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# Dinuclear silver(I) complexes of dibenzo-crown ethers and the mononuclear complex of aminobenzo-crown ether

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#### Abstract

Three silver(I) coordination complexes of crown ethers,  $[Ag([15]C6)(ClO_4)_2](THF)$  (1),  $[Ag(DB[21]C7)(H_2O)]_2(ClO_4)_2$  (2) and  $[Ag(DB[24]C8)(CF_3SO_3)]_2(acetone)_2$  (3) have been synthesized in different solvents and characterized structurally. The mononuclear complex 1 and two different dinuclear complexes 2 and 3 are shown in this work. Silver(I) ions are situated in a distorted pentagonal pyramidal geometry and form close dinuclear complex with DB[21]C7 based on cation- $\pi$  interaction in  $\eta^2$ -fashion. This coordination unit involves  $\sigma$  bonding at a part oxygen atoms of ligand oxygen base cavity and  $\pi$ - $\pi$  interaction between two parallel phenyl groups. But in 3, each DB[24]C8 host contained two silver(I) ions as guest without cation- $\pi$  and  $\pi$ - $\pi$  interaction. (C) 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Silver complexes; Dinuclear complex; Cation $-\pi$  interaction;  $\pi - \pi$  interaction

#### 1. Introduction

It has become a great major goal in coordination chemistry that of constructing coordination host-guest complexes of organic molecules with metal ions via weak non-covalent interactions such as  $\pi$ -stacking, hydrogen bonding, charge transfer interaction and electrostatic interactions [1]. Of these interactions, cation- $\pi$ ,  $\pi$ - $\pi$  and charge transfer have recently received increasing attention [2]. Cation- $\pi$  and charge transfer interactions can not only build novel molecular architectures but also dramatically influence the physical properties of the fused polyaromatic solid surfaces [3] and may cause to potential applications in electrical conductors and photosensitive devices [4,5]. The potential for such an interaction has always been evident from an electrostatic analysis of benzene.

Crown ethers with their unique chemical architecture play a prominent role and open the way to practical designing of complexation for metal ions [6]. Some macrocyclic crown ethers complexes have been reported so far [7,8], but there are few coordination complexes constructed by  $\eta^2$  coordination mode of benzene of dibenzo-crown ether compounds to silver(I) ions which contain metal ions as guest molecules. Such organometallic compounds are noted as a new type of macrocyclic crown ether coordination complexes. This study of the synthesis and structures of silver(I) complexes of 4'-(2,6dinitro-4-trifluoromethyphenyl)-aminobenzo-15-crown-5 ([15]C5), dibenzo-21-crown-7-ether (DB[21]C7) and dibenzo-24-crown-8-ether (DB[24]C8) is a continuation of our previous work [9], in which the formation of silver(I) coordination complexes of dibenzo-18-crown-6ether has adopted  $\eta^2$  fashion to form dinuclear complexes.

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Dibenzo-24-crown-8-ether (DB[24]C8)

Our continuing interest in the construction of supramolecular architecture of metal ions with crown ether include phenyl group lets us consider the incorporation of metal ions into the crown ether systems for the generation of novel molecular or supramolecular networks with potential physicochemical properties. In order to design new types of silver(I) complexes with macrocyclic crown ether ligands, we have chosen the readily available [15]C6, DB[21]C7 and DB[24]C8, wish to synthesize silver(I) complexes to obtain the possibility of unplanarity complexation in the cation $-\pi$  complexes and to examine any unusual coordination and reactivity which the macrocyclic crown ethers ligand might induce. This has prompted us to consider the possibility that the crystal engineering of such a system with designed structures may be realized by using simple controlling factors such as ligand and solvents [10].

In this work, we have synthesized three silver(I) coordination complexes,  $[Ag([15]C5)(ClO_4)](THF)$ ,  $[Ag(DB[21]C7)(H_2O)]_2(ClO_4)_2$  and  $[Ag_2(DB[24]C8)-(ClO_4)_2]$ . The hosts phenyl crown ether using different mode bind with guests silver(I) ions and built into a variety of sterically confining groups which impart

different kinds of symmetry to the hosts. Here, we describe the syntheses and characterization of this system to show how the mobile silver(I) ions are assembled as guests located in the oxygen base cavity of ligand to build up distinctive molecular architectures.

