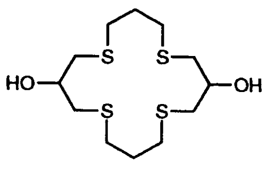
Synthesis and Structural Characterization of Crown Thioether Complexes of Silver(I) and Copper(II)†

Megumu Munakata,* Liang Ping Wu, Mikiko Yamamoto, Takayoshi Kuroda-Sowa and Masahiko Maekawa
Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan

The crown thioether silver(I) complexes $\{[Ag\{(OH)_2[16]aneS_4\}]NO_3\}_\infty$ **1** and $\{[Ag\{(OH)_2[16]aneS_4\}][O_2CMe]\}_\infty$ **2** and the copper(II) complex $[Cu\{(OH)_2[16]aneS_4\}][ClO_4]_2$ **3**, where $(OH)_2[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane-3,11-diol, have been prepared by reaction of $(OH)_2[16]aneS_4$ with the appropriate metal salt. The two silver structures are not isomorphous. Complex **1** crystallizes in the monoclinic space group *C*2 with *a* = 13.500(4), *b* = 9.178(2), *c* = 8.695(4) Å, β = 121.99(2)° and *Z* = 2. Silver(I) is tetrahedrally bound with four thioether groups from four symmetry-related macrocycles and each ligand molecule in turn co-ordinates to four separate silver(I) ions in an exodentate fashion to yield a three-dimensional tetrahedral polymeric network. Complex **2** crystallizes in the orthorhombic space group *Pccn* with *a* = 14.121(9), *b* = 17.203(8), *c* = 15.940(3) Å and *Z* = 8. It contains two types of crystallographically different silver(I) ions, both of which are co-ordinated by four sulfur atoms from four symmetry-related macrocycles in a rather distorted-tetrahedral fashion. The silver atoms are in a two-dimensional sheet arrangement interconnected by the macrocycle. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with *a* = 7.820(2), *b* = 13.853(2), *c* = 9.627(2) Å, β = 90.85(2)° and *Z* = 2. The molecule is a discrete monomer in which the tetradentate macrocycle is in the endodentate conformation with four thioether donors in a precisely square-planar arrangement around the copper.

The chemistry of crown thioethers has grown into a field that is now undergoing explosive development by a number of groups around the world.[1] Interest in this particular sector of macrocyclic chemistry has been focused on the synthesis, conformational analysis and co-ordination chemistry of the wide range of d-[2–27] and p-block[28] ions involved. At the forefront of these studies have been the complexes of 1,4,7-trithiacyclononane ($[9]aneS_3$), 1,4,7,10-tetrathiacyclododecane ($[12]aneS_4$), 1,4,8,11-tetrathiacyclotetradecane ($[14]aneS_4$), 1,5,9,13-tetrathiacyclohexadecane ($[16]aneS_4$) and 1,4,7,10,13,16-hexathiacyclooctadecane ($[18]aneS_6$). An important feature is that these macrocycles have remarkable versatility in adopting unpredictable geometries and stabilizing unusual oxidation states.[9]

Macrocyclic thioether complexes[10–20] of copper-(I) and -(II) have been the subject of much interest for a long time as simple models for blue copper proteins.[11] By contrast, the investigation of corresponding silver(I) complexes has developed only recently.[21–27] The reactions of Ag^I with the tridentate crown thioether $[9]aneS_3$ have been reported in the complex cation $[Ag([9]aneS_3)_2]^+$ in which the Ag^I is sandwiched by two trithia ligands,[24] and in the trimeric cation $[Ag_3([9]aneS_3)_3]^{3+}$ in which the ligands are bridging.[23] Schröder and co-workers[21] have characterized the dinuclear silver(I) complex $[Ag_2([15]aneS_5)_2]^{2+}$ with the pentadentate crown thioether $[15]aneS_5$ (1,4,7,10,13-pentathiacyclopentadecane), in which each macrocycle bridges asymmetrically. In addition, polymeric network structures have been reported by Cooper and co-workers[25] for complexes of Ag^I with tridentate $[12]aneS_3$ (1,5,9-trithiacyclododecane) and hexadentate $[18]aneS_6$. Surprisingly the co-ordination chemistry of Ag^I with tetradentate crown thioethers has received less attention. We report here two complexes of Ag^I and one of Cu^{II} with the tetradentate crown thioether 1,5,9,13-tetrathiacyclohexadecane-3,11-diol, $(OH)_2[16]aneS_4$, involving two different conformational modes of the macrocycle.



$(OH)_2[16]aneS_4$

Although $(OH)_2[16]aneS_4$ is commercially available, its potential for formation of unusual metal complex architecture has not been fully explored. The complexation behaviour for Cu^I has been investigated by polarizing microscopy[29] and the formation constants of the complexes with Ag^I and Hg^{II} have also been measured.[30] However, little information is available concerning the structural chemistry of the ligand except one report on the mononuclear technetium(V) complex $[TcN(Cl)\{(OH)_2[16]aneS_4\}]Cl$.[31]

A particularly active field of chemical research in recent years has been the design of polymeric metal complexes. Lack of knowledge on the structural control of complexes, however, makes dramatic developments difficult in respect of designing syntheses. Our recent efforts have therefore been focused on controlling the structures of polymeric copper(I) and silver(I) complexes.[32–39] We report here the dimensional control of crown thioether complexes by the metal ions and the counter anions.

