Crystal Structures of Macrocyclic Compounds Containing Two 5-Mercapto-3*H*-1,3,4-thiadiazolin-2-one Groups

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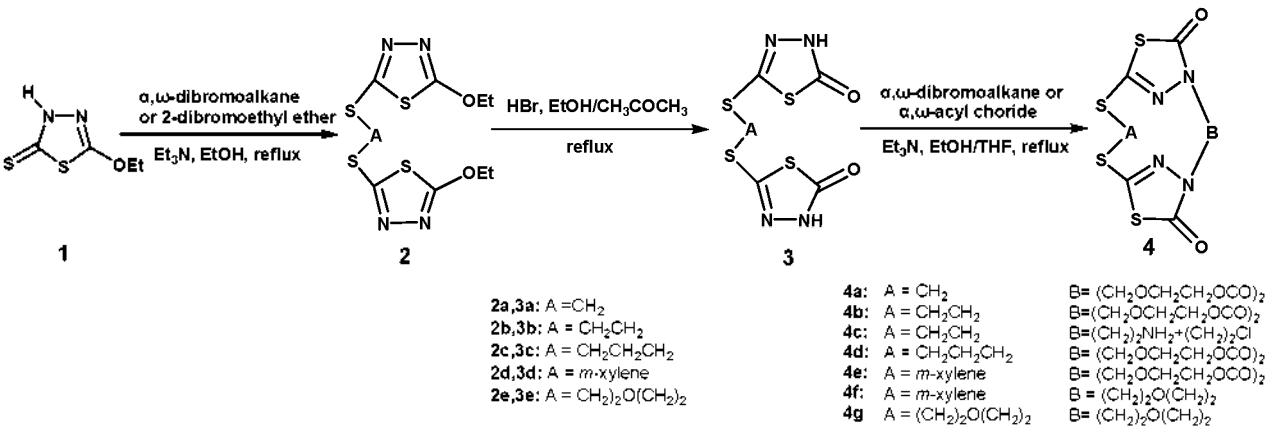
Many macrocylic compounds possessing heterocyclic constituents show unique chemical and biological properties, and the literature contains studies on macrocylic compounds containing 2-imino-5-mercapto-3*H*-1,3,4-thiadiazoline,[1] 5-amino-3*H*-1,3,4-thiadiazolin-2-one,[2] 5-mercapto-3*H*-1,3,4-thiadizolin-2-one,[3-5] 5-amino-3*H*-1,3,4-thiadizoline-2-thione,[6] 5-amino-2*H*-1,2,4,-thiadiazolin-3-one,[7] and 5-amino-2*H*-1,2,4-thiadiazoline-thione[7] groups. The current study focuses on macrocycles composed of two 5-mercapto-3*H*-1,3,4-thiadizolin-2-one units. From 5-mercapto-3*H*-1,3,4-thiadizolin- 2-one, S-bridged macrocyles can be derived, in which the sulfur atoms are directly connected to the heterocyclic rings. To enhance the selectivity of the ligands and the stability of the complexes, various changes in the crown ether structures have been attempted,[8-12] including the replacement of ligand polyether oxygen atoms by surfur or nitrogen atoms and the insertion of aromatic or heterocyclic rings into the macroring. 5-Mercapto-3*H*-1,3,4-thiadizolin-2-one provides rigidity, but also soft donor atoms to form complexes. The sulfur atom is soft and thus useful for forming complexes with transition metals cations like Ag^+ which we performed preliminary trial shown in experimentals.

To form the macrocyclic compound, two of these heterocyclic rings were linked by either ether chains or alkyl chains as shown in Scheme 1. The crystal structures of many of these compounds were determined by interpreting X-ray diffraction patterns. The 15-, 18-, 21-, 22-, 23-, and 25-membered macrocyclic compounds shown in Scheme 1 produce central cavities of different sizes and shapes.

