Steric Control of Selectivity for Lanthanoids in Liquid–Liquid Extraction with Tris- and Tetrakis(pyrazol-1-yl)borate–β-Diketon Mixed-Ligand Systems

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Mixed-ligand chelate extraction of trivalent lanthanoid ions (M^{3+}) into benzene with poly(pyrazol-1-yl)borate ($H_nB(pz)_{4-n}$; $n=0, 1$) and β-diketone was studied. The β-diketones used were dibenzoylmethane (dbm) and dipivaloylmethane (dpm). Lanthanoid ions were extracted as $[M\{H_nB(pz)_{4-n}\}_2(\beta\text{-diketone})]$. The logarithmic extraction constants ($\log K_{ex}$) of the $[HB(pz)_3]^-$ systems were 5—6 higher than those of the $[B(pz)_4]^-$ systems. The highest separability for lanthanide ions was achieved with the $[B(pz)_4]^-$–dbm system. These features of $\log K_{ex}$ were principally governed by intra- and interligand steric contact.

Ligand structure is the most fundamental factor in the discrimination of ion size and the separation of ions. Hydrotris(pyrazol-1-yl)borate ($[HB(pz)_3]^-$) and tetrakis (pyrazol-1-yl)borate ($[B(pz)_4]^-$) consist of the tetrahedral boron atom bonding pyrazol-1-yl groups. They act as bidentate or tripodal tridentate ligands, the coordination taking place through the pyrazole nitrogen atoms, and form a six-membered chelate ring with a boat conformation.[1)] Thus far, ion recognition using these ligands of unique structure has not been clarified.

In a recent study we separated group 2 metals by liquid–liquid extraction with poly(pyrazol-1-yl)borates.[2)] $[HB(pz)_3]^-$ quantitatively extracts both Mg^{2+} and Ca^{2+} as an octahedral bis-ligand complex with C_{3v} symmetry. Although $[B(pz)_4]^-$ extracts Mg^{2+} quantitatively around neutral pH, it barely extracts Ca^{2+}. Such high selectively for Mg^{2+} over Ca^{2+} is not realized with conventional ligands. The high selectivity is derived from the fact that $[B(pz)_4]^-$ cannot open the tripod of the pyrazol rings to the size fitting Ca^{2+} because of the steric contact between the coordinated and noncoordinated pyrazol rings. The ion size discrimination by $[B(pz)_4]^-$ totally differs from that of conventional chelating ligands. The latter depends on the chelate ring size, which is regulated by the kind and number of atoms, as well as the order of the bonds contained in the ring.[3)]

The present study was conducted in order to investigate how poly(pyrazol-1-yl)borates discriminate the size of lanthanoid ions. The separation of individual lanthanoid ions by liquid–liquid extraction is still a challenging theme in ligand design. Many monodentate, chelating and macrocyclic ligand systems, as well as mixed-ligand systems, have been investigated.[4)] However, there have been few studies in which the extraction behavior had been interpreted based upon the complex structure and the strategy to improve the selectivity has been clearly proposed.

In preliminary experiments, the extractability of lanthanoids with $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ was rather low. It was singnificantly enhanced by the presence of a β-diketone ligand, such as dibenzoylmethane (1,3-diphenyl-1,3-propanedione; dbm) or dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione; dpm). Mixed-ligand systems of poly(pyrazol-1-yl)borate and β-diketone for lanthanoid extraction are discussed in this paper.

Experimental

Reagents and Apparatus. Potassium hydrotris(pyrazol-1-yl)borate and potassium tetrakis(pyrazol-1-yl)borate were synthesized from pyrazole and potassium tetrahydroborate according to a method of Trofimenko.[1a)] The crude compounds were recrystallized from a anisole. All other chemicals were reagent-grade materials and distilled water was used throughout.

The pH was measured using a Hitachi–Horiba F-8L pH meter equipped with a glass electrode. The metal ion and ligand concentrations were determined with a Japan Jarrel Ash ICAP-500 inductively coupled argon plasma spectrometer.

