Inorg. Chem. 1994, 33, 2663-2667

Large-Ring S_6-Thiacyclophanes as Ditopic Macrocycles. Synthesis and Structures of 2,5,8,17,20,23-Hexathia[9.9]-*o*-cyclophane, HT[9.9]OC, 2,5,8,17,20,23-Hexathia[9.9]-*m*-cyclophane, HT[9.9]MC, and $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$

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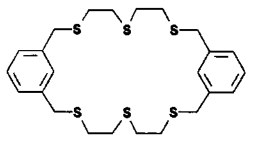
Received January 11, 1994[⊗]

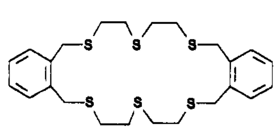
Synthesis of the large-ring thiacyclophanes HT[9.9]MC, **13**, and HT[9.9]OC, **14**, containing two *meta*- or *ortho*-xylyl groups and six sulfur atoms are reported. These compounds were obtained in good yields via a stepwise procedure, employing hydroxy and chloro intermediates, as opposed to a one-pot approach. The crystal structures of both compounds were determined. **13** crystallized in the space group $P2_1/c$ with $a = 9.397(2)$ Å, $b = 17.157(4)$ Å, $c = 9.770(2)$ Å, $\beta = 124.36(1)°$, $V = 1300(1)$ Å^3, and $Z = 2$. The structure refined to $R = 5.24\%$ and $R_w = 6.47\%$ for 920 reflections with $F_o^2 > 3\sigma(F_o^2)$. **14** crystallized in the space group $P2_1/c$ with $a = 5.032(3)$ Å, $b = 8.567(7)$ Å, $c = 29.87(2)$ Å, $\beta = 98.29(7)°$, $V = 1275(2)$ Å^3, and $Z = 2$. The structure refined to $R = 3.11\%$ and $R_w = 3.78\%$ for 1319 reflections with $F_o^2 > 3\sigma(F_o^2)$. The effect of the xylyl groups on the conformation of the macrocycles are described. HT[9.9]OC acts as a ditopic S_6 ligand binding to two $[M(CH_3CN)]^+$ (M = Cu, Ag) moieties to yield the dinuclear complexes $[Cu_2(CH_3CN)_2(HT[9.9]OC)][ClO_4]_2$ and $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$. $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$ crystallized in the space group $C2/c$ with $a = 27.257(4)$ Å, $b = 10.809(4)$ Å, $c = 14.287(4)$ Å, $\beta = 104.60(2)°$, $V = 4073(2)$ Å^3, and $Z = 4$. The structure refined to $R = 4.81\%$ and $R_w = 5.16\%$ for 1352 reflections with $F_o^2 > 3\sigma(F_o^2)$. The two Ag atoms are each coordinated by three S atoms and an CH_3CN group with the *o*-xylyl group chelating rather than bridging. The CH_3CN ligands are oriented on opposite sides of the macrocyclic ring in an *anti*-conformation.

Introduction

The chemistry of crown thioethers is centered around macrocycles containing $-SCH_2CH_2S-$ linkages which are direct analogs of the widely studied crown ethers. Ligands such as 1,4,7-trithiacyclononane (9S3) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) are commercially available, and a great deal is known about the coordination chemistry of these ligands.[1-3] From these studies, it is apparent that one of the major attributes controlling the coordinating ability of a macrocyclic thioether is the conformation or preorganization of the free ligand. With the exception of 9S3, structural data on crown thioethers reveals the tendency of the S donors to adopt exodentate orientations with respect to the macrocyclic cavity[1,2] and there is a strong preference for CS-CC and SC-CS bonds to assume *gauche* and *anti* placements, respectively.[4] These conformational requirements and the degree of donor atom preorganization enhance the coordinating ability and can be controlled somewhat by ligand design.[5] In this regard, we have shown that the *ortho*-xylyl group can have a substantial effect on ligand conformation and coordinative ability of tri- and tetrathiacyclophanes.[6-10] It should also be possible to employ these xylyl groups as rigid spacing units to favor binuclear coordination modes for hexadentate macrocycles.[11-14] This strategy has been employed effectively by Burrows et al.[15] in the synthesis of binuclear Cu(II) complexes. In this paper, we present the stepwise synthesis, spectral characterization, and X-ray structural characterization of the large ring *meta*- and *ortho*-thiacyclophanes HT[9.9]MC, **13**, and HT[9.9]OC, **14**, containing six sulfur atoms. The effect of these xylyl groups on ligand conformation, binding ability, and metal: ligand coordination stoichiometry with Cu(I) and Ag(I) is reported including the X-ray structure of the dinuclear complex $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$.



13, HT[9.9]MC



14, HT[9.9]OC

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

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0020-1669/94/1333-2663$04.50/0

Experimental Section

Since the preparations for **13** and **14** are essentially identical, only the experimental details for **13** are presented. α,α'-Dibromo-*o*-xylene, α,α'-dibromo-*m*-xylene, *o*-xylene-α,α'-dithiol, *m*-xylene-α,α'-dithiol, 2-mercaptoethanol, thionyl chloride, cesium carbonate, and all deuterated solvents were purchased from Aldrich and used as received. $[Cu(CH_3CN)_4][ClO_4]$ was prepared by the literature method.[27] All reactions were conducted under an atmosphere of N_2 using standard Schlenk techniques, and all solvents were degassed prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.1 and 75.4 MHz, respectively, on a Bruker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Canadian Microanalytical Services, Delta, British Columbia, Canada.

