

Assembly of a Cyclic Dimer Silver(I) Complex Encapsulating Two BF_4^- Ions

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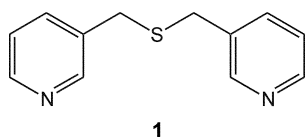
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It is a challenging work to capture ionic species or small molecules as guests. Thus, the construction of self-assembled cyclic oligomer complexes composed of metal centres connected by acyclic organic ligands^{1,2} has been a subject of great interest together with the inclusion phenomena of macrocyclic ligands³ in the supramolecular chemistry. The majority of the organic-inorganic hybrid macrocyclic structures reported so far have been based on bis-monodentate ligands such as 4,4'-bipyridine and its derivatives interconnected by rigid or flexible spacers.² The same type of ligands has been also used for the formation of coordination network.⁴

We are currently engaged in the construction of the coordination polymers by using series of dipicolyl sulfides including **1**, bis(3-pyridylmethyl)sulfide, which is a potentially tridentate ligand to act as a flexible building blocks. In the reaction of **1** with AgBF_4 , in contrast to other reactions we have employed, neither the 1-D nor 2-D coordination polymers have been isolated, but rather discrete cyclic dimer complex was obtained. A remarkable feature of this cyclic structure is the encapsulation of two BF_4^- anions in its 20-membered cavity. Although the rational control of molecular frameworks by anions have become a recent interest in crystal engineering,⁵ little is known about anion-encapsulated M_2L_2 [M: metal, L: ligand] complexes.¹ To our best knowledge, few examples of two BF_4^- -encapsulated M_2L_2 complexes have been reported so far.^{1c} We present here the synthesis and structural details of this complex, which was



characterized by X-ray diffraction and ESI-Mass.

Reaction of **1** with AgBF_4 in the molar ratio 1 : 1 in methanol gave off-white precipitates immediately, which were identified as the discrete complex $[\text{Ag}(\mathbf{1})_2]_2\text{BF}_4$ by the single crystal X-ray analysis. Elemental analysis of the complex is consistent with a 1 : 1 ligand:metal ratio. The IR spectrum shows an intense BF_4^- band at 1053 cm^{-1} . The ESI mass spectrum in DMF shows peaks at m/z 323, 325,

539, 541, 732 and 734 corresponding to $[\text{Ag}(\mathbf{1})]^-$, $[\text{Ag}(\mathbf{1})]^+$, $[\text{Ag}(\mathbf{1})_2]^+$, $[\text{Ag}(\mathbf{1})_2]^-$, $\{[\text{Ag}(\mathbf{1})_2]_2(\text{BF}_4)^-\}$, and $\{[\text{Ag}(\mathbf{1})_2]_2(\text{BF}_4)^+\}$. The crystals with high quality for X-ray analysis were obtained by the vapor diffusion of diethyl ether into the DMSO solution of the precipitates. Crystal parameters and procedural information corresponding to data collection and structure refinements are given in Table 1. The geometric parameters of the complex are shown in Table 2.

According to X-ray crystal structure analysis (Figure 1), the discrete cyclodimeric complex, $[\text{Ag}(\mathbf{1})_2]_2\text{BF}_4$, was constructed. A striking feature is that two BF_4^- anions are positioned in the cavity. In the cationic $[\text{Ag}(\mathbf{1})_2]_2^{2+}$, each Ag atom is coordinated linearly by two pyridine N atoms from two different ligands (**1**) [N-Ag-N $166.4(2)^\circ$] while each ligand binds two Ag atoms in *cis,cis*-mode, leading to the