Acid Dissociation and Distribution of Poly(pyr-

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azol-1-yl)borates. The acid dissociation constants of $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ were determined by potentiometric titration.[5)] Ten cm^3 of an aqueous solution containing 5×10^{-2} M (1 M=1 mol dm^{-3}) of $K[HB(pz)_3]$ or $K[B(pz)_4]$ was titrated with 0.1 M hydrochloric acid in a stream of nitrogen at 25.0±0.1°C.

The distribution was studied in a 30 cm^3 centrifuge tube. An aliquot of benzene (10 cm^3) was equilibrated with an equal volume of an aqueous phase containing 1×10^{-2} M of $K[H_nB(pz)_{4-n}]$ bufferd with 2×10^{-2} M of sodium acetate, 2-(*N*-morpholino)-ethanesulfonic acid (MES), *N*-(2-acetamido)-2-aminoethanesulfonic acid (ACES), 3-(*N*-morpholino) propanesulfonic acid (MOPS), *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS), 2-(cyclohexylamino) ethanesulfonic acid (CHES), or 3-cyclohexylaminopropanesulfonic acid (CAPS) at 25±1°C. After the two phases were separated by centrifugation, the pH of the aqueous phase was measured. The ligand concentration in the aqueous phase was determined from the boron content using the ICAP-500. The concentration in the organic phase was measured after back-extraction into 0.2 M potassium hydroxide.

Distribution of the Lanthanoid Chelates. Lanthanoid ions were extracted in a manner similar to that of ligand extraction. An aliquot of benzene (10 cm^3) containing β-diketone (1×10^{-2} M) and an equal volume of an aqueous phase containing $K[H_nB(pz)_{4-n}]$ (2×10^{-2} M), lanthanoid ion (1×10^{-4} M) and buffer (2×10^{-2} M), were shaken at 25±1°C for 10 or 20 min for $[HB(pz)_3]^-$ or $[B(pz)_4]^-$ systems, respectively. After the two phases were separated, the pH and the metal concentration in the aqueous phase were determined. The metal concentration in the organic phase was similarly determined after back-extraction into 0.3 or 1.0 M nitric acid.

Results

Acid Dissociation Constants and Partition Constants of Poly(pyrazol-1-yl)borates. The poly(pyrazol-1-yl)borates are polyacidic bases. The acid dissociation constants are defined as:

$$K_{a1} = [H^+][HA]/[H_2A^+] \tag{1}$$

and

$$K_{a2} = [H^+][A^-]/[HA], \tag{2}$$

where A^- stands for a poly(pyrazol-1-yl)borate anion. For $[HB(pz)_3]^-$, pK_{a1} and pK_{a2} were 3.64±0.10 and 6.92±0.04, respectively. For $[B(pz)_4]^-$, pK_{a1} was 3.04±0.10 and pK_{a2} was 6.06±0.05. The poly(pyrazol-1-yl)borates were hydrolyzed in water into pyrazole and boric acid. The decomposition rate of the ligands was highest at around pH 3 — 8. The standard deviations for pK_{a1} were larger than those for pK_{a2}, since the alkaline $K[H_nB(pz)_{4-n}]$ solution was titrated with hydrochloric acid, and the pK_{a1} values were slightly affected by hydrolysis. These values seem to be valid, because the same values were obtained when acidic solutions of the ligands were titrated with sodium hydroxide.

The partition constant of poly(pyrazol-1-yl) borates is defined as

$$P_{HA} = [HA]_o/[HA], \tag{3}$$

where subscript o denotes the species in the organic phase. To remove any influence of the hydrolysis, $\log [HA]_o$ was plotted against the shaking time (*t*), and the value at $t=0$ was obtained by extrapolation. Using this value, $\log P_{HA}$ between benzene and aqueous solutions was −0.23±0.06 for $H[HB(pz)_3]$ and 0.39±0.02 for $H[B(pz)_4]$. The pK_a values of poly(pyrazol-1-yl)-borates, which were determined by the distribution method, agreed closely with those obtained by the titration method.

