloroform. $[HL^4]_o = 0.01$ mol dm^{-3}, $[NaClO_4] = 0.1$ mol dm^{-3}. M = Yb (□), Ho (◇), Eu (○), Pr (△) or La (⊕).

mol dm^{-3}) and was found to disappear after adding D_2O. 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. E_{OH} increases as the O···O distance decreases.

Molecular orbital calculations were also made for benzoyl- (HL^5) and trifluoroacetyl-pyrazolone (HL^6) derivatives and 4-benzoyl-3-phenylisoxazolone (HL^7). The O···O distances for HL^5 and HL^6 are similar and longer than those of HL^1–HL^4. HL^7 is characterized by a long O···O distance (2.90 Å), and consequently its E_{OH} is very small.

Distribution of the acylpyrazolone derivatives

In a quantitative treatment for the distribution of the ligands (HA), the acid dissociation constant, K_a, and the partition constant, P_{HA}, are defined as in eqns. (1) and (2) where [HA] and

$$K_a = [H^+][A^-]/[HA] \quad (1)$$

$$P_{HA} = [HA]_o/[HA] \quad (2)$$

$[A^-]$ are the concentrations of the neutral and anionic species of the ligand in the aqueous phase, and the subscript o denotes the species in the organic phase. Thus, the distribution ratio of the ligand, D_{HA}, can be written as in eqn. (3).

$$D_{HA} = [HA]_o/([HA] + [A^-])$$

or

$$D_{HA} = P_{HA}/(1 + K_a[H^+]^{-1}) \quad (3)$$

When $[H^+]$ is much greater than K_a, D_{HA} agrees with P_{HA}, while log D_{HA} agrees with log P_{HA} + pK_a − pH when $[H^+]$ is much less than K_a.

The distribution behaviors of the ligands HL^1–HL^4 between the cyclohexane and aqueous phases are seen in Fig. 1 as a function of pH. The distribution curves are asymptotic to a constant value, log P_{HA}, in a low pH region, and to a straight line with a slope of −1, *i.e.* the theoretical line (eqn. 3) in a high pH region. The acid dissociation constants and the partition constants were calculated treating the distribution curve by the non-linear least-square method on the basis of eqn. (3) and are summarized in Table 2.

The log P_{HA} value increases as the 4-acyl group becomes bulkier. The pK_a value of HL^1 is quite similar to that of HL^5. The increasing pK_a values of HL^1–HL^4 could be ascribed to the electron-donating effect of the methyl group. The acidity of HL^6 is enhanced by the electron-withdrawing trifluoroacetyl group. HL^7 is most characterized by its amazingly strong acidity, which could be brought about by the very long O···O distance, that is the very weak intramolecular hydrogen bond which facilitates the release of hydrogen.

Extraction of lanthanide metal ions

The solvent extraction behaviors of lanthanide metal ions (Ln^{3+}) from a 0.1 mol dm^{-3} sodium perchlorate aqueous phase to a 0.01 mol dm^{-3} acylpyrazolone (HL^1–HL^4, HA) chloroform phase are shown in Fig. 2 as a typical example, in which the logarithmic value of the distribution ratio of the metal ions, log D ($D = [Ln^{3+}]_o/[Ln^{3+}]$), is plotted against the pH of the aqueous phase, where the subscript o denotes the species in the organic phase. The plots are found to fall on straight lines of slopes close to three. In order to clarify the composition of the extracted species, the effect of $[HA]_o$ on log D was also examined. The slopes of the straight lines were found to be close to three, indicating that the extracted species is LnA_3 and hydrolysis is negligible in the present pH range. Based on these slope analyses, the extraction equilibrium can be expressed as in eqn. (4). The extraction constant, K_{ex}, is defined in eqns. (5) and (6). The log K_{ex} values are obtained by substituting the $pH_{1/2}$

$$Ln^{3+} + 3HA_{(o)} \rightleftharpoons LnA_{3(o)} + 3H^{+} \qquad (4)$$

$$K_{ex} = [LnA_3]_o[H^+]^3/[Ln^{3+}][HA]_o^3 = D[H^+]^3/[HA]_o^3 \qquad (5)$$

$$\log K_{ex} = \log D - 3pH - 3\log [HA]_o \qquad (6)$$

values, the pH being read from log D *vs.* pH plots, at which half of the metal ions is extracted (log $D = 0$), in eqn. (6) and are summarized in Table 2. Since the concentration of the lanthanide ion is much lower than that of the extractant, the concentration of the extractant in the organic phase ($[HA]_o$ in eqn. (6)) can be considered equal to the initial concentration.

