Molecular Design of Highly Selective Ligands for Group 13 Metals

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Highly selective ligands for group 13 metal ions (Al<sup>3+</sup>, Ga<sup>3+</sup> and In<sup>3+</sup>) have been successfully designed taking into consideration the bite size (O-O distance in the chelate ring) and the interligand contact in the complex. The complexation of Al<sup>3+</sup> was found to be under the effect of the interligand contact and that of In<sup>3+</sup> the bite size. The appropriate substituents were introduced to β-diketone type ligands to control the bite size and the volume of the ligand.

Keywords Solvent extraction, β-diketone, acylpyrazolone, molecular recognition, substituent effect, bite size, interligand contact, aluminum, gallium, indium

β-Diketones have been proven to be versatile ligands for various metal ions. A large number of studies have been done as chelating reagents, especially in the field of solvent extraction of metal ions for the purpose of separation and concentration. Much attention has also been paid to the structural chemistry of β-diketones involving keto-enol tautomerism and the intramolecular hydrogen bond. However, a systematic study on the correlation between the structure of β-diketones and their selectivity for metal ions seems to be insufficient.

Studies on the solvent extraction of metal ions with acylpyrazolones<sup>6,7</sup> and acylisoxazolones<sup>8</sup> 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 AA and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadione (thenoyltrifluoroacetone, TTA), according to the 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<sup>9</sup> and acylpyrazolones having bulky substituents at the 4-position,<sup>10</sup> it has been found that the separability of lanthanides was clearly improved with those ligands having 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 β-diketone could be suitably modified in the way fitting the geometry of its ring skeleton introducing bulky groups at suitable positions for creating 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 ionic radii very similar to each other, we now expand our research to the metal ions of group 13 with elements of large difference in the 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.<sup>11</sup>

In the present paper, the selectivity of modified β-diketones for Al<sup>3+</sup> (r = 0.53 Å for a coordination number of 6), Ga<sup>3+</sup> (r = 0.62 Å) and In<sup>3+</sup> (r = 0.80 Å)<sup>12</sup> has been examined via the solvent extraction method, and the stability of Al<sup>3+</sup>, Ga<sup>3+</sup> and In<sup>3+</sup> β-diketonates has been discussed based on the structures of the ligands and their metal complexes.

Experimental

Chemicals

1,2-Diphenyl-1,3-butanedione (α-phenylbenzoyl-acetone, PhBA) was synthesized referring to the literature. 1,2-Diphenyl-1,3-butanedione (α-phenylbenzoyl-trifluoroacetone, MBFA)<sup>14</sup> was synthesized according to the method of Jensen. 3-Phenyl-2,4-pentanedione (α-phenylacetylacetone, PhAA), 1-phenyl-1,3-butanedione (benzoyl-acetone, BA), 4,4,4-trifluoro-1-phenyl-

\[ R_1 \text{Ph} \quad R_2 \text{Ph} \quad R_3 \text{Ph} \]
1,3-butane-dione (benzoyl trifluoroacetone, BFA), and 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone, TAA) were purchased from Dojindo and used without further purification.

**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. 1H-NMR spectra were measured with a Varian VX-200 spectrometer (200 MHz) at 25 °C in CDCl3.

Semiempirical MNDO/H17 calculation was performed on fully optimized molecular geometries on a Cray Y-MP2E/264 using MNDO93 (Cray Research Inc.).

**Acid Dissociation Constants (pKₐ)**

The pH measurements for determining pKₐ of AA, BA, PhAA and PhBA were made in aqueous 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 (tetramethylammonium perchlorate) in 25:75 v/v of water-dioxane, and the pH reading correction proposed by Irving and Mannon18 has been adopted. The pKₐ values of the acylpyrazolones were obtained by analyzing the distribution of the ligand between the benzene phase and the 0.1 M sodium perchlorate aqueous phase.19

**Solvent Extraction Procedure**

A 10 cm³ aliquot of an aqueous phase containing 1x10⁻⁴ mol dm⁻³ of metal ion, 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 ligand in a 30 cm³ centrifuge tube at 25 °C until the reaction reached to the 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 agrees well with the initial concentration.

