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Journal of Alloys and Compounds 408–412 (2006) 981–984

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Molecular design of organic ligands highly selective for lanthanide metal ions

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Received 31 July 2004; received in revised form 3 December 2004; accepted 6 December 2004
Available online 24 June 2005

Abstract

Some ß-diketones in which the distance between the two donating oxygens was controlled have been designed and synthesized. The structures of the ß-diketones derivatives were evaluated by semi-empirical MNDO/H molecular orbital calculation and ^{1}H 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 O─O distance becomes shorter, suggesting that the O─O distance is one of the most significant factors that govern the selectivity in the extraction of lanthanide metal ions. The separability of 1-phenyl-3-methyl-4-pivaloy-5-pyrazolone is comparable to that of bis(2-ethylhexyl)phosphoric acid, one of the most selective extractants for lanthanides.

Keywords: Molecular design; Solvent extraction; Separation; Lanthanide metal ions

1. Introduction

ß-Diketones are well known as versatile chelating reagents for metal ions. A large number of studies have been done as chelating reagents especially in the field of the solvent extraction of metal ions for the purpose of separation and concentration [1,2]. Much attention has been also paid to structural chemistry of ß-diketones involving keto–enol tautomerism and the intramolecular hydrogen bond [3,4].

In the course of the studies on the solvent extraction of metal ions with acylpyrazolones or acylisoxazolones, the authors have noticed that improved extraction with strongly acidic extractants is usually accompanied by poor selectivity [5–8]. Examination of the ligand structure by the molecular orbital calculations postulated the relationship among the separation of the two donating oxygens, the acidity of the ligands, and the extractability and separability for metal ions.

In the present paper, some ß-diketones were synthesized, and the solvent extraction of lanthanide metal ions was examined. The separability in the extraction of lanthanide metal ions with these ß-diketones was discussed in terms of the effect of the O–O distance. It was found that the separability with the other ß-diketones could be also explained taking the effect of the bite size into consideration.

2. Experimental

Trifluoroacetylcyclohexanones, α-substituted ß-diketones and acylpyrazolones were prepared according to the literature [9–11]. The solvent extractions were made in the similar manners described in the literature [6–8].

3. Results and discussion

Three series of ß-diketones have been prepared systematically in order to elucidate the effect of the molecular structure of the ß-diketones, especially the O–O distance, on the extractability and separability of lanthanide metal ions: trifluoroacetylcycloalkanones (1) in which the O–O distance is controlled by the ring-structure geometry, the α-substituted

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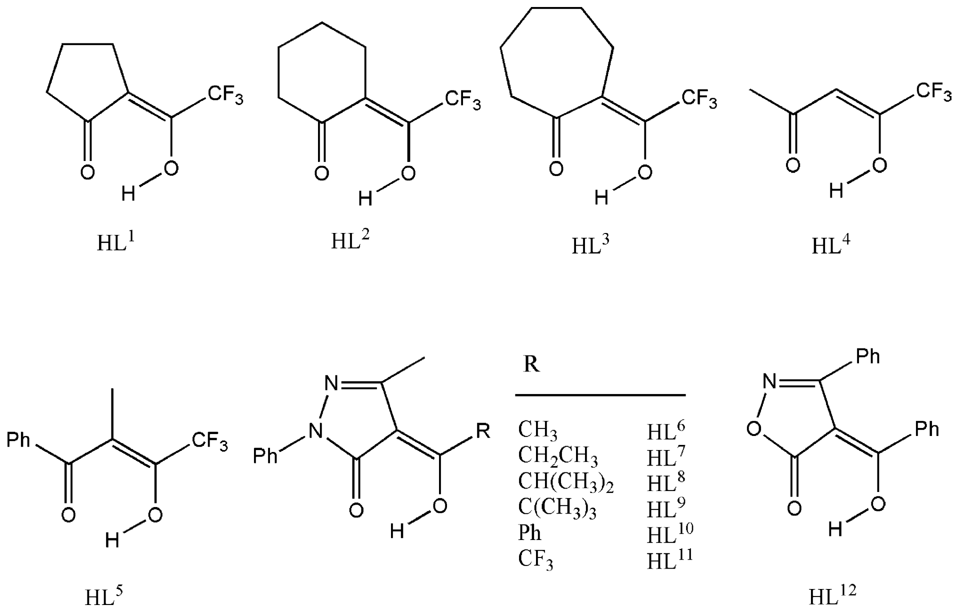
doi:10.1016/j.jallcom.2004.12.089



