ment, and it may be that, once the first bridging ligand is displaced, subsequent attack on the remaining positions is more rapid.

Acknowledgment. We thank the SERC and Verband der Chemischen Industrie for financial support and Professor J. H. Enemark and Dr. M. R. Minelli for measuring the ^{95}Mo NMR spectra.

Registry No. $[Et_4N]_2[Mo_2O_2(4\text{-}MeC_6H_4S)_6(OMe)]$, 69532-73-6; $[Et_4N]_2[Mo_2O_2(SPh)_6(OMe)]$, 69609-04-7; $MoOCl_3(thf)_2$, 20529-42-4; benzoyl chloride, 98-88-4.

Supplementary Material Available: Listings of calculated atomic coordinates, anisotropic thermal parameters, isotropic thermal parameters, bond lengths, bond angles, and observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Wayne State University, Detroit, Michigan 48202,
and University of Wisconsin—Eau Claire, Eau Claire, Wisconsin 54701

Ring Size Effects on the Structure of Macrocyclic Ligand Complexes: Copper(II) Complexes with 12–16-Membered Cyclic Tetrathia Ethers

VIRGINIA B. PETT,[1a] LEONARD L. DIADDARIO, JR.,[1b] EDWARD R. DOCKAL,[1b] PETER W. CORFIELD,[1c] CHRISTOPHER CECCARELLI,[1b] MILTON D. GLICK,*[1b] L. A. OCHRYMOWYCZ,[1d] and D. B. RORABACHER*[1b]

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Crystal structures have been resolved at room temperature for a series of Cu(II) complexes with cyclic tetrathia ether ligands having the general formulation $Cu^{II}([n]aneS_4)(ClO_4)_2(H_2O)_x$, where n represents the total number of carbon and sulfur atoms in the macrocyclic ligand ring (n = 12, 13, 15, 16) and x = 1 for n = 12 or 13 and zero for the other compounds. The respective space groups, lattice constants, and final R factors for these four compounds are as follows: for orthorhombic $Cu^{II}([12]aneS_4)(ClO_4)_2(H_2O)$ space group $Pbc2_1$, a = 9.010 (2) Å, b = 15.775 (3) Å, c = 13.380 (2) Å, Z = 4, R = 0.127, R_w = 0.162; for monoclinic $Cu^{II}([13]aneS_4)(ClO_4)_2(H_2O)$ space group $P2_1/c$, a = 18.073 (3) Å, b = 13.607 (3) Å, c = 18.167 (3) Å, β = 119.759 (1)°, Z = 8, R = 0.081, R_w = 0.116; for monoclinic $Cu^{II}([15]aneS_4)(ClO_4)_2$ space group $P2_1/n$, a = 7.994 (1) Å, b = 9.167 (3) Å, c = 13.978 (3) Å, β = 99.29 (3)°, Z = 2, R = 0.066, R_w = 0.085; for monoclinic $Cu^{II}([16]aneS_4)(ClO_4)_2$ space group $P2_1/c$, a = 7.931 (3) Å, b = 9.613 (5) Å, c = 14.885 (5) Å, β = 110.71 (3)°, Z = 2, R = 0.044, R_w = 0.064. These structures are compared with that previously reported for $Cu^{II}([14]aneS_4)(ClO_4)_2$ to provide a continuous series of homologous macrocyclic complexes in which the internal cavity progresses from dimensions that are too small to accommodate the central metal ion to those that exceed optimal size. In the compounds formed with $[12]aneS_4$ and $[13]aneS_4$, the Cu(II) ion sits 0.53 and 0.38 Å above the plane of the four sulfur donor atoms. In both cases the inner coordination sphere is square pyramidal, being completed by an axially coordinated water molecule. In the complexes formed with the three larger ligands, Cu(II) is coplanar with the four sulfur donor atoms, and two ClO_4^- ions are coordinated axially to form a tetragonal inner coordination sphere. The Cu–S bond lengths increase with increasing ring size, exhibiting average values of 2.30, 2.32, and 2.36 Å for n = 14, 15, and 16, respectively. In the last complex, in fact, the four Cu–S bonds are no longer equivalent: one pair of *trans*-Cu–S bonds is 2.33 Å while the other pair is 2.39 Å. In all five complexes, the axial Cu–O bond distances vary inversely with the average Cu–S bond distances so that, within each of the two types of coordination spheres represented, the total of the inner-sphere bond distances remains virtually constant. A comparison between the bond length totals of the two geometric groups indicates a limiting bonding distance of 3.0 Å for an oxygen donor atom axially coordinated to Cu(II). This agrees well with previous studies of Cu(II) complexes containing oxygen and nitrogen within the equatorial plane. Within the macrocyclic ring itself, there appear to be two mechanisms whereby the ligands attempt to adjust to the spatial requirements of the coordinated metal ion: (i) compression of the C–S–C bond angles and (ii) changes in the torsion angles and ring conformations. The progression of these properties is analyzed in considerable detail.

Introduction

In a series of recent studies on the copper(II) complexes of macrocyclic tetrathia ethers, we have investigated the effect of ring size upon various chemical and physical parameters including substitution kinetics,[2] complex stability constants,[3] standard electrode potentials,[4,5] electron-transfer kinetics,[5] and spectral properties.[6] Whereas the trends observed in several of these properties are presumed to reflect the variations in the coordination geometry forced upon the central metal ion by the constraints of the various macrocyclic ligands, the structural features that account for these variations have not been previously reported except for the copper(II)[7] and copper(I)[8] complexes of the 14-membered cyclic tetrathia ether.

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(1) (a) Present address: The College of Wooster, Wooster, OH 44691. (b) Wayne State University. (c) On leave from King's College, Briarcliff Manor, NY 10510. (d) University of Wisconsin—Eau Claire.

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Table I. Crystal Parameters and Experimental Details for X-ray Diffraction Studies on the Cu([*n*]aneS$_4$)(ClO$_4$)$_2$ Compounds

	n				
	12	13	14	15	16
		(A) Crystal Data			
cryst dimens, mm	0.2 × 0.4 × 0.5	0.4 × 0.6 × 0.9	0.1 × 0.2 × 0.2	0.2 × 0.3 × 0.5	0.1 × 0.2 × 0.6
lattice type	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$Pbc2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
cell dimens, *a*, Å	9.010 (2)	18.073 (3)	7.904 (3)	7.994 (1)	7.931 (3)
b, Å	15.775 (3)	13.607 (3)	8.830 (4)	9.167 (3)	9.613 (5)
c, Å	13.380 (2)	18.167 (3)	16.840 (6)	13.978 (3)	14.885 (5)
β, deg	90	119.759 (1)	126.33 (2)	99.29 (3)	110.71 (3)
cell vol, Å^3	1901.7 (6)	3879 (1)	946.8 (6)	1009.6 (5)	1061.5 (8)
empirical formula	$CuC_8H_{18}S_4Cl_2O_9$	$CuC_9H_{20}S_4Cl_2O_9$	$CuC_{10}H_{20}S_4Cl_2O_8$	$CuC_{11}H_{22}S_4Cl_2O_8$	$CuC_{12}H_{24}S_4Cl_2O_8$
fw	520.93	534.98	530.97	545.02	559.05
no. of waters per formula unit	1	1	0	0	0
no. of formula units per unit cell	4	8	2	2	2
F(000), e	1060	2184	542	558	574
obsd density, g/mL	~1.7	1.84	1.90	1.80	1.71
calcd density, g/mL	1.82	1.83	1.87	1.79	1.75
		(B) X-ray Intensity Measurements			
scan method	θ–2θ	ω	θ–2θ	θ–2θ	θ–2θ
scan range for data collection ±(spectral dispersion cor), deg	1.0	1.0–1.23	1.0	1.0	1.0
max 2θ range, deg	45	45	50	48	45
scan rate, deg/min	2.0	2.0	4.0	2.0	2.0
no. of data between std reflcns	97	97	97	97	97
dec indicated	none	none	none	none	none
linear abs coeff, μ, cm^{-1}	18.92	18.58	19.35	17.81	16.98
extinction and abs cor	no	no	no	no	no
no. of indep reflcns	1487	5517	1378	1781	1390
no. of obsd reflcns	1089	3567	968	1134	1333
criteria for obsd reflcns	$>3\sigma$	$>2.5\sigma$	$>3\sigma$	$>2.5\sigma$	$>2.5\sigma$
		(C) Final Model Refinement			
R, R_w	0.127, 0.162	0.081, 0.116	0.032, 0.038	0.066, 0.085	0.044, 0.064
highest peak on final difference fourier, e/Å^3	2.40	1.64	0.58	0.67	0.92
anisotropic	no	yes	yes	yes	yes
calcd H atom positions	no	yes	yes	no	yes

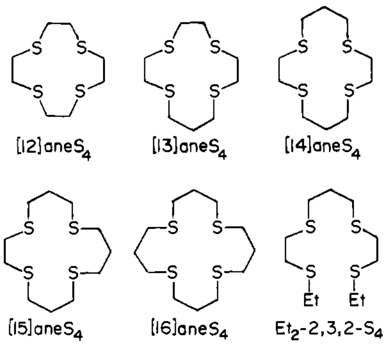

Figure 1. Macrocyclic tetrathia ether ligands discussed in this work.

