

Fe(III).

Fe-TTF compounds have an electrical conductivity in the range of  $10^{-3}$ – $10^{-4}$  S·cm<sup>-1</sup>. Those values are in semiconductor range. This means that partially oxidized TTF are moderately stacked in solid state, and exhibited the electrical conductivity in stacking direction. The values of electrical conductivity are represented in Table 3.

The mid-peak potentials ( $E_{1/2}$ ) of TTF in the prepared compounds are about 0.00 V for TTF<sup>+</sup>/TTF<sup>0</sup> couple and +0.23 V for TTF<sup>2+</sup>/TTF<sup>+</sup> couple. TTF molecule shows similar  $E_{1/2}$  values in this work. Similar results were also reported for TTF and some heavy transition metal compounds.<sup>9</sup>

In summary, TTF reacts with hydrated FeCl<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in methanol to form (TTF)<sub>3</sub>FeCl<sub>3</sub>·0.5CH<sub>3</sub>OH and (TTF)<sub>2.5</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>OH respectively, in both of which charge transfer has occurred to [FeCl<sub>3</sub>]<sup>-</sup> and [Fe(SO<sub>4</sub>)<sub>2</sub>]<sup>-</sup> moiety during the reaction. The partially oxidized TTFs are moderately stacked to exhibit relatively high electrical conductivity. Such inter-stack interactions between TTFs are also supported by the temperature-independent magnetic susceptibility arisen from the TTF radicals. This small and temperature independent magnetic susceptibility, Pauli paramagnetism, is well known in low-dimensional semiconductor as a result of band formation.<sup>10</sup>

**Acknowledgement.** This work is supported by Basic Science Research Program, Ministry of Education KOREA

(BSRI-96-3410).

## References

1. Hatfield, W. E. *Molecular Metals, NATO Conference Series*; Plenum: New York, 1979.
2. Kim, Y. I.; Hatfield, W. E. *Inorg. Chim. Acta* **1991**, *188*, 15.
3. Mallah, T.; Holles, C.; Bott, M.; Kurmoo, M.; Day, P.; Allan, M.; Friend, R. H. *J. Chem. Soc., Dalton Trans.* **1990**, 859.
4. Bozio, R.; Zanon, I.; Gilando, A.; Pecile, C. Y. *J. Chem. Phys.* **1979**, *71*, 2282.
5. Inoue, M. B.; Inoue, M.; Fernando, Q.; Nebesny, K. W. *Inorg. Chem.* **1987**, *25*, 3976.
6. Wudl, F.; Smith, G. H.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453.
7. Sugano, T.; Kuroda, H.; Yakushi, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1041.
8. Torrence, J. B.; Scott, B. A.; Welber, B.; Kaufman, F. B.; Seiden, P. B. *Phys. Rev. B.* **1979**, *19*, 730.
9. Jung, C. K.; Kim, Y. I.; Choi, S. N. *Bull. Korean Chem. Soc.* **1996**, *17*, 1061.
10. Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1.

## Extractive Separation of Alkali Metal Ions by Mono- and Bis-*o*-Xylyl Crown Macrocyclic Compounds in an Aquatic Environment

Yong-Ill Lee\*<sup>†</sup>, Dong-Won Kim<sup>‡</sup>, Ki-Young Choi<sup>†</sup>, Miran Yoo\*,  
Jong Seung Kim\*, Young-Jae Yoo\*, and Wonbo Sim\*

\*Department of Chemistry, Changwon National University, Changwon 641-773, Korea

<sup>‡</sup>Department of Chemistry, Chungbuk National University, Cheongju 360-763, Korea

