Synthesis of Heteromacrocycles as Ligands of a Palladium-Artificial Enzyme and Crystal Structure

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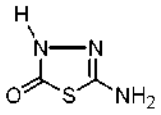
Molecular recognition is a general principle in nature, and the design of artificial receptors (enzymes) for specific target molecules based on molecular recognition is an important theme in bioorganic chemistry. Enzymes are often surrounded by a hydrophobic sheath of amino acids that shields them from undesirable hydrolysis and polymerization reactions, and facilitates their normal functions. The mimicking of metalloenzyme active sites are of particular interest.[1-3] Artificial metalloenzymes possessing molecular-recognition properties have attracted attention since the 1980s. Some compounds have been utilized for enantioselective sulfoxidation,[4,5] hydrogenation,[6,7] or asymmetric allylic alkylation reactions.[8]

In the present work, we have prepared ligands of a palladium-artificial enzyme as amino acid substitutes. 5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**1**)[9] and 5-amino-3*H*-1,3,4-thiadiazolin-2-thione (**2**)[10] -derived mimics of a metalloenzyme active sites were designed. To provide potential chelation sites to allow the formation of palladium ion complexes, 1,3-benzenedimethanethiol was introduced.[11-13] In order to form a hydrogen bond and control the size of the macrocycle cavity, an ether linkage was inserted and compounds **1** and **2** were acylated with acyl halide.



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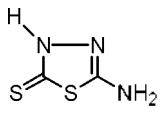

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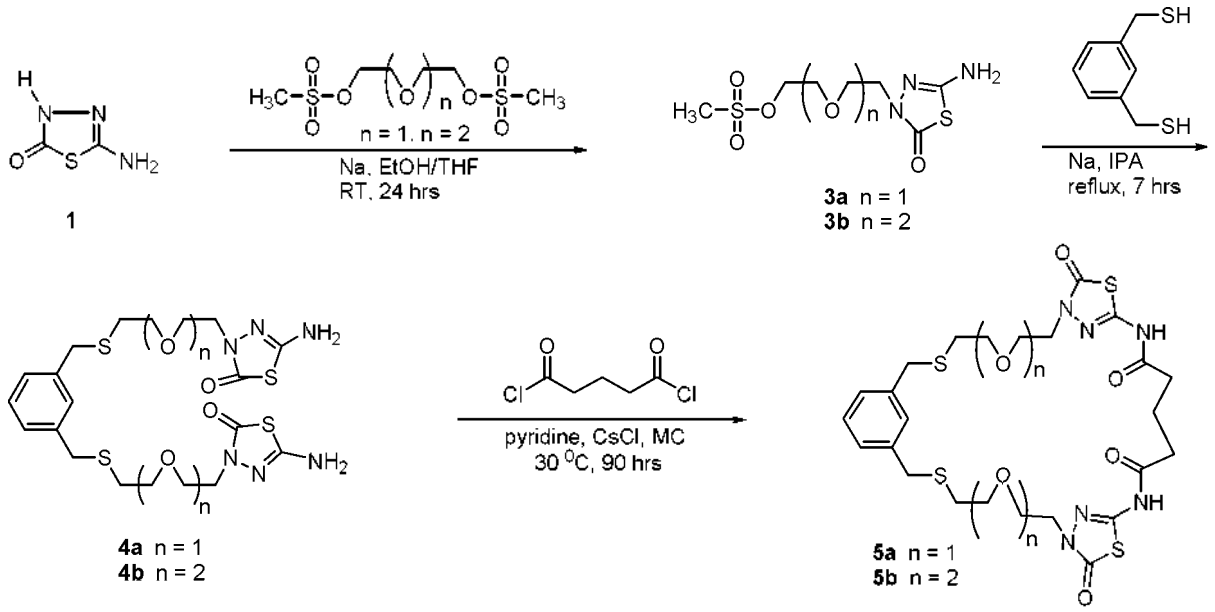
Results and Discussion

