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## Supramolecular Chemistry

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# Supramolecular Assembly of Dumbbell-shaped Disilver Complex from Thiaoxa-macrocycle and 4,4'-Bipyridine

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The 16-membered  $S_2O_3$ -donor macrocycle  $L^1$  (1,11-dithia-3,4;8,9-dibenzo-5,7,14-trioxacyclohexadecane) was synthesized by a dithiol–dihalide coupling reaction under high dilution conditions. Reaction of  $L^1$  with  $AgClO_4$  afforded a half-sandwich type mononuclear silver complex **1**,  $[AgL^1(CH_3CN)](ClO_4)$ , which can then be manipulated to provide a unique dumbbell-shaped disilver complex **2**,  $[(AgL^1)_2(\mu-bpy)](ClO_4)_2$  through a successive reaction with 4,4'-bipyridine (bpy). The macrocyclic mono- and dinuclear silver complexes **1** and **2** as well as  $L^1$  were structurally characterized by X-ray crystallography.

**Keywords:** Thiaoxa-macrocycle; 4,4'-Bipyridine; Self-assembly; Dumbbell-shaped disilver complex; Crystal structure

## INTRODUCTION

Design and synthesis of discrete supramolecular complexes and coordination networks with tailorable structures are fundamental steps to discover and fabricate useful nanomaterials and devices [1–6]. Especially the programmed self-assemblies of the discrete cyclic and acyclic supramolecular oligomer complexes with spacing ligands have attracted intense interest not only for their potential applications but also their fascinating structural topologies [7,8]. So far a number of linked or networked species have been generated with rigid rod-like bidentate spacers such as 4,4'-bipyridine (bpy) and its derivatives [9–13].

Recently, we have 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 complexes, upon varying donor atoms, counterions and

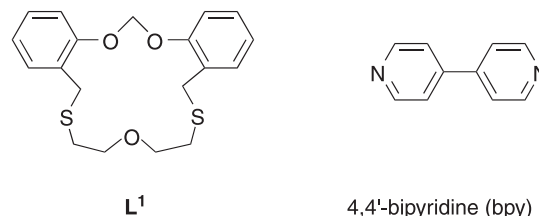
solvents [14–18]. This approach is attractive because the *exo*-coordination of sulfur donors [19] to the metal ion offers the possibility of linking the ligand building blocks in diverse modes. In this work we prepared a half-sandwich type mononuclear complex **1** from the reaction of 16-membered  $S_2O_3$  macrocycle  $L^1$  with  $AgClO_4$ . From the stepwise reaction of **1** with bpy, we were successfully able to isolate the dumbbell-shaped disilver complex **2**.

## RESULTS AND DISCUSSION

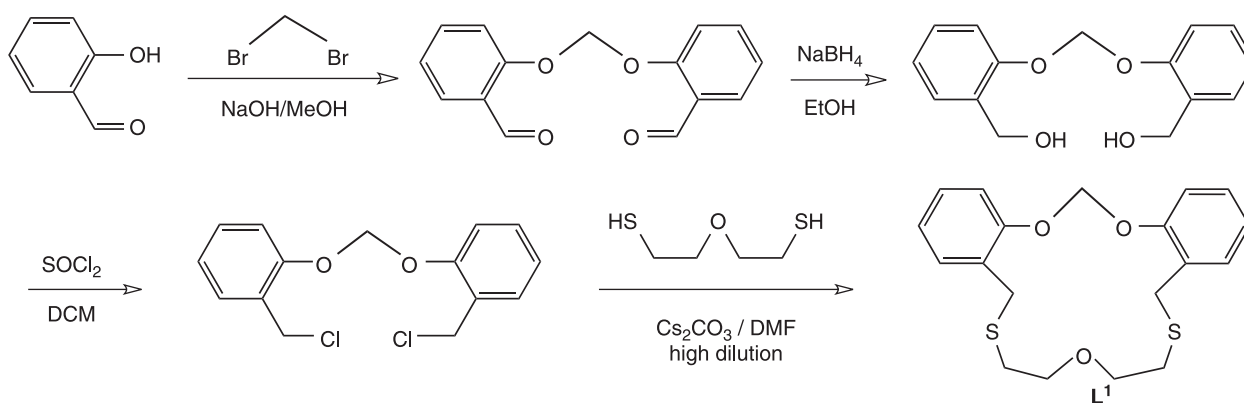
### Ligand Synthesis and Characterization

