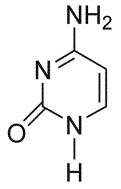
Convergent Synthesis of Macrocycles Composed of 5-Amino-2*H*-1,2,4-thiadiazolin-3-one or 5-Amino-2*H*-1,2,4-thiadiazoline-3-thione and 1,3-Benzenedimethanethiol

Nam Sook Cho,* Young Hoon Kim, and Chun Ho Lee

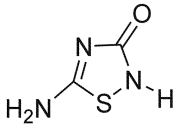
Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea
Received June 28 2004

Key Words : 5-Amino-2*H*-1,2,4-thiadiazolin-3-one, 5-Amino-2*H*-1,2,4-thiadiazoline-3-thione, Macrocycle, 1,3-Benzenedimethanethiol, Host molecule

Transition metal complexes with peripheral sites capable of hydrogen-bonding or π-stacking interactions to form groups have recently been used as hosts to bind neutral guests, such as aliphatic amines,[1] aromatic amines,[2] hydrazines,[3] DNA nucleobases,[4,5] amino acids,[6,7] and barbiturate.[8-18] This form of host is referred to as a metalloreceptor. The construction of hosts with metal ions in the scaffold has allowed the binding of many structurally sophisticated guests. Consequently, the design and study of various metal-containing macrocycles is one of the most active and interesting areas in modern supramolecular chemistry.[1-30] Coordinate covalent bond formation offers new prospects for selective molecular recognition, anion transport, and catalytic activation of electron-rich organic and inorganic substrates. It has long been recognized that multiple complementary interactions between the host and guest are of vital importance in stabilizing host-guest complexes (*e.g.*, the chelation effect). Investigations of host-guest interactions and inclusion phenomena as well as biomimetic studies have become interesting targets. To obtain stable, reversible adducts, there is still a clear need for neutral molecular receptors that are simple and versatile, while they are also selective. This recalls the first stages of enzymatic processes, which involve the formation of a metallo-enzyme-substrate complex. We sought to prepare macrocycles composed of 5-membered cytosine analogues and 1,3-benzenedimethanethiol.



