Improved Separation in the Solvent Extraction of Lanthanides by β-Diketones through a Controlled Separation of the Two Donating Oxygens

Shigeo Umetani,* Yusuke Kawase, Hideki Takahara, Quyen Thi Hanh Le and Masakazu Matsui

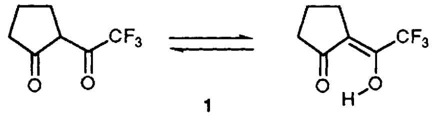
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

The extractability and separability of lanthanides with β-diketones is shown to be governed by the separation of the two donating oxygens.

In the course of our studies on the solvent extraction of lanthanides (Ln^{3+}) with acylpyrazolone or acylisoxazolone derivatives, we have noticed that improved extraction with a strongly acidic extractant is usually accompanied by poor selectivity. The extracting power for 2-thenoyltrifluoroacetone (HTTA, pK_a = 6.23),[1,2] 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP, 3.92)[3,4] and 3-phenyl-4-benzoyl-5-isoxazolone (HPBI, 1.23)[5] increases as their acidity increases, whereas, selectivity becomes poorer. In addition, the distances between the two donating oxygens, estimated by use of a semi-empirical MNDO/H[†] calculation, are *ca.* 2.5, 2.7 and 2.9 Å for HTTA, HPMBP and HPBI, respectively, strongly suggesting a relationship between the oxygen separation and the acidity of the extractant, the extractability and the separability of lanthanides. In order to confirm this, 2-trifluoroacetyl-cyclopentanone **1** and -cyclohexanone **2** have been synthesized and their extraction of lanthanides (Eu^{3+}, Ho^{3+} and Yb^{3+}) has been examined.

Ligands **1** and **2** were synthesized according to the literature.[6] The structure and purity were identified through IR, ^{1}H NMR spectroscopy and elemental analyses.

In general, β-diketone-type chelating agents exhibit keto–enol tautomerism. No signal attributed to a methyne proton of ligand **1** was observed in its ^{1}H NMR spectrum in CDCl$_3$. A trace of a signal attributed to a methyne proton of ligand **2** was observed at δ 3.9 as a triplet. The signals of the hydroxy protons of **1** and **2** appeared at δ 12.9 and 15.1. These NMR data show that **1** and **2** exist quantitatively in enol form. The strong absorptions assigned to C=O stretching occur at 1690 for **1** and 1570 cm^{-1} for **2** in their IR spectra. The NMR and IR data clearly indicate that the intramolecular hydrogen bonding of **1** is weakened owing to the longer O–O distance. The O–O distance obtained by a semi-empirical MNDO/H calculation is 2.55 for **1** and 2.43 Å for **2**. PM3 and AM1 calculations gave similar values.



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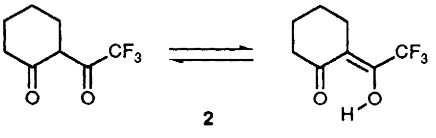

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[†] Semi-empirical calculations, MNDO/H (MNDO calculation that is taking hydrogen bonding into consideration), AM1 and PM3, were performed on fully optimized molecular geometries on a Cray Y-MP2E/264 using UNICHEM (Cray Research Inc.).

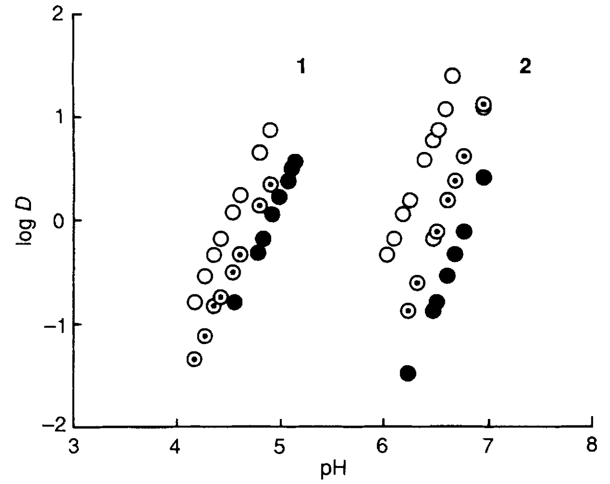

Fig. 1 Extraction of lanthanides into chloroform with **1** and **2**. Conditions as in Table 1. ○ Yb, ⊙Ho, ● Eu.

In Fig. 1 are seen the plots for log D *vs.* pH in the extraction of lanthanides into chloroform with **1** and **2**. Lanthanides are extracted from a much lower pH region with **1** owing to its stronger acidity. The slopes of the straight lines are close to 3. From the effect of the concentration of the extractant (HA) on D, it was deduced that the composition of the extracted species was LnA_3. The overall extraction equilibrium and the extraction constant, K_{ex}, can be expressed as in eqns. (1) and (2), where subscript o stands for the species in the organic phase. The $pH_{1/2}$ values, where half of metal ion is extracted, and the extraction constants obtained on the basis of eqn. (2) are summarized in Table 1 together with the separation factor (SF) defined by the difference in the log K_{ex} values. It is clearly gleamed from Table 1 that the extraction constants for **1** are much larger than those for **2**. On the other hand, the selectivity is significantly better for extractant **2** than for **1**. The SF values between europium and ytterbium are reported to be 0.94 (extractions into benzene), 1.09 and 0.09 (extractions into chloroform) for HTTA,[2] HPMBP[4] and HPBI,[5] respectively. The separation of the heavier lanthanides with **2** is much improved over that for these extractants.

$$Ln^{3+} + 3HA_o \rightleftharpoons LnA_{3,o} + 3H^+ \quad (1)$$

$$K_{ex} = [LnA_3]_o[H^+]^3/[Ln^{3+}][HA]_o^3 = D[H^+]^3/[HA]_o^3 \quad (2)$$

Table 1 Extraction constants of lanthanides into chloroform for the extractants **1** and **2**

	Extractant 1			Extractant 2		
	$pH_{\frac{1}{2}}$[a]	log K_{ex}	SF	$pH_{\frac{1}{2}}$[a]	log K_{ex}	SF
Eu^{3+}	4.90	−10.81		6.81	−16.52	
			0.47			0.78
Ho^{3+}	4.75	−10.34		6.55	−15.74	
			0.72			1.13
Yb^{3+}	4.51	−9.62		6.17	−14.61	

[a] Organic phase: [extractant] = 0.05 mol dm^{-3} in chloroform. Aqueous phase: [$NaClO_4$] = 0.1 mol dm^{-3}, added to keep the ionic strength at 0.1; [Good's buffer] = 0.01 mol dm^{-3}; [Ln^{3+}] = 1 × 10^{-4} mol dm^{-3}. Extractions were made at 25 °C.

Our results show that the O–O distance is one of the factors that govern selectivity, though it cannot be concluded that a smaller O–O distance will always bring good selectivity. Appreciation of the significance of the effect of the O–O distance may help in designing or modifying ligands of high selectivity. The solvent extraction studies with **1** and **2** are now being extended to other metal ions.

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