<sup>†</sup>Department of Chemistry, Mokwon University, Taejon 301-729, Korea

<sup>§</sup>Department of Chemistry, Konyang University, Nonsan 320-711, Korea

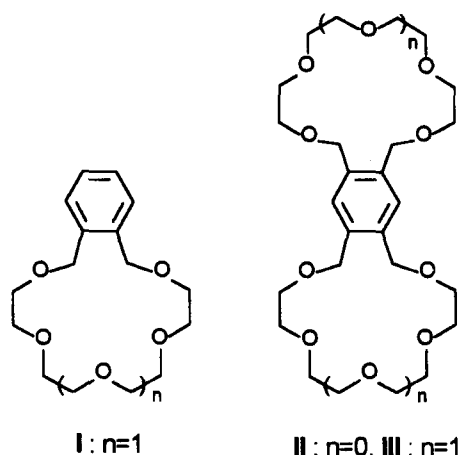
Received June 16, 1997

Synthetic macrocyclic multidentate ligands such as crown ethers become the focus of intense scientific interest for the separation of alkali and alkaline earth metal cations from aqueous solutions and synthetic efforts have been successful in obtaining various macrocyclic compounds.<sup>1-4</sup> Some of the ligands and metal complexes have several potential applications, including medical treatment,<sup>5</sup> imaging,<sup>6</sup> analytical separation of metal cations<sup>7,8</sup> and ion-selective electrodes.<sup>9,10</sup> Recently, Lee *et al.*<sup>11</sup> reported the synthesis of bis-crown ether derivatives, *i.e.* (1,2)(4,5)-bis-*o*-xylyl crown compounds in which the macrocycles are connected to the benzene core *via* Ar-CH<sub>2</sub>-O linkages. However, to the best of our knowledge, no details on their alkali metal cation complexation have been appeared yet. Understanding com-

plexation at the molecular level provides the basis for metal selectivity sequence and binding strength which depends on cavity size, steric factors, conformation, ligand basicity, and rigidity.<sup>12</sup> Although there are several reports on the solvent extraction of alkali metal ions with crown ethers, most experiments employed monocyclic crown ethers as organic ligands. Schlotter *et al.*<sup>13</sup> deduced a qualitative insight in the metal cation complexation properties of benzo-bis-(18-crown-6) from <sup>1</sup>H NMR titration studies using potassium thiocyanate and potassium picrate. They observed the increase of  $\Delta\delta$  (Hz) for benzo-bis-(18-crown-6) in going to host/guest ratios 1:2, compared to the corresponding benzo-(18-crown-6).

In the present paper, mono- and bis-*o*-xylyl crown ethers of different cavity sizes, *i.e.*, mono-*o*-xylyl-(17-crown-5) (I), bis-*o*-xylyl-(14-crown-4) (II), and bis-*o*-xylyl-(17-crown-5)

<sup>†</sup>To whom correspondence should be addressed.



Scheme 1.

(III), were synthesized and their binding properties for alkali metal cations were examined by solvent extraction with a water-chloroform system. Various counter ions including erythrosin B, picrate, iodide, chloride, and nitrate, were used to investigate the counter ion effect in extraction efficiency from aqueous solutions.

### Experimental

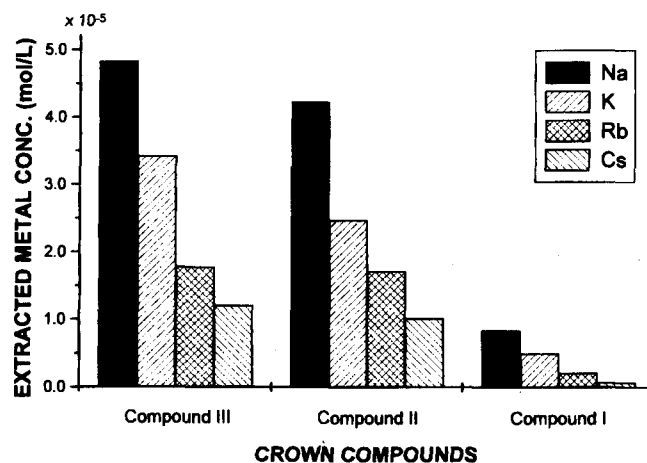
**Materials.** Mono-*o*-xylyl-(17-crown-5) (I) was prepared by Reinhoudt's method<sup>14</sup> and bis-*o*-xylyl (II and III) crown ether compounds were synthesized in our laboratory according to the published procedure.<sup>11</sup> Their properties and analytical data are as follows, (II): colorless needles; mp 114-115 °C; IR (KBr pellet) 3030, 2940, 2860, 1460, 1350, 1290, 1250, 1120, 1090, 985, and 870  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.39 (s, 2H, ArH), 4.76 (s, 8H, ArCH<sub>2</sub>), 3.73 and 3.64 (two s, 24H, OCH<sub>2</sub>CH<sub>2</sub>O), (III): colorless needles; mp 97.5-98.5 °C; IR (KBr pellet) 3040, 2940, 2880, 2850, 1470, 1360, 1350, 1300, 1250, 1100, and 1030  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.43 (s, 2H, ArH), 4.71 (s, 8H, ArCH<sub>2</sub>), 3.72 and 3.66 (two s, 32H, OCH<sub>2</sub>CH<sub>2</sub>O). Sodium, potassium, rubidium and cesium picrates were prepared by the reaction of picric acid and corresponding metal carbonates in hot water and washed with benzene. They were further purified by recrystallization from water. The solutions were prepared using deionized water obtained from a Milli-Q plus reagent water system. All other chemicals were reagent grade purchased from Aldrich and used without any further purification.

