THE SYNTHESIS AND CHARACTERISTICS OF MACROCYCLIC COMPOUNDS CONTAINING 5-MERCAPTO-3*H*-1,3,4-THIADIAZOLIN-2-ONE SUBUNITS

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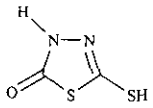
Abstract- The synthesis of six new macrocyclic compounds (**5**) containing two 5-mercapto-3*H*-1,3,4-thiadiazolin-2-one (**1**) subunits linked to the 3 and 5 positions of the heterocyclic units is described. The formation of a complex of **5d** with Ag^+ is also reported.

INTRODUCTION

Polydentate macrocyclic compounds containing heterocyclic rings as subunits possess a variety of interesting properties.[1,2] Most heterocyclic units contain oxygen or nitrogen, which provide the coordination sites allowing the heterocycles to form complexes with metals and act as effective hosts for different kinds of molecules.[1,2] Even though soft sulfur can form complexes with transition metal cations, the studies of synthesis and chemical properties of macrocycles containing sulfur heterocycles compare unfavorably with macrocyclic compounds containing oxygen or nitrogen.[1,2] It reasons from that SCH_2CH_2S linkage favors *anti* arrangements, which leave the sulfur atoms in a poor position for cooperatively binding to an ion. However, trithia-9-crown-3 clearly imparted the unique conformational properties to show high stability and novel structures of its complexes with transition metals.[3] In addition, crown thioethers can induce unusual electronic and redox behavior (stabilization of lower oxidation states).[3d,3g] The interest of these ligand systems has thus been increased.[4] Moreover, a recent report shows that the formation of the *anti*- and *syn*-SCH_2CH_2S linkage is mobile over a NMR time scale at room temperature, and the energy difference between the two forms was calculated to be *ca.* 0.4 kcal mol^{-1}.[5] These results suggested that sulfur containing building blocks might afford particular roles toward preparation of specific receptor molecules. Attention has been drawn to the sulfur donor subunit, 1,3,4-thiadiazole[6-11] for the incorporation of heterocyclic compounds into macrocyclic compounds.

We recently reported the synthesis, tautomeric behavior, and selective alkylation of 5-mercapto-3*H*-1,3,4-

thiadiazolin-2-one (**1**),[12] a compound of biological and analytical interest. Of the four possible tautomers, **1** is believed to exist as a stable thiol-lactam form on the basis of spectroscopic results and *ab initio* calculations.



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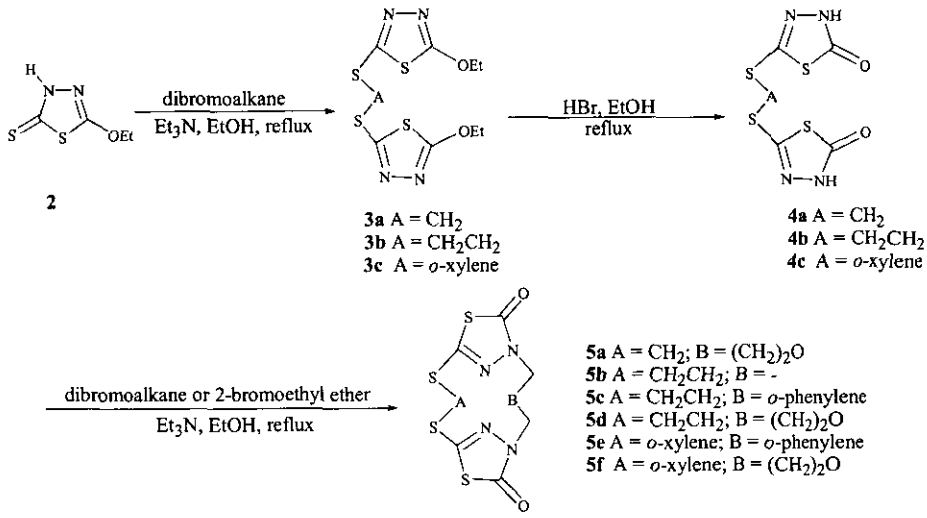
S-Bridged multifunctional macrocycles containing 1,3,4-thiadiazolone (**1**) can be synthesized, in which the sulfur atoms are directly connected to the heterocyclic ring. Guest molecules can form hydrogen bonds with its lactam group. Molecular recognition most commonly occurs through hydrogen bonding. In light of the general interest in the construction of synthetic macrocycles containing heterocyclic subunits, as well as the limited examples of the inclusion of 1,3,4-thiadiazole in a macrocyclic framework, we describe the synthesis and characterization of macrocycles containing **1** herein.