Preparation of *m*-Xylylenebis(1-hydroxy-3-thiapropane), 3. 2-Mercaptoethanol (6.92 g, 0.0885 mol) was added to anhydrous ethanol (250 mL) in which Na metal (2.04 g, 0.0885 mol) had been dissolved and this solution stirred for 1 h. α,α'-Dibromo-*m*-xylene (11.7 g, 0.0443 mol) dissolved in anhydrous ethanol (250 mL) was added dropwise over 1 h while the solution was maintained at reflux. The reaction mixture was then refluxed for a further 4 h, cooled to room temperature, and filtered. The solvent was removed in vacuo yielding an orange-yellow oil which was extracted with diethyl ether (400 mL). The ether extracts were filtered and the solvent removed to yield a colorless oil. Yield: 8.71 g (76%). IR (neat): ν(OH) 3375 cm^{-1} (vs, br). ^1H NMR ($CDCl_3$): δ 7.18 (m, 4H, aromatic), 3.67 (s, 4H, benzylic), 3.58 (q, 4H, CH_2O), 3.13 (t, 2H, OH), 2.55 (t, 4H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.33, 129.08, 128.60, 127.42 (aromatic), 60.42 (CH_2O), 35.61 (benzylic), 33.71 (CH_2S). Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.78; H, 7.02; S, 24.81. Found: C, 55.02, H, 6.90, S, 24.45. Data for **4** are as follows. Yield: 90%. IR (neat): ν(OH) 3380 cm^{-1} (vs, br). ^1H NMR ($CDCl_3$): δ 7.23 (m, 4H, aromatic), 3.90 (s, 4H, benzylic), 3.69 (q, 4H, CH_2O), 2.86 (t, 2H, OH), 2.67 (t, 4H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.95, 130.50, 127.42 (aromatic), 60.61 (CH_2O), 34.82 (benzylic), 33.29 (CH_2S). Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.78; H, 7.02; S, 24.81. Found: C, 55.76, H, 7.07, S, 25.00.

Preparation of *m*-Xylylenebis(1-chloro-3-thiapropane), 5. *Extreme Caution! This compound is a severe vesicant!* The diol, **3**, prepared as described above (3.29 g, 0.0127 mol) was dissolved in CH_2Cl_2 (15 mL). Thionyl chloride (3.64 g, 0.0306 mol; 20% excess) was added slowly via syringe and the mixture stirred for 1 h. A saturated solution of $NaHCO_3$ (30 mL) was added, and this mixture was stirred vigorously for a further 1 h. The two-phase reaction mixture was then filtered through phase separation paper and the organic layer dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo yielding an orange oil. Due to the dangerous nature of this compound, no further purification procedures or elemental analyses were attempted. From the ^1H NMR spectrum, it was estimated that the material prepared in this manner was >98% pure. Yield: 2.89 g (76%). ^1H NMR ($CDCl_3$): δ 7.27 (m, 4H, aromatic), 3.75 (s, 4H, benzylic), 3.53 (t, 4H, CH_2Cl), 2.76 (t, 4H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.33, 129.17, 128.92, 127.77 (aromatic), 42.86 (CH_2Cl), 36.33 (benzylic), 33.41 (SCH_2). Data for **6** are as follows. Yield: 88%. ^1H NMR ($CDCl_3$): δ 7.26 (m, 4H, aromatic), 3.95 (s, 4H, benzylic), 3.56 (t, 4H, CH_2Cl), 2.82 (t, 4H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.76, 130.65, 127.72 (aromatic), 43.01 (CH_2Cl), 33.80 (benzylic), 33.29 (SCH_2).

Preparation of *m*-Xylylenebis(1-hydroxy-3,6-dithiahexane), 7. 2-Mercaptoethanol (0.78 g, 0.010 mol) was added to anhydrous ethanol (250 mL) in which Na metal (0.78 g, 0.010 mol) had been dissolved and this solution stirred for 1 h. **5** (1.48 g, 0.0050 mol) dissolved in anhydrous ethanol (50 mL) was added dropwise over 2 h while the solution was maintained at reflux. The reaction mixture was then refluxed for a further 2 h, cooled to room temperature, and filtered. The solvent was removed in vacuo yielding a thick yellow oil which was extracted with diethyl ether (250 mL). The ether extracts were filtered and the solvent removed to yield a colorless oil. Yield: 1.32 g (70%). IR (neat): ν(OH) 3390 cm^{-1} (vs, br). ^1H NMR ($CDCl_3$): δ 7.21 (m, 4H, aromatic), 3.72 (s, 4H, benzylic), 3.65 (q, 4H, CH_2O), 2.63 (m, 12H, SCH_2), 2.54 (t, 2H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.36, 129.15, 128.69, 127.57 (aromatic), 60.59 (CH_2O), 36.15 (benzylic), 35.13, 31.54, 31.39 (SCH_2). Anal. Calcd for $C_{16}H_{24}O_2S_4$: C, 55.78; H, 7.02; S, 24.81. Found: C, 55.76; H, 7.07, S, 25.00. Data for **8** are as follows. Yield: 84%. IR (neat): ν(OH) 3390 cm^{-1} (vs, br). ^1H NMR ($CDCl_3$): δ 7.23 (m, 4H, aromatic), 3.94 (s, 4H, benzylic), 3.70 (q, 4H, CH_2O), 2.70 (m, 12H, SCH_2), 2.33 (t, 2H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.03, 130.62, 127.51 (aromatic), 60.61 (CH_2O), 35.33 (benzylic), 33.80, 32.18, 31.78 (SCH_2). Anal. Calcd for $C_{16}H_{26}O_2S_4$: C, 55.78; H, 7.02; S, 24.81. Found: C, 55.76, H, 7.07, S, 25.00.