Distribution of Trivalent Lanthanoids. The extracted ratios (%*E*) of some lanthanoids with $[HB(pz)_3]^-$–dpm and $[B(pz)_4]^-$–dpm systems are plotted as a function of the pH in Fig. 1. The %*E* was at maximum and constant when the shaking time was between 5—15 min for the $[HB(pz)_3]^-$ systems and between 5—25 min for the $[B(pz)_4]^-$ systems. The %*E* decreased due to the hydrolysis of $[H_nB(pz)_{4-n}]^-$, as the shaking time was prolonged beyond the above range. The %*E* was independent of the metal ion concentration of 5×10^{-5}—5×10^{-4} M. It was confirmed that the buffers have no influence on the extraction between 1.0×10^{-2} M and 4.0×10^{-2} M. With the $[HB(pz)_3]^-$–dbm and $[HB(pz)_3]^-$–dpm systems, all lanthanoid ions were quantitatively extracted into the benzene phase. However, the %*E* of heavier lanthanoids in the $[B(pz)_4]^-$ systems also reached 100%; La^{3+} in the $[B(pz)_4]^-$–dbm system and La^{3+}–Nd^{3+} in the $[B(pz)_4]^-$–dpm system were not quantitatively extracted. The recovery of these metal ions decreased as the pH increased.

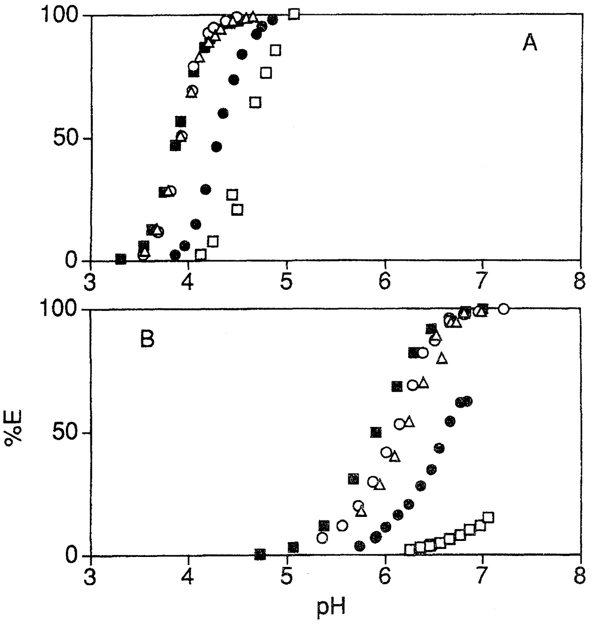

Fig. 1. Plots of %*E* as a function of pH. Initial ligand concentrations are 1×10^{-2} M for Hdpm in benzene, and 2×10^{-2} M for $K[HB(pz)_3]$ (A) or $K[B(pz)_4]$ (B) in the aqueous phase. ■, Yb^{3+}; ○, Dy^{3+}; △, Eu^{3+}; ●, Pr^{3+}; □, La^{3+}.

The overall extraction equilibrium and the extraction constant (K_{ex}) of a lanthanoid ion (M^{3+}) can be described as:

$$M^{3+} + 2HA + HL_o \rightleftharpoons MA_2L_o + 3H^+ \quad (4)$$

$$K_{ex} = [MA_2L]_o[H^+]^3/[M^{3+}][HA]^2[HL]_o \quad (5)$$

$$\log K_{ex} = \log D - 3pH - 2\log[HA] - \log[HL]_o, \quad (6)$$

where L means a β-diketone, and D is the distribution ratio of the lanthanoid ion. The $pK_{a,HL}$ of Hdbm and Hdpm is 9.35 and 11.57, respectively.[6] The logarithmic partition constant of β-diketone ($\log P_{HL}$) between benzene and the aqueous phase is 5.35 for Hdbm and 3.98 for Hdpm.[6] Since these values are sufficiently high, $[HL]_o$ is regarded as begin equal to the initial concentration. To analyze the extraction data graphically, the acid dissociation and distribution of poly(pyrazol-1-yl)borates must be taken into consideration. [HA] is expressed as

$$[HA] = C_{HA,i}/\{P_{HA} + ([H^+]/K_{a1}) + 1 + (K_{a2}/[H^+])\}, \quad (7)$$

where $C_{HA,i}$ means the initial analytical concentration of the poly(pyrazol-1-yl)borate in the aqueous phase. Substitution of Eq. 7 into Eq. 6 and a rearrangement results in

$$\log D = \log K_{ex} + 3pH + 2\alpha + \log[HL]_o, \quad (8)$$

where

$$\alpha = \log C_{HA,i} - \log\{P_{HA} + ([H^+]/K_{a1}) + 1 + (K_{a2}/[H^+])\}, \quad (9)$$