Results

Crystal Structure of Complex **1**.—Direct reaction of an aqueous solution of $AgNO_3$ with 1 molar equivalent of $(OH)_2[16]aneS_4$ in MeCN affords colourless plate crystals of

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

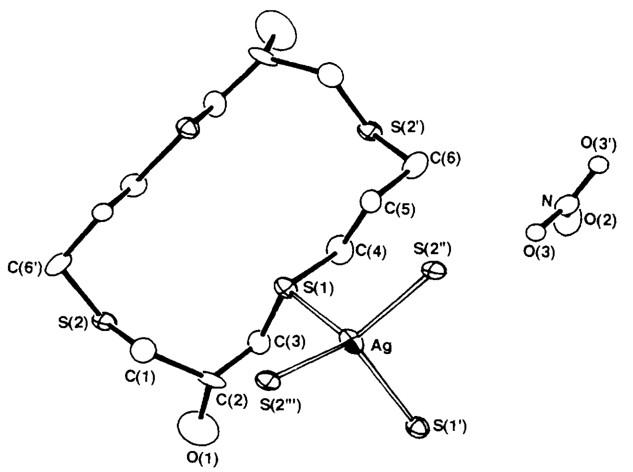


Fig. 1 An ORTEP[40] view of the partial molecular structure of complex **1** with the atom numbering scheme

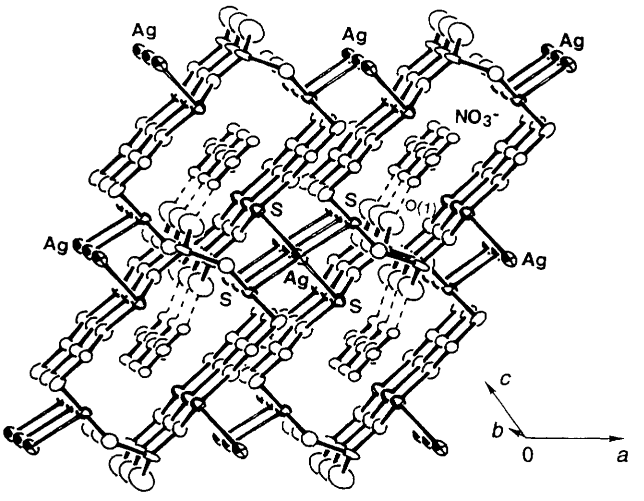


Fig. 2 Packing diagram for complex **1** along the *b* axis. Dashed lines show the hydrogen bonds: O(1) ··· O(2) 2.90(2) Å

$\{[Ag\{(OH)_2[16]aneS_4\}]NO_3\}_\infty$ **1**. The IR spectrum shows an absorption at 1371 cm^{-1} corresponding to N–O stretching vibrations, ν(N–O), as well as other peaks confirming the presence of co-ordinated $(OH)_2[16]aneS_4$. A single-crystal structure determination reveals (Fig. 1) that in this complex each silver(I) ion is co-ordinated by four thioether groups in an essentially tetrahedral geometry with S–Ag–S bond angles ranging from 107.6(1) to 113.9(2)°, and Ag–S distances of 2.643(5) and 2.600(4) Å, Table 1. These four thioether groups are not from a single ligand. Instead, each Ag atom is bound to four different sulfurs from four symmetry-related macrocycles as illustrated by the partial structure in Fig. 2, and each ligand molecule in turn co-ordinates to four separate silver(I) ions in an exodentate fashion. The total crystal structure is built up from these repeating units to give a three-dimensional tetrahedral network. The structure shows that the macrocycle adopts a much more flattened conformation with an opened 16-membered cavity filled with NO_3^-. In this huge polymeric complex each Ag atom is surrounded by eight of its partners interconnected by $(OH)_2[16]aneS_4$ in a tetragonal array. There is extensive hydrogen bonding in the crystal involving the counter anion NO_3^- sitting inside the cavity of the macrocycle and the OH group of the adjacent ligand, H–O(1) ··· O(2) 2.90(2) Å, Fig. 2.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**–**3**

Complex **1**			
Ag–S(1)	2.643(5)	Ag–S(2)	2.600(4)
O(1)–C(2)	1.39(2)		
S(1)–Ag–S(1')	110.7(2)	S(1)–Ag–S(2''')	108.5(1)
S(1)–Ag–S(2")	107.6(1)	S(2")–Ag–S(2''')	113.9(2)
Complex **2**			
Ag(1)–S(1)	2.697(6)	Ag(1)–S(4')	2.546(7)
Ag(2)–S(2)	2.604(7)	Ag(2)–S(3')	2.658(6)
O(1)–C(2)	1.38(3)	O(2)–C(8)	1.62(3)
S(1)–Ag(1)–S(1')	86.9(3)	S(1')–Ag(1)–S(4')	127.0(2)
S(1)–Ag(1)–S(4")	94.8(2)	S(4')–Ag(1)–S(4")	123.6(3)
S(2)–Ag(2)–S(2')	119.2(3)	S(2')–Ag(2)–S(3')	97.3(2)
S(2)–Ag(2)–S(3')	124.7(2)	S(3')–Ag(2)–S(3")	93.0(3)
Complex **3**			
Cu–S(1)	2.356(2)	Cu–S(2)	2.350(2)
Cu ··· O(3)	2.599(4)	O(5)–C(1)	1.408(7)
S(1)–Cu–S(1')	180.0	S(1)–Cu–S(2)	89.46(5)
S(1)–Cu–S(2')	90.54(5)	S(2)–Cu–S(2')	180.0
S(1)–Cu–O(3)	89.5(1)	S(1)–Cu–O(3')	90.5(1)
S(2)–Cu–O(3)	81.6(1)	S(2)–Cu–O(3')	98.4(1)
O(3)–Cu–O(3')	180.0		

