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Exo-coordinated discrete and continuous supramolecular silver(I) complexes with thiaoxa-macrocycles†

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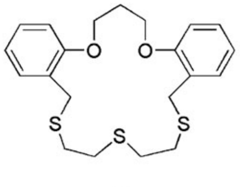
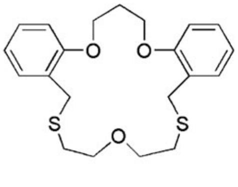
Two thiaoxa-macrocycles (**L^1**: S_3O_2 and **L^2**: S_2O_3) with a dibenzo-subunit were synthesised and structurally characterised by X-ray analysis. Reactions of **L^1** and **L^2** with silver(I) salts (NO_3^- and PF_6^-) afforded the respective ligand- and/or anion-directed complexes **1**–**3** with different topologies; tetranuclear sandwich [Ag_4(**L^1**)$_2$(NO_3)$_4$] (**1**), cyclic tetramer [Ag_4(**L^1**)$_4$](PF_6)$_4$ (**2**) and poly(bicyclic dimer) [Ag(**L^2**)NO_3]$_n$ (**3**). The formation of such supramolecular complexes is discussed in terms of donor or anion effect.

Introduction

The structural modification of macrocyclic ligands and the careful selection of the metal salt system often lead the formation of diverse coordination topologies.[1] For example, the versatility of sulfur-containing macrocycles makes them useful for a range of coordinative products because the sulfur donor is expected to favour binding towards soft metal ions in endo- and/or exocyclic mode.[2] We have worked on the assembly of supramolecular coordination architectures based on the exo-coordination of sulfur-containing macrocycles as well as their applications.[3] A range of mono- and multinuclear complexes of thiaoxa- or thiaoxaaza-macrocycles with discrete and continuous types were reported by us[2a,3] and other workers.[2] We are interested in extending this work in a ligand-directed approach to construct new supramolecular structures. In this work, we examine the donor and anion as controlling factors to direct the assembly of silver(I) complexes. Based on these considerations, we synthesised thiaoxa-macrocycles **L^1** and **L^2**. **L^1** and **L^2** have a same framework but one sulfur donor in **L^1** was replaced by one oxygen atom in **L^2**; the variation may trigger a change for the resulting complexes. In the view of silver(I) salt systems employed, it is becoming apparent that the variation of one donor plays an important role in the topologies of resulting complexes.



L^1



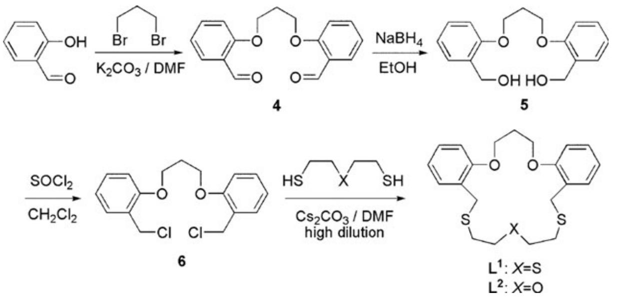
L^2

Results and discussion

Synthesis and characterisation of ligands

Synthesis of the ligands began with salicylaldehyde. Dichloride **6** was prepared through dialdehyde **4** and dialcohol **5**.[4] **L^1** and **L^2** were obtained by coupling reactions for macrocyclisation from dichloride **6** and corresponding dithiols in the presence of Cs_2CO_3 under high dilution condition in reasonable yields (**L^1**: 45%, **L^2**: 41%). The ^{1}H and ^{13}C NMR spectra together with elemental analysis and mass spectra were clearly in agreement with the proposed structures (Scheme 1).

Structures of the macrocycles prepared were also characterised in the solid state by single-crystal X-ray crystallography (Fig. 1). Colourless crystals of **L^1** and **L^2** suitable for X-ray analysis were obtained by slow evaporation from the respective solutions in dichloromethane. Notably, sulfur



Scheme 1 Synthesis of ligands.