Figures 2, 3, and 4 show plots of $\log D - 2\alpha - \log[HL]_o$ vs. pH, $\log D$ vs. $\log C_{HA,i}$, and $\log D$ vs. $\log C_{HL,o,i}$ for the extraction of La^{3+}, Eu^{3+}, and Lu^{3+} with $[B(pz)_4]^-$-dbm system, keeping the rest of the variables constant. At the lower pH and $C_{HL,o,i}$ regions of the $[B(pz)_4]^-$ systems, the slopes of the plots decreased. This may have been caused by the ion-pair extraction of MA_2^+. Except for these regions, all of the plots of all the systems gave straight lines with slopes very close to 3 for $\log D - 2\alpha - \log[HL]_o$ vs. pH, 2 for $\log D$ vs. $\log C_{HA,i}$, and 1 for $\log D$ vs. $\log C_{HL,o,i}$. These results confirm the validity of Eqs. 4 and 8. The associations of ligands were negligible under these conditions. The $\log K_{ex}$ values were obtained from $\log D - 2\alpha - \log[HL]_o$ vs. pH plots by a linear least-squares fit, and are listed in Table 1.

Discussion

Heteroleptic lanthanoid complexes of $[M\{H_nB(pz)_{4-n}\}_2(\beta\text{-diketone})]$ similar to the extracted species in the present study have been prepared and characterized by several workers.[7] The X-ray structures of some of these compounds have been determined. The lanthanoid ions are eight coordinate and have different geometries, depending upon the species. The geometry of $[Ce\{HB(pz)_3\}_2(acac)]$ (acac=acetylacetone) is that of a distorted bicapped trigonal prismatic (BCTP).[7b,7c] For $[Yb\{HB(pz)_3\}_2(acac)]$, although the geometry of the ytterbium ion is derived from a square antiprism (SAP), a distortion takes the geometry along a pathway towards dodecahedral or BCTP.[7b,7c] The coordination geometry of $[Yb\{HB(pz)_3\}_2(dpm)]$ is best described as SAP.[7a] These findings suggest that the BCTP geometries are preferred by large lanthanoid ions, and that SAP geometries are preferred by small lanthanoid ions and bulky β-diketones. The geometry change is derived from the steric contact between the ligands, which should affect the stability and extraction constants of the complexes.

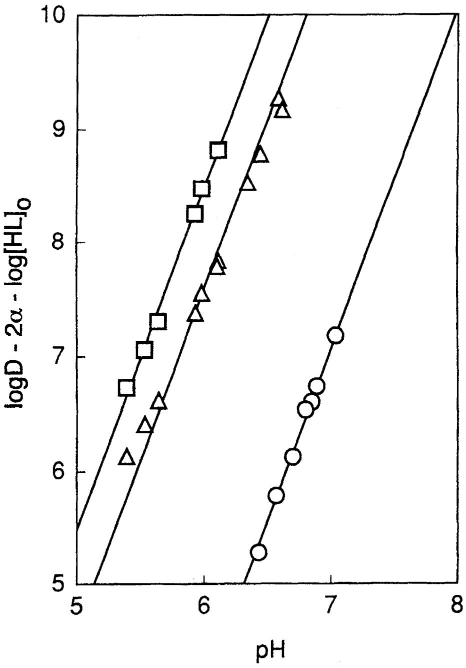

Fig. 2. Plots of $\log D - 2\alpha - \log[HL]_o$ vs. pH for the extraction of La^{3+}, Eu^{3+}, and Lu^{3+} with the $[B(pz)_4]^-$-dbm system. The initial concentration was 1×10^{-2} M for Hdbm in benzene, and 2×10^{-2} M for $K[B(pz)_4]$ in the aqueous phase. Solid lines, of which the slope is 3, were obtained by the least-squares fit. □, La^{3+}; △, Eu^{3+}; ○, Lu^{3+}.

