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A Poly(bicyclic dimer) and a Cyclic Tetramer: Ligand Isomerism of S_2O_2 Macrocycles During the Assembly of Supramolecular Silver(I) Complexes

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Two isomeric S_2O_2 macrocycles (L^1 and L^2) with a 14-membered cavity have been synthesised as a model system with different binding modes. Self-assembly reactions of L^1 and L^2 with silver perchlorate afford the respective ligand-directed cyclic oligomer complexes with different shapes: a poly(bicyclic dimer) (**1**) and a discrete cyclic tetramer (**2**). The formation of these supramolecular complexes is discussed in terms of conformational discrimination of two isomeric macrocycles due to ring rigidity and interdonor distances.

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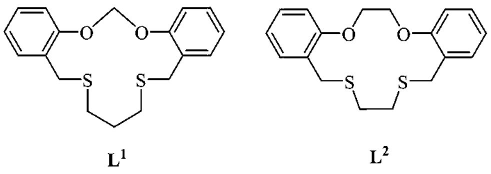
Introduction

The programmed self-assembly of discrete supramolecular complexes and coordination networks has attracted intense interest not only for their potential applications as new functional materials but also their fascinating structural topologies.[1] A cyclic oligomer complex, which is one of the entities in the former category, has been reported to be capable of selective recognition and separation of guest species, including small molecules and anions.[2] As a methodology of emerging significance in supramolecular chemistry, there is an interest in understanding the factors that influence the way in which metal complexes self-assemble into cyclic oligomers. Rigid rod-like didentate ligands such as 4,4′-bipyridyl derivatives, together with corner-piece complexes based on late transition metal ions, are known to form a range of metallacycles.[3]

Besides its formation of numerous cyclic oligomer complexes with multidentate N-donor ligands, the soft silver(I) ion has a high affinity for sulfur ligands, such as linear thioethers, and such compounds can be used as building blocks to construct discrete metallomacrocyclic frameworks as well as network species. For their supramolecular assembly, the choice of length of the spacer unit in the ligand, anions and solvent are crucial to the structure of the final product.

Recently, we proposed the *exo* coordination properties of S/O or S/O/N donor macrocycles, which afford diverse types of supramolecular complexes, including cyclic oligomer silver(I) complexes, upon varying donor atoms, counteranions and solvents.[4] This approach is attractive because the *exo* coordination of sulfur donors[5] to the metal ion offers the possibility of linking the ligand building blocks in diverse modes. We are interested in extending this to a ligand-directed approach, such as ligand isomerism,[6] in order to construct new supramolecular structures, including cyclic oligomer complexes based on dithiaoxa macrocycles. By using two positional isomers with different interdonor distances (L^1 and L^2), we succeeded in generating two different cyclic oligomer complexes (**1** and **2**).



L^1 L^2

Results and Discussion

Synthesis and Characterisation of Ligands

Synthesis of the ligands began with salicylaldehyde (Scheme 1). Dichlorides (*m* = 0 and 1) were prepared using a known procedure,[7] and L^1 and L^2 were obtained by macrocyclisation coupling reactions between these dichlorides and dithiols in the presence of Cs_2CO_3 under high-dilution condition in reasonable yield (28 and 41%, respectively). The ^1H and ^{13}C NMR spectra together with elemental analyses and mass spectra are clearly in agreement with the proposed structures.