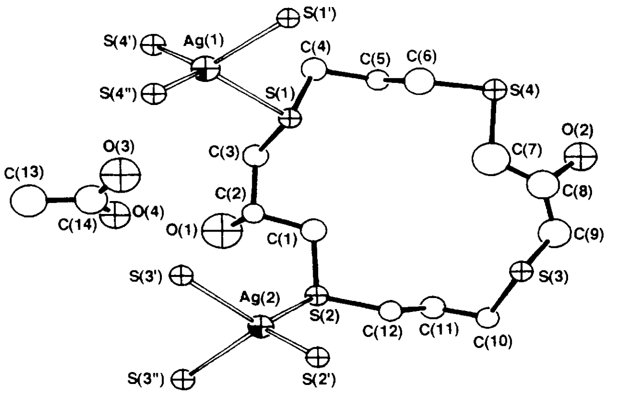


Fig. 3 An ORTEP view of the partial molecular structure of complex **2** with the atom numbering scheme

Crystal Structure of Complex **2**.—Crystals of $\{[Ag\{(OH)_2[16]aneS_4\}][O_2CMe]\}_\infty$ suitable for X-ray analysis were obtained by reaction of AgO_2CMe with 1 molar equivalent of $(OH)_2[16]aneS_4$ using acetone as a diffusion solvent. The structure and atom labelling scheme is depicted in Fig. 3. There are two types of crystallographically different silver(I) ions in the complex and both of them are co-ordinated by four thioether groups in a rather distorted-tetrahedral fashion. As in **1**, these four thioether groups come from each of four symmetry-related ligands and each ligand molecule is in turn co-ordinated to four separate Ag atoms with the *exo* conformation to yield a polymeric network structure. Fig. 4 indicates a portion of the polymer. The variation of the Ag–S bond lengths for Ag(1), 2.546(7) and 2.697(6) Å, Table 1, is significantly greater than that for Ag(2), 2.658(6) and 2.604(7) Å. The variation of S–Ag(1)–S angles in the range 86.9(3)–127.0(2)° is also remarkable compared with 93.0(3)–124.7(2)° for S–Ag(2)–S, suggesting that the co-ordination sphere of Ag(1) involves a more severe distortion from regular tetrahedral. The silver atoms in the crystal are in a two-dimensional sheet arrangement in which atoms Ag(1) and

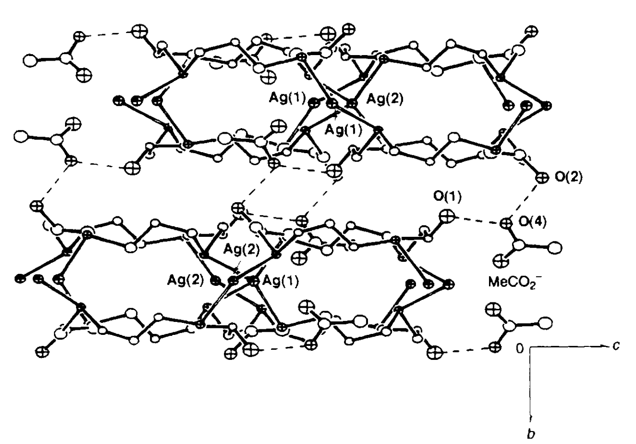


Fig. 4 Packing diagram for complex **2** along the *a* axis. Dashed lines show the hydrogen bonds: O(1) • • • O(4) 2.54(3), O(2) • • • O(4) 2.67(3) Å

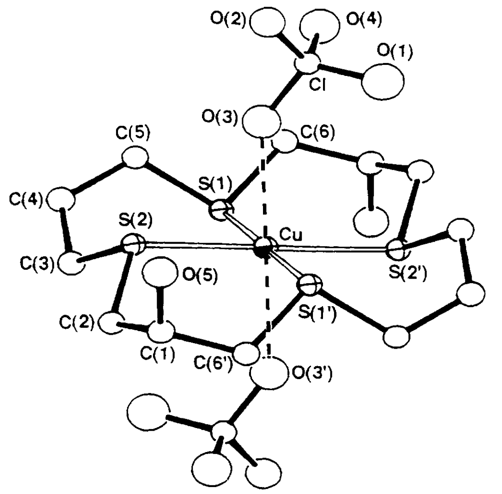


Fig. 5 An ORTEP view of the molecular structure of complex **3** with the atom numbering scheme

Ag(2) are stacked alternately along a diagonal to the *a* and *c* axes of the unit cell. Strong hydrogen bonding links the $MeCO_2^-$ anion and the OH group of two adjacent $(OH)_2[16]aneS_4$ ligands, O(1) • • • O(4) 2.54(3) and O(2) • • • O(4) 2.67(3) Å, holding the sheets together to give a three-dimensional network, Fig. 4.