Synthesis of  $L^1$  began with salicylaldehyde (Scheme 1). Dichloride was prepared using a known procedure [14].  $L^1$  was obtained by coupling reactions for macrocyclization from dichloride and dithiol in the presence of  $Cs_2CO_3$  under high dilution condition in reasonable yield (28%). The  $^1H$  and  $^{13}C$  NMR spectra together with mass spectrum show clear agreement with the proposed structure.

Structure of  $L^1$  was also characterized in solid state by single-crystal X-ray crystallography (Fig. 1 and Table I). Colorless crystals of  $L^1$  suitable for X-ray analysis were obtained by slow evaporation from



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SCHEME 1 Synthesis of  $L^1$ .

the solution of methanol. In crystal,  $L^1$  shows two independent conformation with no significant difference. The macrocyclic ring is relatively flattened and their two oxygen atoms oriented *endo*-dentate, while the two sulfur atoms are arranged *exo*-dentate with respect to the ring cavity [20,21]. The torsion angles (172.8–174.5°) for S–C–C–O segments are in general indicative of an *anti-anti* arrangement.

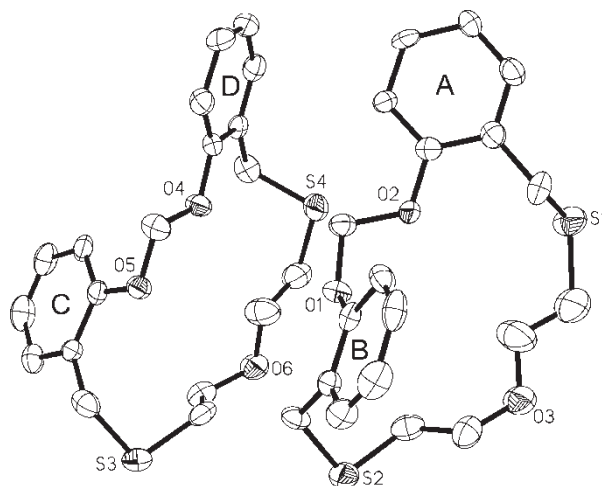
### Preparation of Mono- and Disilver Complexes (1 and 2)

Treatment of  $L^1$  with silver perchlorate in a 1:1 molar ratio in acetonitrile has resulted in the formation of a half-sandwich type acetonitrile-solvated complex **1** (Scheme 2). Thus, it would be interesting to prepare a new complex with extended structure by using **1** as precursor for further reaction with the bridging ligand. Fortunately, an assembly reaction between **1** and bpy produced **2** which is isolated as the coordinately linked macrocyclic disilver complex (Scheme 2). The complex cation of **2**,  $[(AgL^1)_2(\mu\text{-bpy})]^{2+}$  was prepared by facile loss of acetonitrile