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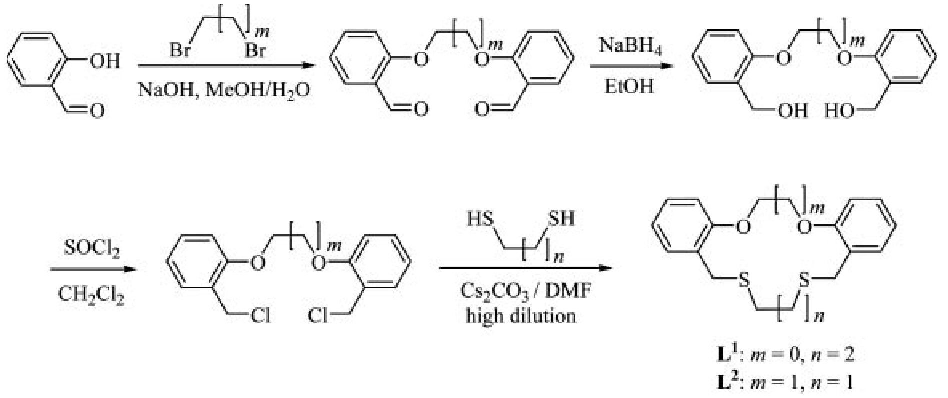
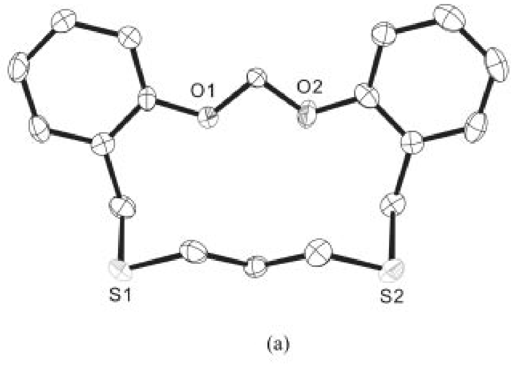
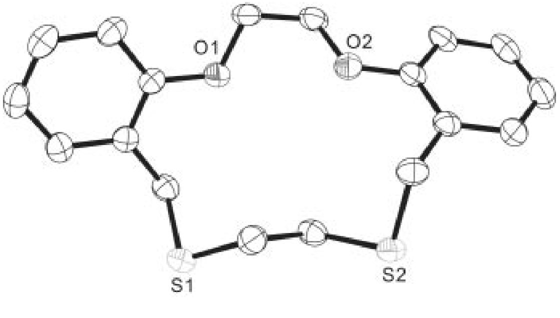


Scheme 1. Synthesis of ligands.

The structures of these macrocycles were also characterised in the solid state by single-crystal X-ray crystallography. Colourless crystals of **L^1** and **L^2** suitable for X-ray analysis were obtained by slow concentration of their respective solutions in methanol (**L^1**) or dichloromethane (**L^2**). Crystals of **L^1** and **L^2** (Figure 1) have the acentric space groups *Pc* and $P2_12_12_1$, respectively. The conformations of the ring cavities in the two molecules differ only in their inter-donor distances. In both cases, the macrocyclic rings are relatively flattened and the two oxygen atoms are oriented endodentate, whilst the two sulfur atoms are arranged exodentate with respect to the ring cavity.[5] As expected, the observed S···S distance in **L^1** (5.627 Å) is significantly longer than that of **L^2** (4.387 Å).



(a)



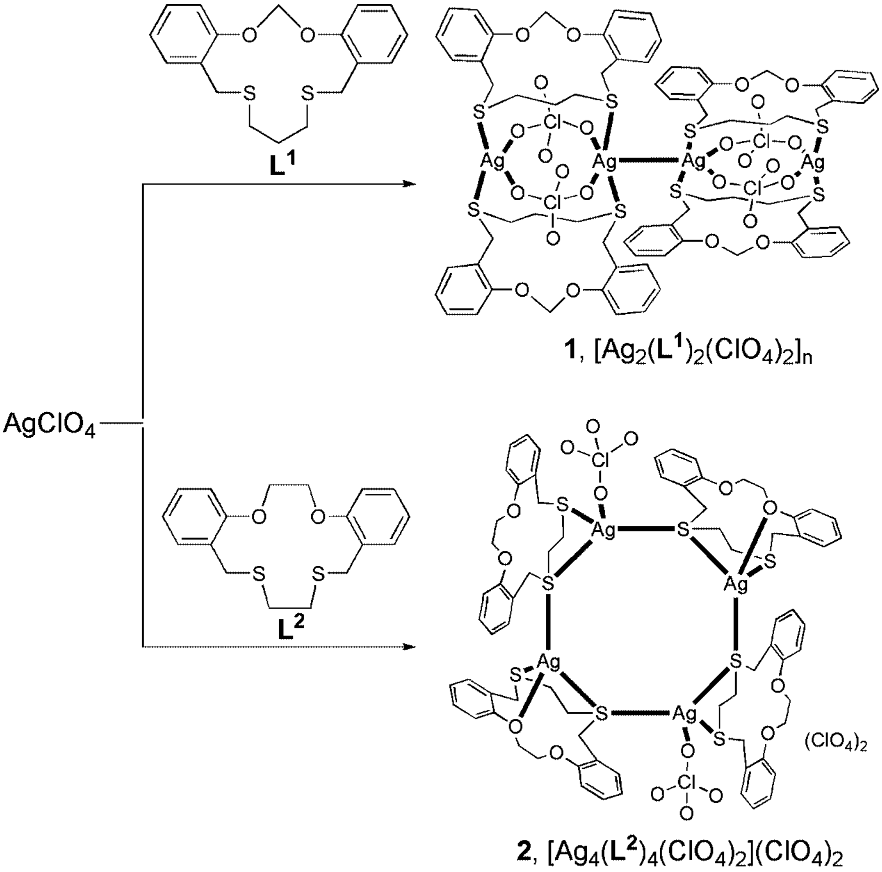
(b)

