CHAPTER V

METAL ION GUEST RESPONSIVE OF BENZOXAZINE DIMERS VIA MOLECULAR ASSEMBLY AND STOICHIOMETRIC INCLUSION PHENOMENA OF CYCLIC DERIVATIVES

Abstract

A series of benzoxazine dimers (**1-9**), esterified dimers (**10-18**), and the benzoxazine dimer based cyclic derivatives (**19-22**) are prepared. Metal ion guest responsive properties based on; (i) the substituent groups at both ortho and para positions on phenol rings as well as aza group, (ii) the ester group at benzene ring, and (iii) the cyclization of dimers, are clarified. Ion extraction of benzoxazine dimers is improved by two folds compared to the substituted group at aza group is bulky or the hydroxyl group at phenol is esterified. Stoichiometric host-guest ratio for 1:1 and 2:1 dependent on type of metal ions is observed in the case of the cyclic derivatives with ether linkage as confirmed by ^{1}H NMR.

Introduction

For the past three decades, host-guest compounds or inclusion compounds have received much attention owing to the understanding of the interaction at molecular level.[1-2] The induced molecular recognition properties are known to be based on the non-covalent interaction or secondary forces between hosts and guests.[1-3] Various hosts either with specific functional groups, such as hydroxyl, ester, ether, amide, sulfonyl group and phenyl ring, etc., or definite size, have been designed and developed in order to achieve the unique supramolecular structures.

Polybenzoxazines are known as a novel type of phenolic resin with excellent thermal properties.[4] Although various derivatives have been reported, most are related to the difunctional benzoxazines with the objectives to improve the materials as well as the optimal processing conditions. Considering the open ring benzoxazines, we originally proposed that the basic unit is resembled to that of calixarenes with an aza methylene linkage (Scheme I).[5] It is necessary to note that the open ring benzoxazines can be prepared in regular alignment only if the backbone unit involves with mono-functional benzoxazines as shown in Scheme II.

Recently, our group has focused on the controlled structure benzoxazines by using *p*-substituted phenol. Our studies found an important information that the *p*-substituted phenols self-terminate at dimer level (Scheme III) via Mannich reaction and, as a result, the polymerization cannot proceed to a large molecular weight. The dimers obtained are so stable with inter and intramolecular hydrogen bonds that the asymmetric reaction is inevitably occurred.[6]

Sone et al. reported that the acyclic *p*-substituted phenol-formaldehyde oligomers show the inclusion properties to entrap neutral molecules.[7] Here, the structure of benzoxazine dimer can be expected to be a host molecule since it provides the site to interact with metal ions via molecular assembly through the lone pair electrons at hydroxyl and aza groups, similar to those phenol derivatives. By using the dimer as a backbone unit, we previously succeeded in preparation of a 30-membered ring macrocyclic benzoxazine via ester and ether linkage. It is also another important point to clarify the inclusion phenomena of these macrocyclic benzoxazines.

The present article, thus, focuses on (i) the possibility whether the benzoxazine dimer acts as a host molecule, (ii) the influence of the structure on the guest responsive properties, and (iii) the speculated inclusion phenomena of benzoxazine dimers and their cyclic derivatives. The clarification of host-guest properties induced from benzoxazine dimers will not only support us to propose a novel host compound but also be a guideline to develop supramolecular structured benzoxazines.

Experimental Section

Chemicals. Barium chloride, lithium hydroxide and deuterated chloroform ($CDCl_3$) were purchased from Fluka Chemicals (Buchs, Switzerland). Sodium hydroxide, cesium carbonate, potassium hydroxide, chloroform, magnesium chloride, calcium chloride, and picric acid were the products of Ajax chemicals (Australia). All chemicals were analytical grade and used without further purification.

Syntheses. A series of benzoxazine dimers; *N,N*-Bis(3,5-dimethyl-2-hydroxy benzyl)methylamine **1**, *N,N*-Bis(5-methyl-2-hydroxybenzyl)methylamine **2**, *N,N*-Bis (5-ethyl-2-hydroxybenzyl)methylamine **3**, *N,N*-Bis(3,5-dimethyl-2-hydroxybenzyl) propylamine **4**, *N,N*-Bis(5-methyl-2-hydroxybenzyl)propylamine **5**, *N,N*-Bis(5-ethyl-2-hydroxybenzyl)propylamine **6**, *N,N*-Bis(3,5-dimethyl-2-hydroxybenzyl)cyclohexyl amine, **7**, *N,N*-Bis(5-methyl-2-hydroxybenzyl)cyclohexylamine **8**, *N,N*-Bis(5-ethyl-2-hydroxybenzyl)cyclohexylamine **9**, were prepared as reported elsewhere[8-9] and used as starting materials (Scheme IV).

Preparation of *N,N*-Bis(2-benzoyl-3,5-dimethyl benzyl)methylamine 10, *N,N*-Bis(2-benzoyl-5-methylbenzyl)methylamine 11, *N,N*-Bis(2-benzoyl-5-ethyl benzyl)methylamine 12, *N,N*-Bis(2-benzoyl-3,5-dimethyl benzyl)propylamine 13, *N,N*-Bis(2-benzoyl-5-dimethylbenzyl)propylamine 14, *N,N*-Bis(2-benzoyl-5-ethyl benzyl)propylamine 15, *N,N*-Bis(2-benzoyl-3,5-dimethylbenzyl)cyclohexylamine 16, *N,N*-Bis(2-benzoyl-5-ethylbenzyl)cyclohexylamine 17, *N,N*-Bis(2-benzoyl-5-ethylbenzyl)cyclohexylamine 18. Benzoxazine dimer **1** (5 mmol) were dissolved in dichloromethane (50 mL) and followed by adding NaOH (20 mmol) in water (50 mL). A solution of benzoyl chloride (10 mmol) in CH_2Cl_2 (50 mL) was added dropwisely to the mixture. The reaction was proceeded at room temperature for 6 h. The organic phase was collected and extracted by water for several times. The product was dried over sodium sulfate and the solvent was removed to obtain crude product. The product was recrystallized in isopropanol to obtain a clear and colorless crystal. Similarly, **11-18** were prepared as the procedures of **10** using **2-9** as starting materials, respectively. The product was characterized by FT-IR, ^{1}H NMR, and EA.

Compound **10:** 95% yield; FTIR (KBr, cm^{-1}): 1737 (vs, C=O), 1484 (s, tetrasubstituted benzene), 1265 (vs, C-N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.05 (3H, s, N-**CH$_3$**), 2.15 (6H, s, Ar-**CH$_3$**), 2.30 (6H, s, Ar-**CH$_3$**), 3.35 (4H, s, Ar-**CH$_2$**-N), 6.98 (2H, s, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{33}H_{33}NO_4$: C, 78.11; H, 6.51; and N, 2.76. Found: C, 77.99; H, 6.54; and N, 2.78.