Scheme 1. ß-Diketones employed in the present work.

ß-diketones (2), by the steric effect of bulky substituents at their α-position, the heterocyclic 4-substituted pyrazolones (3), by the steric effect between the 3-methyl group and the bulky 4-acyl substituents. The structures of the ß-diketones in use are shown in Scheme 1.

3.1. *Trifluoroacetylcycloalkanones*

The distances between the two donating oxygens for the enol forms of HL^1, HL^2 and HL^3 were obtained by semi-empirical MNDO/H calculations and are seen in Table 1 together with that of trifluoroacetylacetone (HL^4), the conventional ß-diketone analogous to HL^1, HL^2 and HL^3. It is clear that the O–O distance for HL^1 is longer than those for HL^2 and HL^3 as predicted from their cyclic structures. The O–O distances for the anionic form and the lithium complexes were also calculated by MNDO/H, and either of them for HL^1 is longer than those for HL^2 and HL^3. In the case of the calculation for the anionic form, the enol moiety was fixed on a plane. 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. The calculated hydrogen bond energy for HL^1 is 4.37 and 4.60 kcal/mol smaller than that of HL^2 and HL^3, respectively. The ^{1}H NMR spectra in $CDCl_3$ show the evidence for the hydrogen bond strength. The sharp signals assigned to the hydroxyl protons of HL^2 and HL^3 appeared at δ 15.07 and 15.94, respectively; whereas, a very broad signal was observed at δ 12.9 for 1. It was reported that the hydrogen-bonded enolic proton signal appears at that low magnetic field. These signals did not move through changing the concentration (0.01–0.1 mol dm^{-3}) and was found to disappear 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–O separation.

Complexation of trifluoroacetylcycloalkanones with lanthanides has been investigated via the solvent extraction technique. The solvent extraction behaviors of lanthanides (Ln^{3+}) from a 0.1 mol dm^{-3} sodium perchlorate aqueous phase to a 0.05 mol dm^{-3} trifluoroacetylcycloalkanone (HA) chloroform phase were examined. The logarithmic value of the distribution ratio of 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

Table 1
Structural comparison of HL^1–HL^4

	HL^1	HL^2	HL^3	HL^4
O—O distance (Å)				
HA	2.55	2.43	2.42	2.50
A^-	2.99	2.75	2.74	3.08
LiA	2.86	2.69	2.68	2.89
E_{OH} (kcal/mol)	10.00	14.37	14.60	14.02
^{1}H NMR (—OH, ppm, $CDCl_3$)	12.9 (Very broad)	15.07 (Sharp)	15.94 (Sharp)	14.06 (Very broad)

Table 2
Extraction parameters for lanthanides with HL^1–HL^3

	HL^1		HL^2		HL^3	
	$\log K_{ex}$	SF	$\log K_{ex}$	SF	$\log K_{ex}$	SF
La^{3+}	−13.26		–		–	
		1.46		–		–
Pr^{3+}	−11.80	–	−17.27	–	−17.55	–
	–	0.99		0.75	–	1.32
Eu^{3+}	−10.81	–	−16.52	–	−16.23	–
	0.47	–	0.78	–	0.63	–
Ho^{3+}	−10.34	–	−15.74	–	15.60	–
	–	0.72	–	1.13	–	1.04
Yb^{3+}	−9.62	–	−14.61		−14.56	–
SF(Yb–Pr)	–	2.18	–	2.66	–	2.99

