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Dinuclear silver(I) complexes of N, N'-dibenzyl-4,13-diaza-18-crown-6-ether and dibenzo-24-crown-8-ether

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Abstract

Three silver(I) coordination complexes of diaza- and dibenzo-crown ethers, $[Ag(DDAC)](CF_3SO_3)$ (1), $[Ag_2(DDAC)(CF_3SO_3)_2]$ (2) and $[Ag_2(DB24C8)(CF_3SO_3)_2]$ (3) have been synthesized by using different molar ratios of ligand to silver triflate salt, and characterized structurally. A large excess of DDAC ligand leads to mononuclear complex 1, and a large excess of silver triflate gives rise to dinuclear complex 2, based on metal-heteroatom and metal-oxygen interactions. Ligand DB24C8 coordinates two silver(I) ions to afford dinuclear complex 3.

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1. Introduction

Macrocyclic ligands have long been employed for studies involving transition metal ion recognition [1,2]. There has been tremendous development with respect to cyclic type ligands like crown ethers [3] which are able to perform specific functions. When the macrocyclic ligands are bound to polymeric supporting materials, the resulting materials can serve as ion sensors, exchange resins, metal ion extractors, phase transfer catalysts, mimics of enzyme systems and photoresponsive chromophores [4–6].

Cryptand type ligands, crown ether systems are suitable to be used in the design of complexation agents for metal ions [7–13]. We have been continuously studying dibenzo-crown ether complexes with

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silver(I) ions [14,15], because these silver(I) complexes used usually involve the oxygen base cavities and π -donor phenyl groups. Same as the reported example [16], two different coordination complexes can be constructed by using different molar ratios of crown ether ligand to silver(I) ion in this work. The macrocyclic crown ether and cryptand ligands were incorporated into the dimers.

In this work, two cryptand type ligands of crown ethers, N, N'-dibenzyl-4,13-diaza-18-crown-6-ether (DDAC) and dibenzo-24-crown-8-ether (DB24C8), as a continuation of our previous work [15], have been selected as ligands to synthesize three silver(I) coordination complexes, [Ag(DDAC)](CF₃SO₃) (1), [Ag₂-(DDAC)-(CF₃SO₃)₂] (2) and [Ag₂(DB24C8)(CF₃SO₃)₂] (3). The cryptand crown ether hosts, diaza-crown ether and dibenzo-crown ether, using different coordination modes bind the guest silver(I) ions and build up distinctive molecular architectures.

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

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 DDAC was 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. All crystallizations of the silver complexes were performed in the dark.

2.2. Syntheses

2.2.1. $[Ag(DDAC)](CF_3SO_3)$ (1)

To a toluene solution (8 ml) containing Ag-(CF₃SO₃) (12.6 mg, 0.048 mmol), DDAC (106.2 mg, 0.24 mmol) was added. The mixture was stirred at room temperature for 20 min and filtered. A portion of the filtrate (2 ml) was introduced into a 7 mm glass tube and layered with *n*-hexane as a diffusion solvent. After the glass tube was sealed under argon and left standing at room temperature for one week, colorless block crystals of 1 suitable for X-ray determination were isolated. The theoretical value of elemental analysis and the isolated yield (21.4 mg, 18%) are based on the formula without THF molecules. Anal. Calc. for AgSF₃O₇N₂C₂₇H₃₈: C, 46.36; H, 5.48; N, 4.00. Found: C, 46.35; H, 5.06; N, 3.96%. Main IR bands (KBr, v/cm^{-1}): 2858(m), 1494(w), 1452(m), 1266(s), 1145(s), 1106(s), 1030(s), 749(m), 709(m), 638(s).

2.2.2. $[Ag_2(DDAC)(CF_3SO_3)_2]$ (2)

A solution of DDAC (12.8 mg, 0.03 mmol) in toluene (10 ml) was treated with Ag(CF₃SO₃) (38.8 mg, 0.30 mmol). The above procedure was repeated to yield colorless platelet single crystals of **2** (13.4 mg, yields 26%). *Anal.* Calc. for Ag₂S₂F₆O₁₀N₂C₂₈H₃₈: C, 34.42; H, 4.09; N, 2.81. Found: C, 35.16; H, 4.00; N, 2.93%. Main IR bands (KBr, ν/cm^{-1}): 2887(m), 2370(w), 1458(w), 1285(s), 1267(s), 1148(s), 1106(s), 1036(s), 736(m), 708(m), 638(m).