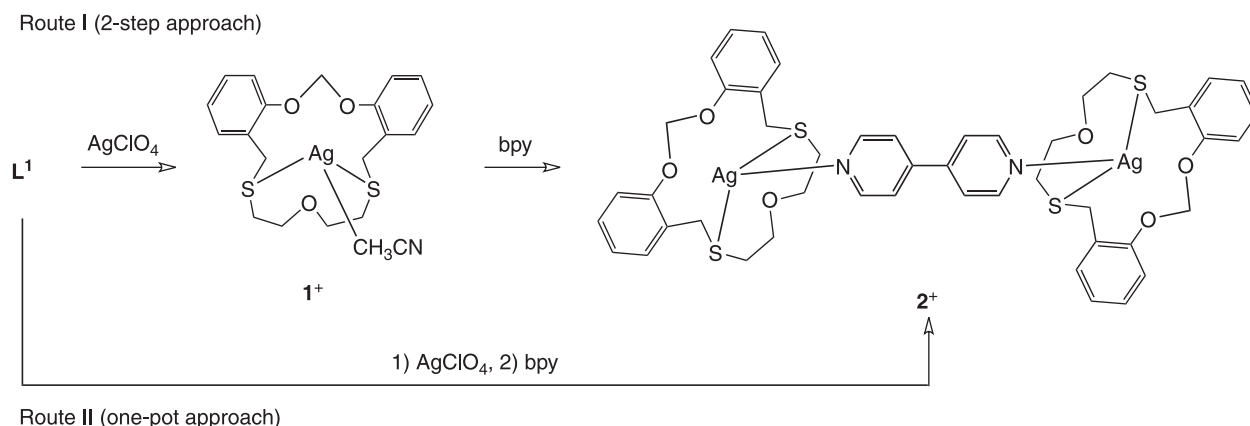
as illustrated in Route I. Indeed, the Route II that exploits the straightforward one-pot reaction also resulted in the isolation of **2**. The complexes **1** and **2** were characterized by single crystal X-ray diffraction techniques.

A colorless precipitate was obtained from  $L^1$  and  $AgClO_4$  in dichloromethane/methanol (v/v 1:1). Single crystals of the product suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into the acetonitrile solution. The crystallographic analysis confirms that the product is a mononuclear silver complex **1** of formula  $[AgL^1(CH_3CN)](ClO_4)$  (Fig. 2 and Table II). The coordination geometry of the silver atom is distorted trigonal plane with two coordination sites being occupied by the sulfur atoms of  $L^1$  [Ag1-S1 2.543(2) and Ag-S2 2.520(2) Å] and the third site is occupied by a nitrogen atom of the acetonitrile [Ag-N 2.308(5) Å]. Accordingly, the silver atom is shifted by about 0.84 Å outward from the center of two sulfur atoms. The conformation of the macrocycle is different from that in free  $L^1$  because of the flexible nature of the thioether moiety. In view of the torsion angles between the neighboring donor atoms, the aliphatic segments of S–C–C–O show a *gauche-gauche* arrangement. Three oxygen donors weakly interact with silver atom [Ag···O1 2.744(4), Ag···O2 2.792(4) and Ag···O3 3.139(4) Å] by long-range interaction. The uncoordinated  $ClO_4^-$  ion (not shown) only acts as the counterion to balance the charge.

As a second step, bpy was employed as a spacer ligand to react with **1**. The reaction of **1** with bpy in DMSO followed by vapor diffusion of diethyl ether afforded crystalline product **2**. X-ray structure analysis reveals that **2** is an interesting discrete complex of

FIGURE 1 Crystal structure of  $L^1$  showing independent two molecules.TABLE I Selected interatomic distances (Å), torsion angles (°) and dihedral angles (°) for  $L^1$ 

S1···S2	7.264 (4)	S1···S2	7.226 (3)
S1–C–C–O3	173.18 (96)	O3–C–C–S2	172.75 (52)
S3–C–C–O6	–172.78 (48)	O6–C–C–S4	–174.50 (70)
ring A···ring B	57.11 (22)	ring C···ring D	60.16 (23)



