Ditopic Crown Thioethers. Synthesis and Structures of *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$, *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$, and *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$ (L = 2,5,8,17,20,23-Hexathia[9](1,2)[9](4,5)cyclophane)

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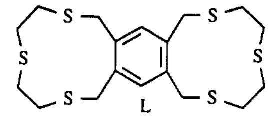
The thiacyclophane 2,5,8,17,20,23-hexathia[9](1,2)[9](4,5)cyclophane (L) is a crown thioether containing two S_3 coordination sites separated by an aromatic spacing unit. The template reaction of 2 equiv of $[Me_4N]_2[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]$ with 1 equiv of tetrabromodurene produces $[Mo_2(CO)_6(L)]$. Displacement of L with $[Me_4N]_2[SCH_2CH_2SCH_2CH_2S]$ regenerates $[Me_4N]_2[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]$ and gives L in 20% overall yield. The reaction of L with 2 equiv of $[Cu(CH_3CN)_4][ClO_4]$ or $AgBF_4$, in the presence of ancillary phosphine ligands, yields binuclear complexes. Employing simple monodentate phosphines such as PPh_2Me or PPh_3, the complexes have an anti arrangement, with the metal centers on opposite sides of the aromatic ring, while the use of the bidentate phosphine $Ph_2PCH_2CH_2PPh_2$ gives a syn arrangement, with metal ions on the same side of the aromatic ring. All complexes were characterized by ^1H and $^{31}P\{^1H\}$ NMR, and X-ray crystal structures were obtained for *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$ (**1a**), *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$ (**2b**), and *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$ (**3**). Complex **1a**, $C_{45}H_{53}Cu_2Cl_5O_8P_2S_6$, crystallized as a $CHCl_3$ solvate in a triclinic crystal system, space group $P\bar{1}$ with $a = 15.192(7)$ Å, $b = 16.943(8)$ Å, $c = 11.725(6)$ Å, $\alpha = 96.86(5)°$, $\beta = 112.34(4)°$, $\gamma = 92.73(5)°$, $V = 2757(2)$ Å^3, and $Z = 2$. The structure refined to $R = 7.94\%$ and $R_w = 7.63\%$ for 2727 reflections with $F_o^2 > 3\sigma(F_o^2)$. The complex shows an anti conformation of the $CuPS_3$ sites with Cu···Cu′ separations of 8.502(4) and 8.528(4) Å for the two independent molecules. Complex **2b**, $C_{54}H_{56}Ag_2B_2F_8P_2S_6$, crystallized in a triclinic crystal system, space group $P\bar{1}$ with $a = 11.402(6)$ Å, $b = 11.713(5)$ Å, $c = 10.986(3)$ Å, $\alpha = 99.76(3)°$, $\beta = 96.54(3)°$, $\gamma = 86.86(4)°$, $V = 1436(1)$ Å^3, and $Z = 1$. The structure refined to $R = 6.09\%$ and $R_w = 6.68\%$ for 2949 reflections with $F_o^2 > 3\sigma(F_o^2)$. The complex shows an anti conformation of the two $AgPS_3$ sites with a Ag···Ag′ separation of 7.617(4) Å. Complex **3**, $C_{44}H_{50}Cu_2F_{12}P_4S_6$, crystallized in a monoclinic crystal system, space group $C2/c$ with $a = 26.33(2)$ Å, $b = 12.658(2)$ Å, $c = 17.771(9)$ Å, $\beta = 117.74(4)°$, $V = 5241(5)$ Å^3, and $Z = 4$. The structure refined to $R = 7.42\%$ and $R_w = 7.45\%$ for 1282 reflections with $F_o^2 > 3\sigma(F_o^2)$. The complex shows a syn conformation of the two $CuPS_3$ sites with $Ph_2PCH_2CH_2PPh_2$ bridging the two Cu atoms and a Cu···Cu′ separation of 5.886(7) Å.

Introduction

Crown thioether ligands containing six or more S donor atoms have the potential to coordinate two metal centers[1,2] thereby acting as ditopic ligands. There are, however, major problems associated with preparing binuclear complexes employing this type of flexible, macrocyclic ligand. (1) A macrocycle with a large central cavity will often prefer to encapsulate a single metal ion[1,2] rather than coordinate two metal centers. This competition between mononuclear and binuclear complex reduces the possibility of systematically preparing a series of complexes containing two metals. (2) Even if binuclear complexes are easily attainable, there is often little control over the relative orientation of the metal atoms. The known structures of binuclear complexes of crown thioethers ($[Cu_2(CH_3CN)_2(18S6)][ClO_4]_2$,[3] $[Cu_2(24S8)][BF_4]_2$,[4] $[Cu_2(28S8)][ClO_4]_2$,[4] $[Rh_2(Me_5Cp)_2Cl_2(18S6)][BPh_4]_2$,[5] and $[Rh_2(1,5\text{-}COD)_2(20S6)][BF_4]_2$[6]) demonstrate this problem quite dramatically.[7] In each complex, the metal centers are oriented on opposite sides of the macrocycle ring removing any possibility of cooperativity or communication between the metal ions. For example, the macrocycle 18S6 is known to encapsulate a number of transition metals and forms both mononuclear, $[Cu(18S6)]^+$, and binuclear, $[Cu_2(CH_3CN)_2(18S6)]^{2+}$, complexes with Cu(I).[3,8] In the binuclear complex, the coordination sites that might be used for cooperative binding of a substrate molecule, those containing the ancillary CH_3CN ligands, are directed away from each other and the macrocyclic ring adopts an "inside-out" conformation.

We report herein the synthesis and coordination chemistry of 2,5,8,17,20,23-hexathia[9](1,2)[9](4,5)cyclophane (L), the first example of a crown thioether ligand designed specifically for binuclear coordination. The compartmentalized nature of the ligand favors a 2:1, metal to ligand ratio and the presence of a rigid aromatic spacing unit allows for increased control over the relative orientation of the two metal centers. Part of this work has been the subject of a preliminary communication.[9]



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(7) Abbreviations used for crown thioether ligands: 9S3, 1,4,7-trithiacyclononane; 18S6, 1,4,7,10,13,16-hexathiacyclooctadecane; 20S6, 1,4,7,11,14,17-hexathiacycloeicosane; 24S8, 1,4,7,10,13,16,19,22-octathiacyclotetracosane; 28S8, 1,4,8,11,15,18,22,25-octathiacyclooctacosane.