Compound **11:** 95% yield; FTIR (KBr, cm^{-1}): 1738 (vs, C=O), 1499 (s, trisubsubstited benzene), 1266 (vs, C-N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.05 (3H, s, N-**CH$_3$**), 2.30 (6H, s, Ar-**CH$_3$**), 3.45 (4H, s, Ar-**CH$_2$**-N), 6.98 (2H, d, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.10 (2H, d, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{31}H_{29}NO_4$: C, 77.66; H, 6.05; and N, 2.92. Found: C, 77.71; H, 6.12; and N, 2.89.

Compound **12:** 95% yield; FTIR (KBr, cm^{-1}): 1738 (vs, C=O), 1498 (s, trisubsubstited benzene), 1264 (vs, C-N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.25 (6H, t, Ar-CH_2-**CH_3**), 2.05 (3H, s, N-**CH_3**), 2.65 (4H, q, Ar-**CH_2**-CH_3), 3.45 (4H, s, Ar-**CH_2**-N), 6.98 (2H, d, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.10 (2H, d, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{33}H_{33}NO_4$: C, 78.11; H, 6.51; and N, 2.76. Found: C, 78.12; H, 6.48; and N, 2.73.

Compound **13:** 95% yield; FTIR (KBr, cm^{-1}): 1734 (vs, C=O), 1498 (m, tetrasubstituted benzene), 1264 (s, C-N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.75 (3H, t, N-CH_2-CH_2-**CH_3**), 1.45 (2H, m, N-CH_2-**CH_2**-CH_3), 2.10 (6H, s, Ar-**CH_3**), 2.22 (6H, s, Ar-**CH_3**), 2.35 (2H, t, N-**CH_2**-CH_2-CH_3), 3.45 (4H, s, Ar-**CH_2**-N), 6.98 (2H, d, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.10 (2H, d, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{35}H_{37}NO_4$: C, 78.50; H, 6.92; and N, 2.62. Found: C, 78.48; H, 6.87; and N, 2.65.

Compound **14:** 95% yield; FTIR (KBr, cm^{-1}): 1737 (vs, C=O of ester), 1497 (m, trisubstituted benzene), 1268 (vs, C-N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.75 (3H, t, N-CH_2-CH_2-**CH_3**), 1.45 (2H, m, N-CH_2-**CH_2**-CH_3), 2.18 (6H, s, Ar-**CH_3**), 2.35 (2H, t, N-**CH_2**-CH_2-CH_3), 3.45 (4H, s, Ar-**CH_2**-N), 6.98 (2H, d, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.10 (2H, d, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{33}H_{33}NO_4$: C, 78.11; H, 6.51; and N, 2.76. Found: C, 78.07; H, 6.46; and N, 2.78.

Compound **15:** 95% yield; FTIR (KBr, cm^{-1}): 1734 (vs, C=O), 1497 (m, trisubstituted benzene), 1267 (vs, C-N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.75 (3H, t, N-CH_2-CH_2-**CH_3**), 1.25 (6H, t, Ar-CH_2-**CH_3**), 1.45 (2H, m, N-CH_2-**CH_2**-CH_3), 2.35 (2H, t, N-**CH_2**-CH_2-CH_3), 2.65 (4H, q, Ar-**CH_2**-CH_3), 3.45 (4H, s, Ar-**CH_2**-N), 6.98 (2H, d, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.10 (2H, d, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{35}H_{37}NO_4$: C, 78.50; H, 6.92; and N, 2.62. Found: C, 78.53; H, 6.90; and N, 2.59.

Compound **16:** 95% yield; FTIR (KBr, cm^{-1}): 1731 (vs, C=O), 1482 (s, tetrasubstituted benzene), 1265 (vs, C-N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (4H, m, CH_2), 1.60 (2H, m, CH_2), 1.82 (4H, dt, CH_2), 2.05 (3H, s, N-**CH_3**), 2.15 (6H, s, Ar-**CH_3**), 2.60 (1H, t, CH), 3.35 (4H, s, Ar-**CH_2**-N), 6.98 (2H, s, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{38}H_{41}NO_4$: C, 79.30; H, 7.13; and N, 2.43. Found: C, 79.28; H, 7.11; and N, 2.47.

Compound **17:** 95% yield; FTIR (KBr, cm^{-1}): 1738 (vs, C=O), 1497 (m, trisubstituted benzene), 1267 (vs, C-N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (4H, m, CH_2), 1.60 (2H, m, CH_2), 1.82 (4H, dt, CH_2), 2.40 (6H, s, Ar-**CH_3**), 2.50 (1H, t, CH), 3.55 (4H, s, Ar-**CH_2**-N), 6.98 (2H, d, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.10 (2H, d, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{36}H_{37}NO_4$: C, 78.98; H, 6.76; and N, 2.56. Found: C, 78.88; H, 6.78; and N, 2.55.

Compound **18:** 95% yield; FTIR (KBr, cm^{-1}): 1737 (vs, C=O), 1498 (m, trisubstituted benzene), 1267 (vs, C-N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (4H, m, CH_2), 1.25 (6H, t, Ar-CH_2-**CH_3**), 1.45 (2H, m, N-CH_2-**CH_2**-CH_3), 1.60 (2H, m, CH_2), 1.82 (4H, dt, CH_2), 2.35 (2H, t, N-**CH_2**-CH_2-CH_3), 2.50 (1H, t, CH), 2.65 (4H, q, Ar-**CH_2**-CH_3), 3.55 (4H, s, Ar-**CH_2**-N), 6.98 (2H, d, Ar-**H**), 7.05 (2H, s, Ar-**H**), 7.10 (2H, d, Ar-**H**), 7.45 (4H, t, Ar-**H**), 7.62 (2H, t, Ar-**H**), 8.20 (4H, d, Ar-**H**). Anal. calcd for $C_{38}H_{41}NO_4$: C, 79.30; H, 7.13; and N, 2.43. Found: C, 79.27; H, 7.15; and N, 2.44.

Preparation of Cyclic Benzoxazines. Benzoxazine dimers based cyclic esters (**19-20**) were prepared as reported elsewhere.[10-11] Benzoxazine dimers based cyclic ethers (**21-22**) were prepared as follows. Potassium *tert*-butoxide (2.1 mmol, 0.236 g) was added to the solution of **2** (1 mmol, 0.271 g) in toluene (150 mL). The solution was refluxed for 30 min. Ditosylated diethylene glycol in toluene (50 mL) was added dropwise to the solution of **2**. The reaction was refluxed for 4 days. The

organic solution was collected and washed by water (50 mL) for three times. The solution was dried over sodium sulfate and the solvent was removed to obtain a yellow solid product. The product was recrystallized in isopropanol to obtain a white solid product. Compound **3** (0.299 g, 1 mmol) was used to prepare **22.** The procedures were the same as **21**. The products were characterized by FTIR, ^{1}H-NMR, TOF-MS, and EA.