We now wish to report the detailed structural parameters of the Cu(II) complexes formed with the 12-, 13-, 15-, and 16-membered cyclic tetrathia ether ligands as determined by X-ray crystallographic techniques. The specific ligands involved are as follows (see Figure 1): 1,4,7,10-tetrathiacyclododecane ([12]aneS$_4$); 1,4,7,10-tetrathiacyclotridecane ([13]aneS$_4$); 1,4,8,12-tetrathiacyclopentadecane ([15]aneS$_4$); 1,5,9,13-tetrathiacyclohexadecane ([16]aneS$_4$).

The structures of these four complexes and the structure previously reported for the Cu(II) complex with 1,4,8,11-tetrathiacyclotetradecane ([14]aneS$_4$)[7] are compared to provide an overview of the structural changes brought about by stepwise increases in the cyclic ligand ring size. To the best of our knowledge, the current work represents the first definitive study dealing with the trends in the specific coordination geometry of the central metal ion as a function of the ligand cavity size for a series of ligands, involving a constant number of donor atoms, where the ring size is varied stepwise from dimensions that are too small to accommodate the metal ion through those that are too large to provide optimal coordination.

The crystals obtained for these compounds, as described below, were beset by problems of disorder and high thermal motion, precluding the highest quality structure determinations. Nonetheless, the key structural features of chemical consequence are clear, thereby permitting us to analyze the effects of ring size upon the geometry of the copper coordination sphere.

Experimental Section

All cyclic polythia ether ligands were synthesized by methods previously described[10] and were purified by liquid chromatography and recrystallization from chloroform. Crystals of the Cu(II) complexes were formed by dissolving equimolar quantities of Cu(ClO$_4$)$_2$ and the appropriate ligand in 80% methanol and slowly evaporating at room temperature.

Selected crystals were mounted on pulled glass fibers with epoxy resin. All diffraction data were collected at ambient temperature on a Syntex P2$_1$ diffractometer with Mo Kα radiation (λ = 0.71069 Å) diffracted from a highly oriented graphite monochromator in the parallel mode with a takeoff angle of 4°. Initial examination by rotation and axial photographs and by preliminary data sets yielded approximate lattice constants and established the symmetry. The final crystal parameters resulted from least-squares analyses of 15 reflections, with 2θ between 15 and 30°, and are tabulated in Table I.

For each crystal the intensities were measured by the θ–2θ technique, with the exception of the [13]aneS$_4$ complex, for which the ω-scan method was used. Three standard reflections, measured every 97

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Table II. Atomic Coordinates for $Cu^{II}([12]aneS_4)(ClO_4)_2(H_2O)$ with Estimated Standard Deviations[a]

atom	x	y	z
Cu	0.1265 (3)	0.1299 (2)	0.2500 (0)
Cl(1)	0.3395 (8)	0.4704 (5)	0.2539 (12)
Cl(2)	0.7933 (8)	0.2516 (10)	0.0001 (12)
S(1)	0.0784 (13)	0.0193 (7)	0.1380 (9)
S(2)	0.2781 (13)	0.2018 (7)	0.1411 (11)
S(3)	0.2646 (12)	0.1950 (7)	0.3800 (10)
S(4)	0.0837 (12)	0.0307 (7)	0.3749 (9)
O	−0.0685 (24)	0.2040 (12)	0.2603 (26)
O(1)	0.4276 (55)	0.4841 (33)	0.1729 (41)
O(2)	0.4403 (39)	0.4448 (24)	0.3228 (29)
O(3)	0.2434 (37)	0.4031 (23)	0.2367 (39)
O(4)	0.2893 (52)	0.5260 (29)	0.3185 (36)
O(5)	0.7369 (32)	0.2402 (21)	−0.0954 (29)
O(6)	0.6962 (40)	0.2931 (22)	0.0612 (32)
O(7)	0.9050 (44)	0.1891 (26)	0.0084 (33)
O(8)	0.8217 (45)	0.3295 (25)	−0.0416 (32)
C(1)	0.2082 (83)	0.0641 (45)	0.0457 (58)
C(2)	0.3408 (49)	0.1152 (26)	0.0582 (38)
C(3)	0.4413 (43)	0.2216 (23)	0.2265 (29)
C(4)	0.4368 (46)	0.1839 (28)	0.3220 (37)
C(5)	0.2634 (48)	0.1066 (26)	0.4773 (32)
C(6)	0.2467 (45)	0.0257 (25)	0.4428 (33)
C(7)	0.1820 (55)	−0.0561 (30)	0.3110 (36)
C(8)	0.1087 (38)	−0.0711 (21)	0.2177 (24)

[a] The estimated standard deviations given in parentheses correspond to the least significant digits in the adjacent values. This convention is used throughout this paper.

reflections, were statistically constant for all crystals studied. The scan ranges and scan rates are given in Table I. Backgrounds were measured at each end of the scan.

Standard computer programs modified for local use were employed.[11] Correction for Lorentz-polarization effects, but not for absorption, was made. The atomic positions and thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares techniques. The quantity minimized was $\sum w_i(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, respectively. Correction for anomalous dispersion of the copper atom was applied. Discrepancy factors were defined as follows:

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

Results

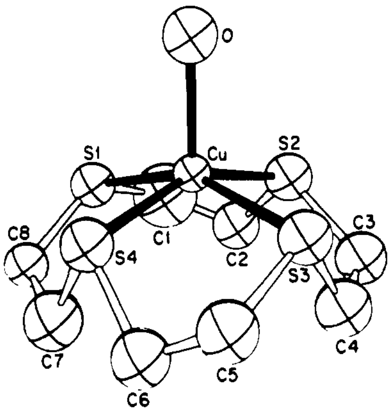

Figure 2. Atom-labeling scheme for the $Cu^{II}([12]aneS_4)$ complex. The copper atom is positioned 0.53 Å above the plane of the four sulfur atoms. The apical oxygen atom is from the coordinated water molecule.

Table III. Bond Lengths and Bond Angles in $Cu^{II}([12]aneS_4)(ClO_4)_2(H_2O)$

	Bond Lengths (Å)		
Cu–S(1)	2.34 (1)	S(4)–C(6)	1.73 (4)
Cu–S(2)	2.30 (1)	S(4)–C(7)	1.84 (5)
Cu–S(3)	2.37 (1)	C(1)–C(2)	1.45 (8)
Cu–S(4)	2.32 (1)	C(3)–C(4)	1.41 (6)
Cu–O	2.11 (2)	C(5)–C(6)	1.37 (6)
S(1)–C(1)	1.84 (8)	C(7)–C(8)	1.43 (6)
S(1)–C(8)	1.80 (3)		
S(2)–C(2)	1.85 (5)	O–O(5)	2.75 (4)
S(2)–C(3)	1.89 (4)	O–O(8)	2.88 (4)
S(3)–C(4)	1.74 (4)	O–O(7)	3.39 (4)
S(3)–C(5)	1.91 (4)	Cu–O(1)	4.74 (5)
	Bond Angles (deg)		
S(1)–Cu–S(2)	94.1 (6)	Cu–S(3)–C(5)	100 (1)
S(2)–Cu–S(3)	86.5 (4)	Cu–S(4)–C(6)	106 (1)
S(3)–Cu–S(4)	81.4 (4)	Cu–S(4)–C(7)	95 (2)
S(4)–Cu–S(1)	85.8 (3)	C(1)–S(1)–C(8)	127 (3)
S(1)–Cu–S(3)	152.8 (4)	C(2)–S(2)–C(3)	104 (2)
S(2)–Cu–S(4)	152.6 (4)	C(4)–S(3)–C(5)	104 (2)
S(1)–Cu–O	107.4 (8)	C(6)–S(4)–C(7)	79 (2)
S(2)–Cu–O	105.2 (8)	S(1)–C(8)–C(7)	117 (3)
S(3)–Cu–O	98.6 (8)	S(1)–C(1)–C(2)	131 (6)
S(4)–Cu–O	100.8 (9)	S(2)–C(2)–C(1)	103 (4)
Cu–S(1)–C(1)	91 (2)	S(2)–C(3)–C(4)	117 (3)
Cu–S(1)–C(8)	101 (1)	S(3)–C(4)–C(3)	113 (3)
Cu–S(2)–C(2)	101 (1)	S(3)–C(5)–C(6)	103 (3)
Cu–S(2)–C(3)	99 (1)	S(4)–C(6)–C(5)	117 (3)
Cu–S(3)–C(4)	96 (2)	S(4)–C(7)–C(8)	108 (3)

Structure Determination of $Cu^{II}([12]aneS_4)(ClO_4)_2 \cdot H_2O$. The position of the copper atom was found from a Patterson map, and the rest of the structure appeared in the difference map. The space group is *Pbc*2_1, but continual difficulty in the determination and refinement of the structure resulted from the fact that the Cu, S, and Cl atoms, which account for three-fourths of the X-ray scattering, are in positions very close to those expected for the centric space group *Pbcm*. Thus, the macrocyclic cation has a nearly perfect mirror plane that is perpendicular to the plane of the ligand S atoms and passes through the copper atom. The cation is positioned in the unit cell so that this plane is perpendicular to the *c* axis, mimicking what would be the mirror plane in *Pbcm*. Our attempts to break the pseudosymmetry by moving pseudorelated atoms independently were unsuccessful.