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Experimental Section

$[Me_4N][Mo(SCH_2CH_2SCH_2CH_2S)(CO)_3]$,[10] $[Cu(CH_3CN)_4][ClO_4]$,[11] and $[Cu(CH_3CN)_4][PF_6]$[11] were prepared by the literature methods. $Mo(CO)_6$, $AgBF_4$, 3-thiapentane-1,5-dithiol, tetrabromodurene, bis(diphenylphosphino)ethane (dppe), a 25% (w/w) solution of $[Me_4N][OH]$ in methanol, and all deuterated solvents were purchased from Aldrich and used as received. All reactions were conducted under an atmosphere of N_2 using standard Schlenk techniques and all solvents were degassed prior to use. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.1, 75.4, and 121.5 MHz, respectively, on a Brüker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analysis were performed by Microanalytical Services, New Westminister, British Columbia, Canada.

Preparation of 2,5,8,17,20,23-Hexathia[9](1,2)[9](4,5)cyclophane (L). 3-Thiapentane-1,5-dithiol (13.705 g, 88.8 mmol) was added to a 25% (w/w) solution of $[Me_4N][OH]$ in methanol (16.191 g, 177.6 mmol). The mixture was stirred at room temperature for 12 h to give a milky white suspension of $[Me_4N]_2[SCH_2CH_2SCH_2CH_2S]$ and the methanol removed in vacuo. $Mo(CO)_6$ (23.443 g, 88.8 mmol) was refluxed in CH_3CN (100 mL) for 6 h and then cooled to room temperature. The resulting orange solution of *fac*-$Mo(CH_3CN)_3(CO)_3$ was then added via cannula to the flask containing the freshly prepared $[Me_4N]_2[SCH_2CH_2SCH_2CH_2S]$. The mixture was stirred for 12 h resulting in a bright yellow suspension of $[Me_4N]_2[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]$. To this suspension was added tetrabromodurene (19.972 g, 44.4 mmol) followed by enough CH_3CN to bring the total volume to 300 mL. This reaction mixture was stirred at room temperature for 24 h during which time the suspension changed in color from bright yellow to yellow-brown. The solvent was then removed in vacuo and the residue washed with methanol (50 mL). The resulting brown residue was dissolved in dimethylsulfoxide (100 mL) and this solution added to a flask containing $[Me_4N]_2[SCH_2CH_2SCH_2CH_2S]$ (26.69 g, 88.8 mmol) prepared as described above. The mixture was stirred at room temperature for 48 h after which H_2O (200 mL) was added and the solution extracted with diethyl ether (3 × 300 mL). The combined ether fractions were evaporated to dryness and the residue dissolved in CH_2Cl_2 (50 mL) and dried over anhydrous $MgSO_4$. After filtration, the CH_2Cl_2 solution was slowly added dropwise to a boiling solution of absolute ethanol (200 mL) and the solution filtered while hot. The solution was then reduced to a volume of 50 mL, cooled to room temperature and the resulting white solid isolated by filtration. Recrystallization by vapor diffusion of hexanes into a chloroform solution of the compound produced colorless crystalline material. Yield: 3.86 g (20%). Mp: 245 °C. NMR (δ, ppm): ^1H ($CDCl_3$, 300 K) 7.71 (s, 2H, aromatic), 3.91 (s, 8H, benzylic), 2.8–2.5 (m, 16H, SCH_2); $^{13}C\{^1H\}$ 136.52, 132.29 (aromatic), 32.06 (benzylic), 31.93 (CH_2S), 31.81 (CH_2S). Anal. Calcd for $C_{18}H_{26}S_6$: C, 49.71; H, 6.04; S, 44.25. Found: C, 49.66; H, 6.00; S, 44.31.

Preparation of *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$ (1a). ***Caution! Perchlorate salts of metal complexes with organic ligands are explosive.***[12] $[Cu(CH_3CN)_4][ClO_4]$ (0.214 g, 0.653 mmol), PPh_2Me (0.130 g, 0.653 mmol), and L (0.142 g, 0.327 mmol) were dissolved in 4:1 $CH_3CN/CHCl_3$ (30 mL) and stirred at room temperature for 12 h. The solvents were removed in vacuo and the resulting white solid recrystallized from $CHCl_3$. Yield: 0.303 g (80%). NMR (δ, ppm): ^1H ($CDCl_3$, 300 K) 7.0–7.5 (m, 22H, L and PPh_2Me aromatic), 4.21 (d, 4H, ^2J = 11.3 Hz, benzylic), 3.85 (d, 4 H, ^2J = 11.3 Hz, benzylic), 3.35 (m, 4H, SCH_2), 3.06 (m, 12H, SCH_2), 1.70 (d, 6H, $^2J_{PH}$ = 5.0 Hz, PCH_3); $^{31}P\{^1H\}$ −12.80. Anal. Calcd for $C_{45}H_{53}Cl_5Cu_2O_8P_2S_6$: C, 42.20; H, 4.18. Found: C, 42.14; H, 4.14.

Preparation of *anti*-$[Cu_2(L)(PPh_3)_2][ClO_4]_2$ (1b). ***Caution! Perchlorate salts of metal complexes with organic ligands are explosive.***[12] $[Cu(CH_3CN)_4][ClO_4]$ (0.152 g, 0.465 mmol), PPh_3 (0.122 g, 0.465 mmol), and L (0.101 g, 0.232 mmol) were dissolved in 1:1 CH_3CN/CH_2Cl_2 (40 mL) and stirred at room temperature for 12 h. The solvents were removed in vacuo and the resulting white solid recrystallized from CH_3CN/diethyl ether. Yield: 0.202 g (68%). NMR (δ, ppm): ^1H ($CDCl_3$, 300 K) 6.9–7.7 (m, 32H, L and PPh_3 aromatic), 4.21 (d, 4H, ^2J = 11.3 Hz, benzylic), 3.96 (d, 4H, ^2J = 11.3 Hz, benzylic), 3.46 (m, 4H, SCH_2), 2.90 (m, 12H, SCH_2); $^{31}P\{^1H\}$ 5.56. Anal. Calcd for $C_{54}H_{56}Cl_2Cu_2O_8P_2S_6$: C, 50.45; H, 4.40. Found: C, 50.39; H, 4.33.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$, *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$, and *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$

formula	$C_{45}H_{53}Cu_2$-$Cl_5O_8P_2S_6$	$C_{54}H_{56}Ag_2$-$B_2F_8P_2S_6$	$C_{44}H_{50}Cu_2$-$F_{12}P_4S_6$
fw	1280.69	1348.81	1250.33
a, Å	15.192(7)	11.402(6)	26.33(2)
b, Å	16.943(8)	11.713(5)	12.658(2)
c, Å	11.725(6)	10.986(3)	17.771(9)
α, deg	96.86(5)	99.76(3)	
β, deg	112.34(4)	96.54(3)	117.74(5)
γ, deg	92.73(5)	86.86(4)	
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
V, Å^3	2757(2)	1436(1)	5241(5)
ρ, g/cm^{-3}	1.542	1.559	1.584
Z	2	1	4
μ, cm^{-1}	13.40	10.01	12.37
λ, Å	0.710 69	0.710 69	0.710 69
T, °C	24	24	24
$R(F_o)$,[a] %	7.94	6.09	7.42
$R_w(F_o)$,[a] %	7.63	6.68	7.45