2.2.3. $[Ag_2(DB24C8)(CF_3SO_3)_2]$ (3)

Similar to the previous complexes, DB[24]C8 (44.8 mg, 0.10 mmol) was added to a solution of AgCF₃SO₃ (51.4 mg, 0.20 mmol) in toluene, and yielded colorless platelet single crystals of **3** (26.9 mg, yield 28%). *Anal.* Calc. for Ag₂S₂F₆O₁₄C₂₆H₃₂: C, 32.42; H, 6.88. Found: C, 32.05; H, 6.56%. Main IR bands (KBr, ν/cm^{-1}): 3547(m), 2910(s), 1597(s), 1504(s), 1456(s), 1352(s), 1278(s), 1224(s), 1160(s), 1116(s), 1083(s), 1047(s), 1033(s), 951(s), 938(s), 905(m), 746(m), 634(s).

2.3. Crystallography

Single crystal X-ray data for all complexes were measured on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at -123 ± 1 °C for 1 and 2, and 26.0 ± 1 °C for 3. Details 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

3.1.1. Syntheses

It is noted that in the preparations described above different metal:ligand ratios were used. Generally, coordination of an aromatic ligand to silver ions can be achieved via a stoichiometric reaction [17,18], but sometimes an excess of ligand or metal ion has to be used to obtain coordinated complexes [19-23]. In this work, the complexes presented here are prepared via reactions of excess ligand or metal ion. In the experiments, when the molar ratios of M:L were 5:1, 1:10 and 1:2 for 1, 2 and 3, respectively, crystallized solids were isolated at room temperature, and the different molar ratios led to different crystal structures. Reasons for the use of silver salt excesses in 3 are as follows: (i) The solvent toluene may form metal complexes in solution with silver ions [24] which partially consumes the metal salt. Thus, the preparation of silver(I) complexes in toluene sometimes requires an excess of the silver salt

Table 1 Crystallographic data for complexes 1–3

Complex	1	2	3			
Formula	$AgSF_{3}O_{7}N_{2}C_{27}H_{38}$	$Ag_{2}S_{2}F_{6}O_{10}N_{2}C_{28}H_{38}$	$AgSF_3O_7C_{13}H_{16}$			
Formula weight	699.53	1912.92	481.19			
Crystal system	monoclinic	triclinic	monoclinic			
Space group	$P2_1/n$ (#14)	P1 (#2)	$P2_1/c$ (#14)			
a (Å)	11.261(3)	12.603(6)	10.0449(3)			
b (Å)	13.523(4)	15.094(7)	21.051(3)			
<i>c</i> (Å)	20.222(6)	10.252(6)	8.6860(5)			
α (°)		98.76(2)				
β (°)	109.870(3)	100.34(2)	110.4894(6)			
γ (°)		109.46(1)				
$V(Å^3)$	2896(1)	1760(1)	1720.5(2)			
Ζ	4	2	4			
F(000)	1440.00	960.00	960.00			
T (°C)	-123.0	-123.0	26.0			
ρ (g/cm ³)	1.604	1.804	1.858			
λ, Å (Mo Kα)	0.71069	0.71069	0.71069			
μ (cm)	8.33	13.15	13.53			
Number of reflections measured	9062 (total)	19999 (total)	20973 (total)			
	6594 (unique)	7949 (unique)	2018 (unique)			
Number of observed reflections $[I > 2\sigma(I)]$	6049	5651	3912			
Number of variable parameters	370	452	274			
Residuals: R ; $R_{\rm w}$	0.026; 0.053	0.066; 0.128	0.055; 0.108			
Goodness-of-fit	1.07	1.07	1.44			
$R = \sum F_{\rm o} - F_{\rm c} / \sum F_{\rm o} . R_{\rm w} = \left[\sum w(F_{\rm o}^2 - F_{\rm c}^2)^2 / \sum w(F_{\rm o}^2)^2\right]^{1/2}.$						

[25]. (ii) When a compound (complex) in solution is "incongruently saturating", its crystal cannot be obtained via a stoichiometric reaction [26]. We examined

the effect of a different molar ratio on the nature of the final product. The reactivity of $AgCF_3SO_3$ with DB24C8 was systematically studied in toluene with