Preparation of *m*-Xylylenebis(1-chloro-3,6-dithiahexane), 9. *Extreme Caution. This compound is a severe vesicant!* The diol, **7**, prepared as described above (17.74 g, 0.069 mol) was dissolved in CH_2Cl_2 (30 mL). Thionyl chloride (19.60 g, 0.165 mol; 20% excess) was added slowly via syringe and the mixture stirred for 1 h. A saturated solution of $NaHCO_3$ (30 mL) was added, and this mixture was stirred vigorously for a further 1 h. The two-phase reaction mixture was then filtered through phase separation paper and the organic layer dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo yielding an orange oil. Due to the dangerous nature of this compound, no further purification procedures or elemental analyses were attempted. From the ^1H NMR spectrum, it was estimated that the material prepared in this manner was >98% pure. Yield: 18.0 g (88%). ^1H NMR ($CDCl_3$): δ 7.26 (m, 4H, aromatic), 3.95 (s, 4H, benzylic), 3.56 (t, 4H, CH_2Cl), 2.82 (t, 4H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.76, 130.65, 127.72 (aromatic), 43.01 (CH_2Cl), 33.80 (benzylic), 33.29 (SCH_2). Data for **10** are as follows. Yield: 80%. ^1H NMR ($CDCl_3$): δ 7.26 (m, 4H, aromatic), 3.94 (s, 4H, benzylic), 3.57 (t, 4H, CH_2Cl), 2.67–2.85 (m, 12H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.98, 130.63, 127.54 (aromatic), 43.02 (CH_2Cl), 34.22 (benzylic), 33.77, 32.32, 31.93 (SCH_2).

Preparation of 2,5,8,17,20,23-Hexathia[9.9]-*m*-cyclophane, HT[9.9]MC, 13. Cs_2CO_3 (3.83 g, 11.74 mmol) was suspended in DMF (700 mL) under an atmosphere of N_2(g). To this mixture was added a solution of **9** (1.784 g, 5.87 mmol) and *m*-xylene-α,α'-dithiol, **11** (1.00 g, 5.87 mmol), in DMF (125 mL). The addition was over a period of 20 h with the reaction temperature maintained at 55–60 °C. After addition, the mixture was cooled to room temperature and stirred for a further 12 h. The DMF was removed under vacuum and the resulting residue extracted with CH_2Cl_2 (150 mL). The CH_2Cl_2 solution was then washed with 0.1 M NaOH (2 × 50 mL) and the organic fractions dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was recrystallized from acetone. Yield: 1.87 g (81%). Mp: 142–142.5 °C. ^1H NMR ($CDCl_3$): δ 7.19–7.33 (m, 8H, aromatic), 3.90 (s, 8H, benzylic), 2.85 (s, 16H, SCH_2CH_2S). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.72, 130.14, 127.83 (aromatic), 38.33 (benzylic), 37.12 (SCH_2CH_2S). Anal. Calcd for $C_{24}H_{32}S_6$: C, 56.21; H, 6.29; S, 37.51. Found: C, 56.00, H, 6.09, S, 38.10. Data for **14** are as follows. Yield: 92%. Mp: 152–153 °C. ^1H NMR ($CDCl_3$): δ 7.29 (m, 8H, aromatic), 3.94 (s, 8H, benzylic), 2.76 (m, 16H, SCH_2CH_2S). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.93, 130.38, 127.65 (aromatic), 33.85 (benzylic), 32.59, 32.39 (SCH_2CH_2S). Anal. Calcd for $C_{24}H_{32}S_6$: C, 56.21; H, 6.29; S, 37.51. Found: C, 55.91, H, 6.05, S, 38.16.

Preparation of $[Cu_2(HT[9.9]OC)(CH_3CN)_2][ClO_4]_2$. *Caution! Perchlorate salts with organic ligands are potentially explosive.* $[Cu(CH_3CN)_4][ClO_4]$ (0.128 g, 0.390 mmol) was dissolved in CH_3CN (15 mL). The ligand, HT[9.9]OC, **14** (0.100 g, 0.195 mmol), dissolved in CH_2Cl_2 (15 mL) was then added via syringe and this colorless mixture stirred at room temperature for 12 h. The solvent was then removed in vacuo, with the white residue redissolved in CH_3CN (10 mL). Diffusion of diethyl ether into this solution gave $[Cu_2(\mathbf{14})(CH_3CN)_2][ClO_4]_2$ as a white microcrystalline solid. Yield: 0.147 g (90%). ^1H NMR (CD_3CN): δ (ppm) 7.34 (m, 8H, aromatic), 3.98 (s, 8H, benzylic), 2.85 (m, 16H, SCH_2CH_2S). $^{13}C\{^1H\}$ NMR (CD_3CN): δ (ppm) 135.98, 132.26, 129.30 (aromatic), 35.72, 34.58, 34.43 (aliphatic). Anal. Calcd for $C_{28}H_{38}Cl_2Cu_2N_2O_8S_6$: C, 36.51; H, 4.17. Found: C, 36.30, H, 4.09.