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† Electronic supplementary information (ESI) available: Fig. S1: ^{1}H NMR spectra of free **L^1**, **L^1** + $AgNO_3$ (1.0 equiv.) and **L^1** + $AgPF_6$ (1.0 equiv.) in CD_3CN–DMSO-d_6 (1 : 1). Fig. S2. ^{1}H NMR spectra of free **L^2** and **L^2** + $AgNO_3$ (1.0 equiv.) in CD_3CN–DMSO-d_6 (1 : 1). See DOI: 10.1039/b710581a

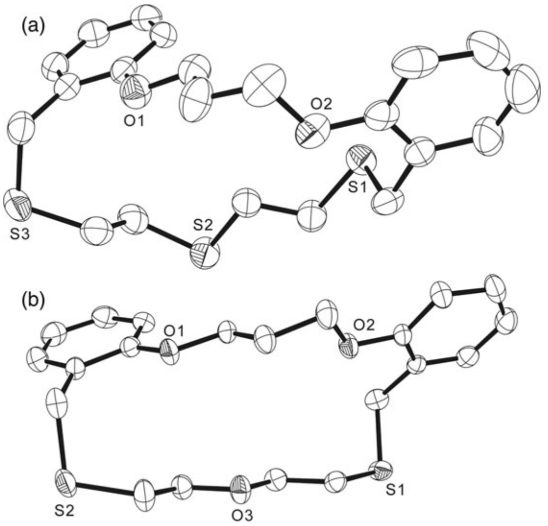


Fig. 1 Molecular structures of (a) $\mathbf{L^1}$ and (b) $\mathbf{L^2}$. Thermal ellipsoids are drawn at the 30% probability level.

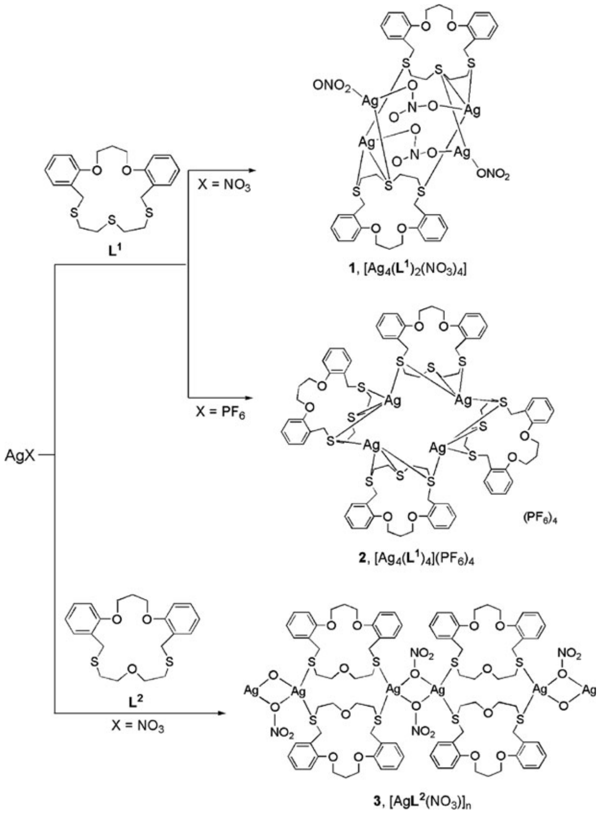
atoms are oriented in an exodentate fashion. The macrocyclic ring of $\mathbf{L^1}$ is slightly twisted and torsion angles between donor atoms are indicative of *anti* arrangements [S1–C–C–S2 172.5(2) and S2–C–C–S3 172.1(2)°]. $\mathbf{L^2}$ has a non-folded configuration with the two exodentate sulfur donors separated as far as possible; they lie, together with the centroid of aromatic rings, at the corners of a pseudo-rectangular plane. The aliphatic segment between donor atoms spans also *anti* arrangements with characteristic torsion angles [S1–C–C–O3 179.8(2) and S2–C–C–O3 171.8(3)°].

Complex syntheses and structural description

In complexation, silver nitrate and hexafluorophosphate were used to examine the anion effect on the resulting complexes. Using these reaction systems, we obtained three supramolecular complexes **1–3** with different topologies (Scheme 2), and their structures were characterised by X-ray analysis (Fig. 2–4).