Not only did this pseudo mirror plane hinder the determination of precise positions for the light atoms but it also led to problems in refining the heavy-atom positions. Whenever the S atoms were allowed to refine anisotropically, they inevitably moved to positions consistent with space group *Pbcm*, resulting in unrealistic bond distances, although the ring geometry and difference maps clearly indicate a noncentric arrangement. For this reason, the atomic positions after refinement with isotropic temperature factors best describe the structure (Table II). Because of the refinement problems, residual indices were fairly high ($R = 0.127$, $R_w = 0.162$). Hydrogen atom positions were not assigned.

The structure of the $Cu^{II}([12]aneS_4)$ complex with the atom-labeling scheme is shown in Figure 2. The four sulfur atoms lie virtually in a single plane with the copper atom centered at 0.53 Å above this plane. The inner coordination sphere of the copper is completed by a water oxygen atom bonded axially to produce a five-coordinate copper ion with overall square-pyramidal geometry. Interatomic distances and

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(11) Local versions of the following computer programs were used: (a) SYNCOR, W. Schmonsees' program for data reduction. (b) FASTES, W. Schmonsees' program for generation of normalized structure factors. (c) REL, R. E. Long's program for phase determination by Sayre's method. (d) FORDAP, A. Zalkin's Fourier program. (e) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function-and-error program. (f) ORTEP, C. K. Johnson's program for drawing crystal models. (g) MULTAN78, P. Main's system for solutions of crystal structures using the tangent formula of Karle and Hauptman. (h) HFINDR, A. Zalkin's program to calculate hydrogen atom positions. (i) PLANES, D. L. Smith's program to calculate least-squares planes. (j) INFO, A. Zalkin's program to calculate density, molecular weight, and reciprocal cell dimensions. (k) TRACER, Lawton and Jacobson's program for cell reduction. (l) EQUIV, local program for averaging equivalent reflections.

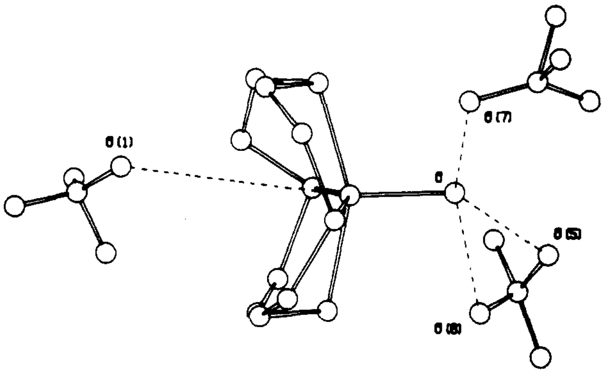

Figure 3. View of the Cu^{II}([12]aneS_4) complex showing the positioning of the perchlorate anions relative to the cationic unit. The O(1) oxygen of the first perchlorate is nearly aligned on the Cu–O (H_2O) axis. The apparent H bond interactions between the apical water and the O(5), O(7), and O(8) atoms of the second perchlorate are designated by dashed lines.

angles are given in Table III.

Although the perchlorate ions do not appear to be coordinated to the copper ion, one perchlorate oxygen lies below the square pyramid in a position that is nearly on the axis defined by the copper and the water oxygen (see Figure 3) with a Cu–O distance of 4.74 (5) Å. Three oxygens of the second perchlorate are positioned sufficiently close to the coordinated water molecule to suggest weak hydrogen bonding to the water hydrogens (interatomic distances: O–O(5), 2.75 (4) Å; O–O(7), 3.39 (4) Å; O–O(8), 2.88 (4) Å).

Structure Determination of Cu^{II}([13]aneS_4)$(ClO_4)_2$·H_2O. Axial rotation photographs and preliminary data set showed the crystal system to be monoclinic with the only systematic absences ($k = 2n + 1$ for $0k0$) indicating space group $P2_1$ or $P2_1/m$. By application of direct methods, with the assumption of space group $P2_1$, all 8 copper atoms and more than half the 32 sulfur atoms in the asymmetric unit were located. The copper and the sulfur atom positions were related by *B* centering. Even though the lighter atoms might not conform to the *B* centering, it became obvious that finding all 200 nonhydrogen atoms in the asymmetric unit would not be possible with ordinary small-molecule methods. A primitive cell[12] was chosen; 118 low-intensity data with noninteger *hkl* were deleted. Refinement was continued in space group $P2_1/c$.

All hydrogen atom positions were calculated for a C–H bond distance of 1.08 Å, and their contributions were included in F_0. Final least-squares refinement for all atomic position coordinates (with 361 variables) yielded $R = 0.081$, $R_w = 0.116$.

The resultant structure of the Cu^{II}([13]aneS_4) complex with the atom-labeling scheme is shown in Figure 4. The atomic coordinates are listed for all atoms except the hydrogens in Table IV, and the interatomic distances and angles are given in Table V.

The data show that the structure of the [13]aneS_4 complex is very similar to that of the [12]aneS_4 complex with the four sulfur donor atoms coplanar and the copper atom situated 0.38 Å above the sulfur plane. The lone water molecule is axially bonded to the copper atom to produce a square-pyramidal complex.

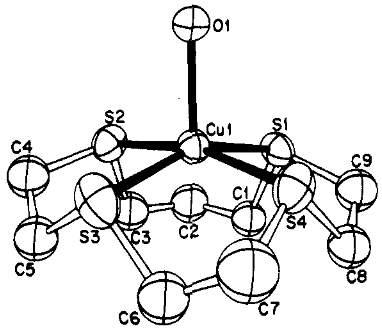

Figure 4. Atom-labeling scheme for the Cu(1) cationic unit in the Cu^{II}([13]aneS_4)$(ClO_4)_2(H_2O)$ crystal. The copper atom is positioned 0.38 Å above the plane of the four sulfur donor atoms with all carbon atoms below this plane. The apical oxygen atom is from the coordinated water molecule.

Table IV. Atomic Coordinates for Cu^{II}([13]aneS_4)$(ClO_4)_2(H_2O)$

atom	*x*	*y*	*z*
Cu(1)	0.3562 (1)	0.2375 (1)	0.8414 (1)
Cu(2)	0.8574 (1)	0.2434 (1)	0.5142 (1)
O(1)	0.4259 (7)	0.2516 (7)	0.7749 (7)
O(2)	0.9286 (8)	0.2463 (9)	0.6513 (7)
S(1)	0.4294 (3)	0.1038 (3)	0.9274 (3)
S(2)	0.4426 (3)	0.3486 (3)	0.9485 (3)
S(3)	0.2519 (3)	0.3568 (3)	0.7828 (3)
S(4)	0.2504 (3)	0.1275 (3)	0.7530 (3)
S(5)	0.9466 (3)	0.3503 (3)	0.4951 (3)
S(6)	0.9284 (3)	0.1076 (3)	0.5004 (2)
S(7)	0.7245 (3)	0.1420 (3)	0.4819 (3)
S(8)	0.7638 (3)	0.3736 (3)	0.4852 (3)
C(1)	0.4234 (10)	0.1260 (12)	1.0243 (10)
C(2)	0.4766 (12)	0.2124 (14)	1.0739 (12)
C(3)	0.4383 (11)	0.3086 (14)	1.0410 (11)
C(4)	0.3744 (11)	0.4536 (13)	0.9158 (11)
C(5)	0.2809 (11)	0.4314 (12)	0.8740 (10)
C(6)	0.1651 (12)	0.2749 (13)	0.7754 (12)
C(7)	0.1543 (14)	0.1882 (16)	0.7233 (14)
C(8)	0.2608 (11)	0.0355 (12)	0.8353 (10)
C(9)	0.3520 (11)	0.0056 (12)	0.8804 (11)
C(10)	0.9470 (10)	0.3094 (13)	0.3996 (10)
C(11)	0.9813 (14)	0.2117 (16)	0.4059 (14)
C(12)	0.9242 (11)	0.1281 (13)	0.3996 (11)
C(13)	0.8497 (9)	0.0133 (11)	0.4711 (9)
C(14)	0.7597 (10)	0.0477 (12)	0.4207 (10)
C(15)	0.6615 (13)	0.2224 (15)	0.3987 (13)
C(16)	0.6619 (15)	0.3183 (18)	0.4230 (14)
C(17)	0.7830 (11)	0.4354 (13)	0.4072 (11)
C(18)	0.8787 (12)	0.4599 (14)	0.4540 (11)
Cl(1)	0.2251 (3)	0.2213 (3)	1.0415 (3)
Cl(2)	0.5038 (3)	0.5068 (3)	0.7674 (3)
Cl(3)	0.9981 (3)	0.0010 (3)	0.7629 (3)
Cl(4)	0.7262 (3)	0.2676 (3)	0.1842 (3)
O(3)	0.1639 (11)	0.2091 (16)	1.0660 (12)
O(4)	0.2053 (14)	0.1631 (15)	0.9721 (13)
O(5)	0.3032 (10)	0.1857 (17)	1.1045 (10)
O(6)	0.2242 (18)	0.3155 (14)	1.0107 (21)
O(7)	0.5339 (11)	0.4778 (10)	0.8525 (9)
O(8)	0.4243 (12)	0.4640 (14)	0.7166 (14)
O(9)	0.4895 (20)	0.6064 (15)	0.7639 (12)
O(10)	0.5577 (15)	0.4747 (27)	0.7422 (13)
O(11)	1.0288 (13)	0.0951 (12)	0.7868 (12)
O(12)	1.0673 (11)	−0.0577 (13)	0.7755 (12)
O(13)	0.9322 (13)	0.0005 (23)	0.6825 (11)
O(14)	0.9699 (11)	−0.0291 (9)	0.8182 (9)
O(15)	0.6708 (17)	0.2518 (22)	0.1046 (12)
O(16)	0.7754 (20)	0.3433 (15)	0.2112 (12)
O(17)	0.7207 (14)	0.2066 (14)	0.2425 (11)
O(18)	0.7859 (25)	0.2142 (29)	0.1738 (24)