The synthetic procedures are similar to those previously reported for macrocycles composed of two 5-mercapto-3*H*-1,3,4-thiadiazolin-2-ones and two xylenes.[4] The synthesis starts with a regioselective *S*-alkylation of 5-ethoxy-1,3,4-thidiazoline-2-thione (**1**) under basic conditions.[3] The reaction of **1** with the appropriate α,ω-dibromoalkane or 2-dibromoethyl ether in the presence of triethylamine in ethanol yielded *S*-alkylated dimers (**2**). The structure of **2** was determined by interpreting both ^{1}H and ^{13}C NMR spectra. Signals corresponding to the SCH_2 group appeared at 3.41 and 31.6 ppm in the ^{1}H and ^{13}C NMR spectra of **2e**, respectively, while the thiadiazole carbon atoms C(2) and C(5) resonated at 175.8 and 158.3 ppm, respectively. These results are similar to those previously reported.[3,4] The ethoxy group of **2** was cleanly dealkylated with HBr to give compound **3**. The formation of **3** was also confirmed by ^{1}H and ^{13}C NMR and IR spectra. The ethoxy group was replaced by a lactam NH (12.92 - 13.91 ppm in the ^{1}H NMR) and the chemical shifts of the ring carbon atoms C(2) and C(5) were shifted upward relative to those of **2**. A similar pattern was described in previous reports.[3,4] The IR spectrum shows a strong carbonyl band at 1645 - 1670 cm^{-1}, which suggests that **3** exists as a lactam. The NH of **3** is acidic enough to be either alkylated or acylated under basic conditions (triethylamine) with alkyl bromide and acyl halide, respectively.

The final step is ring formation by either [2+2] alkylation or [2+2] acylation between **3** and the corresponding 2-dibromoethylamine, 2-dibromoethyl ether, or triethyleneglycol bis-(chloroformate). Macrocycle structures were firmly established by ^{1}H and ^{13}C NMR, IR spectroscopy, high-resolution MS,



Scheme 1. Synthesis of macrocyclic compounds containing 5-mercapto-3*H*-1,3,4-thiadiazolin-2-ones.

Table 1. Crystal data and structure refinement parameters for **4c**, [$C_{10}H_{14}N_5O_2S_4Cl$].

Chemical formula	$C_{10}H_{14}ClN_5O_2S_4$
Formula weight	399.95
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C* 2/*c*
Unit cell dimensions	a = 18.687(4) Å, α = 90.0° b = 9.0420(18) Å, β = 127.15(3)° c = 12.043(2) Å, γ = 90.0°
Volume	1621.9(8) Å^3
Z, Calculated density	4, 1.638 mg/m^3
Crystal size	0.40 × 0.20 × 0.13 mm
Theta range for data collection	2.64 to 25.0°
Goodness-of-fit on F^2	1.057
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0373, wR_2 = 0.0913
R indices (all data)	R_1 = 0.0569, wR_2 = 0.0994
Largest diff. peak and hole	0.483 and -0.275 e Å^{-3}

Table 2. Selected bond distances (Å) and angles (°) for **4c**, [$C_{10}H_{14}N_5O_2S_4Cl$].

C(1)-S(2)	1.820(3)	(2)-C(3)	1.746(3)
C(3)-N(7)	1.280(4)	(3)-S(4)	1.744(3)
S(4)-C(5)	1.778(3)	C(5)-O(8)	1.215(4)
C(8)-O(9)	1.221(5)	S(30)-C(29)	1.760(8)
C(5)-N(6)	1.356(4)	N(6)-N(7)	1.382(3)
(6)-C(9)	1.448(4)	C(9)-C(10)	1.513(5)
C(10)-N(11)	1.484(4)		
C(1)-S(2)-C(3)	101.0(1)	S(4)-C(3)-N(7)	115.5(2)
C(3)-S(4)-C(5)	88.9(1)	S(4)-C(5)-N(6)	107.1(2)
C(5)-N(6)-N(7)	117.8(2)	C(5)-N(6)-C(9)	124.4(3)

