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Solvent Extraction of Divalent Metals as Dihydrobis(1-pyrazolyl)borate Chelates

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The extraction behavior of divalent metals (M^{2+}) with dihydrobis(1-pyrazolyl)borate ligand ($H_2B(pz)_2^-$) has been studied. Divalent transition metals form $[M\{H_2B(pz)_2\}_2]$ chelates readily and are extracted into the organic phase. The extraction constants of the first-row transition metals increase in the order Mn(II)<Fe(II)<Co(II)<Ni(II)<Cu(II)>Zn(II), which is in accordance with the Irving and Williams' order for complex stability. Although Be^{2+} is slightly extracted by $H_2B(pz)_2^-$, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} are not extracted, whether a synergistic agent such as trioctylphosphine oxide and tetrabutylammonium chloride is added or not. The characteristics of $H_2B(pz)_2^-$ in the extractability of metal ions are ascribed to that the basicity of coordinating nitrogen atoms is increased by negative charge of the molecule and inductive effect of the boron atom, and that adduct formation is restricted by the steric hindrance.

The poly(1-pyrazolyl)borates, which were first reported by Trofimenko,[1-3] are unique uninegative ligands of the general formula, $H_nB(pz)_{4-n}^-$ (n is 0, 1 or 2, and pz stands for 1-pyrazolyl group), and a wide variety of their chelates of various elements continues to provide a fascinating and fertile field of research to coordination chemists.[4-6] Dihydrobis(1-pyrazolyl)borate ligand ($H_2B(pz)_2^-$) is bidentate, coordination taking place through the pyrazole nitrogen atoms. The $H_2B(pz)_2^-$ is similar to the anion derived from an enolized β-diketone such as acetylacetone and thenoyltrifluoroacetone, and forms bis neutral $[M\{H_2B(pz)_2\}_2]$ chelates with divalent metal ions (M^{2+}). The $H_2B(pz)_2^-$ chelates are different from β-diketonates in that the chelate ring has a boat type configuration, and the metal ion is screened by the ligand moieties as shown in Fig. 1, where the square-planar Ni(II) chelate is presented as an example.[7] Further replacement of the remaining borate hydrogens by pyrazolyl groups to form hydrotris- and tetrakis(1-pyrazolyl)borate compounds ($HB(pz)_3^-$ and $B(pz)_4^-$) provides a series of tridentate chelating ligands, which form complexes with not only d-block elements but also main-group metals.

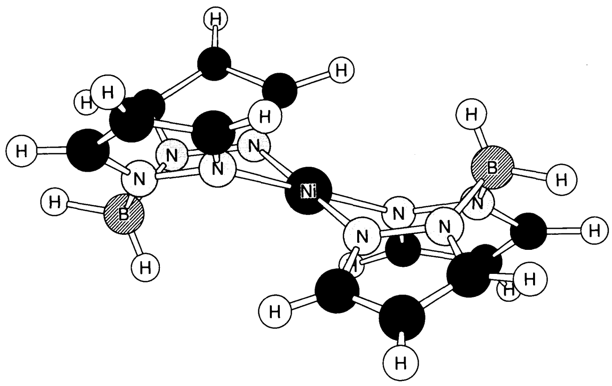


Fig. 1. Pseudochair conformation of the square-planar $[Ni\{H_2B(pz)_2\}_2]$ chelate.

These ligands seem very attractive from a view point of ligand design for selective complexation of metal ions, because they have the unique structures as stated above and their electronic and steric parameters can be altered by a proper choice of substituents. The studies, however, have scarcely been reported on chelate chemistry in the solution phase using the $H_nB(pz)_{4-n}^-$ and analogous ligands.[8] In the first place, we report here the solvent extraction of divalent metals with $H_2B(pz)_2^-$ in order to clarify the characteristics of the chelating reagent for selective extraction of metals.

Experimental

Reagents and Apparatus. Potassium dihydrobis(1-pyrazolyl)borate was synthesized from pyrazole and potassium tetrahydroborate according to the method of Trofimenko.[3] The crude compound was recrystallized from anisole. The $H_2B(pz)_2^-$ was recrystallized from water as a tetrabutylammonium salt for elementary analysis (Found: C, 67.59; H, 11.35; N, 18.02%. Calcd for $C_{22}H_{44}N_5B$: C, 67.88; H, 11.30; N, 17.98%. mp 129 °C). All other chemicals were reagent-grade materials, and distilled water was used throughout.