RESULTS AND DISCUSSION

The preparation of macrocycles containing heterocycle (**1**) was accomplished by the method outlined in Scheme 1 with three steps. From Scheme 1, it is readily apparent that these macrocycles were designed to form 12-, 14-, 15-, 16-, and 17-membered macrocycles to produce central holes of different sizes and shapes. The macrocycles were derived from 5-ethoxy-1,3,4-thidiazoline-2-thione (**2**). **2** is regioselectively *S*-alkylated in basic conditions.[12] The reaction of **2** with the appropriate α,ω-dibromoalkanes in the presence of triethylamine in ethanol gave the *S*-alkylated dimers (**3**). The well-defined ^{1}H and ^{13}C NMR spectra reveal the structure of **3**. In the case of **3b**, signals corresponding to the SCH_2 group appeared at 3.6 and 33.6 ppm in the ^{1}H and ^{13}C NMR spectra, respectively, while the thiadiazole carbon atoms C(2) and C(5) resonated at 176.0 and 157.6 ppm, respectively. All of these values are within their normal characteristic ranges. The chemical shifts of SCH_2 are almost identical with those of ethylene in 1,2-bis[(5-thiomethyl-1,3,4-thiadiazol-2-yl)thio]ethane (3.8 and 33.2 ppm).[9] In the ^{13}C NMR spectra, the thione of **2** (184.2 ppm) typically changed to the thio of **3** (157.6 ppm).[9] The selective dealkylation of the ethoxy group in *S*-alkyl-5-ethoxy-1,3,4-thiadiazole with HBr was previously reviewed.[12] The ethoxy group of **3** was cleanly dealkylated with HBr to give compound (**4**). The formation of **4** was confirmed by ^{1}H and ^{13}C NMR and IR spectra. The ethoxy group was replaced by a lactam NH (13.0-13.2 ppm) in the ^{1}H NMR and the chemical shifts of the ring carbon atoms C(2) and C(5) were shifted upwards compared to **3**. A similar pattern was observed between 2-ethoxy-5-methylthio-1,3,4-thiadiazole and 5-methylthio-3*H*-1,3,4-thiadiazolin-2-one.[12] In addition, IR spectrum shows a strong carbonyl band at 1650-1660 cm^{-1}. This suggests that **4** exists in a lactam form like 5-methylthio-3*H*-1,3,4-thiadiazolin-2-one.[12] Like 5-methylthio-3*H*-1,3,4-thiadiazolin-2-one,[12] the NH of **4** is acidic enough to be alkylated in triethylamine

