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Steric Effects of Polymethylene Chain Length on the Liquid-Liquid Extraction of Copper(II) with Bis(4-acylpyrazol-5-one) Derivatives

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A novel family of bis(4-acylpyrazol-5-one) derivatives in which two 1-phenyl-3-methyl-4-acylpyrazol-5-one subunits are linked by a polymethylene chain $-(CH_2)_n-$ of various lengths (n = 0–8, 10, 20) has been designed. The distribution curves show that each bis(4-acylpyrazol-5-one) derivative is a diprotic acid, H_2BPn. The acidity constants pK_1 and pK_2 indicate that H_2BPn exists as a rigid molecule because of the electrostatic repulsion of negative charge on two β-diketone donor sites. In complexation of Cu(II) with H_2BPn, which is quadridentate with two β-diketone donor sites, the polymethylene chain length affects the complex formation and the stoichiometry of the complex through a steric effect. The results on the extraction demonstrate that the extracted Cu(II) species is Cu(BPn) (n = 8, 10, 20) and $Cu(HBPn)_2$ or $Cu_2(BPn)_2$ with H_2BPn (n = 1–7). In the extraction constants of $Cu_2(BPn)_2$, a conspicuous gap was observed between complexes with H_2BPn composed of even-numbered and odd-numbered polymethylene chains. This even–odd gap can be attributed to conformational isomerism of hydrogen atoms in the polymethylene chains.

Introduction

The 1-phenyl-3-methyl-4-acylpyrazol-5-one derivative is well-known as a β-diketone type chelating ligand coordinating to a metal ion with oxygen atoms as "hard" Lewis base. The derivatives are stable and easy to be synthesized. Metal ions are extracted from a relatively low pH medium. These ligands have a strong affinity with such "hard" Lewis acid metal ions as alkali-, alkaline-earth, and lanthanide-metal ions.[1-10]

We designed a novel family of bis(4-acylpyrazol-5-one) derivatives, shown in Figure 1, in which two 1-phenyl-3-methyl-4-acylpyrazol-5-one subunits are linked by polymethylene chains of varying lengths $-(CH_2)_n-$ (n = 0–8, 10, 20). Since the bis(4-acylpyrazol-5-one) derivatives have two β-diketone donor sites on both sides of the polymethylene chain, it is expected to form specific complexes depending on the polymethylene chain length. Previously, with the use of some of these ligands, liquid–liquid extractions of several metal ions have been investigated by the present authors, Dong et al.,[11] and Tayeb et al.[12] In this paper, a complex of Cu(II) that is a quadridentate square-planar Lewis acid has been investigated in order to explore the effect of polymethylene chain length of bis(4-acylpyrazol-5-one) derivatives on the extraction of Cu(II).

Experimental Section

Chemicals. Bis(4-acylpyrazol-5-one) derivatives were synthesized from 1-phenyl-3-methylpyrazol-5-one and the corresponding acid dichlorides by a method analogous to Jensen's.[13] The crude products were purified by recrystallization from 1,4-dioxane and dried in vacuo at ca. 80 °C. All of the other chemicals were reagent grade and were utilized without further purification.

Anal. Calcd for $C_{22}H_{18}O_4N_4$ (**H_2BP0**): C, 65.67; H, 4.51; N, 13.92. Found: C, 65.28; H, 4.43; N, 13.86. ^1H NMR ($CDCl_3/Me_4Si$): δ 15.64 (s, 2 H, OH), 7.81–7.84, 7.47–7.51, 7.33–7.37 (m, 10 H, Ph), 2.55 (s, 6 H, CH_3). Mp: 250 °C.

Anal. Calcd for $C_{23}H_{20}O_4N_4$ (**H_2BP1**): C, 66.34; H, 4.84; N, 13.45. Found: C, 66.04; H, 4.80; N, 13.43. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.79–7.81, 7.45–7.52, 7.34 (m, 10 H, Ph), 2.55 (s, 6 H, CH_3), 1.49–1.71 (m, 2 H, CH_2). Mp: 221 °C.