The synthesis of ligands containing two units of 5-amino-3*H*-1,3,4-thiadiazolin-2-one (**1**) were accomplished according to Scheme 1. The difference between **3a** and **3b** is the length of the chain, which influences the size of the macrocycle cavity. According to the regiospecific *N*-alkylation of **1**, the reaction of **1** with tri(ethyleneglycol) dimethanesulfonate in the presence of $NaOC_2H_5$ in ethanol gave the *N*-alkylated product (**3b**). The formation of **3b** was confirmed by ^1H and ^{13}C NMR spectra. The NH signal of compound (**1**) was replaced by that of NCH_2 at δ 3.90 and 46.0 in the ^1H and ^{13}C NMR spectra, respectively. To introduce 1,3-bezenedimethanthiol, the compound was *S*-alkylated with **3b** under basic conditions (NaOCH $(CH_3)_2$- $(CH_3)_2CHOH$. The formation of **4b** was also confirmed by ^1H and ^{13}C NMR spectra. The SH signal of 1,3-bezene-



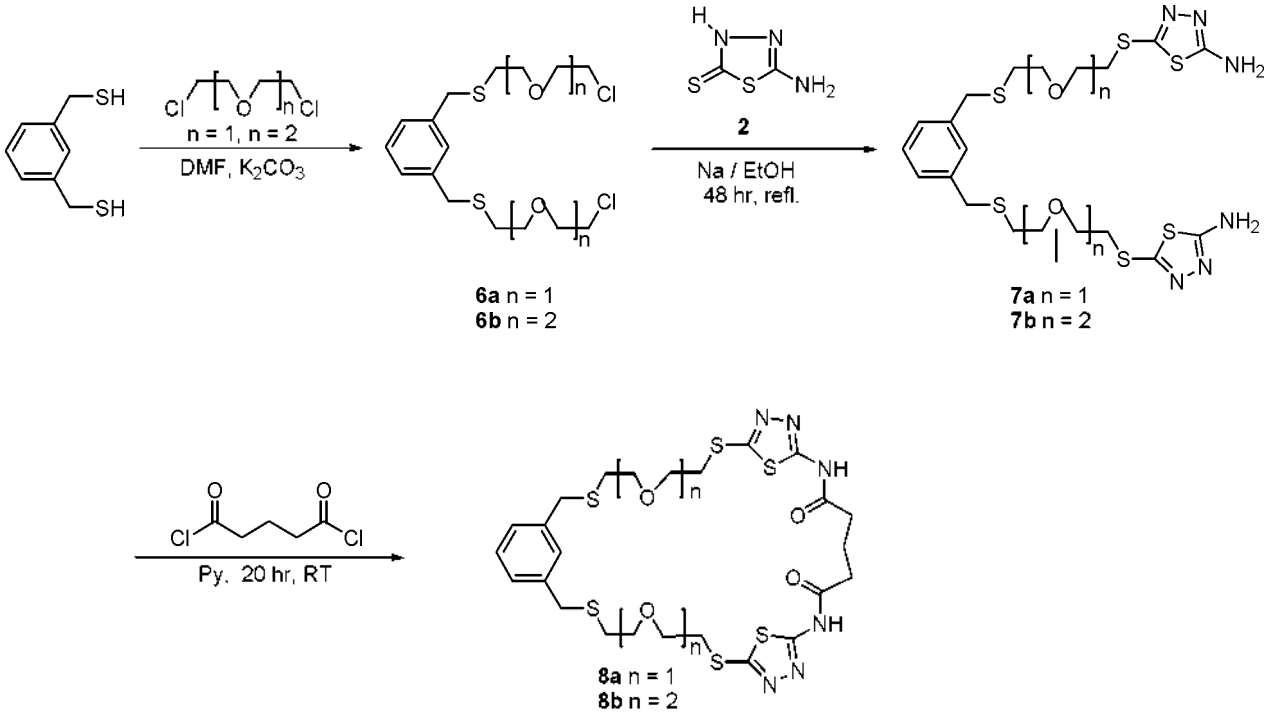
1

3a n = 1
3b n = 2

4a n = 1
4b n = 2

5a n = 1
5b n = 2

Scheme 1. Synthesis of heteromacrocycles containing two units of 5-amino-3*H*-1,3,4-thiadiazolin-2-one (**1**).