From the reactions of $\mathbf{L^1}$ with silver(I) salts (**1**: NO_3^- and **2**: PF_6^-), two complexes **1** and **2** were prepared as follows. Each colourless precipitate was obtained from $\mathbf{L^1}$ with the corresponding silver(I) salts in dichloromethane–methanol and single crystals of the respective complexes suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into the acetonitrile solution.

The crystal structure of **1** is shown in Fig. 2, with selected geometric parameters presented in Table 1. The X-ray analysis revealed that **1** is a unique tetranuclear sandwich-type (4 : 2) complex $[Ag_4(\mathbf{L^1})_2(NO_3)_4]\cdot 2CH_2Cl_2$. The asymmetric unit of **1** contains one $\mathbf{L^1}$, two silver atoms and two nitrate ions. The structural unit shown in Fig. 2(a) is generated through inversion symmetry. Ag1 is four-coordinated by two S donors from one $\mathbf{L^1}$, one S donor from adjacent $\mathbf{L^1}$ and one bridging bidentate nitrate ion. Bond angles around Ag1 vary considerably (90.1–150.1°). Ag2 is in a distorted trigonal plane with the coordination sites occupied by the S2 atom, one mono- and one bridging bidentate nitrate ions, allowing the formation of a twelve-membered ring composed of four Ag atoms, two S



Scheme 2 Complexes prepared.

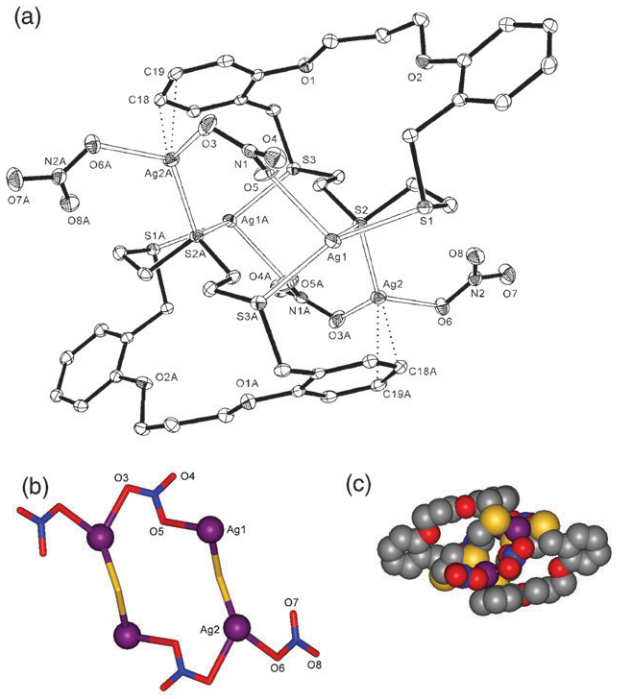


Fig. 2 Tetranuclear sandwich (4 : 2) structure of **1**, $[Ag_4(\mathbf{L^1})_2(NO_3)_4]\cdot 2CH_2Cl_2$: (a) general view, (b) cyclic tetranuclear core, and (c) space-filling view. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Symmetry operation: (A) $-x + 1, -y, -z + 1$.