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

Preparation of *anti*-$[Ag_2(L)(PPh_2Me)_2][BF_4]_2$ (2a). $AgBF_4$ (0.076 g, 0.392 mmol), PPh_2Me (0.078 g, 0.392 mmol), and L (0.085 g, 0.196 mmol) were dissolved in 3:1 CH_3CN/CH_2Cl_2 (50 mL) and stirred at room temperature for 12 h. The solvents were removed in vacuo and the resulting white solid recrystallized from CH_3CN/diethylether. Yield: 0.180 g (75%). NMR (δ, ppm): ^1H ($CDCl_3$, 300 K) 7.0–7.7 (m, 22H, L and PPh_2Me aromatic), 4.05 (d, br, 4H, benzylic), 3.55 (d, br, 4H, benzylic), 3.35–2.95 (m, 16H, SCH_2), 1.69 (s, br, 6H, PCH_3); $^{31}P\{^1H\}$ −2.90 (d, br). Anal. Calcd for $C_{44}H_{52}Ag_2B_2F_8P_2S_6$: C, 43.15; H, 4.29. Found: C, 43.08; H, 4.19.

Preparation of *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$ (2b). $AgBF_4$ (0.090 g, 0.460 mmol), PPh_2Me (0.121 g, 0.460 mmol), and L (0.100 g, 0.230 mmol) were dissolved in 1:1 CH_3CN/CH_2Cl_2 (40 mL) and stirred at room temperature for 12 h. The solvents were removed in vacuo and the resulting white solid recrystallized from CH_3CN/diethyl ether. Yield: 0.263 g (85%). NMR (δ, ppm): ^1H ($CDCl_3$, 300 K) 7.0–7.5 (m, 32H, L and PPh_3 aromatic), 4.23 (d, 4H, ^2J = 11.0 Hz, benzylic), 3.76 (d, 4H, ^2J = 11.0 Hz, benzylic), 3.0–3.4 (m, 16H, SCH_2); $^{31}P\{^1H\}$ 14.50 (dd, $^1J_{AgP}$ = 590.0 and 511.8 Hz). Anal. Calcd for $C_{54}H_{56}Ag_2B_2F_8P_2S_6$: C, 48.08; H, 4.19. Found: C, 47.99; H, 4.10.

Preparation of *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$ (3). $[Cu(CH_3CN)_4][PF_6]$ (0.136 g, 0.366 mmol), dppe (0.073 g, 0.183 mmol), and L (0.079 g, 0.183 mmol) were dissolved in 1:1 CH_3CN/CH_2Cl_2 (40 mL) and stirred at room temperature for 12 h. The solvents were removed in vacuo and the resulting white solid recrystallized from acetone. Yield: 0.125 g (53%). NMR (δ, ppm): ^1H ($CDCl_3$, 300 K) 7.0–7.5 (m, 22H, L and dppe, aromatic), 4.18 (d, 4H, ^2J = 11.5 Hz, benzylic), 3.88 (d, 4H, ^2J = 11.5 Hz, benzylic), 3.45 (m, 4H, SCH_2), 2.99 (m, 12H SCH_2); $^{31}P\{^1H\}$ −11.88. Anal. Calcd for $C_{44}H_{50}Cu_2F_{12}P_4S_6$: C, 42.26; H, 4.04. Found: C, 42.20; H, 3.98.

General X-ray Diffraction Data Collection, Solution, and Refinement. Diffraction experiments were performed on a four-circle Rigaku AFC6 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 data collection parameters are summarized in Table 1 and the supplementary material. 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 (2θ < 30, 40, 45, and 50°). Empirical absorption coefficients were calculated and absorption corrections applied to the data. The data were processed using the TEXSAN software[13] package running on a VAX 3520 computer. Refinements were carried out by using full-matrix least-squares techniques on F by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[14] and anomalous dispersion terms[15,16] were taken from the usual sources. Fixed H-atom contributions were

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Table II. Selected Positional Parameters and *B*(eq)[a] for *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$

atom	*x*	*y*	*z*	*B*(eq)
		Molecule 1		
Cu1	0.2812(2)	0.0100(1)	0.0035(2)	3.9(1)
S1	0.1894(3)	0.1011(3)	–0.1048(5)	5.0(2)
S2	0.3519(4)	–0.0149(3)	–0.1401(5)	5.2(3)
S3	0.2012(3)	–0.1188(3)	–0.0494(5)	4.2(2)
P1	0.3647(4)	0.0260(3)	0.2068(5)	3.7(2)
C1	0.0357(11)	–0.0497(11)	–0.069(2)	3.6(4)
C2	–0.0063(12)	0.0751(10)	–0.018(2)	3.7(4)
C3	0.0324(12)	0.0282(11)	–0.085(2)	3.3(4)
C4	0.0643(13)	0.0644(11)	–0.175(2)	5.2(5)
C5	0.220(2)	0.0901(13)	–0.242(2)	7.2(6)
C6	0.298(2)	0.055(2)	–0.240(3)	11.2(9)
C7	0.274(2)	–0.102(2)	–0.233(3)	13(1)
C8	0.2465(14)	–0.1587(12)	–0.163(2)	5.7(5)
C9	0.0763(14)	–0.1092(12)	–0.141(2)	5.7(5)
C10	0.2892(7)	0.0198(8)	0.2943(10)	3.3(4)
C16	0.4456(7)	0.1139(6)	0.2865(13)	4.0(4)
C22	0.4404(14)	–0.0553(12)	0.249(2)	5.9(5)
		Molecule 2		
Cu2	0.2439(2)	0.4720(1)	0.5483(2)	4.6(1)
S4	0.3595(4)	0.5590(3)	0.7066(5)	5.9(3)
S5	0.1924(4)	0.4172(4)	0.6898(5)	6.0(3)
S6	0.2948(4)	0.3539(3)	0.4929(5)	5.6(3)
P2	0.1434(4)	0.5346(3)	0.4045(5)	4.1(2)
C23	0.4628(12)	0.4376(11)	0.540(2)	4.1(4)
C24	0.5240(13)	0.5730(11)	0.567(2)	5.1(5)
C25	0.4888(13)	0.5119(12)	0.613(2)	4.5(4)
C26	0.476(1)	0.5289(12)	0.732(2)	6.0(5)
C27	0.340(2)	0.528(2)	0.843(3)	12(1)
C28	0.270(2)	0.475(2)	0.830(3)	11.0(8)
C29	0.256(1)	0.3290(13)	0.702(2)	6.3(5)
C30	0.256(2)	0.2921(13)	0.583(2)	7.5(6)
C31	0.4239(13)	0.3655(11)	0.576(2)	5.3(5)
C32	0.0507(7)	0.4686(7)	0.2801(10)	4.0(4)
C38	0.1943(9)	0.5995(7)	0.3275(11)	4.2(4)
C44	0.0768(14)	0.5964(12)	0.467(2)	5.8(5)

[a] $B(\mathrm{eq}) = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*a_i\cdot a_j$.