Preparation of $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$. $AgBF_4$ (0.056 g, 0.288 mmol) and HT[9.9]OC, **14** (0.074 g, 0.144 mmol), were dissolved in CH_3CN (15 mL) and this pale yellow mixture was stirred at room temperature for 12 h. The volume of solvent was reduced by half, and after standing for 12 h $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$ crystallized as pale golden prisms suitable for single-crystal X-ray diffraction studies. Yield: 0.138 g (90%) as acetonitrile disolvate. ^1H NMR (CD_3CN): δ (ppm) 7.31 (m, 8H, aromatic), 3.89 (s, 8H, benzylic), 2.83 (m, 16H, SCH_2CH_2S). $^{13}C\{^1H\}$ NMR (CD_3CN): δ (ppm) 135.99, 132.00, 128.86 (aromatic), 34.71, 33.43, 32.50 (aliphatic). Anal. Calcd for $C_{32}H_{44}Ag_2B_2F_8N_4S_6$: C, 36.03; H, 4.17. Found: C, 35.98, H, 4.14.

General X-ray Crystallography. Diffraction experiments were performed on a four-circle Rigaku AFC6S diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell constants and orientation matrices for data collection were obtained from 25 centered reflections (15° < 2θ < 35°). Machine parameters, crystal data, and

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Table 1. Summary of Crystallographic Data for HT[9.9]MC, 13, HT[9.9]OC, 14, and $[Ag_2(CH_3CN)_2(HT[9.9[OC)][BF_4]_2$

	compound		
	HT[9.9]MC, **13**	HT[9.9]OC, **14**	$[Ag_2(CH_3CN)_2$-$(HT[9.9[OC)][BF_4]_2$
formula	$C_{24}H_{32}S_6(m)$	$C_{24}H_{32}S_6(o)$	$C_{28}H_{38}Ag_2B_2F_8N_2S_6$
fw	512.96	512.96	984.40
a, Å	9.397(2)	5.032(3)	27.257(4)
b, Å	17.157(4)	8.567(7)	10.809(4)
c, Å	9.770(2)	29.87(2)	14.287(4)
β, deg	124.36(1)	98.29(7)	104.60(2)
V, Å^3	1300(1)	1275(2)	4073(2)
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
Z	2	2	4
ρ, g/cm^3	1.31	1.33	1.49
λ, Å	0.71069	0.71069	0.71069
μ/cm^{-1}	5.15	5.15	13.18
T, °C	24	24	24
$R(F_o)$,[a] %	5.24	3.11	4.81
$R_w(F_o)$,[a] %	6.47	3.78	5.16

[a] $R = \sum \| F_o| - |F_c| / \sum |F_o\|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$, and $w = 1/\sigma^2(F)$.

Table 2. Selected Positional Parameters and B(eq) Values (Å^2) for HT[9.9]MC, 13

atom	x	y	z	B(eq)
S(1)	0.4752(2)	0.0646(1)	0.1836(3)	5.7(1)
S(2)	0.4052(3)	−0.1730(1)	0.3110(3)	6.9(1)
S(3)	0.8753(3)	−0.2854(1)	0.7337(3)	5.7(1)
C(7)	0.7011(8)	0.0823(4)	0.3446(9)	5.3(3)
C(8)	0.4572(8)	−0.0399(4)	0.1835(8)	5.3(3)
C(9)	0.460(1)	−0.0721(4)	0.328(1)	6.5(4)
C(10)	0.658(2)	−0.2234(6)	0.476(2)	11.6(6)
C(11)	0.627(2)	−0.2266(6)	0.577(2)	11.0(6)
C(12)	0.991(1)	−0.2089(4)	0.8844(9)	5.9(3)

Table 3. Selected Bonding Parameters for HT[9.9]MC, 13

	Distances (Å)		
S(1)–C(7)	1.818(7)	S(1)–C(8)	1.801(8)
S(2)–C(9)	1.787(8)	S(2)–C(10)	2.16(1)
S(3)–C(11)	2.19(1)	S(3)–C(12)	1.807(7)
C(6)–C(7)	1.513(9)	C(8)–C(9)	1.498(10)
C(10)–C(11)	1.18(1)	C(12)–C(2)′	1.507(9)
	Angles (deg)		
C(7)–S(1)–C(8)	103.3(3)	C(9)–S(2)–C(10)	100.4(4)
C(11)–S(3)–C(12)	98.5(4)	C(1)–C(2)–C(12)′	121.6(7)
C(3)–C(2)–C(12)′	120.4(7)	C(1)–C(6)–C(7)	120.4(6)
C(5)–C(6)–C(7)	120.8(6)	C(6)–C(7)–S(1)	114.5(5)
S(1)–C(8)–C(9)	114.5(5)	C(8)–C(9)–S(2)	114.9(6)
S(2)–C(10)–C(11)	87(1)	C(10)–C(11)–S(3)	86(1)
S(3)–C(12)–C(2)′	115.9(5)		