1

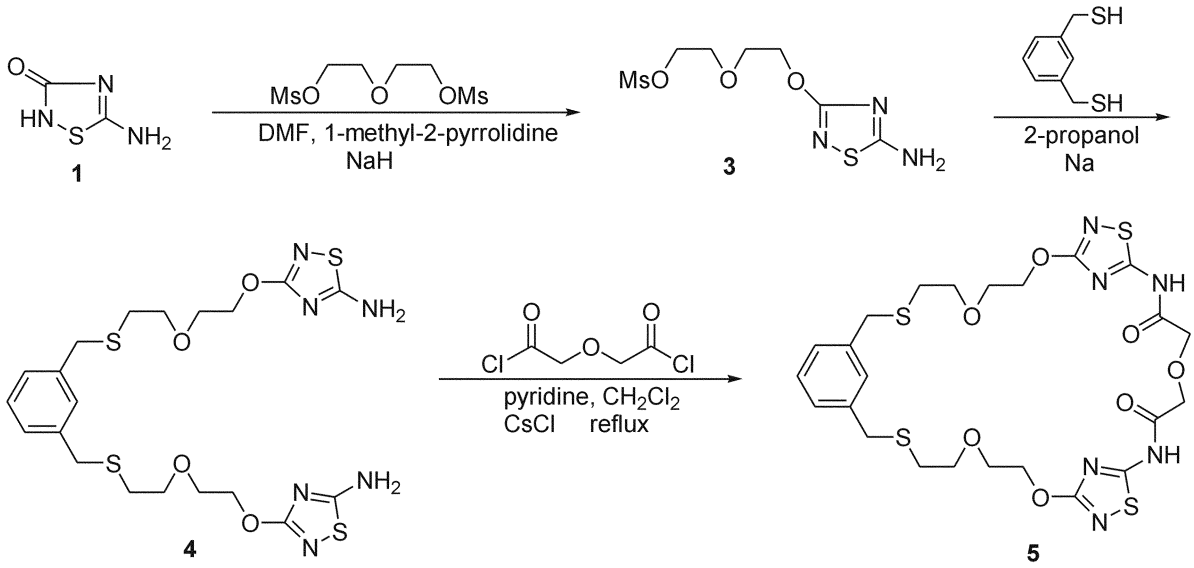


2

Compound **1**[31,32] is an analogue of cytosine in which the C=C double bond moiety is replaced with a sulfur atom. In compound **2**,[33] the carbonyl group of compound **1** is replaced with a thione. These compounds can provide sites for hydrogen bond formation and 1,3-benzenedimethanethiol can supply the chelation sites to construct complexes with metal ions.[1-4,21,23,27]

Results and Discussion

Compound (**1**) is regiospecifically *O*-alkylated under NaH basic conditions to give 5-amino-3-alkoxy-1,2,4-thiadiazole. Using this reaction, a macrocycle **5**, containing two 5-amino-1,2,4-thiadiazole subunits linked to the 3- and 5-positions of the heterocyclic unit was prepared from **1**, as shown in Scheme 1. The anion of compound **1** was prepared in the presence of NaH in 1-methyl-2-pyrrolidinone and DMF; it was alkylated with ethylene glycol dimethanesulfonate to afford the *O*-alkylated compound (**3**). The formation of **3** was confirmed by its ^{1}H and ^{13}C NMR spectra. In **3**, the NH of compound **1** was replaced by an $OCH_2CH_2OCH_2CH_2OMs$ signal at 4.44, 4.38, 3.80, and 3.09 ppm in the ^{1}H NMR spectrum and 69.4, 69.2, 68.8, 67.8, and 37.6 ppm in the ^{13}C NMR spectrum. In the ^{13}C NMR, the lactam part of **1** (175.4 ppm) changed to a lactim group in **3** (183.0 ppm). To provide possible chelation sites that allow the formation of complexes with metal ions, the 1,3-benzenedimethanethiol anion was produced in a 2-propanol solution of sodium 2-propanoxide and alkylated with **3** to give an *S*-alkylated compound (**4**). The formation of **4** was also confirmed by its ^{1}H and ^{13}C NMR spectra. In **4**, the SH of 1,3-benzenedimethanethiol was replaced by a $SCH_2CH_2OCH_2CH_2O$-1,2,4-thiadiazole signal at 6.64, 4.42, 3.74, 3.62, and 2.60 ppm in the ^{1}H spectrum and 183.0, 167.0, 71.2, 69.1, 68.2, and 30.9 ppm in the ^{13}C NMR spectrum. The disappearance of the mesyl group of compound **3** at 3.09 and 37.6 ppm in the ^{1}H and ^{13}C NMR spectra, respectively and the appearance of a 1,3-xylenyl group at 7.27-7.17 and 3.74 ppm in the ^{1}H spectrum and 138.6, 129.6, 128.6, 127.6, and 36.7 ppm in the ^{13}C NMR spectrum also supported the formation of **4**. The target macrocycle was obtained *via* cyclization involving *N*,*N*-diacylation of **4** at the NH_2 of the 1,2,4-thiadiazole rings using diglycolyl chloride with a high dilution technique. The diglycolyl chloride solution was added to CH_2Cl_2 solution of **4** over a 24 hr period. The structure of the macrocycle was firmly established by ^{1}H and ^{13}C NMR, IR, and HRMS. The successful macrocyclization of **4** to **5** was supported by evidence of *N*-acylation, indicated by the $NHCOCH_2$ group that replaced NH_2 at 12.91, and 4.51 ppm in the ^{1}H spectrum and 167.2