Table 1 shows that the $\log K_{ex}$ values of the $[HB(pz)_3]^-$ systems are 4.69—6.30 higher than those of the $[B(pz)_4]^-$ systems containing the same β-diketone. Therefore, $[HB(pz)_3]^-$ is a much more powerful extractant for lanthanoid ions than $[B(pz)_4]^-$, although the difference in pK_a of $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ is small and the $[B(pz)_4]^-$ complexes are probably more hydrophobic than the $[HB(pz)_3]^-$ complexes. The separation factor between La^{3+} and Yb^{3+}, which is a difference in $\log K_{ex}$, of the $[B(pz)_4]^-$ systems is higher than that of the corresponding $[HB(pz)_3]^-$ systems: 4.42 for $[B(pz)_4]^-$-dbm, 3.46 for $[HB(pz)_3]^-$-dbm, 2.72 for $[B(pz)_4]^-$-dpm, and 2.35 for $[HB(pz)_3]^-$-dpm. These features are most appropriately interpreted as being due

Table 1. log K_{ex} for Lanthanoids(III) is Mixed Ligand Systems

	$[HB(pz)_3]^-$–dbm	$[HB(pz)_3]^-$–dpm	$[B(pz)_4]^-$–dbm	$[B(pz)_4]^-$–dpm
La^{3+}	−7.83±0.05	−7.98±0.07	−13.92±0.04	−14.11±0.15
Ce^{3+}	−6.95±0.10	−7.12±0.13	−12.31±0.07	−12.83±0.26
Pr^{3+}	−6.56±0.05	−7.06±0.06	−11.91±0.25	−12.65±0.24
Nd^{3+}	−6.14±0.06	−6.78±0.06	−11.54±0.21	−12.56±0.18
Sm^{3+}	−5.03±0.09	−5.88±0.22	−10.37±0.10	−11.67±0.33
Eu^{3+}	−4.80±0.08	−5.80±0.13	−10.41±0.16	−11.78±0.15
Gd^{3+}	−4.92±0.09	−5.75±0.11	−10.44±0.15	−12.05±0.13
Tb^{3+}	−4.48±0.14	−5.47±0.26	−10.14±0.05	−11.71±0.14
Dy^{3+}	−4.27±0.09	−5.69±0.13	−10.12±0.13	−11.62±0.10
Ho^{3+}	−4.53±0.22	−5.57±0.17	−9.83±0.15	−11.81±0.17
Er^{3+}	−4.39±0.22	−5.89±0.17	−9.79±0.17	−11.79±0.11
Tm^{3+}	−4.42±0.03	−5.92±0.29	−9.66±0.20	−11.46±0.23
Yb^{3+}	−4.37±0.07	−5.63±0.17	−9.50±0.12	−11.39±0.14
Lu^{3+}	−4.83±0.06	−5.84±0.18	−9.52±0.05	−11.53±0.27

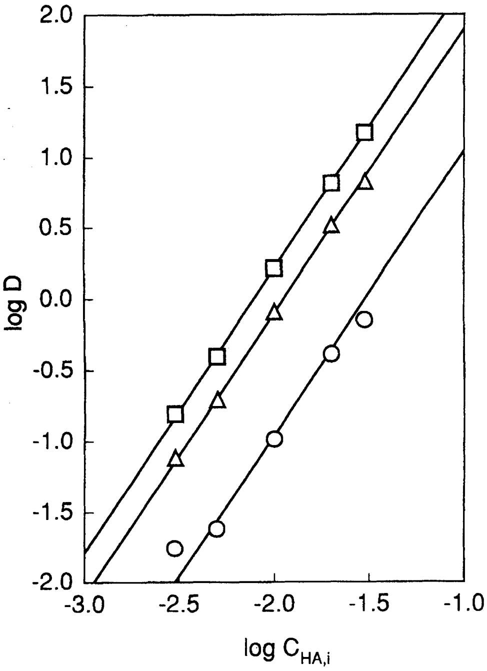

Fig. 3. Plots of log D vs. log $C_{HA,i}$ for the extraction of La^{3+}, Eu^{3+}, and Lu^{3+} with the $[B(pz)_4]^-$–dbm system. The initial concentration was 1×10^{-2} M for Hdbm in benzene, and the equilibrium pH was 7.09 for La^{3+}, 5.83 for Eu^{3+}, and for 5.61 Lu^{3+}. Solid lines, of which the slope is 2, were obtained by the least-squares fit. □, La^{3+}; △, Eu^{3+}; ○, Lu^{3+}.