Figure 1. Molecular structures of **L^1** (a) and **L^2** (b). Thermal ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å]: **L^1**: S1···S2 5.627(2); **L^2**: S1···S2 4.387(1).

Complex Syntheses and Structural Description

Two crystalline supramolecular complexes were obtained from the assembly reactions of the ligands with silver perchlorate. A colourless precipitate was obtained from **L^1** and $AgClO_4$ in methanol/water, and colourless single crystals of **1** suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into a nitromethane solution of this complex. Similarly, a colourless precipitate was obtained from **L^2** and $AgClO_4$ in dichloromethane/methanol, and colourless single crystals of **2** suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into its DMF solution (Scheme 2).

The X-ray analysis revealed that **1** is a poly(bicyclic dimer) $[\{Ag_2(\mathbf{L^1})_2(ClO_4)_2\}CH_3NO_2]_n$ (Figure 2a). The bicyclic dimer unit of **1** contains two bridging Ag atoms, two macrocycles, two perchlorate ions and one noncoordinating nitromethane molecule (not shown). Each five-coordinate Ag atom[8] that lies outside the cavity bridges two S donors from two different macrocycles in a bent fashion [S1–Ag1–S1C 161.95(6)°] such that the two metal centres point towards each other. However, the separation of the two Ag atoms [Ag1···Ag1A 4.8611(12) Å] is far from the range of an argentophilic interaction.[9] Interestingly, two diagonally opposite ClO_4^- anions weakly bridge two Ag atoms in a bidentate manner to form a three-dimensional bicycle. It is known that in most reported $AgClO_4$ complexes with dithioether ligands, the ClO_4^- anions usually take the role of a monodentate ligand or intercalating anion. However, the ClO_4^- anions in **1** coordinate to two Ag atoms in the rare η^2-double-bridge mode through two O atoms to form an eight-membered ring.[8] Several cases of bicyclic dimeric $AgClO_4$ complexes with acyclic dithioethers[8] were ex-