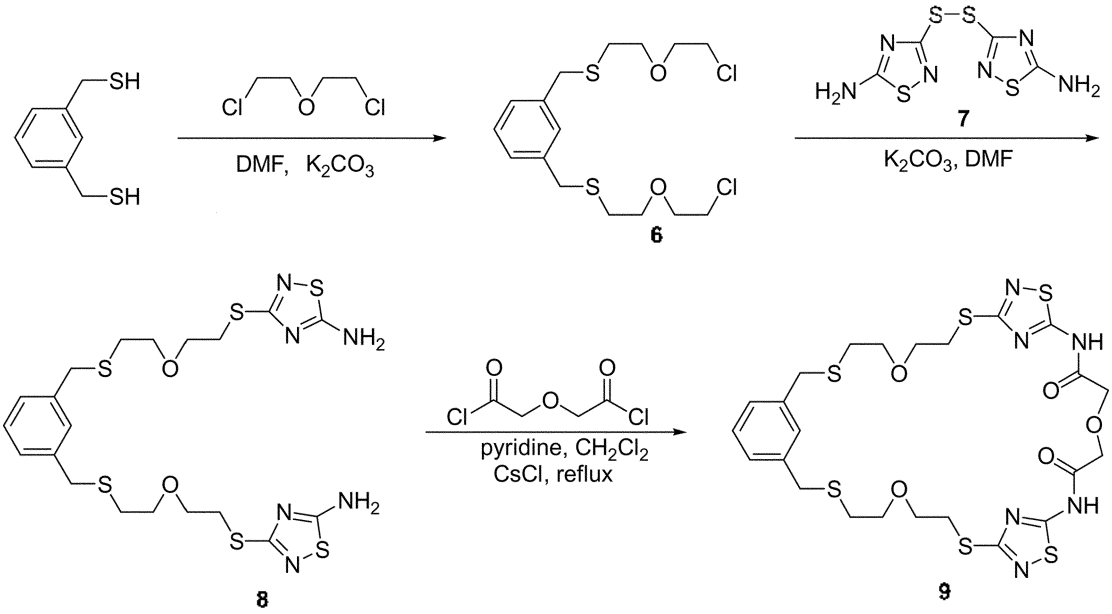


Scheme 1. Synthesis of macrocycle containing two 5-amino-2*H*-1,2,4-thiadiazolin-3-one subunits.

and 71.8 ppm in the ^{13}C NMR spectrum. The IR spectrum also shows the carbonyl group of the amide at 1701 cm^{-1}. FAB-HRMS clearly supported the structure of **5** (Cald 643.1137, Found 643.1134).

We reported the synthesis of bis(5-amino-1,2,4-thiadiazolyl)-3,3'-disulfide (**7**) and the *S*-alkylation of compound (**7**) at the 3-position under basic conditions to afford 3-alkylthio-5-amino-1,2,4-thiadiazole.[33] Using this reaction, macrocycle **8** was synthesized, and it had the same scaffold as macrocycle **5**. The only structural difference between **8** and **5** was the atom linking the 1,2,4-thiadiazole subunit, which is sulfur in **8** and oxygen in **5**. Macrocycle **8** was synthesized as shown in Scheme **2**. The synthesis sequence of **8** differs from that of **5**. The chelation sites were built first and then the 1,2,4-thiadiazole rings were introduced. Therefore, the *S*-alkylation of 1,3-benzenedimethanethiol was performed with 1,5-dichloro-3-oxapentane, which was the similar method as used to convert **3** to **4**, to prepare **6**. The formation of **6** was confirmed by its ^1H and ^{13}C NMR spectra. In **6**, the SH of 1,3-benzenedimethanethiol was replaced by a $SCH_2CH_2OCH_2CH_2Cl$ signal at 3.71, 3.63, 3.56, and 2.56 ppm, and 70.2, 69.9, 43.6, and 30.3 ppm in the ^1H and ^{13}C NMR spectra, respectively.