formula  $[(\text{AgL}^1)_2(\mu\text{-bpy})](\text{ClO}_4)_2$ ; an imposed inversion symmetry exists about the center of the  $\text{bpy}$  (Fig. 3 and Table III). The coordination environment of **2** is similar to that of **1** except the coordinated acetonitrile is replaced by bridging  $\text{bpy}$  ligand which leads the formation of the dumbbell-like structure. Accordingly, the overall coordination of each metal ion is also three-coordinate. Thus, **2** might be regarded as an extension of **1** through  $\text{bpy}$  bridging two adjacent silver centers. The cation part consists of two silver atoms bridged by one  $\text{bpy}$  ligand and further coordinated to an  $\text{L}^1$  with  $\text{Ag}\cdots\text{Ag}$  separation of  $11.680(1)$  Å. The bond distances of  $\text{Ag-S1}$  [ $2.501(1)$ ] and  $\text{Ag-S2}$  [ $2.471(1)$  Å] are shorter than those of **1**, while that of  $\text{Ag-N1}$  [ $2.319(4)$  Å] is longer than  $2.308(5)$  Å observed in **1**. The bond angles of  $\text{S-Ag-N}$  [ $\text{S1-Ag1-N1}$   $112.22(10)$  and  $\text{S2-Ag1-N1}$   $114.53(10)$ ] are larger than those of **1**, while that of  $\text{S1-Ag-S2}$  is smaller than  $141.42(6)^\circ$  observed in **1**. The differences of bond angles around silver center may be due to the steric effect of  $\text{bpy}$ . To our knowledge, binuclear complexes formed by  $\text{bpy}$  bridging ligand have well been documented in previous works [22,23],

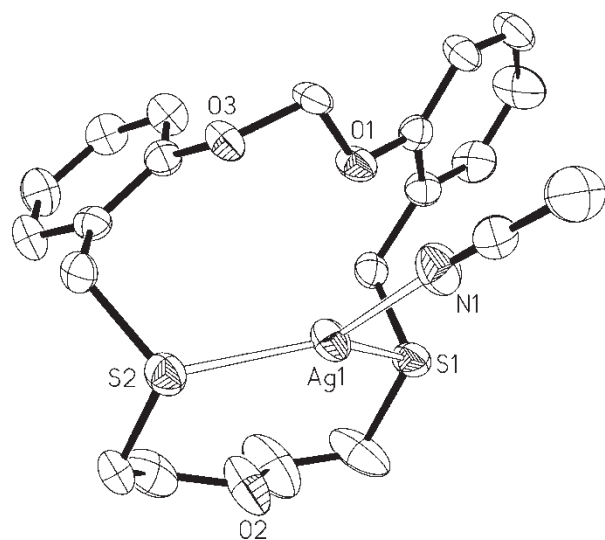


FIGURE 2 Crystal structure of **1**,  $[\text{AgL}^1(\text{CH}_3\text{CN})]\text{ClO}_4$ .

**2** is the first example of a macrocyclic disilver complex bridged by  $\text{bpy}$ .

### Mass and NMR Studies

The FAB mass spectra for the complexes were also obtained (Fig. 4). The mass spectra of **1** and **2** contain peaks at  $m/z$  469 and 547, which correspond to  $[\text{AgL}^1]^+$  and  $[(\text{AgL}^1)_2(\mu\text{-bpy})]^{2+}$ , respectively. The relative abundances of their isotope patterns are in good agreement with those of simulated ones.

To provide insight into the complexes in solution state, NMR studies were carried out for the parallel system.  $^1\text{H}$  NMR spectra of free and complexed  $\text{L}^1$ s (**1** and **2**) are shown in Fig. 5. The signals of four methylene ( $\text{H}_1$  and  $\text{H}_{6-8}$ ) and aromatic protons ( $\text{H}_{2-5}$ ) for  $\text{L}^1$  were well resolved and identified (Fig. 5a). In case of monomeric silver complex **1** (Fig. 5b), every protons of the ligand except  $\text{H}_8$  shifted downfield, suggesting the stable complex formation. The order of magnitude of the chemical shift variation is  $\text{H}_7$  ( $\Delta\delta = 0.44$  ppm)  $>$   $\text{H}_6$  ( $\Delta\delta = 0.21$  ppm)  $>$   $\text{H}_8$  ( $\Delta\delta = 0.15$  ppm),  $\text{H}_1$  ( $\Delta\delta = 0.11$  ppm), indicating 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. In case of the dumbbell-like complex **2** (Fig. 5c), every protons of the ligand shows no significant chemical shifts than **1** (Fig. 5b) imply that the coordination environment of **2** is not different with **1**. The bridging of  $\text{bpy}$  to both silver centers in **2** is indicated by the presence of two resonance in its  $^1\text{H}$ -NMR spectrum. The results above described indicate the formation of the