Crystal Structure of Complex **3**.—Treatment of $Cu(ClO_4)_2 \cdot 6H_2O$ with $(OH)_2[16]aneS_4$ in MeOH at ambient temperature gave a black cloudy suspension which upon addition of a small amount of Et_2O deposited black plates of $[Cu\{(OH)_2[16]aneS_4\}][ClO_4]_2$. The molecular structure together with the atomic numbering scheme is given in Fig. 5 and selected interatomic distances and angles are in Table 1. The structure consists of a centrosymmetric mononuclear $[Cu\{(OH)_2[16]aneS_4\}]^{2+}$ cation and two weakly co-ordinating ClO_4^- anions. Discounting interactions between copper and perchlorate, the Cu^{II} is co-ordinated by four thioether donors in an exact square-planar arrangement (D_{4h} symmetry) even though the macrocycle itself is strongly pleated and twisted. Since the Cu atom is located at an inversion centre, the CuS_4 chromophore is crystallographically constrained to be coplanar. In addition, although not required by symmetry, the two independent Cu–S bonds are equal in length and the S–Cu–S angles are 90° indicating a perfect square-planar co-ordination environment around the metal. The Cu–S thioether bond distances of 2.350(2) and 2.356(2) Å compare well with those found in $[Cu([16]aneS_4)][ClO_4]_2$.[18] The axial co-ordination sites of the copper(II) ion are occupied by two O atoms from two symmetry-related perchlorate anions, at Cu • • • O(3) 2.599(4) Å, to complete an approximate octahedral CuS_4O_2 chromophore.[40] Although the O(3) atom cannot be viewed as directly bonded to the metal ion, the Cu • • • O distance is short enough to suggest at least some weak or semi-co-ordination.[41] The infrared spectrum of **3** shows a strong and slightly split band at 1103 cm^{-1} owing to the ν_3 mode of the ClO_4^-, consistent with its bonding interaction with copper. There is also extensive intermolecular hydrogen bonding in the crystal between the counter anion ClO_4^- and the OH group of an adjacent $(OH)_2[16]aneS_4$ ligand, H–O • • • $OClO_3^-$ 2.855(6) Å (Fig. 6).

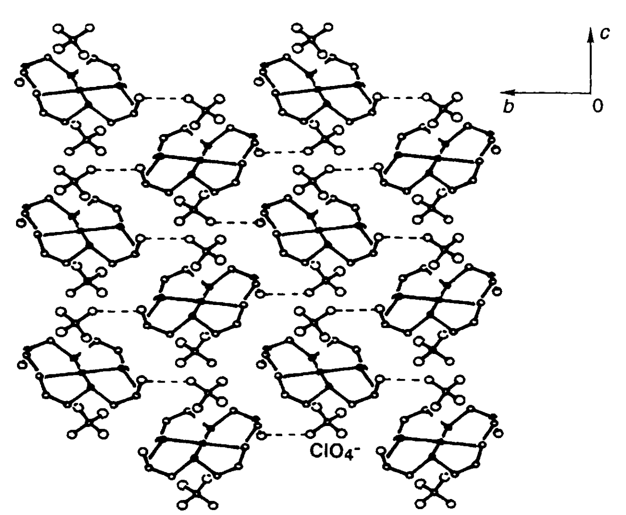


Fig. 6 Packing diagram for complex **3** along the *a* axis. Dashed lines show the hydrogen bonds: O(2) • • • O(5) 2.855(6) Å

Discussion

Although we have tried to synthesize the corresponding copper(I) complex with $(OH)_2[16]aneS_4$ by using tetrakis(acetonitrile)copper(I) perchlorate, the copper(I) ion was found to be oxidized to copper(II) even under an argon atmosphere. The structure determinations of the three complexes have revealed two different types of bonding for the potentially quadridentate macrocyclic ligand $(OH)_2[16]aneS_4$. In the compound with copper perchlorate (**3**), $(OH)_2[16]aneS_4$ adopts the *endo* conformation with the copper(II) lying strictly inside the macrocyclic ring. On the other hand, in the two polymeric silver complexes the metal ions have distorted-tetrahedral geometries and the ligand is turned 'inside out' and adopts the exodentate conformation in each case. Even between the two silver complexes, **1** and **2**, the structural differences are significant. Such a change of the metal ion or counter anion leading to a totally different structure indicates both the remarkable versatility and flexibility of the ligand, which has been characterized in other crown thioether complexes, and the marked influence of the cations and anions involved.

Previous conformational analyses[1,5,8,18] on $[14]aneS_4$, $[16]aneS_4$ and other macrocyclic thioethers revealed that, with the exception of $[9]aneS_3$, each crown thioether has a strong preference for exodentate orientation with respect to the macrocyclic cavity. Crystals of the various forms of free $[14]aneS_4$ have been shown to have *exo* conformations.[41] Molecular mechanics studies[8] on $[16]aneS_4$ also showed that the lowest-energy conformation is quadrangular with the sulfur atoms at the corners of a square, which disfavours endodentate chelation. Thus the *exo* conformational mode of $(OH)_2[16]aneS_4$ observed in our two silver(I) complexes lent further support to these general conclusions. In contrast, the formation of the *endo*-type complex of this ligand in **3** is presumed to require reorganization of the macrocycle as in $[Cu([16]aneS_4)][ClO_4]_2$.[18]