Compound **21**: 80% yield; R_f = 0.0 (5% MeOH in $CHCl_3$); mp = 185°C; FTIR (KBr, cm^{-1}): 1504 (vs, trisubstituted benzene), 1253 (vs, C-N stretching), 1140 (s, C-O-C). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.20 (6H, s, N-CH_3), 2.27 (12 H, s, Ar-CH_3), 3.59 (8H, s, N-CH_2), 3.85 (8H, t, CH_2-O), 4.02 (8H, t, CH_2-O), 6.69 (4H, d, Ar-H), 6.95 (4H, d, Ar-H), 7.20 (4H, s, Ar-H). MALDI-TOF MS: m/z = 682. Anal. calcd. for $C_{42}H_{54}N_2O_6$: C, 73.90: H, 7.91; N, 4.11. Found: C, 73.86; H, 7.93; N, 4.07.

Compound **22**: 75% yield; R_f = 0.0 (5% MeOH in $CHCl_3$); mp = 186°C; FTIR (KBr, cm^{-1}): 1503 (vs, trisubstituted benzene), 1248(vs, C-N stretching), 1133 (s, C-O-C). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.20 (12H, t, Ar-CH_2-**CH_3**), 2.22 (6H, s, N-CH_3), 2.58 (8 H, q, Ar-**CH_2**-CH_3), 3.65 (8H, s, N-CH_2), 3.89 (8H, t, CH_2-O), 4.05 (8H, t, CH_2-O), 6.72 (4H, d, Ar-H), 6.98 (4H, d, Ar-H), 7.25 (4H, s, Ar-H). MALDI-TOF MS: m/z = 738. Anal. calcd. for $C_{46}H_{62}N_2O_6$: C, 74.80: H, 8.40; N, 3.79. Found: C, 74.78; H, 8.39; N, 3.81.

Ion Extraction Property of Benzoxazine Dimers and Derivatives. Ion extraction was qualitatively and quantitatively analyzed by Pedersen's technique.[1] All benzoxazine derivatives (**1-22**) were dissolved in chloroform at $7x10^{-3}$, $7x10^{-2}$, $3.8x10^{-2}$, $7x10^{-1}$, and $3.8x10^{-1}$ M. Alkali and alkaline earth metal picrates aqueous solutions were prepared at $7x10^{-5}$ M. Both solutions were mixed and left for 10 min before measuring the concentration of metal picrates. The concentration was determined by a UV-Vis Perkin-Elmer Lambda-16 Spectrophotometer at λ 354 nm ($\varepsilon = 1.45 \times 10^4$ $M^{-1}cm^{-1}$). In the case of the cyclic derivatives, the organic phase was

collected and further studied for the host-guest ratio by a ^{1}H NMR ACF 200 MHz of Bruker, Switzerland.

Results and Discussion

Ion Extraction Ability. Figure 1 summarizes the ion interaction ability of **1-3**, which are different in substituted group at ortho and para positions while the substituted group at aza position is maintained. When the concentration of **1-3** is increased, the extracted potassium ion increased gradually. At the equimolar concentration of host and guest ($7x10^{-5}$ M), the extraction is ~10% while the concentration of host at $7x10^{-2}$ M, the extraction is accomplished for ~40-50%. Hampton et al.[12] reported that a series of macrocyclic benzoxazines performed low ion extraction percentage, less than 0.2 % at the host and metal picrate concentrations of $5x10^{-3}$ M, owing to the strong intramolecular hydrogen bond. Recently, our group[6,12] reported the unique intramolecular hydrogen bond in the dimers by X-ray structural analysis. This hydrogen bond generates a six-membered ring of O--H--N and prevents the symmetric reaction.[6]

Taking the above informations into our consideration, an intramolecular hydrogen bond might play an important role for **1-9**. Figure 1 demonstrates that when the host concentration ($7x10^{-2}$ M) is increased to 1000 times of that of picrate ($7x10^{-5}$ M), the ion extraction ability of dimer is achieved for only 20-40%. This indicates that the host-guest formation might form as a molecular assembly controlled by hydrogen bond (see Proposed ion interaction system). Here, **1** with more methyl substituted groups at both positions might form a loose assembly structure owing to the steric effect, and as a result, accept more number of guests.

Sone et al.[7] reported that the inclusion compound of phenol-formaldehyde oligomers is enhanced when the phenol unit has a bulky group at the para position. Taking this into our consideration, **3**, which has more bulky group than **2**, shows higher ion extraction percentage.

Electron density of the host molecules is another important factor to be considered in the system. In the case of **1**, two methyl groups provide more electrons to the system than that of **2** or **3** while **3** provides more electrons to the system than **2**. As a result, the ion extraction percentage is in the order of **1**>**3**>**2**. Similarly, other

alkali and alkaline earth metal ions; lithium, sodium, magnesium, calcium, and barium, show the extraction percentage increases as increasing the concentration of **1-3**.

Effect of Substituent Groups on Aza-methylene Linkage. Chirachanchai et al.[13] determined the crystal structure of a series of benzoxazine dimers to find the hydrogen bonding network and found that the substituted group at aza linkage affects the packing structure. In order to identify the effect of substitutent group at aza linkage in ion interaction, a series of dimers (**4-9**) was studied.

As demonstrated in Figure 2, the ion extraction percentage is increased gradually when the functional group changed from methyl to propyl and cyclohexyl groups. The dimers, **7-9,** with cyclohexyl group on aza-methylene linkage show the high extraction percentage (approximately 70-80%). In addition, **4-6**, with propyl group also show an increase of extraction ability. This suggests that the bulky group substituted on aza linkage enhance the ion interaction ability. When the substituted groups at both para-position on phenol and aza units are bulky, as seen in the case of **9**, the extraction ability is up to 85%.

Comparing to **5** and **8**, the compounds **4** and **7** with the same substituent group at para position but methyl group at ortho position should perform high ion extraction percentage owing to their loose packing structures in liquid state. Unexpectedly, we found the results are in contrast. This indicates the effect of substituted aza group is so significant that the substituent groups at para and ortho affect little.

Effect of Ester Group on Phenol Unit. If the ion extraction ability is influenced by hydrogen bonding, esterification of the dimers will enhance the extraction ability. As shown in Figures 1 and 3, the esterfied dimers **10-12** give the higher extraction percentage than **1-3** for two times. It is necessary to note that **10-12** at the concentration $7x10^{-2}$ M can extract almost all of potassium picrate (~100%). The results suggest two important factors involved in the ion interaction ability, which are hydrogen bond and the electron density. The decreasing of

hydrogen bond and the increasing of electron density enhance the interaction between benzoxazine dimer and metal ions.

Figure 4 shows that all esterified dimers **10-18** perform the similar level of extraction ability. This might be related to the influence of esterification, which is so significant that the effects from the substituent groups of phenol and aza group were rarely observed.