Scheme 2. Synthesis of heteromacrocycles containing two units of 5-amino-3*H*-1,3,4-thiadiazolin-2-thione (**2**).

dimethanthiol was replaced by a SCH_2 at δ 2.61 and 30.8 in the ^1H and ^{13}C NMR spectra, respectively. 1,3-Benzenedimethanethiol supplies the chelation sites to form complexes with palladium ions.[11-13]

To obtain the target macrocycle containing two 5-amino-3*H*-1,3,4-thiadiazoline-2-ones and one 1,3-benzenedimethanethiol from **4b**, we attempted Cs^+-mediated cyclization.[14] which involves *N,N'*-diacylation of **4b** at the NH_2 group of the 1,3,4-thiadiazole rings using diglycolyl chloride with a high-dilution technique. Glutaryl chloride was added to a CH_2Cl_2 solution of **4b** over a 72 h period. The structure of the macrocycle was established using ^1H and ^{13}C NMR, IR, and FAB-HRMS spectra. The successful macrocyclization of **4b** to **5b** was supported by evidence of *N*-acylation, which indicated that a $NHCOCH_2$ group replaced the NH_2 functional group at δ 11.88 and 3.84 in the ^1H NMR spectrum, and at δ 166.7 and 45.6 ppm in the ^{13}C NMR spectrum. The IR spectrum also displays the carbonyl group of the amide at 1653 cm^{-1}. FAB-HRMS spectra clearly supported structure **5b** (729.1869).

The synthesis of ligands containing two 5-amino-3*H*-1,3,4-thiadiazolin-2-thione (**2**) units was accomplished according to Scheme 2. The difference between **6a** and **6b** is the length of the chain. As α,α'-*m*-xylenedithiol is a palladation chelation site,[11-13] an α,α'-*m*-xylenedithiol moiety was introduced to the macrocyclic compounds to chelate palladium.

According to the regiospecific *S*-alkylation, compound **2** with the appropriate chloride (**6a** or **6b**) in the presence of NaOEt in ethanol gave an (*S*)-alkylated dimer (**7a** or **7b**), as shown in the previous method.[15] Again, the difference between **7a** and **7b** is the length of the chain, which influences the size of the macrocycle cavity. To obtain target macrocycles containing two 2-amino-5-alkylthio-1,3,4-thiadiazole and one 1,3-benzenedimethanethiol from **2**, we attempted Cs^+-mediated[11-13] cyclization involving *N,N'*-diacylation of **7b** at the NH_2 of the 1,3,4-thiadiazole rings using glutaryl chloride with a high-dilution technique to synthesize ligands of **8a** and **8b**. Glutaryl chloride was added to a CH_2Cl_2 solution of **7b** over a 20 h period. The structure of the macrocycle was established using ^1H and ^{13}C NMR, IR, and FAB-HRMS. The successful macrocyclization of **7b** to **8b** was supported by evidence of *N*-acylation, which indicated that an $NHCOCH_2$ group replaced

Table 1. Crystal data and structure refinement for macrocycle, **8b**, $[C_{29}H_{10}N_6O_6S_6]$.

Chemical formula	$C_{29}H_{10}N_6O_6S_6$
Formula weight	761.03
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.9202(11)Å, α = 76.545(8)°
	b = 9.9488(12)Å, β = 84.623(8)°
	c = 21.220(2)Å, γ = 83.502(7)°
Volume	1815.3(4) $Å^3$
Z, Calculated density	2, 1.392 Mg/m^3
F(000)	800
Crystal size	0.50 × 0.32 × 0.23 mm
Theta range for data collection	1.98 to 26.00 °
Reflections collected / unique	11350/7088 [R_{int} = 0.0227]
Goodness-of-fit on F^2	1.034
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0675, wR_2 = 0.1864
R indices (all data)	R_1 = 0.1144, wR_2 = 0.2201
Largest diff. peak and hole	1.146 and -0.588 e $Å^{-3}$

Table 2. The selected bond distances (Å) and angles (°) for macrocyle, **8b**, [$C_{29}H_{40}N_6O_6S_6$].