To introduce the 1,2,4-thiadiazole rings, the *S*-alkylation of bis(5-amino-1,2,4-thiadiazolyl)-3,3'-disulfide (**7**) was performed at the 3-position of **7** in the presence of K_2CO_3. The structure of **8** was confirmed by ^1H and ^{13}C NMR. The chlorine of **6** was replaced by a 1,2,4-thiadiazole ring signal



Scheme 2. Synthesis of macrocycle containing two 5-amino-2*H*-1,2,4-thiadiazoline-3-thione subunits.

at 8.03 ppm and 183.7 and 166.5 ppm, respectively. The S-alkylation was strongly supported by the typical chemical shift in which CH_2Cl changes to 3.24 and 30.9 ppm from 3.72 and 42.8 ppm in the ^1H and ^{13}C NMR spectra, respectively. Target macrocycle **9** was obtained by cyclization using *N,N*-diacylation following the acylation procedure used for **4**. The structure of **9** was determined using the same method as for **5**.

Experimental Section

The IR spectra were recorded on a Jasco Report-100 spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained using a JEOL JNM-AL400 spectrometer at 400 MHz and 100 MHz respectively with tetramethylsilane as the internal reference. NMR measurements were performed at the Central Research Facilities of Chungnam National University. Elemental analyses were carried out on an EA 1110 (CE Instrument). FAB-HRMS spectra were obtained on a JEOL-JMS HX-100/110A spectrometer at Korea Basic Science Institute, Taeduk, Taejon.

The synthesis of 5-amino-2*H*-1,2,4-thiadiazolin-3-one (**1**)[31,32] and bis(5-amino-1,2,4-thiadiazolyl)-3,3'-disulfide[33] followed the previous literature procedures.

5-(5-Amino-1,2,4-thiadiazol-3-yl)oxa-3-oxapentyl methanesulfonate (3). Compound (**1**) (5.0 g, 42.68 mmol) was dissolved in heated anhydrous 1-methyl-2-pyrrolidinone (150 mL) and DMF (35 mL) at 50 °C. The clear reaction solution was cooled to room temperature, and 60% NaH (2.6 g, 64.00 mmol) was added to the above solution and the reaction mixture was stirred for 60 min at room temperature. The ethylene glycol dimethanesulfonate (16.8 g, 64.00 mmol) was added to the reaction mixture and heated to 55-60 °C for 3 hr. The reaction mixture was cooled to room temperature and ice water (300 mL) was added to the reaction mixture. The aqueous solution was extracted with chloroform (300 mL × 3). The organic solution was dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent *n*-hexane : ethyl acetate = 1 : 9) to afford the product (3.5 g, 29.7%).

Liquid, R_f: 0.46 (*n*-hexane : ethyl acetate = 1 : 9). IR (KBr, cm^{-1}): 3321, 1617, 1539, 1507, 1334, 1173. ^1H NMR (400 MHz, $CDCl_3$, δ): 6.82 (2H, s, NH_2), 4.44 (2H, m, CH_2O), 4.38 (2H, m, CH_2OMs), 3.80 (4H, m, 2 x CH_2O), 3.09 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 183.0 (O-C=N), 166.8 (H_2N-C=N), 69.4 (NH_2N=COCH_2), 69.2 (MsOCH_2), 68.8 (MsOCH$_2$$CH_2$), 67.8 ($NH_2N$=COCH$_2$$CH_2$), 37.6 ($CH_3$). FAB-HRMS cald for $C_7H_{14}N_3O_5S_2$, 284.0375, found 284.0378.

1,3-Bis[5-(5-amino-1,2,4-thiadiazol-3-yl)oxa-3-oxapentylthiomethyl]benzene (4). 1,3-Benzenedimethanethiol (0.50 mL, 3.38 mmol) was dissolved in a freshly prepared 2-propanol solution (70 mL) of sodium 2-propanoxide (0.59 g, 7.13 mmol). Compound (**3**) (0.30 g, 6.81 mmol) was added to the above solution and the reaction mixture was heated at reflux over 3 hr. After cooling the reaction mixture at room temperature, solvent was removed under reduced pressure. The residue was purified by chromatography (SiO_2; eluent $CHCl_3$: MeOH = 15 : 1) to afford product (0.30 g, 16.3%).