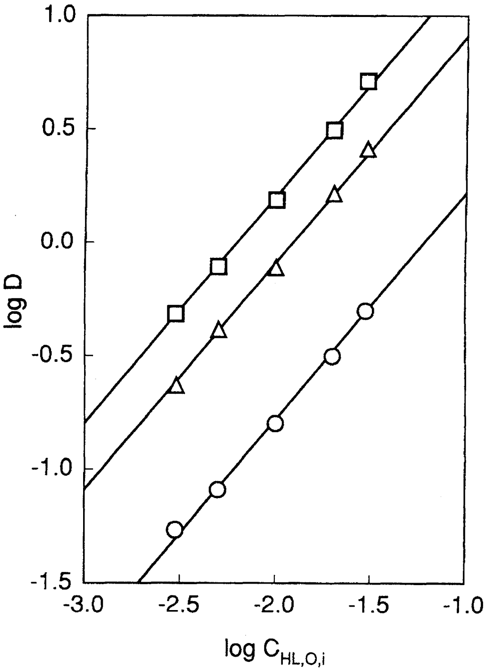

Fig. 4. Plots of log D vs. log $C_{HL,o,i}$ for the extraction of La^{3+}, Eu^{3+}, and Lu^{3+} with the $[B(pz)_4]^-$–dbm system. The initial concentration was 2×10^{-2} M for $K[B(pz)_4]$ in the aqueous phase, and the equilibrium pH was 6.83 for La^{3+}, 5.53 for Eu^{3+}, and for 5.39 Lu^{3+}. Solid lines, of which the slope is 1, were obtained by the least-squares fit. □, La^{3+}; △, Eu^{3+}; ○, Lu^{3+}.

to two kinds of steric effects on the stability constant of the mixed-ligand complex (β_{MA2L}). The K_{ex} is represented as:

$$K_{ex} = P_{MA2L}\beta_{MA2L}K_{a2}^2K_{a,HL}/P_{HL}$$

and

$$\log K_{ex} = \log P_{MA2L}\beta_{MA2L} - 2pK_{a2} - pK_{a,HL} - \log P_{HL}, \quad (10)$$

where P_{MA2L} is the partition constant of the complex. We have not determined the P_{MA2L} values. The determination was difficult, because the P_{MA2L} values were considerably high. We therefore, discuss the steric effect using log $P_{MA2L}\beta_{MA2L}$ in the following. It is expected that P_{MA2L} is higher for the $[B(pz)_4]^-$ systems than for the $[HB(pz)_3]^-$ systems. P_{MA2L} probably decreases as the lanthanoide ion size decreases. In Fig. 5, log $P_{MA2L}\beta_{MA2L}$ is plotted against the crystal radii (r) of the eight-coordinate lanthanoid ions.[8] The tetrad effect[9] is evident in the plot for all of the systems. The log $P_{MA2L}\beta_{MA2L}$ values of the $[B(pz)_4]^-$–dbm system increases uniformly with the decrease in r. In the other

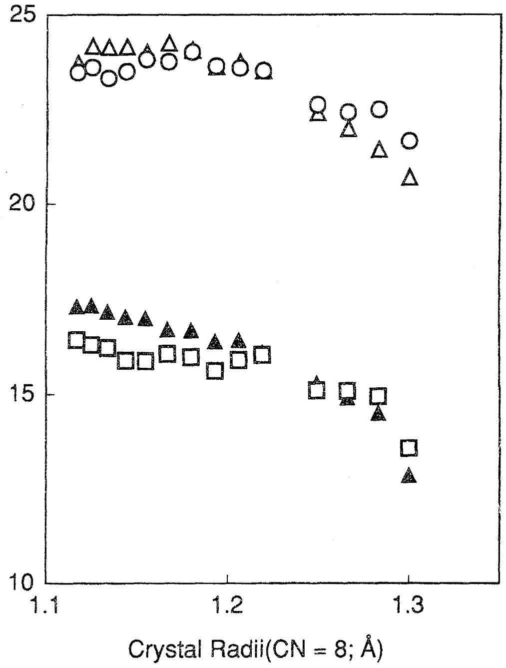

Fig. 5. Variation of $\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ with crystal radii of lanthanoids(III). △, $[\mathrm{HB(pz)_3}]^-$–dbm; ○, $[\mathrm{HB(pz)_3}]^-$–dpm; ▲, $[\mathrm{B(pz)_4}]^-$–dbm; □, $[\mathrm{B(pz)_4}]^-$–dpm.

