Journal of Inclusion Phenomena and Macrocyclic Chemistry **39:** 235–239, 2001.

Synthesis and X-Ray Crystal Structures of Novel Oxathiadibenzocrown Ethers *

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(Received: 7 March 2000; in final form: 2 September 2000)

Key words: oxathia macrocycles, synthesis, cyclization, X-ray crystal structures.

Abstract

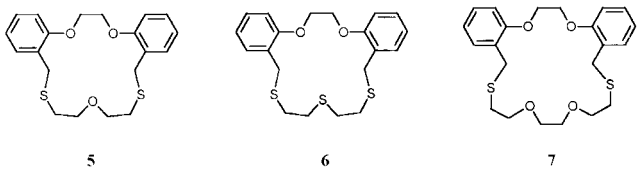
The novel 1,12-dithia macrocycles based on dibenzo substituents, **5** (S_2O_3), **6** (S_3O_2) and **7** (S_2O_4) have been synthesized by cesium carbonate promoted ring closure reactions of 2,2′-(ethylenedioxy)bis(benzyl chloride), **3**, with the appropriate dithiols under high dilution condition in reasonable yields. The structures of macrocycles **6** and **7** have been characterized by X-ray crystallography.

Introduction

The syntheses and coordination chemistry of oxathia macrocycles is an intensive area of study, and numerous related macrocycles as well as their soft and heavy metal ion complexes are known [1-4]. The dibenzo macrocycles as large as 17–19 membered rings with mixed donor sets are of particular interest due to a restricted environment. Most of the related studies, however, have focused only on 1,12-diaza type N/O and N/S mixed macrocycles or their derivatives because of the well established synthetic procedure and the variety of coordination properties [5–11].

In spite of a great number of studies on the oxathia macrocycles [1–4] and the dibenzo-1,12-diaza macrocycles [5–11], the study on the corresponding dithia-macrocycles having 1,12-dithia-3,4;9,10-dibenzo-5,8-dioxa moieties have not been reported. For over a decade, synthesis, coordination and analytical application of cyclic and acyclic O/S and N/S donor ligands have been our interest [12–15].

Herein we describe the syntheses of macrocycles **5-7** and the X-ray crystal structures of macrocycles **6** and **7**. These potentially penta- or hexadenate ligands can be expected to be ionophores for soft metal ions, such as Ag(I), Hg(II) and platinum group metal ions.



5 6 7

Figure 1. The structures of macrocycles **5–7**.

* Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. 82283 (70 pages).

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Experimental

Melting points are uncorrected. Infrared spectra were measured on Mattson Genesis Series FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500 and 125.7 MHz, respectively. Microanalyses were done by an Elemental Analysen Systeme Vario EL and mass spectra were obtained on a Kratos Profile HV-3 spectrometer at Korea Basic Science Institute Pusan Branch, respectively. Thin-layer chromatography was carried out on plates coated with Merck silica UV-254. For flash column chromatography, Merck silica gel 60 (No. 9385, 230-400 mesh) was used.

Synthesis of macrocycle **5**

Dialdehyde **1** was obtained by reaction of salicylaldehyde with dibromoethane [11]. The reduction of dialdehyde **1** with sodium borohydride followed by chlorination with thionyl chloride gave 2,2′-(ethylenedioxy)bis(benzyl chloride) **3** [11].

Macrocycle **5** was synthesized under high dilution employing the cyclization procedure of Buter and Kellogg [16]. Cesium carbonate (5.76 g, 0.0177 mol) was dissolved in DMF (1000 mL) in a 3L round-bottom flask. 2,2′-oxydiethanethiol (2.212 g, 0.0160 mol) and dichloride **3** (5.00 g, 0.0160 mol) were dissolved in DMF (30 mL) and placed in a 50 mL glass syringe. Under a nitrogen atmosphere, the contents of the syringe were added dropwise at regular speed (a rate of 0.6 mL h^{-1}) into the DMF solution by the aid of microprocessor controlled syringe pump at 45–50 °C for 50 h. The mixture was kept for a further 10 h. After cooling to room temperature the reaction mixture was filtered and evaporated. Water (100 mL) was added, and the mixture was extracted with 3 × 70 mL of dichloromethane. The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was removed to give a yellow oil.