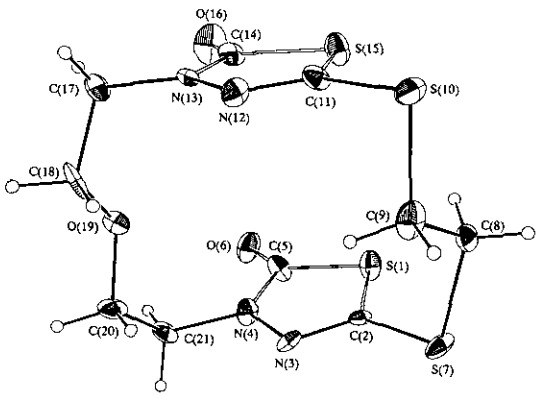
Scheme 1



with alkyl bromide. Thus, the finl step is ring formation, an [2+2] alkylation, between 4 and the corresponding α,ω-dibromoalkane or 2-bromoethyl ether. The structures of the macrocycles were firmly established by ^{1}H and ^{13}C NMR, IR spectroscopy, and high-resolution MS and elemental analysis. The successful macrocyclization of **4b** to **5d** was supported by the evidence of *N*-alkylation, which was provided with the appearance of an NCH_2 group instead of NH at 3.7 and 47.3 ppm in the ^{1}H and ^{13}C NMR spectra, respectively, and the strong carbonyl band at 1680 cm^{-1}. It is worth noting that with the cyclization, the bridged methylene is shielded relative to the methylene in the acycle counterpart, as shown by proton and carbon downfield shifts.[8] This is probably due to the anisotropic effect of the juxtaposed heterocyclic moieties.[8] Macrocycles (**5c**, **5e** and **5f**) showed this trend of chemical shifts. On the other hand, the bridged methylenes of **5a**, **5b** and **5d** show deshielding relative to the methylene in the *counterpart acylcle* (**4**). However, macrocycle (**5d**) was clearly characterized by a single-crystal X-Ray diffraction study. As Figure 1 the X-Ray crystal structure of **5d** is a 15-membered macrocycle, which is composed of the C-N-N atoms of 1,3,4-thiadiazolone rings, *syn*-ethyl ether, and an *S-anti* conformation within the ethylene. Two of the 1,3,4-thiadiazolone rings are planar and are roughly parallel to each other. There is an angle of 8.3° between the two rings. In addition, the molecular ion peak (*m/z*, 364) and microanalytical data clearly support the molecular formula $C_{10}H_{12}N_4S_4O_3$. The macrocycles (**5**) were derived from **2** with overall yields of 3-14 % after recrystallization from the appropriate solvent.

Furthermore, we wish to report the results of preliminary complexation studies of macrocycle host (**5d**) since macrocycles (**5**) can potentially coordinate transition metal cations. Most of the macrocycles were precluded from the study of complex formation because of solubility problems. Some macrocyclic compounds containing 1,3,4-thiadiazoles were reported to be efficient complexing agents for silver ion.[6a]

Figure 1. The molecular structure of the macrocycle (**5d**), showing the atomic numbering used for the crystallographic analysis.



The complexation reaction of **5d** with a silver salt was carried out. The macrocycle was dissolved in dry THF at room temperature and then treated with a THF solution of $AgClO_4$. After 1 hour of stirring at room temperature, a white solid separated from the solution. We attempted to obtain single-crystals of this complex from a variety of solvents, but in all cases we obtained either powders or small quantities of crystals unsuitable for single-crystal X-Ray diffraction study. Although we don't yet know the actual structure of the resulting complex, its stoichiometry (1:1, host:metal) is obvious on the basis of microanalytical data. It is hard to speculate the structure without clear evidence because co-ordination of Ag(I) is very irregular. The two, four, five and six co-ordination are known.[3a,3e] The IR spectrum absorption bands are characteristic of noncoordinated counter anions at 1092 cm^{-1} (lit.,[5] 1081-1098 cm^{-1}). Unfortunately, it was impossible to determine whether the NMR spectrum of the complex differs from that of macrocycle (**5d**) because of its very low solubility in appropriate deuterated organic solvents. Surprisingly, however, the potential coordinate sites of **5d** [N(3), S(7), S(10), N(12), and O(19)] are within 0.017 Å of lying in the same plane. This plane is almost perpendicular (85.9°) to the heterocyclic ring formed by C(11), N(12), N(13), C(14) and S(15). The size and shape of the central hole, as well as the rigidity and solubility of the molecule, are controlled by the nature of the spacers linked to the 3 and 5- positions of the 1,3,4-thiadiazolone units. The larger members of this series with more binding sites are required for the most efficient binding with various guest molecules and transition metals.

EXPERIMENTAL

All melting points were determined on an electrically heated Thomas-Hoover capillary melting point apparatus and were uncorrected. The IR spectra were recorded on a Jasco Report-100 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker ARX-400 spectrometer at 400 MHz and 100 MHz respectively with tetramethylsilane as internal reference. Electron impact MS spectra were performed with a JEOL JMS-SX 102A spectrometer (70 eV) at the Korea Basic Science Institute, Taejon,

Korea. Elemental analyses were run on an Elementar Analysensysteme GmbH Vario EL at the Korea Basic Science Institute, Seoul, Korea. The progress of reaction and purity of products were traced with TLC. 5-Ethoxy-1,3,4-thiadiazoline-2-thione (**2**) was prepared as previously reported.[12]

General procedure for the synthesis of α,ω-bis[(5-ethoxy-1,3,4-thiadiazoline-2-yl)thio]- alkane (3). The mixture of compound (**2**), (1 g, 6.2 mmol), α,ω-dibromoalkane (3.1 mmol) and triethylamine (3.3 mL, 24.8 mmol) in ethanol (20 mL) was heated under reflux until the compound (**2**) was disappeared on TLC. The solvent was evaporated under reduced pressure to leave a solid residue, which was washed with water. The crude product was recrystalized from the appropriate solvent.