A Hitachi-Horiba F-8L pH meter equipped with a glass electrode was used for pH measurement. Metal ion and ligand concentrations were determined with a Japan Jarrel Ash ICAP-500 inductively coupled argon plasma emission spectrometer or a Hitachi 180-80 Zeeman atomic absorption spectrometer.

Protonation and Distribution of the Ligand. Protonation constants of $H_2B(pz)_2^-$ were determined by potentiometric titration. Ten ml of aqueous solution containing 5×10^{-2} M (1 M=1 mol dm^{-3}) of $K[H_2B(pz)_2]$ was titrated with 0.1 M hydrochloric acid in a stream of nitrogen at 25.0±0.1 °C.

The extraction experiment was performed in a 30 ml glass-stoppered centrifuge tube. An aliquot of an organic phase (10 ml) was equilibrated with the equal volume of an aqueous phase containing 1×10^{-2} M of $K[H_2B(pz)_2]$ and 2×10^{-2} M of sodium acetate, 2-morpholinoethanesulfonic acid (MES), 3-morpholino-1-propanesulfonic acid (MOPS), 3-[tris(hydroxymethyl)methylamino]-1-propanesulfonic acid (TAPS), 2-(cyclohexylamino)ethanesulfonic acid (CHES), or 3-cyclohexylamino-1-propanesulfonic acid (CAPS) as a buffer for

1 min at 25±1 °C. After the two phases were separated centrifugally, pH of the aqueous phase was measured. The ligand concentration in the aqueous phase was determined from the boron contents using the ICAP-500. The concentration in the organic phase was measured after back-extracted into 1×10^{-2} M sodium hydroxide.

Distribution of the Metal Chelates. The extraction of divalent metals with $H_2B(pz)_2^-$ was accomplished in the similar way to the ligand extraction. An organic phase (10 ml) and the equal volume of an aqueous phase containing $K[H_2B(pz)_2]$ (1×10^{-2} M), a divalent metal ion (1×10^{-4} M) and the buffer (2×10^{-2} M) were shaken for 1 h at 25±1 °C. The two phases were separated, and the metal concentration in the aqueous phase was determined by atomic emission or absorption spectrometry. The concentration in the organic phase was similarly determined after back-extracted into 1.0 or 3.0 M hydrochloric acid.

Results and Discussion

Protonation and Distribution of the Ligand. The $H_2B(pz)_2^-$ (A^-) is considered to be protonated as shown in Scheme 1. The acid dissociation constants of the protonated ligand are defined as

$$K_{a1} = [A^-][H^+]/[HA], \qquad (1)$$

$$K_{a2} = [HA][H^+]/[H_2A^+], \qquad (2)$$

where brackets represent the molar concentration. These values were determined by the pH titration, because the ligand molecule has no absorption peaks above 230 nm. From the inflection points on the titration curve, pK_{a1} and pK_{a2} were found to be 8.70±0.03 and 4.99±0.07, respectively. These values are substantially higher than that of pyrazole (pK_a=2.60).[9] Therefore, the basicity of the coordinating nitrogen atoms in $H_2B(pz)_2^-$ increases in comparison with that in a pyrazole molecule, because of negative charge of the molecule and electron donation from the central boron atom to the pyrazolyl groups. This is one of the most striking characteristics of the $H_nB(pz)_{4-n}^-$. Such an effect is not exerted, when heterocyclic rings are bonded by a carbon atom to form a chelating reagent. For example, the pK_a values of 2,2′-bipyridyl (pK_{a1}=4.42, pK_{a2}=1.5)[9] and 1,10-phenanthroline (pK_{a1}=4.96, pK_{a2}=1.9)[9] are lower than that of pyridine (pK_a=5.31).[9] The $H[H_2B(pz)_2]$ resembles 8-quinolinol (HOx: pK_{a1}=9.23, pK_{a2}=4.92)[9], in terms of having similar chemical forms, i.e., cationic, neutral and anionic forms in acidic, neutral and basic media, respectively, as well as similar pK_a values. The molar fraction of the three species of $H[H_2B(pz)_2]$ is shown in Fig. 2 as a function of pH.