Anal. Calcd for $C_{24}H_{22}O_4N_4$ (**H_2BP2**): C, 66.97; H, 5.15; N, 13.02. Found: C, 67.15; H, 4.12; N, 12.98. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.79–7.82, 7.44–7.47, 7.28–7.32 (m, 10 H, Ph), 3.25 (s, 4 H, CH_2CH_2), 2.58 (s, 6 H, CH_3). Mp: 227 °C.

Anal. Calcd for $C_{25}H_{24}O_4N_4$ (**H_2BP3**): C, 67.56; H, 5.44; N, 12.60. Found: C, 67.67; H, 5.39; N, 12.46. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.80–7.83, 7.42–7.47, 7.27–7.31 (m, 10 H, Ph), 2.90–2.94 (t, 4 H, CH_2), 2.49 (s, 6 H, CH_3), 2.18–2.25 (m, 2 H, CH_2). Mp: 176 °C.

Anal. Calcd for $C_{26}H_{26}O_4N_4$ (**H_2BP4**): C, 68.11; H, 5.72; N, 12.22. Found: C, 68.54; H, 5.71; N, 12.06. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.80–7.83, 7.42–7.47, 7.27–7.31 (m, 10 H, Ph), 2.80–2.86 (t, 4 H, CH_2), 2.49 (s, 6 H, CH_3), 1.85–1.92 (m, 4 H, CH_2). Mp: 199 °C.

Anal. Calcd for $C_{27}H_{28}O_4N_4$ (**H_2BP5**): C, 68.63; H, 5.97; N, 11.86. Found: C, 68.08; H, 5.97; N, 11.34. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.82–7.84, 7.42–7.47, 7.27–7.30 (m, 10 H, Ph), 2.77–2.81 (t, 4 H, CH_2), 2.48 (s, 6 H, CH_3), 1.79–1.87 (m, 4 H, CH_2), 1.50–1.58 (m, 2 H, CH_2). Mp: 155 °C.

Anal. Calcd for $C_{28}H_{30}O_4N_4$ (**H_2BP6**): C, 69.12; H, 6.21; N, 11.51. Found: C, 69.29; H, 6.21; N, 11.52. ^1H NMR ($CDCl_3/Me_4Si$): δ 7.82–7.84, 7.43–7.47, 7.28–7.30 (m, 10 H, Ph), 2.74–2.78 (t, 4 H, CH_2), 2.48 (s, 6 H, CH_3), 1.77–1.81 (m, 4 H, CH_2), 1.47–1.51 (m, 4 H, $(CH_2)_2$). Mp: 216 °C.

Anal. Calcd for $C_{29}H_{32}O_4N_4$ (**H_2BP7**): C, 69.58; H, 6.44; N, 11.19. Found: C, 69.52; H, 6.53; N, 11.01. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.81–7.84, 7.42–7.47, 7.26–7.30 (m, 10 H, Ph), 2.73–2.76 (t, 4 H, CH_2), 2.48 (s, 6 H, CH_3), 1.73–1.78 (m, 4 H, CH_2), 1.43–1.48 (m, 6 H, $(CH_2)_3$). Mp: 124 °C.

Anal. Calcd for $C_{30}H_{34}O_4N_4$ (**H_2BP8**): C, 70.02; H, 6.66; N, 10.89. Found: C, 70.10; H, 6.65; N, 10.80. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.81–7.84, 7.41–7.42, 7.27–7.30 (m, 10 H, Ph), 2.72–2.76 (t, 4 H, CH_2), 2.48 (s, 6 H, CH_3), 1.72–1.79 (m, 4 H, CH_2), 1.40 (m, 8 H, $(CH_2)_4$). Mp: 136 °C.

Anal. Calcd for $C_{32}H_{38}O_4N_4$ (**H_2BP10**): C, 70.83; H, 7.06; N, 10.32. Found: C, 71.11; H, 7.05; N, 10.31. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.81–7.84, 7.42–7.47, 7.27–7.30 (m, 10 H, Ph), 2.71–2.75 (t, 4 H, CH_2), 2.48 (s, 6 H, CH_3), 1.71–1.78 (m, 4 H, CH_2), 1.37–1.41 (m, 12 H, $(CH_2)_6$). Mp: 152 °C.