Bis[(5-ethoxy-1,3,4-thiadiazol-2-yl)thio]methane (3a). Yield; 86%, mp 91-93 ℃ (from EtOH) R_f; 0.47 (ethyl acetate: *n*-hexane = 3 : 7), IR (KBr); 2950(CH), 1550 (C=N), 1260, 1060. ^{1}H NMR (400 MHz, $CDCl_3$); 5.0 (2H, s, CH_2), 4.6 (4H, q, 7.1 Hz, 2 x CH_2), 1.5 (6H, t, 7.1 Hz, 2 x Me). ^{13} C NMR (100 MHz, $CDCl_3$); 176.4 (C=N), 156.5 (C-S), 70.3 (OCH_2), 37.5, (SCH_2), 15.1 (Me). *Anal.* Calcd for $C_9H_{12}N_4O_2S_4$: C, 32.1; H, 3.6; N, 16.7. Found: C, 31.3; H, 3.8; N, 17.2.

1,2-Bis[(5-ethoxy-1,3,4-thiadiazol-2-yl)thio]ethane (3b). Yield; 52%, mp 102-103 ℃ (from EtOH), R_f; 0.34 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3025, 2970 (CH), 1520 (C=N), 1270, 1060. ^{1}H NMR (400 MHz, $CDCl_3$); 4.7 (4H, q, 7.1 Hz, 2 x CH_2), 3.6 (4H, s, 2 x CH_2), 1.5 (6H, t, 7.1 Hz, 2 x Me). ^{13} C NMR (100 MHz, $CDCl_3$); 176.0 (C=N), 157.6 (C-S), 70.1 (OCH_2), 33.6 (SCH_2), 15.1 (Me). *Anal.* Calcd for $C_{10}H_{14}N_4O_2S_4$: C, 34.3; H, 4.0; N, 16.0. Found: C, 34.3; H, 4.2; N, 16.0.

α,α'-Bis[(5-ethoxy-1,3,4-thiadiazol-2-yl)thio]-*o*-xylene (3c). Yield; 62%, mp 73-74 ℃ (from *n*-hexane), R_f; 0.68 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3000, 2970 (CH), 1520 (C=N), 1270, 1050. ^{1}H NMR (400 MHz, $CDCl_3$); 7.4 - 7.3 (4H, m, Ph), 4.6 - 4.5 (8H, q + s, 2 x OCH_2 + 2 x SCH_2), 1.5 (6H, t, 6.3 Hz, 2 x Me). ^{13} C NMR (100 MHz, $CDCl_3$); 176.1 (C=N), 157.6 (C-S), 135.3, 131.9, 129.2 (Ph), 70.0 (OCH_2), 36.1 (SCH_2), 15.1 (Me). *Anal.* Calcd for $C_{16}H_{18}N_4O_2S_4$: C, 45.0; H, 4.3; N, 13.1. Found: C, 44.4, H, 4.3; N, 13.4.

General procedure for the synthesis of α,ω-bis[(5-oxo-1,3,4-thiadiazoline-2-yl)thio]alkane (4). To a solution of compound (**3**) (6 mmol) in ethanol (20 mL), was added HBr (47 %, 3.5 mL, 30 mmol), in one portion. The mixture was heated under reflux until the compound (**3**) was disappeared on TLC. The solvent evaporated under reduced pressure to leave a solid residue, which was washed with water. The crude product was recrystallized from the appropriate solvents.