Figure 3 represents the logarithm of distribution ratio of the ligand (log D_{HA}) between aqueous and chloroform phases as a function of pH;

$$D_{HA} = C_{HA,o}/C_{HA}, \qquad (3)$$

where C_{HA} means the analytical molar concentration of the ligand and the subscript o denotes the species in the organic phase. The log D_{HA} vs. pH plot can be reproduced using Eqs. 1, 2 and

$$P_{HA} = [HA]_o/[HA], \qquad (4)$$

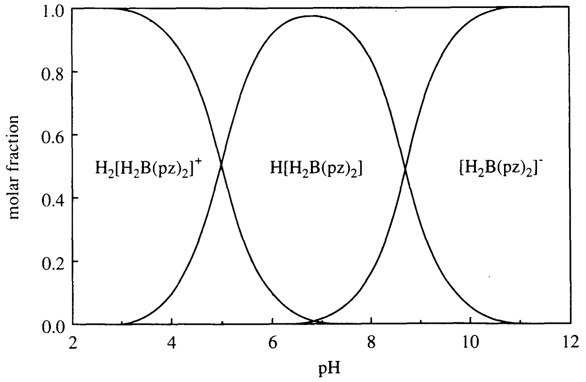


Fig. 2. Molar fraction of the protonated and deprotonated forms of $H_2B(pz)_2^-$ as a function of pH.

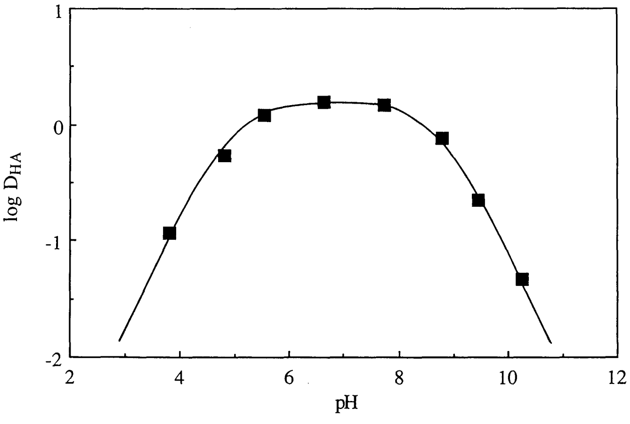
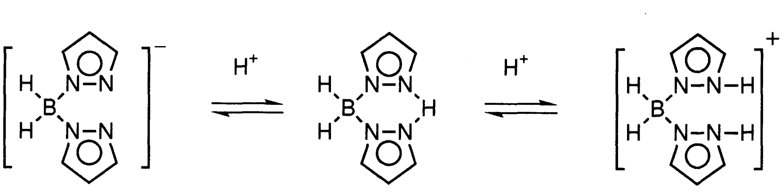


Fig. 3. Distribution of $H[H_2B(pz)_2]$ between chloroform and water as a function of pH. The solid curve was obtained by the non-linear least-squares method.



Scheme 1.

where P_{HA} is the partition constant of the ligand. By a non-linear least-squares method, $pK_{a1}=8.72\pm0.05$, $pK_{a2}=4.96\pm0.06$, and $\log P_{HA}=0.20\pm0.03$ were obtained. These pK_a values agree well with those observed by the titration.

It is reported that the oxidative and hydrolytic stability of the $H_nB(pz)_{4-n}^-$ decreases with increasing number of hydrogens attached to the boron atom.[3] In the present work, the aqueous solution of $K[H_2B(pz)_2]$ was prepared just before the experiments. The decomposition rate of the ligand was dependent on pH of the aqueous phase. When the pH was much higher than pK_{a1} or lower than pK_{a2}, the decomposition was proved to be negligible for a few hours by ^1H NMR. When the ligand existed in the form of $H[H_2B(pz)_2]$ in the aqueous phase, the ligand concentration in the organic phase decreased with an increase in shaking time (t/min) and was expressed at pH 6.25 by

$$\ln[HA]_o=-5.10-1.42\times10^{-3}\,t \quad (n=5,\ r^2=0.999). \qquad (5)$$

$\log D_{HA}$ determined after 1 min of shaking is thought to be the value at equilibrium and hardly affected by the ligand decomposition.