S(1)-C(2)	1.735(4)	S(1)-C(47)	1.808(5)
S(6)-C(2)	1.734(4)	S(6)-C(5)	1.720(4)
N(3)-N(4)	1.383(5)	N(4)-C(5)	1.279(5)
C(8)-O(9)	1.221(5)	S(30)-C(29)	1.760(8)
S(30)-C(31)	1.774(7)		
C(2)-S(1)-C(47)	99.9(2)	C(2)-S(6)-C(5)	85.8(2)
N(4)-C(5)-S(6)	115.5(3)	N(3)-N(4)-C(5)	112.8(3)
C(29)-S(30)-C(31)	103.4(3)		

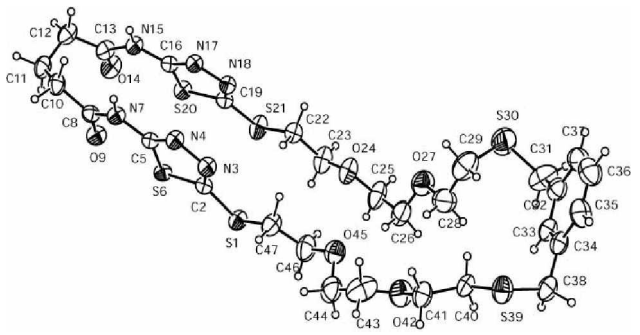


Figure 1. ORTEP diagram of macrocycle, **8b**, [$C_{29}H_{40}N_6O_6S_6$], showing the atom numbering scheme.

the NH_2 at 13.64 and 3.84 ppm in the ^1H spectrum, and at 160.0 and 36.6 ppm in the ^{13}C NMR spectrum. The IR spectrum also showed the carbonyl group of the amide at 1653 cm^{-1}. FAB-HRMS clearly supported structure (**8b**) (761.1414). Moreover, the structure of the macrocycle (**8b**) was verified using X-ray crystallography. The crystallographic data and structure refinement parameters for **8b** [$C_{29}H_{40}N_6O_6S_6$] are summarized in Table 1. The selected bond distances and angels are summarized in Table 2. An ORTEP view including the atomic numbering scheme is depicted in Figure 1.

Experimental Section

The synthesis of 5-amino-3*H*-1,3,4-thiadiazolin-2-one (**1**),[9] 5-(5-amino-2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)-3-oxopentyl methanesulfonate (**3a**).[16] *α,α'*-bis-[5-(5-amino-2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)-3-oxopentylthio]-*m*-xylene (**4a**).[16] tri(ethyleneglycol)dimethanesulfonate,[17] and 1,3-benzenedimethanethiol[18] were followed the previous procedures.

1-(5-Amino-2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)-3,6-dioxaoctyl-8-methanesulfonate (3b). The synthesis of **3b** followed the same procedure of the preparation of **3a**. Yield 24.2%. Oil. R_f: 0.18 ($CHCl_3$: MeOH = 15 : 1). IR (cm^{-1}): 3320 (NH_2), 1613 (C=O), 1611 (NH), 1348, 1178 ($S(=O)_2$), 1131 (C-N). ^1H NMR (400 MHz, $CDCl_3$-d_6, δ): 4.70 (2H, br, NH_2), 4.37 (2H, t, CH_2N, J = 5.2 Hz), 3.90 (2H, t, CH_2OMs, J = 5.6 Hz), 3.75 (4H, m, $NCH_2(CH_2O)_2$), 3.64 (4H, m, $MsOCH_2(CH_2O)_2$), 3.09 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$-d_6, δ): 167.5 (C=O), 150.6 (C=N), 70.5, 70.2, 69.4, 68.9, 68.0 ($5OCH_2$), 46.0 (NCH_2), 37.7 (CH_3). Anal. Calcd for $C_9H_{17}N_3O_6S_2$: C 33.02; H 5.23; S 19.59. Found: C 33.04; H 5.24; S 19.58.