Table 1. Crystal data and structure refinement for macrocycles **6** and **7**

	Macrocycle **6**	Macrocycle **7**
Formula	$C_{20}H_{24}O_2S_3$	$C_{22}H_{28}O_4S_2$
M	392.57	420.56
T, K	293(2)	293(2)
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a/Å	12.4884(11)	10.4516(8)
b/Å	12.9887(12)	8.1969(7)
c/Å	12.6390(11)	25.8695(19)
β/°	98.515(2)	96.738(2)
V/Å^3	2027.5(3)	2201.0(3)
Z	4	4
D_c/g cm^{-3}	1.286	1.269
μ/mm^{-1}	0.376	0.266
F(000)	832	896
Crystal size, mm	0.40 × 0.35 × 0.35	0.28 × 0.20 × 0.10
Theta range for data collection, deg	2.26–28.35	2.03–28.29
Limiting indices	$-15 \le h \le 13$	$-12 \le h \le 13$
	$-17 \le k \le 16$	$-7 \le k \le 10$
	$-16 \le 1 \le 15$	$-19 \le l \le 34$
Reflections collected	13134	13951
Independent reflections	4930 ($R_{int} = 0.0486$)	5277 ($R_{int} = 0.0609$)
Completeness to theta, %	97.4 (=28.25)	96.8 (=28.29)
Absorption correction	None	None
Data/restraints/parameters	4930/0/226	5277/0/253
GOF on F^2	1.002	1.003
Final R_1, wR_2		
Indices [$I > 2\sigma(I)$]	0.0645, 0.1770	0.0644, 0.1505
(all data)	0.1396, 0.2105	0.1548, 0.1856
Largest diff. peak and hole/e Å^{-3}	0.583, −0.423	0.533, −0.243

Flash column chromatography (SiO_2, *n*-hexane : ethyl acetate/ 9 : 1) afforded the product as a white solid in 26% yield (1.560 g). M.p. 90–92 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86–7.40 (m, 8 H, aromatic), 4.39 (s, 4 H, OCH_2CH_2O), 3.93 (s, 4 H, ArCH_2), 3.54 (t, J 6.4 Hz, 4 H, CH_2OCH_2), 2.66 (t, J 6.4 Hz, 4 H, SCH_2CH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) 159.85, 131.04, 128.52, 128.11, 121.73, 111.89, 71.52, 67.67, 31.58, 30.70; IR (KBr disk) 2921.64, 2854.14, 2352.74, 1598.70, 1492.64, 1448.28 cm^{-1}; Mass spectrum *m/z* 376 (M, 14%), 317 (9), 299 (29), 267 (9), 240 (34), 211 (9), 195 (6), 165 (27), 145 (16), 133 (81), 121 (58), 107 (92), 91 (100), 77 (79), 61 (31), 51 (27). *Anal. Calcd* for $C_{20}H_{24}O_3S_2$: C, 63.80; H, 6.42. *Found*: C, 64.01; H, 6.57.

Synthesis of macrocycle **6**

The synthetic procedure is almost the same as for macrocycle **5** except the use of 2-mercaptoethyl sulfide as a dithiol. Flash column chromatography (SiO_2, *n*-hexane : ethyl acetate/ 9 : 1) afforded the product as a white solid in 57% yield. M.p. 101–102 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.93–7.41 (m, 8 H, aromatic), 4.40 (s, 4 H, OCH_2CH_2O), 3.87 (s, 4 H, ArCH_2), 2.65 (s, overlapped, 8 H, SCH_2CH_2S); ^{13}C NMR (125 MHz, $CDCl_3$) 156.21, 130.56, 128,15, 127.31, 111.75, 99.68, 67.40, 31.87, 31.70, 29.52; IR (KBr disk) 3022.68, 2924.58, 2873.72, 1597.27, 1491.77, 1450.48, 1244.93 cm^{-1}; Mass spectrum *m/z* 392 (M, 32%); 376 (15), 352 (21), 330 (30), 317 (9), 299 (52), 273 (24), 240 (59), 211 (35), 197 (36), 181 (15), 165 (50), 149 (44), 133 (100), 121 (84), 107 (99), 91 (50), 78 (80), 57 (30), 47 (25). *Anal. Calcd* for $C_{20}H_{24}O_2S_3$: C, 61.19; H, 6.16. *Found*: C, 61.24; H, 6.22.