$\log P_{HA}$ was rather low not only for chloroform but also for carbon tetrachloride (0.23) and heptane (−0.33).

Distribution of Divalent Transition Metals. The extraction of trace amounts of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 10^{-2} M $K[H_2B(pz)_2]$ in the aqueous phase into chloroform was investigated for various acidic aqueous solutions. The distribution ratio of a metal (D_M) was independent of the shaking time of 1 to 120 min;

$$D_M=C_{M,o}/C_M, \qquad (6)$$

where C_M signifies the analytical molar concentration of the metal ion. Thus, the extraction equilibrium of the chelates is reached rapidly, and the chelates extracted into the organic phase is decomposed only slowly. Plots of $\log D_M$ vs. pH with a constant ligand concentration is shown in Fig. 4. The extractability increases in the order Mn(II)<Cd(II)<Fe(II)<Co(II)<Ni(II)<Zn(II)<Cu(II). For the first-row metal ions, this order is in accordance with the Irving and Williams' order for complex stability.[10] This suggests that these divalent metals react with $H_2B(pz)_2^-$ to form MA_2 type chelates. It has been reported that the chelates which precipitate from the aqueous solution of $H_2B(pz)_2^-$ are MA_2 type, and that the configuration about the metal is square planar for Ni(II) and Cu(II), and tetrahedral for Mn(II), Fe(II), Co(II) and Zn(II).[2,3,7]

A plot of $\log D_M$ against $\log C_{HA}$ for Zn(II) at a constant pH is shown in Fig. 5. A slope of 2.0 indicates that the extracted species are MA_2, and that no further additon of the protonated ligand to this extracted form occurs in the ligand concentration range studied. The distribution of Zn(II) was independent of the metal concentrations in the range 1×10^{-5}—1×10^{-3} M, when the pH and ligand concentration in the aqueous phase were maintained constant. Hence, no polymeric species of the extracted chelates are formed in the chloroform layer. The same results were obtained for the other metal ions. The predominance of the MA_2 form for the $H_2B(pz)_2^-$ chelates is a contrast to β-diketonates and 8-quinolinolates for which various associative equilibria have been observed.[11,12]

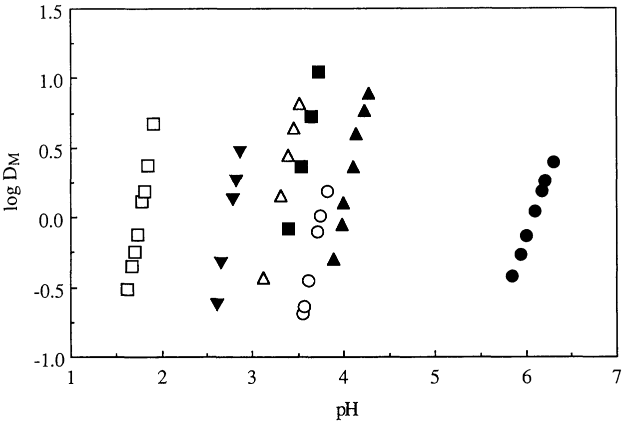


Fig. 4. Plots of $\log D_M$ vs. pH. Initial concentrations in the aqueous phase are 1×10^{-2} M for $K[H_2B(pz)_2]$ and 1×10^{-4} M for metal ions. Organic phase is chloroform. □, Cu(II); ▼, Zn(II); △, Ni(II); ■, Co(II); ○, Fe(II); ▲, Cd(II); ●, Mn(II).