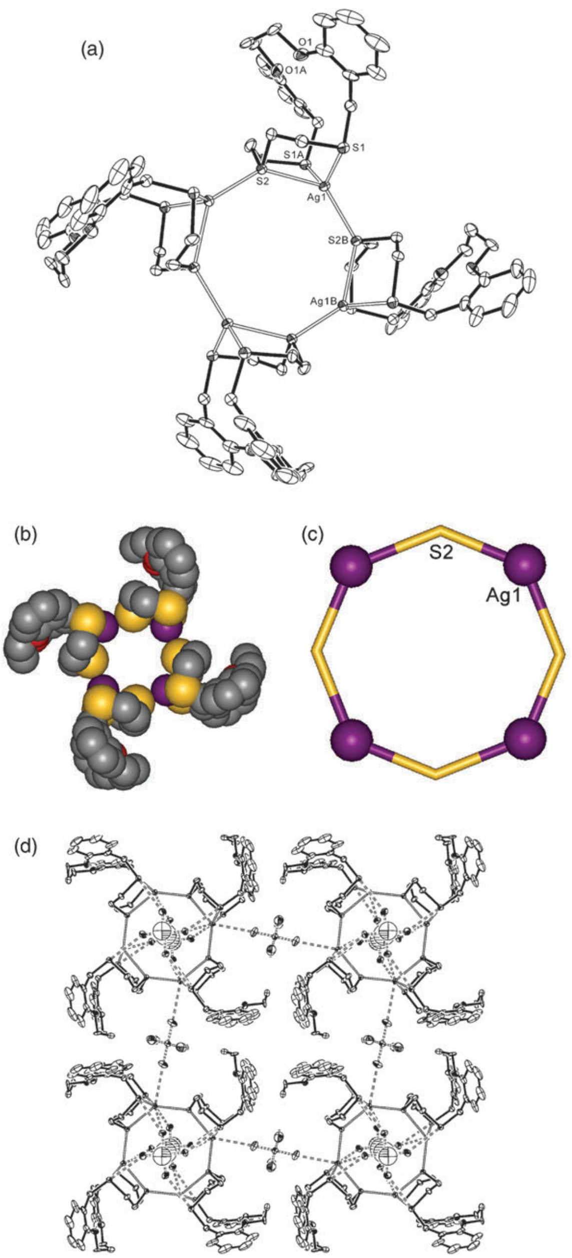


Fig. 3 Cyclic tetramer structure of **2**, $[Ag_4(\mathbf{L}^1)_4](PF_6)_4 \cdot 4CH_2Cl_2$: (a) general view, (b) space-filling view, (c) octagonal Ag_4S_4 core, and (d) packing view. Hydrogen atoms, non-coordinating anions and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Symmetry operations: (A) x, y, $-z + 1$, (B) y, $-x$, z.

atoms, and two bridging bidentate nitrate ions (Fig. 2(b)). In fact, Ag2 is shifted by 0.70 Å towards an adjacent aromatic ring from the O_2S trigonal plane and interacts with two C atoms (C18A and C19A) in the aromatic ring leading to an η^2-type cation–π interaction[5] [dotted lines, Ag2···C19A 2.524(2), Ag2···C18A 2.728(3) Å]. The bond angles around Ag2 show a Y-shaped geometry [O6–Ag2–S2 127.4(5), S2–Ag2–O3A 126.7(3), O6–Ag2–O3A 79.7(9)°]. Complex **1** adopts an elliptical-cage-like conformation (Fig. 2(c)) but no solvent molecule is included inside. Instead, two non-coordinating dichloromethane molecules exist in the crystal lattice. The conformation of $\mathbf{L}^1$ in **1** is different from that in free $\mathbf{L}^1$ in the view of torsion angles between the neighbouring donor atoms, the aliphatic segment of S–C–C–S–C–C–S shows an *anti–anti* arrangement in free $\mathbf{L}^1$, while in **1**, it changes to an *anti–gauche* arrangement.

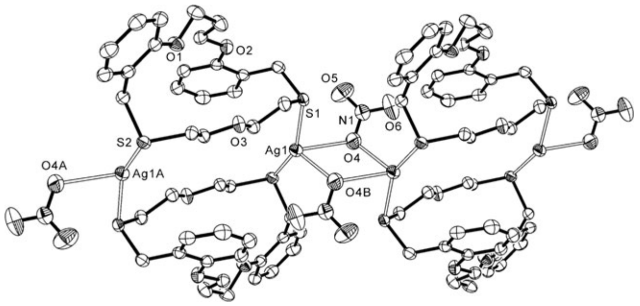


Fig. 4 Poly(cyclic dimer) structure of **3**, $[Ag(\mathbf{L}^2)NO_3]_n$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Symmetry operations: (A) $-x + 1$, $-y + 1$, $-z + 1$, (B) $-x + 1$, $-y + 2$, $-z + 1$.