Table 1. Crystallographic Data for $[\text{Ag}(\mathbf{1})_2]_2\text{BF}_4$

formula	$\text{C}_{24}\text{H}_{24}\text{Ag}_2\text{B}_2\text{F}_8\text{N}_4\text{S}_2$
f.w.	821.95
space group	$C2/c$
<i>a</i> , Å	13.627(1)
<i>b</i> , Å	14.009(2)
<i>c</i> , Å	15.609(2)
β , °	106.977(2)
<i>V</i> , Å ³	2580.1(5)
<i>Z</i>	4
<i>D</i> _{calc} , g cm ⁻³	1.916
μ , mm ⁻¹	1.597
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0596 <i>wR</i> ₂ = 0.1478

$$R_1 = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}, wR_2 = \frac{[\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}}$$

Table 2. Selected Geometric Parameters (Å, °) for $[\text{Ag}(\mathbf{1})_2]_2\text{BF}_4$

Ag(1)-N(1)	2.152(5)	Ag(1)-N(2) ⁱ	2.141(5)
N(1)-Ag(1)-N(2) ⁱ	166.5(2)		
Ag(1)⋯Ag(1) ^j	7.212(2)	Ag(1)⋯F(3)	3.31(4)
Ag(1)⋯F(4)	3.56(1)	Ag(1) ^j ⋯F(2)	3.468(6)
Ag(1)⋯S(1) ⁱⁱ	3.106(2)		
C(2)-C(6)-S(1)-C(7)	89.1(6)	C(6)-S(1)-C(7)-C(8)	73.0(5)
Dihedral angle between two pyridine rings		1.79(5)	

Symmetry transformations used to generate equivalent atoms: i) $-x - 1/2, -y + 1/2, -z + 1$; ii) $-x + 1/2, y + 1/2, (-z + 1/2) + 1$

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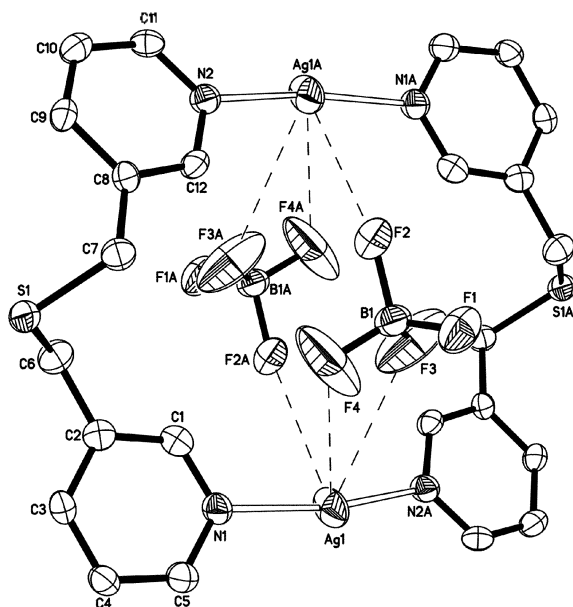


Figure 1. Structure of complex $[\text{Ag}(\text{I})]_2 \cdot 2\text{BF}_4$ with atomic labeling scheme. Hydrogen atoms are omitted for clarity.

formation of a 20-membered macrocyclic motif. Two pyridine rings coordinated to the Ag atom are tilted by $13.7(1)^\circ$ with respect to each other. The Ag-N distances [Ag(1)-N(1) 2.152(5) Å, Ag(1)-N(2A) 2.141(5) Å] are shorter than those found in the silver(I)-bis(2-pyridylmethyl)sulfide complex.⁶ The asymmetric unit contains one Ag atom, one ligand, and one BF_4^- anion by a crystallographic inversion center at the midpoint between the two Ag atoms. Each non-coordinating S atom oriented *exo*-fashion, and thus the pseudo-rectangular framework of the molecule is folded into the stair-shape. The dimension of the pseudo-rectangle is defined by the distances between the centroids of pyridyl rings (6.6×7.0 Å) and intramolecular Ag...Ag separation [7.212(2) Å]. This is in contrast to the two-fold symmetric dimer of bis(2-pyridylmethyl)sulfide, an isomer of **1**, in which three-coordinate Ag atoms are bound in N-Ag-N fashion together with the each S donor to form a cyclic dimer with a much smaller empty cavity.⁶ Each BF_4^- ion is located slightly above and below the folded rectangular plane and with the distance Ag(1)...F(3) of 3.31(6) Å, which indicates a long range interaction.