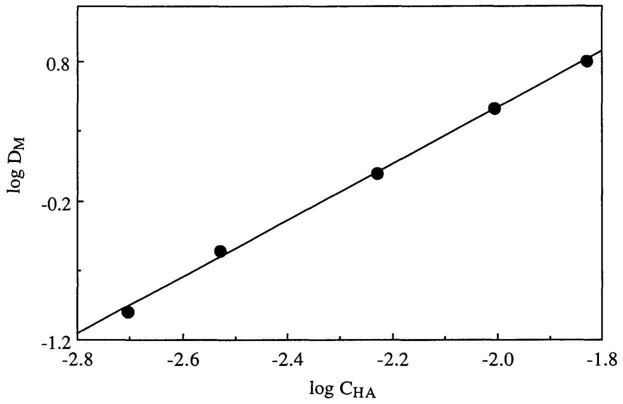


Fig. 5. Plot of $\log D_M$ vs. $\log C_{HA}$ for Zn(II) at pH 2.80. Initial concentration of Zn(II) in the aqueous phase is 1×10^{-4} M, and organic phase is chloroform. The solid line is best-fit one, of which slope is 2.0.

To compare the extraction behavior of the transition metals by $H_2B(pz)_2^-$ with that by other chelating ligands, the extraction constants are calculated. The extraction equilibrium and constant for $H_2B(pz)_2^-$ chelates can be defined as

$$M^{2+}+2HA \rightleftharpoons MA_{2,o}+2H^+ \qquad (7)$$

$$K_{ex}=[MA_2]_o[H^+]^2/[M^{2+}][HA]^2. \qquad (8)$$

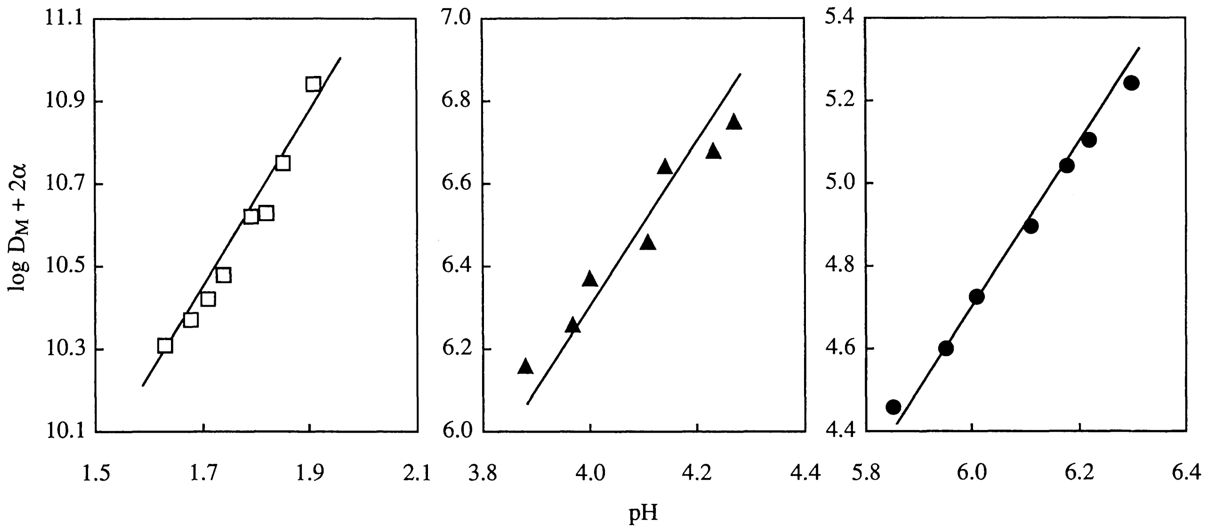


Fig. 6. Plots of log D_M+2α vs. pH. □, Cu(II); ▲, Cd(II); ●, Mn(II). Solid lines show Eq. 11, where the slopes are 2 and log K_{ex} values are listed in Table 1.

Table 1. Logarithms of the Extraction Constants (log K_{ex}) for Divalent Transition Metal Ion Chelates

Metal ion	$H[H_2B(pz)_2]$[a]	HBA[b]	HOx[c]	HDDC[d]
Mn(II)	−7.31±0.01	−14.63	−9.32	−4.42
Fe(II)	−0.77±0.02	—	—	1.20
Co(II)	0.38±0.03	−11.11	−2.16[d]	2.33
Ni(II)	1.00±0.05	−12.12	−2.18	11.58
Cu(II)	7.03±0.02	−4.17	1.77	13.70
Zn(II)	3.07±0.02	−10.79	−2.41[d]	2.96
Cd(II)	−1.70±0.04	−14.11	−5.29[d]	5.41

a) This work. b) Benzoylacetone in benzene. Ref. 11. c) 8-Quinolinol in chloroform. Ref. 11. d) Diethyldithiocarbamic acid in carbon tetrachloride. Ref. 13. d) Complexes of type $ML_2(HL)_2$ are formed.