# 2. Experimental

# 2.1. General procedures

All reactions and manipulations were performed under an argon atmosphere by using Schlenk techniques. All chemicals were reagent grade and used as supplied without further purification. Solvents were dried and distilled by using standards methods before use. Reagent grade [15]C6, DB[21]C7 and DB[24]C8 were purchased from Tokyo Chemical Industry Co., Ltd., whereas silver perchlorate and all other chemicals were purchased from Wako Pure Chemical, Inc. and used as received. The IR spectra were measured as KBr disks on a JASCO FT/IR-8000 spectrometer at room temperature (r.t.). All crystallizations of the silver complexes were performed in the dark.

Safety Note: Perchlorate salts with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with the necessary precautions.

#### 2.2. Syntheses

### 2.2.1. $[Ag([15]C5)(ClO_4)](THF)$ (1)

To a THF solution (10 ml) containing silver perchlorate (22.54 mg, 0.1 mmol), [15]C5 (10.34 mg, 0.02 mmol) was added. The mixture was stirred at r.t. for 20 min and filtered. A portion of the filtrate (2 ml) was introduced into a 7 mm glass tube and layered with *n*pentane as a diffusion solvent. The glass tube was then sealed under Argon and left standing at r.t. for 5 days, orange yellow block crystals of **1** suitable for X-ray determination were isolated. *Anal.* Calc. For AgCl-F<sub>3</sub>O<sub>14</sub>N<sub>3</sub>C<sub>25</sub>H<sub>30</sub>: C, 37.65; H, 3.76. Found: C, 37.81; H, 3.75%. Main IR bands (KBr,  $\nu$  (cm<sup>-1</sup>)): 2875(m), 1638(s), 1543(s), 1513(s), 1314(s), 1287(s), 1131(s), 937(m), 625(m). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  H 9.90 (s, H), 8.58 (s, 2H), 7.08 (s, H), 7.06 (d, H), 6.88 (d, H), 4.24 (t, 4H), 4.01 (t, 4H), 3.87 (s, 8H).

### 2.2.2. $[Ag(DB[21]C7)(H_2O)]_2(ClO_4)_2$ (2)

A solution of DB[21]C7 (36.0 mg, 0.1 mmol) in acetone (10 ml) was treated with  $Ag(ClO_4) \cdot H_2O$  (45.0 mg, 0.2 mmol). After stirring for 20 min the reaction mixture was filtered. The filtrate was transferred to a 7 mm diameter glass tube under argon and was layered by *n*-pentane as a diffusion solvent. The glass tube was sealed under argon and standing at r.t. for 6 days

Table 1 Crystallographic data for complexes 1, 2 and 3

Complex	1	2	3
Formula	AgClF <sub>3</sub> O <sub>14</sub> N <sub>3</sub> C <sub>25</sub> H <sub>30</sub>	$Ag_2Cl_2O_{24}C_{44}H_{60}$	Ag <sub>2</sub> Cl <sub>2</sub> O <sub>16</sub> C <sub>24</sub> H <sub>32</sub>
Formula weight	796.84	1259.59	863.15
Crystal system	triclinic	triclinic	monoclinic
Space group	P1 (#2)	P1 (#2)	$P2_1/c$ (#14)
a (Å)	13.262(3)	10.512(1)	8.734(1)
b (Å)	14.210(3)	13.610(2)	9.8652(7)
c (Å)	8.498(1)	9.3476(7)	17.1773(6)
α (°)	99.255(2)	91.287(3)	
$\beta$ (°)	92.340(2)	109.996(1)	95.4652(7)
γ (°)	107.876(7)	108.392(5)	
V (Å <sup>3</sup> )	1497.4(5)	1179.7(2)	1473.2(2)
Z	2	1	2
<i>F</i> (000)	808.00	644.00	864.00
<i>T</i> (°C)	-123.0	-123.0	-123.0
$\rho  (\mathrm{g}  \mathrm{cm}^{-3})$	1.767	1.773	1.946
$\lambda$ (Å) (Mo K $\alpha$ )	0.71069	0.71069	0.71069
$\mu (\mathrm{cm}^{-1})$	8.54	10.31	15.83
Number of reflections measured	23 026 (total)	18970 (total)	15632 (total)
	6744 (unique)	5393(unique)	3331 (unique)
Number of observed reflections $[I > 2\sigma(I)]$	6415	5051	3192
Number of variable parameters	490	415	265
Residuals: R; Rw	0.029, 0.075	0.022, 0.050	0.022;0.050
Goodness-of-fit	1.05	1.10	1.04