***α,α'*-Bis-[8-(5-amino-2,3-dihydro-2-oxo-1,3,4-thiadiazol-3-yl)-3,6-dioxaoctylthio]-*m*-xylene (4b).** The synthesis of **4b** followed the same procedure of the preparation of **4a**. Yield 65%. Oil. R_f: 0.55 (*n*-hexane : ethyl acetate : EtOH = 5 : 3 : 2). IR (cm^{-1}): 3310 (NH_2), 1672 (C=O), 1610 (NH). ^1H NMR (400 MHz, $CDCl_3$-d_6, δ): 7.24-7.15 (4H, m, C_6H_4), 5.24 (4H, br, $2NH_2$), 3.86 (4H, t, $2CH_2N$, J = 5.2 Hz), 3.71-3.68 (8H, m, $2OCH_2$ + $2CH_2C_6H_4$), 3.57-3.54 (12H, m, 3 $(CH_2O)_2$), 2.58 (4H, t, $2CH_2S$, J = 6.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$-d_6, δ): 167.4 (C=O), 150.9 (C=N), 138.5, 129.4, 128.6, 127.6 (C_6H_4), 70.7, 70.23, 70.15, 68.2 ($4OCH_2$), 46.1 (NCH_2), 36.5 ($C_6H_4CH_2S$), 30.8 (SCH_2). Anal. Calcd for $C_{24}H_{36}N_6O_6S_4$: C 45.55; H 5.73; S 20.27. Found: C 45.54; H 5.72; S 20.28.

9,13,19,23,36,37-Hexaaza-6,16-dioxa-3,11,21,29-tetrathiotetracyclo-[29,3,1,1,^{9,12}1^{20,23}]-heptatriaconta-1(35),12(36),20(37),31(32),33(34)-pentaene-10,14,18,22,-tetraone (5a). To a solution of **3a** (3.5 g, 6.4 mmol) in methylene chloride (300 mL), pyridine (1.0 mL, 12.9 mmol) and cesium chloride (1.1 g, 6.5 mmol) were added. Solution of glutaryl chloride (1.7 g, 9.8 mmole) in methylene chloride (250 mL) was added for 72 h using syringe pump. After addition of glutaryl chloride solution, the reaction mixture was stirred for additional 24 h. The end point of reaction was checked by TLC. The salt was filtered off and the solution was washed with saturated NaCl solution and dried with $MgSO_4$. The solvent was distilled off to give oily product. First precipitation induced by addition of acetone (5 mL). And then methylene chloride was added to afford crude precipitate product. The crude product was recrystallized from C_2H_5OH to afford pure product (0.3 g, 7%). mp: 218-220 °C. R_f: 0.33 ($CHCl_3$: MeOH = 9 : 1). IR (KBr, cm^{-1}): 3434 (C=ONH), 1671 (C=O), 1628 (C=ONH). ^1H NMR (DMSO-d_6, 400 MHz, δ): 11.94(2H, br, 2NH), 7.20-7.04 (4H, m, C_6H_4), 3.90 (4H, t, $2CH_2N$, J = 5.2 Hz), 3.67 (8H, m, $2CH_2O$ + $2CH_2C_6H_4$), 3.54 (4H, t, $C=OCH_2$), 2.49 (4H, t, $2CH_2O$, J = 6.0 Hz), 2.34 (4H, t, $2CH_2S$, J = 6.4 Hz), 1.82 (2H, t, $CH_2CH_2CH_2$, J = 6.0 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 171.2 (C=O), 166.7 (CH_2C=O), 142.4 (C=N), 138.6, 129.1, 127.8, 127.1 (C_6H_4), 70.3, 45.7 ($2OCH_2$), 45.7 (CH_2), 35.4 (NCH_2), 33.6 ($C_6H_4CH_2$), 30.1 (SCH_2), 19.8 ($CH_2CH_2CH_2$). FABHRMS calcd. for $C_{25}H_{33}N_6O_6S_4$ 641.1344, found 641.1340.