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.

Structure Determination of *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$ (1a). Colorless crystals of **1a** were grown by slow evaporation of a chloroform solution of the compound. A statistical analysis of intensity distributions was consistent with space group $P\bar{1}$ and this was confirmed by a successful solution refinement. A total of 9686 reflections were collected and 2732 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The positions of the copper atoms were determined by the Patterson method and the remaining non-hydrogen atoms located from difference Fourier map calculations. In the final cycles of refinement, the copper, sulfur, phosphorus, chlorine, and oxygen atoms were assigned anisotropic thermal parameters. All the carbon atoms were assigned individual isotropic thermal parameters with those in the phenyl groups of PPh_2Me input as rigid groups. The $CHCl_3$ molecule of solvation exhibited 2-fold disorder for Cl4 as a result of rotation about a 2-fold axis. This disorder was modeled successfully with site occupancy factors of 50%; no attempt was made to include the H atom. This resulted in $R = \sum\|F_o| - |F_c\|/\sum|F_o| = 0.0794$ and $R_w = (\sum w(|F_o|-|F_c|)^2/\sum wF_o^2)^{1/2} = 0.0763$ at final convergence. A goodness of fit calculation resulted in a value of 1.949. The Δ/σ value for any parameter in the final cycle was less than 0.01. A final difference Fourier map calculation showed no peaks of chemical significance. Selected atomic positional parameters are summarized in Table II and selected bond distances and angles are summarized in Table III. Listings of atomic positional parameters, nonessential bonding parameters, thermal parameters, and hydrogen atom parameters are deposited as supplementary material.

Table III. Selected Bond Distances and Angles for *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$

	Molecule 1		
	Distances (Å)		
Cu1–S1	2.294(6)	P1–C10	1.81(1)
Cu1–S2	2.328(7)	P1–C16	1.79(1)
Cu1–S3	2.341(5)	P1–C22	1.83(2)
Cu1–P1	2.209(5)	C1–C2′	1.36(3)
S1–C4	1.80(2)	C1–C3	1.36(4)
S1–C5	1.84(3)	C1–C9	1.53(3)
S2–C6	1.77(3)	C2–C3	1.36(3)
S2–C7	1.80(3)	C3–C4	1.49(3)
S3–C8	1.80(2)	C5–C6	1.34(3)
S3–C9	1.82(2)	C7–C8	1.46(4)
	Nonbonding Distance (Å)		
	Cu1···Cu1′	8.502(4)	
	Angles (deg)		
S1–Cu1–S2	92.7(2)	C2–C1–C9	119(2)
S1–Cu1–S3	112.7(2)	C3–C1–C9	122(2)
S1–Cu1–P1	126.0(2)	C1–C2–C3	124(2)
S2–Cu1–S3	92.6(2)	C1–C3–C2	117(2)
S2–Cu1–P1	122.2(2)	C1–C3–C4	125(2)
S3–Cu1–P1	106.0(2)	C2–C3–C4	119(2)
C4–S1–C5	100.7(10)	C3–C4–S1	112(1)
C6–S2–C7	97.5(13)	S1–C5–C6	120(2)
C8–S3–C9	104.1(9)	C5–C6–S2	125(3)
C10–P1–C16	103.5(7)	S2–C7–C8	116(2)
C10–P1–C22	103.8(9)	C7–C8–S3	117(2)
C16–P1–C22	103.2(7)	S3–C9–C1	111(1)
	Molecule 2		
	Distances (Å)		
Cu2–S4	2.307(5)	P2–C32	1.81(1)
Cu2–S5	2.347(8)	P2–C38	1.82(2)
Cu2–S6	2.291(6)	P2–C44	1.77(2)
Cu2–P2	2.219(6)	C23–C24′	1.34(3)
S4–C26	1.79(2)	C23–C25	1.38(3)
S4–C27	1.86(4)	C23–C31	1.50(3)
S5–C28	1.76(3)	C24–C25	1.39(3)
S5–C29	1.81(2)	C25–C26	1.48(3)
S6–C30	1.80(3)	C27–C28	1.31(5)
S6–C31	1.82(2)	C29–C30	1.46(3)
	Nonbonding Distance (Å)		
	Cu2···Cu2′	8.528(4)	
	Angles (deg)		
S4–Cu2–S5	91.8(2)	C24–C23–C31	117(2)
S4–Cu2–S6	115.1(2)	C25–C23–C31	124(2)
S4–Cu2–P2	112.6(2)	C23–C24–C25	123(2)
S5–Cu2–S6	92.3(2)	C23–C25–C24	118(2)
S5–Cu2–P2	119.3(2)	C23–C25–C26	123(2)
S6–Cu2–P2	120.7(2)	C24–C25–C26	120(2)
C26–S4–C27	101.4(13)	C25–C26–S4	111(1)
C28–S5–C29	98.3(12)	S4–C27–C28	122(2)
C30–S6–C31	102.3(10)	C27–C28–S5	126(3)
C32–P2–C38	105.4(6)	S5–C29–C30	114(2)
C32–P2–C44	102.4(7)	C29–C30–S6	118(2)
C38–P2–C44	104.8(9)	S6–C31–C23	108(1)

Structure Determination of *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$ (2b). Colorless crystals of **2b** were grown by slow evaporation of an acetonitrile solution of the compound. A statistical analysis of intensity distributions were consistent with space group $P\bar{1}$ and this was confirmed by a successful solution refinement. A total of 5053 reflections were collected and 2949 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The position of the silver atom was determined by the Patterson method and the remaining non-hydrogen atoms were located from difference Fourier map calculations. In the final cycles of refinement, the silver, phosphorus, sulfur, fluorine, carbon and boron atoms were assigned anisotropic thermal parameters. This resulted in $R = 0.0609$ and $R_w = 0.0668$ at final convergence. A goodness of fit calculation resulted in a value of 2.023. The Δ/σ value for any parameter in the final cycle was less than 0.001. A final difference Fourier map calculation showed no peaks of chemical significance. Selected atomic positional parameters are summarized in Table IV and selected bond distances and angles are summarized in Table V. Listings of atomic positional parameters, nonessential bonding

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

(15) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1974**, *17*, 781.