Proposed Ion Interaction Structure. Yamagishi et al.[14-15] reported the metal ion extraction by acyclic all-ortho *p-tert*-butylphenol-formaldehyde accomplished for ~10-80 % where the concentration of host is 1000 times to that of metal guests. The proposed host-guest formation is based on the pseudo-cyclic conformation of molecular assembly. Here, we originally propose the ion interaction properties of benzoxazine dimers, thus, it is important to clarify the speculated the system. As shown in Figures 1-4, the ion extraction percentage for each benzoxazine dimer is found to be in the range of 30-95%. However, this can be achieved when the concentration of dimer is higher than that of metal ion 1000 times. It is important to note that all dimers, although they do show the marked ion extraction ability, the selectivity is not observed.

In our case, we proposed that the molecular assembly between metal ions and benzoxazine dimers is controlled by the hydrogen bonding network and the electron density. As a result, the ion interaction appears to be insignificant in selectivity. However, the ion interaction is enhanced when the bulky and ester groups involve in the dimer structure.

Stoichiometric Ion Interaction of Cyclic Compounds. In our related work, a series of cyclic benzoxazines are successfully prepared as reported elsewhere.[11] Here, benzoxazine dimer based cyclic esters (**19-20**) and benzoxazine dimer based cyclic ethers (**21-22**) are applied as hosts. Figure 5 shows the extraction percentage of sodium, potassium and cesium observed by UV at the equimolar concentration of host and metal species. The metal ions were not responsive for **19-20** while the interaction with **21-22** was obvious. It is necessary to note that the extraction

percentage for **21-22** is either 50 or 100%, which can be calculated to be integral numbers of molar ratios, which are 2:1 and 1:1. This suggests that host-guest formation might be in a stoichiometric ratio.

^{1}H NMR is an effective method to qualitatively and quantitatively study the inclusion phenomena.[16] Here, we used samples from liquid-liquid extraction system using picrate salt. Thus, the picrate peak at 8.8 ppm will be observed whenever the host-metal complexes are formed. As shown in Tables 1 and 2, **21- 22** give the δ_H values shifted after extraction with picrate salts, especially the ones belonging to the methylene linkage and ethylene glycol unit. It is important to note that the chemical shift after ion extraction appears to be the same even the type of metal ions are varied. This might be due to the fact that **21-22** perform similar inclusion compound structure.

Considering the molar ratio of host-guest, the peak integration of picrate and aromatic proton is determined. Figures 6-7 indicate that **21** performs host-guest ratio at 2:1 (host:guest) for all ions while that of **22** at 1:1 for Na^+ and K^+ and 2:1 for Cs^+. This implies the specific cyclic structures play an important role to interact with metal ions. In other word, **22** with more bulky group at para position might form a larger cavity to entrap metal ion guest. In conclusion, a stoichiometric ratio of **21** and **22** are clarified to be dependent on the size of the metal species.

The reason why **19** and **20** do not show ion extraction ability is another important point to be further studied. The terephthaloyl ester group on **19-20** may generate the steric effect preventing the precise cavity formation for metal ion guest. In order to confirm our speculation, we are now studying the ethylene ester linkage derivatives as well as X-ray structure of **19-20**.

Conclusions

Although only few linear oligomers that perform inclusion phenomena have been reported[7,14-15], the present work accomplished a novel type of acyclic host molecules. Ion extraction studies based on varying the concentration of dimers and metal ion indicated that the benzoxazine dimers form a molecular assembly to interact with metal ions. By changing the dimer structure systematically, the hydrogen bonds and electron density are clarified to be main factors in the assembly

formation. The substituted group at aza position and the esterification on phenol ring strongly enhanced the ion extraction ability. When the benzoxazine dimer was modified to be a cyclic ether linkage derivative, the host-guest ratio was confirmed for the first time in our studies to be a stoichiometric ratio, indicating that the host-guest phenomena based on the interaction of host and guest species.

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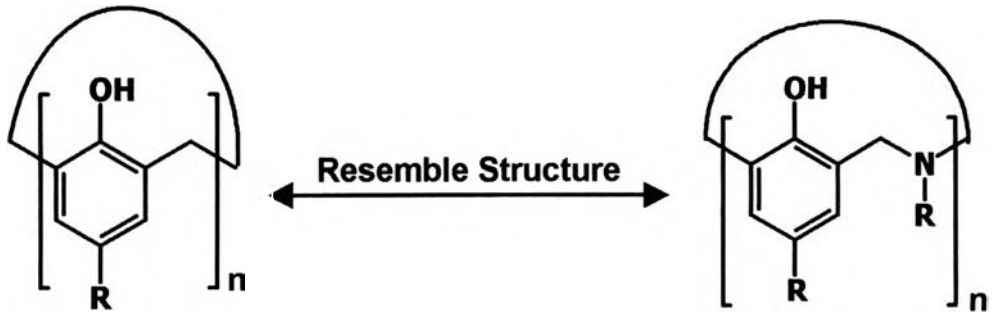
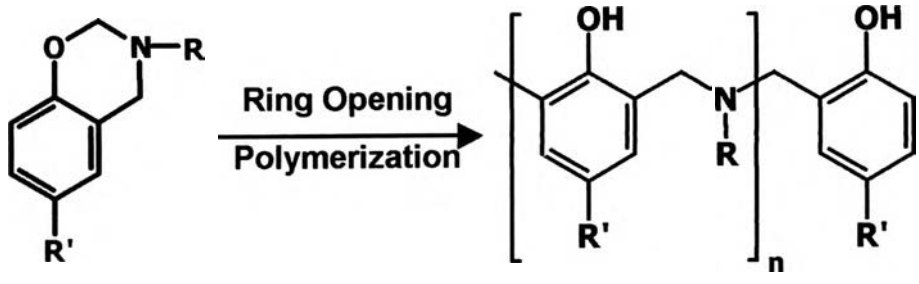
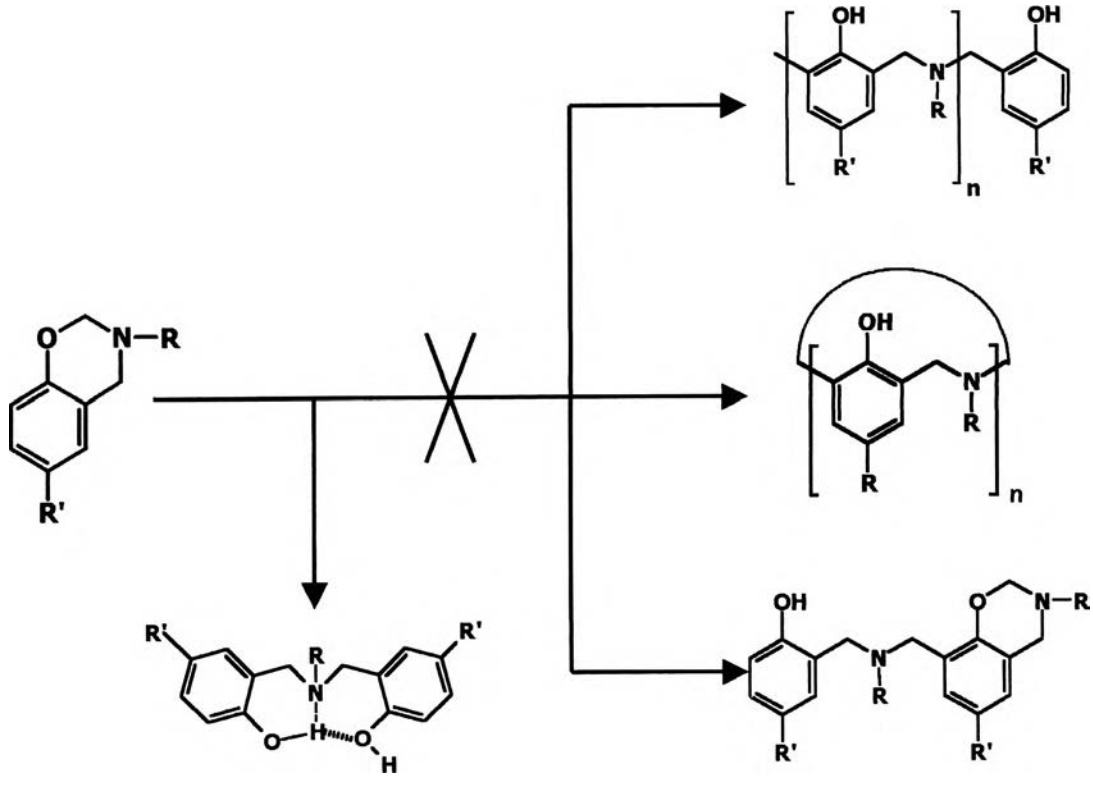