**Results and Discussion**

**Molecular Orbital Calculations**

The distances between the two donating oxygens were estimated by semi-empirical MNDO/H17 calculation which is the MNDO17 calculation that takes the hydrogen bond into consideration. The distances between the two donating oxygens of AA and BA are 2.50 and 2.51 Å, respectively, whereas those for PhAA and PhBA are reduced to 2.44 Å. A shortening of this distance was made by introducing a phenyl group to the α-position of AA and BA. The steric repulsion raised between the phenyl group and the two terminal groups in the structure of AA and BA brings a narrowing of this distance. This structural change is also supported by 1H-NMR data. The very broad peaks assigned to the enolic proton (-OH) for AA and BA appear at 15.44 and 16.15 ppm, respectively, while those for PhAA and PhBA are very sharp and shift downfield to 16.77 and 17.39 ppm, respectively. The sharp and downfield signal of the enolic proton is caused by the strong intramolecular hydrogen bonding due to the narrow O-O separation.

In addition, the facts that the enolic proton signals correspond to one proton and there were observed no methyne protons for PhAA and PhBA indicate that both PhAA and PhBA exist quantitatively in the enol form in CDCl3. It has been reported that the presence of an α-substituent usually favors the keto tautomer,4 and our previous results14 are in agreement with this tendency. The results obtained here agree with the report5 demonstrating that the α-aryl group markedly increases the enol content unlike other α-substituents such as the methyl or bromo groups.

**Equilibrium Analysis**

The complexations of the two extractants PhAA and PhBA with Al³⁺ and In³⁺, compared to those of AA and BA, have been investigated via the solvent extraction method. The extraction behaviors significantly changed through the introduction of a phenyl group to the α-position. The solvent extractions of Al³⁺ and In³⁺ from a 0.1 mol dm⁻³ sodium perchlorate aqueous phase to a 0.1 mol dm⁻³ PhAA benzene phase are shown in Fig. 1. Almost 100% of Al³⁺ is extracted around pH 4.6 with PhAA, while In³⁺ is totally unextracted below pH 5. A similar result was also obtained for PhBA.

To clarify the composition of the extracted species, the effects of pH and log [HA] on log D (D = [M³⁺]/[M³⁺]) was also examined. Here, HA...
Interligand Contact in Al and In $\text{Bdiketonates}$

The intracomplex interligand contacts should have great influence on the stability of Al $\text{Bdiketonates}$, which could be deduced from the extraction order of Al$^{3+}$ and In$^{3+}$ with $\text{Bdiketonates}$. In general, the organic ligands including $\text{Bdiketonates}$ form more stable complexes with metal ions having smaller ionic radii when their 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 Al$^{3+}$ and In$^{3+}$, the reverse in the extraction order is frequently seen depending on the bulkiness of the ligands. Al$^{3+}$ is extracted better than In$^{3+}$ with AA and BA. In the case of bulky $\text{Bdiketonates}$, such as DBM and TTA, 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 $\text{Bdiketonates}$. It should be noted here that the O-O distances of AA, BA, TTA and DBM are similar to each other according to the molecular orbital calculations. Although Al$^{3+}$ is completely isolated from In$^{3+}$ by PhAA and PhBA, the extractions were disturbed compared to those for AA and BA, i.e., the distribution curves log D vs. pH of Al$^{3+}$ for PhAA and PhBA shifted more to the alkaline region than those of AA and BA. The poor extractions of Al$^{3+}$ with PhAA and PhBA are partly ascribed to the lower acidity, though this is not so important because differences of the pK$_a$ values are very small. It could be also attributed to the interligand contact in the Al complex. The steric crowding of the ligands is enhanced by the $\alpha$-phenyl group which disturbs the free rotation of the terminal methyl or phenyl groups. The free rotation is expected to diminish the interligand contact.