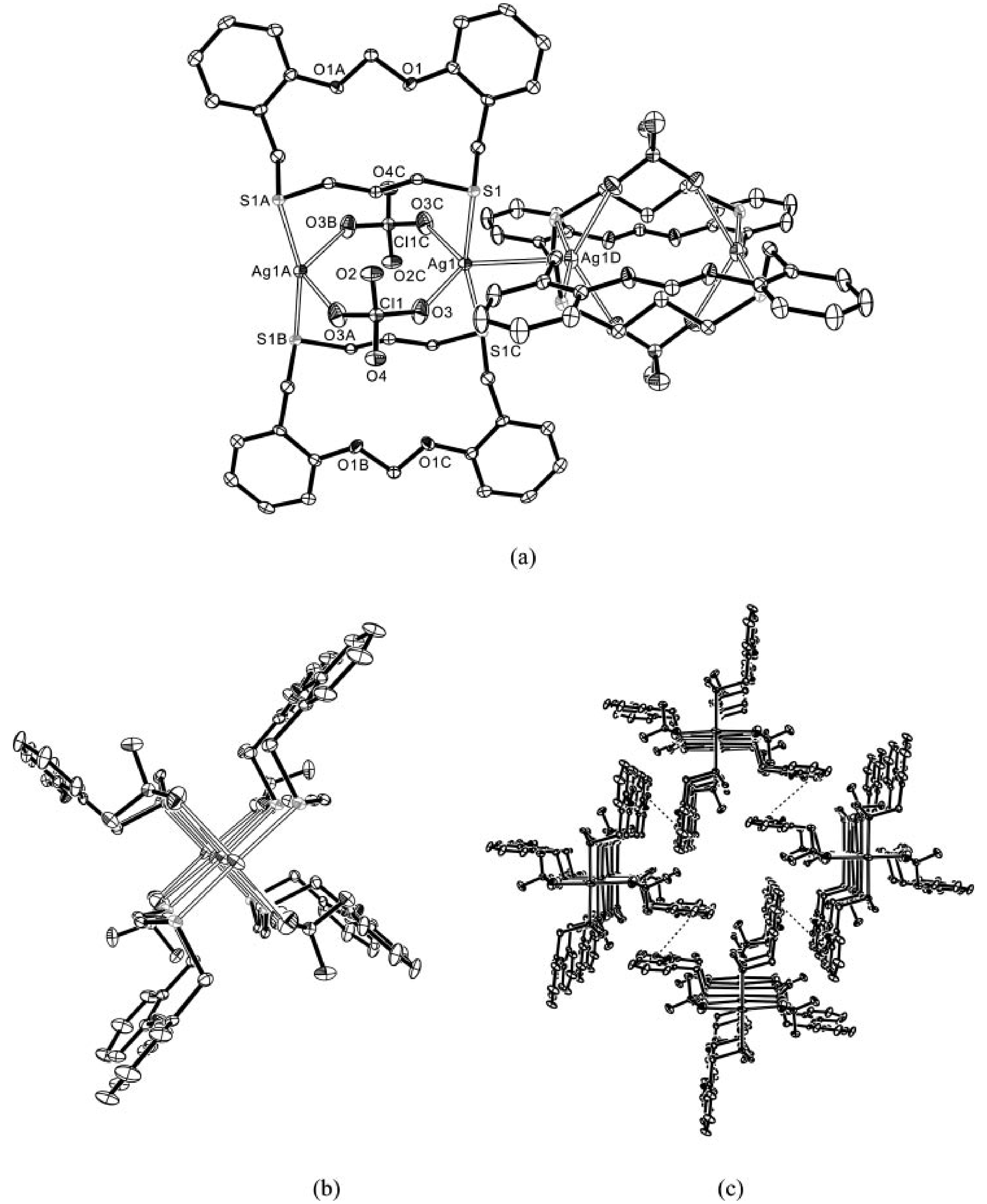
Scheme 2. Complexes prepared.

tracted from the Cambridge Crystallographic Database (CCDC).[10] As we understand, however, this is the first example of a bicyclic dimeric $AgClO_4$ complex based on a cyclic analogue. The bicyclic dimer unit is further held together by Ag–Ag contacts[9] [3.129(1) Å] to form a polymeric chain of the bicyclic dimer unit. Some d^{10} metal ions show a tendency to form metal–metal bonds, and Ag–Ag contacts in the range 2.80–3.30 Å have been reviewed.[9] The two repeating adjacent bicyclic dimer units of **1** are perpendicular to each other and show a propeller-like side view (Figure 2b). In this case, no significant change of the S···S distance (5.622 Å for **1**) is observed compared with that for $\mathbf{L^1}$ (5.627 Å).

In the packing structure (Figure 2c), each 1D network is arranged side by side with an adjacent one such that they form an offset face-to-face-type π-π stacking interaction[11] through the aromatic rings. The dihedral angle between the two aromatic rings is 13.0(3)°, thereby indicating a slightly tilted orientation. The intercentroid distance between two aromatic rings is 4.153 Å, which falls at the mean of the literature range (3.7–4.6 Å) for such an interaction.[11]