Synthesis of macrocycle **7**

The synthetic procedure for **7** is almost the same for macrocycle **5** except for the use of 2,2′-(ethylenedioxy)diethanethiol as a dithiol. Flash column chromatography (SiO_2, *n*-hexane : ethyl acetate/ 7 : 3) afforded the product as a white solid in 44% yield. M.p. 79–80 °C ; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83–7.30 (m, 8 H, aromatic), 4.32 (s, 4 H, ArOCH_2), 3.81 (s, 4 H, ArCH_2), 3.54 (t, J 6.6 Hz, 4 H, OCH$_2$CH$_2$S), 3.46 (s, 4 H, CH$_2$OCH_2CH_2OCH$_2$), 2.64 (t, J 6.6 Hz, 4 H, SCH_2CH$_2$O); ^{13}C NMR (125 MHz, $CDCl_3$) 156.74, 130.95, 128.54, 128.53, 121.68, 112.17, 71.59, 71.01, 67.43, 32.15, 31.03; IR (KBr disk) 3060.31, 2916.08, 2854.14, 1586.35, 1491.50, 1449.05, 1240.02 cm^{-1}; Mass spectrum *m/z* 420 (M, 18%); 352 (19), 332 (9), 316 (11), 299 (57), 271 (35), 239 (80), 227 (7), 211 (30), 197 (29), 180 (12), 165 (41), 145 (42), 133 (90), 121 (100), 107 (92), 91

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for macrocycle **6**

	x/a	y/b	z/c	$U_{(eq)}$
S(1)	5271(1)	2005(1)	4502(1)	80(1)
S(3)	1001(1)	1115(1)	6515(1)	93(1)
S(2)	2214(1)	336(1)	3534(1)	88(1)
C(1)	3030(2)	4789(2)	5409(3)	51(1)
C(2)	4734(2)	4060(2)	6134(2)	48(1)
C(3)	5139(3)	5003(3)	6550(2)	56(1)
C(4)	6172(3)	5046(3)	7125(3)	65(1)
C(5)	6800(3)	4199(3)	7299(3)	72(1)
C(6)	6408(3)	3258(3)	6890(3)	64(1)
C(7)	5379(3)	3173(2)	6309(2)	53(1)
C(9)	4156(7)	855(4)	4058(4)	175(4)
C(10)	3416(5)	1469(5)	3637(4)	146(3)
C(13)	584(3)	2427(3)	6677(3)	67(1)
C(14)	−66(2)	2850(2)	5679(2)	51(1)
C(15)	−1122(3)	2534(2)	5351(3)	59(1)
C(16)	−1690(3)	2836(3)	4386(3)	61(1)
C(17)	−1209(3)	3477(3)	3745(3)	56(1)
C(18)	−173(2)	3841(2)	4044(2)	49(1)
C(19)	404(2)	3528(2)	5014(2)	46(1)
C(20)	1995(2)	4472(2)	4754(2)	50(1)
O(2)	1440(2)	3825(2)	5395(2)	54(1)
O(1)	3735(2)	3916(2)	5559(2)	52(1)
C(8)	4959(3)	2165(2)	5842(3)	63(1)
C(12)	1521(4)	1233(4)	5244(4)	106(2)
C(11)	1921(5)	307(4)	4895(4)	106(2)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for macrocycle **7**