 $R = \Sigma ||F_0| - |F_0|| / \Sigma |F_0|. \ R_{\omega} = [\Sigma \ \omega \ (F_0^2 - F_c^2)^2 / \Sigma \ \omega \ (F_0^2)^2]^{1/2}.$ 

colorless platelet single crystals of **2** were obtained. Anal. Calc. For Ag<sub>2</sub>Cl<sub>2</sub>O<sub>24</sub>C<sub>44</sub>H<sub>60</sub>: C, 41.92; H, 4.76. Found: C, 41.93; H, 4.74%. Main IR bands (KBr, v (cm<sup>-1</sup>)): 2931(m), 1593(m), 1505(s), 1454(m), 1254(s), 1212(m), 1107(s), 946(m), 626(m). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ H 7.05(t, 4H), 6.97 (d, 4H), 4.27 (t, 8H), 4.04 (t, 4H), 3.94 (t, 4H), 3.85(s, 4H).

#### 2.2.3. $[Ag_2(DB[24]C8)(ClO_4)_2](3)$

Similar to the synthesis of 2, DB[24]C8 (44.8 mg, 0.1 mmol) was added to a solution of  $Ag(ClO_4) \cdot H_2O$  (45.0 mg, 0.2 mmol) in acetone (10 ml). The mixture was stirred at r.t. for 20 min, and the resultant colorless solution was filtered. The filtrate was introduced into a 7 mm diameter glass tube under argon and was layered by n-pentane as a diffusion solvent. The glass tube was sealed under argon and wrapped with aluminum foil. The filtrate was left standing at r.t. for 6 days, the colorless block single crystals of 2 were obtained. Anal. Calc. For Ag<sub>2</sub>Cl<sub>2</sub>O<sub>16</sub>C<sub>24</sub>H<sub>32</sub>: C, 33.37; H, 3.71. Found: C, 32.34; H, 3.73%. Main IR bands (KBr, v (cm<sup>-1</sup>): 3425(w), 2924(m), 1592(m), 1503(s), 1455(m), 1255(s), 1216(m), 1089(s), 938(m), 753(m), 625(s). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ H 7.15 (t, 4H), 7.04 (d, 4H), 4.34 (t, 8H), 3.93 (t, 8H), 3.81 (s, 8H).

# 2.3. <sup>1</sup>H NMR measurement

<sup>1</sup>H NMR spectra were measured on a JEOL GSX 270 FT NMR spectrometer. The transients of 3000–5000

were accumulated using 4.0  $\mu$ s (45° pulse) and 16 K data points were collected over a bandwidth of 15 KHz. The probe temperature was set at 23 °C and a 5 mm diameter sample tube was used. All deuterated solvents were dried by molecular sieves before use. Tetramethylsilane was used as an internal reference.

#### 2.4. Crystallography

The single crystal X-ray measurements for all complexes were made on a Quantum CCD area detector coupled with a Rigaku AFC8 diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71069 Å) at a temperature of  $-123 \pm 1$  °C. A suitable single crystal was mounted on a glass fiber. Intensity data were collected by using standard scan techniques  $(\omega - 2\theta)$  to a maximum  $2\theta$  value of 55.0° for 1, 55.4° for 2 and 3, respectively. All intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR88 [11] for 1, SAPI91 [12] for 2, SIR97 [13] for 3) expanded using Fourier techniques [14]. All non-H atoms were refined with anisotropic thermal parameters. The final cycle of full-matrix leastsquares refinements [15] for all the structures was performed on these data having  $I > 2\sigma(I)$  and included anisotropic thermal parameters for non-hydrogen atoms. Reliability factors are defined as  $R = \Sigma ||F_0|$  –  $|F_{\rm c}||\Sigma|F_{\rm o}|$  and  $R_{\omega} = [\Sigma \omega (F_{\rm o}^2 - F_{\rm c}^2)^2 / \Sigma \omega (F_{\rm o}^2)^2]^{1/2}$ . All crystallographic computations were performed using the TEXSAN package [16]. Details of the X-ray experi-