In the present work the metal-ion size seems to be one of the major factors controlling the bonding mode of $(OH)_2[16]aneS_4$. Glick and co-workers[18] studied several copper(II) complexes of 12- through 16-membered S_4 macrocyclic thioethers in an attempt to find the ring-size effects on the general structural morphology. It was found 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}. In a series of metal complexes of $[14]aneS_4$ such as $[Ni([14]aneS_4)][BF_4]_2$[7] and $[Cu([14]aneS_4)][ClO_4]_2$[11] the metal ion is centred in the plane of the four sulfur atoms with the ligand adopting the same *endo* conformation in each case. However, with larger metal ions such as Hg^{II} (ref. 4) and Cu^{I} (refs. 10 and 13) a switch from the *endo* to the *exo* conformation is observed because of the relatively small cavity in the centre of the macrocyclic ligand with respect to the metal-ion size. In analogous metal complexes of the more flexible 16-membered ring $[16]aneS_4$ this pattern still exists. Structural data for the complexes of Fe^{II},[2] Hg^{II} (ref. 8) and Ni^{II} (ref. 42) show that the metal ion in each is encircled by an ample macrocyclic ring and its co-ordination sphere is completed by apical counter anions. Copper(II) ion is about the same size as Ni^{II} or Fe^{II} and there is little doubt about the *endo* conformation of $(OH)_2[16]aneS_4$ in the copper(II) complex. What would happen with an even larger metal ion such as Ag^{I}? The crystallographic results for **1** and **2** have shown that Ag^{I} is too big to fit in the cavity of the macrocycle, which forces four sulfur-donor atoms to point towards the outside of the 16-membered macrocyclic ring and donate to four separate metal ions. The present paper represents the first structural evidence for an *exo* conformation of a 16-membered crown thioether about a transition-metal ion.

Another example to demonstrate the importance of macrocyclic cavity size in determining the conformation of the macrocycle is provided by the crystal structure of $[Ag([16]aneS_6)][ClO_4]$[22] ($[16]aneS_6$ = 1,3,6,9,11,14-hexathiacyclohexadecane) in which the macrocycle is similar to that of $(OH)_2[16]aneS_4$ except that it contains two extra sulfur atoms in place of two carbon atoms. In this complex, although a distorted-tetrahedral co-ordination sphere around Ag is still maintained from four sulfur atoms, a monomeric structure with *endo* conformation of the ligand is observed. This is obviously attributable to the larger size of the sulfur-donor atoms, which might be expected to increase the cavity size of the macrocycle.

The metal-ion size in respect to the cavity size of the macrocycle, although important, is not the only factor to be considered here. While Cu^{II} generally prefers a square-coplanar to a tetrahedral co-ordination sphere, most silver(I) crown thioether complexes exhibit idealized tetrahedral geometry. Thus the generation of two silver complexes of $(OH)_2[16]aneS_4$ having a polymeric tetrahedral network structure must result in part from the strong tendency of Ag^{I} to achieve a tetrahedral co-ordination sphere which cannot be obtained simply by distortion or rearrangement of the 16-membered macrocycle. The same conclusion has been reached previously for the copper(I) complex $[Cu([14]aneS_4)]ClO_4$.[10,13]

Crown thioethers co-ordinated in the *exo* conformation in complexes usually tend to bridge metal ions, and are expected to form an extensive polymeric network structure. It is noteworthy that in metal-ion complexes of crown thioethers with polymeric structure such as $\{[Hg([14]aneS_4)I_2]\}_\infty$,[4] $\{[Cu([14]aneS_4)]ClO_4\}_\infty$,[13] $\{[Ag([18]aneS_6)Br]\}_\infty$,[25] $\{[Ag([12]aneS_3)(CF_3SO_3)]\cdot MeCN\}_\infty$ ($[12]aneS_3$ = 1,5,9-trithiacyclododecane),[25] and the two silver complexes of this work the metal ion has a tetrahedral environment, presumably due to the steric requirements. In other words, no structural evidence appears to exist for a polymeric complex of this type involving a square-planar or octahedral co-ordination environment about the metal ion. This study and previous structural work on transition-metal complexes of crown thioethers offer a guide to the future design of unique polymeric metal complex architecture.

A second point of interest in the present study is that $(OH)_2[16]aneS_4$ having two hydroxyl groups shows a unique ability to form hydrogen bonds. The common feature of the three complexes in this paper is the presence of the extensive intermolecular hydrogen-bonding network connecting the cations and the counter anions. Similar hydrogen bonding has been observed in $[TcN(Cl)\{[16]aneS_4(OH)_2\}]Cl$.[31] Such hydrogen bonding is also an important factor in determining the conformation of the ligand in the two silver(I) polymeric structures reported here. In contrast to **1** in which NO_3^- is connected to only one hydroxyl group with relatively medium strength (O $\cdots$ O 2.90 Å), Fig. 2, the counter anion $MeCO_2^-$ in