The extraction constant can be expressed in terms of the stability constant, β_3 ($[LnA_3]/[Ln^{3+}][A^-]^3$), the partition constants for HA, P_{HA} ($[HA]_o/[HA]$), and LnA_3, P_{LnA} ($[LnA_3]_o/[LnA_3]$), and the acid dissociation constant, K_a, as in eqn. (7).

$$K_{ex} = \beta_3 P_{LnA} K_a^{3} P_{HA}^{-3} \qquad (7)$$

Strong acidity will give enhanced extractability though K_a and β_3 compensate each other to some extent.[1,3] It is also known that P_{LnA} and P_{HA}^{-3} offset each other in the solid, which arises from regular solution theory in chelate extraction systems.[1,3] The linear relationship between log K_{ex} and pK_a in the extraction of tervalent europium with 4-acyl-5-pyrazolone derivatives can be seen in a previous paper,[16] demonstrating that the extractability in the extraction of lanthanide ions is mainly governed by the acidity of the ligands. However, the origin of the separability is not accessible. When the nature of the target metal ion is analogous like the lanthanide ions, the steric effect of the ligands, and the conformational and electronic effect of the donor atoms, could be responsible.

As seen in Table 2, for each ligand the log K_{ex} value increases as the atomic number of the lanthanide metal ion increases, in other words as the ionic radius decreases. It also gradually increases as the pK_a value decreases, in other words as the acidity is enhanced for HL^1–HL^3. The log K_{ex} values for HL^5 are similar to those for HL^1–HL^3,[4] for their acidity is comparable, and those for HL^6 and HL^7 are much greater because of their strong acidity.[4,7] It is quite interesting that the log K_{ex} values for HL^4 are much smaller than those for HL^1–HL^3 and HL^5, although its acidity is comparable. X-Ray crystallographic studies indicate that β-diketones exist in the enol form with the β-diketone moiety consisting of the two carbonyl groups and the carbon in the α-position on a plane. After the release of the enolic proton, molecular orbital calculations indicate that the planar structure collapses and the anionic form reaches the most stable conformation. The crystallographic studies also demonstrate that the β-diketone moiety in the lanthanide complexes as well as other metal complexes is usually kept on the plane or close to coplanar, meaning that the anionic form in the most stable conformation is required to adjust itself to be planar on chelation. The energy required to rearrange the ligand conformation is obtained by MNDO/H calculation to be 4.19, 4.29, 5.01 and 11.40 kcal mol^{-1} for HL^1–HL^4, respectively. The increasing energy is attributable to the steric repulsion between the 3-methyl and the 4-acyl groups. The steric repulsion for HL^4 is especially large, which could be considered the reason why the extraction constants for HL^4 are much smaller than those for HL^1–HL^3.

Separability for lanthanide metal ions

The separation factor (SF) is defined as the difference in the log K_{ex} values for two metal ions and is summarized in Table 2. The separation factors between lanthanum and ytterbium, SF(Yb–La), are 4.47, 4.41, 4.65 and 4.97 for HL^1–HL^4, respectively. As seen in Table 2, the extraction separability for the lanthanide metal ions improves as the O···O distances becomes shorter. The SF values are plotted against the O···O distance in Fig. 3. This tendency is also seen for other acylpyrazolones. The SF(Yb-La) values for HL^5 and HL^6 are reported to be 2.94[4] and 3.03,[6] respectively. Although the nature of the acyl group is quite different, the separability for HL^5 and HL^6 is very similar. The phenyl group in HL^5 is aromatic, while the CF_3 group in HL^6 is aliphatic analogous to those in HL^1–HL^4 but strongly electron withdrawing. This indicates that the O···O distance rather than the steric and electronic nature of the substituent is significant for the separation of the lanthanide metal ions. HL^7 is structurally analogous to acylpyrazolones and is known as one of the most powerful extractants owing to its extremely strong acidity. However, the separability for lanthanide ions is very low. Its pK_a and SF value were reported to be 1.23 and 1.47,[7] respectively. It is quite interesting that the low separability for this extractant can also be rationalized in terms of the O···O distance. A similar relationship between the O···O distance and the extraction separability for the lanthanide metal ions is seen for trifluorothenoylacetone (HL^8, SF = 3.79),[17] benzoyltrifluoroacetone (HL^9, 3.75) and benzoyltrifluoro-α-methylacetone (HL^{10}, 4.44),[14] although the extractions were made into benzene and it is not possible simply to compare with the separability for HL^1–HL^7. Here, the O···O distances for HL^8 and HL^9 are similar and that for HL^{10} is less than that for HL^9 owing to the α-methyl substituent. This also indicates that the O···O distance rather than the steric and electronic factors is responsible for the separation of the lanthanide metal ions.