Liquid, R_f: 0.10 ($CHCl_3$: MeOH = 15 : 1). IR (KBr, cm^{-1}): 3400, 3018, 1506, 1336, 1215, 1052, 1027. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.27-7.17 (4H, m, C_6H_4), 6.64 (4H, br, $2NH_2$), 4.43(4H, m, 2CH_2OHet), 3.74 (8H, m, 2CH_2 + 2C$H_2C_6H_4$), 3.62 (4H, t, J = 6.41 Hz, $2CH_2$), 2.60 (4H, t, J = 6.41 Hz, $2CH_2S$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 183.0 (O-C=N), 167.0 (H_2NC=N), 138.6, 129.6, 128.6, 127.6 (C_6H_4), 70.2 (CH_2OHet, 69.1 ($CH_2OCH_2CH_2S$), 68.2 ($CH_2OCH_2CH_2S$), 36.7 ($C_6H_4CH_2$), 30.9 (SCH_2). FAB-HRMS: $C_{20}H_{29}O_4N_6S_4$, (M+1) 545.1133, found: 545.1138.

11,14,20,23,38,39-Hexaaza-6,9,17,25,28-pentaoxa-3,12,22,31-tetrathiotetracyclo-[31,3,1,1,^{10,13}1,^{21,24}]-nonatriaconta-1(37),10(11),13(38),21(39),23(24),33(34),35(36)-heptaene-15,19-dione (5). Compound (**4**) (0.3 g, 0.55 mmol) was dissolved in dichloromethane (100 mL) and pyridine (90 mL, 1.10 mmol) and diglycolyl chloride (0.094 g, 0.55 mmol) was added to the above solution over 24 hr. The solution was heated at reflux for additional 20 hr. After cooling the reaction mixture at room temperature, ice water (50 mL) was added to the reaction mixture and the mixture was stirred for 30min. The organic layer was separated and dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by chromatography (SiO_2; eluent $CHCl_3$: MeOH = 30 : 1) to afford colorless solid product (0.070 g, 19.7%).

Mp: 176.5-178.0 °C, R_f: 0.49 ($CHCl_3$: MeOH = 30 : 1). IR (KBr, cm^{-1}): 3435, 3165, 3090, 2929, 1701, 1579, 1279, 1120, 1086. ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6, δ) 12.91 (2H, br, 2NH), 7.29 (1H, s, CH of C_6H_4), 7.27-7.19 (3H, m, (CH)$_3$ of C_6H_4), 4.48 (4H, m CH_2OHet), 4.41 (4H, s, ((CO)CH_2O). 3.79 (4H, s, $C_6H_4CH_2S$). 3.77 (4H, m, CH_2CH_2OHet). 3.68 (4H, t, J = 6.23 Hz, SCH_2CH_2O). 2.28 (4H, t, J = 6.23 Hz, CH_2S). ^{13}CNMR (75 MHz, $CDCl_3$ + DMSO-d_6, δ) 175.4 (O-C=N), 168.7 (C=O), 167.2 (S-C=N), 139.9, 129.4, 128.5, 127.9 (C_6H_4), 71.8 ((C=O)CH_2O) 70.2 (CH_2OHet), 69.0 (HetOCH_2CH_2OC H_2CH_2S), 68.8 (HetOCH$_2$CH$_2$OCH_2CH_2S), 36.7 ($CH_2C_6H_4$), 31.0 (SCH_2). FAB-HRMS Cald for $C_{24}H_{31}N_5O_7S_4$ 643.1137, Found 643.1134.