Assuming that the concentration of the metal chelates in the aqueous phase is negligible,

$$D_M = [MA_2]_o/[M^{2+}] \tag{9}$$

Since the initial concentration of the ligand in the aqueous phase ($C_{HA,i}$) is much higher than that of the metal ion, the equilibrium HA concentration in the aqueous phase is deduced as Eq. 10, taking into account the protonation and the distribution of the ligand,

$$[HA] = C_{HA,i}/\{P_{HA} + ([H^+]/K_{a2}) + 1 + (K_{a1}/[H^+])\} \tag{10}$$

Substitution of Eqs. 9 and 10 into Eq. 8 and rearrangement result in

$$\log D_M + 2\alpha = 2\text{pH} + \log K_{ex}, \tag{11}$$

where

$$\alpha = \log\{P_{HA} + ([H^+]/K_{a2}) + 1 + (K_{a1}/[H^+])\} - \log C_{HA,i}. \tag{12}$$

Figure 6 realizes the plots of log D_M+2α vs. pH for Cu(II), Cd(II), and Mn(II). log K_{ex} is obtained from these plots by a linear least-squares method; solid lines in Fig. 6 are best fit.

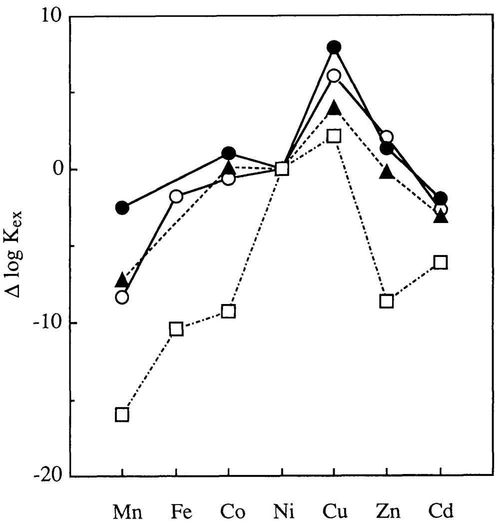


Fig. 7. Selectivity patterns in extraction of divalent transition metal ions with bidentate ligands. Δlog K_{ex} is obtained for each ligand by subtracting log K_{ex} of Ni(II) from log K_{ex} of the metal. ○, $H[H_2B(pz)_2]$; ●, HBA; ▲, HOx; □, HDDC.

log K_{ex} values are listed in Table 1 with those for chelates of other bidentate ligands (HL).[11,13] Since HL is highly hydrophobic and the addition of HL can occur, K_{ex} for these ligands except $H[H_2B(pz)_2]$ is defined as

$$K_{ex} = [ML_2(HL)_r]_o[H^+]^2/[M^{2+}][HL]_o^{2+r}. \tag{13}$$

The log K_{ex} values for $H[H_2B(pz)_2]$ are higher than those for benzoylacetone (HBA) and HOx, and as great as those for diethyldithiocarbamic acid (HDDC). Therefore, $H_2B(pz)_2^-$ is a powerful chelating ligand for extraction of the divalent transition metals.

The selectivity of these ligands toward the divalent transition metals is clearly compared in Fig. 7, where Δlog K_{ex} that is obtained for each ligand by subtracting log K_{ex} of Ni(II) from log K_{ex} of the metal is plotted.