	x/a	y/b	z/c	$U_{(eq)}$
S(1)	987(1)	9848(1)	1538(1)	68(1)
S(2)	5955(1)	8437(1)	1542(1)	79(1)
O(1)	2155(2)	6690(3)	634(1)	75(1)
O(2)	3515(2)	13270(3)	2087(1)	83(1)
O(3)	5962(3)	12243(4)	1737(1)	106(1)
O(4)	4653(2)	6929(3)	355(1)	70(1)
C(1)	2575(3)	5815(5)	210(1)	78(1)
C(2)	1331(3)	5925(4)	930(1)	63(1)
C(3)	617(3)	4550(5)	764(2)	80(1)
C(4)	−212(4)	3876(5)	1088(2)	93(1)
C(5)	−315(4)	4544(6)	1567(2)	96(1)
C(6)	411(3)	5884(5)	1731(2)	78(1)
C(7)	1235(3)	6591(4)	1420(1)	61(1)
C(8)	2006(3)	8054(4)	1612(1)	62(1)
C(9)	1903(3)	11256(4)	1969(1)	65(1)
C(10)	2971(3)	12083(4)	1729(1)	68(1)
C(11)	4480(4)	14243(5)	1900(2)	85(1)
C(12)	5766(4)	13604(6)	2038(2)	99(1)
C(13)	7024(4)	11260(6)	1998(2)	108(2)
C(14)	7229(3)	9955(6)	1624(2)	99(1)
C(15)	6663(3)	6998(5)	1124(1)	74(1)
C(16)	6787(3)	7667(4)	596(1)	66(1)
C(17)	7932(4)	8322(5)	472(2)	86(1)
C(18)	8017(5)	9009(6)	−13(2)	106(2)
C(19)	6959(5)	9041(5)	−373(2)	97(1)
C(20)	5820(4)	8366(5)	−269(1)	81(1)
C(21)	5734(3)	7667(4)	212(1)	64(1)
C(22)	3554(3)	6809(5)	−22(1)	76(1)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized Uij tensor.

(53), 78 (58), 61 (29), 45 (17). *Anal. Calcd* for $C_{22}H_{28}O_4S_2$: C, 62.83; H, 6.71. *Found*: C, 63.12; H, 6.67.

X-Ray crystallographic determinations

All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated MoK_α (λ = 0.71073 Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The two-dimensional diffraction images were collected, each of which was measured for 30 s. The frame data were processed to give structure factors using the program SAINT [17]. The structure was solved by a direct method and refined by full matrix least squares against F^2 for all data using SHELXTL software [18]. All non-H atoms were refined with anisotropic displacement parameters.

Results and Discussion

Syntheses of macrocycles **5-7**

Dialdehyde **1** was obtained by the reaction of salicylaldehyde with dibromoethane [11]. The reduction of dialdehyde **1** with sodium borohydride followed by the chlorination with thionyl chloride yielded 2,2′-(ethylenedioxy)bis(benzyl chloride), **3**, as a key precursor [11].

We accomplished the syntheses of novel 1,12-dithia type macrocycles based on dibenzo substituents **5–7** by the reactions of aromatic dichloride **3** with corresponding aliphatic dithiols. Several attempts of final cyclization of precursor **3** with appropriate dithiols were inefficient or extremely low yielding. For example, a conventional coupling reaction in the presence of KOH in alcoholic solvent [19] failed to give the expected macrocycle **5** but resulted in ethylation of **3** by solvent to give undesired **4**. Replacement of the alcoholic solvent by DMF in the presence of cesium carbonate [16] afforded the desired macrocycle **5** with poor yield of ca. 5%. The conditions employed with cesium carbonate in DMF under high dilution by using the syringe pump were successful in giving macrocycle **5–7**. The yields from precursor **3** after purification were increased remarkably and optimized (**5**: 26%, **6**: 57% and **7**: 44%).

X-Ray crystal structures of macrocycles **6** *and* **7**

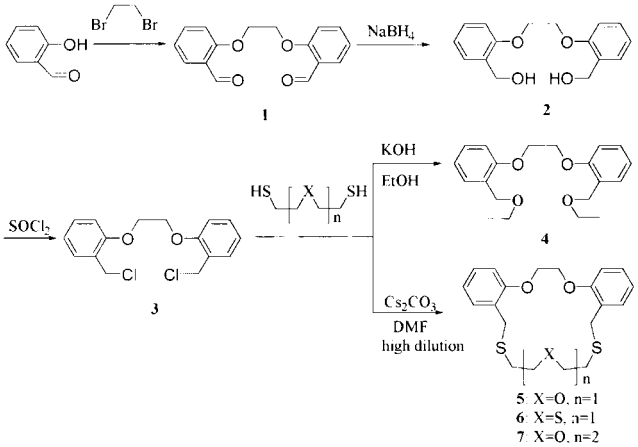
Colorless crystals of macrocycles **6** and **7** suitable for X-ray analyses were obtained by slow evaporation of a 10% ethylacetate/*n*-hexane mixture solution at room temperature over a period of two days. The crystallographic data for macrocycles **6** and **7** are listed in Table 1 while the final atomic parameters are listed in Tables 2 and 3. Structural perspec-