To examine the role of anions in the formation of $\mathbf{L}^1$ complexes, the reaction was repeated with $AgPF_6$, and the complex **2** was isolated. The crystal structure of **2** is shown in Fig. 3, with selected geometric parameters presented in Table 2. The structure of **2** is more challenging. An X-ray analysis revealed that **2** is a unique cyclic tetramer (4 : 4) complex $[Ag_4(\mathbf{L}^1)_4](PF_6)_4 \cdot 4CH_2Cl_2$ (Fig. 3(a)). Since **2** has crystallographically imposed $4/m$ symmetry, the asymmetric unit contains half a molecule of $\mathbf{L}^1$ and half a silver atom. The silver atom is in a distorted tetrahedral environment with the coordination sites occupied by facial mode of three S atoms from one $\mathbf{L}^1$ and one S atom from an adjacent $\mathbf{L}^1$ in a bent arrangement. The continual symmetry operations lead to a cyclic form, which is made up of four ligands and four silver atoms with a windmill-like conformation. Consequently, the repeating S2–Ag1–S2B–Ag1B bonding leads to an octagonal scaffold with an Ag_4S_4 core (Fig. 3(c)). The distance between two opposite silver atoms in the octagonal plane is 6.563(5) Å. The aliphatic segment of S–C–C–S–C–C–S shows an *anti–anti* arrangement in free $\mathbf{L}^1$, while in **2**, it changes to a *gauche–gauche* arrangement. In the packing structure, each tetramer is arranged in length and breadth with an adjacent one by long-range interaction of Ag···F (3.161 Å) through the bridging PF_6^- ions such that they form a layered array (Fig. 3(d)). The octagonal cavity is blocked by two trapping PF_6^- ions above and beneath through the Ag···F interactions

Table 1 Selected bond lengths (Å) and angles (°) for **1**[a]

Ag1–S3A	2.469(1)	Ag1–S1	2.475(1)
Ag1–S2	2.811(1)	Ag1–O5	2.555(2)
Ag2–O6	2.347(2)	Ag2–S2	2.502(1)
Ag2–O3A	2.524(2)		
S3A–Ag1–S1	150.1(2)	S3A–Ag1–O5	90.2(6)
S1–Ag1–O5	115.0(6)	S3A–Ag1–S2	120.8(2)
S1–Ag1–S2	82.0(2)	O5–Ag1–S2	78.3(5)
O6–Ag2–S2	127.4(5)	O6–Ag2–O3A	79.7(6)
S2–Ag2–O3A	126.7(5)		

[a] Symmetry operation: (A) $-x + 1$, $-y$, $-z + 1$.

Table 2 Selected bond lengths (Å) and angles (°) for **2**[a]

Ag1–S2B	2.532(4)	Ag1–S1	2.565(3)
Ag1–S2	2.681(4)		
S1–Ag1–S1A	124.5(13)	S2B–Ag1–S1	113.7(7)
S1–Ag1–S2	83.6(7)	S2B–Ag1–S2	134.3(16)

[a] Symmetry operations: (A) x, y, $-z + 1$, (B) y, $-x$, z.

(3.450 Å). Some other examples of the cyclic tetrameric silver(I) complexes $[Ag_4\mathbf{L}_4]^{4+}$ with dithia- and trithia-macrocycles (**L**) have been reported by us[6] and other workers.[7]

In the reactions of $\mathbf{L^2}$, only the crystalline product with $AgNO_3$ was available. A colourless precipitate was obtained from the reaction of $\mathbf{L^2}$ and $AgNO_3$ in dichloromethane–methanol. Colourless single crystals of **3** $[Ag(\mathbf{L^2})NO_3]_n$ suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into the acetonitrile solution.

The crystal structure of **3** is shown in Fig. 4, with selected geometric parameters presented in Table 3. An X-ray analysis revealed that **3** has a one-dimensional double-stranded polymeric chain structure. The asymmetric unit contains one $\mathbf{L^2}$, one silver atom and one nitrate ion. The rhomboid Ag–$(NO_3)_2$–Ag units are located at the centre of four $\mathbf{L^2}$ and each cluster core is tetrahedrally coordinated by two sulfur donors from two adjacent $\mathbf{L^2}$ by Ag–S bonds and two oxygen atoms from two bridging nitrate ions forming an infinite poly(cyclic dimer) structure. An alternating arrangement of a pair of macrocycles and a square-dimeric Ag–$(NO_3)_2$–Ag unit forms a large cyclic dimer, corresponding to eighteen-membered ring. It is noteworthy that the similarities of S···S distances between free $\mathbf{L^2}$ [7.909(1) Å] and **3** [7.878(1) Å] as well as the retention of *anti–anti* arrangement for the aliphatic segment of S–C–C–S–C–C–S before and after complexation. These results suggest that $\mathbf{L^2}$ is well preorganised for the complexation. Some discrete and polymeric species linked with the square-dimer Ag–$(NO_3)_2$–Ag unit have been reported previously.[8] To our knowledge, however, **3** is the first example in which the sulfur-containing ligand is employed for the construction of the Ag–$(NO_3)_2$–Ag linking unit based species. This result also shows that the nitrate anion as a second coordinating species has a remarkable influence on the structure and topology of the assembled product.