systems, $\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ is almost independent of r of $\mathrm{Sm^{3+}}$–$\mathrm{Lu^{3+}}$.

Firstly, the steric effect of the poly(pyrazol-1-yl)borates on β_{MA2L} is discussed. Although P_{MA2L} is expected to be higher for the $[\mathrm{B(pz)_4}]^-$ complexes, $\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ of the $[\mathrm{HB(pz)_3}]^-$ complexes is 6.4—8.1 higher than that of the $[\mathrm{B(pz)_4}]^-$ complexes. This is caused by a difference in β_{MA2L}. While higher β_{MA2L} values of the $[\mathrm{HB(pz)_3}]^-$ systems are partly due to the higher basicity of $[\mathrm{HB(pz)_3}]^-$, the difference in β_{MA2L} is very large compared with the difference in K_{a} of $[\mathrm{HB(pz)_3}]^-$ and $[\mathrm{B(pz)_4}]^-$. Moreover, the variation in $\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ is larger for $[\mathrm{B(pz)_4}]^-$ systems than that for $[\mathrm{HB(pz)_3}]^-$ systems. The coordination around the boron atom of $[\mathrm{HB(pz)_3}]^-$ is not very crowded. The pyrazol-1-yl groups can rotate freely around the B–N bond, and the ligand takes a conformation suitable for tripodal tridentate coordination. When $[\mathrm{HB(pz)_3}]^-$ coordinates to a large metal ion, the bite size (intraligand distance between the donor atoms) is widened by opening the tripod of the pyrazol-1-yl groups. Since the increase in the strain energy[3] of $[\mathrm{HB(pz)_3}]^-$ accompanying the deformation should be reasonably small, the ligand forms stable complexes with metal ions of various sizes. Hence, for the $[\mathrm{HB(pz)_3}]^-$ systems, β_{MA2L} should decrease slightly among with an increase in r, because of a drop in the electrostatic interaction.

The coordination around the boron atom of $[\mathrm{B(pz)_4}]^-$ is crowded by the four pyrazol-1-yl groups. When $[\mathrm{B(pz)_4}]^-$ takes a tridentate coordination, the intraligand contact between the coordinated and noncoordinated pyrazol-1-yl groups must cause a substantial increase in the strain energy. Opening the tripod of the pyrazol-1-yl groups is restricted by the steric contact. This restriction was quite evident in our previous study.[2] Both $[\mathrm{HB(pz)_3}]^-$ and $[\mathrm{B(pz)_4}]^-$ readily produce bis-ligand complexes of $\mathrm{Mg^{2+}}$ in which the ligands are tridentate with a bite size of 2.94—2.91 Å. Although $[\mathrm{HB(pz)_3}]^-$ forms a six-coordinate $[\mathrm{Ca\{HB(pz)_3\}_2}]$ complex of which the bite size is 3.11 Å, $[\mathrm{B(pz)_4}]^-$ can hardly form a similar complex. In addition, the bite size of complexed tridentate $[\mathrm{B(pz)_4}]^-$ is reportedly smaller than 3.0 Å[10] with the only exception being $[\mathrm{Cd\{B(pz)_4\}_2}]$.[11] The bite size of $[\mathrm{HB(pz)_3}]^-$ is 2.99 Å in $[\mathrm{Yb\{HB(pz)_3\}_2(acac)}]$ and 3.06 Å in $[\mathrm{Ce\{HB(pz)_3\}_2(acac)}]$.[7] These bite sizes are very large for $[\mathrm{B(pz)_4}]^-$ to adopt. Therefore, β_{MA2L} for $[\mathrm{B(pz)_4}]^-$ is much lower than that for $[\mathrm{HB(pz)_3}]^-$, and sharply decreases as r increases. This intraligand contact dominates the difference between the $\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ vs. r plots of $[\mathrm{HB(pz)_3}]^-$ and $[\mathrm{B(pz)_4}]^-$ systems.