Table 4. Selected bond lengths (Å), bond angles (°) and torsional angles (°) for macrocycle **6**

S(1)—C(8)	1.805(3)	S(1)—C(9)	2.062(8)
S(3)—C(13)	1.802(4)	S(3)—C(12)	1.826(5)
S(2)—C(11)	1.811(5)	S(2)—C(10)	2.092(7)
C(1)—O(1)	1.431(3)	C(2)—O(1)	1.361(4)
C(19)—O(2)	1.367(3)	C(20)—O(2)	1.417(3)
C(8)—S(1)—C(9)	96.19(19)	C(13)—S(3)—C(12)	99.6(2)
C(11)—S(2)—C(10)	101.5(2)	C(19)—O(2)—C(20)	118.9(2)
C(2)—O(1)—C(1)	117.3(2)		
C(8)—S(1)—C(9)—C(10)	93.9(4)	S(1)—C(9)—C(10)—S(2)	−167.3(2)
C(9)—C(10)—S(2)—C(11)	79.1(4)	C(10)—S(2)—C(11)—C(12)	69.9(5)
S(2)—C(11)—C(12)—S(3)	169.3(3)	C(11)—C(12)—S(3)—C(13)	179.8(4)
O(1)—C(1)—C(20)—O(2)	70.6(3)		

Table 5. Selected bond lengths (Å), bond angles (°) and torsional angles (°) for macrocycle **7**

S(1)—C(9)	1.800(3)	S(1)—C(8)	1.812(3)
S(2)—C(14)	1.817(4)	S(2)—C(15)	1.815(4)
O(1)—C(2)	1.369(4)	O(1)—C(1)	1.423(4)
O(2)—C(11)	1.414(4)	O(2)—C(10)	1.415(4)
O(4)—C(21)	1.370(4)	O(4)—C(22)	1.420(4)
C(12)—O(3)	1.389(5)	C(13)—O(3)	1.471(5)
C(9)—S(1)—C(8)	101.05(15)	C(14)—S(2)—C(15)	99.79(18)
C(2)—O(1)—C(1)	118.1(3)	C(11)—O(2)—C(10)	114.4(2)
C(12)—O(3)—C(13)	109.6(4)	C(21)—O(4)—C(22)	118.2(3)
C(8)—C(1)—C(9)—C(10)	82.1(3)	S(1)—C(9)—C(10)—O(2)	165.5(2)
C(9)—C(10)—O(2)—C(11)	−175.6(3)	C(10)—O(2)—C(11)—C(12)	92.8(4)
O(2)—C(11)—C(12)—O(3)	74.0(4)	C(11)—C(12)—O(3)—C(13)	158.9(3)
C(12)—O(3)—C(13)—C(14)	−174.5(3)	O(3)—C(13)—C(14)—S(2)	−71.0(4)
O(4)—C(22)—C(1)—O(1)	66.2(4)		



Scheme 1. Syntheses of macrocycles **5–7**.

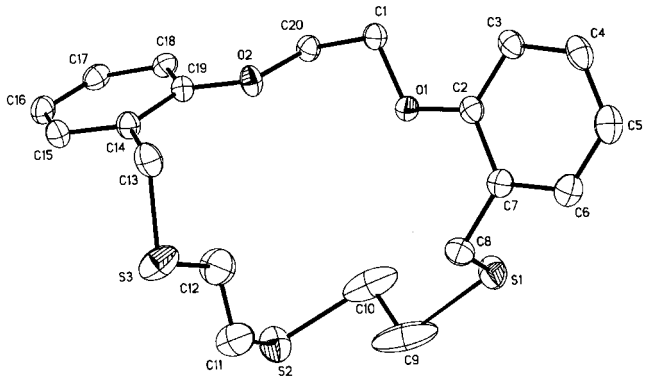


Figure 2. ORTEP plot of macrocycle **6**.

tive views of macrocycles **6** and **7** are shown in Figures 2 and 3, respectively. Selected bond lengths, bond angles and torsional angles for macrocycles **6** and **7** are compiled in Tables 4 and 5, respectively.