Table 2 Crystal and refinement data for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{12}H_{24}AgNO_5S_4$	$C_{14}H_{27}AgO_4S_4$	$C_{12}H_{24}Cl_2CuO_{10}S_4$
M	498.44	495.47	591.00
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*2	*Pccn*	$P2_1/c$
a/Å	13.500(4)	14.121(9)	7.820(2)
b/Å	9.178(2)	17.203(8)	13.853(2)
c/Å	8.695(4)	15.940(3)	9.627(2)
β/°	121.99(2)		90.85(2)
U/Å^3	913.8(2)	3872.2(1)	1042.8(3)
Z	2	8	2
D_c/g cm^{-3}	1.811	1.700	1.882
F(000)	508	2032	606
Crystal size/mm	0.10 × 0.15 × 0.08	0.10 × 0.10 × 0.05	0.10 × 0.10 × 0.05
μ(Mo-Kα)/cm^{-1}	15.51	14.59	17.40
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan rate/° min^{-1}	4.0	8.0	4.0
$2\theta_{max}$/°	55.0	54.9	55.0
No. reflections measured	1168	4935	2662
No. observed [$F_o > 3\sigma(F_o)$]	725	1319	1364
No. parameters	105	199	133
R	0.061	0.084	0.042
R'	0.061	0.095	0.046
Goodness of fit	1.81	3.30	1.39

Table 3 Atomic coordinates for complex **1**

Atom	*x*	*y*	*z*
Ag	0	0	0
S(1)	−0.0188(3)	0.1636(5)	0.2334(6)
S(2)	−0.3108(3)	0.3456(5)	0.1829(5)
O(1)	−0.288(2)	0.378(2)	−0.163(3)
O(2)	$\frac{1}{2}$	0.298(2)	$\frac{1}{2}$
O(3)	0.414(1)	0.099(2)	0.387(2)
N	$\frac{1}{2}$	0.165(3)	$\frac{1}{2}$
C(1)	−0.300(2)	0.211(2)	0.041(3)
C(2)	−0.226(2)	0.268(2)	−0.038(3)
C(3)	−0.105(1)	0.318(2)	0.102(2)
C(4)	0.118(2)	0.261(2)	0.392(3)
C(5)	0.209(1)	0.156(2)	0.518(2)
C(6)	0.326(2)	0.232(2)	0.663(3)

Table 4 Atomic coordinates for complex **2**

Atom	*x*	*y*	*z*
Ag(1)	$\frac{3}{4}$	$\frac{1}{4}$	0.3374(2)
Ag(2)	$\frac{1}{4}$	$\frac{1}{4}$	0.4122(2)
S(1)	0.6532(4)	0.1771(4)	0.4602(3)
S(2)	0.3095(4)	0.1289(4)	0.4949(4)
S(3)	0.3504(4)	0.1741(4)	0.7974(3)
S(4)	0.7030(5)	0.1254(4)	0.7619(4)
O(1)	0.436(2)	0.061(2)	0.358(2)
O(2)	0.571(1)	0.048(1)	0.887(1)
O(3)	0.545(2)	0.183(2)	0.211(2)
O(4)	0.468(1)	0.079(1)	0.202(1)
C(1)	0.436(2)	0.124(2)	0.492(1)
C(2)	0.469(2)	0.123(1)	0.404(1)
C(3)	0.580(2)	0.100(1)	0.409(2)
C(4)	0.748(2)	0.118(2)	0.497(2)
C(5)	0.726(2)	0.089(1)	0.590(1)
C(6)	0.722(2)	0.159(2)	0.651(1)
C(7)	0.568(2)	0.119(2)	0.755(2)
C(8)	0.517(3)	0.112(2)	0.831(2)
C(9)	0.424(2)	0.100(2)	0.847(2)
C(10)	0.261(2)	0.111(2)	0.746(1)
C(11)	0.283(2)	0.085(2)	0.665(2)
C(12)	0.278(1)	0.149(1)	0.603(1)
C(13)	0.497(2)	0.146(3)	0.075(2)
C(14)	0.498(2)	0.138(2)	0.167(2)

2 is located between the two-dimensional sheets of the cations and involved in rather strong hydrogen bonds (O···O 2.54 and 2.67 Å), Fig. 4. As a result there is appreciable constraint in the latter structure including severely distorted tetrahedral CuS_4 and a much twisted macrocycle. Further investigation on this system with other anions is underway to clarify this point. Moreover, this type of hydrogen-bonding interaction also affects the bond length between the carbon atom and the attached hydroxyl group. As seen in Table 1, the C–O distances in **1** [1.39(2) Å] and **3** [1.408(7) Å] are comparable, while the corresponding bond lengths of O(1)–C(2) [1.38(3) Å] and O(2)–C(8) [1.62(3) Å] for **2** differ significantly. The unusual long bond distance of O(2)–C(8) in **2** appears to be due to the asymmetric hydrogen bonding of the $MeCO_2^-$ anion to both hydroxyl groups, Fig. 4.

In conclusion copper(II) ion forms a monomeric complex with $(OH)_2[16]aneS_4$ of *endo* conformation because the metal ion prefers a square-planar geometry and fits well the cavity size of the ligand. On the other hand silver(I) ion forms a polymeric complex with the ligand in exodentate conformation because of the large metal-ion size and the tetrahedral co-ordination mode. The structures and dimensionalities of the polymeric silver(I) complexes are further modified by the counter anion because of hydrogen bonding between the hydroxyl groups of the ligand and the counter anion. The dimensionality of the $(OH)_2[16]aneS_4$ complex is thus controlled by the counter anion as well as the metal ion.