Anal. Calcd for $C_{42}H_{58}O_4N_4$ (**H_2BP20**): C, 73.87; H, 8.56; N, 8.20. Found: C, 73.91; H, 8.62; N, 8.08. ^1H NMR ($CDCl_3/Me_4Si$): δ 10 (br, 2 H, OH), 7.82–7.84, 7.42–7.46, 7.28–7.30 (m, 10 H, Ph), 2.71–2.75 (t, 4 H, CH_2), 2.48 (s, 6 H, CH_3), 1.71–1.78 (m, 4 H, CH_2), 1.26–1.41 (m, 32 H, $(CH_2)_{16}$). Mp: 140 °C.

Apparatus. Flame and flameless atomic absorption measurements were made with a Hitachi polarized Zeeman atomic absorption spectrophotometer, Model 180-80. A Shimadzu UV-180 spectrometer with 1-cm quartz cells was used for spectrophotometric measurement. The pH measurements were performed with a Horiba F-8L pH meter, equipped with a glass electrode.

Procedure. The ionic strength of the aqueous solution in the procedures described below was controlled to 0.1 M with sodium perchlorate (*Caution*: potential explosion hazard[14]).

(a) Distribution of Bis(4-acylpyrazol-5-one) Derivatives. A 50-mL aliquot of an aqueous solution containing 0.1 M sodium perchlorate and 1×10^{-2} M sodium acetate as a buffer component was adjusted to the

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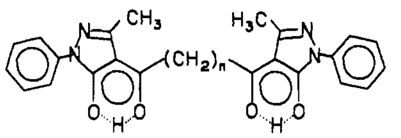

Figure 1. Structure of bis(4-acylpyrazol-5-one) derivatives.

desired pH with a hydrochloric acid or sodium hydroxide solution. The aqueous phase was shaken with an equal volume of 1,2-dichloroethane containing 1 × 10^{-3} M H_2BPn in a 100-mL separatory funnel for 1 h in a thermostated room at 25 ± 1 °C. The pH of the aqueous phase measured after two-phase separation was taken as the equilibrium value. The bis(4-acylpyrazol-5-one) concentration in 1,2-dichloroethane was determined spectrophotometrically. The H_2BPn derivatives except H_2BP0 and H_2BP1 have strong absorption (ϵ = ca. 4 × 10^4) at 270 nm. H_2BP0 and H_2BP1 have broad absorption at 240 (ϵ = 2.70 × 10^4) and 235 nm (ϵ = 2.47 × 10^4), respectively. The H_2BPn concentration in the aqueous phase was also determined after a back-extraction into 1,2-dichloroethane.

(b) Distribution of Cu(II). A 10-mL aliquot of an aqueous solution containing the desired amount of Cu(II), 0.1 M sodium perchlorate, and 1 × 10^{-2} M sodium acetate was put in a 30-mL glass-stoppered centrifuge tube. An equal volume of 1,2-dichloroethane containing 1 × 10^{-3} M H_2BPn was added and the reaction was mechanically shaken vigorously for 1 h in a thermostated room at 25 ± 1 °C. The shaking time of 1 h was found to be long enough for equilibration. After two-phase centrifugal separation, the pH of the aqueous phase measured was taken as the equilibrium value. The concentration of Cu(II) in the aqueous phase was determined by flame or flameless atomic absorption spectrometry. The concentration of Cu(II) in the organic phase was measured also after back-extraction into hydrochloric acid solution.

The sum of the H_2BPn and Cu(II) concentrations determined in each phase coincided well with the concentration initially taken.

Results and Discussion

Treatment of Extraction Data. For the distribution of a diprotic acid, bis(4-acylpyrazol-5-one) derivative (H_2BPn) acidity constants, K_1 and K_2, and the partition constant, P_{H_2BPn}, are defined as follows:

$$K_1 = \frac{[H^+][HBPn^-]}{[H_2BPn]} \qquad K_2 = \frac{[H^+][BPn^{2-}]}{[HBPn^-]} \tag{1}$$

$$P_{H_2BPn} = \frac{[H_2BPn]_{org}}{[H_2BPn]} \tag{2}$$

where subscript "org" denotes the species in the organic phase. Thus, the distribution ratio of H_2BPn, D_{H_2BPn}, can be written as

$$D_{H_2BPn} = \frac{[H_2BPn]_{org}}{[H_2BPn] + [HBPn^-] + [BPn^{2-}]} = \frac{P_{H_2BPn}}{1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2}} \tag{3}$$