Bis[(5-oxo-1,3,4-thiadiazol-2-yl)thio]methane (4a). Yield; 90%, mp 154-156 ℃ (from EtOH: toluene = 1:1); R_f; 0.48 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3100 (NH), 1680 (C=O), 1500 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$); 13.2 (2H, br, 2 x NH), 4.9 (2H, s, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 171.6

(C=O), 146.2 (C-S), 36.7 (SCH_2). *Anal.* Calcd for $C_5H_4N_4O_2S_4$: C, 21.4; H, 1.4; N, 20.0. Found: C, 21.6; H, 1.4; N, 19.7.

1,2-Bis[(5-oxo-1,3,4-thiadiazol-2-yl)thio]ethane (4b). Yield; 77%, mp 204-207 ℃ (from DMF: H_2O = 3:1), R_f; 0.19 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3200 (NH), 3050 (CH), 1680 (C=O),1510 (C=N), 1060. ^{1}H NMR (400 MHz, $CDCl_3$); 13.0 (2H, br, 2 x NH), 3.4 (4H, s, 2 x CH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 171.3 (C=O), 147.4 (C-S), 32.0 (SCH_2). *Anal.* Calcd for $C_6H_6N_4O_2S_4$: C, 24.5; H, 2.1; N, 19.0. Found: C, 23.8; H, 2.5; N, 18.8.

α,α'-Bis[(5-oxo-1,3,4-thiadiazol-2-yl)thio]-*o*-xylene (4c). Yield; 85%, mp 160-162 ℃ (from EtOH: toluene = 1:1), R_f; 0.35 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3200 (NH), 2900 (CH), 1680 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$); 13.1 (2H, br, 2 x NH), 7.5-7.4 (4H, m, Ph), 4.5 (4H, s, 2 x CH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 171.5 (C=O), 147.5 (C-S), 134.7, 130.8, 128.3 (Ph), 34.1 (SCH_2). *Anal.* Calcd for $C_{12}H_{10}N_4O_2S_4$: C, 38.9; H, 2.7; N, 15.1. Found: C, 38.3; H, 2.7; N, 15.4.

General procedure for the synthesis of macrocycles (5).

Compound (**4**) (1.7 mmol) was dissolved in ethanol (20 mL) with triethylamine (1.21 mL, 8.5 mmol). To the solution was added an appropriate either 2-bromoethyl ether or α,ω-dibromoalkane (2.6 mmol), with stirring. The resulting mixture was heated under reflux until the compound (**4**) was disappeared on TLC. The solvent was evaporated under the reduced pressure to leave a solid residue, which was washed with water. The crude product was recrystallized from the appropriate solvents.

Macrocycle (5a). Yield; 32%, mp 216-218 ℃ (from EtOH: toluene = 1:1); R_f; 0.44 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 2900 (CH), 1680 (C=O), 1300, 1120. ^{1}H NMR (400 MHz, $CDCl_3$); 4.9 (2H, s, SCH_2), 4.0 (4H, t, 4.8 Hz, 2 x OCH_2), 3.7 (4H, t, 4.8 Hz, 2 x NCH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 169.4 (C=O), 142.8 (C-S), 66.3 (OCH_2), 46.7 (NCH_2), 38.6 (SCH_2). HRMS Calcd for $C_9H_{10}N_4O_3S_4$, 349.9636; found, 349.9636.

Macrocycle (5b). Yield; 37%, mp 210 ℃ (from DMF), R_f; 0.73 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3000, 2900 (CH), 1680 (C=O), 1060. ^{1}H NMR (400 MHz, $CDCl_3$); 4.2 (4H, s, 2 x NCH_2), 3.4 (4H, s, 2 x SCH_2). ^{13}C NMR (400 MHz, $CDCl_3$); 169.0 (C=O), 144.5 (C-S), 46.1 (NCH_2), 33.4 (SCH_2). EIMS (*m/z*) 320 (M^+, 34.7%). *Anal.* Calcd for $C_8H_8N_4O_2S_4$: C, 30.0; H, 2.5; N, 17.5. Found: C, 30.0; H, 2.4; N, 17.5.