and elemental analysis. Successful macrocyclization of compounds **3c** to **4c** was demonstrated by *N*-alkylation, as evidenced by the appearance of an NCH_2 group in place of the NH group at 3.68 and 44.8 ppm in the ^{1}H and ^{13}C NMR spectra, respectively, and the strong carbonyl band at 1674 cm^{-1}. The **4c** was isolated as HCl salt. Macrocycle **4c** was further characterized by single-crystal X-ray diffraction studies. The crystallographic data and structure refinement parameters for **4c** [$C_{10}H_{14}N_5O_2S_4Cl$] are summarized in Table 1, and the selected bond distances and bond angles are given in Table 2. An ORTEP view including the atomic numbering scheme is shown in Figure 1. The molecule exhibits a C_2-axis passing through atom N11 and the middle point of two C1 atoms. Hydrogen bonds N11-H···C12 serve to hold the macrocycles together. As shown in Figure 1, the X-ray crystal structure of **4c** is a 15-membered macrocycle composed of the C-N-N atoms of 1,3,4-thiadiazolone rings, *syn*-ethyl amine, and an *S-anti* conformation within the ethylene. Two of the 1,3,4-thiadiazolone rings are planar. The molecular ion peak (*m/z* 364) and microanalytical data support the molecular formula $C_{10}H_{15}N_5S_4O_2Cl$. Macrocycle **4c** was derived from **1** with an overall yield of 10 - 13% after recrystallization.

The structures of macrocycles **4b**,[13] **4f**,[14] and **4g**,[15] as determined by X-ray diffraction, are summarized in Figures 2, 3, and 4, respectively. Macrocycle **4b** is a 22-membered ring and **4f** and **4g** have an 18-membered ring structure. Compounds **4b**, **4c**, and **4g** exhibit a similar ring configuration pattern yielding a relatively large central cavity. The spacers between 5 and 5' are CH_2CH_2 and $(CH_2CH_2)O$ and the 3-3' spacers are $(CH_2CH_2)N$, $(CH_2CH_2)O$, and $(CH_2OCH_2CH_2OCO)_2$, respectively. However in **4f**, *m*-xylene and $(CH_2CH_2)O$ spacers allow benzene and the two, nearly parallel 1,3,4-thiadiaole rings to form a cage. The crystal structures show that the size and shape of the central cavity, 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.

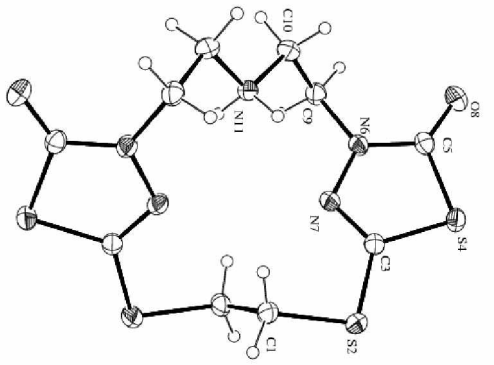


Figure 1. ORTEP diagram of **4c**, [$C_{10}H_{14}N_5O_2S_4Cl$], showing the atom numbering scheme and Cl anion is omitted for clarity.

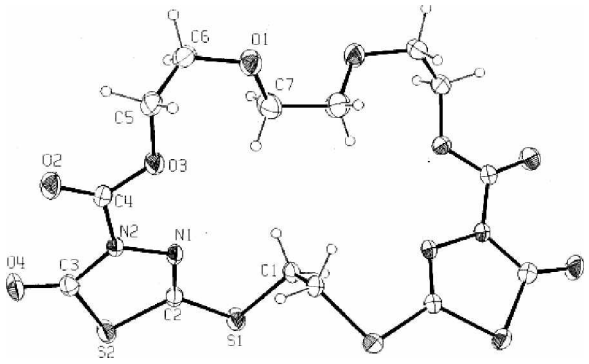


Figure 2. ORTEP diagram of macrocycle **4b** [$C_{14}H_{16}N_4O_8S_4$] showing the atom numbering scheme.[13]

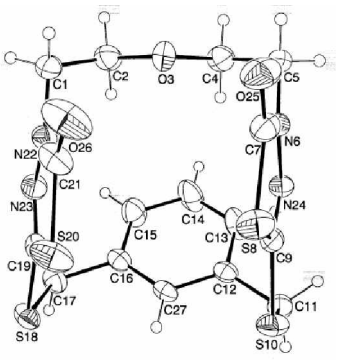


Figure 3. ORTEP diagram of macrocycle **4f** [$C_{16}H_{16}N_4O_2S_4$] showing the atom numbering scheme.[14]

