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Preparation of Novel Selenacrown Ethers and Their Complexing Abilities with Transition Metal and Heavy Metal Cations

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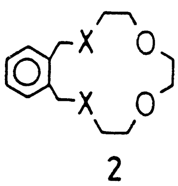
Cyclic polyselenaethers were prepared and their extraction abilities toward transition metal and heavy metal cations were determined. Toward methylmercury(II) cation, the extraction abilities of these selenacrown ethers were higher than those of structually corresponding thiacrown ethers. Also the structures of the complexes of these selenacrown ethers with transition metal and heavy metals were discussed.

It is well known that some of the transition metal cations and the heavy metal cations form complexes with various thiacrown ethers.1,2) In particular, toward transition and heavy metal cations (for example Cu^{+}, Pd^{2+}, Ag^{+}, Pt^{2+}, and Hg^{2+}), thiacrown ethers are the excellent complexing agents.3) On the other hand, it has been reported that the liner selenaethers form complexes with Ni^{2+}, Pd^{2+}, and Pt^{2+}.2,4) However, only a few examples of macrocyclic polyselenaethers have been reported. Pinto et al.5) synthesized some selenacrown ethers and discussed their structures. Misumi et al.6) reported the preparation of cyclophanes containing selenium atoms instead of methylene groups. However, the complexing abilities of the selenacrown ethers were not discussed. We wish to report here the preparation of novel selenacrown ethers and their ability for complexing with transition metal and heavy metal cations.

The reaction of α,α'-diselenocyanato-o-xylene(**1**) with 1,3-dibromopropane in dry tetrahydrofuran gave 1,6-diselena-3,4-benzocyclononane(**3b**) and 1,6,10,15-tetraselena-3,4:12,13-dibenzocyclooctadecane(**4b**) in 55 and 18% yields, respectively. Other compounds (**2a**-**5a**, **2b**, and **5b**) were prepared by a similar reaction.7) The extraction abilities of these selena and thiacrown ethers are summarized in Table 1. Among the transition metal and heavy metal cations, Cu^{+},



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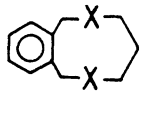

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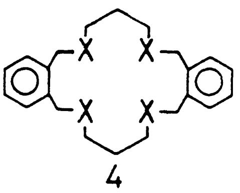

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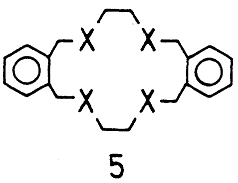

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a:X=S, b:X=Se

Table 1. Extraction of Metal Picrate from the Aqueous to the Organic Phase (%)$^{a)}$

Compd.	Co^{2+}	Ni^{2+}	Cu^{+} c)	Cu^{2+}	Pd^{2+} d)	Ag^{+}	$MeHg^{+}$ b,e)	Hg^{2+} b)
2a	1	2	86	5	70	97	5	90
2b	1	1	82	2	72	97	49	87
3a	0	0	19	0	68	80	1	2
3b	0	1	44	3	74	83	1	12
4a	0	2	68	2	54	100	13	11
4b	0	1	56	2	73	91	57	10
5a	0	1	50	1	62	92	4	13
5b	0	1	57	3	69	47	54	55

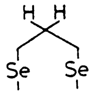
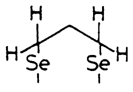
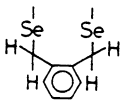
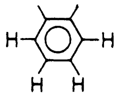
a) Water and dichloromethane(equal volumes). Metal nitrate = 0.1M, crown ether = 7 x 10^{-4}M, picric acid = 7 x 10^{-5}M. b) Metal chlorides were used instead of nitrate. c) $CuSO_4$ and $(NH_3OH)_2SO_4$ were used instead of nitrate. d) Concentration of metal salt was 1 x 10^{-3}M. e) Concentration of metal salt was 1 x 10^{-2}M.

Pd^{2+} and Ag^{+} were well extracted by both selena and thiacrown ethers. However, toward methylmercury(II) cation, selenacrown ethers exhibited higher extraction abilities than structurally related thiacrown ethers, except for **3b** which has no incorporating cavity. In order to determine the structure of the complexes of **4a** and **4b** with CH_3HgCl, ^1H NMR spectra of the mixture of **4a** and/or **4b** with CH_3HgCl were obtained in $CDCl_3$ and/or dimethyl sulfoxide-d_6(DMSO-d_6). However the chemical shifts of the complexes showed no changes compared with those of metal free ligands. Therefore, it was thought that, in such polar solvents, the complexes were decomposed, or the coordination of selenium and/or sulfur atoms of the ligands to CH_3Hg^{+} was presumably very weak. Similarly, toward palladium(II) cation, selenacrown ethers exhibited slightly higher extraction abilities than thiacrown ethers. **2a** and **2b**, which contain oxygen atoms besides selenium and/or sulfur atoms, showed excellent extraction abilities toward mercury(II) cation compared with **3a**-**5b**, which contain only selenium and/or sulfur atoms as a potential donor. This result suggested that, in the case of **2a** and **2b**, mercury(II) atoms were coordinated by oxygen atoms as well as selenium and/or sulfur atoms. In order to define the compositions and the structures of the complexes of **2a** and **2b** with Hg^{2+},