Simultaneous Effects of the Bite Size and the Interaligand 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 TAA, BFA and MBFA. Al$^{3+}$ was better extracted than In$^{3+}$ with TAA; the O-O distance of TAA 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 BFA, its O-O distance (2.52 Å) and pK$_a$ are still similar to those of TAA. The extraction of Al$^{3+}$ with BFA 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 to the $\alpha$-position of BFA to obtain its derivative MBFA, the O-O distance and pK$_a$ are reduced. Because of the lower acidity and the enhanced interligand contact caused by the $\alpha$-methyl group as in the case of PhAA and PhBA, the extraction of Al$^{3+}$ decreased; however, the influence of the narrowed O-O distance is markedly seen for the In$^{3+}$ extraction. The extraction of In$^{3+}$ drastically decreased, consequently, Al$^{3+}$ was extracted much better than In$^{3+}$ resulting in a facilitated separation.

Extraction with Acylpyrazolones

Five acylpyrazolone derivatives have been prepared as seen in the scheme. They are 1-phenyl-3-methyl-4-acetyl (HPMAP), 1-benzoyl (HPMBP), 1-(1-naphthoyl) (HPM1NP), 2-(2-naphthoyl) (HPM2NP), and -pivaloyl (HPMPIP)-pyrazolones. The O-O distances were estimated by...
the MNDO/H calculation. The O-O distances of the acyl-pyrazolones except for HPMPiP are 2.60 - 2.65 Å, while that of HPMPiP is 2.46 Å. The 1H-NMR spectra show the evidence for the hydrogen bond strength. The signal assigned to the hydroxyl proton of HPMPiP appeared at 14.9 ppm; whereas those for the other acylpyrazolones are too broad to observe at 10-20 ppm.

Fig. 2 Extraction of Al^{3+} into benzene with acyl-pyrazolones. [acylpyrazolone]_o = 5x10^{-3} mol dm^{-3} in benzene. [NaClO_4] = 0.1 mol dm^{-3}.

Being derived from the five membered heterocyclic 4-pyrazolone, the O-O distances of the present acylpyrazolone derivatives except for HPMPiP are longer than those of the conventional β-diketones. Owing to their long O-O distances, the extraction of In^{3+} was not disturbed and was made at pH 1-2. The extraction of Al^{3+} was seen in the higher pH region, although the ionic radius of Al^{3+} is much smaller than that of In^{3+}. Considering that the acylpyrazolones themselves are bulky ligands and their acidities are quite similar, it is clear that the extraction of Al^{3+} is under the effect of the interligand contact. As seen in Fig. 2, it was found that the extraction reduces as the substituent at the 4-position becomes bulkier. The quantitative separation of Al^{3+} from In^{3+} can be readily achieved with the naphthoylpyrazolones. The extraction of In^{3+} does not depend on the size of the substituents. The effect of the interligand contact is also seen in the extraction of Ga^{3+}. While the ionic radius of Ga^{3+} is smaller than that of In^{3+}, their extractions were similar. In addition, the extractability decreases as the substituents becomes bulkier like the case of Al^{3+}. All of the acylpyrazolones examined are available to quantitatively separate Al^{3+} and Ga^{3+}. Owing to the steric repulsion between the 4-pivaloyl and 3-methyl groups, the O-O distance of HPMPiP is narrowed and the extraction of In^{3+} came close to that of Al^{3+}, resulting in a quantitative separation of Ga^{3+} from Al^{3+} and In^{3+}.

From our results so far, there are two factors governing the complexion of group 13 metal ions 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 on organic ligands, especially on the concepts of their complexion with metal ions, and confirms our suggestion for a perspective strategy for designing novel ligands of high selectivity from well-known typical ones.

References

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