Calixarenes **Pseudocyclic / Cyclic Benzoxazine**

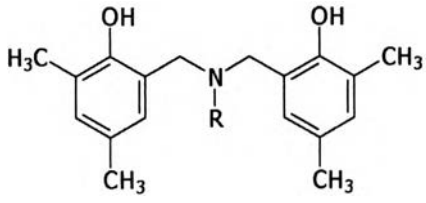
Scheme I. (Apirat et al.)



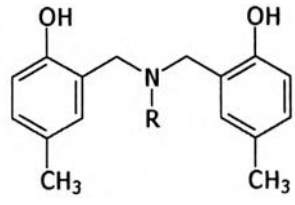
Scheme II. (Apirat et al.)



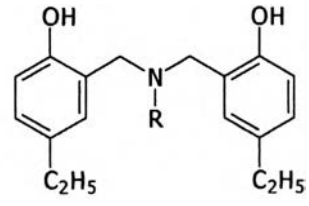
Scheme III. (Apirat et al.)



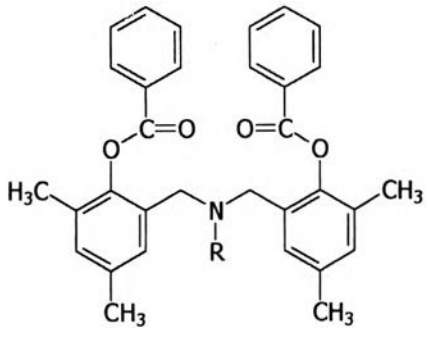
R = -CH_3 (1)
= -C_3H_7 (4)
= -C_6H_{11} (7)



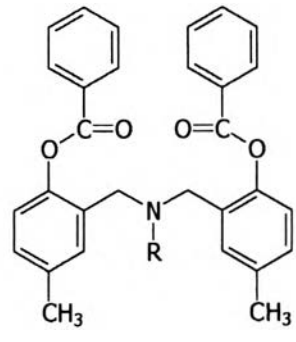
R = -CH_3 (2)
= -C_3H_7 (5)
= -C_6H_{11} (8)



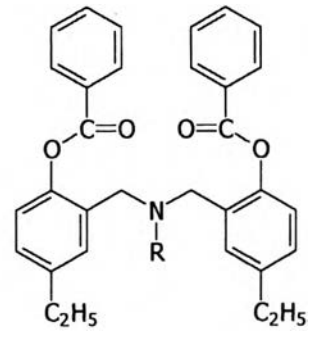
R = -CH_3 (3)
= -C_3H_7 (6)
= -C_6H_{11} (9)



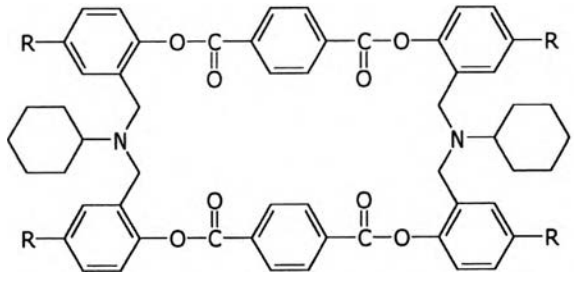
R = -CH_3 (10)
= -C_3H_7 (13)
= -C_6H_{11} (16)



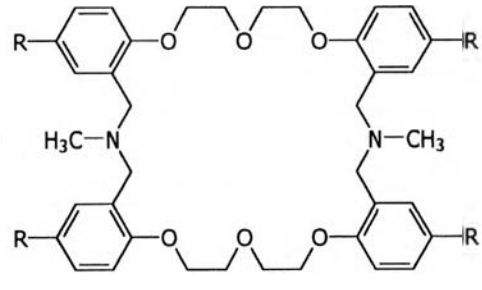
R = -CH_3 (11)
= -C_3H_7 (14)
= -C_6H_{11} (17)



R = -CH_3 (12)
= -C_3H_7 (15)
= -C_6H_{11} (18)



R = -CH_3 (19)
= -C_2H_5 (20)



R = -CH_3 (21)
= -C_2H_5 (22)

Scheme IV. (Apirat et al.)

Figure Captions

Figure 1. Extraction percentage of potassium picrate at the concentration of $7x10^{-5}$ M by (■) **1**, (◆) **2**, and (▲) **3** with various concentrations in $CHCl_3$ at 25°C.

Figure 2. Extraction percentage of potassium picrate at the concentration of $7x10^{-5}$ M by **1-9** at the concentration of $7x10^{-2}$ M in $CHCl_3$ at 25°C.

Figure 3. Extraction percentage of potassium picrate at the concentration of $7x10^{-5}$ M by (■) **10**, (◆) **11**, and (▲) **12** with various concentrations in $CHCl_3$ at 25°C.

Figure 4. Extraction percentage of potassium picrate at the concentration of $7x10^{-5}$ M by **10-18** at the concentration of $7x10^{-2}$ M in $CHCl_3$ at 25°C.