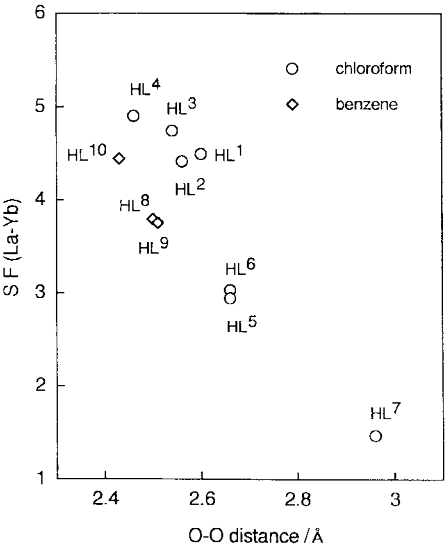

Fig. 3 Effect of the O···O distance of SF(La–Yb).

The ligand in the organic phase is distributed into the aqueous phase and releases hydrogen to form the anionic species followed by complex formation with metal ions. This metal complex is distributed to the organic phase because of the high hydrophobicity. The heat of formation of the anionic species was obtained by MNDO/H calculation, varying the distance between the two donating oxygens. The β-diketone moiety including the two carbonyl groups and the carbon in the α position was fixed on a plane through the calculation, for the β-diketone moiety is usually kept on the plane or close to coplanar in the lanthanide complexes. Plots of H_f (heat of formation) *vs.* the distance between the two donating oxygens are seen in Fig. 4. The O···O distances of the most stable structure are 3.05, 3.00, 2.98 and 2.84 Å for HL^1–HL^4, respectively. Since the ionic radius of lanthanide ions becomes smaller as the atomic number increases, the charge density increases as the atomic number increases. Consequently, lanthanides

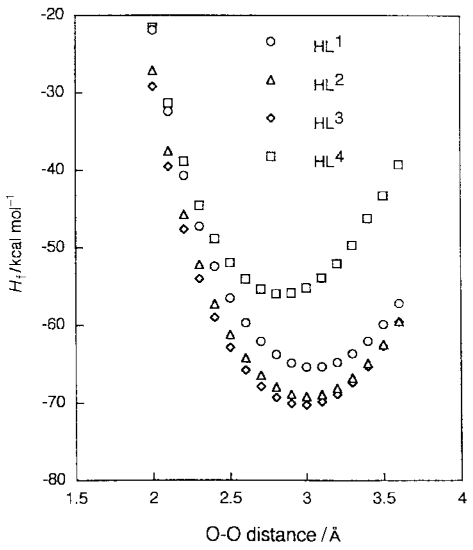

Fig. 4 Plots of the heat of formation (H_f) *vs.* the O···O distance for the anionic form of HL^1–HL^4. H_f was calculated by MNDO/H.

are well extracted in the order in which the atomic number decreases. According to X-ray crystallographic studies, the O···O distance in the lanthanide β-diketonates is in many cases 2.7–2.9 Å.[18–21] It is reported that the distance between the central lanthanide ion and the oxygen atom in water of hydration decreases as the atomic number increases,[22] which suggests that the conformation of the two donating oxygens in the β-diketone is also affected by the ionic radii of the central lanthanide ions. It is shown in Fig. 4 that some amount of energy is needed to arrange their conformation to fit the complex structure. Even more energy is required to complex smaller metal ions. This means that the selectivity obtained by the difference in the charge density is offset to some extent by the energy which is required to rearrange the conformation of the ligand. On the other hand, less energy is required for the ligands having shorter O···O distances to rearrange their conformation. The selectivity would not be reduced so much as in the case of the ligands having longer O···O distances.

The separability of the 4-pivaloyl derivative (HL^4) is equal to that of bis(2-ethylhexyl) hydrogenphosphate, one of the most selective extractants for lanthanides.[23,24]

Conclusions

Our results suggest that the O···O distance is one of the most important factors that governs the selectivity. The separability for the lanthanide metal ions with ligands of shorter O···O distance is found to be better. The concept obtained in the present work is universal and applicable to a wide range of multidentate ligands. Appreciation of the significance of the effect of the O···O distance, and furthermore the geometry of the donating atoms and the rigidity of the ligands, would help in designing or modifying ligands of high selectivity.

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