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

Table IV. Selected Positional Parameters and B(eq)[a] for *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$

atom	x	y	z	B(eq)
Ag	0.10298(7)	0.27158(7)	0.22019(8)	3.74(4)
S1	0.1251(2)	0.1797(2)	0.4232(2)	3.5(1)
S2	0.3087(2)	0.1653(2)	0.1883(2)	4.4(1)
S3	0.2311(2)	0.4536(2)	0.2651(2)	3.8(1)
P1	−0.0903(2)	0.2644(2)	0.1060(2)	2.9(1)
C1	−0.1180(8)	0.5050(8)	0.5271(8)	3.2(4)
C2	−0.0407(9)	0.4139(8)	0.5495(8)	3.2(4)
C3	0.0754(8)	0.4045(8)	0.5240(8)	3.0(4)
C4	0.1493(9)	0.2998(9)	0.5515(9)	4.3(5)
C5	0.2796(10)	0.1049(9)	0.4205(10)	4.8(5)
C6	0.3104(11)	0.0670(11)	0.2907(14)	6.8(7)
C7	0.4039(9)	0.2768(11)	0.266(1)	6.9(7)
C8	0.3780(8)	0.3945(9)	0.2411(10)	4.4(5)
C9	0.2405(9)	0.4929(9)	0.4342(9)	4.1(5)
C10	−0.0850(7)	0.2056(8)	−0.0565(8)	2.8(4)
C16	−0.1683(8)	0.4049(8)	0.1092(8)	2.8(4)
C22	−0.1948(8)	0.1757(8)	0.1579(9)	3.1(4)

[a] $B(\mathrm{eq}) = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i{}^*a_j{}^*a_i{\cdot}a_j$.

Table V. Selected Bond Distances and Angles for *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$

	Distances (Å)		
Ag–S1	2.618(3)	P1–C10	1.807(9)
Ag–S2	2.626(3)	P1–C16	1.824(9)
Ag–S3	2.597(3)	P1–C22	1.822(10)
Ag–P1	2.407(3)	C1–C2′	1.383(11)
S1–C4	1.824(10)	C1–C3	1.412(13)
S1–C5	1.825(11)	C1–C9	1.503(13)
S2–C6	1.739(14)	C2–C3	1.379(13)
S2–C7	1.783(13)	C3–C4	1.503(13)
S3–C8	1.807(10)	C5–C6	1.54(2)
S3–C9	1.829(10)	C7–C8	1.46(2)
	Nonbonding Distances (Å)		
Ag···Ag′	7.617(4)		
	Angles (deg)		
S1–Ag–S2	83.19(10)	C2–C1–C9	118.7(9)
S1–Ag–S3	106.98(9)	C3–C1–C9	123.0(9)
S2–Ag–S3	82.14(9)	C1–C2–C3	124.4(9)
S1–Ag–P1	115.73(9)	C1–C3–C2	117.4(8)
S2–Ag–P1	135.51(9)	C1–C3–C4	123.7(9)
S3–Ag–P1	123.94(9)	C2–C3–C4	118.8(9)
C4–S1–C5	103.1(5)	C3–C4–S1	110.1(7)
C6–S2–C7	105.3(7)	S1–C5–C6	115.1(8)
C8–S3–C9	102.3(5)	C5–C6–S2	120.7(9)
C10–P1–C16	105.7(4)	S2–C7–C8	118.3(9)
C10–P1–C22	104.6(4)	C7–C8–S3	116.3(8)
C16–P1–C22	103.5(4)	S3–C9–C1	108.4(6)
C2–C1–C3	118.2(9)		

parameters, thermal parameters, and hydrogen atom parameters are deposited as supplementary material.

Structure Determination of *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$ (3). Colorless crystals of 3 were grown by slow evaporation of an acetone solution of the compound. A statistical analysis of intensity distributions and a determination of observed extinctions were consistent with space group $C2/c$ and this was confirmed by a successful solution refinement. A total of 4840 reflections were collected and 1282 unique reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ were used in the refinement. The position of the copper atom was determined by the Patterson method and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of refinement, the copper, sulfur, and phosphorus atoms were assigned anisotropic thermal parameters. All the carbon atoms were assigned isotropic thermal parameters with those in the phenyl groups of $PPh_2CH_2CH_2PPh_2$ input as rigid groups. The $PF_6{}^-$ anion exhibited a 2-fold disorder for F3, F4, F5, and F6 as a result of rotation about a 4-fold axis. This disorder was successfully modelled with site occupancy factors of 60% and 40%. The two fully occupied fluorine sites were refined anisotropically and the partially occupied sites were refined isotropically. This resulted in $R = 0.0742$ and $R_w = 0.0745$ at final convergence. A goodness of fit calculation resulted in a value of 1.876. The Δ/σ value for any parameter in the final cycle was less than 0.02. A final difference Fourier map calculation showed no peaks of chemical significance. Selected atomic positional parameters are summarized in Table VI and selected bond distances and angles are summarized in Table VII. Listings of atomic positional parameters, nonessential bonding parameters, thermal parameters, and hydrogen atom parameters are deposited as supplementary material.

Table VI. Selected Positional Parameters and B(eq)[a] for *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$

atom	x	y	z	B(eq)
Cu	0.38590(10)	0.3543(2)	0.1003(2)	3.5(1)
S1	0.4250(2)	0.4569(4)	0.0313(4)	4.4(3)
S2	0.2925(2)	0.3704(4)	−0.0112(3)	4.1(3)
S3	0.3645(2)	0.4386(4)	0.1965(3)	3.7(2)
P1	0.4299(2)	0.1997(4)	0.1173(3)	2.9(2)
C1	0.4392(8)	0.592(1)	0.2144(13)	4.0(5)
C2	0.5237(8)	0.593(1)	0.1959(12)	3.5(4)
C3	0.4634(8)	0.595(1)	0.1625(13)	4.0(5)
C4	0.4297(9)	0.592(2)	0.0671(14)	5.3(5)
C5	0.3643(8)	0.459(2)	−0.0709(13)	4.8(5)
C6	0.3067(8)	0.469(1)	−0.0739(12)	4.1(5)
C7	0.2621(8)	0.447(2)	0.0445 (12)	4.3(5)
C8	0.2891(8)	0.424(2)	0.1378(13)	4.5(5)
C9	0.3764(9)	0.581(2)	0.1878(13)	4.9(5)
C10	0.3949(5)	0.0805(9)	0.1251(8)	2.8(4)
C16	0.4426(6)	0.1779(9)	0.0261(7)	2.5(4)
C22	0.5009(8)	0.1920(13)	0.2072(11)	3.3(4)

[a] $B(\mathrm{eq}) = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i{}^*a_j{}^*a_i{\cdot}a_j$.