Electrospray ionisation (ESI) mass study

We also carried out ESI-mass experiments for **1** in solution state to compare with that in solid state. The mass spectrum of $\mathbf{L^1}$ with a mixture of two equivalent silver(I) nitrate was dominated by mono- to tetranuclear species such as $[Ag(\mathbf{L^1})_2]^+$ (m/z 921.9), $[Ag_2(\mathbf{L^1})_2(NO_3)]^+$ (m/z 1090.9), $[Ag_3(\mathbf{L^1})_2(NO_3)_2]^+$ (m/z 1261.8), $[Ag_4(\mathbf{L^1})_3(NO_3)_3]^+$ (m/z 1430.7) (Fig. 5). The results show that species **1** also exist in solution state as a stable form.

Table 3 Selected bond lengths (Å) and angles (°) for **3**[a]

Ag1–S2A	2.454(1)	Ag1–S1	2.463(1)
Ag1–O4B	2.503(3)	Ag1–O4	2.576(2)
S2A–Ag1–S1	151.2(1)	S2A–Ag1–O4B	118.9(1)

[a] Symmetry operations: (A) $-x + 1$, $-y + 1$, $-z + 1$, (B) $-x + 1$, $-y + 2$, $-z + 1$.

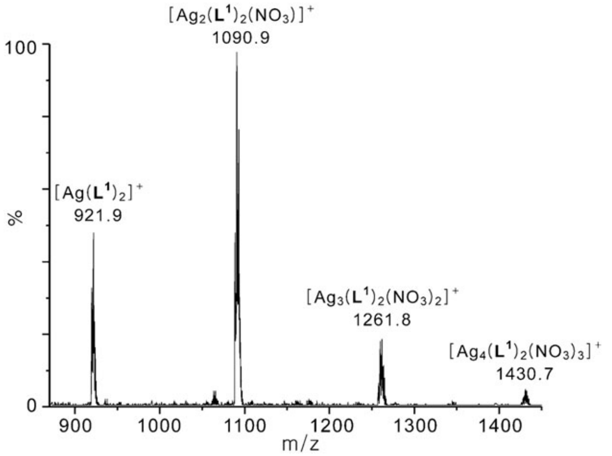


Fig. 5 ESI-mass spectrum of **1**. The complex solution was prepared by dissolving $\mathbf{L^1}$ and silver(I) nitrate (2 equiv.) in acetonitrile.

In addition, comparative NMR studies were carried out for the complex system (Fig. S1 and S2, ESI†). In the case of silver(I) complexes, the peaks for methylene protons adjacent to the sulfur donors show larger downfield shifts suggesting that the silver(I) is strongly coordinated by sulfur donors, and the oxygen atoms interact with the silver(I) weakly, similar to the case in the solid state.

Conclusions

The preparation and structural characterisation of three types of silver(I) complexes **1–3** derived from thiaoxa-macrocycles have been presented. The versatility of results is emphasised on the influences of the variation of anions and donor atoms on the respective supramolecular complexes. For example, comparing the structures between **1** and **2** afforded a good case for the anion effect on the frameworks of complexes. The NO_3^- ions in **1** possessing stronger coordination or donor ability than PF_6^- occupy the coordination site bridging two silver atoms or terminating the structure and, consequently, allow the formation of high nuclear species. In case of **2**, however, the preference of assembly of the cyclic tetramer is due to the weaker affinity of PF_6^- towards silver atom which leads the anion to be excluded from the coordination sphere. On going from **1** to **3**, we observed that replacement of one sulfur to oxygen donor induced the formation of an infinite structure because of the reduced chance of Ag–S bond formation. It is concluded that these results show donors and anions have a great influence on the structures of the resulting supramolecular complexes.