$[HA]_o = 0.05\,mol\,dm^{-3}$ in chloroform.

are found to fall on straight lines. The slopes of the lines are 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 plots, $\log D - 3pH$ versus $\log [HA]_o$, were found to be close to three, indicating that the extracted species is LnA_3. Based on these slope analyses, the extraction equilibrium can be expressed as follows:

$$Ln^{3+} + 3HA_o = LnA_{3,o} + 3H^+ \tag{1}$$

The extraction constant, K_{ex}, is defined in Eqs. (2) and (3).

$$K_{ex} = \frac{[LnA_3]_o[H^+]^3}{[Ln^{3+}][HA]_o^3} = D\frac{[H^+]^3}{[HA]_o^3} \tag{2}$$

$$\log K_{ex} = \log D - 3pH - 3\log[HA]_o \tag{3}$$

The $\log K_{ex}$ values are summarized in Table 2. The most distinguishing difference in the extraction behavior is the extraction pH region. Lanthanides were extracted at about a 1.5–2 lower pH region by HL^1 than by HL^2 and HL^3.

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. Although the separability between La and Pr cannot be compared, the SF values for HL^2 and HL^3 are superior to those for HL^1 except for that between Pr and Yb for HL^2. The SF values between Pr and Yb are 2.18, 2.66 and 2.99 for HL^1, HL^2 and HL^3, respectively. It is clear that the O–O distance is responsible for the selectivity.

The possible explanation for the role of the O–O distance and the ligand rigidity in the complexation of trifluoroacetylcyclohexanone with lanthanides could be postulated as follows. The ligand in the organic phase is distributed into the aqueous phase and releases hydrogen to form the anionic species followed by the complex formation with metal ions. This metal complex is distributed to the organic phase owing to 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 ß-diketone moiety including the two carbonyl groups and the carbon in the α-position were fixed on a plane through the calculation, for the ß-diketone moiety is usually kept on the plane or close to coplanar in the lanthanide complexes. The plots of heat of formation (Hf) versus the distance between the two donating oxygens indicates that the most stable structures are given when their O–O distances are 2.99, 2.75 and 2.74 Å for HL^1, HL^2 and HL^3, respectively. Because the ionic radius of lanthanide ions becomes smaller as the atomic number increases, the charge density increases as the atomic number increases. Consequently, lanthanides are well extracted in the order in which the atomic number increases. According to the X-ray crystallographic studies, the O–O distance in lanthanide ß-diketonates is in many cases 2.7–2.9 Å [12]. In the case of HL^1, some amount of energy is needed to arrange its 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 arrange the conformation of the ligand. On the other hand, less energy is required for HL^2 and HL^3 to arrange their conformation. The selectivity would not be reduced so much as in the case of HL^1.

3.2. α-Substituted ß-diketones

An introduction of a methyl group to the α-position in the molecular structure of benzoyltrifluoroacetone (BFA) gave α-methyl benzoyltrifluoroacetone (HL^5). Their O–O distances were estimated by MNDO/H to be 2.51 and 2.42 Å, respectively. ^1H NMR spectrum data in $CDCl_3$ clearly show that the intramolecular hydrogen bonding of HL^5 is strengthened (rather sharp OH-peak at $\delta = 15.8$ ppm) owing to its smaller O–O distance, comparing to that of BFA (very broad OH-peak at $\delta = 15.2$ ppm). Their dissociation constants, pK_a, were measured by potentiometric titration method in water–dioxane (25:75, v/v) to be 8.10 for BFA and 10.35 for MBFA.