Results

Ligand Synthesis and Characterization. The thiacyclophane ligand 2,5,8,17,20,23-hexathia[9](1,2)[9](4,5)cyclophane (L) was prepared via the template reaction of tetrabromodurene with $[Me_4N]_2[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]$. This is a modified version of the method used by Sellmann[10] for the preparation of 1,4,7-trithiacyclononane (9S3) and involves the three-step process outlined in eqs 1–3.

$$Mo(CO)_3(CH_3CN)_3 + [Me_4N]_2[SCH_2CH_2SCH_2CH_2S] \rightarrow [Me_4N]_2[Mo(SCH_2CH_2SCH_2CH_2S)(CO)_3] \quad (1)$$

$$2[Me_4N]_2[Mo(SCH_2CH_2SCH_2CH_2S)(CO)_3] + 1,2,4,5\text{-}(BrCH_2)_4C_6H_2 \rightarrow [Mo_2(CO)_6(L)] + 4[Me_4N]Br \quad (2)$$

$$[Mo_2(CO)_6(L)] + 2[Me_4N]_2[SCH_2CH_2SCH_2CH_2S] \rightarrow 2[Me_4N]_2[Mo(SCH_2CH_2SCH_2CH_2S)(CO)_3] + L \quad (3)$$

This synthetic procedure produces L as a stable, colorless crystalline solid in 20% overall yield. L is quite soluble in most polar organic solvents particularly CH_2Cl_2 and $CHCl_3$ and to a lesser extent CH_3CN, ethanol and acetone. The ^1H NMR spectrum shows single resonances for the aromatic and benzylic protons at δ 7.71 and 3.91 ppm and an AA′BB′ multiplet for the CH_2CH_2 chain protons centered at 2.65 ppm. The resonances due to the aliphatic portion of the molecule are almost identical to those found for 2,5,8-trithia[9]-*o*-cyclophane, TT[9]OC, which contains only one of the thioether chains attached to the aromatic ring.[17] Interestingly, the value of δ 7.71 ppm for the single aromatic resonance of L is quite different from that found for analogous oxygen containing macrocycles which show values of δ ranging from 7.38 to 7.43 ppm for ortho substitution and values of δ ranging from 7.55 to 7.65 ppm for meta substitution.[18] This may be related to the conformation of the aliphatic ring as macrocycles containing sulfur prefer exodentate donor atoms while

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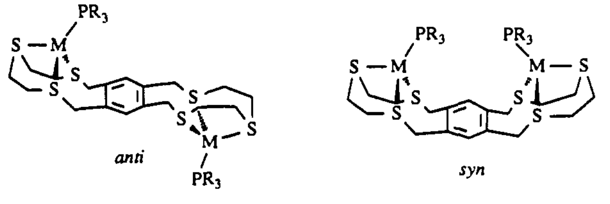
[17] de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1990**, *29*, 4090–4095.
[18] Lee, W. Y.; Sim, W.; Park, O. S. *Synlett.* **1992**, 157–159.

Table VII. Selected Bond Distances and Angles for *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$

	Distances (Å)		
Cu–S1	2.330(8)	P1–C10	1.81(1)
Cu–S2	2.341(5)	P1–C16	1.82(2)
Cu–S3	2.297(7)	P1–C22	1.81(2)
Cu–P1	2.222(6)	C1–C2′	1.43(3)
S1–C4	1.81(2)	C1–C3	1.34(4)
S1–C5	1.78(2)	C1–C9	1.50(3)
S2–C6	1.82(2)	C2–C3	1.41(3)
S2–C7	1.82(3)	C3–C4	1.51(3)
S3–C8	1.77(2)	C5–C6	1.50(3)
S3–C9	1.85(2)	C7–C8	1.50(3)
		C22–C22′	1.54(4)
	Nonbonding Distances (Å)		
Cu···Cu′	5.886(7)	P1···P1′	4.432(9)
	Angles (deg)		
S1–Cu–S2	93.0(2)	C2–C1–C9	116(2)
S1–Cu–S3	117.0(2)	C3–C1–C9	126(2)
S1–Cu–P1	103.5(3)	C1–C2–C3	121(2)
S2–Cu–S3	93.7(2)	C1–C3–C2	121(2)
S2–Cu–P1	117.9(2)	C1–C3–C4	124(2)
S3–Cu–P1	126.9(2)	C2–C3–C4	116(2)
C4–S1–C5	103.0(9)	C3–C4–S1	109(1)
C6–S2–C7	103.8(10)	S1–C5–C6	117(2)
C8–S3–C9	103.8(9)	C5–C6–S2	115(1)
C10–P1–C16	104.7(7)	S2–C7–C8	114(1)
C10–P1–C22	104.0(7)	C7–C8–S3	117(2)
C16–P1–C22	103.7(9)	S3–C9–C1	106(1)
C2–C1–C3	118(2)	P1–C22–C22′	112(2)

those containing oxygen prefer endodentate donor atoms. Obviously one must take care in assigning ring substitution patterns based solely on trends in these NMR parameters.

Synthesis and Characterization of Complexes. The reaction of 1 equiv of L with 2 equiv of $[Cu(CH_3CN)_4][ClO_4]$ or $AgBF_4$, in CH_3CN in the presence of 2 equiv of PR_3 (PPh_2Me, PPh_3) gave, in good yield, the complexes *anti*-$[M_2(L)(PR_3)_2][X]_2$ (M = Cu, X = ClO_4, L = PPh_2Me (**1a**), L = PPh_3 (**1b**); M = Ag, X = BF_4, L = PPh_2Me (**2a**), L = PPh_3 (**2b**)). These complexes are all air stable, white crystalline solids with good solubility in polar organic solvents, most notably acetonitrile. None of the silver complexes showed sensitivity to light in either solution or the solid state. ^1H NMR spectra for the complexes with monodentate PR_3 ancillary ligands establish that the structures are symmetrical with only one set of resonances being observed for L and PR_3. The most significant feature is the splitting of the benzylic proton resonance, a singlet in L, into a pair of doublets. This is a direct result of forming the seven-membered chelate rings which place the benzylic protons in axial and equatorial positions on the ring. This is also a very useful diagnostic tool and can be used to monitor the extent of complexation of L for a particular reaction. $^{31}P\{^1H\}$ NMR spectra are also consistent with symmetrical bimetallic complexes since only single resonances, shifted downfield from free phosphine, were observed. Although these observations infer that the metal binding sites are equivalent, it is not possible to distinguish between a syn conformation in which both metals are on the same side of the macrocyclic ring and an anti conformation in which the metals occupy binding sites on opposite sides of the ring.