Experimental

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 FT-IR spectrophotometer, and the NMR spectra were recorded with a Bruker 300 MHz spectrometer. Mass spectra were obtained on a QTRAP-3200 spectrometer at the Central Laboratory of Gyeongsang National University.

Synthesis and characterisation of $\mathbf{L^1}$

Cesium carbonate (7.47 g, 23.0 mmol) was dissolved in DMF (1000 cm^3) in a 3-liter round-bottom flask. 2-Mercaptoethyl sulfide (2.36 g, 12.3 mmol) and 2,2′-(propyleneoxy)bis(benzyl chloride) (4.0 g, 12.3 mmol) was dissolved in DMF (30 cm^3) and this solution was added to a 50-cm^3 glass syringe. Under a nitrogen atmosphere, the contents of the syringe was added dropwise (a rate of 0.6 cm^3 h^{-1}) into a DMF solution of Cs_2CO_3 at 45–50 °C for 50 h. The reaction mixture was kept for a further 10 h with rapid stirring, allowed to cool to room temperature, then filtered. The filtrate was evaporated 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 evaporated to dryness. Flash column chromatography on silica gel using 50% dichloromethane–*n*-hexane as the eluent led to the isolation of $\mathbf{L^1}$ as a colourless crystalline product in 45% yield. Mp 110–112 °C. $C_{21}H_{26}O_2S_3$ (406.62): calc.: C 62.03, H 6.44 S 23.66; found: C 62.42, H 6.10, S 23.96%. IR (KBr) 2931, 2871, 1602, 1496, 1447, 1415, 1286, 1237, 1093, 1047, 756 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–6.88 (m, 8 H, Ar), 4.26 (t, 4 H, OCH_2), 3.82 (s, 4 H, $ArCH_2$), 2.54 (m, 8 H, SCH_2CH_2), 2.38 (m, 2 H, $OCH_2CH_2CH_2O$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$); δ 156.34, 131.07, 128.50, 126.90, 121.06, 111.11, 64.25, 32.91, 31.29, 29.71, 29.36 ppm. ESI-MS *m*/*z* 407.9 (MH$^+$).

Synthesis and characterisation of $\mathbf{L^2}$

The synthetic procedure was almost the same as for $\mathbf{L^1}$ except for the use of 2-Mercaptoethyl ether. Flash column chromatography (SiO_2; *n*-hexane–ethyl acetate 9 : 1) afforded the product as a white solid in 41% yield. Mp 99–101 °C. $C_{21}H_{26}O_3S_2$ (390.56): calc.: C 64.58, H 6.71, S 16.42; found: C 64.30, H 6.38, S 16.30%. IR (KBr) 2931, 2861, 1904, 1787, 1594, 1496, 1450, 1414, 1352, 1300, 1237, 1098, 1022, 750, 668 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32–6.87 (m, 8 H, Ar), 4.24 (t, 4 H, OCH_2), 3.81 (s, 4 H, $ArCH_2$), 3.40 (t, 4 H, OCH_2CH_2S) 2.61 (t, 4 H, SCH_2CH_2O), 2.40 (t, 2 H, $OCH_2CH_2CH_2O$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.33, 131.00, 128.39, 127.70, 121.12, 111.18, 70.69, 64.38, 30.26, 29.84, 29.29 ppm. ESI-MS *m*/*z* 391.3 (MH$^+$).

$[Ag_4(\mathbf{L^1})_2(NO_3)_4]\cdot 2CH_2Cl_2$ (1)

A colourless precipitate was obtained by mixing of $\mathbf{L^1}$ and $AgNO_3$ (2 equiv.) in dichloromethane–methanol. Colourless crystals were obtained by vapour diffusion of diethyl ether into the acetonitrile solution. Yield: 60%. Mp (decomp.) > 140 °C. $[Ag_4(\mathbf{L^1})_2(NO_3)_4]\cdot 2CH_2Cl_2$: calc.: C 31.79, H 3.39, S 11.57, N 3.37; found: C 32.02, H 3.47, S 11.89, N 3.40%. IR (KBr) 2942, 1597, 1493, 1458, 1390 (NO_3^-), 1294, 1248, 1104, 1047, 755. ESI-MS *m*/*z* 1430.7 $[Ag_4(\mathbf{L^1})_2(NO_3)_3]^+$.