Table 5 Atomic coordinates for complex **3**

Atom	*x*	*y*	*z*
Cu	0	0	0
Cl	−0.2261(2)	−0.0263(1)	0.3519(1)
S(1)	0.2692(2)	−0.0351(1)	0.1008(1)
S(2)	0.0536(2)	0.1655(1)	0.0320(1)
O(1)	−0.3538(7)	−0.0842(4)	0.2897(7)
O(2)	−0.3029(7)	0.0448(3)	0.4367(5)
O(3)	−0.1260(7)	0.0182(4)	0.2469(5)
O(4)	−0.1192(7)	−0.0862(4)	0.4330(5)
O(5)	−0.2977(7)	0.2492(3)	−0.0542(5)
C(1)	−0.1906(8)	0.2263(4)	−0.1658(6)
C(2)	−0.0025(8)	0.2317(4)	−0.1252(6)
C(3)	0.2856(7)	0.1804(4)	0.0227(6)
C(4)	0.3738(8)	0.1515(4)	0.1589(6)
C(5)	0.3025(7)	0.0620(4)	0.2259(6)
C(6)	−0.2448(8)	0.1307(4)	−0.2301(6)

Experimental

All preparations were performed using usual Schlenk techniques. The reagents $AgNO_3$ and AgO_2CMe were obtained from Wako Co., Japan; $(OH)_2[16]aneS_4$ (Aldrich) was used without further purification, and $Cu(ClO_4)_2 \cdot 6H_2O$ was dried for 7 h at 60 °C under reduced pressure. All solvents were dried and distilled by standard methods before use. Infrared spectra were measured as KBr discs on a JASCO FT/IR-8000 spectrometer over the range 200–4000 cm^{-1}.

Preparations.—$\{[Ag\{(OH)_2[16]aneS_4\}]NO_3\}_\infty$ **1**. A solution of $AgNO_3$ (17.0 mg, 0.10 mmol) in water (1.5 cm^3) was placed in a glass tube (diameter 5 mm) and a solution of $(OH)_2[16]aneS_4$ (32.9 mg, 0.10 mmol) in MeCN (1.5 cm^3) gently added. The glass tube was then sealed and allowed to stand at ambient temperature for 2 d, giving colourless plates, yield ≈60% (Found: C, 28.40; H, 4.40; N, 3.00. Calc. for $C_{12}H_{24}AgNO_5S_4$: C, 28.90; H, 4.80; N, 2.80%).

$\{[Ag\{(OH)_2[16]aneS_4\}][O_2CMe]\}_\infty$ **2**. An aqueous solution (2.0 cm^3) of AgO_2CMe (21.7 mg, 0.13 mmol) and a solution of $(OH)_2[16]aneS_4$ (42.7 mg, 0.13 mmol) in MeCN (2.0 cm^3) were mixed and stirred for 10 min under Ar. The resultant colourless solution was filtered and the filtrate transferred to a glass tube (diameter 5 mm) and then layered with acetone (2.0 cm^3). The tube was allowed to stand at ambient temperature for 4 d, giving colourless plates in the diffusion solvent, yield ≈45% (Found: C, 34.20; H, 5.25. Calc. for $C_{14}H_{27}AgO_4S_4$: C, 33.95; H, 5.50%).

$[Cu\{(OH)_2[16]aneS_4\}][ClO_4]_2$ **3**. Dropwise addition of the solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (25.0 mg, 0.067 mmol) in MeOH (2.0 cm^3) to a solution of $(OH)_2[16]aneS_4$ (20.1 mg, 0.062 mmol) in MeOH (4.0 cm^3) produced a black cloudy suspension which was stirred for 1 h at room temperature. Removal of the black solid through filtration gave a clear dark yellow-green solution, which was sealed in a glass tube with Et_2O (2.0 cm^3). After standing at ambient temperature for 1 week black plate single crystals were obtained, yield ≈20% (Found: C, 24.20; H, 3.95. Calc. for $C_{12}H_{24}Cl_2CuO_{10}S_4$: C, 24.35; H, 4.05%).

Crystallography.—Details of the crystal data collection and processing, structure analysis and refinement for complexes **1**–**3** are given in Table 2. The unit-cell data and intensities were collected on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). All three structures were solved by a direct method (MITHRIL)[43] and refined by full-matrix least-squares minimization of $\Sigma w(|F_o| - F_c|)^2$ with anisotropic thermal parameters for all the non-hydrogen atoms. Isotropic hydrogen atoms were located by Fourier-difference synthesis and refined on the associated C or O atoms. All of the calculations were performed using the TEXSAN crystallographic software package[44] on a micro VAX computer. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}$, where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 45. The final atomic coordinates are given in Tables 3–5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

This work was partially supported by a Grant-in Aid for Science Research [nos. 0723226 and 07241260 (priority areas)] from the Ministry of Education, Science and Culture in Japan. The authors are also grateful to Kinki University for financial support (GG 1100).

References

1 S. R. Cooper and S. C. Rawle, *Struct. Bonding (Berlin)*, 1990, **72**, 1; A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1; S. R. Cooper, *Acc. Chem. Res.*, 1988, **21**, 141.

2 A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh, A. Houlton and J. Silver, *J. Chem. Soc., Chem. Commun.*, 1989, 1774.

3 T. Adachi, M. D. Durrant, D. L. Hughes, C. J. Pickett, R. L. Richards, J. Talarmin and T. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1992, 1464.