Since the distribution ratio D of Cu(II) is independent of the concentration of such aqueous species as sodium acetate and sodium perchlorate, it might be concluded that the ion-pair formation is negligible and only the chelate extraction takes place. Then, the chelate extraction equilibrium can be expressed in terms of an extraction equation of the following general form:

$$iM^{2+} + (j + k)H_2BPn_{org} \rightleftarrows M_i(BPn)_j(HBPn)_{k,org} + (2j + k)H^+ \tag{4}$$

where M^{2+} represents the aqueous divalent metal ion, $M_i(BPn)_j(HBPn)_{k,org}$ denotes extractable metal complex, and i indicates the degree of polymerization, j the number of ligands that coordinate with both β-diketone donor sites as a diprotic acid, and k the number of ligands that coordinate with only one side of the β-diketone donor site as a monoprotic acid.

Application of the law of mass action of eq 4 leads to the expression

$$\log D - (i - 1) \log [M^{2+}] = \log K_{ex} + (j + k) \log [H_2BPn]_{org} + \log i + (2j + k) \text{ pH} \tag{5}$$

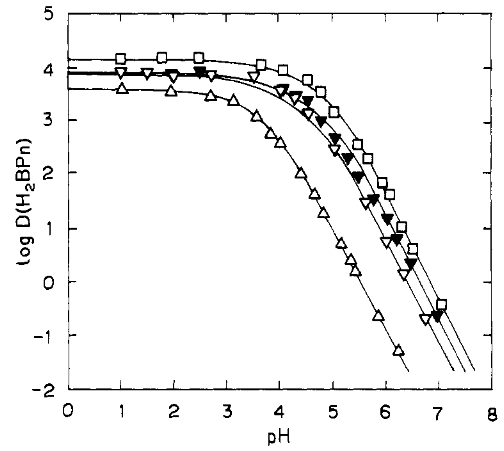

Figure 2. Extraction of H_2BPn (n = 0, 2, 3, 4) between 1,2-dichloroethane and water as a function of pH: (△) H_2BP0; (▽) H_2BP2; (▼) H_2BP3; (□) H_2BP4. The aqueous phase was 0.1 M sodium perchlorate and 0.01 M sodium acetate; the organic phase was 1 × 10^{-3} M H_2BPn in 1,2-dichloroethane.

in which K_{ex} represents the extraction constants. It can hence be seen that

$$\frac{\partial(\log D)}{\partial(\log [M^{2+}])} = i - 1 \tag{6}$$

$$\frac{\partial(\log D - (i - 1) \log [M^{2+}])}{\partial(\text{pH})} = 2j + k \tag{7}$$

$$\frac{\partial(\log D - (i - 1) \log [M^{2+}])}{\partial(\log [H_2BPn]_{org})} = j + k \tag{8}$$

Evaluation of these partial derivatives by the slope analysis method allowed the stoichiometry of the extraction equation to be elucidated for each of the investigated systems.

Design of Bis(4-acylpyrazol-5-one) Derivatives. In order to estimate the steric effect of polymethylene chain between two 1-phenyl-3-methyl-4-acylpyrazol-5-one groups, bis(4-acylpyrazol-5-one) derivatives were synthesized by inserting various lengths of polymethylene groups $-(CH_2)_n-$ (n = 0–8, 10, 20) between two 1-phenyl-3-methyl-4-acylpyrazol-5-one groups. Examination of an HGS molecular model indicates that polymethylene chain length is required to be at least 8 ($n \geq 8$) in order to put a metal ion between both sides with two β-diketone donor sites and to form a stable complex of 1:1 metal to ligand stoichiometry. Thus, bis(4-acylpyrazol-5-one) derivatives whose polymethylene chain lengths were up to n = 8 were used as chelating ligands.

In general, β-diketone type chelating agents have a keto–enol tautomerism. However, the absence of a methyne proton (CH) peak for the 4-positions of pyrazole rings characteristic of a keto form in the ^{1}H NMR spectrum indicates that bis(4-acylpyrazol-5-one) derivatives in $CDCl_3$ exist quantitatively as an enol form, as shown in Figure 1, and those in 1,2-dichloroethane, which was used as the organic solvent in this work, can also be regarded as having an enol form, for similar structures and relatively low dielectric constants.