TABLE II Selected bond lengths (Å), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) for **1**

$\text{Ag1-S1}$	2.543 (2)	$\text{Ag1-S2}$	2.520 (2)
$\text{Ag1-N1}$	2.308 (5)	$\text{S1-Ag1-N1}$	109.94 (14)
$\text{S1-Ag1-S2}$	141.42 (6)	$\text{S2-Ag1-N1}$	108.60 (14)
$\text{S1-C-C-O2}$	$-62.53 (1.08)$	$\text{O2-C-C-S2}$	60.97 (71)

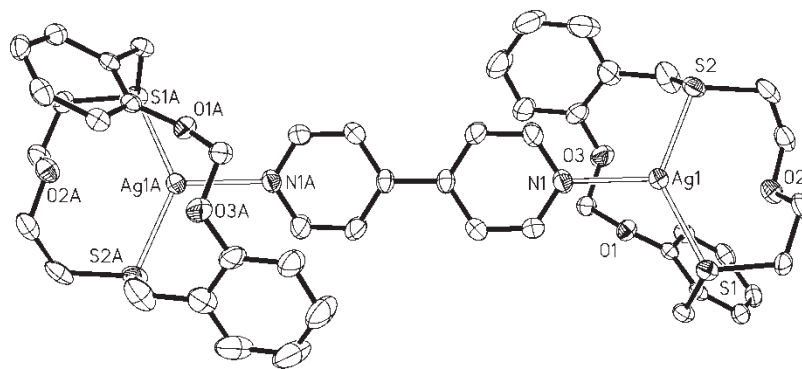


FIGURE 3 Crystal structure of **2**,  $[(\text{AgL}^1)_2(\mu\text{-bpy})](\text{ClO}_4)_2$ . Symmetry operation: A)  $-x + 1, -y + 1, -z$ .

dumbbell-like complex **2** which is also similar to the case in solid state.

## CONCLUSION

We have prepared the dumbbell-like disilver complex involving two  $\text{L}^1$ s and one bpy. The utility of bpy as a bridging ligand for Ag(I) complexes is demonstrated. From the reaction of  $\text{L}^1$  with  $\text{AgClO}_4$ , monomeric  $[\text{AgL}^1(\text{CH}_3\text{CN})]\text{ClO}_4$  (**1**) which containing one coordinating acetonitrile molecule was obtained. The dumbbell-like complex  $[(\text{AgL}^1)_2(\mu\text{-bpy})](\text{ClO}_4)_2$  (**2**) was afforded from the reaction between **1** with bpy by facile change of acetonitrile with bpy. From the  $^1\text{H-NMR}$  experiments, it is concluded that the complex **2** is also retained in solution. The results illustrate an extension to the chemistry of dumbbell-like linear assembly by using a bridging co-ligand.

## EXPERIMENTAL

### General Methods

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 on a JEOL JMS-700 spectrometer at the Central Laboratory of Gyeongsang National University, respectively.

TABLE III Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **2**

Ag1-S1	2.501 (1)	Ag1-S2	2.471 (1)
Ag1-N1	2.319 (4)	S1-Ag1-S2	132.60 (4)
S1-Ag1-N1	112.22 (10)	S2-Ag1-N1	114.53 (10)
S1-C-C-O2	-60.44 (47)	O2-C-C-S2	-58.08 (49)

Symmetry operation: A)  $-x + 1, -y + 1, -z$ .