The reaction of 1 equivalent of L with 2 equiv of $[Cu(CH_3CN)_4][PF_6]$, in CH_3CN, in the presence of one equivalent of $Ph_2PCH_2CH_2PPh_2$ gave, in good yield, the complex *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$ (**3**) as an air stable, crystalline solid. As with the monodentate phosphine complexes **1a**, **1b**, **2a**, and **2b**, ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** are indicative of a symmetrical species. Therefore **3** most likely contains L in the syn conformation with the two Cu(I) centers positioned in close proximity linked by a bridging $Ph_2PCH_2CH_2PPh_2$ unit. Although, an anti conformation for the complex with $Ph_2PCH_2CH_2PPh_2$ units bridging intermolecularly to form a polymeric compound is possible, the solubility characteristics of **3** are too similar to those of complexes **1a**, **1b**, **2a**, and **2b** for this to be the case.

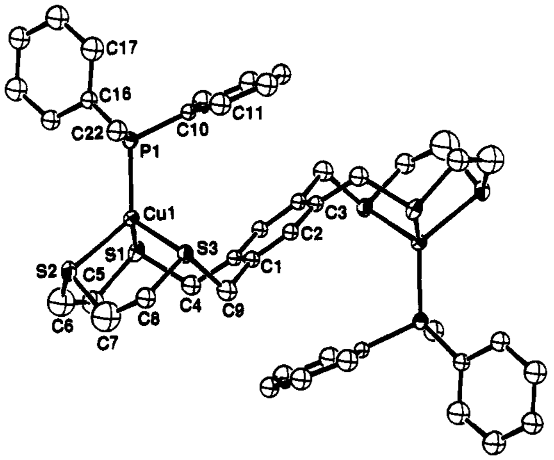


Figure 1. Perspective ORTEP drawing of the *anti*-$[Cu_2(L)(PPh_2Me)_2]^{2+}$ cation of **1a** (molecule 1), showing the atom numbering scheme. Thermal ellipsoids of 30% are shown.

X-ray Structure of *anti*-$[Cu_2(L)(PPh_2Me)_2][ClO_4]_2$ (1a). Complex **1a** crystallizes with two molecules per asymmetric unit. The two molecules each have a crystallographically imposed center of symmetry and differ only slightly; by the rotational positioning of one of the phenyl rings on the PPh_2Me ligand. The X-ray structure of **1a** verifies (Figure 1; only molecule 1 is shown) that L acts as a ditopic ligand coordinating to two Cu atoms via two sets of S_3 donors with the fourth site on each Cu atom occupied by a PPh_2Me ligand. For each binuclear complex, the Cu atoms are in identical, distorted tetrahedral environments bonded to three S atoms and a P atom: Cu1–S1 2.294(6), Cu1–S2 2.328(7), Cu1–S3 2.341(5), and Cu1–P1 2.209(5) Å for molecule 1; Cu2–S4 2.307(5), Cu2–S5 2.347(8), Cu2–S6 2.291(6), Cu2–P2 2.219(6) Å for molecule 2. The S1–Cu1–S2, S2–Cu1–S3, S4–Cu2–S5, and S5–Cu2–S6 angles involving the five-membered chelate rings are 92.7(2), 92.6(2), 91.8(2), and 92.3(2)°, respectively, and the S1–Cu1–S3 and S4–Cu2–S6 angles associated with the seven-membered chelate rings spanning the durene unit are 112.7(2) and 115.1(2)°. The coordination about Cu(I) in both molecules of **1a** compares well to that found for $[Cu(PPh_2Me)(TT[9]OC)][ClO_4]$,[19] which has the same structural features as *one* of the S_3 coordination sites of **1a**. Overall, the ligand adopts an anti conformation that places the two copper centers on opposite sides of the central aromatic ring with nonbonding Cu–Cu distances of Cu1···Cu1′ 8.502(4) and Cu2···Cu2′ 8.528(4) Å.

X-ray Structure of *anti*-$[Ag_2(L)(PPh_3)_2][BF_4]_2$ (2b). Complex **2b** has a crystallographically imposed center of symmetry. The X-ray structure of **2b** shows (Figure 2) that L also acts as a ditopic ligand for Ag(I) coordinating to two Ag atoms via two sets of S_3 donors with the fourth site on each Ag atom occupied by a PPh_3 ligand. The Ag atoms are in identical, distorted tetrahedral environments bonded to three S atoms, Ag–S1 2.618(3), Ag–S2 2.626(3), Ag–S3 2.597(3) Å, and a P atom, Ag–P1 2.407(3) Å. The S1–Ag–S2 and S2–Ag–S3 angles involving the

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[19] de Groot, B.; Giesbrecht, G. R.; Loeb, S. J.; Shimizu, G. K. H. *Inorg. Chem.* **1991**, *30*, 177–182.

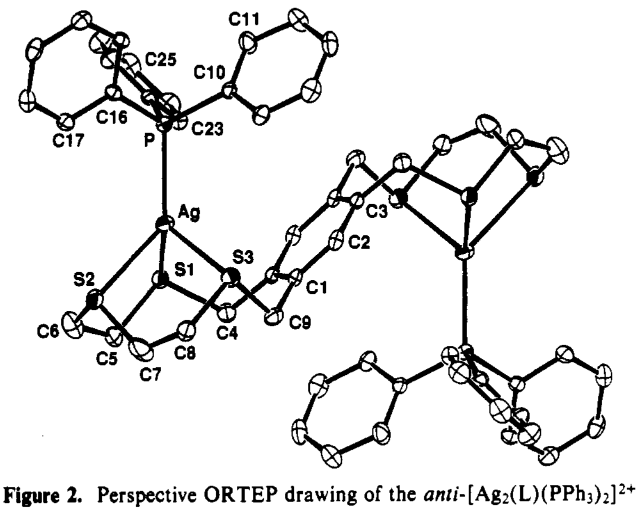


Figure 2. Perspective ORTEP drawing of the *anti*-$[Ag_2(L)(PPh_3)_2]^{2+}$ cation of **2b**, showing the atom numbering scheme. Thermal ellipsoids of 30% are shown.