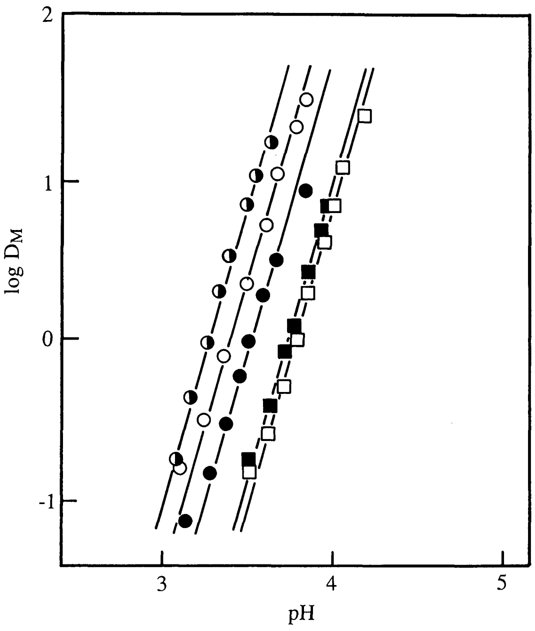


Fig. 8. Solvent effects on the extraction of Co(II) with $H_2B(pz)_2^-$. Initial concentrations in the aqueous phase are 1×10^{-2} M for $K[H_2B(pz)_2]$ and 1×10^{-4} M for Co(II). ◑, dichloromethane; ○, chloroform; ●, carbon tetrachloride; ■, cyclohexane; □, hexane.

The selectivity pattern of $H[H_2B(pz)_2]$ is similar to that of HBA and HOx, and different from that of HDDC. This suggests that the coordinating nitrogen atoms in $H_2B(pz)_2^-$ are a rather hard base.

Figure 8 shows log D_M of Co(II) vs. pH at a constant concentration of $K[H_2B(pz)_2]$ using dichloromethane, chloroform, carbon tetrachloride, cyclohexane and hexane as an organic phase. Because the Co(II) chelate has a tetrahedral structure, it is an originally coordinatively saturated compound and does not contain free coordination positions which are usually occupied by water molecules. As shown in Fig. 8, the extractability of the Co(II) chelate is enhanced in the order, hexane (dielectric constant, 1.88)<cyclohexane (2.02)<carbon tetrachloride (2.24)<chloroform (4.81)<dichloromethane (8.93).[14] This order is the same as that of increasing dielectric constant of these solvents. Since the increase in the extractability is essentially attributed to the magnitude of solvation energy of the MA_2 chelate in the organic phase, the Co(II) chelate may be a moderately polar molecule.

Distribution of Group II Metals. Magnesium, calcium, strontium, and barium could not be extracted by $H_2B(pz)_2^-$, whether a synergistic agent such as trioctylphosphine oxide and tetrabutylammonium chloride was added or not. This is a distinct difference between $H[H_2B(pz)_2]$ and HOx. The steric hindrance by the $H_2B(pz)_2^-$ moiety prevents the formation of complexes such as $MA_2(HA)_r$ and MA_3^-, which are common types of the extracted species of alkaline earth metal ions with HOx.[11]

On the other hand, Be^{2+} was slightly extracted by $H_2B(pz)_2^-$, and the maximum extracted percentage was 10% about pH 6.5. The extracted species is assumed to be tetrahedral $[Be\{H_2B(pz)_2\}_2]$. This chelate is not so stable in the aqueous solution, because the large portion of Be^{2+} remained in the aqueous phase as the aqua ion in the lower pH range and precipitated as the hydroxide in the higher pH range.

Conclusions

Dihydrobis(1-pyrazolyl)borate is a bidentate ligand, and similar to HOx in the protonation behavior and the selectivity for divalent transition metals. Although $H_2B(pz)_2^-$ is a powerful extraction reagent for first-row transition metals, it can not extract group II metals in contrast to HOx. The characteristics of $H_2B(pz)_2^-$ in the extractability of metal ions are ascribed to that the coordinating nitrogen atoms have appropriate basicity and hardness for complex formation with the divalent first-row transition metals, and that adduct formation is restricted by the steric hindrance.

It is interesting that $HB(pz)_3^-$ and $B(pz)_4^-$ are tridentate ligands and react readily with not only transition metals but also group II metals in aqueous solution. The reason should be that $HB(pz)_3^-$ and $B(pz)_4^-$ are sterically very efficient to occupy six coordination sites of the metal ions. The solvent extraction of metal ions with these ligands is going to be reported in forthcoming papers.

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