### Synthesis of $\text{L}^1$

Cesium carbonate (11.22 g, 34.44 mmol) was dissolved in DMF (1000 mL) in a 3-liter round-bottom flask. Bis(2-mercaptoethyl)oxide (3.11 g, 22.54 mmol) and dichloride (6.70 g, 22.54 mmol) was dissolved in DMF (30 mL) and this solution was added to a 50 mL glass syringe. Under a nitrogen atmosphere, the contents of the syringe was added dropwise (a rate of 0.6 mL/h) into a DMF solution of  $\text{Cs}_2\text{CO}_3$  at 45–50°C for 50 h [24]. 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 20% ethyl acetate/*n*-hexane as the eluent led to the isolation of  $\text{L}^1$  as a colorless crystalline product in 28% yield. Mp 76–78°C. IR (KBr,  $\text{cm}^{-1}$ ): 2923, 2852, 1585, 1487, 1452, 1255, 1213, 1110, 999, 748. ESI-mass ( $m/z$ ): 362 ( $\text{M}^+$ ).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44 (d, 2H,  $\text{H}_5$ ), 7.28 (dd, 2H,  $\text{H}_3$ ), 5.86 (s, 2H,  $\text{H}_1$ ), 3.87 (s, 4H,  $\text{H}_6$ ), 3.31 (t,  $J$  = 6.7 Hz, 4H,  $\text{H}_8$ ), 2.57 (t,  $J$  = 6.7 Hz,  $\text{H}_7$ ) ppm.  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ) 154.39, 131.19, 128.33, 122.71, 113.49, 90.90, 70.62, 30.43, 29.84 ppm. The proton numbers in NMR data indicate the nonequivalent protons represented Fig. 5.

### Synthesis of Complex **1**, $[\text{Ag}(\text{L}^1)(\text{CH}_3\text{CN})](\text{ClO}_4)$

Silver perchlorate (0.29 g, 0.14 mmol) was dissolved in methanol (2.0 mL) and was added to the solution of  $\text{L}^1$  (0.50 g, 0.14 mmol) in dichloromethane (2.0 mL). The solution was stirred at room temperature. A fine powder, which precipitated from the solution, was filtered off. Single crystals suitable for X-ray crystallography were prepared by the vapor diffusion of diethyl ether into the acetonitrile solution of the complex. FAB-mass ( $m/z$ ): 469  $^{107}\text{AgL}^1+$ .  $^1\text{H NMR}$  [300 MHz,  $\text{CD}_3\text{CN}:\text{DMSO}-d_6$

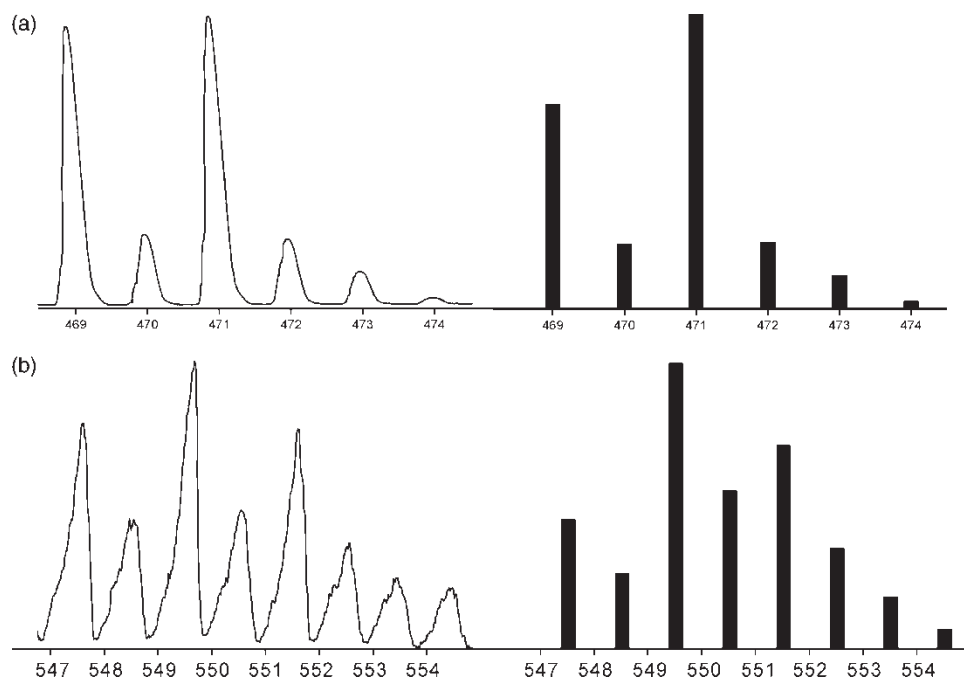


FIGURE 4 Observed isotropic distribution for (a)  $[AgL^1]^+$  and (b)  $[(AgL^1)_2(\mu-bpy)]^{2+}$  in the FAB mass spectra of **1** and **2**. The bars represent the predicted mass spectral distribution for this ion.