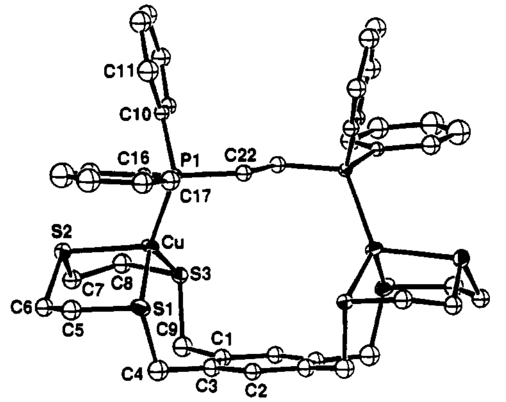


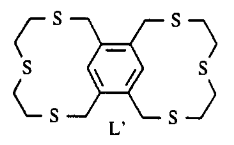
Figure 3. Perspective ORTEP drawing of the *syn*-$[Cu_2(L)(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]^{2+}$ cation of **3**, showing the atom numbering scheme. Thermal ellipsoids of 30% are shown.

five-membered chelate rings are 83.19(1) and 82.14(9)°, respectively, and the S1–Ag–S3 angle associated with the seven-membered chelate ring is 106.98(9)°. The coordination about Ag(I) in **2b** compares well to that found for $[Ag(PPh_3)(TT[9]OC)][BF_4]$,[19] which has the same structural features as *one* of the S_3 coordination sites of **2b**. As in **1a**, the ligand adopts an anti conformation that places the two silver centers on opposite sides of the aromatic ring with a nonbonding Ag–Ag distance of Ag···Ag′ 7.617(4) Å.

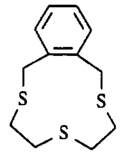
X-ray Structure of *syn*-$[Cu_2(L)(\mu\text{-}PPh_2CH_2CH_2PPh_2)][PF_6]_2$ (3). Complex **3** has crystallographically imposed 2-fold symmetry relating the two coordination sites. The X-ray structure of **3** demonstrates (Figure 3) that L can also accommodate a coordination mode that places the two metal atoms on the same side of the aromatic ring. Most significantly, this coordination mode allows for the incorporation of bridging ligands or substrate molecules. As in **1a**, each Cu atom is coordinated by a set of S_3 donors with the fourth site occupied by a phosphine ligand. Again, the Cu atoms are in identical, distorted tetrahedral environments bonded to three S atoms, Cu–S1 2.330(8), Cu–S2 2.341(5), Cu–S3 2.297(6) Å, and a P atom, Cu–P1 2.209(5) Å. The S1–Cu–S2 and S2–Cu–S3 angles involving the five-membered chelate rings are 93.0(2) and 93.7(2)°, respectively, and the S1–Cu1–S3 angle associated with the seven-membered chelate ring is 117.0(2)°. Unlike **1a** and **2b**, the ligand adopts an syn conformation that places the two copper centers on the same side of the aromatic ring resulting in a much closer metal to metal distance. The Cu–Cu distance of Cu···Cu′ 5.886(7) Å in this syn conformation is ideal for bridging the diphosphine ligand $PPh_2CH_2CH_2PPh_2$ with a P–P distance of P1···P1′ 4.432(9) Å.

Discussion

Our investigations into the coordination chemistry of TT[9]OC showed clearly that a ditopic ligand, such as L, based on the 1,2,4,5 (ortho) substitution pattern of a durene fragment, had the potential to bring two S_3 sites into close proximity.[17,19-21] Indeed, the compartmentalized nature of L separates the S_6 donor set into equivalent S_3 binding sites which can each coordinate *facially* to a metal center. The standard method of preparing TT[9]OC and related trithiacyclophanes is to perform a Cs^+ mediated ring closure employing, for example, α,α'-dibromo-*o*-xylene and $HSCH_2CH_2SCH_2CH_2SH$ which gives TT[9]OC in high yield.[19] However, for similar reactions with 1,2,4,5-tetrabromodurene, *both* ortho and meta ring closures are possible and attempts to prepare L by this method yielded the meta analog 2,5,8,17,20,23-hexathia[9](2,4)[9](5,1)cyclophane (L′) exclusively. The fact that meta ring closure is more favorable was also observed in the synthesis of trithiacyclophanes and can be attributed to the larger amount of ring strain involved in the ortho isomer and the better "fit" of the $-SCH_2CH_2SCH_2CH_2S-$ linkage with a *m*-xylyl unit.[17] The use of $Mo(SCH_2CH_2SCH_2CH_2S)$ as the source of the $-SCH_2CH_2SCH_2CH_2S-$ fragment circumvents these problems since coordination of $-SCH_2CH_2SCH_2CH_2S-$ creates a more suitable fit, or template, for formation of the ortho isomer.[10] $[Mo_2(CO)_6(L)]$ is the only complex intermediate containing CO that can be detected (infrared) and it is presumed to have an anti conformation with structural details similar to those observed for $[Mo(CO)_3(TT[9]OC)]$.[17]



L′



TT[9]OC

In the coordination of L to group 11 metals, the use of a simple monodentate ligand such as PPh_2Me or PPh_3 results in the formation of **1a**, **1b**, **2a**, and **2b** in which L adopts an anti conformation. This conformation maximizes the separation between the two coordination sites and is probably the favored conformation on steric grounds. The use of a bidentate ligand such as $Ph_2PCH_2CH_2PPh_2$ yields **3** in which L adopts a syn conformation. It appears that intramolecular bridging between adjacent metal atoms in the syn conformation of the ligand is favored over intermolecular linking of the fragments in the anti conformation. In **3**, the syn conformation places the Cu atoms at a distance of 5.886(7) Å and the P1···P1′ separation is 4.432(9) Å. Thus, this conformation produces a relatively large cavity into which $PPh_2CH_2CH_2PPh_2$ or some other similarly sized, substrate molecule could coordinate. The flexibility of L and the dependence of the metal–metal separation and cavity size on metal and bridging ligand type are currently being investigated. The resemblance of a single S_3 binding site of L to the S_3 set of TT[9]OC or 9S3 is notable and it may be possible to develop binuclear chemistry with L, based on the known chemistry of these ligands.[1,2,17,19-21]

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Supplementary Material Available: Listings of crystallographic data collection parameters, positional parameters, thermal parameters, nonessential bond distances and angles, and hydrogen atom parameters (16 pages). Ordering information is given on any current masthead page.

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