12,16,22,26,42,43-Hexaaza-6,9,29,32-tetraoxa-3,14,24,35-tetrathiotetracyclo-[35,3,1,1,^{12,15}1^{23,26}]-hitetraconta-1(41),15(42),23(43),37(38),39(40)-pentaene-13,17,21,25,-tetraone (5b). The synthesis of **5b** followed the same procedure of the preparation of **4a**. Yield 5%. mp: 228-230 °C. R_f: 0.36 ($CHCl_3$: MeOH = 9 : 1). IR (KBr, cm^{-1}): 3206 (C=ONH), 1653 (C=O), 1576 (C=ONH). ^1H NMR (DMSO-d_6, 400 MHz, δ): 11.88 (2H, br, 2NH), 7.18-7.07 (4H, m, C_6H_4), 4.03(4H, t, $2CH_2N$, J = 5.2 Hz), 3.84 (4H, t, $C=OCH_2$), 3.76-3.70 (8H, m, $2CH_2O$ + $2CH_2C_6H_4$), 3.40 (12H, m, $6CH_2O$), 2.31 (4H, t, $2CH_2S$, J = 7.2 Hz), 1.76 (2H, q, $CH_2CH_2CH_2$, J = 6.4 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 171.2 (C=O), 166.7 (CH_2C=O), 142.4 (C=N), 138.6, 129.2, 128.1, 127.3 (C_6H_4), 70.1, 69.6, 69.3, 67.0 ($4OCH_2$), 45.6 ($C=OCH_2$), 35.3 (NCH_2), 33.7 ($C_6H_4CH_2$), 30.1(SCH_2), 19.7 ($CH_2CH_2CH_2$). FABHRMS calcd. for $C_{29}H_{40}N_6O_8S_4$ 729.1869, found 729.1870.

The synthesis of 5-amino-3*H*-1,3,4-thiadiazolin-2-thione

(**2**).[10] α,α`-bis(5-chloro-3-oxapentylthio-*m*-xylene (**6a**).[15] α,α`-bis(8-chloro-3,5-dioxaoctylthio)-*m*-xylene (**6b**).[15] α,α`-bis [5-(5-amino-1,3,4-thiadiazol-2-yl)thio-3-oxapentylthio)-*m*-xylene (**7a**).[15] α,α`-bis[8-(5-amino-1,3,4-thiadiazol-2-yl)thio-3,5-dioxaoctylthio]-*m*-xylene (**7b**)[15] were followed the previous procedures.

11,12,14,20,22,23-Hexaaza-6,28-dioxa-3,9,25,31,38,39-hexathiotetracyclo-[31,3,1,1,^{10,13}1^{21,24}]-nonatriaconta-1(37),10(11),12(13),21(22),23(24),33(34),35(36)-heptaene-15,19-dione (8a). To a solution of **7a** (0.15 g, 0.26 mmol) in methylene chloride (50 mL), pyridine (5 mL) and cesium chloride (0.2 g, 1.2 mmol) were added. Solution of glutaryl chloride (0.07 g, 0.39 mmole) in methylene chloride (50 mL) was added for 12 h using syringe pump. After addition of glutaryl chloride solution, the reaction mixture was stirred for additional 40 h. The end point of reaction was checked by TLC. The salt was filtered off and the solution was washed with 1 N HCl and saturated NaCl solution and dried with $MgSO_4$. The solvent was distilled off to give oily product. The residue was column chromatographed using *n*-hexane : ethyl acetate : ethanol (5 : 3 : 1) as eluent affording white solid product (52.4 mg, 30%). mp: 157-159 °C. R_f: 0.45 (*n*-hexane : ethyl acetate : ethanol = 5 : 3 : 1). IR (KBr pellet, cm^{-1}): 3155 (NH), 1699 (C=O), 1560 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.52 (2H, br, 2NH), 7.23-7.12 (4H, m, C_6H_4), 3.71 (4H, s, $2C_6H_4SC\underline{H}_2$), 3.63 (4H, t, J = 6.4 Hz, $2CH_2O$), 3.49 (4H, t, J = 6.4 Hz, $2OCH_2$), 3.33-3.30 (8H, m, $2CH_2S$, $2COCH_2$), 2.49 (4H, t, J = 6.4 Hz, $2C_6H_4CH_2SC\underline{H}_2$), 1.99 (2H, quintet, J = 6.4 Hz, $CH_2C\underline{H}_2CH_2$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.9 (S-C=S), 158.8 (C=O), 158.3 (N-C=N), 138.7, 129.3, 128.4, 127.3 (C_6H_4), 69.9, 68.8 (CH_2OCH_2), 35.3 (O=C-$\underline{C}H_2$), 34.0 ($C_6H_4\underline{C}H_2S$), 33.6 (CH_2S), 29.9 ($C_6H_4CH_2S\underline{C}H_2$), 20.00 ($CH_2\underline{C}H_2CH_2$). FABHRMS calcd for $C_{25}H_{33}N_6O_4S_6$ 673.0888, found 673.0883.