Distribution of Bis(4-acylpyrazol-5-one) Derivatives. Figure 2 shows the dependence of the logarithm of the distribution ratio of bis(4-acylpyrazol-5-one) derivatives, log D_{H_2BPn} (n = 0–4), on the pH. The slopes of the distribution curves successively change from 0 via −1 to −2. This behavior shows that the bis(4-acylpyrazol-5-one) derivative is a diprotic acid, H_2BPn, which has a two-step protonation. The log D_{H_2BPn} value at slope 0 and the pH values of intersections of tangents with slope 0, −1, and −2 indicate log P_{H_2BPn}, pK_1, and pK_2, respectively according to eq 3. The pK_1, pK_2, and log P_{H_2BPn} values obtained by a nonlinear least-squares method using these experimental data are reported in Table I. The similar curves were also obtained for the bis(4-acylpyrazol-5-one) derivatives of $n > 5$, but those P_{H_2BPn} values were

Table I. Acidity Constants of H_2BPn at 25 °C[a]

H_2BPn	$\log P_{H_2BPn}$	pK_1	pK_2
$n = 0$	3.60 ± 0.03[b]	3.30 ± 0.07[b]	4.11 ± 0.07[b]
$n = 2$	3.91 ± 0.07	4.07 ± 0.10	4.73 ± 0.12
$n = 3$	3.92 ± 0.07	4.22 ± 0.15	4.98 ± 0.15
$n = 4$	4.16 ± 0.03	4.41 ± 0.11	5.00 ± 0.12

[a] Aqueous phase: $[NaClO_4] = 0.1$ M; $[CH_3COONa] = 0.01$ M. Organic phase: $[H_2BPn] = 1 \times 10^{-3}$ M in 1,2-dichloroethane. [b] Standard deviation.

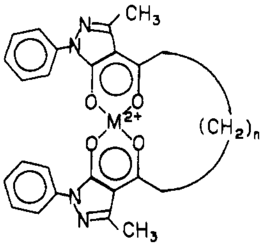

Figure 3. Extracted complex of 1:1 ligand to Cu(II) stoichiometry.

so high that the acidity constants, pK_1 and pK_2, could not be obtained. The P_{H_2BPn} values increase with an increase in polymethylene chain length, reflecting mainly the increase of a hydrophobic characteristic.

Bjerrum[15] suggested that ΔpK ($= pK_2 - pK_1$) of an aliphatic dicarboxylic acid, $HOOC(CH_2)_nCOOH$, should be statistically log 4 (=0.60), but ΔpK of the aliphatic dicarboxylic acid is more than 0.60. The excess value ($= \Delta pK - 0.60$) was attributed to the electrostatic repulsion of the negative charge on carboxyl groups by Ingold and other workers,[16-18] because the electrostatic repulsion inhibits formation of the dianion. As Hunter[19] pointed out in addition to the electrostatic effect, the intramolecular hydrogen bonding in the monoanion will increase the excess value, particularly when the structure is optimum for the formation of an intramolecular hydrogen bond between the proton of the un-ionized carboxyl group and an oxygen of the neighboring carboxylate anion. The effects of intramolecular hydrogen bond on the excess values have been also studied by Westheimer[20] and Kolthoff,[21-23] and comments have been made on the effect of structure and solvent.

From the analogy with the structure of aliphatic dicarboxylic acid, the similar discussion could also be applied to H_2BPn. However, the excess value of H_2BPn is significantly smaller than that of the corresponding aliphatic dicarboxylic acid. Therefore, since the structure of β-diketone is quite different from that of carboxyl group and two bulky 1-phenyl-3-methyl-4-acylpyrazol-5-one rings would cause a steric hindrance, H_2BPn might be regarded as a rigid molecule without intramolecular hydrogen bond. The mutual repulsion of the negative charges on both β-diketone donor sites might make an intrinsically flexible polymethylene chain simulate the behavior of a rigid molecule.