Several macrocyclic compounds containing 1,3,4-thiadiazoles have been reported as being efficient complexing agents for silver ion.[16] To assess this ability for the macrocycles described herein, complexation studies of the macrocyclic host **4g**

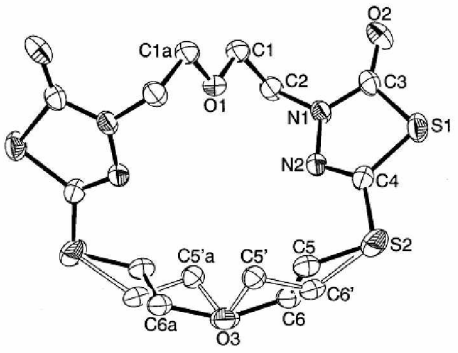


Figure 4. ORTEP diagram of macrocycle **4g** [$C_{12}H_{16}N_4O_3S_4$] showing the atom numbering scheme.[15]

were performed with a silver salt. The formation of a white precipitate was observed upon exposure of the macrocycle to a THF solution containing $AgClO_4$. Despite using a variety of solvents, single crystals of the white solid complex were unobtainable, yielding either powders or small quantities of crystals unsuitable for X-ray diffraction studies. Although the actual structure of the complex is unknown, the stoichiometry (1 : 1, host : metal) was deduced from microanalytical data. To speculate on the structure of the complex is difficult without clear evidence because the coordination of Ag(I) is typically irregular, and coordinations of two, four, five, and six atoms are known.[17,18] The IR absorption bands are characteristic of free counter anions at 1085 cm^{-1} (literature range 1081 - 1098 cm^{-1}).[19] Unfortunately, determining whether the NMR spectrum of the complex differs from that of macrocycle **4g** was impossible because of its very low solubility in deuterated organic solvents.

Experimental Section

The synthesis of 5-ethoxy-1,3,4-thiadiazoline-2-thione,[20] bis[(5-ethoxy-1,3,4-thiadizole-2-yl)thio]methane,[3] bis[(5-ethoxy-1,3,4-thiadizole-2-yl)thio]ethane,[3] α,α'-bis[(5-ethoxy-1,3,4-thiadizole-2-yl)thio]-*m*-xylene[4] were followed the previous procedures. The synthesis of bis[(5-ethoxy-1,3,4-thiadiazol-2-yl)thio]alkane (**2**), bis[(5-oxo-4*H*-1,3,4-thiadiazolin-2-yl)thio]alkane(**3**) and macrocycles (**4**) generally followed the procedures reported for the synthesis of macrocyles composed of two 5-mercapto-2,3-dihydro-1,3,4-thiadiazol-2-ones and two xylenes.[4]

1,3-Bis[(5-ethoxy-1,3,4-thiadiazol-2-yl)thio]propane (2c). R_f: 0.50 (hexane : EA (5 : 5)), yield 84.3 % (from hexane : EA (7 : 3)), m.p.: 52 °C - 53.5 °C. IR (KBr pellet, cm^{-1}): 2987, 2930 (CH), 1630 (CN) 1256, 1060. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.59 (4H, q, J = 7.4 Hz, OCH_2), 3.34 (4H, t, J = 6.9 Hz, SCH_2), 2.32 (2H, quin, J = 7.2 Hz, CH_2), 1.50 (6H, t, J = 8.5 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.2 (C=N), 157.4 (C-S), 69.3 (OCH_2), 32.2 (SCH_2), 28.9 (CH_2), 14.4 (CH_3). Anal. Calcd. for $C_{11}H_{16}N_4O_2S_4$: C, 36.24; H, 4.42; N, 15.37; S, 35.19. Found: C, 36.28; H, 4.40; N, 15.35; S, 35.17.