Table 4. Selected Positional Parameters and B(eq) Values (Å^2) for HT[9.9]OC, 14

atom	x	y	z	B(eq)
S(1)	0.4490(2)	0.1350(1)	0.44538(2)	3.9(1)
S(2)	0.9371(2)	0.37605(9)	0.56044(3)	4.2(1)
S(3)	0.2893(1)	0.54772(9)	0.32864(3)	4.2(1)
C(7)	0.6141(6)	0.2291(4)	0.40225(9)	4.0(2)
C(8)	0.5502(6)	0.2610(4)	0.49338(9)	3.2(2)
C(9)	0.8445(6)	0.2603(4)	0.5098(1)	3.2(2)
C(10)	0.8100(7)	0.2505(4)	0.6009(1)	4.2(3)
C(11)	0.9032(7)	0.2999(4)	0.6495(1)	3.2(2)
C(12)	0.1343(6)	0.3727(3)	0.3473(1)	4.2(3)

Table 5. Selected Bonding Parameters for HT[9.9]OC, 14

	Distances (Å)		
S(1)–C(7)	1.819(3)	S(1)–C(8)	1.809(3)
S(2)–C(9)	1.813(3)	S(2)–C(10)	1.803(3)
S(3)–C(11)	1.804(3)	S(3)–C(12)	1.814(3)
C(6)–C(7)	1.504(4)	C(8)–C(9)	1.491(4)
C(10)–C(11)	1.520(4)	C(12)–C(1)′	1.502(4)
	Angles (deg)		
C(7)–S(1)–C(8)	101.0(1)	C(9)–S(2)–C(10)	99.2(1)
C(11)–S(3)–C(12)	102.5(1)	C(1)–C(6)–C(7)	122.1(2)
C(2)–C(1)–C(12)′	119.6(2)	C(6)–C(1)–C(12)′	121.6(2)
C(5)–C(6)–C(7)	119.2(3)	C(6)–C(7)–S(1)	109.5(2)
S(1)–C(8)–C(9)	114.3(2)	C(8)–C(9)–S(2)	113.3(2)
S(2)–C(10)–C(11)	112.5(2)	C(10)–C(11)–S(3)	116.1(2)
S(3)–C(12)–C(1)′	108.6(2)		

data collection parameters are summarized in Table 1. The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collections. The intensity data were collected using the ω–2θ scan technique, in four shells ($2\theta < 30, 40, 45,$ and $50°$). Empirical absorption coefficients were small, and thus, no absorption corrections were applied to the data. The data were processed using the TEXSAN software package running on a VAX 3520 computer.[28] Refinements were carried out by using full-matrix least-squares techniques on F by minimizing the function $w(|F_o|-|F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[29] and anomalous dispersion terms[30,31] were taken from the usual sources. Fixed H-atom contributions were included with C–H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameter of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued.

Structures of 13, 14, and $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$. Colorless crystals of **13** and **14** and golden yellow crystals of $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$ were grown by slow evaporation of acetone, benzene, and acetonitrile solutions, respectively. Statistical analysis of intensity distributions and a determination of observed extinctions were consistent with the space group $P2_1/c$ for both **13** and **14** and the space group $C2/c$ for $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$. These were confirmed by successful solution refinements. A total of 1282 reflections were collected, and 920 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of **13**, while a total of 1382 reflections were collected and 1319 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of **14** and a total of 3796 reflections were collected and 1352 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$. The positions of the silver and sulfur atoms were determined by direct methods from the initial E-maps with highest figure of merit. The remaining non-hydrogen atoms were located from difference Fourier map calculations. In the final cycles of refinement for **13** and **14**, the sulfur atoms and carbon atoms were all assigned anisotropic thermal parameters. This resulted in $R = 0.0524$ and $R_w = 0.0647$ for **13** and $R = 0.0311$ and $R_w = 0.0378$ for **14** at final convergence. In the final cycles of refinement for $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$, the silver, sulfur, nitrogen, boron, and fluorine atoms were all assigned anisotropic thermal parameters, while the carbon atoms were assigned isotropic thermal parameters. This resulted in $R = 0.0481$ and $R_w = 0.0516$ for $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$ at final convergence. The Δ/σ value for any parameter in the final cycles was less than 0.001 and final difference Fourier map calculations showed no peaks of chemical significance. Selected atomic positional parameters are summarized in Tables 2, 4, and 7, and selected bond distances and angles are summarized in Tables 3, 5, and 8. Full listings of atomic positional parameters (Tables S-II, S-VI, and S-X), nonessential bonding parameters (Tables S-III, S-VII, and S-XI), thermal parameters (Tables S-IV, S-VIII, and S-XII), and hydrogen atom parameters (Table S-V, S-IX, and S-XIII) are deposited as supplementary material.

Results

The hexathiacyclophanes **13** and **14** were obtained in good yields (>60% overall) by employing a five-step procedure. Scheme 1 outlines these synthetic steps using the *meta* compounds as examples; the route is identical for the *ortho* versions as indicated. In a typical preparation, the reaction of α,α'-dibromoxylenes, **1** and **2**, with 2 equiv of 2-mercaptoethanol in refluxing sodium ethoxide solution yielded the dihydroxy intermediates, **3** and **4**.