**Extraction Procedure.** Solvent extractions were carried out by shaking vigorously equal volumes (10 mL) of  $2.5 \times 10^{-5}$  M of crown ether in chloroform and  $1.0 \times 10^{-4}$  M of alkali metal picrate in aqueous solution placed in a stoppered test tube for 40 min at 25 °C. The pH of aqueous solution was adjusted to 8.0 with 0.01 M tetramethylammonium hydroxide. The two phases were allowed to separate and then the chloroform layer was kept aside. The 5 mL of organic phase was taken and the solvent was removed in vacuum, then the residue was dissolved in 5 mL of acetonitrile. The concentration of the metal picrate extracted from aqueous phase was determined by the absorption at 380 nm in UV/VIS spectrophotometer.

To investigate the counter ion effect in extraction experiment, atomic absorption spectrophotometer (Varian AA 100 plus) was used to determine the concentration of sodium in aqueous solutions. Sodium concentration in the extracted aqueous solution was calculated using an established calibration curve with five different sodium standard solutions ( $1.0 \times 10^{-5}$ - $1.0 \times 10^{-4}$  M) with various counter ions, *i. e.*, erythrosin B, picrate, iodide, chloride, and nitrate.

### Results and Discussion

The stoichiometry of the crown ether/cation complexes was determined by solvent extraction to elucidate the cation binding ability of crown compounds I, II and III, in which an excess metal picrate concentration ( $1.0 \times 10^{-4}$  M) in aqueous phase and a constant crown ether concentration ( $2.5 \times 10^{-5}$  M) in organic phase were used for completion of the extraction. Tetramethylammonium cation used for pH adjustment in aqueous phase can not interact with crown ethers because of larger ion sizes than cavity size, which is also supported by the well-known fact that the interaction between crown ethers and ammonium cations decreases in the following order, primary > secondary > tertiary > quaternary.<sup>15</sup> Chloroform was used as the water immiscible solvent. It is not only a good solvent for the bis-*o*-xylyl crown ethers but also the dissociation of the extracted complex in it is negligible. The comparison of the extraction efficiency to alkali metals such as sodium, potassium, rubidium and cesium with three different crown compounds using picrate as a counter anion was shown in Figure 1. The sequence of extractability for alkali metal cations is  $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$  with xylyl crown derivatives, I, II and III, depending on the size-relationship of cation and crown ether cavity. It should, in particular, be noted that the extractability of bis-*o*-xylyl-(17-crown-5) (III) for sodium cation is about six times higher than that of mono-*o*-xylyl-(17-crown-5) (I), even though III has only two crown rings in the structure. The concentration ratio of extracted sodium metal to bis-*o*-xylyl (17-crown-5) (III) is nearly 2.0, which indicates the 2:1 stoichiometry of the complex. For the extraction of  $\text{K}^+$ ,  $\text{Rb}^+$ ,



**Figure 1.** Profile for the extraction of alkali metals (sodium, potassium, rubidium and cesium) in an aquatic environment, with mono-*o*-xylyl-(17-crown-5) (I), bis-*o*-xylyl-(14-crown-4) (II), and bis-*o*-xylyl-(17-crown-5) (III) using picrate as a counter anion.

**Table 1.** Effect of counter anion for sodium metal extraction with bis-*o*-xylyl-(17-crown-5): III and mono-*o*-xylyl-(17-crown-5): I at 25 °C and pH 8.0

Counter ion	bis- <i>o</i> -xylyl (17-crown-5) (III)		mono- <i>o</i> -xylyl (17-crown-5) (I)	
	Extracted sodium concentration (mol/L)	Relative extraction efficiency (%)	Extracted sodium concentration (mol/L)	Relative extraction efficiency (%)
Picrate	$4.831 \times 10^{-5}$	96.6	$0.843 \times 10^{-5}$	33.7
Iodide	$4.091 \times 10^{-5}$	81.8	$0.690 \times 10^{-5}$	27.6
Erythrosin B	$3.092 \times 10^{-5}$	61.8	$1.972 \times 10^{-5}$	78.9
Nitrate	$2.796 \times 10^{-5}$	55.9	$0.416 \times 10^{-5}$	16.6
Chloride	$1.214 \times 10^{-5}$	24.2	$0.072 \times 10^{-5}$	2.88