1,5-Bis[(5-ethoxy-1,3,4-thiadiazol-2-yl)thio]-3-oxapentane (2e). R_f: 0.38 (hexane : EA (7 : 3)), yield 67% (from hexane : EA (7 : 3)), m.p.: 142 °C - 144 °C, IR (KBr pellet, cm^{-1}): 2981, 2935 (CH), 1685, 1508. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.56 (4H, q, J = 6.9 Hz, OCH_2CH_3), 3.83 (4H, t, J = 6.0 Hz, OCH_2), 3.41 (4H, t, J = 6.8 Hz, SCH_2), 1.46 (6H, t, J = 6.9 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.8 (C=N), 158.3 (C-S), 70.0 (OCH_2), 46.7 (OCH_2), 31.6 (SCH_2), 15.1 (CH_3). Anal. Calcd. for $C_{12}H_{16}N_4O_3S_4$: C, 36.53; H, 4.60; N, 14.20; S, 32.51. Found: C, 36.56; H, 4.62; N, 14.17; S, 32.56.

1,3-Bis[(5-oxo-4*H*-1,3,4-thiadiazolin-2-yl)thio]propane (3c). R_f: 0.65 (hexane : EA (5 : 5)), yield 84.0% (from EtOH), m.p.: 156 °C - 158 °C. IR (KBr pellet, cm^{-1}): 3221 (NH), 3040 (CH), 16720 (C=O). ^{1}H NMR (400 MHz, DMSO, δ): 12.93 (2H, s, NH), 3.21 (4H, t, J = 7.2 Hz, SCH_2), 2.05 (2H, quin, J = 7.1 Hz, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.3 (C=O), 148.1 (C-S), 31.0 (SCH_2), 29.0 (CH_2). Anal. Calcd. for $C_7H_8N_4O_2S_4$: C, 27.26; H, 2.62; N, 18.17; S, 41.59. Found: C, 27.27; H, 2.62; N, 18.18; S, 41.57.

1,5-Bis[(5-oxo-4*H*-1,3,4-thiadiazolin-2-yl)thio]-3-oxapentane(3e). R_f: 0.55 (hexane : EA (5 : 5)), yield 98% (from EtOH), m.p.: 162 °C - 164 °C. IR (KBr pellet, cm^{-1}): 3167, 3121 (CH), 1645 (C=O), 1497 (C=N). ^{1}H NMR (400 MHz, DMSO, δ): 12.92 (2H, s, NH), 3.68 (4H, t, J = 6.0 Hz, OCH_2), 3.25 (4H, t, J = 6.4 Hz, SCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ) : 171.4 (C=O), 148.5 (C-S), 68.5 (SCH_2), 32.1 (CH_2). Anal. Calcd. for $C_8H_{10}N_4O_3S_4$: C, 28.39; H, 2.98; N, 16.55; S, 37.90. Found: C, 28.38; H, 2.95; N, 16.56; S, 37.92.

4,17,24,25-tetraaza-6,9,12,15-tetraoxa-2,19,21,23-tetrathiatricyclo-[18,3,1^{1,4}1^{17,20}]-pentacosa-1(24),20(25)-diene-3,5,16,18-tetraone (4a). R_f: 0.20 hexane : EA : acetone (8 : 16 : 1), yield 74.2% (from acetone : chloroform (4 : 1)). m.p.: 160 °C - 162 °C. IR (KBr pellet, cm^{-1}): 3000, 2927 (CH), 1780 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.89 (2H, s, SCH_2), 4.55 (4H, m, OCH_2), 3.84 (4H, m, OCH_2), 3.71 (4H, s, OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.6 (C=O), 149.6 (amide C=O), 148.6 (C-S), 71.6, 69.3, 68.4 (OCH_2), 34.0 (SCH_2). Anal. Calcd. for $C_{13}H_{14}N_4S_4O_8$: C, 32.36; H, 2.92; N, 11.62; S, 26.58. Found: C, 32.38; H, 2.95; N, 11.68; S, 26.54. MS (EI) *m/z*: 482 (M^-).

4,17,25,26-Tetraaza-6,9,12,15-tetraoxa-2,19,21,24-tetrathiatricyclo-[18,4,1^{1,4}1^{17,20}]-pentacosa-1(25),20(26)-diene-3,5,16,18-tetraone (4b). R_f: 0.34 (hexane : EA : EtOH (5 : 3 : 1)), yield 48% (from acetone : chloroform (4 : 1)), m.p.: 250 °C - 252 °C. IR (KBr pellet, cm^{-1}): 3000, 2910 (CH), 1780 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.56 - 4.54 (4H, m, OCH_2), 3.85 - 3.83 (4H, m, OCH_2), 3.75 (4H, s, SCH_2), 3.65 (4H, s, OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.5 (C=O), 149.2 (amide C=O), 147 (C-S), 71.3, 70.2, 68.7, 68.5, 68.2, 67.2 (OCH_2), 31.1 (SCH_2). Anal. Calcd. for $C_{14}H_{16}N_4S_4O_8$: C, 33.86; H, 3.25; N, 11.28; S, 25.83. Found: C, 33.87; H, 3.21; N, 11.29; S, 25.89. MS (EI) *m/z*: 496 (M^-).