The relationship of the perchlorate ions to the copper–polythia ether units is shown in Figure 5. This illustrates the primary difference in the two asymmetric cationic units, namely the differing orientation of the perchlorate ion lying below the plane of the four sulfur atoms, one unit having a single perchlorate oxygen aligned on the Cu–water oxygen axis (with the Cu(2)–O(17) distance of 4.31 Å) and the second unit having two perchlorate oxygens on either side of this axis (Cu(1)–O(4), 4.53 Å; Cu(1)–O(6), 4.85 Å). As with the

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[12] The possibility that the structure might be orthohombic (space group *Pnam*) was considered and rejected for a number of reasons (Pett, V. B. Ph.D. Disseration, Wayne State University, Detroit, MI, 1979).

Table V. Bond Lengths and Bond Angles in $Cu^{II}([13]aneS_4)(ClO_4)_2(H_2O)$

	Bond Lengths (Å)		
Cu(1)-S(1)	2.334 (4)	Cu(2)-S(5)	2.321 (4)
Cu(1)-S(2)	2.3326 (4)	Cu(2)-S(6)	2.333 (4)
Cu(1)-S(3)	2.310 (5)	Cu(2)-S(7)	2.313 (5)
Cu(1)-S(4)	2.330 (5)	Cu(2)-S(8)	2.322 (5)
Cu(1)-O(1)	2.14 (1)	Cu(2)-O(2)	2.16 (2)
Cu(1)-O(5)[a]	4.06 (2)	Cu(2)-O(18)[c]	3.76 (3)
O(1)-O(9)[b]	2.79 (2)	O(2)-O(18)[c]	2.86 (4)
O(1)-O(5)[a]	2.90 (2)	O(2)-O(12)[d]	2.96 (2)
O(1)-O(8)	3.07 (2)	O(2)-O(11)	3.02 (2)
S(1)-C(1)	1.84 (2)	S(5)-C(10)	1.83 (2)
S(1)-C(9)	1.81 (2)	S(5)-C(18)	1.84 (2)
S(2)-C(3)	1.80 (2)	S(6)-C(12)	1.82 (2)
S(2)-C(4)	1.81 (2)	S(6)-C(13)	1.79 (2)
S(3)-C(5)	1.79 (2)	S(7)-C(14)	1.83 (2)
S(3)-C(6)	1.87 (2)	S(7)-C(15)	1.85 (2)
S(4)-C(7)	1.75 (2)	S(8)-C(16)	1.78 (2)
S(4)-C(8)	1.89 (2)	S(8)-C(17)	1.82 (2)
C(1)-C(2)	1.50 (2)	C(10)-C(11)	1.45 (3)
C(2)-C(3)	1.46 (2)	C(11)-C(12)	1.45 (2)
C(4)-C(5)	1.50 (2)	C(13)-C(14)	1.49 (2)
C(6)-C(7)	1.46 (2)	C(15)-C(16)	1.38 (3)
C(8)-C(9)	1.49 (2)	C(17)-C(18)	1.54 (3)
	Bond Angles (deg)		
S(1)-Cu(1)-S(2)	90.9 (2)	S(5)-Cu(2)-S(6)	91.2 (2)
S(2)-Cu(1)-S(3)	89.6 (2)	S(6)-Cu(2)-S(7)	88.4 (2)
S(3)-Cu(1)-S(4)	86.0 (2)	S(7)-Cu(2)-S(8)	86.4 (2)
S(4)-Cu(1)-S(1)	87.7 (2)	S(8)-Cu(2)-S(5)	88.3 (2)
S(1)-Cu(1)-S(3)	156.7 (2)	S(5)-Cu(2)-S(7)	157.8 (2)
S(2)-Cu(1)-S(4)	165.3 (2)	S(6)-Cu(2)-S(8)	163.2 (2)
S(1)-Cu(1)-O(1)	98.7 (3)	S(5)-Cu(2)-O(2)	95.8 (4)
S(2)-Cu(1)-O(1)	94.3 (3)	S(6)-Cu(2)-O(2)	95.4 (3)
S(3)-Cu(1)-O(1)	104.5 (3)	S(7)-Cu(2)-O(2)	104.4 (4)
S(4)-Cu(1)-O(1)	100.3 (3)	S(8)-Cu(2)-O(2)	101.4 (4)
Cu(1)-S(1)-C(1)	103.3 (5)	Cu(2)-S(5)-C(10)	106.4 (6)
Cu(1)-S(1)-C(9)	102.1 (6)	Cu(2)-S(5)-C(18)	101.3 (6)
Cu(1)-S(2)-C(3)	106.0 (6)	Cu(2)-S(6)-C(12)	100.4 (7)
Cu(1)-S(2)-C(4)	100.1 (6)	Cu(2)-S(6)-C(13)	101.7 (5)
Cu(1)-S(3)-C(5)	100.1 (6)	Cu(2)-S(7)-C(14)	99.6 (5)
Cu(1)-S(3)-C(6)	94.5 (6)	Cu(2)-S(7)-C(15)	96.0 (7)
Cu(1)-S(4)-C(7)	105.0 (7)	Cu(2)-S(8)-C(16)	103.2 (8)
Cu(1)-S(4)-C(8)	98.9 (5)	Cu(2)-S(8)-C(17)	97.5 (6)
C(1)-S(1)-C(9)	99.9 (7)	C(10)-S(5)-C(18)	100.2 (8)
C(3)-S(2)-C(4)	101.5 (8)	C(12)-S(6)-C(13)	100.4 (7)
C(5)-S(3)-C(6)	104.8 (8)	C(14)-S(7)-C(15)	102.9 (9)
C(7)-S(4)-C(8)	104.4 (9)	C(16)-S(8)-C(17)	104 (1)
S(1)-C(1)-C(2)	112 (1)	S(5)-C(10)-C(11)	114 (1)
S(1)-C(9)-C(8)	116 (1)	S(5)-C(18)-C(17)	113 (1)
S(2)-C(3)-C(2)	114 (1)	S(6)-C(12)-C(11)	111 (1)
S(2)-C(4)-C(5)	115 (1)	S(6)-C(13)-C(14)	115 (1)
S(3)-C(5)-C(4)	109 (1)	S(7)-C(14)-C(13)	108 (1)
S(3)-C(6)-C(7)	111 (1)	S(7)-C(15)-C(16)	115 (2)
S(4)-C(7)-C(6)	113 (1)	S(8)-C(16)-C(15)	116 (2)
S(4)-S(8)-C(9)	105 (1)	S(8)-C(17)-C(18)	105 (1)
C(1)-C(2)-C(3)	115 (2)	C(10)-C(11)-C(12)	116 (2)

[a] Transformed by $-\frac{1}{2}+x, \frac{1}{2}-y, z$. [b] Transformed by $\frac{3}{2}-x, -\frac{1}{2}+y, 1-z$. [c] Transformed by $\frac{1}{2}+x, \frac{1}{2}-y, z$. [d] Transformed by $\frac{3}{2}-x, \frac{1}{2}+y, 2-z$.

preceding complex, three perchlorate oxygens are positioned sufficiently close to the coordinated water molecule to suggest that they may be involved in weak hydrogen-bonding interactions (O(1)–O(5), 2.90 (2) Å; O(1)–O(8), 3.07 (2) Å; O(1)–O(9), 2.79 (2) Å and O(2)–O(11), 3.02(2) Å; O(2)–O(12), 2.96 (2) Å; O(2)–O(18), 2.86 (4) Å).