Table 2 Selected bond lengths (Å) and bond angles (°) for complexes 1, 2 and 3

Complex 1 Bond lengths					
Ag(1)–O(5)	2.444(2)	Ag(1)–O(6)	2.479(1)	Ag(1)-O(7)	2.402(2)
Ag(1)-O(8)	2.568(2)	Ag(1)-O(9)	2.414(2)	Ag(1)-O(10)	2.515(2)
Bond angles					
O(5) - Ag(1) - O(10)	94.48(8)	O(5) - Ag(1) - O(6)	67.30(5)	O(5) - Ag(1) - O(7)	135.85(5)
O(5) - Ag(1) - O(8)	124.09(5)	O(5) - Ag(1) - O(9)	64.93(5)	O(6) - Ag(1) - O(10)	93.90(5)
O(6) - Ag(1) - O(9)	118.92(6)	O(6) - Ag(1) - O(7)	69.79(6)	O(6) - Ag(1) - O(8)	117.45(5)
O(7) - Ag(1) - O(8)	68.95(5)	O(7) - Ag(1) - O(9)	132.69(5)	O(7) - Ag(1) - O(10)	98.28(8)
O(9) - Ag(1) - O(10)	125.11(7)	O(8)-Ag(1)-O(9)	66.55(6)	O(8) - Ag(1) - O(10)	136.61(7)
Complex 2 Bond lengths					
Ag(1)-O(5)	2.633(2)	Ag(1)–O(6)	2.547(1)	Ag(1)–O(7)	2.406(1)
Ag(1)-O(8)	2.310(1)	Ag(1)-C(20)	2.598(2)	Ag(1)-C(21)	2.572(2)
C(11)-C(12)	1.418(2)	C(20)-C(21)	1.387(3)	O(5)-Ag(1)-O(6)	59.55(4)
Bond angles					
O(5) - Ag(1) - O(7)	123.89(4)	O(5) - Ag(1) - O(8)	87.13(5)	O(5) - Ag(1) - C(20)	86.61(5)
O(5) - Ag(1) - C(21)	103.61(5)	O(6) - Ag(1) - O(7)	65.96(4)	O(6) - Ag(1) - O(8)	137.26(5)
O(6) - Ag(1) - C(20)	105.94(5)	O(6) - Ag(1) - C(21)	92.20(4)	O(7) - Ag(1) - O(8)	129.04(6)
O(7) - Ag(1) - C(20)	121.42(5)	O(7) - Ag(1) - C(21)	90.39(5)	O(8) - Ag(1) - C(20)	97.14(5)
O(8) - Ag(1) - C(21)	123.29(5)	C(20)-Ag(1)-C(21)	31.11(6)		
Complex 3 Bond lengths					
Ag(1)-O(1)	2.686(1)	Ag(1) - O(1)	2.509(1)	Ag(1)-O(2)	2.405(1)
Ag(1)-O(3)	2.585(1)	Ag(1)-O(4)	2.542(1)	Ag(1)-O(5)	2.494(2)
Bond angles					
O(1) - Ag(1) - O(3)	135.06(4)	$O(1) - Ag(1) - O(1^*)$	90.64(4)	O(1) - Ag(1) - O(2)	69.61(4)
$O(1^*)-Ag(1)-O(4)$	67.05(4)	O(1) - Ag(1) - O(4)	146.65(4)	O(1) - Ag(1) - O(5)	111.01(5)
$O(1^*)-Ag(1)-O(5)$	87.31(5)	$O(1^*)-Ag(1)-O(2)$	136.43(4)	$O(1^*)-Ag(1)-O(3)$	128.97(4)
O(2)-Ag(1)-O(3)	66.71(4)	O(2)-Ag(1)-O(4)	109.12(4)	O(2)-Ag(1)-O(5)	135.63(5)
O(4) - Ag(1) - O(5)	93.10(5)	O(3) - Ag(1) - O(4)	61.97(4)	O(3) - Ag(1) - O(5)	93.34(5)
$Ag(1) - O(1) - Ag(1^*)$	89.36(4)				

ments and crystal data are summarized in Table 1. Selected bond lengths and angles for the three complexes are given in Table 2.