4,7,10,18,19,-Pentanaza-2,1213,17-tetrathiatricyclo[15,2,1^{1,4},1^{10,13}] nonadeca-1(18),13(19)-diene-3,11-dione hydrochloride (4c). R_f: 0.38 (hexane : EA : EtOH (5 : 3 : 1)), yield 32.5%, m. p.: 292 °C - 295 °C. IR (KBr pellet, cm^{-1}): 3426 (NH), 2938 (CH), 1674 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 4.24 (4H, m, $NH_2^+\underline{CH_2}$), 3.68 (4H, m, NCH_2), 3.55 (4H, s, SCH_2); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 169.8 (C=O), 148.4 (C-S), 48.2 ($NHCH_2$), 44.8 (NCH_2), 33.8 (SCH_2). Anal. Calcd. for $C_{10}H_{16}N_5S_4O_2Cl$: C, 30.03; H, 3.53; N, 17.51. Found: C, 30.2; H, 3.56; N, 17.54. MS (EI) *m/z*: 364 (M^-).

4,7,26,27-Tetraaza-6,9,12,15-tetraoxa-2,19,21,25-tetrathiatricyclo-[18,5,1^{1,4},1^{17,20}]-hexaisa-1(26),20(27)-diene-3,5,16,18-tetraone (4d). R_f: 0.50 (hexane : EA : acetone (8 : 16 : 1)), yield 74.3% (from acetone : chloroform (4 : 1)), m.p.: 145 °C - 146 °C. IR (KBr pellet, cm^{-1}): 3006, 2911 (CH), 1776 (C=O). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 4.50 - 4.53 (4H, m, $COOCH_2$), 3.83 - 3.86 (4H, m, OCH_2), 3.69 (4H, s, OCH_2), 3.34 (4H, t, J = 7.4 Hz, SCH_2), 2.37 (2H, quin, J = 7.1 Hz, $CH_2CH_2CH_2$); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 167.2 (C=O), 149.9 (amide C=O), 150.3 (amide C=O), 148.1 (C-S),147.7 (C-S), 71.2, 70.8, 68.9, 68.6, 68.2, 67.9 (OCH_2), 30.5, 30.1 (SCH_2), 27.3 (CH_2). Anal. Calcd. for $C_{15}H_{18}N_4S_4O_8$: C, 35.28; H, 3.55; N, 10.98; S, 25.12. Found: C, 35.28; H, 3.56 ; N, 10.97; S, 25.25. MS (FAM) *m/z*: 510 (M^-).

7,20,31,32-Tetraaza-9,12,15,18-tetraoxa-3,5,22,24-tetrathiatricyclo[24,3,1^{4,7},1,^{20,23}]-doyriconta-1(30),4(31),23(32),26(27),28(29)-pentane-6,8,18,21-tetraone (4e). R_f: 0.21 (hexane : EA (5 : 5)), yield 56% (from acetone : chloroform (4 : 1)), IR (KBr pellet, cm^{-1}): 2887(CH), 1782 (C=O), 1517, m.p.: 120 °C - 120.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.60 (1H, m, C_6H_4), 7.35 - 7.36 (3H, m, C_6H_4), 4.54 - 4.56 (4H, m, $COOCH_2$), 4.34 (4H, s, SCH_2), 3.84 - 3.86 (4H, m, OCH_2), 3.70 (4H, s, OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.5 (C=O), 149.7 (amide C=O), 147.9 (C-S), 135.9, 131.4, 129.2, 129.0 (C_6H_4), 70.9, 68.7, 67.6 (OCH_2), 51.8 (SCH_2). Anal. Calcd. for $C_{20}H_{20}N_4S_4O_8$: C, 41.95; H, 3.52; N, 9.79; S, 22.40. Found: C, 42.95; H, 3.58; N, 9.73; S, 22.48. MS (FAM) *m/z*: 572 (M^-).