Macrocycle (5c). Yield; 32%, mp 260-262 ℃ (from DMF), R_f; 0.61 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3000, 2950 (CH), 1700, 1680 (C=O), 1550 (C=N), 1060. ^{1}H NMR (400 MHz, $CDCl_3$); 7.3-7.5 (4H, m, Ph), 5.2 (4H, s, 2 x NCH_2), 3.3 (4H, s, 2 x SCH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 170.7 (C=O), 146.7 (C-S), 135.1, 131.2, 129.7 (Ph), 47.2 (NCH_2), 31.2 (SCH_2). HRMS Calcd for $C_{14}H_{12}N_4O_2S_4$, 395.9843; found, 395.9846.

Macrocycle (5d). Yield; 34%, mp 156-158 ℃ (from EtOH); R_f; 0.62 (ethyl acetate: *n*-hexane = 1 : 1). IR (KBr); 2900 (CH), 1680 (C=O), 1280, 1120.^{1}H NMR (400 MHz, $CDCl_3$); 4.0 (4H, t, 4.6 Hz, 2 x OCH_2), 3.7 (4H, t, 4.6 Hz, 2 x NCH_2), 3.5 (4H, s, 2 x SCH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 168.8 (C=O), 145.1 (C-S), 67.2 (OCH_2), 47.1(NCH_2), 33.6 (SCH_2). EIMS (*m/z*) 364 (M^+, 100%). *Anal.* Calcd for $C_{10}H_{12}N_4O_3S_4$: C, 33.0; H, 3.3; N, 15.4; S, 35.2. Found: C, 33.2; H, 3.3; N, 15.5; S, 34.5.

Macrocycle (5e). Yield; 48%, mp 248-250 ℃ (from DMF), R_f; 0.66 (ethyl acetate: *n*-hexane = 3 : 7). IR (KBr); 3100, 2950 (CH), 1700 (C=O), 1500 (C=N), 1080 (Ph). ^{1}H NMR (400 MHz, $CDCl_3$); 7.4 - 7.2 (8H, m, 2 x Ph), 5.4 (4H, s, 2 x NCH_2), 4.4 (4H, s, 2 x SCH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 168.7 (C=O), 146.5 (C-S), 134.4, 134.1, 130.8, 129.4, 128.6, 128.3 (Ph), 47.3 (NCH_2), 32.4 (SCH_2). HRMS Calcd for $C_{20}H_{16}N_4O_2S_4$, 472.0156; found, 472.0150.

Macrocycle (5f). Yield; 51%, mp 198-200 ℃ (from acetone:), R_f; 0.26 (ethyl acetate: *n*-hexane = 1:1). IR (KBr); 2900 (CH), 1700 (C=O), 1510 (C=N), 1300, 1080.^{1}H NMR (400 MHz, $CDCl_3$); 7.5 - 7.3 (4H, m, Ph), 4.6 (4H, s, 2 x SCH_2), 4.1 (4H, t, 4.8 Hz, 2 x OCH_2), 3.8 (4H, t, 4.8 hz, 2 x NCH_2). ^{13}C NMR (100 MHz, $CDCl_3$); 169.7 (C=O), 147.2 (C=N), 135.4, 132.4, 130.0 (Ph), 68.2 (OCH_2), 48.1 (NCH_2), 34.5 (SCH_2). HRMS Calcd for $C_{16}H_{16}N_4O_3S_4$, 440.0105; found, 440.0102.

X-Ray crystal structure of macrocycle (5d)

Direct methods (SHELX86)[13] (all non-H atoms) followed by full-matrix least-squares refinement (SHELX97)[14] on F^2 with all non-H atoms anisotropic. Hydrogen atoms were located from ΔF synthesis and positionally refined with a Flake parameter, -0.3 (3). Final R_1 [$F \geq 4\sigma(F)$] and wR_2 [all data] were *0.0572 and 0.1289 for 190 refined parameters*, S[F^2] 1.152. And $(\Delta/\sigma)_{max}$ was 0.000. Maximum and minimum features in ΔF synthesis are 0.762 and -0.693 e Å^{-3}, respectively.