1,3-Bis(5-chloro-3-oxapentylthiomethyl)-benzene (6). The reaction mixture of 1,3-benzenedimethanethiol (20.0 g, 0.117 mol), 2-chloroethyl ether (87.8 g, 0.470 mol) and powder K_2CO_3 (64.8 g, 0.469 mol) were heated to 50-55 °C in DMF (150 mL) over 3 hr. The solvent was removed under reduced pressure. The reaction residue was dissolved in $CHCl_3$ (1000 mL) and H_2O (500 mL). The organic layer was separated and washed with H_2O (500 mL) and dried with $MgSO_4$ and the solvent was removed. The crude product was purified by chromatography (SiO_2; eluent *n*-hexane : ethyl acetate = 5 : 1) to give a colorless oil product (21.6 g, 48.0%).

Liquid, yield: (1.2 g, 55%), R_f: 0.43 (*n*-hexane : ethyl acetate = 4 : 1). IR (KBr, cm^{-1}): 2956 (CH), 1604 (C=O). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.30-7.01 (4H, m, C_6H_4), 3.78 (4H, s, 2$C_6H_4CH_2S$), 3.71 (4H, t, J = 5.50 Hz, $2CH_2Cl$), 3.63

(4H, t, J = 5.50 Hz, 2C$\underline{H}_2$CH$_2$Cl), 3.56 (4H, t, J = 6.60 Hz, SCH$_2$C$\underline{H}_2$O), 2.56 (4H, t, J = 6.60 Hz, 2C$_6$H$_4$CH$_2$SC$\underline{H}_2$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 138.8, 129.4, 128.4, 127.5 (C$_6$H$_4$), 71.2, 69.9 (CH$_2$OCH$_2$), 43.6 (CH$_2$Cl), 35.3 (C$_6$H$_4$C$\underline{H}_2$S), 30.0 (C$_6$H$_4$CH$_2$S$\underline{C}$H$_2$). Anal. Calcd for $C_{16}H_{24}Cl_2O_2S_2$: C 50.70; H 6.31; S 16.73. Found: C 50.75; H 6.34; S 17.08.

1,3-Bis{[5-(5-amino-1,2,4-thiadiazol-3-yl)thio]-3-oxapentylthiomethyl}-benzene (8). To a suspension of K_2CO_3 (3.27 g, 23.66 mmol) in anhydrous DMF (60 mL), were added compound (**6**) (2.26 g, 5.89 mmol) and compound (**7**) (7, 3.21 g, 12.14 mmol) in DMF (10 mL) over 10 min. The reaction mixture was heated at 50-55 °C for 5 hr and then heated at 70 °C for 15 hrs. The solvent was removed under reduced pressure and the residue was dissolved in H_2O (50 mL) and ethyl acetate (200 mL). The organic layer was separated and dried with anhydrous $MgSO_4$. Solvent was removed under reduced pressure to afford product. The crude product was purified by chromatography (SiO_2; eluent chloroform : methanol = 20 : 1) to give oil product (1.18 g, 34.7%).

R_f: 0.13 ($CHCl_3$: MeOH = 15 : 1). IR (KBr, cm^{-1}): 3300, 3141, 2918, 1610, 1515. ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ): 8.03 (4H, s, 2NH), 7.17-7.27 (4H, m, C$_6$H$_4$), 3.76 (4H, s, C$_6$H$_4$C$\underline{H}_2$S), 3.62 (4H, t, J = 6.23 Hz, 2SCH$_2$CH$_2$OC$\underline{H}_2$CH$_2$), 3.53 (4H, t, J = 6.60 Hz, SCH$_2$C$\underline{H}_2$OCH$_2$CH$_2$), 3.24 (4H, t, J = 6.23 Hz, SCH2CH$_2$OCH$_2$C$\underline{H}_2$), 2.55 (4H, t, J = 6.60 Hz, C$_6$H$_4$CH$_2$SC$\underline{H}_2$). ^{13}C NMR (DMSO-d$_6$, 100 MHz, δ): 183.7 (S-C=N), 166.5 (N-C=N), 139.5, 130.1, 129.1, 128.1 (C$_6$H$_4$), 70.5, 69.6, (C$\underline{H}_2$OC$\underline{H}_2$), 36.0 (C$_6$H$_4$C$\underline{H}_2$S), 30.9, (SCH$_2$C$\underline{H}_2$-OCH$_2$C$\underline{H}_2$), 30.7 (C$_6$H$_4$CH$_2$S$\underline{C}$H$_2$). FAB-HRMS Cald for $C_{20}H_{29}O_2N_6S_6$, 577.0676; Found 577.0676.