Structure Determination of $Cu^{II}([15]aneS_4)(ClO_4)_2$. The data showed systematic absences consistent with space group $P2_1/n$.[13] The Patterson map showed the copper atom to be at the origin. Since the ligand has no center of symmetry, the structure is necessarily disordered. Refinement of a disordered model in space group $P2_1/n$ with the carbons in the ethylene bridge (C(10) and C(11)) and the opposing propylene bridge (C(4), C(5), and C(6)) at half-occupancy gave $R = 0.066$, $R_w = 0.085$ (82 variables). The long C–S bond lengths remaining for C(6)–S(1′) and C(4)–S(2), as well as the long C(10)–C(11) bond length, are presumed to be artifacts of the disordered model used. In other parts of the ring the bond lengths and angles are normal.

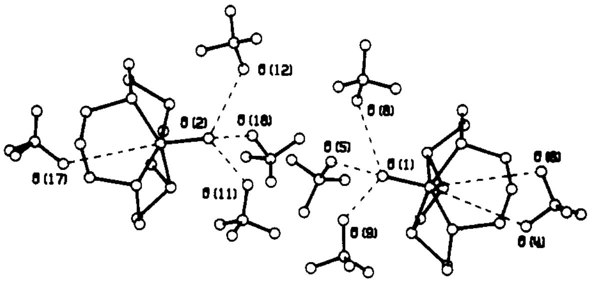

Figure 5. View of the $Cu^{II}([13]aneS_4)$ complex showing the two asymmetric cationic units and their positioning relative to the perchlorate anions. Note the difference in the positions of the perchlorates that lie "below" the plane of the sulfur donor atoms for the two cationic units. The possible interactions of the oxygens from these perchlorates with the copper atoms as well as the apparent H bond interactions between the apical waters and the adjacent perchlorate oxygens are designated by dashed lines.

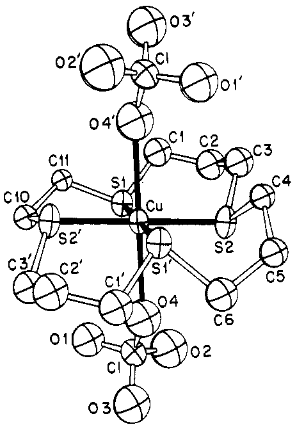

Figure 6. Atom-labeling scheme for the $Cu^{II}([15]aneS_4)$ complex showing the positioning of the copper atom within the center of the four sulfur atoms. The axially coordinated oxygens are from the two perchlorate anions. The $Cu^{II}([14]aneS_4)$ complex (not shown—see ref 7) is virtually identical except for the absence of the carbon corresponding to C(5).

Table VI. Atomic Coordinates for $Cu^{II}([15]aneS_4)(ClO_4)_2$

atom	x	y	z
Cu	0.0	0.0	0.0
S(1)	0.2824 (3)	0.0616 (3)	0.0504 (2)
S(2)	−0.0113 (3)	−0.1053 (3)	0.1492 (2)
C(1)	0.2967 (15)	0.1580 (14)	0.1650 (9)
C(2)	0.2508 (18)	0.0556 (15)	0.2449 (11)
C(3)	0.0611 (16)	0.0300 (13)	0.2435 (9)
C(4)	−0.2412 (27)	−0.0714 (28)	0.1640 (16)
C(5)	−0.3349 (29)	−0.2058 (29)	0.1126 (17)
C(6)	−0.2938 (35)	−0.2472 (32)	0.0100 (21)
C(10)	0.2375 (28)	0.1442 (28)	−0.1459 (17)
C(11)	0.3169 (27)	0.2009 (26)	−0.0349 (17)
Cl	0.2064 (3)	−0.3463 (3)	−0.0677 (2)
O(1)	0.3159 (12)	−0.2641 (10)	−0.1188 (7)
O(2)	0.2946 (15)	−0.3953 (13)	0.0196 (9)
O(3)	0.1383 (14)	−0.4652 (12)	−0.1249 (8)
O(4)	0.0727 (13)	−0.2543 (11)	−0.0517 (7)

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[13] This nonconventional setting was used so that β would be close to 90°, in order to avoid correlation problems during the least-squares refinement.

Table VII. Bond Lengths and Bond Angles in $Cu^{II}([15]aneS_4)(ClO_4)_2$

Bond Lengths (Å)			
Cu-S(1)	2.323 (3)	S(2)-C(4)	1.91 (2)
Cu-S(2)	2.313 (3)	S(2')-C(10)	1.84 (2)
Cu-O(4)	2.53 (1)	C(1)-C(2)	1.55 (2)
S(1)-C(1)	1.82 (1)	C(2)-C(3)	1.53 (2)
S(1)-C(11)	1.80 (2)	C(4)-C(5)	1.56 (3)
S(1)-C(6)	1.91 (3)	C(5)-C(6)	1.57 (4)
S(2)-C(3)	1.83 (1)	C(10)-C(11)	1.66 (3)
Bond Angles (deg)			
S(1)-Cu-S(2)	90.3 (1)	C(3)-S(2)-C(4)	90.6 (8)
S(1)-Cu-O(4)	93.0 (2)	C(3')-S(2')-C(10)	110.2 (9)
S(2)-Cu-O(4)	85.3 (2)	S(1)-C(1)-C(2)	110.6 (9)
Cu-S(1)-C(1)	102.5 (7)	S(1)-C(11)-C(10)	109 (1)
Cu-S(1)-C(11)	102.5 (7)	S(2)-C(3)-C(2)	108.0 (9)
Cu-S(1')-C(6)	101.3 (8)	S(2)-C(4)-C(5)	103 (2)
Cu-S(2)-C(3)	108.2 (4)	S(2')-C(10)-C(11)	108 (1)
Cu-S(2)-C(4)	102.0 (6)	S(1')-C(6)-C(5)	103 (2)
Cu-S(2')-C(10)	103.9 (7)	C(1)-C(2)-C(3)	116 (1)
C(1)-S(1)-C(11)	104.1 (9)	C(4)-C(5)-C(6)	117 (2)
C(1')-S(1')-C(6)	87 (1)		

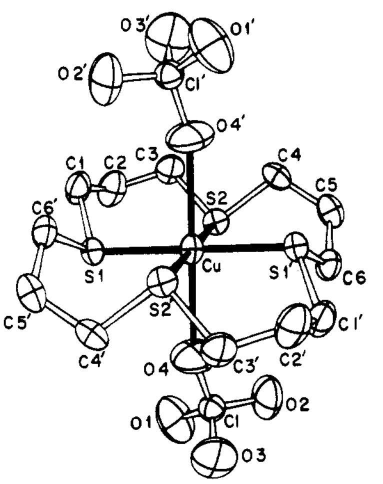

Figure 7. Atom-labeling scheme for the $Cu^{II}([16]aneS_4)$ complex. The axially coordinated oxygens are from the two perchlorate anions.

The general structure of the $Cu^{II}([15]aneS_4)$ complex with the atom-labeling scheme is shown in Figure 6. The atomic coordinates are listed for all atoms in Table VI while the interatomic bond distances and bond angles are given in Table VII.

In the $[15]aneS_4$ complex, the copper atom and all four sulfur atoms are required by symmetry to be coplanar. The inner coordination sphere of the copper atom is completed by axial coordination to the two perchlorate ions, resulting in a tetragonal complex.

Structure Determination of $Cu^{II}([16]aneS_4)(ClO_4)_2$. The structure was initially solved in space group *Pc*. With 242 variables, the refinement yielded $R = 0.040$, $R_w = 0.056$. However, the C–C bond lengths varied from 1.42 to 1.62 Å and there were many correlation coefficients above 50%, indicating the likelihood of a center of symmetry.

The peak profiles for 010, 030, 050 were weak and excessively noisy and were not of Gaussian shape; these reflections were removed from the data set and the atom positions refined in space group $P2_1/c$. Positions of all hydrogen atoms were calculated. After full-matrix least-squares refinements of 124 variables (all atoms with anisotropic thermal parameters), $R = 0.044$, $R_w = 0.064$.

The general structure of the $Cu^{II}([16]aneS_4)$ complex with the assigned atom-labeling scheme is shown in Figure 7. The atomic coordinates are listed for all atoms (except calculated hydrogens) in Table VIII while the interatomic distances and bond angles are given in Table IX.