Complexation of macrocycle (5d)

To a solution of macrocycle (**5d**) (70 mg, 0.19 mmol) in THF (6 mL) was added $AgClO_4$ (40 mg, 0.19 mmol) in THF (3 mL). The reaction mixture was stirred for 1 h at rt. The solid formed was filtered and crystallized from dioxane to give white adduct [Ag(**5d**)]ClO_4 (97 mg, 80 %), mp 243-245 °C. IR (KBr); 2930(CH), 1690, 1660 (C=O), 1307, 1092 (ClO_4); *Anal.* Calcd for $C_{10}H_{12}N_4O_7AgClS_4$: C, 21.0; H, 2.1; N, 9.8; S. 22.5. Found: C, 21.8; H, 1.9; N, 9.7; S. 23.0.

ACKNOWLEDGMENTS

This work was supported by the Korea Science and Engineering Foundation (971-0302-023-02) and the Ministry of Education, Korea (BSRI-98-3433).

REFERENCES

1. B. Dietrich, P. Viout, and J-M Lehn, 'Macrocyclic Chemistry: Aspect of Organic and Inorganic Supramolecular Chemistry,' VCH, Weinheim, 1993.
2. F. Vögle, 'Supramolecular Chemistry,' Wiley, Chichester, 1991.
3. (a) H. W. Roesky, H. Hofmann, P. G. Jones, W. Pinkert, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1215. (b) A. J. Blake, A. J. Holder, T. I. Hyde, Y. V. Roberts, A. J. Lavery, and M. Schröder, *J. Organomet. Chem.*, 1987, **323**, 261. (c) A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J, Lavery, M. O. Odulate, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 118. (d) J. Clarkson, R. Yagbasan, P. J. Blower, S. C. Rawle, and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1987, 950. (e) P. J. Blower, J. A. Clarkson, S. C. Rawle, J. R. Hartman, R. E. Wolf, Jr., R. Yagbasan, S. G. Bott, and S. R. Cooper, *Inorg. Chem.*, 1989, **28**, 4040. (f) A. L. Blake, J. A. Greig. A. J. Holder, T. I. Hyde, A. Taylor, and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 197. (g) S. R. Cooper, S. C. Rawle, R. Yagbasan, and D. J. Watkin, *J. Am. Chem. Soc.*, 1991, **113**, 1600.
4. (a) B. De Groot and S. J. Loeb, *Inorg. Chem.*, 1991, **30**, 3103. (b) S. R. Cooper, S. C. Rawle, R. Yagbasan, and D. J. Watkin, *J. Am. Chem. Soc.*, 1991, **113**, 1600. (c) S. R. Cooper, *Acc. Chem. Res.*, 1988, **21**, 141. (d) R. E. Wolf, Jr, J. R. Hartman, J. M. E. Storey, B. M. Foxman, and S. R. Cooper, *J. Am. Chem. Soc.*, 1987, **109**, 4328. (e) J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1202. (f) J. R. Hartman, E. J. Hintsa, and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1208.
5. B. Blackwell, S. M. Ngola, H. Peterson, S. Rosenfeld, and C. W. Tingle, *J. Org. Chem.*, 1998, **63**, 181.
6. (a) P. Molia, A. Tarrago, C. Gaspar, and A. Espinosa, *J. Org. Chem.*, 1994, **59**, 3665. (b) P. Molia, A. Espnsa, A. Tarraga, F. H. Cano, and Ma. C. Foces-Foces, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1159.
7. F. Bottino and S. Pappalardo, *Tetrahedron*, 1982, **38**, 665.
8. S. Papparlardo, F. Bottino, and C. Tringali, *Heterocycles*, 1984, **22**, 1339.
9. S. Papparlardo, F. Bottino, and C. Tringali, *J. Org. Chem.*, 1987, **52**, 405.
10. S. Papparlardo, F. Bottino, and C. Tringali, *J. Org. Chem.*, 1987, **52**, 4309.
11. F. Bottino, U. Chiacchio, F. R. Fronczek, and S. Papparlardo, *J. Org. Chem.*, 1989, **54**, 2024.
12. N. S. Cho, C. K. Park, H. S. Kim, E. S. Choi, and S. K. Kang, *Bull. Korean Chem. Soc.*, 1998, **19**, 103 (*Chem. Abstr.*, 1998, **128**, 243634).
13. G. M. Sheldrick, SHELXS-86, *Acta Crystallogr., Sect. A,* 1990, **46**, 467.
14. G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

Received, 17th June, 1999