Extraction of Cu(II). It is well-known that Cu(II) reacts with β-ketones to form a square-planar chelate with a coordination number of 4 and is able to be extracted in a lower pH region, where β-diketones exist mainly as the undissociated form. In chelation of Cu(II) with H_2BPn, which is a quadridentate ligand with two β-diketone donor sites, polymethylene chain length would affect the mode and stoichiometry of the chelate formation.

Table II. Summary of Results on Extraction of Cu(II) with H_2BPn[a]

	slope		
H_2BPn	eq 6	eq 7	eq 8
$n = 1$	1.10 ± 0.33[b] (4)[c]	3.97 ± 0.41 (23)	1.91 ± 0.10 (4)
$n = 2$	1.04 ± 0.20 (4)	3.89 ± 0.42 (5)	2.02 ± 0.38 (4)
	−0.05 ± 0.07 (5)	2.08 ± 0.10 (15)	1.99 ± 0.06 (6)[d]
$n = 3$	0.91 ± 0.31 (8)	4.14 ± 0.30 (21)	2.04 ± 0.29 (14)
$n = 4$	1.02 ± 0.27 (15)	3.98 ± 0.46 (23)	2.06 ± 0.26 (15)
	0.16 ± 0.23 (12)	0.98 ± 0.36 (4)	1.98 ± 0.20 (4)[d]
$n = 5$	1.19 ± 0.20 (4)	4.00 ± 0.50 (4)	2.16 ± 0.20 (6)
$n = 6$	0.89 ± 0.12 (5)	4.04 ± 0.54 (5)	1.90 ± 0.45 (4)
$n = 7$	1.03 ± 0.27 (12)	3.98 ± 0.38 (24)	2.07 ± 0.27 (30)
$n = 8$	−0.03 ± 0.02 (9)	2.04 ± 0.08 (14)	0.97 ± 0.13 (12)
$n = 10$	−0.01 ± 0.17 (8)	2.15 ± 0.05 (8)	1.05 ± 0.07 (8)
$n = 20$	−0.11 ± 0.18 (8)	2.09 ± 0.21 (8)	1.03 ± 0.16 (6)

[a] Aqueous phase: $[NaClO_4] = 0.1$ M; $[CH_3COONa] = 0.01$ M. Organic phase: H_2BPn (n = 0–8, 10, 20) in 1,2-dichloroethane. [b] Standard deviation. [c] Number of points. (Given in parentheses). [d] $[Cu^{2+}]$ is lower than ca. 5×10^{-6} M.

For instance, H_2BPn (n = 8, 10, 20), which have polymethylene chains long enough to put Cu(II) between both β-diketone donor sites, are expected to form complexes of 1:1 Cu(II) to ligand stoichiometry, as shown in Figure 3. In fact, as seen in Table II, plots of log $[Cu^{2+}]$, pH, and log $[H_2BPn]$ vs log D exhibited slopes of 0, 2, and 1, respectively. Consequently, the values for i, j, and k were obtained as 1, 1, and 0, respectively. Substituting $i = 1$, $j = 1$, and $k = 0$ in eq 4 and 5 yields

$$Cu^{2+} + H_2BPn_{org} \rightleftarrows Cu(BPn)_{org} + 2H^+ \qquad (9)$$

$$\log D = \log K_{ex} + \log [H_2BPn]_{org} + 2\ pH \qquad (10)$$

where the partial derivatives in eq 6–8 are 0, 2, and 1, respectively.

The extraction of Cu(II) was made with 1-phenyl-3-methyl-4-octanoylpyrazol-5-one (HPMOP), which is structurally similar to H_2BP8, with a view to characterizing bis(4-acylpyrazol-5-one) derivatives under the same condition as employed for H_2BPn. According to the results of the slope analysis, Cu(II) was found to be extracted into 1,2-dichloroethane as $Cu(PMOP)_2$. Then the extraction equilibrium and the extraction constant, K_{ex}, can be written as follows:

$$Cu^{2+} + 2HPMOP_{org} \rightleftarrows Cu(PMOP)_{2,org} + 2H^+ \qquad (11)$$

$$\log D = \log K_{ex} + 2 \log [HPMOP]_{org} + 2\ pH \qquad (12)$$

The $pH_{1/2}$ values, the pH values where $\log D = 0$, were found to be 2.71 for HPMOP and 1.55 for H_2BP8. Therefore, it is clear that the extraction of Cu(II) with H_2BP8 was made from a lower pH region than that with HPMOP. Substituting $\log D = 0$ and pH = 2.71 in eq 12 gives $\log K_{ex} = 0.58$ for HPMOP. On the other hand, $\log K_{ex}$ of one of the most commonly used β-diketones, 2-thenoyltrifluoroacetone, in chloroform was −1.25.[24] Although there is some difficulty in comparing the extraction behaviors of Cu(II) complexes whose composition is not the same, the difference in the $pH_{1/2}$ value should be significant. The pK_1 and pK_2 values for H_2BP8 are supposed to be larger than 4, for the pK values increase with an increase of the polymethylene chain length as seen in Table I. Considering that HPMOP, whose pK is 4.07,[9] is a stronger acid than H_2BP8, this large extractability of H_2BP8 could be attributed to the stable complex formation brought about by its molecular structure, which can allow it to act as a quadridentate ligand.

The extraction characteristics with H_2BPn (n = 0–7) were quite different from those with H_2BPn (n = 8, 10, 20). The slope of unity in log D vs log $[Cu^{2+}]$ plots indicates $i = 2$. Independence of metal ion concentration is a prerequisite for the conventional slope analysis. Therefore, the slope analysis of this case must have been made by reference to the Preston[25] treatment. The slope analysis of pH and log $[H_2BPn]$ has been made vs log D − log

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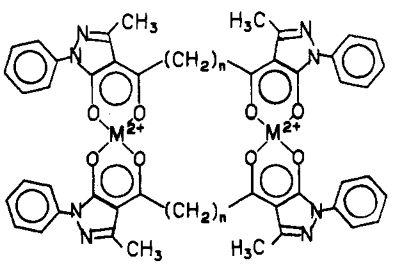

Figure 4. Extracted complex of 2:2 ligand to Cu(II) stoichiometry.

$[Cu^{2+}]$ according to eq 7 and 8. Plots of log D – log $[Cu^{2+}]$ vs pH and log $[H_2BPn]$ (n = 1–7) exhibit slopes of 4 and 2, respectively. Consequently values for j and k were obtained as 2 and 0, respectively. Substituting $i = 2, j = 2$ and $k = 0$ in eq 4 and 5 gives

$$2Cu^{2+} + 2H_2BPn_{org} \rightleftarrows Cu_2(BPn)_{2,org} + 4H^+ \qquad (13)$$

$$\log D - \log [Cu^{2+}] = \log K_{ex} + 2 \log [H_2BPn]_{org} + \log 2 + 4\ \mathrm{pH} \qquad (14)$$

where the partial derivatives in eq 6–8 are 1, 4, and 2, respectively. The extracted species with H_2BPn (n = 1–7) can be regarded as a dimer, $Cu_2(BPn)_2$, in which two Cu(II) moieties are inserted between two rigid H_2BPn layers like a sandwich, as shown in Figure 4.

H_2BP0, analogous in structure to oxalic acid, is peculiar. This has two β-diketone donor sites located directly side by side without a polymethylene chain. The examination of an HGS model reveals that the dimer can not be formed because of restriction of the structure, and at least $i = 3$, i.e. a trimer of 3:3 Cu(II) to ligand stoichiometry, is necessary to form a complex.

In addition to the 2:2 complex as mentioned above, another type of complex could be observed for H_2BP2 and H_2BP4 at a low Cu(II) concentration. It was found that the plot of log D vs log $[Cu^{2+}]$ consists of two rectilinear sections with a sharp discontinuity in slope at concentration of ca. 5×10^{-6} M, and the slopes changes from 0 to 1. In order to confirm the composition of the extracted species, extraction experiments for the slope analysis were made in the $[Cu^{2+}]$ range where the slope of log D vs log $[Cu^{2+}]$ is 0. The stoichiometry of a complex below 5×10^{-6} M is deduced from the slope of the relevant section of the plots of log D vs log $[Cu^{2+}]$, pH, log $[H_2BP4]$, and the observed values are 0, 2, and 2, respectively. Then the values of i, j, and k were obtained as 1, 0, and 2, respectively. Substituting $i = 1, j = 0$ and $k = 2$ in eq 4 and 5 yields