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(28) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(29) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(30) Ibers, J. A.; Hamilton, H. A. *Acta Crystallogr.* **1974**, *17*, 781.

(31) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

Table 6. Comparison of Torsional Angles for HT[9.9]MC, 13, and HT[9.9]OC, 14

torsional angle[a]	HT[9.9]OC, **14**	HT[9.9]MC, **13**
C(1)–C(6)–C(7)–S(1)	87.9(3)	93.1(6)
C(6)–C(7)–S(1)–C(8)	−165.6(2)	84.9(6)
C(7)–S(1)–C(8)–C(9)	−65.0(3)	74.3(6)
S(1)–C(8)–C(9)–S(2)	−175.7(1)	169.6(4)
C(8)–C(9)–S(2)–C(10)	72.5(2)	103.1(6)
C(9)–S(2)–C(10)–C(11)	169.2(2)	100.1(7)
S(2)–C(10)–C(11)–S(3)	82.9(1)	176.0(3)
C(10)–C(11)–S(3)–C(12)	−85.2(3)	110.1(7)
C(11)–S(3)–C(12)–C(1)′ [b]	180.0(2)	
C(11)–S(3)–C(12)–C(2)′ [c]		69.9(6)
S(3)–C(12)–C(1)′–C(6)′ [b]	88.8(3)	
S(3)–C(12)–C(2)′–C(1)′ [c]		−62.3(8)
C(12)′–C(1)–C(6)–C(7)[b]	1.25(3)	
C(12)′–C(2)–C(1)–C(6)[c]		178.4(6)
C(2)–C(1)–C(6)–C(7)[c]		−178.3(6)

[a] Sign is positive for a clockwise rotation of 1 to 4 viewed down the 2–3 bond. [b] A torsional angle associated with *ortho* substitution of the aromatic ring. [c] A torsional angle associated with *meta* substitution of the aromatic ring.

Table 7. Selected Positional Parameters and B(eq) Values (Å^2) for $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$

atom	x	y	z	B(eq)
Ag	0.29080(4)	0.0714(1)	0.47986(8)	3.80(5)
S(1)	0.3203(1)	−0.0205(3)	0.3347(3)	3.4(2)
S(2)	0.2456(1)	0.2394(3)	0.3587(3)	3.3(2)
S(3)	0.3635(1)	0.1367(3)	0.6140(2)	2.9(2)
N(1)	0.2313(5)	−0.074(1)	0.4858(9)	5.4(7)
C(7)	0.3849(5)	0.038(1)	0.3518(9)	3.5(3)
C(8)	0.2838(5)	0.074(1)	0.2386(9)	3.9(3)
C(9)	0.2760(5)	0.209(1)	0.262(1)	3.4(3)
C(10)	0.1828(5)	0.178(1)	0.305(1)	3.4(3)
C(11)	0.3525(5)	0.302(1)	0.630(1)	3.7(3)
C(12)	0.4162(5)	0.144(1)	0.5549(8)	2.7(3)
C(13)	0.1958(7)	−0.123(2)	0.473(1)	5.2(4)
C(14)	0.1480(8)	−0.192(2)	0.457(1)	8.1(5)

Table 8. Selected Bonding Parameters for $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF]_2$

	Distances (Å)		
Ag–S(1)	2.603(4)	Ag–S(2)	2.595(4)
Ag–S(3)	2.487(4)	Ag–N(1)	2.27(1)
S(1)–C(7)	1.83(1)	S(1)–C(8)	1.80(1)
S(2)–C(9)	1.82(1)	S(2)–C(10)	1.82(1)
S(3)–C(11)	1.84(1)	S(3)–C(12)	1.84(1)
N(1)–C(13)	1.08(2)	C(1)–C(12)	1.49(2)
C(6)–C(7)	1.51(2)	C(8)–C(9)	1.52(2)
C(10)–C(11)	1.51(2)	C(13)–C(14)	1.47(2)
	Angle (deg)		
S(1)–Ag–S(2)	85.7(1)	S(1)–Ag–S(3)	112.1(1)
S(1)–Ag–N(1)	97.6(3)	S(2)–Ag–S(3)	117.9(1)
S(2)–Ag–N(1)	106.5(3)	S(3)–Ag–N(1)	127.2(3)
C(7)–S(1)–C(8)	103.6(6)	C(9)–S(2)–C(10)	100.0(6)
C(11)–S(3)–C(12)	101.0(6)	C(6)–C(1)–C(12)	123(1)
C(2)–C(1)–C(12)	116(1)	C(1)–C(6)–C(7)	124(1)
C(5)–C(6)–C(7)	118(1)	S(1)–C(7)–C(6)	107.7(9)
S(1)–C(8)–C(9)	117.5(9)	S(2)–C(9)–C(8)	117(1)
S(2)–C(10)–C(11)	111.6(9)	S(3)–C(11)–C(10)	112(1)
S(3)–C(12)–C(1)	111.8(9)	N(1)–C(13)–C(14)	178(2)