Secondly, to examine the effect of β-diketone on $\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ the difference between $\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ for $[\mathrm{M\{H}_n\mathrm{B(pz)}_{4-n}\}_2\mathrm{(dbm)}]$ and $[\mathrm{M\{H}_n\mathrm{B(pz)}_{4-n}\}_2\mathrm{(dbm)}]$, $\Delta\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$, is plotted against r in Fig. 6. $\Delta\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ decreases with a decrease in r, and is negative for small ions. This feature is attributable to steric crowding around the donor atom of β-diketone. The van der Waals volumes of the pivaloyl and phenyl groups are 45.84 and 54.69 $\mathrm{cm^3}$, respectively.[12] Whereas the phenyl group is planner, the pivaloyl group is spherical and its volume is

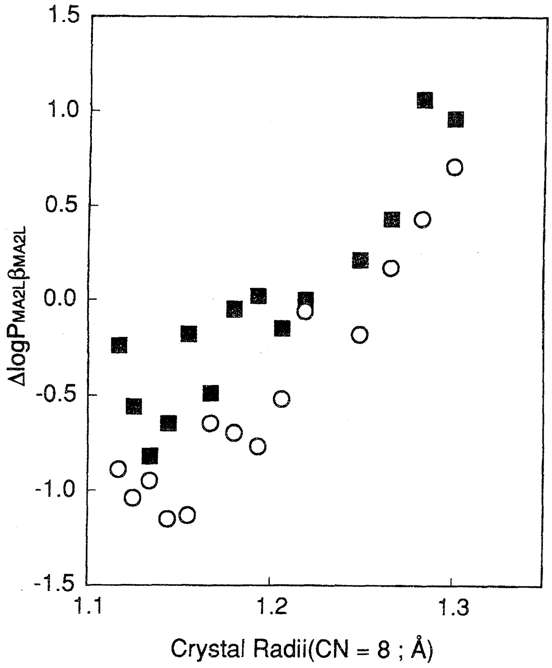

Fig. 6. Variation of $\Delta\log P_{\mathrm{MA2L}}\beta_{\mathrm{MA2L}}$ with crystal radii of lanthanoids(III). ■, $[\mathrm{HB(pz)_3}]^-$ system; ○, $[\mathrm{B(pz)_4}]^-$ system.

located in the vicinity of the carbonyl group. Thus, when dpm is the coligand, the coordination around the metal ion is more crowded. Interligand contact cannot be avoided and reduces the complex stability of the small lanthanoid ions. This interligand contact is the other steric factor which dominates the stability and extractability of the mixed-ligand complexes. Actually, when pivaloyl-*d*-camphor, which is bulkier than dpm, was employed with $[HB(pz)_3]^-$, none of the examined lanthanoids (Lu^{3+}, Tb^{3+}, and Eu^{3+}) were extracted into benzene.

Conclusion

From poly(pyrazol-1-yl)borate–β-diketone mixed-ligand systems, trivalent lanthanoid ions are extracted into benzene as $[M\{H_nB(pz)_{4-n}\}_2(\beta\text{-diketone})]$. The stability and extractability of $[M\{H_nB(pz)_{4-n}\}_2(\beta\text{-diketone})]$ complexes are governed by intra- and interligand contact. The intraligand contact between the pyrazol-1-yl groups in the poly(pyrazol-1-yl)borates prevents $[B(pz)_4]^-$ from opening the bite size. As a results, $[B(pz)_4]^-$ is a less powerful, but more selective, ligand for small lanthanoid ions than $[HB(pz)_3]^-$. The interligand contact, which is easily modified by the choice of the bulky substituents on the carbonyl carbon atom of β-diketone, destabilizes the complexes of small lanthanoid ions. Improved separability is attained with $[B(pz)_4]^-$ and a non-bulky β-diketone that minimizes the interligand contact.

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