#### 3. Results

# 3.1. Syntheses and infrared spectroscopy

A ligand generally is coordinated to metal ions via a stoichiometric reaction [4,17], but the complexes presented here are prepared via reactions of excess metal ions with the ligand [15]C6, DB[21]C7 and DB[24]C8. In the experiments, when the molar ratio of metal ions to ligand is less than 2 for these complexes, it is very difficult to obtain the single crystals at r.t. The reason for this phenomenon is twofold, (i) solvent may react with silver(I) ions to form a complex [18] which consumes partial silver(I) ions; (ii) when a complex formed in solution is 'incongruently saturating' [19], its crystal cannot be obtained via a stoichiometric reaction.

The interest in the IR spectra of these compounds lies mainly in the coordinative interactions associated with the ligand and the counteranions. A broad strong absorption occurs in the region 1034-1254 cm<sup>-1</sup> in these complexes, and their peaks are shifted to slightly different frequencies compared with the normal absorption of AgClO<sub>4</sub> at 1140, 1109, 1087 cm<sup>-1</sup>. This suggests that the perchlorate groups in these complexes are present not as ionic species, but as coordinated ones [20]. The coordination of silver(I) ions to oxygen, carbon or carbon–carbon  $\pi$  bonds of crown ether can also be seen by comparing the spectra of 1–3 with that of the three free ligand.

#### 3.2. Description of the structure

# 3.2.1. *Mononuclear complex of* [*Ag*([15]C6)(*ClO*<sub>4</sub>)](*THF*) (1)

The molecular structure of complex 1 together with the numbering scheme is shown in Fig. 1. The X-ray diffraction analysis of 1 reveals a mononuclear complex of silver(I) located in oxygen base cavity of ligand, and the uncoordination molecules of THF molecules are distributed independently in a column in a region of void space in the lattice interstices. The central silver(I)



Fig. 1. Molecular structure and atom numbering of 1.

ions, coordinated to six oxygen atoms, is bonded to five oxygen atoms from [15]C5 ligand at Ag–O distances ranging from 2.402(2) to 2.568(2) Å, the last coordination sites are interestingly completed by one oxygen atoms from perchlorate group at Ag–O distance of 2.515(2)Å. Not as other two dibenzo crown ether ligands in this work, [15]C6 does not offer  $\pi$ -donor from bezene ring to coordinate to silver(I) ions to form metal– $\pi$  bond. The steric structure of [15]C6 could be thought of as the one important effect factor. From the angles data surrounding silver(I) ions with oxygen atoms from ligand oxygen base cavity, we know that silver(I) ions positions are slightly over to the oxygen atoms cavity plane, and are situated in the space of distorted octahedral geometry.

# 3.2.2. Dinuclear complex of

# $[Ag(DB[21]C7)(H_2O)]_2(ClO_4)_2$ (2)

The unit-cell contents, as determined by the structural study, showed that the stoichiometry of the complex was a 1:1:2 metal-to-ligand-to-water tertiary system; however, molecules of perchlorate anion exist independently of the complex in lattice interstices. The molecular structure of 2 together with the atomic numbering scheme is given in Fig. 2. This compound can be regarded as both a coordination dimer and a stacking dimer. The dinuclear complex structure shows each silver(I) ion is bonded to one hydrate oxygen at Ag-O bond length of 2.310(1) Å and three ligand oxygens at Ag–O distance ranging from 2.406(1) to 2.633(2) Å, whereas carbon–carbon  $\pi$  coordination of DB[21]C7 with silver(I) in  $\eta^2$ -mode and rise to a cavities space with  $5.62 \times 3.42$  Å, in which no any molecular is included. The Ag–C bond lengths range from 2.598(2) to 2.585(2) Å within the limits from 2.47 to 2.77 Å in the reported silver(I)-aromatic complexes [4,21]. The distance of two parallel phenyl groups of 3.424 Å is very short, indicating presence of strong  $\pi - \pi$  interaction [22]. Each DB[21]C7 ligand symmetrically  $\eta^2$ -interacts with one silver(I) ions linked with each other. Similar to complex [Ag(DB[18]C6)(ClO<sub>4</sub>)](THF) in our previous



(b)



Fig. 2. Partial labeling (a) and schematic view (b) of silver(I)– DB[21]C7 dinuclear unit.

work [9], the silver(I) ions in 2 are coordinated to four oxygens of which three oxygens of ligand and one hydrate oxygen instead of one perchlorate oxygen in complex [Ag(DB[18]C6)(ClO<sub>4</sub>)](THF). The perchlorate anions are not coordinated to silver(I) ions and only exist independently of the complex in a column in a region of void space in the lattice formed by two dinuclear units (Fig. 3). Above these results, we hope to obtain new porous complex via using large excess



Fig. 3. The view down crystallographic packing of 2.

molar ratio between silver salt and ligand, in which ions as guests locate in the cavity of the polymer network. This work is underway in our laboratory.