The reaction of $\mathbf{L^2}$ with $AgClO_4$ in dichloromethane/methanol afforded a colourless precipitate. Vapour diffusion of diethyl ether into a DMF solution of this precipitate gave a crystalline product **2**. An X-ray analysis revealed that **2** is a cyclic tetramer $[Ag_4(\mathbf{L^2})_4(ClO_4)_2](ClO_4)_2\cdot 2MeOH$ with inversion symmetry (Figure 3a). Tetranuclear Ag^I complexes $[Ag_4\mathbf{L}_4]^{4+}$ of trithiamacrocycles (**L**) with similar cyclic tetrameric structure have been reported by Loeb et al.[12] Ag1, which lies outside the cavity, is bonded to one O and two S atoms of one macrocycle as well as to one S atom of the adjacent macrocycle to form a distorted tetragonal environment, whereas tetrahedrally coordinated Ag2 is surrounded by two S atoms of one macrocycle and one S atom of an adjacent macrocycle. The fourth site is occupied by an O atom of ClO_4^- in a monodentate manner. Consequently, the repeating Ag1–S–Ag2–S bonding leads to an octagonal scaffold with an Ag_4S_4 core. The two coordinating ClO_4^- ions are attached to the exterior and two other ClO_4^- ions are included in the octagonal cavity. The resulting 3D structure of **2** is "doughnut"-like and has a diameter of approximately 13.8 Å and a thickness of 7.4 Å. The S···S distances in **2** (3.432 and 3.635 Å) are shorter than that in $\mathbf{L^2}$ (4.387 Å) due to conversion of the torsion angle between the two S atoms from *anti* to *gauche* upon complexation.

The FAB mass spectra of **1** and **2** contain peaks at *m*/*z* = 439 and 979, which correspond to $[Ag_2(\mathbf{L^1})_2]^{2+}$ and $[Ag_4(\mathbf{L^2})_4(ClO_4)_2]^{2+}$, respectively, according to their isotope patterns (Figure 4).



(a)

(b)

(c)

Figure 2. Poly(bicyclic dimer) structure of **1**: (a) general view, (b) side view and (c) packing arrangement showing π-π stacking (dashed line). Hydrogen atoms and non-coordinating nitromethane molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ag1–S1 2.4243(14), Ag1–S1C 2.4243(13), Ag1–Ag1D 3.1285(11), Ag1···Ag1A 4.8611(12), S1···S1A 5.6217(24); S1–Ag1–S1C 161.95(6), S1C–Ag1–Ag1D 80.98(3), S1–Ag1–Ag1D 80.98(3). Symmetry operations: A: x, y, $-z + 1$; B: $2 - x$, $-y$, $1 - z$; C: $-x + 2$, $-y$, z; D: $y + 1$, $-x + 1$, $-z + 3/2$.

Conclusion

The preparation and structural characterisation of two types of cyclic oligomer silver(I) complexes derived from isomeric S_2O_2 macrocycles have been presented. The tendency to adopt these respective arrangements shows the possibility that the metal coordination mode can be controlled by tuning the inter-donor distances in the backbone of each bound ligand.