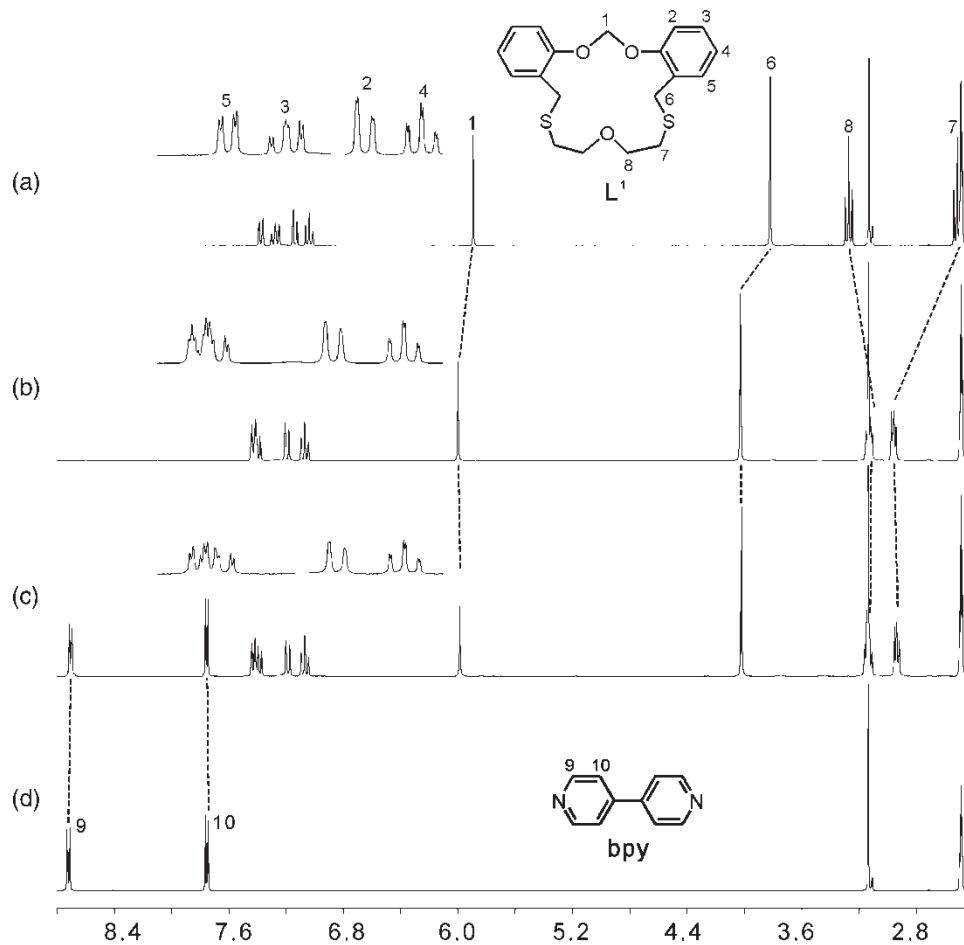


FIGURE 5  $^1H$ -NMR spectra of (a) free  $L^1$ , (b)  $L^1$  +  $AgClO_4$  (1.0 equiv) and (c)  $L^1$  +  $AgClO_4$  (1.0 equiv) + bpy (0.5 equiv) and (d) bpy only in  $CD_3CN:DMSO-d_6$  (1:1).