4 N. Galešić, M. Herceg and D. Sevdić, *Acta Crystallogr., Sect. C*, 1986, **42**, 565.

5 T. F. Lai and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 1982, 1465.

6 A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1989, 1675.

7 P. H. Davis, L. K. White and R. L. Belford, *Inorg. Chem.*, 1975, **14**, 1753.

8 W. N. Setzer, Y. Tang, G. J. Grant and D. G. VanDerveer, *Inorg. Chem.*, 1991, **30**, 3652.

9 A. J. Blake, M. A. Halcrow and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1994, 1631 and refs. therein.

10 L. L. Diaddario, jun., E. R. Dockal, M. D. Glick, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg. Chem.*, 1985, **24**, 356.

11 M. D. Glick, D. P. Gavel, L. L. Diaddario and D. B. Rorabacher, *Inorg. Chem.*, 1976, **15**, 1190.

12 J. M. Desper and S. H. Gellman, *J. Am. Chem. Soc.*, 1991, **113**, 704.

13 E. R. Dockal, L. L. Diaddario, M. D. Glick and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1977, **99**, 4530.

14 R. O. Gould, A. J. Lavery and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1985, 1492.

15 J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1202.

16 P. W. R. Corfield, C. Ceccarelli, M. D. Glick, I. W. Y. Moy, L. A. Ochrymowycz and D. B. Rorabacher, *J. Am. Chem. Soc.*, 1985, **107**, 2399.

17 B. de Groot and S. J. Loeb, *Inorg. Chem.*, 1989, **28**, 3573.

18 V. B. Pett, L. L. Diaddario, jun., E. R. Dockal, P. W. Corfield, C. Ceccarelli, M. D. Glick, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg. Chem.*, 1983, **22**, 3661.

19 A. J. Blake, A. Taylor and M. Schröder, *Polyhedron*, 1990, **9**, 2911.

20 A. J. Blake, R. O. Gould, A. J. Holder, A. J. Lavery and M. Schröder, *Polyhedron*, 1990, **9**, 2919.

21 A. J. Blake, R. O. Gould, G. Reid and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1990, 974.

22 B. de Groot and S. J. Loeb, *Inorg. Chem.*, 1991, **30**, 3103.

23 H. J. Küppers, K. Wieghardt, Y. H. Tsay, C. Krüger, B. Nuber and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 575.

24 J. Clarkson, R. Yagbasan, P. J. Blower, S. C. Rawle and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1987, 950.

25 P. J. Blower, J. A. Clarkson, S. C. Rawle, J. R. Hartman, R. E. Wolf, jun., R. Yagbasan, S. G. Bott and S. R. Cooper, *Inorg. Chem.*, 1989, **28**, 4040.

26 G. Wu, W. Jiang, J. D. Lamb, J. S. Bradshaw and R. M. Izatt, *J. Am. Chem. Soc.*, 1991, **113**, 6538.

27 A. J. Blake, R. O. Gould, A. J. Holder, T. I Hyde and M. Schröder, *Polyhedron*, 1989, **8**, 513.

28 G. R. Willey, A. Jarvis, J. Palin and W. Errington, *J. Chem. Soc., Dalton Trans.*, 1994, 255; A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1992, 2987; G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 591.

29 F. Neve and M. Ghedini, *Inorg. Chim. Acta*, 1994, **217**, 1.

30 M. Hojo, M. Hagiwara, H. Nagai and Y. Imai, *J. Electroanal. Chem., Interfacial Electrochem.* 1987, **234**, 251.

31 H. J. Pietzsch, H. Spies, P. Leibnitz and G. Reck, *Polyhedron*, 1993, **12**, 2995.

32 M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota and S. Kitagawa, *Inorg. Chem.*, 1995, **34**, 2705.

33 S. Kawata, S. Kitagawa, M. Kondou, I. Furuchi and M. Munakata, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1759.

34 M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Honda and S. Kitagawa, *J. Chem. Soc., Dalton Trans.*, 1994, 2771.

35 M. Munakata, T. Kuroda-Sawa, M. Maekawa, M. Nakamura, S. Akiyama and S. Kitagawa, *Inorg. Chem.*, 1994, **33**, 1284.

36 M. Munakata, S. Kitagawa, N. Ujimaru, M. Nakamura, M. Maekawa and H. Matsuda, *Inorg. Chem.*, 1993, **32**, 826.

37 S. Kitagawa, M. Munakata and T. Tanimura, *Inorg. Chem.*, 1992, **31**, 1714.

38 S. Kitagawa, S. Matsuyama, M. Munakata and T. Emori, *J. Chem. Soc., Dalton Trans.*, 1991, 2869.

39 S. Kitagawa, S. Matsuyama, M. Munakata, N. Osawa and H. Masuda, *J. Chem. Soc., Dalton Trans.*, 1991, 1717.

40 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976. B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, pp. 594–744.

41 G. H. Robinson and S. A. Sangokoya, *J. Am. Chem. Soc.*, 1988, **110**, 1494; R. E. Wolf, J. R. Hartman, J. M. E. Storey, B. M. Foxman and S. R. Cooper, *J. Am. Chem. Soc.*, 1987, **109**, 4328.

42 A. J. Blake, M. A. Halcrow and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1992, 2803.

43 MITHRIL, an integrated direct method computer program, University of Glasgow; C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 42.

44 TEXSAN-TEXRAY, Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985.

45 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 24*th March* 1995; *Paper* 5/01904D