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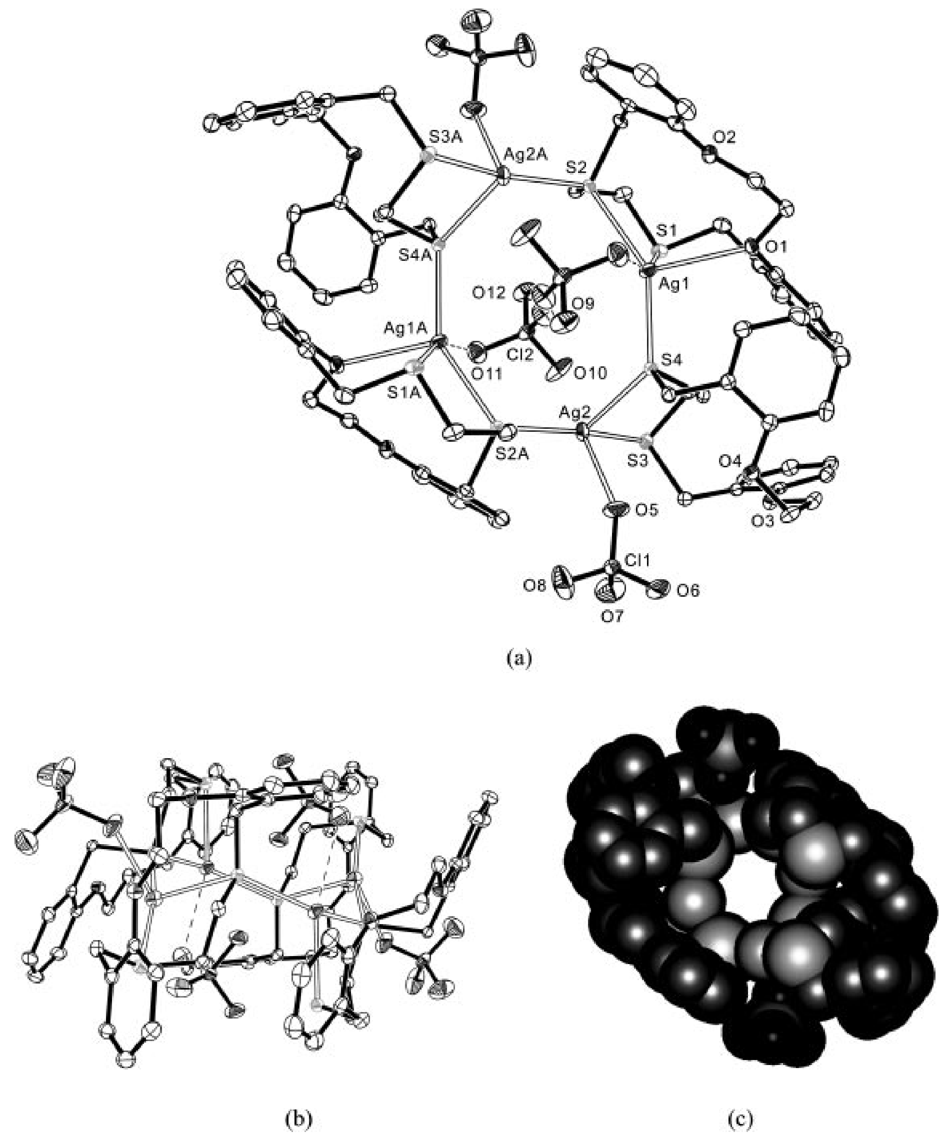

Figure 3. Cyclic tetramer structure of **2**: (a) top view, (b) side view and (c) space-filling view (noncoordinating anions are omitted). Hydrogen atoms and noncoordinating methanol molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ag1–S1 2.6102(14), Ag1–S2 2.6322(14), Ag1–S4 2.5245(12), Ag2–S3 2.4855(13), Ag2–S4 2.6990(13); S1–Ag1–S2 81.79(4), S4–Ag1–S2 145.60(4), S4–Ag1–S1 113.43(4), S3–Ag2–S4 88.92(4), Ag1–S4–Ag2 120.60(5); S1···S2 3.4320(18), S3···S4 3.6346(17), Ag1···Ag2 4.5381(7), Ag1···Ag1A 5.6148(9). Symmetry operation: A: $-x + 1$, $-y + 1$, $-z + 1$.

Experimental Section

General Remarks: Chemical reagents and solvents were purchased commercially and used as received without further purification. Infrared spectra were measured with a Mattson Genesis Series FTIR spectrophotometer, and the NMR spectra were recorded with a Bruker 300 MHz spectrometer. Mass spectra were obtained with a JEOL JMS-700 spectrometer at the Central Laboratory of Gyeongsang National University.