According to the packing structure (Figure 2), the deviation from the linearity of N-Ag-N angle is due to the weak intermolecular Ag...S interaction (3.106(2) Å). Furthermore, the cyclic dimmers pack in layers, allowing offset π - π stacking⁷ with the separation between the centroids of 3.69 Å. The dihedral angle between the pyridyl ring planes is $1.79(5)^\circ$.

In conclusion, unusual twenty-membered cyclic dimer encapsulating two BF_4^- anions was obtained by the self-assembly of the tridentate N_2S donor ligand (**1**) and silver ion. We are currently investigating the subtle factors influencing the formation of discrete or continuous complexes using dipicolyl sulfide derivatives including **1**.

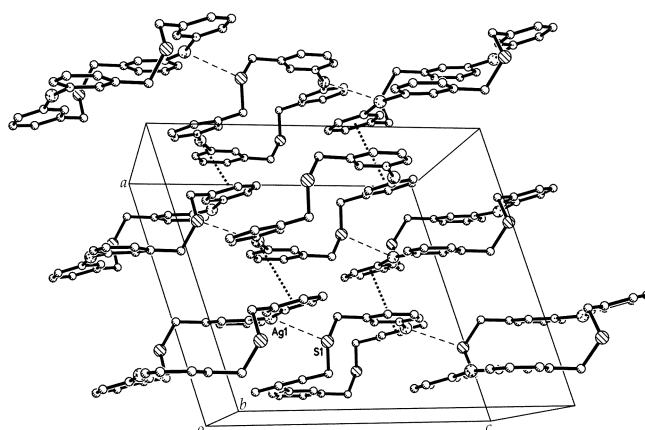


Figure 2. Projection showing the stair-shaped cyclic dimers with the Ag...S and π - π interactions for $[\text{Ag}(\text{I})]_2 \cdot 2\text{BF}_4$. BF_4^- ions and H atoms are omitted for clarity.

Experimental Section

Synthesis. The ligand **1**, bis(3-pyridylmethyl)sulfide, was conveniently synthesized by the reaction of Na_2S and 3-picolyl chloride hydrochloride, and the detailed procedure will be described in elsewhere. Reaction of **1** (50.0 mg, 0.231 mmol) with AgBF_4 (50.0 mg, 0.257 mmol) in methanol gave off-white precipitate immediately. Analytical data for $\{[\text{Ag}(\text{I})](\text{BF}_4)\}_2$: Mp. 209–213 °C (dec.). Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{Ag}_2\text{B}_2\text{F}_8\text{N}_4\text{S}_2$: C, 35.07; H, 2.94; N, 6.82; S, 7.80. Found: C, 34.97; H, 3.05; N, 6.43; S, 8.23%. IR (KBr, cm^{-1}): 3448 (br), 1582, 1474, 1423, 1053 (s, br, BF_4^-), 813, 711. ESI-MS: m/z 323 $^{107}\text{Ag}(\text{I})^+$, 325 $^{109}\text{Ag}(\text{I})^+$, 539 $^{107}\text{Ag}(\text{I})_2^-$, 541 $^{109}\text{Ag}(\text{I})_2^-$, 732 $\{[\text{Ag}(\text{I})]_2(\text{BF}_4)\}^+$, 734 $\{[\text{Ag}(\text{I})]_2(\text{BF}_4)\}^-$.

Crystallographic Structure Determination. All data were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å) radiation source and a CCD detector at ambient temperature. 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 and no correction was applied for absorption or decay. The frame data were processed to give structure factors using the program SAINT.⁸ The structure was solved by direct methods and refined by full matrix least squares methods on F^2 for all data using SHELXTL software.⁹ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the parent atom.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center [CCDC deposit number 205088]. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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