Figure 5. Extraction percentage of (□)sodium picrate, (⊡) potassium picrate, and (⊟) cesium picrate at the concentration of $7x10^{-5}$ M by **19-22** in $CHCl_3$ at 25°C.

Figure 6. ^1H NMR spectra of (a) **21** and (b) complex of **21** and cesium ion.

Figure 7. ^1H NMR spectra of (a) **22** and (b) complex of **22** and potassium ion.

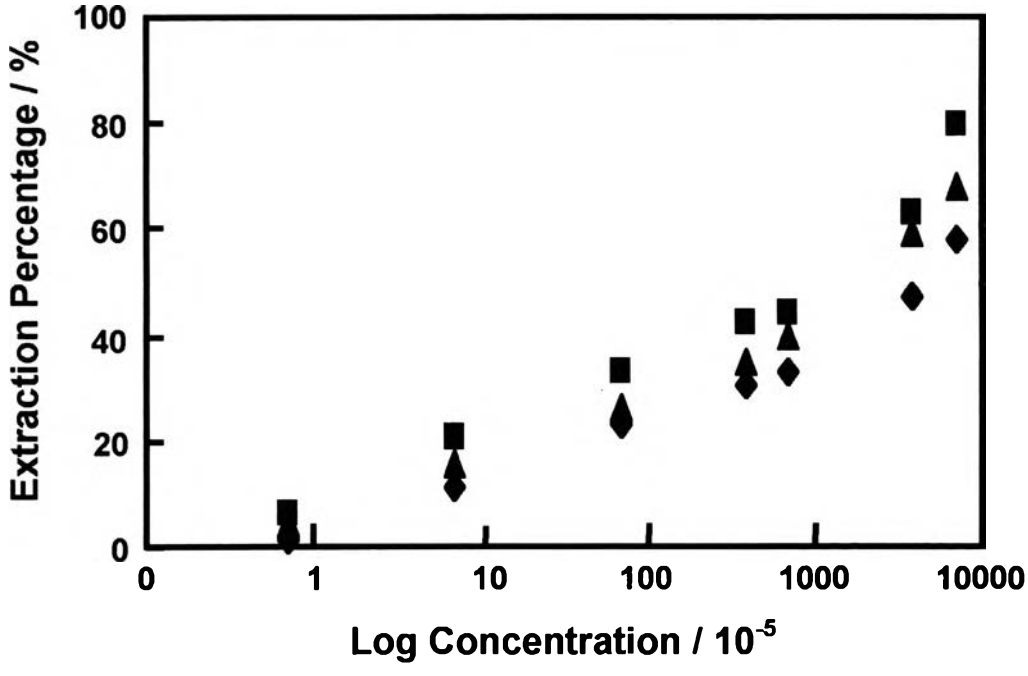


Figure 1. (Apirat et al.)

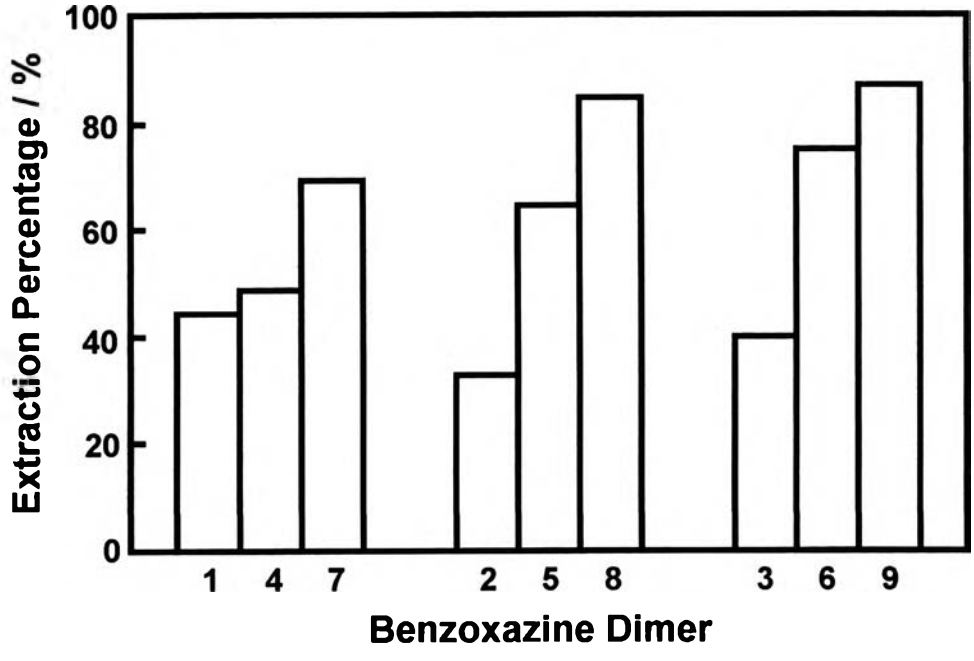


Figure 2. (Apirat et al.)

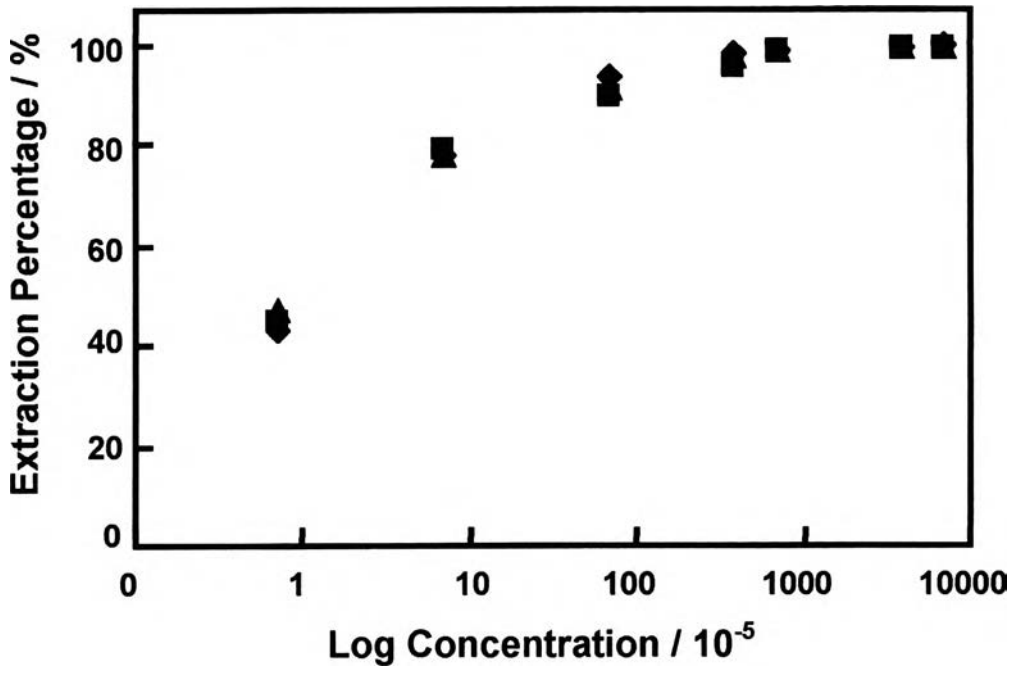


Figure 3. (Apirat et al.)