From the data, it is obvious that BFA, with its smaller pK_a and larger O–O distance, can extract lanthanides better: the K_{ex} values for BFA are in fact 10^5–10^6 times larger than those for MBFA. Otherwise, as a result of the diminution of the O–O distance, HL^5 separates lanthanides better than BFA: the separation factor for La and Yb, found to be 4.68 for HL^5 exceeds that for BFA which is 3.90.

It should be noticed that the presence of an α-substituent in the structure of ß-diketone is often followed by a notable decrease of the percentage enol tautomer of the extractant, thus hinders the solvent extraction procedure. In fact, a bromo group has been introduced to dibenzoylmethane (DBM) and BFA to obtain α-BrDBM and α-BrBFA with shorter O–O distances. However, due to the predomination of their keto forms, the attempt to get their solvent extraction data was failed. Our study will be expanded further with phenyl group as α-substituent for enol rich ß-diketone derivatives, such as phenyl acetylacetone (PAA) and phenyl benzoylacetone (PBA).

Table 3
Structural comparison of HL^6–HL^{12}

	HL^6	HL^7	HL^8	HL^9	HL^{10}	HL^{11}	HL^{12}
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)	13.93	14.95	15.41	18.38	12.43	10.74	5.71

Table 4
The log K_{ex} values for lanthanide metal ions with acylpyrazolones

	HL^6	HL^7	HL^8	HL^9
La^{3+}	−9.82	−9.97	−10.19	−14.22
Pr^{3+}	−8.22	−8.46	−8.72	−12.49
Eu^{3+}	−7.13	−7.26	−7.43	−11.13
Ho^{3+}	−6.24	−6.39	−6.46	−10.28
Yb^{3+}	−5.35	−5.56	−5.54	−9.25
SF(Yb–La)	4.47	4.41	4.65	4.97

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

3.3. Acylpyrazolones

The O–O distances obtained by MNDO/H for various acylpyrazolones and acylisoxazolone are shown in Table 3. The distance between the two donating oxygens of HL^6 is 2.60 Å and shortens as the 4-acyl group becomes bulkier. A shortening of this distance was made by introducing a bulky group to the 4-position of the pyrazolone ring. 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. No enolic proton peak is usually observed for acylpyrazolones, although they exist quantitatively in the enol form in the organic solvent, which can be assured by the lack of the peak for the methyne proton at the 4-position. However, a moderately sharp peak was observed at 14.9 ppm only for HL^9, whose O–O distance is the shortest among the acylpyrazolones examined in the present work. The intramolecular hydrogen bond energy (E_{OH}) increases as the O–O distance decreases.

Molecular orbital calculations were also made for benzoyl-(HL^{10}) and trifluoroacetylpyrazolone (HL^{11}) derivatives and 3-phenyl-4-benzoyl-isoxazolone (HL^{12}). The O–O distances for HL^{10} and HL^{11} are similar and longer than those of HL^6–HL^9. HL^{12} is characterized by the long O–O distance (2.90 Å), and consequently its E_{OH} is very small.

The separation factors between lanthanum and ytterbium, SF(Yb–La), are 4.47, 4.41, 4.65 and 4.97 for HL^6–HL^9, respectively. As seen in Table 4, the extraction separability for the lanthanide metal ions improves as the O–O distance becomes shorter. This tendency is also seen for the other acylpyrazolones. The SF(Yb–La) values for HL^{10} and HL^{11} are reported to be 2.94 [5] and 3.03 [7], respectively. Although the nature of the acyl group is quite different, the separability for HL^{10} and HL^{11} is very similar. The phenyl group in HL^{10} is aromatic, while the CF_3 group in HL^{11} is aliphatic analogous to HL^6–HL^9 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^{12} 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(Yb–La) values were reported to be 1.23 and 1.47 [8], respectively. It is quite interesting that the low separability for the extractant HL^{12} can also be rationalized in terms of the O–O distance. The separability of the 4-pivaloy derivative (HL^9) is equal to that of bis(2-ethylhexyl)phosphoric acid, one of the most selective extractants for lanthanides [13].

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