Table VIII. Atomic Coordinates for $Cu^{II}([16]aneS_4)(ClO_4)_2$

atom	*x*	*y*	*z*
Cu	0.0	0.0	0.0
S(1)	−0.1653 (2)	−0.0792 (1)	−0.155
S(2)	0.2275 (2)	0.0898 (1)	−0.0540 (1)
C(1)	−0.1745 (8)	0.0547 (7)	−0.2435 (4)
C(2)	0.0087 (8)	0.0873 (7)	−0.2480 (4)
C(3)	0.1248 (8)	0.1817 (6)	−0.1675 (4)
C(4)	0.3080 (8)	0.2438 (5)	0.0212 (4)
C(5)	0.4468 (8)	0.2035 (6)	0.1189 (4)
C(6)	0.4002 (7)	0.0728 (6)	0.1640 (4)
Cl	0.2721 (2)	−0.3400 (1)	0.0605 (1)
O(1)	0.2909 (8)	−0.4075 (6)	−0.0190 (4)
O(2)	0.4383 (6)	−0.2774 (6)	0.1173 (3)
O(3)	0.2186 (8)	−0.4353 (6)	0.1162 (4)
O(4)	0.1426 (7)	−0.2338 (6)	0.0279 (5)

Table IX. Bond Lengths and Bond Angles in $Cu^{II}([16]aneS_4)(ClO_4)_2$

Bond Lengths (Å)			
Cu-S(1)	2.3314 (13)	S(2)-C(4)	1.83 (1)
Cu-S(2)	2.3874 (17)	C(1)-C(2)	1.51 (1)
Cu-O(4)	2.4824 (50)	C(2)-C(3)	1.52 (1)
S(1)-C(1)	1.82 (1)	C(4)-C(5)	1.52 (1)
S(1)-C(6')	1.82 (1)	C(5)-C(6)	1.53 (1)
S(2)-C(3)	1.82 (1)		
Bond Angles (deg)			
S(1)-Cu-S(2)	90.37 (5)	C(3)-S(2)-C(4)	96.6 (3)
S(1)-Cu-O(4)	85.9 (2)	S(1)-C(1)-C(2)	113.0 (4)
S(2)-Cu-O(4)	91.7 (2)	S(1')-C(6)-C(5)	110.1 (4)
Cu-S(1)-C(1)	110.2 (2)	S(2)-C(3)-C(2)	112.5 (4)
Cu-S(1)-C(6')	104.7 (2)	S(2)-C(4)-C(5)	110.5 (4)
Cu-S(2)-C(3)	110.5 (2)	C(1)-C(2)-C(3)	114.0 (5)
Cu-S(2)-C(4)	103.0 (2)	C(4)-C(5)-C(6)	115.0 (4)
C(1)-S(1)-C(6')	98.8 (3)		

With the larger $[16]aneS_4$ ligand, the copper atom and the four sulfur atoms remain coplanar (as required by the space group symmetry), but two *trans*-Cu–S bonds are significantly elongated relative to the other two Cu–S bonds. The two perchlorate anions complete the tetragonal inner coordination sphere by occupying the axial sites.

Discussion

Ring Size Effects on the General Structural Morphology. The structures of the copper(II) complexes of the 12–16-membered S_4 macrocyclic ligands exhibit two distinct geometries. When the ring contains 14 or more atoms, the sulfur donor atoms lie in a square-planar arrangement around the central copper ion with perchlorate oxygens coordinated axially at significantly greater bond distances to complete an overall tetragonal geometry. The observation that macrocyclic tetrathia ethers must contain a minimum of 14 atoms in order to provide a central cavity large enough to accommodate a divalent, first-row transition metal ion such as Cu^{II} is in accordance with the conclusions reached previously by Busch and co-workers[14,15] and contrasts with a minimum requirement of 13 atoms for the corresponding tetraaza ligands.[16]

For the $[12]aneS_4$ and $[13]aneS_4$ ligands, the copper atom is forced to sit above the plane of the four sulfur donor atoms with a water oxygen coordinated axially to produce a five-coordinate square-pyramidal complex. In contrast to these observations, Rosen and Busch observed the formation of 2:3 complexes for these same two ligands reacting with Ni(II) (i.e., $Ni_2L_3^{4+}$) in which each nickel ion was coordinated to a ligand that was in a folded conformation while the third ligand served

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(15) Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262.

(16) Iitaka, Y.; Shina, M.; Kimura, E. *Inorg. Chem.* **1974**, *13*, 2886.

Table X. Comparative Structural Properties of the Cu(II)-Tetrathia Ether Complexes

ligand	ligand cavity diam in CuL complex, Å	copper-donor bond lengths, Å			ΣR	equatorial planarity
		donor	range	av		
[12]aneS_4	4.52	4 S	2.30-2.37	2.33	11.44	S coplanar; Cu +0.53 Å
		1 H_2O	2.11	2.11		
[13]aneS_4	4.58	4 S	2.31-2.33	2.32	11.44	S ±0.08 Å, ±0.03 Å[b]; Cu +0.38 Å, +0.37 Å[b]
		1 H_2O	2.14, 2.16[b]	2.15		
[14]aneS_4[c]	4.61	4 S	2.30-2.31	2.30	14.52	S coplanar; Cu coplanar
		2 ClO_4^-	2.65	2.65		
[15]aneS_4	4.63	4 S	2.31-2.32	2.32	14.33	S coplanar; Cu coplanar
		2 ClO_4^-	2.53	2.53		
[16]aneS_4	4.72	4 S	2.33, 2.39	2.36	14.40	S coplanar; Cu coplanar
		2 ClO_4^-	2.48	2.48		
Et_2-2,3,2-S_4[d]		4 S	2.32-2.34	2.33	14.43	3 S coplanar, 1 S +0.78 Å; Cu coplanar
		1 H_2O	2.30	2.30		
		1 ClO_4^-	2.81	2.81		

[a] Ligand cavity calculated as sum of two Cu-S distances for coplanar complexes; sum of two S distances from axial Cu-O-S plane for complexes in which Cu lies above equatorial plane. [b] First value listed is for cation 1; second value is for cation 2. [c] Reference 7. [d] Et_2-2,3,2-S_4 is an open-chain homologue to [14]aneS_4 with terminal ethyl groups.[30]

to bridge the two metal centers.[15]

Similarly folded conformers have been observed in other complexes involving macrocyclic ligands with small internal cavities. The 12-membered tetraaza macrocycle [12]aneN_4 is folded when coordinated to Co(III) with two cis nitro groups completing the octahedral coordination sphere.[16] And in the case of the Cu(II) complex with the corresponding 12-membered cyclic tetraether [12]aneO_4 (i.e., 12-crown-4) Steiner and co-workers found that the macrocycle was folded with chloride ions coordinated at the two remaining cis sites.[17] In fact, to the best of our knowledge, the current tetrathia ether complexes are the only known examples of first-row transition metal ion complexes involving small cyclic tetrafunctional ligands having all *chalcogen* donor atoms, in which the ligands are *not* coordinated in a folded conformation.

Other examples in which Cu(II) is coordinated to tetrafunctional cyclic ligands in an out-of-plane conformation do exist, however. The geometry of the Cu^{II}([12]aneS_4)(H_2O)·2ClO_4 compound, as revealed in the current work, is virtually identical with that reported for the Cu^{II}([12]aneN_4)(NO_3)·NO_3 compound.[18] In fact, even the distance of the copper atom above the donor plane is strikingly similar for these two compounds, being 0.53 and 0.51 Å, respectively.

Other examples of Cu(II) coordinated above the plane of the donor atoms have been observed by Anderson and co-workers for complexes involving unsaturated 14-membered cyclic and open-chain N_4 ligands.[19] And Moore and co-workers have observed both folded (bridged) and square-pyramidal complexes between Hg(II) and [14]aneS_4, depending on the counteranions present during crystallization.[20]

The pattern that emerges from these and other studies suggests that, when the cavity of a cyclic ligand is too small to accommodate the metal ion, the presence of other strongly coordinating donor atoms tends to favor folded complexes, whereas the presence of only weakly coordinating competitive donor atoms (or increased ligand rigidity caused by unsaturation or ring substitution) tends to favor square-pyramidal complexes.

Table XI. Comparative C-S-C Bond Angles in Uncomplexed and Complexed Thioether Ligands

compd	C-S-C angle, deg	ref
Uncomplexed Ligands		
bis(trifluoromethyl)sulfide	106	23
[9]aneS_3	103	27
[14]aneS_4	102, 104	26
Complexed Ligands		
bis(μ-chloro)bis[chloro(5,8-dithiadodecane)-copper(II)]	103	24
bis(2,5-dithiahexane)copper(II)	100, 104	25
Cu^{II}(Et_2-2,3,2-S_4)	100-105	30
Cu^{II}([13]aneS_4)	100-105	this work
Cu^{II}([14]aneS_4)	105	7
Ni^{II}([14]aneS_4)	103	28
Cu^{II}([15]aneS_4)	87-110	this work
Cu^{II}([16]aneS_4)	97-99	this work
$Mo^{II}_2(SH)_2$([16]aneS_4)$_2$	94-98	21

When complexed with each of the three larger cyclic tetrathia ethers, the Cu(II) lies in the plane of the four sulfur donor atoms. The optimal fit of Cu(II) appears to occur with the [14]aneS_4 ligand since the average Cu-S bond distance is at a minimum of 2.30 Å in this complex. As the ring is expanded, the average Cu-S bond length increases slightly (Table X), but no other gross changes in the morphology of the complex are observed. In the [16]aneS_4 complex two trans Cu-S bonds are elongated to 2.39 Å while the other two Cu-S distances are increased only slightly to 2.33 Å. Although two distinct pairs of Cu-S bonds are observed in the solid crystal, the resonance Raman spectrum indicates that all four Cu-S bonds are equivalent in solution,[6] presumably as a result of rapid interconversion of the two axes within the equatorial plane.