11,14,20,23,38,39-Hexaaza-6,17,28-trioxa-3,9,12,22,25,31-hexathiotetracyclo-[31,3,1,1^{10,13},1,^{21,24}]-nonatriaconta-1(37),10(11),13(38),21(39),23(24),33(34),35(36)-heptaene-15,19-dione (9). The synthesis of macrocycle (**9**) followed the same procedure of preparation of compound (**5**). The crude product was purified by chromatography (SiO_2; eluent *n*-hexane : ethyl acetate = 1 : 1) to afford product (33.9%).

Liquid. R_f: 0.43 (chloroform : methanol = 15 : 1). IR (KBr, cm^{-1}): 3119, 2914, 1684, 1558. ^{1}H NMR (400 MHz, acetone-d$_6$, δ): 7.32-7.23 (4H, m, C$_6$H$_4$), 4.63 (4H, s, 2COCH$_2$O), 3.82 (4H, s, 2C$_6$H$_4$C$\underline{H}_2$S), 3.71 (4H, t, J = 6.23 Hz, 2Het-SCH$_2$C$\underline{H}_2$O), 3.64 (4H, t = 6.60 Hz, 2C$_6$H$_4$CH$_2$SCH$_2$C$\underline{H}_2$O), 3.39 (4H, t = 6.23 Hz, 2HetSC$\underline{H}_2$CH$_2$O), 2.57 (4H, t = 6.60 Hz, 2C$_6$H$_4$CH$_2$SC$\underline{H}_2$CH$_2$O). ^{13}C NMR (100 MHz, acetone-d$_6$, δ): 175.9 (S-C=N), 170.6 (C=O), 167.3 (N-C=N), 140.1, 130.6, 129.3, 128.6 (C$_6$H$_4$), 72.2 ((CO)CH$_2$O), 71.3, 70.0 (CH$_2$OCH$_2$), 37.0 (C$_6$H$_4$C$\underline{H}_2$), 32.2 (HetS$\underline{C}$H$_2$CH$_2$O), 31.3 (C$_6$H$_4$CH$_2$S$\underline{C}$H$_2$). FAB-HRMS Cald for $C_{24}H_{31}O_5N_6S_6$, 675.0680; Found 675.0681.

Acknowledgement. This work was supported by a Grant from Chungnam National University in 2003.