7,13,24,25-Tetraaza-10-oxa-3,5,15,17-tetrathiatricyclo [17,3,1,^{4,7} 1^{13,16}]-pentacosa-1(23),4(24), 16(25), 19(20), 21(22)-pentaene-6,8,18,21-tetraone (4f). R_f: 0.75 (hexane : EA (5 : 5)), yield 55%, m.p.: 148 °C - 149 °C. IR (KBr pellet, cm^{-1}): 2940, 2859 (CH), 1692 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.63 (1H, m, C_6H_4), 7.20 - 7.26 (3H, m, C_6H_4), 4.24 (4H, s, SCH_2), 3.93 (4H, t, J = 4.8 Hz, OCH_2), 3.44 (4H, t, J = 5.2 Hz, NCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 169.6 (C=O), 145.7 (C-S), 137.4, 128.4, 128.2, 127.6 (C_6H_4), 67.8 (OCH_2), 46.8 (NCH_2), 33.3 (SCH_2). Anal. Calcd. for $C_{16}H_{16}N_4O_3S_4$: C, 43.62; H, 3.66; N, 12.72; S, 29.11. Found: C, 43.65; H, 3.58; N, 12.70; S, 29.15. MS (FAM) *m/z*: 440 (M^-).

1,7,20,21-Tetraaza-4,14-dioxa-9,11,17,18-tetrathiapentacyclo[16,2,1,1^{7,10}]-docosa-10(22),18(21)-diene-8,20-dione (4g). R_f: 0.63 (hexane : EA :ethanol (5 : 3 : 1)), yield 57% (from acetone), m.p.: 148 °C - 150 °C. IR (KBr pellet, cm^{-1}): 2893 (CH), 1683 (C=O), 1283. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 4.05 (4H, t, J = 4.8 Hz, OCH_2CH_2N), 3.80 (4H, t, J = 6.4 Hz, SCH_2CH_2O), 3.77 (4H, t, J = 5.2 Hz, OCH_2CH_2N), 3.23 (4H, t, J = 6.8 Hz, SCH_2); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 169.7 (C=O), 146.8 (C-S), 68.8 (OCH_2CH_2N), 68.0 (SCH_2CH_2O), 47.1 (NCH_2), 31.6 (SCH_2). Anal. Calcd. for $C_{12}H_{16}N_4S_4O_4$: C, 35.28; H, 3.95; N, 13.72; S, 31.39. Found: C, 35.30; H, 3.92; N, 13.73; S, 31.38. MS (FAM) *m/z*: 408 (M^-).

X-ray data of macrocycle (4c). Compound (**4c**) was crystallized from slow evaporation of a solution of DMSO. X-ray intensity data were collected on a CAD-4 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 295 K. The unit cell dimensions were determined on the basis of 25 reflections in the range of $11.39° < \theta < 14.03°$. The data was collected by the $\omega/2\theta$ scan mode. 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.[21] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms (B_{iso} = 1.2B_{eq}).

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-726078). 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: +44-1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

1,7,20,21-Tetraaza-4,14-dioxa-9,11,17,18-tetrathiapentacyclo-[16,2,1,1^{7,10}]-docosa-10(22),18(21)-diene-8,20-dione (4g)-AgClO$_4$ complex. Macrocyclic compound (**4g**, 0.1 g, 0.25 mmol) was dissolved in THF (10 mL). $AgClO_4$ (51 mg, 0.25 mmol)-THF solution (10 mL) was added and stirred for 1 hr. White solid was collected and washed with THF and $CHCl_3$. 0.11 g (74.2%), m.p: 241 °C - 243 °C. IR (KBr pellet, cm^{-1}): 3031 (CH), 1667 (C=O), 1664 (C=O), 1133, 1085 (ClO_4). Anal. Calcd. for $C_{12}H_{16}N_4S_4O_8AgCl$: C, 23.4; H, 2.6; N, 9.1; S, 20.8. Found: C, 23.2; H, 2.6; N, 9.0; S, 20.6.

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