TABLE IV Crystal data and refinement parameters

Compound	L <sup>1</sup>	1	2
Formula	C <sub>19</sub> H <sub>22</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>21</sub> H <sub>25</sub> AgClNO <sub>7</sub> S <sub>2</sub>	C <sub>24</sub> H <sub>26</sub> AgClNO <sub>7</sub> S <sub>2</sub>
M	362.49	610.86	647.90
Crystal system	Orthorhombic	Orthorhombic	Triclinic
<i>a</i> (Å)	14.7902 (19)	11.6095 (11)	7.7085 (8)
<i>b</i> (Å)	12.1426 (17)	12.6302 (11)	11.4723 (12)
<i>c</i> (Å)	20.637 (3)	16.3734 (15)	15.1202 (16)
$\alpha$ (°)	90	90	74.455 (2)
$\beta$ (°)	90	90	87.249 (2)
$\gamma$ (°)	90	90	75.321 (2)
<i>V</i> (Å <sup>3</sup> )	3706.3 (9)	2400.8 (4)	1245.9 (2)
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.299	1.690	1.727
$\mu$ (mm <sup>-1</sup> )	0.301	1.167	1.130
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> - 1
<i>Z</i>	8	4	2
<i>F</i> (000)	1536	1240	658
Dimensions (mm)	0.20 × 0.20 × 0.30	0.20 × 0.10 × 0.10	0.10 × 0.10 × 0.10
<i>T</i> (K)	298 (2)	173 (2)	173 (2)
2 $\theta$ <sub>max</sub> (°)	56.60	56.62	56.58
No. measured	23227	15372	8060
No. unique	7631	5649	5604
Parameters	433	298	325
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0569	0.0518	0.0433
<i>wR</i> <sub>2</sub> (all data)	0.1857	0.1116	0.1096

(1:1),  $\delta$ ]: 7.40–7.37 (m, 4H, H<sub>5</sub> and H<sub>3</sub>), 7.21 (d, 2H, H<sub>2</sub>), 7.07 (dd, 2H, H<sub>4</sub>), 5.99 (s, 2H, H<sub>1</sub>), 4.03 (s, 4H, H<sub>6</sub>), 3.12 (t, 4H, H<sub>8</sub>), 2.96 (t, 4H, H<sub>7</sub>) ppm. The proton numbers in NMR data indicate the nonequivalent protons represented Fig. 5.

### Synthesis of Complex 2, [(AgL<sup>1</sup>)<sub>2</sub>( $\mu$ -bpy)](ClO<sub>4</sub>)<sub>2</sub>

A slightly excess amount of bpy (0.028 g, 0.177 mmol) was added a solution of **1** (0.090 g, 0.147 mmol) in DMSO (5.0 mL). The mixture was stirred for about 1 h. Single crystals suitable for X-ray crystallography were prepared by the vapor diffusion of diethyl ether into the DMSO solution. FAB-mass (*m/z*): 547 [(<sup>107</sup>AgL<sup>1</sup>)<sub>2</sub>(bpy)]<sup>2+</sup>. <sup>1</sup>H NMR [300 MHz, CD<sub>3</sub>-CN:DMSO-*d*<sub>6</sub> (1:1),  $\delta$ ]: 8.69 (d, 2H, H<sub>9</sub>), 7.76 (d, 2H, H<sub>10</sub>), 7.44–7.37 (m, 4H, H<sub>3</sub> and H<sub>5</sub>), 7.18 (d, 2H, H<sub>2</sub>), 7.07 (dd, 2H, H<sub>4</sub>), 5.99 (s, 2H, H<sub>1</sub>), 4.02 (s, 4H, H<sub>6</sub>), 3.13 (t, 4H, H<sub>8</sub>), 2.93 (t, 4H, H<sub>7</sub>). The proton numbers in NMR data indicate the nonequivalent protons represented Fig. 5.

### X-ray Crystallography

All data were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  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 the SAINT [25]. The structure was

solved by direct methods and refined by full matrix least squares methods on *F*<sup>2</sup> for all data using SHELXTL software [26]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined with a riding model with *U*<sub>iso</sub> constrained to be 1.2 times *U*<sub>eq</sub> of the parent atom. Crystallographic data are summarized in Table IV. Supplementary crystallographic data associated to L<sup>1</sup>, **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 633501–633503.

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