The Cu-S bond length is remarkably constant (differing by 0.09 Å at most) throughout this series of complexes. Besides the movement of the Cu(II) into or out of the plane of the sulfur atoms, conformational changes in the ligand backbone contribute to the maintenance of optimum bond length. The diameter of the macrocyclic cavity increases by only 0.20 Å while four carbon atoms are added to the macrocyclic ring. It appears that the increased ligand strain necessary to compress a large macrocycle such as [16]aneS_4 around the Cu(II) is balanced by the Cu-S bond energy that is thereby retained. The flexibility of these macrocyclic ligands is demonstrated further by the significant variations in the size of the central cavity of [16]aneS_4 as exhibited in three of its metal complexes for which structural parameters are available:

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(20) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1978**, 394.

Table XII. Comparative Torsion Angles and Chelate Ring Conformations in the Cu^{II}-Tetrathia Ether Complexes

Chelate Rings

ligand	atoms in ring	ring[a]	torsion angles,[b] deg						ring conformation	lone pairs on sulfurs
[12]aneS$_4$	5	Cu-S(1)-C(8)-C(7)-S(4)	−20	−14	+52	−61	+40		half-chair	down-down
	5	Cu-S(4)-C(6)-C(5)-S(3)	−36	+60	−56	+25	+10		intermediate	down-down
	5	Cu-S(3)-C(4)-C(3)-S(2)	−40	+57	−45	+6	+22		half-chair	down-down
	5	Cu-S(2)-C(2)-C(1)-S(1)	−24	+40	−51	+29	+4		envelope	down-down
[13]aneS$_4$	6	Cu(1)-S(1)-C(1)-C(2)-C(3)-S(2)	−54	+70	−79	+76	−66	+53	chair	down-down
	5	Cu(1)-S(2)-C(4)-C(5)-S(3)	+1	−34	+58	−50	+23		envelope	down-down
	5	Cu(1)-S(3)-C(6)-C(7)-S(4)	−37	+59	−50	+14	+18		half-chair	down-down
	5	Cu(1)-S(4)-C(8)-C(9)-S(1)	−31	+55	−56	+27	+8		envelope	down-down
[14]aneS$_4$[c]	6	Cu-S(2)-C(5)-C(4)-C(3)-S(1)	−57	+66	−75	+77	−72	+60	chair	down-down
	5	Cu-S(1)-C(2)-C(1)-S(2′)	−11	+46	−67	+51	−18		half-chair	down-up
	6	Cu-S(2′)-C(5′)-C(4′)-C(3′)-S(1′)	same as first ring						chair	up-up
	5	Cu-S(1′)-C(2′)-C(1′)-S(2)	same as second ring						half-chair	up-down
[15]aneS$_4$	6	Cu-S(1)-C(1)-C(2)-C(3)-S(2)	−52	+66	−79	+79	−68	+54	chair	down-down
	6	Cu-S(2)-C(4)-C(5)-C(6)-S(1′)	−32	+87	−47	−41	+87	−37	twist boat	down-up
	6	Cu-S(1′)-C(1′)-C(2′)-C(3′)-S(2′)	same as first ring						chair	up-up
	5	Cu-S(2′)-C(10)-C(11)-S(1)	+9	−39	+58	−47	+19		half-chair	up-down
[16]aneS$_4$	6	Cu-S(1)-C(1)-C(2)-C(3)-S(2)	−45	+65	−79	+78	−62	+44	chair	down-down
	6	Cu-S(2)-C(4)-C(5)-C(6)-S(1′)	−33	+83	−42	−46	+83	−30	twist boat	down-up
	6	Cu-S(1′)-C(1′)-C(2′)-C(3′)-S(2′)	same as first ring						chair	up-up
	6	Cu-S(2′)-C(4′)-C(5′)-C(6′)-S(1)	same as second ring						twist boat	up-down

Macrocyclic Rings (C-S Torsion Angles Only)

ligand	ring	torsion angles,[b] deg			
[12]aneS$_4$	...C(1)-S(1)-C(8)...C(7)-S(4)-C(6)...	−75	+86	−165	+152
	...C(5)-S(3)-C(4)...C(3)-S(2)-C(2)...	−73	+159	−99	+142
[13]aneS$_4$	...C(9)-S(1)-C(1)...C(3)-S(2)-C(4)...	+79	−175	+170	−75
	...C(5)-S(3)-C(6)...C(7)-S(4)-C(8)...	+147	−160	+90	−163
[14]aneS$_4$[c]	...C(1′)-S(2)-C(5)...C(3)-S(1)-C(2)...	−159	+169	−177	+154
[15]aneS$_4$	...C(11)-S(1)-C(1)...C(3)-S(2)-C(4)···	+159	−174	+171	+164
	...C(6)-S(1′)-C(1′)...C(3′)-S(2′)-C(10)...	+165	+167	+179	+154
[16]aneS$_4$	...C(6′)-S(1)-C(1)···C(3)-S(2)-C(4)...	−164	−174	+169	+165

[a] For each Cu^{II}([*n*]aneS$_4$) complex, the successive bonds within each *chelate* ring are listed sequentially from left to right by proceeding in a clockwise manner as viewed along the Cu-O axis from the side opposite the lone-pair electrons on the S(1) and S(2) donor atoms (i.e., as one looks at the [12]- and [13]aneS$_4$ complexes in Figures 2 and 4 from the "bottom" side and the [15]- and [16]aneS$_4$ complexes in Figures 6 and 7 from the "top" side). From this perspective the lone-pair electrons on both S(1) and S(2) are observed to be "down" in all five complexes (as shown in the last column). As one proceeds down the third (ring) column for each complex, the individual chelate rings are listed as they appear in the same clockwise sequence. The first chelate ring listed for each complex was selected on the basis of maximizing the similarities in the torsion angle and ring conformational trends among the various complexes. For the *macrocyclic* ring bonds, the same clockwise sequence is used, but only the C-S-C ring segments are listed since the torsion angles for all other bonds are included in the chelate rings. [b] For the *chelate* rings, the torsion angles are listed sequentially from left to right for each bond represented in the ring by starting with the first Cu-S bond. Thus, in the first chelate ring listed for the [12]aneS$_4$ complex the torsion angles are as follows: for S(4)-Cu-S(1)-C(8), $\tau_0 = -20°$; for Cu-S(1)-C(8)-C(7), $\tau_1 = -14°$; ... for C(7)-S(4)-Cu-S(1), $\tau_4 = +40°$. For the *macrocyclic* rings, the torsion angles are also listed sequentially from left to right for the C-S bonds given. Thus, for the [12]aneS$_4$ complex, the C-S torsion angles are as follows: for C(2)-C(1)-S(1)-C(8), $\tau = -75°$; for C(1)-S(1)-C(8)-C(7), $\tau = +86°$; for C(8)-C(7)-S(4)-C(6), $\tau = -165°$; etc. [c] The torsion angles for the [14]aneS$_4$ complex were calculated from the data in ref 7. (For the seven torsion angles given in Table III of that reference, the sign convention used was opposite to that used in this paper.)

4.72 Å with Cu(II), 4.90 Å with Mo(II),[21a] and 5.17 Å with Hg(II).[21b]

Trends in Ligand Bond Angles and Ring Conformations. As the size of the macrocyclic ring increases, there appear to be two mechanisms whereby the ligands adjust to the spatial requirements of the coordinated metal ion. The first of these involves a compression of the C-S-C bond angles, which can be attributed to the ability of sulfur to mix d orbitals into the C-S bond. As shown in Table XI, uncomplexed thioether ligands (including [14]aneS$_4$) and noncylic thioether complexes with Cu(II) (including Cu^{II}(Et$_2$-2,3,2-S$_4$), the open-chain analogue of the current series of complexes) exhibit C-S-C bond angles ranging from 100 to 106°. If these complexes can be considered to be normal, then the copper(II) complexes with the smaller macrocyclic ligands have C-S-C bond angles that are also in the normal range. By contrast, the complexes formed with the larger [15]- and [16]aneS$_4$ ligands have C-S-C angles that deviate significantly from this range, presumably in response to the need to compress the ring in an attempt to achieve optimal coordinate bonding distances

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(22) The conformations of the five-membered rings were determined by calculating the pseudorotation angles (*P*) according to the formula

$$\tan P = \frac{(\tau_1 + \tau_4) - (\tau_0 + \tau_3)}{2\tau_2(\sin 36 + \sin 72)}$$

The torsion angles (τ_n) were defined so that at $P = 0°$ the S-C-C-S torsion angle would be maximally positive, characteristic of the symmetrical twist form. Thus, $\tau_0, \tau_1, ..., \tau_4$ represent the torsion angles about the Cu-S, S-C, C-C, C-S, and S-Cu bonds, respectively (Altona, C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 8205).

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between the copper and sulfur atoms.

The second mechanism involves changes in the torsion angles and ring conformations, for which the calculated values are listed in Table XII. These torsion angles are divided into two categories: (i) those torsion angles that are incorporated into the chelate rings and (ii) the C–C–S–C torsion angles that are a part of the peripheral macrocyclic ring but not of the chelate rings. For the larger [14]-, [15]-, and [16]aneS_4 complexes, where the carbon atom chains are puckered above and below the copper–sulfur atom plane, the peripheral C–C–S–C torsion angles of the macrocyclic rings are uniformly anti (averaging 166°), while these same angles fall into two distinct ranges for the [12]- and [13]aneS_4 complexes (in which all carbon atoms are on the opposite side of the S_4 plane from the copper atom), about half being anti (the absolute values ranging from 142 to 175°) and the remainder being essentially gauche (ranging from 73 to 99°). The chelate ring torsion angles are always gauche or eclipsed (ranging from 1 to 87°), presumably as a result of the constraints imposed by these relatively small five- and six-membered rings.