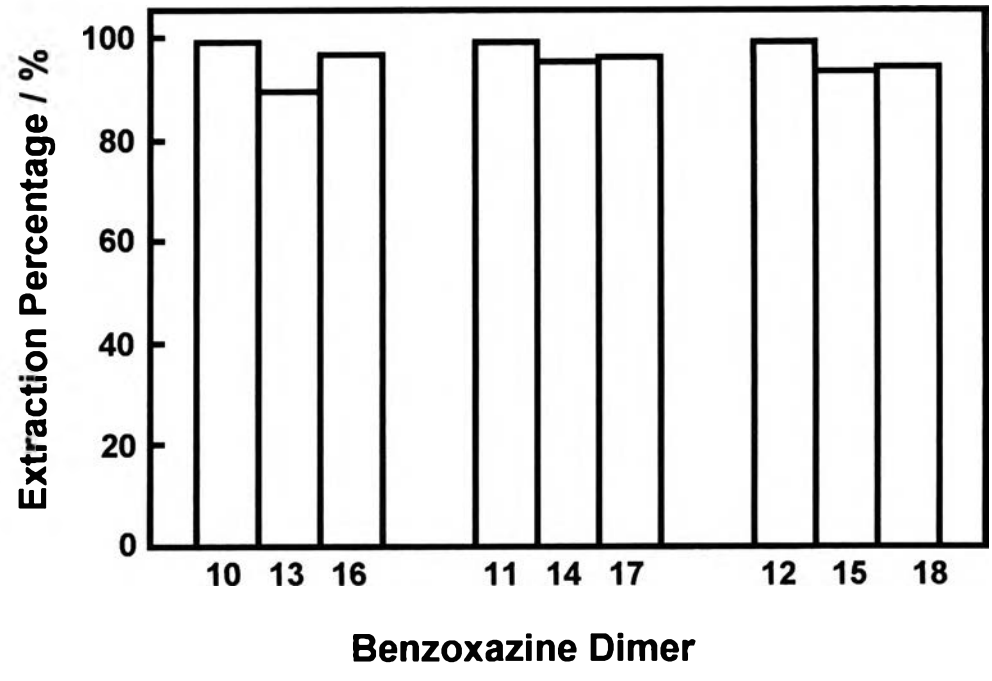


Figure 4. (Apirat et al.)

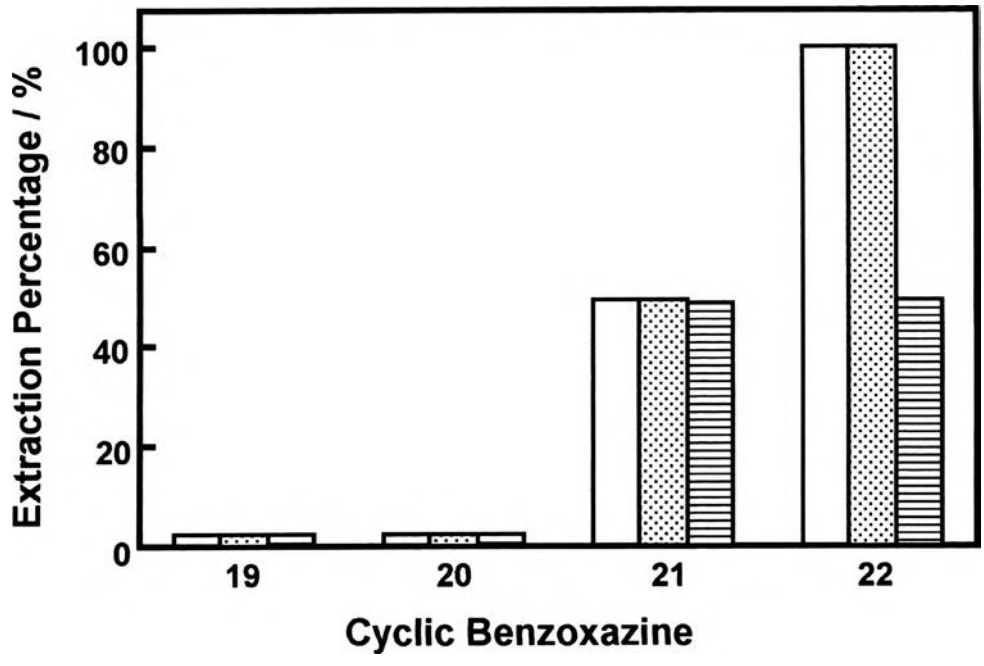


Figure 5. (Apirat et al.)