# 3.3. Dinuclear complex of [Ag<sub>2</sub>(DB[24]C8)(ClO<sub>4</sub>)<sub>2</sub>] (3)

Fig. 4 depicts a perspective view with atom numbering of the molecule. Complex 3 is a 2:1:2 metal-to-ligand-toanion tertiary system, but without participation of molecules of solvent in lattice. The crystallographic studies revealed that the structure contains a dinuclear core, in which each silver(I) ion is octahedrally coordinated to five oxygen atoms of ligand and one oxygen atom of the two symmetry related disorder perchlorate anions. In the unit, each dibenzo-crown ether ligand host contained two silver(I) ions as guest and a pair of silver(I) atoms lead to  $Ag \cdot \cdot Ag$  distance of 3.66 Å with  $Ag(1)-O(1)-Ag(1^*)$  bond angle of 89.36(4)°. Within unit each silver(I) is bonded to one disorder perchlorate oxygen at Ag–O distance of 2.494(2) Å and five oxygens of the ligand at Ag–O bond length range from 2.405(1) to 2.585(1) Å. Different from complex 2, silver(I) ions are not coordinated to phenyl group, whereas silver(I) ions are coordinated to disorder perchlorate oxygen lying the symmetry position. Some properties of the crown ether complex of silver perchlorate have been reported [6–9], but its structure remains unknown until this work. On the other hand, the present structure differs significantly from that of the reported silver(I) crown ether complex, where the nuclear complex,  $[Ag_2(DB[24]C8)(ClO_4)_2]$ , is based on two symmetry silver(I) ions coordinated to five oxygens of ligand and related disorder perchlorate without cation  $-\pi$  interaction.



Fig. 4. Molecular structure and atom numbering of 3.

# 3.4. <sup>1</sup>H NMR spectra

The observed <sup>1</sup>H NMR chemical shifts of silver(I) complexes 1-3 and their free ligands are listed in Table 3. The present silver(I) complexes and ligands were assigned on the basis of previously reports [9,23,24]. As shown in Table 3, the coordination chemical shifts of complexes have some changes occur with slightly shifted to low field comparison with free ligand, in which the proton chemical shift of silver(I)- $\pi$  site is small relatively similar to the report <sup>1</sup>H NMR data [24]. In 1, from the comparison with two phenyl groups of free ligand, the coordination shifts of change of one near oxygen base cavity (3-H, 4-H) are larger than that of the far one (1-H). The <sup>1</sup>H NMR singnals of the final product **1** were assigned to the 1-H, NH, 2-H, 3-H, 4-H, 5-H, 6-H and 7-H positions, respectively. The final product is a mononuclear silver(I) complex.

### 4. Discussion

The three crown ether hosts are coordinated to silver(I) ions as guest in their oxygen base cavity in this work. The structure of these silver(I) complexes display different characteristics with cation being encapsulated in an oxygen environment. Complex 1 consists of mononuclear unit with THF being situated in lattics interstices. Dibenzo-crown ether possess hard oxygen cavities constructed and soft  $\pi$ -donor benzene rings and subsequently cation  $-\pi$  interaction and  $\pi - \pi$ interaction do occur in the dinuclear silver(I) complexes 2. In 3, there are no cation  $-\pi$  interaction or  $\pi - \pi$ interaction, but two silver(I) ions guests located in the one oxygen base cavity form the other dinuclear complex type with Ag...Ag distance at 3.66 Å, and the complex unit shows symmetry structure. The crystallographic results of the present silver(I) complexes indicated that the structure conformation is prominently depended on the property of the crown ether ligand.