14,15,17,23,25,26-Hexaaza-6,9,31,34-tetraoxa-3,12,28,37,44,45-hexathiotetracyclo-[37,3,1,1^{13,16},1^{24,27}]-pentatetraconta-1(43),13(14),15(16),24(25),26(27),39(40),41(42)-heptaene-18,22-dione (8b). The synthesis of **4b** followed the same procedure of the preparation of **4a**. The product residue was column chromatographed using *n*-hexane: THF (1 : 1.5) as eluent affording white solid product (12.9%). It also purified by recystalized with THF. mp: 167.2 °C. R_f: 0.27 (*n*-hexane : THF = 1 : 1.5). IR (KBr pellet, cm^{-1}): 3206 (NH), 1653 (C=O), 1576 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.64 (2H, bs, 2NH), 7.32-7.23 (4H, m, C_6H_4), 3.84 (4H, t, J = 6.42 Hz, $2CH_2CO$), 3.78 (4H, s, $2C_6H_4C\underline{H}_2S$), 3.67 (4H, t, J = 3.67 Hz, CH_2O), 3.64-3.59 (8H, m, $2OCH_2C\underline{H}_2O$), 3.42 (4H, t, J = 3.416 Hz, CH_2O), 2.84 (4H, t, J = 5.81 Hz, $C\underline{H}_2CH_2C\underline{H}_2$), 2.61 (4H, t, $2C_6H_4CH_2SC\underline{H}_2$), 2.28 (2H, m, $CH_2C\underline{H}_2CH_2$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.1 (S-C=N), 160.0 (C=O), 160.7 (N-C=N), 138.9, 129.8, 129.0, 127.8 (C_6H_4), 71.2, 70.7, 70.4, 69.6 (CH_2OCH_2), 36.6 ($\underline{C}H_2CH_2\underline{C}H_2$), 35.8 ($C_6H_4\underline{C}H_2S$), 34.0 ($CH_2S$), 30.5 ($C_6H_4CH_2S\underline{C}H_2$), 21.7 ($CH_2\underline{C}H_2CH_2$). ^{13}C NMR (DMSO-$d_6$, 100 MHz, δ): FABHRMS calcd for $C_{28}H_{39}N_6O_2S_6$ 761.1412, found 761.1414.

X-ray data of macrocycle (8b). X-ray intensity data were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Structure was solved by applying the direct method using a SHELXS-97 and refined by a full-matrix least-squares calculation on F^2 using SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically. The amine H atoms, H7 and H15, were located in a difference map and refined freely. The other hydrogen atoms were placed in ideal positions and were riding on their respective carbon atoms (B_{iso} = 1.2 B_{eq}).

Crystallogrphic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-720138). The data can be obtained free of charge *via* www.ccdc.cam.ac.uk/deposit (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-01223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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