Synthesis and Characterisation of L^1: Cesium carbonate (11.22 g, 34.46 mmol) was dissolved in DMF (1000 mL) in a 3-L, round-bottomed flask. 1,3-Propanedithiol (2.12 g, 22.5 mmol) and the dichloride (6.7 g, 22.5 mmol) were dissolved in DMF (30 mL) and this solution was taken up in a 50-mL glass syringe. Under nitrogen, the contents of the syringe were added dropwise (0.6 mL h^{-1}) to the DMF solution of Cs_2CO_3 at 45–50 °C over 50 h. The reaction mixture was rapidly stirred for a further 10 h, cooled to room temperature and filtered. The filtrate was concentrated and the residue was partitioned between water and dichloromethane. The aqueous phase was separated and extracted with two further portions of dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and then concentrated to dryness. Flash column chromatography on silica gel with 20% ethyl acetate/*n*-hexane as the eluent led to the isolation of L^1 as a colourless crystalline product in 28% yield. M.p. 78–80 °C. $C_{18}H_{20}O_2S_2$ (332.48): calcd. C 65.02, H 6.06; found C 64.79, H 6.12. IR (KBr): $\tilde{\nu}$ = 2924, 2290, 1590, 1491, 1415 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.04 (m, 8 H, Ar), 5.83 (s, 2 H, OCH_2), 3.69 (s, 4 H, $ArCH_2$), 2.34 (t, J = 7.57 Hz, 4 H, SCH_2CH_2), 1.63 (t, J = 2.24 Hz, 2 H, SCH_2CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ =

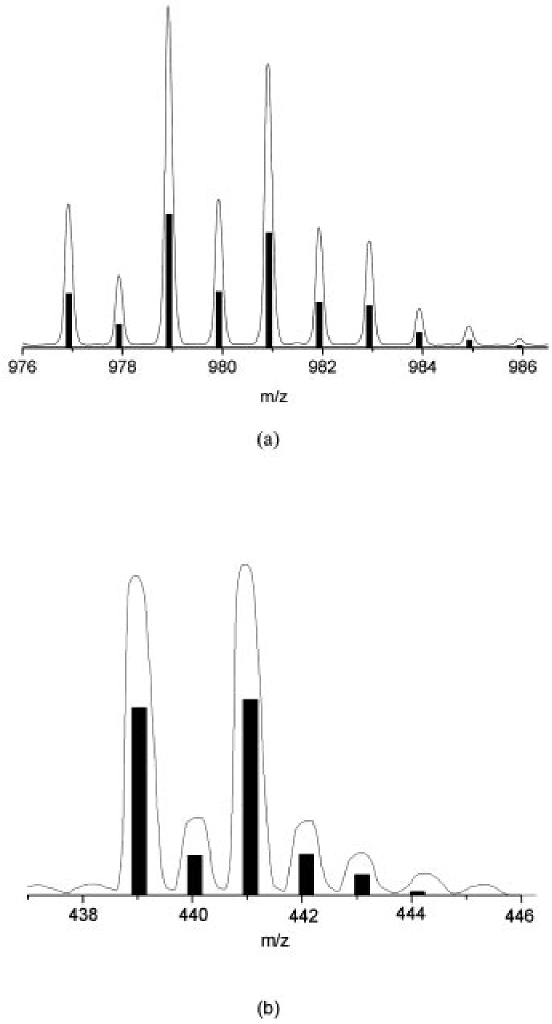

Figure 4. Observed isotopic distribution for $\mathbf{1}^{2+}$ (a) and $\mathbf{2}^{2+}$ (b) in the FAB mass spectra of **1** and **2**. The bars represent the predicted mass spectral distribution for this ion.

154.73, 130.95, 128.21, 123.09, 114.58, 92.19, 31.10, 29.82, 28.81 ppm. FAB-MS: m/z = 332 [M^+].

Synthesis and Characterisation of $\mathbf{L^2}$: The synthetic procedure was almost the same as for $\mathbf{L^1}$ except for the use of a different dichloride (m = 1) and 1,2-ethanedithiol as the thiol (Scheme 2). Flash column chromatography (SiO_2; n-hexane/ethyl acetate, 1:1) afforded the product as a white solid in 41% yield. M.p. 128–130 °C. $C_{18}H_{20}O_2S_2$ (332.48): calcd. C 65.02, H 6.06, S 19.29; found C 64.88, H 6.25, S 19.47. IR (KBr): $\tilde{\nu}$ = 2921, 2358, 1592, 1490, 1452, 1288 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.87–7.38 (m, 8 H, Ar), 4.34 (s, 4 H, OCH_2), 3.78 (s, 4 H, $ArCH_2$), 2.73 (s, 4 H, SCH_2CH_2S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.95, 131.02, 128.59, 128.06, 121.52, 111.07, 66.65, 31.61, 28.17 ppm. FAB-MS: m/z = 332 [M^+].