The average Ag–O distances of 2.511, 2.474 and 2.524 Å observed for **1**, **2** and **3**, respectively, are within the normal range observed in silver(I) carboxylate, oxalate and crown ether complexes [4,9,17,25,26]. The average Ag–C distance of 2.585 Å in **2** has very closely length and fall under 2.40–2.76 Å observed for silver(I) aromatic complexes [27]. In addition, the Ag–O bond length of silver(I) with hydrate in **2** is shorter than that of silver(I) with perchlorate group in **1** and **3**. It can be thought that the steric structure and chemical property of ligand, coordinated molecular groups, silver(I)– $\pi$  interaction and solvent effect the construction of silver(I) complexes.

Similar to our previous work [9], complex 2 shows the silver(I) ions interact with DB[21]C7 ligand at the hard donor crown ether oxygen atoms and soft donor

Table 3 Observed <sup>1</sup>H NMR chemical shifts of silver(I) complexes and ligands <sup>a</sup>

Complex and ligand	$\delta$ (ppm)								
	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	NH
Complex 1	8.58	7.08	7.06	6.88	4.24	4.01	3.87	3.87	9.90
[15]05	8.55	6.90	6.89	6.76	4.07	3.83	3.67	3.67	9.92
Complex 2	7.05	6.97	4.27	4.04	3.85	3.94			
DB[21]07	6.95	6.87	4.14	3.89	3.76	3.84			
Complex 3	7.15	7.04	4.34	3.93	3.81				
DB[24]O8	6.95	6.88	4.13	3.84	3.75				

<sup>a</sup> Solvent: CD<sub>3</sub>COCD<sub>3</sub>.

benzene ring carbon atoms as well as  $\pi - \pi$  interaction of two parallel benzene ring plane in dinuclear unit. The difference is that silver(I) ions of 2 coordinated to one hydrate oxygen instead of one perchlorate oxygen in [Ag(DB[18]C6)(ClO<sub>4</sub>)](THF). The distance of two parallel phenyl at 3.424 Å is shorter than that in [Ag(DB[18]C6)(ClO<sub>4</sub>)](THF) at 3.531 Å, it leads to stronger  $\pi - \pi$  interaction. The interest in complex 3 is that two silver(I) ions guests were located in the one oxygen base cavity to be coordinated to one ligand without cation  $-\pi$  and  $\pi - \pi$  interaction suggesting that when four and five oxygens of ligand are stereospecifically coordinated to silver(I) ions, the phenyl groups can not be coordinated to silver(I) ions. Furthermore, from the comparison of structures of [Ag(DB[18]C6)- $(ClO_4)$ ](THF) [9], [Ag(DB[21]C7)(H<sub>2</sub>O)]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and  $[Ag_2(DB[24]C8)(ClO_4)_2]$ , as well known as the ligand oxygen base cavity size change, the guest number and coordination fashion are apparently different. When the ligand includes eight oxygen atoms, two silver(I) ions locate in one oxygen base cavity of DB[24]C8 to coordinate to oxygen atoms, without silver(I)- $\pi$  interaction and  $\pi - \pi$  interaction. This indicates that the structure construction process in such dibenzo crown ether silver(I) complexes system is strongly depend on the ligand.

In conclusion, with the salt silver perchlorate and crown ether ligand, three distinct coordination compounds, 1-3, have been synthesized at r.t. One mononuclear and two types of dinuclear complexes are shown in present work. In complex 2 based on cation $-\pi$ interaction, in particular, the coordination unit involved both  $\sigma$  bonding at an oxygen group and strong  $\pi - \pi$ bonding between two parallel phenyl groups. There still are challenges in understanding why silver(I) ions coordinated to part oxygen atoms of DB[21]C7 and uncoordinated oxygen atoms have not coordinated to another silver(I) ions to form one- or two-dimensional structure. It is believed that self-assembly of crown ether compounds with transition metal ions can be constructed using the stereospecific crown ether as well as the mole ration and the solvent effect. It is unambiguously demonstrated that the ligand structure and molar ratio of ligand:metal act as a gate blocking the guest molecules entering into the host cavity in DB[21]C7 system in this work. Further studies of silver(I)–DB[21]C7 compounds with different silver salts in large excess molar ratio are currently underway.

# 5. Supplementary material

Complete tables of bond lengths and angels, final atomic coordinates and equivalent isotropic thermal parameters, calculated hydrogen atom parameters, anisotropic thermal parameters, and structure factors for three structures are available from the authors. Details of the crystal structure determinations of the compounds reported are also available upon request from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK.

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