According to Figure 2, two aromatic planes of macrocycle **6** are highly twisted forming a dihedral angle of 63.17(10)°. In thia-crown ethers there is often a pronounced tendency to place the sulfur atoms *exodentate* to the macrocyclic cavity [20]. In the 17-membered ring of macrocycle **6** the three sulfur atoms tend to be as far apart as possible causing a sequence of *gauche-anti-gauche-gauche-anti-anti*

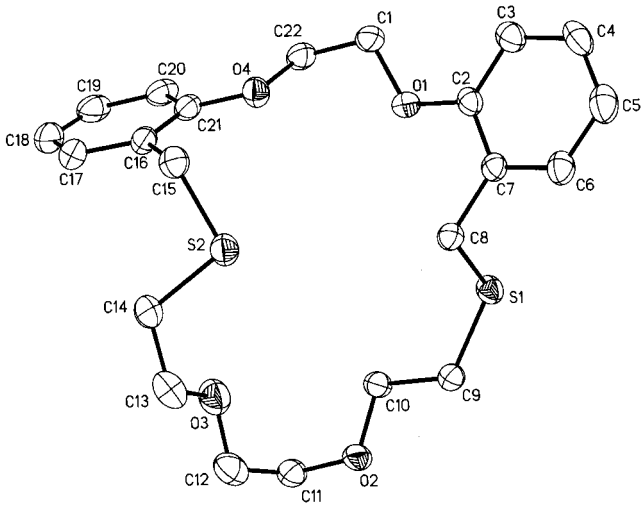


Figure 3. ORTEP plot of macrocycle **7**.

(beginning from a C(8)—S(1) bond) torsional angles. All of sulfides of the —SCH_2CH_2S— units are indeed arranged *anti* and, as a consequence, *exodentate*. Whereas two phenolic oxygen atoms show *endo*-fashion orientations and the torsional angle of O(1)—C(1)—C(20)—O(2) is 70.6(3)°.

From extensive work on the substituted cyclic and acyclic hydrocarbons, it is known that 1,4-interactions between heteroatoms (E = O, N or S) in the E—C—C—E bond depend on whether E is a first- or second-row element [21, 22]. For example, N and O heteroatoms stabilize the *gauche* conformation because of the dispersion forces between the hetero E atoms. In contrast, for E=S, the larger size of the atoms causes greater repulsion between electrons, which disfavors *gauche* conformations. Therefore, it is experimentally suggested that the tendency of 1,4-interactions to decrease is in the order C—S $\gg$ C—C > C—O [20]. The present rules readily apply to the structure of macrocycle **6** shown in Figure 2.

The conformation of the larger macrocycle **7** in Figure 3, however, differs from that of **6** considerably. Unlike the macrocycle **6**, the S(1) and O(2) atoms in macrocycle **7** are directed out of the cavity whereas S(2) and O(3) are directed inside of the cavity and give the molecule an elliptical shape. The dihedral angles between two aromatic planes (52.70°) and torsional angle of two phenolic O atoms (O(1)—C(1)—C(22)—O(4) 66.2(4)°) are smaller than those of macrocycle **6**.

Exodentate conformations disfavor chelation by macrocyclic polyethers. The conformations may have important consequences in chelation of metal ions. To access an encirculating chelate complex, the macrocycles need to undergo a significant conformational change from its *exo*- to higher energy *endo*-forms. Especially for macrocycle **6**, a non-encirculating complex, such as an *exodentate* or sandwich type complex with a soft metal ion, e.g., Ag(I), are expected. The investigations on the metal ion binding, such as solvent extraction and crystal structures of complexes with soft and heavy metal ions are in progress in this laboratory.

Acknowledgements

The support of the LG Yonam Foundation for the visiting research abroad is gratefully acknowledged. This work was also supported by Korea Research foundation (99-005-D00004). S. S. L. thanks Professor L. F. Lindoy in Sydney University for an intensive and fruitful exchange of ideas. We acknowledge helpful discussion from Dr. Ki-Min Park and Mr. Il Yoon in Gyeongsang National University for X-ray data.

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