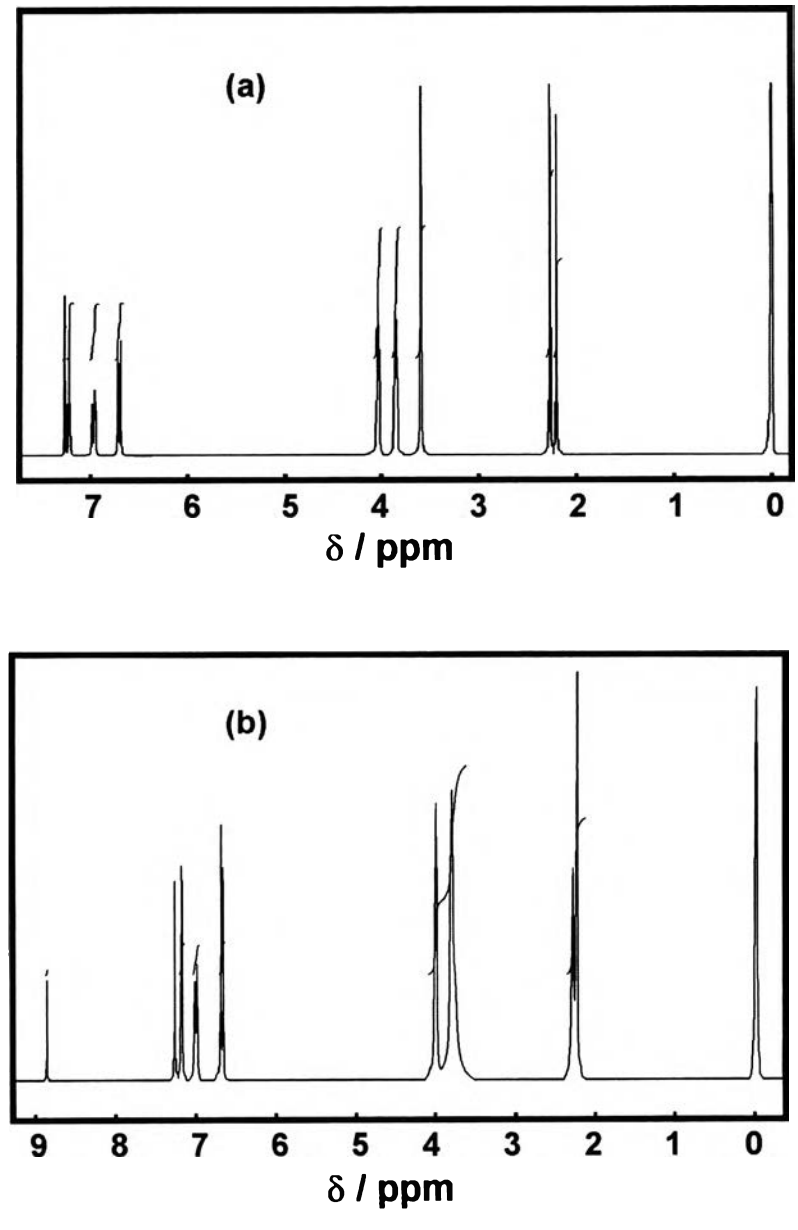


Figure 6. (Apirat et al.)

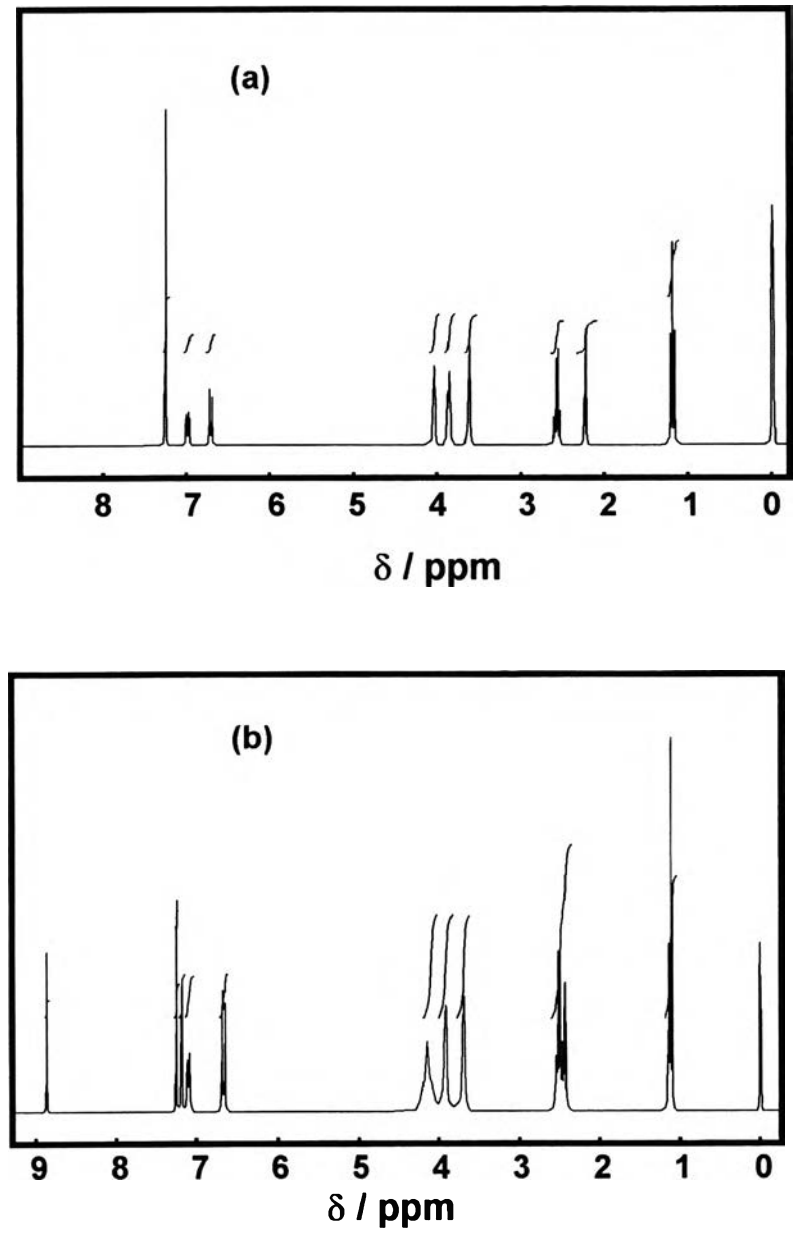
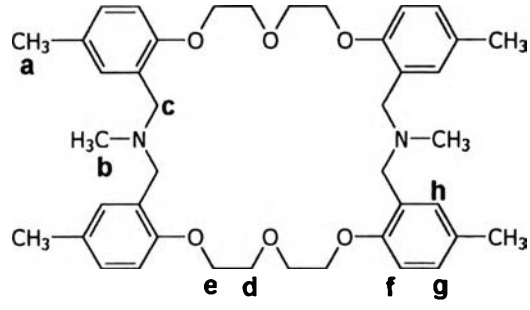


Figure 7. (Apirat et al.)

Table Captions

Table 1. ^{1}H NMR data of **21** and **21**-metal ion complexes

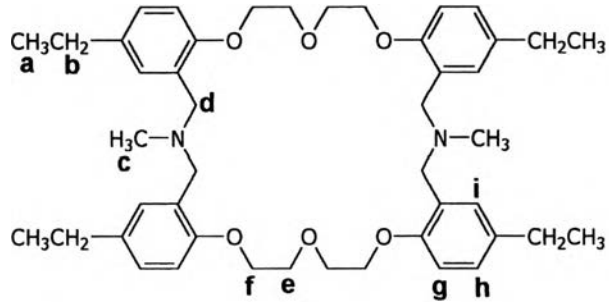
Table 2. ^{1}H NMR data of **22** and **22**-metal ion complexes



21

position	Chemical Shift / ppm			
	21	**21**-Na^+ complex	**21**-K^+ complex	**21**-Cs^+ complex
a	2.27	2.32	2.32	2.30
b	2.21	2.25	2.25	2.25
c	3.60	3.78	3.78	3.78
d	3.87	3.85	3.78	3.78
e	4.05	3.98	3.98	4.01
f	6.95	7.02	7.02	7.01
g	6.70	6.68	6.68	6.68
h	7.21	7.15	7.18	7.18

Table 1. (Apirat et al.)



22

position	Chemical shift / ppm			
	22	**22**-Na^+ complex	**22**-K^+ complex	**22**-Cs^+ complex
a	1.21	1.15	1.15	1.16
b	2.58	2.52	2.52	2.52
c	2.22	2.44	2.42	2.37
d	3.65	4.15	4.18	3.92
e	3.89	3.69	3.69	3.75
f	4.05	3.91	3.91	3.92
g	6.72	6.68	6.68	6.69
h	6.98	7.11	7.11	7.08
i	7.25	7.21	7.21	7.21

Table 2. (Apirat et al.)