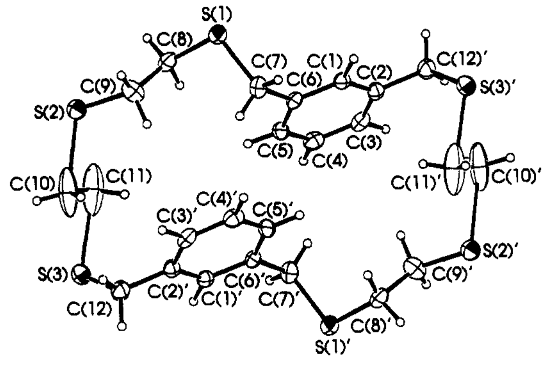
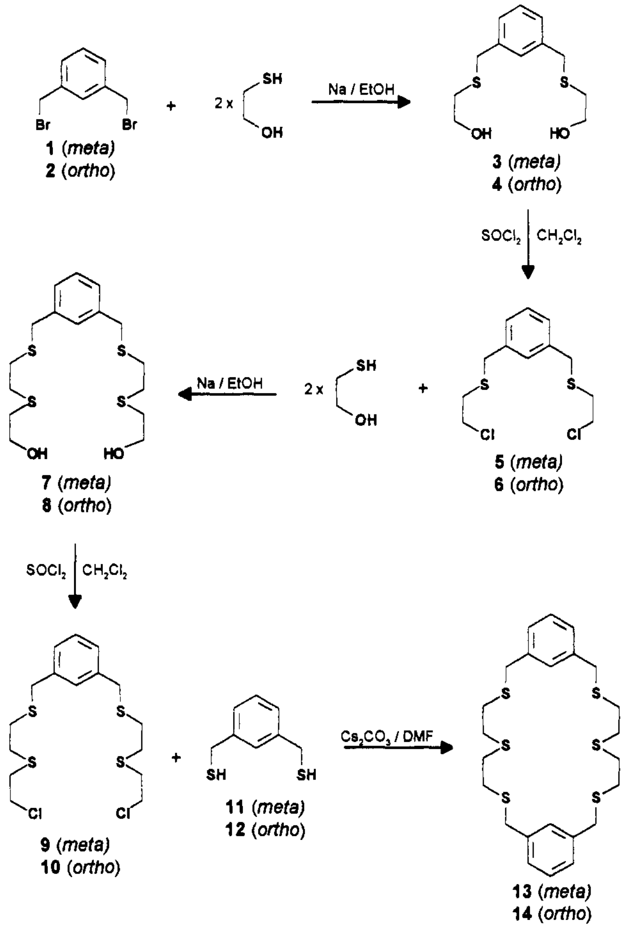


Figure 1. Perspective ORTEP diagram of compound **13** showing the atom-numbering scheme. Thermal ellipsoids of 30% are shown.

Scheme 1



The dihydroxy intermediates were then treated with thionyl chloride to give the dichloro products, **5** and **6**. The dichloro derivatives, **5** and **6**, undergo further reaction with 2 more equivalents of 2-mercaptoethanol to yield the dihydroxy intermediates, **7** and **8**, and then again with thionyl chloride to yield **9** and **10**. The cyclization reaction between **9** or **10** and the appropriate xylene-α,α'-dithiol, **11** or **12**, then proceeded by employing Kellogg's Cs^+-mediated method,[16] to yield the macrocycles **13** and **14**.

A perspective ORTEP drawing of **13** is shown in Figure 1. This hexadentate macrocycle containing the *meta*-xylyl units shows all six sulfur atoms to have adopted an exodentate orientation and all C–S bond placements to be *gauche*. The overall conformation is rather unusual as the macrocycle appears to curl in on itself and with no visibly defined macrocyclic cavity. A perspective ORTEP drawing of **14** is shown in Figure 2. The structure shows this macrocycle adopts a much more flattened conformation with an opened 22-membered cavity. For **14**, only four of the six sulfur atoms were oriented in an exodentate manner and four of eight CC–SC linkages assumed *gauche* placements. It should be noted that, with its much studied coordination chemistry, 18S6 also shows four of six sulfur atoms to be exodentate in a similar free ligand structure.[4]

Reaction of **14** with 2 equiv of $[Cu(CH_3CN)_4][ClO_4]$ or $AgBF_4$ in acetonitrile yielded products which were found by elemental analysis to contain two metal atoms bound to the macrocycle ligand: $[Cu_2(CH_3CN)_2(HT[9.9]OC)][ClO_4]_2$ and $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$. NMR spectroscopy indicated that these complexes are symmetrical, and the most likely

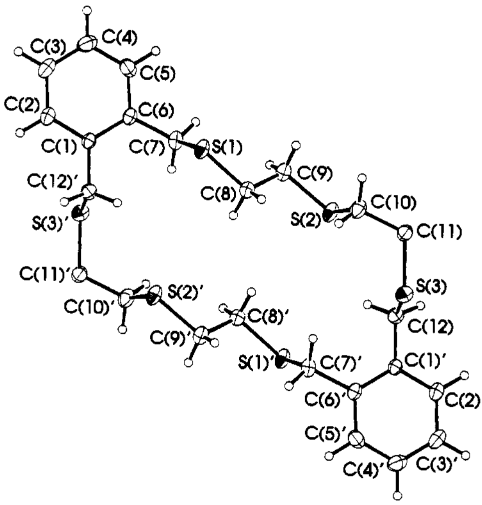


Figure 2. Perspective ORTEP diagram of compound **14** showing the atom-numbering scheme. Thermal ellipsoids of 30% are shown.