$[Ag_4(\mathbf{L^1})_4](PF_6)_4\cdot 4CH_2Cl_2$ (2)

A colourless precipitate was obtained by mixing of equimolar amounts of $\mathbf{L^1}$ and $AgPF_6$ in dichloromethane–methanol. Colourless crystals were obtained by vapour diffusion of diethyl ether into the acetonitrile solution. Yield: 70%. Mp (decomp.) > 169 °C. $[Ag_4(\mathbf{L^1})_4](PF_6)_4\cdot 4CH_2Cl_2$: calc.: C 35.50, H 3.79, S 12.92; found: C 35.13, H 3.69, S 13.11%. IR (KBr) 2866, 2365, 1599, 1493, 1455, 1240, 1104, 1060, 845 (PF_6^-), 758, 734, 559 cm^{-1}. ESI-MS *m*/*z* 513.6 $[Ag_4(\mathbf{L^1})_4]^{4+}$.

$[Ag(\mathbf{L^2})NO_3]_n$ (3)

A colourless precipitate was obtained from the reaction of $\mathbf{L^2}$ with $AgNO_3$ (1 equiv.) in dichloromethane–methanol. Colourless single crystals were obtained by vapour diffusion of diethyl ether into the acetonitrile solution. Yield: 30%. Mp (decomp.) > 195 °C. $[Ag(\mathbf{L^2})NO_3]$: calc.: C 45.01, H 4.68, N 2.50, S 11.44; found C 45.36, H 4.58, N 2.62, S 11.48%. IR (KBr) 2931, 2877, 1594, 1496, 1387 (NO_3^-), 1289, 1245, 1123, 845, 761 cm^{-1}.

Table 4 Crystal and experimental data

	$\mathbf{L^1}$	$\mathbf{L^2}$	**1**	**2**	**3**
Formula	$C_{21}H_{26}O_2S_3$	$C_{21}H_{26}O_3S_2$	$C_{44}H_{56}Ag_4Cl_4N_4O_{16}S_6$	$C_{88}H_{112}Ag_4Cl_8F_{24}O_8P_4S_{12}$	$C_{21}H_{26}Ag_1N_1O_6S_2$
M_r	406.60	390.54	1662.57	2977.46	560.42
T/K	298(2)	173(2)	173(2)	173(2)	298(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Tetragonal	Triclinic
Space group	$Pca2_1$	Cc	$P\bar{1}$	$P4/mnc$	$P\bar{1}$
Z	8	4	1	2	2
a/Å	13.2221(9)	11.8755(7)	9.5230(6)	15.8399(1)	8.8853(1)
b/Å	12.4315(8)	11.3829(6)	12.0312(7)	15.8399(1)	11.1795(1)
c/Å	25.7337(2)	15.7149(9)	14.1546(8)	22.847(3)	12.8220(2)
α/°	90	90	73.512(1)	90	70.863(2)
β/°	90	108.787(1)	86.303(1)	90	87.579(2)
γ/°	90	90	67.543(1)	90	71.115(2)
V/Å^3	4229.9(5)	2011.1(2)	1435.4(2)	5732.5(9)	1135.6(2)
D_c/g cm^{-3}	1.277	1.290	1.923	1.725	1.639
$2\theta_{max}$/°	56.68	52.74	52.74	52.04	52.72
R	0.0467	0.0379	0.0239	0.0806	0.0287
wR	0.1011	0.1226	0.0547	0.1821	0.0742
No. reflections used [$I > 2\sigma(I)$]	9258	2780	5745	2913	4564
R_{int}	0.0385	0.0318	0.0166	0.2592	0.0355

X-Ray crystallography

All data were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation source and a CCD detector. The 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 to give structure factors using SAINT.[9] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 for all data using SHELXTL software.[10] The non-hydrogen atoms were refined anisotropically. Relevant crystal data collection and refinement data for the crystal structures of **L^1**, **L^2**, **1**, **2** and **3** are summarised in Table 4.

CCDC reference numbers 645646 (for **L^1**), 645647 (for **L^2**), 645642 (for **1**), 645643 (for **2**) and 645644 (for **3**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710581a

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