$[Ag_2(L^1)_2(ClO_4)_2]\cdot 2H_2O$ (1): A colourless precipitate was obtained by mixing of equimolar amounts of $\mathbf{L^1}$ and $AgClO_4$ in methanol/water. The product was filtered off and washed with methanol and dried under vacuum. Yield: 78%. M.p. 180–181 °C. $C_{36}H_{44}Ag_2Cl_2O_{14}S_4$ (1115.63): calcd. C 38.76, H 3.98, S 11.50; found C 38.75, H 3.96, S 11.49. IR (KBr): $\tilde{\nu}$ = 2928, 1595, 1492, 1454, 1418, 1294, 1226, 1097 (ClO_4^-), 1001, 756, 621 cm^{-1}. FAB-MS: m/z = 439 $[Ag_2(\mathbf{L^1})_2]^{2+}$.

$[Ag_4(L^2)_4(ClO_4)_2](ClO_4)_2\cdot 1.5MeOH$ (2): Reaction of $\mathbf{L^2}$ with $AgClO_4$ in dichloromethane/methanol afforded a colourless precipitate. Vapour diffusion of diethyl ether into a DMF solution gave rise to a crystalline product. The product for microanalysis was dried under vacuum. Yield: 90%. M.p. 159–160 °C. $C_{73.5}H_{86}Ag_4Cl_4O_{25.5}S_8$ (2207.26): calcd. C 40.44, H 4.28; found C 40.00, H 3.93. IR (KBr): $\tilde{\nu}$ = 2932, 1593, 1493, 1452, 1246, 1097 (ClO_4^-), 930, 758, 621 cm^{-1}. FAB-MS: m/z = 979 $[Ag_4(\mathbf{L^2})_4]^{2+}$.

CAUTION! *Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.*

X-ray Crystallography: All data were collected with a Bruker Smart diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The first 50 frames were retaken after complete data collection. The crystal showed no significant decay. The frame data were processed with

Table 1. Crystal and experimental data.

	$\mathbf{L^1}$	$\mathbf{L^2}$	**1**	**2**
Empirical formula	$C_{18}H_{20}O_2S_2$	$C_{18}H_{20}O_2S_2$	$C_{37}H_{43}Ag_2Cl_2NO_{14}S_4$	$C_{74}H_{88}Ag_4Cl_4O_{26}S_8$
Formula mass	332.46	332.46	1140.60	2223.20
Temperature [K]	173(2)	298(2)	173(2)	173(2)
Crystal system	monoclinic	orthorhombic	tetragonal	monoclinic
Space group	Pc	$P2_12_12_1$	$P4_2/m$	$P2_1/c$
Z	2	4	2	2
a [Å]	4.6632(4)	8.7160(8)	11.7322(8)	16.8393(9)
b [Å]	11.9310(11)	11.6729(11)	11.7322(8)	13.5962(7)
c [Å]	14.8994(13)	16.7701(15)	15.979(2)	20.7473(11)
β [°]	97.685(2)	90	90	110.8510(10)
V [Å^3]	821.51(13)	1706.2(3)	2199.5(3)	4439.0(4)
D_X [$g\,cm^{-3}$]	1.344	1.294	1.722	1.663
$2\theta_{max}$ [°]	56.56	56.52	52.7	56.6
R	0.0645	0.0476	0.0455	0.0511
wR	0.1247	0.0994	0.0856	0.1442
No. of reflection used [$I > 2\sigma(I)$]	3271 (R_{int} = 0.0532)	4096 (R_{int} = 0.0658)	2342 (R_{int} = 0.1156)	10421 (R_{int} = 0.0311)

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SAINT to give the structure factors.[13] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 for all data with SHELXTL.[14] The non-hydrogen atoms were refined anisotropically. In **2**, the ten peaks which were found to have an electron density of more than 1 e Å^{-3} in the final difference Fourier map are the ghosts of methanol. Relevant crystal data collection and refinement data for the crystal structures of **L^1**, **L^2**, **1** and **2** are summarised in Table 1. CCDC-292047 (**L^1**), -292048 (**L^2**), -292049 (**1**) and -292050 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

Acknowledgments

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