References

1. Kickham, J. E.; Loeb, S. J. *Inorg. Chem.* **1995**, *34*, 5656.
2. Kickham, J. E.; Loeb, S. J. *Inorg. Chem.* **1994**, *33*, 4351.
3. Kickham, J. E.; Loeb, S. J. *J. Chem. Soc. Chem. Commun.* **1993**, 1848.
4. Kickham, J. E.; Loeb, S. J.; Murphy, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 7031.
5. Shionoya, M.; Kimura, E.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 6730.
6. Van Staveren, C. J.; Van Eerden, J.; Van Veggel, F. C. J. M.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4994.
7. Reetz, M. T.; Neimeyer, C. M.; Hermes, M.; Goddard, M. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1017.
8. Alberts, A. H.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3375.
9. Aoyama, Y.; Yamagishi, A.; Asagawa, M.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1988**, *110*, 4076.
10. Aoyama, Y.; Asakawa, M.; Yamagishi, A.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1990**, *112*, 3145.
11. Mizutani, T.; Ema, T.; Yoshida, T.; Kuroda, Y.; Ogoshi, H. *Inorg. Chem.* **1993**, *32*, 2072.
12. Mizutani, T.; Ema, T.; Tomita, T.; Kuroda, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1994**, *116*, 4240.
13. Corradini, R.; Dossena, A.; Impellizzeri, G.; Maccarrone, G.; Marchelli, R.; Rizzarelli, E.; Sartor, G.; Vecchio, G. *J. Am. Chem. Soc.* **1994**, *116*, 10267.
14. Kuroda, Y.; Kato, Y.; Higashioji, T.; Hasegawa, J.; Kawanami, S.; Takahashi, M.; Shiraishi, N.; Tanabe, K.; Ogoshi, H. *J. Am. Chem. Soc.* **1995**, *117*, 10950.
15. Zheng, J.-Y.; Konishi, K.; Aida, T. *Tetrahedron* **1997**, *53*, 9115.
16. Mizutani, T.; Yagi, S.; Honmaru, A.; Murakami, S.; Furusyo, M.; Takagishi, T.; Ogoshi, H. *J. Org. Chem.* **1998**, *63*, 8769.
17. Clark, J. L.; Stezowski, J. *J. Am. Chem. Soc.* **2001**, *123*, 9880.
18. Clark, J. L.; Booth, B. R.; Stezowski, J. J. *J. Am. Chem. Soc.* **2001**, *123*, 9889.
19. Brown, S. E.; Haskard, C. A.; Easton, C. J.; Lincoln, S. F. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1013.
20. Crumbliss, A. L.; Batinic-Haberle, I.; Spasojevic, I. *Pure & Appl. Chem.* **1996**, *68*, 1225.
21. Cameron, B. R.; Loeb, S. J.; Yap, G. P. A. *Inorg. Chem.* **1997**, *36*, 5498.
22. Furusho, Y.; Kimura, T.; Mizuno, Y.; Aida, T. *J. Am. Chem. Soc.* **1997**, *119*, 5267.
23. Murphy, S. L.; Loeb, S. J.; Shimizu, G. K. H. *Tetrahedron* **1998**, *54*, 15137.
24. Sugasaki, A.; Ikeda, M.; Takeuchi, M.; Robertson, A.; Shinkai, S. *J. Chem. Soc. Perkin Trans. 1* **1999**, 3259.
25. Seneque, O.; Rager, M.-N.; Giorgi, M.; Reinaud, O. *J. Am. Chem. Soc.* **2000**, *122*, 6183.
26. Mitoka, Y.; Tsukiji, S.; Hiraoka, T.; Kasahi, N.; Shinkai, S.; Hamachi, I. *Tetrahedron Lett.* **2001**, *42*, 7059.
27. Van Manen, H.-J.; Fokkens, R. H.; Nibbering, N. M. M.; Van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Org. Chem.* **2001**, *66*, 4643.
28. Kubo, Y.; Ohno, T.; Yamanaka, J.; Tokita, S.; Iida, T.; Ishimaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 12700.
29. Smith, C. B.; Stephens, A. K. W.; Wallwork, K. S.; Lincoln, F.; Taylor, M. R.; Wainwright, K. P. *Inorg. Chem.* **2002**, *41*, 1093.
30. Chiba, J.; Tanaka, K.; Ohshiro, Y.; Miyake, R.; Hiraoka, S.; Shiro, M.; Shionoya, M. *J. Org. Chem.* **2003**, *68*, 331.
31. Cho, N. S.; Ra, C. S.; Ra, D. Y.; Song, J. S.; Kang, S. K. *J. Heterocyclic Chem.* **1996**, *33*, 1201.
32. Ra, D. Y.; Cho, N. S.; Moon, J. H.; Kang, S. K. *J. Heterocyclic Chem.* **1998**, *35*, 1435.
33. Cho, N. S.; Kim, Y. H.; Park, M. S.; Kim, E. H.; Kang, S. K.; Park, C. *Heterocycles* **2003**, *60*, 1401.