$$Cu^{2+} + 2H_2BPn_{org} \rightleftarrows Cu(HBPn)_{2,org} + 2H^+ \qquad (15)$$

$$\log D = \log K_{ex} + 2 \log [H_2BPn]_{org} + 2\ \mathrm{pH} \qquad (16)$$

where partial derivatives in eq 6–8 are 0, 2, and 2, respectively. Accordingly, the extracted species is a complex of 1:2 Cu(II) to ligand stoichiometry, where Cu(II) is coordinated by two H_2BP4 through one β-diketone donor site as a monoprotic acid, as shown in Figure 5. When Cu(II) is higher than 5×10^{-6} M, the same results as 2:2 complex were obtained, where partial derivatives in eq 6–8 are 1, 4, and 2, respectively.

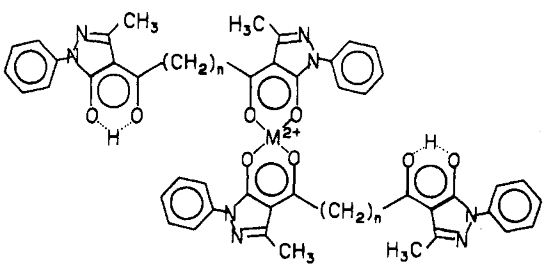

Figure 5. Extracted complex of 1:2 ligand to Cu(II) stoichiometry.

Table III. Extraction Constants of H_2BPn at 25 °C[a]

		log K_{ex}		
H_2BPn	extracted complex	1:1[b]	1:2[c]	2:2[d]
$n = 1$	$Cu_2(BP1)_2$			2.18[d]
$n = 2$	$Cu(HBP2)_2$, $Cu_2(BP2)_2$		0.92[c]	0.30[d]
$n = 3$	$Cu_2(BP3)_2$			2.70[d]
$n = 4$	$Cu(HBP4)_2$, $Cu_2(BP4)_2$		1.04[c]	1.10[d]
$n = 5$	$Cu_2(BP5)_2$			1.62[d]
$n = 6$	$Cu_2(BP6)_2$			0.18[d]
$n = 7$	$Cu_2(BP7)_2$			1.78[d]
$n = 8$	Cu(BP8)	–0.10[b]		
$n = 10$	Cu(BP10)	–0.18[b]		
$n = 20$	Cu(BP20)	–1.06[b]		

[a] Aqueous phase: $[NaClO_4]$ = 0.1 M; $[CH_3COONa]$ = 0.01 M. Organic phase: H_2BPn (n = 0–8, 10, 20) in 1,2-dichloroethane. [b] $\log K_{ex} = \log D - \log [H_2BPn]_{org} - 2\ \mathrm{pH}$. [c] $\log K_{ex} = \log D - 2 \log [H_2BPn]_{org} - 2\ \mathrm{pH}$. [d] $\log K_{ex} = \log D - \log [Cu^{2+}] - 2 \log [H_2BPn]_{org} - \log 2 - 4\ \mathrm{pH}$.

The above observation prompts us to consider the following. In relatively low Cu(II) concentration region, the extracted complex with H_2BPn (n = 2, 4) should be 1:2 Cu(II) to ligand stoichiometry owing to the deficiency of Cu(II). When the amount of Cu(II) is increased, two hydrogen ions are replaced by a Cu(II), and a dimer of 2:2 Cu(II) to ligand stoichiometry is formed.

Compositions of the extracted species of Cu(II) with H_2BPn and the extraction constants obtained from the slope analyses are summarized in Table III. By comparison of the extraction constants of complexes of 2:2 Cu(II) to ligand stoichiometry, the conspicuous gap between H_2BPn with even-numbered and odd-numbered polymethylene chains is recognized. As polymethylene chain may be regarded as a rigid model, examination of an HGS model indicates that steric hindrance with odd-numbered polymethylene chain is smaller than that with even-numbered polymethylene chain. The odd-numbered polymethylene chain exists as a staggered conformational isomer where hydrogen atoms in methylene groups can be as far as possible from each other. On the other hand, the even-numbered polymethylene chain is compelled to exist as an eclipsed conformational isomer where hydrogen atoms in methylene groups are near each other.