Table 2. Molar Ratio and Decomposing Points(Dp.) of the Complexes **6**-**11**

Complexes	Ligand	Metal salt	Molar ratio	Dp./°C
6	**3b**	$Hg(SCN)_2$	1 : 2	>250
7	**3b**	$HgCl_2$	2 : 1	>220
8	**3b**	$Pd(CH_3CN)_2Cl_2$	1 : 1	>210
9	**4b**	$Hg(SCN)_2$	1 : 2	>160
10	**4b**	$HgCl_2$	1 : 2	>300
11	**4b**	$AgCF_3SO_3$	1 : 2	>205

Table 3. ^{1}H NMR Spectral Data (δ/ppm, in DMSO-d_6)

Compd.				
3b	1.98 (br, 2H)	2.66 (t, J=5.6 Hz, 4H)	3.89 (s, 4H)	7.27-7.14 (m, 4H)
6	2.34-2.00 (m, 2H)	2.87-2.63 (m, 4H)	4.13 (br, 4H)	7.58-7.16 (m, 4H)
7	1.98 (br, 2H)	2.59-2.50 (m, 4H)	3.90 (s, 4H)	7.26-7.14 (m, 4H)
8	2.81-2.72 (m, 2H)	3.08-2.99 (m, 4H)	4.31 (d, J=11.8 Hz, 2H) 4.22 (d, J=11.8 Hz, 2H)	7.46-7.32 (m, 4H)
4b	2.09 (f, J=8.0 Hz, 4H)	2.74 (t, J=7.4 Hz, 8H)	4.00 (s, 8H)	7.33-7.14 (m, 8H)
9	2.20 (f, J=6.9 Hz, 4H)	2.98 (t, J=6.7 Hz, 8H)	4.22 (s, 8H)	7.39-7.21 (m, 8H)
10	2.14 (f, J=7.2 Hz, 4H)	2.86 (t, J=7.0 Hz, 8H)	4.10 (s, 8H)	7.37-7.19 (m, 8H)
11	2.28 (f, J=6.3 Hz, 4H)	2.96 (t, J=6.4 Hz, 8H)	4.28 (s, 8H)	7.32-7.23 (m, 8H)

90 MHz ^{1}H NMR titration curves, which plotted the changes of the chemical shifts vs. molar ratio(ligand : metal salt), were obtained in DMSO-D_6, using **2a** or **2b** as the ligand and $Hg(SCN)_2$ as the mercury salt. The inflecting points were observed at a molar ratio of 1 : 3 (ligand : metal salt) in both **2a** and **2b**, and appeared in those methylene protons adjacent to the selenium, sulfur and oxygen atoms. Therefore, it was thought that mercury(II) cation was coordinated by oxygen atoms besides selenium and/or sulfur atoms.

The complex **7** was prepared as follows. A solution of **3b**(10 mg, 3.29×10^{-5} mol) in acetonitrile(3 ml) and a solution of mercury(II) chloride(4 mg, 1.47×10^{-5} mol) in acetonitrile(3 ml) were mixed and concentrated to ca. 3 ml. The mixture was allowed to stand at room temperature; colorless powders of **7** were formed. Other complexes were prepared by a similar method. The compositions of these complexes were confirmed by elemental analyses. The results are summarized in Table 2 and ^{1}H NMR spectral data of **3b**, **4b**, and **6-11** are summarized in Table 3. In the ^{1}H NMR, the chemical shifts of the protons of complex **6** were shifted downfield to 0.17-0.24 ppm compared with those of **3b** by the complexation. While in complex

7, the signals of the ^{1}H NMR spectrum were not shifted compared with **3b** so the complex was presumably decomposed in DMSO-d_6. Therefore, the structure of **7** was not assigned. In complex **8** all proton signals showed considerable downfield shift (0.19-0.79 ppm), especially the signals of the benzyl protons which appeared as a doublet of doublet. This result suggested that the nine-membered ring of **3b** was fixed by the coordination of two selenium atoms to palladium atoms. Although **3b** formed complexes having different compositions depending on the metal salts employed, the composition of the complexes of **4b** was not affected by the kind of metal salt. The elemental analyses and the ^{1}H NMR spectral data suggested that, in **9-11**, each of the two selenium atoms, segregated by an o-xylyl group, were coordinated with one metal atom.

The above results suggested that the selenacrown ethers form complexes with various transition metal and heavy metal cations, and in particular, that their extraction abilities toward methyl mercury(II) cation are higher than those of the corresponding thiacrown ethers. Moreover, it was revealed that the manner of the selenium atom coordination with metal cations is mainly affected by the structure of the ligand molecule and the kind of metal salt.

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7) Satisfactory elemental analyses and mass spectral data were obtained for all new compounds. **2a**, Yield, 11%, Mp, 112.0-114.0 °C. **2b**, Yield, 10%, Mp, 124.0-125.0 °C. **3a**, Yield, 67%, Mp, 83.0-85.0 °C. **3b**, Yield, 55%, Mp, 86.0-87.0 °C. **4a**, Yield, 10%, Mp, 203.0-204.0 °C. **4b**, Yield, 18%, Mp, 188.0-189.0 °C. **5a**, Yield, 5%, Mp, 142.0-144.0 °C. **5b**, Yield, 9%, Mp, 186.0-188.0 °C.

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