Table 2 Selected bond lengths (Å) and bond angles (°) for complexes $1{-}3$

Complex 1					
Bond lengths Ag(1)–O(3) Ag(1)–N(2)	2.598(1) 2.316(2)	Ag(1)-O(4)	2.686(2)	Ag(1)–N(1)	2.305(2)
Bond angles O(3)-Ag(1)-O(4) O45)-Ag(1)-N(1) Ag(1)-O(3)-C(21) Ag(1)-O(4)-C(24) Ag(1)-N(1)-C(25) Ag(1)-N(2)-C(26)	63.6(4) 113.8(4) 110.7(8) 103.9(1) 108.4(1) 107.0(1)	O(3)-Ag(1)-N(1) O(4)-Ag(1)-N(2) Ag(1)-O(3)-C(23) Ag(1)-N(1)-C(19) Ag(1)-N(2)-C(16)	71.7(4) 73.6(4) 117.5(1) 113.9(1) 111.5(1)	O(3)-Ag(1)-N(2) N(1)-Ag(1)-N(2) Ag(1)-O(4)-C(17) Ag(1)-N(1)-C(22) Ag(1)-N(2)-C(18)	121.9(4) 166.1(4) 102.5(9) 108.4(1) 111.8(9)
Complex 2					
Bond lengths Ag(1)–O(1) Ag(1)–N(1) Ag(2)–O(8)	2.511(4) 2.287(4) 2.252(3)	Ag(1)–O(2) Ag(2)–O(6) Ag(2)–N(2)	2.589(4) 2.592(4) 2.325(4)	Ag(1)–O(3) Ag(2)–O(7)	2.203(4) 2.506(5)
Bond angles O(1)-Ag(1)-O(2) O(2)-Ag(1)-O(3) O(6)-Ag(2)-O(7) O(7)-Ag(2)-O(8)	115.5(1) 105.2(1) 121.5(1) 113.4(1)	O(1)-Ag(1)-O(3) O(2)-Ag(1)-N(1) O(6)-Ag(2)-O(8) O(7)-Ag(2)-N(2)	121.4(2) 73.7(1) 113.0(1) 74.5(1)	O(1)-Ag(1)-N(1) O(3)-Ag(1)-N(1) O(6)-Ag(2)-N(2) O(8)-Ag(2)-N(2)	78.8(2) 161.5(2) 71.0(1) 163.5(2)
Complex 3					
Bond lengths Ag(1)–O(1)	2.450(4)	Ag(1)–O(5)	2.538(5)	Ag(1)–O(6)	2.634(6)
Bond angles Ag(1)–O(1)–C(1)	112.3(3)	Ag(1)–O(1)–C(2)	113.6(4)		

different M:L ratios. Reactions similar to that described in the experimental section but performed with M:L ratios of 1:1 led to no evidence for formation of an isolable complex. In order to obtain polymeric complexes by connecting silver(I) ions and the phenyl group of DDAC besides silver(I) locating in the cavities, a large excess of silver triflate was used with L:M = 1:10 which led to dinuclear complex **2**. The effect of a different molar ratio was studied by employing a large ligand excess with L:M = 5:1. The result was the mononuclear complex **1**.

3.1.2. Infrared spectroscopy

In the IR spectra of 1–3, a broad strong absorption occurs in the region $638-1254 \text{ cm}^{-1}$, and their peaks are shifted to slightly different frequencies compared with the normal absorption of AgCF₃SO₃ at 1256, 1179, 1037, and 629 cm⁻¹. This suggests that the triflate groups in these complexes are present not as ionic species, but as coordinated ones [27]. The coordination of silver(I) ions to oxygen or nitrogen atoms of diaza-crown ether and dibenzo-crown ether can also be seen by comparing the spectra of 1–3 with those of the two free ligands (DDAC at 1453, 1123, 1056, 749, 701 cm⁻¹, DB24C8 at 1594, 1507, 1357, 1225, 960, 740 cm⁻¹).

3.2. Description of the structures

3.2.1. Mononuclear complex $[Ag(DDAC)](CF_3SO_3)$ (1)

Molecules of triflate anion exist independently of the complex in lattice interstices. The molecular structure of complex 1 together with the numbering scheme is shown in Fig. 1. The silver(I) ion is in a distorted tetrahedral environment, being coordinated by two nitrogen atoms and two oxygen atoms on the same side of the N–Ag–N system, in which Ag–O bond lengths are 2.598(1) and 2.686(2) Å and Ag–N bond lengths are 2.305(2) and



Fig. 1. ORTEP view of the molecular structure of 1.

2.315(2) Å. The O–Ag–O and N–Ag–N angles are $63.6(4)^{\circ}$ and $166.13(4)^{\circ}$, respectively. The remaining two ligand oxygen atoms are not involved in coordination, and the triflate ion only plays a charge-balance and space-filling role.

3.2.2. Dinuclear complex $[Ag_2(DDAC)(CF_3SO_3)_2]$ (2)

An ORTEP drawing of complex 2 with the atom numbering scheme is shown in Fig. 2. The symmetric unit contains two independent dinuclear molecules each located at an inversion center. The coordination environment of each metal atom is almost tetrahedral, comprising of three oxygen atoms of which two are from DDAC and one from a triflate group, plus a nitrogen atom. The DDAC ligand thus contains two silver(I) centers in its heterocyclic hard donor cavity with Ag–O bond lengths ranging from 2.203(4) to 2.592(4) Å and Ag–N bond lengths of 2.287(4) and 2.325(4) Å. The present Ag–O bond lengths are well within the normal range 2.17–2.61 Å observed in silver(I)–crown ether complexes [15] and the Ag–N bond lengths are normal



Fig. 2. Molecular structure of the dinuclear unit of 2.



Fig. 3. Molecular structure of the dinuclear unit of 3.

compared with those in previously reported crystatesilver(I) complexes [10].