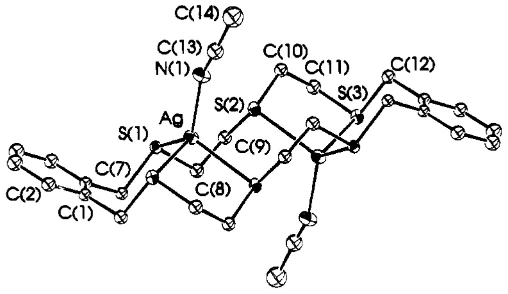


Figure 3. Perspective ORTEP diagram of $[Ag_2(CH_3CN)_2(HT[9.9]OC)]^{2+}$ showing the atom-numbering scheme. Thermal ellipsoids of 30% are shown.

structure is one in which the macrocycle assumes a conformation that places the two metal binding sites on opposite sides of the ring, an *anti* conformation, analogous to that found by X-ray crystallography for the structure of $[Cu_2(18S6)(CH_3CN)_2]^{2+}$ [23] (18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane). This was confirmed by the X-ray structure of $[Ag_2(CH_3CN)_2(HT[9.9]OC)][BF_4]_2$. A perspective ORTEP drawing of the dication $[Ag_2(CH_3CN)_2(HT[9.9]OC)]^{2+}$ is shown in Figure 3. The molecule sits on a crystallographic center of symmetry so the coordination sites are identical. The Ag^+ ion is coordinated by three S atoms of the macrocycle with Ag–S(1) = 2.603(4), Ag–S(2) = 2.595(4), and Ag–S(3) = 2.487(4) Å and an acetonitrile N atom with Ag–N(1) = 2.27(1) Å. Coordination results in the formation of two chelate rings and a bridging link to the other binding site. One chelate ring is a simple five-membered ring with an ethylene backbone and S(1)–Ag–S(2) = 85.7(1)°, while the other is seven-membered resulting from the coordination of both xylyl S atoms and has a much larger bite angle, S(1)–Ag–S(3) = 112.1(1)°. This leaves the other pair of ethylene chains to act as the link between the coordination sites.

The analogous reactions with **13** yielded only products of very low solubility which exhibited complex NMR spectra. There are a number of examples known of unusual polymeric and oligomeric structures of Cu(I) and Ag(I) with crown thioethers resulting from the exodentate coordination of a metal or bridging between metals employing exodentate sulfur atoms.[24-26] It is likely that the curled conformation of **13** favors one or more of these coordination modes producing oligomeric or polymeric material.

Discussion

This stepwise synthetic route, employing hydroxy and chloro intermediates, was used instead of the one-pot approach employed by others in the syntheses of large-ring thioether macrocycles.[17,18,20] Although this synthetic route is multistep and involves the use of dangerous chloro intermediates, it is the method of choice for the syntheses of these macrocycles. The one-pot approach, a 2 + 2 cyclization, has been employed for **14** but gave the desired product in only 4% yield with the major product being the 1 + 1 cyclization product TT[9]OC.[19] The attempted preparation of **13** by this one-pot route gave only the 1 + 1 cyclization product, TT[9]MC.[19] Kellogg has recently reported a synthetic method employing a B/Al–alkoxide couple which gives 2 + 2 cyclization products, in good yield, for the reaction of bis(2-mercaptoethyl sulfide) with 2-substituted 1,3-dihalopropane derivatives.[20] However, attempts by Kellogg to apply this technique to the preparations of **13** and **14**, via the cyclization of bis(2-mercaptoethyl sulfide) and *meta* or *ortho* α,α'-dibromoxylene, gave only the 1 + 1 cyclization products in *ca.* 85% yield.

The effect of incorporating an *ortho*- or *meta*-xylyl fragment into the macrocyclic framework is very different. The general observations are that incorporation of a *meta*-xylyl fragment does not significantly alter the preferred orientations of individual bond placements, but incorporation of an *ortho*-xylyl fragment introduces a corner piece into the framework and therefore necessitates some conformational reorganization on the part of the macrocycle.

The purpose of introducing xylyl fragments into an S_6 macrocycle was to compartmentalize the six thioether donors into two components of S_3 for facial coordination to separate metal centers. It appears from these preliminary results that this strategy was only partly successful. For HT[9.9]MC, incorporation of the *meta*-xylyl unit results in a very rigid conformation for the macrocycle which favors exodentate coordination and aggregation upon interaction with metal ions. For HT[9.9]OC the *ortho*-xylyl group allows for a more open and flexible conformation for the macrocycle, and this results in this molecule acting as a ditopic ligand as demonstrated by the formation of the dinuclear complexes $[M_2(CH_3CN)_2(HT[9.9]OC)]^{2+}$ (M = Cu, Ag). Although, the *o*-xylyl units do not act as the spacing units between the binding sites as designed, but rather chelate directly to a single metal, the formation of dinuclear complexes is favored over encapsulation of a single metal ion which is the basic problem in using simple crown thioethers such as 18S6 as ditopic ligands.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research. G.H.K.S. is grateful for the awarding of an NSERC postgraduate scholarship. H. A. Jenkins is thanked for the synthesis of HT[9.9]OC.

Supplementary Material Available: Listings of crystallographic data collection parameters, positional parameters, thermal parameters, nonessential bonding parameters, and hydrogen atom parameters (11 pages). Ordering information is given on any current masthead page.