The close similarities in torsion angles among the various six- and five-membered chelate rings and the progressive trends in chelate ring conformations as the macrocyclic ring size is increased are particularly striking. For all of the tetragonal complexes (i.e., those with [14]-, [15]-, and [16]aneS_4), the crystallographic inversion center requires that the lone electron pairs on S(1) and S(2) point in the same direction with respect to the Cu–S_4 plane ("down"), while the lone electron pairs on S(1′) and S(2′) point in the opposite direction ("up") as shown in Figures 6 and 7. The six-membered chelate rings that incorporate sulfur atoms whose lone electron pairs are oriented in the *same* direction ("down–down" or "up–up") are in the chair conformation in these three structures with torsion angles that are virtually constant; the only significant variation in these rings is a slight decrease in the two Cu–S torsion angles for the [16]aneS_4 complex, presumably influenced, at least in part, by the lengthening of one pair of *trans*-Cu–S bonds as discussed in the preceding section. Likewise, the six-membered chelate ring in the [13]aneS_4 complex (which, of necessity, incorporates sulfurs whose lone electron pairs are oriented in the *same* direction) is in a virtually identical chair conformation. By contrast, the six-membered chelate rings in the [15]- and [16]aneS_4 complexes which incorporate sulfur atoms whose lone electron pairs are oriented in the *opposite* direction ("down–up" or "up–down") are forced into the twist-boat conformation rather than the more stable chair. The torsion angles in the twist-boat rings are also very similar for these two complexes despite the changes in the overall macrocyclic ring size.

In the [13]aneS_4 complex, the two five-membered rings adjacent to the six-membered ring are in the envelope conformation with the C(5) and C(8) atoms representing the flaps in these envelopes. The fourth ring is in the half-chair (or twist) conformation such that one carbon and one sulfur atom are twisted out of plane (in contrast to the tetragonal complexes in which the two carbon atoms are twisted out of plane in the half-chair rings). Thus, in Cu^{II}([13]aneS_4), as viewed in Figure 4, S(3) is above and C(6) below the Cu(1)–S(4)–C(7) plane. In Cu^{II}([12]aneS_4) there are two such chelate rings in the half-chair conformation. In these rings, as viewed in Figure 2, S(3) lies above and C(6) below the Cu–S(2)–C(3) plane and S(4) is above and C(7) below the Cu–S(1–)C(8) plane. For the two remaining rings, one is in the envelope conformation with C(2) as the flap while the remaining ring is intermediate between the half-chair and envelope conformations, although it more nearly approximates an envelope.

From the foregoing observations, a distinct trend in the chelate ring conformations is evident as the macrocyclic ring is increased stepwise from 12 to 16 atoms (see Table XII). In the [12]aneS_4 complex, two trans chelate rings are in the half-chair conformation while the other two are in the envelope or near-envelope form. The addition of one carbon atom to the macrocyclic ligand transforms one of the half-chair rings into a six-membered chair but has little other effect except to alter the near-envelope (intermediate) ring into a more perfect envelope conformation. The addition of a second carbon atom to the ligand converts the other half-chair ring into a six-membered chair. The resulting expansion of the central cavity to a diameter capable of accommodating the central copper atom, however, results in the inversion of two adjacent sulfur atoms, which converts the two remaining five-membered rings from the envelope to the more stable half-chair conformation. The sequential addition of two more carbons into the macrocyclic ring then transforms each of these half-chair rings into six-membered twist-boat rings.

Donor Selectivity at Axial Sites. Since the crystals of all five Cu(II) complexes were grown under identical conditions, involving the presence of only stoichiometric quantities of perchlorate ion (from $Cu(ClO_4)_2$), it is interesting to note that H_2O serves as the lone axial ligand in the two five-coordinate square-pyramidal complexes while ClO_4^- occupies both axial sites in the three tetragonal complexes. The stronger Cu–O interaction in the five-coordinate complexes probably accounts for the selection of the more basic water oxygen over the perchlorate oxygen in these complexes. However, in these complexes, one or more of the perchlorate oxygens appears to be hydrogen bonded to the coordinated water while another ClO_4^- is aligned with the Cu–O axis on the opposite side of the ring with an average (nonbonding) Cu–O distance of 4.5 Å (Figures 3 and 5). These interactions may contribute to the overall stability of the species observed in the crystalline state.

Constancy of Total Coordination Sphere. In conjunction with the foregoing observations on the selectivity of the coordinated axial donors, it is interesting to note that, as the Cu(II) ion is displaced further from the sulfur donor plane, the axial Cu–O bond shortens perceptibly from an average of 2.15 (2) Å for Cu^{II}([13]aneS_4) to 2.11 (2) Å for Cu^{II}([12]aneS_4). Apparently, this shortening of the Cu–O bond compensates for the slight lengthening of the four Cu–S bonds from an average distance of 2.32 Å for the [13]aneS_4 complex to 2.33 Å for [12]aneS_4. Similarly, in the three tetragonal complexes formed with the larger cyclic ligands, the Cu–O bond distances to the two axial perchlorates shorten markedly as the in-plane Cu–S bonds lengthen with increasing ring size.

The forgoing observations are consistent with the general correlations made by Gazo, Bersuker, and co-workers on a large number of Cu(II) complexes involving O_6, N_6, or N_4O_2 donor sets.[29] In emphasizing the unusual plasticity of the coordination sphere in Cu(II) complexes, these authors observed that the *sum* of the six coordinate bond lengths ($\sum R$) remained virtually constant for a common donor set despite large changes in the extent of tetragonal distortion. These constant sums pertained regardless of the nature of the ligands of which the donor atoms were a part (e.g., oxygen in H_2O, OH^-, NO_3^-, NO_2^-).

In our series of complexes, involving a different set of donor atoms (S_4O_2 or S_4O), we observe a similar phenomenon. As shown in Table X, the sum of the five donor atoms in the [12]aneS_4 and [13]aneS_4 complexes is 11.44 Å, while the [14]aneS_4, [15]aneS_4, and [16]aneS_4 complexes have bond length sums of 14.52, 14.33, and 14.40 Å, respectively. Furthermore, in the closely related Cu(II) complex with the

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open-chain tetrathia ether 3,6,10,13-tetrathiapentadecane (Et_2-2,3,2-S_4),[30] where one sulfur donor atom is out of plane and the axial ligands consist of one water and one perchlorate at unequal Cu–O distances, the sum of the six bond lengths is 14.43 Å.

Taking the difference between the average value of $\sum R$ for the four six-coordinate complexes (~14.4 Å) and the corresponding value for the two five-coordinate complexes (11.4 Å), we obtain a difference of 3.0 Å. This should correspond to the limiting bonding distance of an axial Cu–O bond, being nearly identical with the 3.1-Å limiting Cu–O distance obtained by Gazo et al. in their series of O_6 and N_4O_2 complexes.[29] Furthermore, the difference between the $\sum R$ value obtained for our S_4O_2 coordination sphere (14.4 Å) and the corresponding value obtained in Gazo et al. for O_6 complexes (12.6 Å) yields a total increase in the bonding distance of 1.8 Å for the four equatorial Cu–S bond distances relative to four equatorial Cu–O bonds or an average bond difference of 0.45 Å. This agrees well with the difference of 0.44 Å in the Pauling crystal radii for sulfur and oxygen as recorded for S^{2-} (1.84 Å) and O^{2-} (1.40 Å).[31]

From the foregoing empirical correlations we conclude that, despite restrictions caused by ring strain, out-of-plane displacements of the central copper atom, changes in coordination number, and back-bonding of the sulfur to the copper, the total coordination sphere of copper in all of the tetrathia ether complexes is well within the normal limits of copper complexes. Nonetheless, the changes in overall structure are reflected in considerable variations in the physical properties of these complexes.[2-6] These will continue to be investigated and interpreted in terms of the structural parameters that have now been established.

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Registry No. Cu^{II}([12]aneS_4)$(ClO_4)_2(H_2O)$, 87350-93-4; Cu^{II}([13]aneS_4)$(ClO_4)_2(H_2O)$, 87350-95-6; Cu^{II}([15]aneS_4)$(ClO_4)_2$, 87370-88-5; Cu^{II}([16]aneS_4)$(ClO_4)_2$, 87350-96-7.

Supplementary Material Available: Listings of the thermal parameters for all four compounds, the calculated atomic coordinates for the hydrogen atoms in Cu^{II}([13]aneS_4)$(ClO_4)_2(H_2O)$ and Cu^{II}([16]aneS_4)$(ClO_4)_2$, and the structure factors for all four compounds (47 pages). Ordering information is given on any current masthead page.

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