3.2.3. Dinuclear complex $[Ag_2(DB24C8)(CF_3SO_3)_2]$ (3)

Fig. 3 depicts a perspective view with the atom numbering of centrosymmetric complex 3, in which each silver(I) ion is octahedrally coordinated by two triflate oxygens with an average Ag–O length of 2.586 Å and five oxygens of the ligand with an average Ag–O bond length of 2.450 Å. Each DB24C8 host molecule contains two silver(I) ions as guests with a Ag···Ag distance of 3.95 Å. Unlike dinuclear silver(I) coordination complexes of the dibenzo-crown ether family in our previous works, [Ag(DB[18]C6)(ClO₄)](THF) [15a], the silver(I) ions are not coordinated to phenyl groups.

4. Discussion

In this work, the diaza- and dibenzo-crown ether hosts accommodate silver(I) ions as guests in their cyclic hard donor base cavities. The structures of these three silver(I) complexes display different characteristics with the cation being encapsulated in a macrocyclic environment with different L:M stoichiometries. A large excess of DDAC ligand leads to mononuclear complex 1, and a large excess of silver triflate gives rise to dinuclear complex 2 based on metal-heteroatom and metal-oxygen interactions. DB24C8 coordinates to two silver(I) ions to afford dinuclear complex 3.

The average Ag–O bond lengths of 2.642, 2.442 and 2.540 Å observed for 1, 2 and 3, respectively, are within the normal range observed in silver(I)-crown ether complexes [10]. The average Ag-N bond lengths of 2.310 Å in 1 and 2.306 Å in 2 are virtually the same and a little longer than that in the silver(I) complex of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, but slight shorter than that in the silver(I) complex of N-methylated (L^2) and N-benzylated 1,4,10,13-tetraoxa-7, 16-diazacyclooctadecane (L^3) [10]. In the present complexes, each silver(I) ion is not coordinated to all oxygen and nitrogen atoms as in $[Ag(L^3)]PF_6$ [10]. In addition, triflate oxygen atoms are not coordinated to silver(I) ions in 1, but are coordinated to silver(I) ions in 2, and the Ag–O bond length of silver(I) with triflate is shorter than that of silver(I) with the ligand oxygen atoms.

Furthermore, the crown ether hosts in this work are not involved in coordination of the phenyl group to silver(I) via a π interaction, as our previous work in DB18C6–Ag(I) complexes [15a] (Fig. 4). Two symmetry-related silver(I) ions can be located in the oxygen base cavity of DB24C8 without silver(I)– π interaction and π – π interaction (Fig. 4(c)). On the other hand, even though DDAC has the same size, six-membered hard donor cavity as that of DB18C6, the silver(I) guest number and coordination fashion differ distinctly. The coordination unit of DB18C6-Ag(I) complexes can involve both σ bonding at an oxygen group and silver– π as well as π – π interaction between two parallel phenyl groups (Fig. 4(a)). DDAC only contains two symmetry-related silver(I) ions in its



Fig. 4. Schematic view of dinuclear Ag(I) complexes with dibenzo- and diaza-crown ethers. $[Ag(DB18C6)(CF_3SO_3)]_2(acetone)_2$ (a), $[Ag_2(DDAC)(CF_3SO_3)_2]$ (b), $[Ag_2(DB24C8)(CF_3SO_3)_2]$ (c).

six-membered heterocyclic hard donor cavity without silver– π and π - π interaction (Fig. 4(b)). This case is the same as the formation of the Ag(I)–DB24C8 complex with a eight-membered hard donor cavity. This indicates that the structure construction process in the crown ether–silver(I) complex system is strongly dependent on the ligand: cavity size and the existence of heteroatoms as well as flexibility of the phenyl group.

In conclusion, with the cryptand type ligands, two distinct coordination complexes 1 and 2, have been synthesized with different L:M stoichiometry. With regard to silver(I) complexes with diaza- and dibenzocrown ethers (Fig. 4), there are two kinds of substantial dinuclear complexes. The ligand DB18C6 is based on the silver(I)– π interaction, in which the coordination unit involves both σ bonding at oxygen donor sites and π - π interaction between two phenyl groups. The other kind comprise dinuclear complex 2 and 3 in this work, in which two silver(I) ions occupy the cyclic or heterocyclic base cavity to coordinate to oxygen atoms without Ag(I)– π interaction or π – π interaction. It is believed that self-assembly of macrocyclic cryptand or dibenzo-crown ether compounds with transition metal ions can be constructed using stereospecific diaza- and dibenzocrown ethers ligands (cavity size, the existence of heteroatoms as well as the flexibility of phenyl groups) and the molar ratio effect [10].

5. Supplementary material

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-220695, 220694 and 220693 for complex **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http// www.ccdc.cam.ac.uk).

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