Cs<sup>+</sup> by compound I, II and III, similar experiments were also carried out. The extractability of bis-crown to these metal ions was also much higher than that of mono-crown compound. It is generally accepted that the complex stoichiometry depends significantly upon the size-relationship of cation and crown ether cavity. Different extractability between II and III which have different ring cavity sizes may be expected but no remarkable differences could be observed due to the flexibility of CH<sub>2</sub> unit in Ar-CH<sub>2</sub>-O. It is also found that the flexibility of CH<sub>2</sub> unit in side arm of 1,7-dioxa-4,10,13-triazacyclopentadecane-4,10,10-tripropionic acid (N-pr<sub>3</sub>[15]ane N<sub>3</sub>O<sub>2</sub>) gives a different selectivity for metal cation binding even though it causes a little decrease in stability.<sup>16</sup>

Comparative work on the effect of counter anion for metal ion extraction with bis-*o*-xylyl-(17-crown-5) (III) and mono-*o*-xylyl-(17-crown-5) (I) at 25 °C and pH 8.0 was illustrated in Table 1. Relative extraction efficiency was determined in percent based on the molar concentration of crown ether,  $5.0 \times 10^{-5}$  M for III and  $2.5 \times 10^{-5}$  M for I. The order of extractability of sodium in aqueous solution with compound I for various counter anions was erythrosin B >> picrate > iodide > nitrate > chloride. Erythrosin acts as a very effective counter ion which has a high molar volume as well as planner structure with monocyclic compound in metal ion extraction by forming an extensive ion-pair during extraction as in the case of Cryptand 221.<sup>17</sup> On the other hand, with the use of bis-*o*-xylyl (17-crown-5) (III) as a ligand for the extraction of sodium, the extractability decreases in the order of picrate > iodide > erythrosin B > nitrate > chloride. Taking these results into account, it can be concluded that picrate is suitable as a counter anion for

metal binding with bis-*o*-xylyl compounds. Bulky erythrosin B may cause the strong repulsion between bound counter anions and the subsequently bound ones, and therefore, additional binding of cations may become difficult with bulky counter anion.

**Acknowledgment.** This work was supported by the Basic Science Research Institute Program, Ministry of Education of Korea, Project BSRI 96-3435, 1996 and the Institute for Basic Science, Changwon National University.

## References

- An, H.; Bradshaw, J. S.; Izatt, R. M. *Chem. Rev.* **1992**, *92*, 543.
- Fenton, D. E. In *Comprehensive Coordination Chemistry* (Wilkinson, G. (Ed.), Pergamon Press: Oxford, U. K. 1987; Vol. 3, p 1.
- Bajaj, A. V.; Poonia, N. S. *Coord. Chem. Rev.* **1988**, *87*, 55.
- Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1991**, *91*, 1721.
- Martell, A. E.; Motekaitis, R. J.; Murase, I.; Sala, L. F.; Stoldt, R.; Ng, C. Y.; Rosenkrantz, H.; Metterville, J. J. *Inorg. Chim. Acta* **1987**, *138*, 215.
- Schwartz, S. W.; Mathias, C. J.; Sun, Y.; Dilley, W. G.; Wells, S. A. Jr.; Martell, A. E.; Welch, M. J. *J. Nucl. Med. Biol.* **1991**, *18*, 477.
- Beklemishev, M. K.; Elshani, S.; Wai, C. M. *Anal. Chem.* **1994**, *66*, 3521.
- Mohite, B. S.; Zambare, D. N.; Mahadik, B. E. *Anal. Chem.* **1994**, *66*, 4097.
- Oggenfuss, P.; Morf, W. E.; Oesch, U.; Ammann, D.; Pretsch, E.; Simon, W. *Anal. Chim. Acta* **1986**, *180*, 299.
- Yoshio, M.; Noguch, H. *Anal. Lett.* **1982**, *15*, 1197.
- Lee, W. Y.; Sim, W.; Park, O. S. *Synlett.* **1992**, 157
- Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.
- Schlotter, J. J. H.; Mertens, I. J. A.; Wageningen, A. M. A.; Mulders, F. P. J.; Zwikker, J. W.; Buschmann, H. J.; Jenneskens, L. W. *Tetrahedron Letts.* **1994**, *35*, 7255.
- Gray, R. T.; Reinhoudt, D. N.; Smith, C. J.; Veenstra, M. I. *Rec. Trav. Chim.* **1976**, *95*, 258.
- Kimura, K.; Kitazawa, S.; Maeda, T.; Shono, T. *Fresenius Z Anal. Chem.* **1982**, *313*, 132.
- Choi, K. Y.; Lee, Y. I.; Kil, H. S.; Kim, D. W.; Chung, Y. S.; Kim, C. S.; Hong, C. P.; Sim, W. *Microchem. J.* **1996**, *53*, 180.
- Gandhi, M. N.; Khopkar, S. M. *Anal. Sci.* **1992**, *8*, 233.