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Binuclear Silver (I) Complex with Double Armed Diaza-Crown Ether Containing Short Metal-Metal Separation

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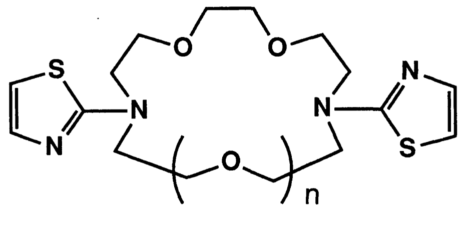
Binuclear silver (I) complexes of double armed diaza-crown ethers, 7, 16-bis(2'-thiazoyl)-1, 4, 10, 13-tetraoxa-7, 16-diazacyclooctadecane and 7, 13-bis(2'-thiazoyl)-1, 4, 10-trioxa-7, 13-diazacyclopentadecane were prepared. In these complexes, two Ag^+ cations were cooperatively coordinated by thiazole-functionalized side arm and parent diaza-crown ring, and their Ag···Ag' separations (2.790 and 2.969 Å) were either shorter (≈0.1 Å) or slightly longer (≈0.08 Å) than the intermetallic distance (2.889 Å), respectively.

Armed macrocycles and their metal complexes have recently attracted much interest. When cation-ligating side arms were attached at appropriate positions on the macrocyclic ligand, cooperative binding of pendant arm and macro-ring offered characteristic cation binding and chemical functions.[1] Here, we report that 7, 16-bis(2'-thiazoyl)-1, 4, 10, 13-tetraoxa-7, 16-diazacyclooctadecane (**1**) and 7, 13-bis(2'-thiazoyl)-1, 4, 10-trioxa-7, 13-diazacyclopentadecane (**2**) having thiazole-functionalized arms uniquely form binuclear Ag^+ complexes in which the Ag···Ag' separations are either shorter (≈0.1 Å) or slightly longer (≈0.08 Å) than the intermetallic distance (2.889 Å), respectively. Although macrocyclic complexes of Ag^+ ion are quite common,[2] few binuclear complexes have been isolated. Furthermore, such short metal-metal distances have rarely been achieved in 15- and 18-membered macrocyclic ligands.[3]



1 n = 2
2 n = 1

We successfully crystallized two different types of binuclear Ag$^+$ complexes with thiazole-functionalized diaza-crown ethers **1** and **2**.$^{4,5)}$ Typically, functionalized diaza-18-crown-6 **1** forms a binuclear Ag$^+$complex, in which two Ag$^+$ ions have exactly centrosymmetrical coordination structure and are closely located at 2.790 Å (Fig. 1). Remarkably, this Ag···Ag' separation is shorter than in metallic silver (2.889(6) Å).$^{6)}$ Short Ag···Ag' distances have been observed in rigid 1,3-bifunctional bidentate ligands,$^{7)}$ but have rarely been attained using flexible, macrocyclic ligands. Probably, the unique ligand geometry and donor combination of the diaza-crown ether **1** offer a short Ag···Ag' distance. Each silver is basically coordinated by two nitrogen atoms of thiazole and crown rings, N(7) and N(11'). The Ag-N(11') and the Ag-N(7) distances are 2.199(4) and 2.374(5) Å, and similar to those reported for mononuclear Ag$^+$ complexes with common nitrogen donors.$^{8)}$

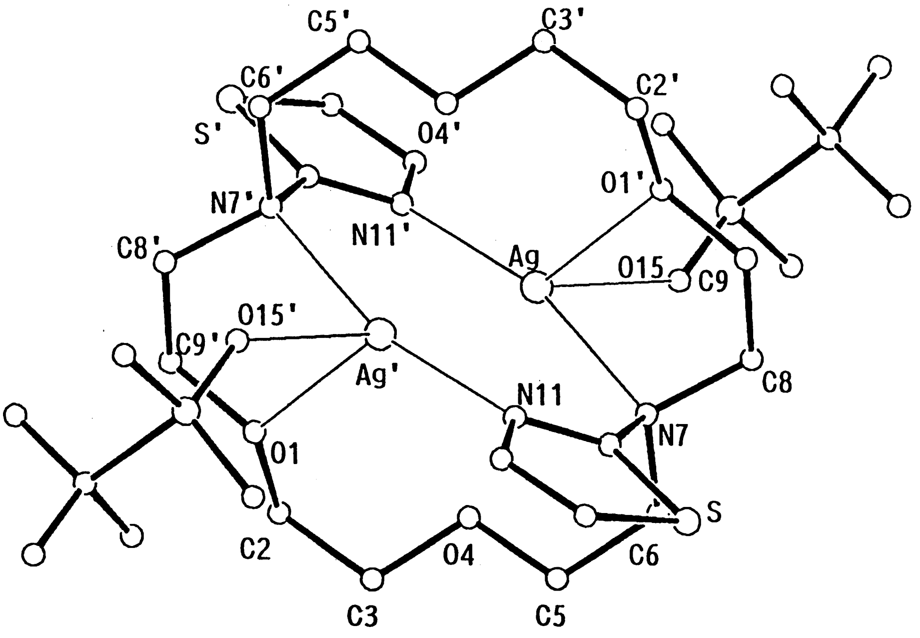


Fig. 1. Perspective drawing of **1**-(AgOSO$_2$CF$_3$)$_2$ complex. Selected distances (Å) and angles (deg): Ag-N(7), 2.374(5); Ag-O(15), 2.535(4); Ag-O(1'), 2.554(5); Ag-N(11'), 2.199(4); O(4)-Ag-N(7), 64.9(2); O(4)-Ag-O(15), 100.6(1); O(4)-Ag-O(1'), 131.7(2); N(7)-Ag-O(15), 88.9(1); N(7)-Ag-O(1'), 68.7(2); O(15)-Ag-O(1'), 91.1(1).

Functionalized diaza-15-crown-5 **2** also forms a binuclear Ag$^+$ complex, the crystal structure of which is largely different from that with diaza-18-crown-6 **1**. Interestingly, the two Ag$^+$ ions are closely spaced (Ag···Ag 2.969(1) Å) but in asymmetrical environments (Fig. 2). One, Ag(1), is strongly linked to two thiazole nitrogens, N(17) and N(21), and to an oxygen of counter-anion, O(24). The second silver, Ag(2), is interacted with a nitrogen atom and three oxygen atoms of diaza-crown ring, N(7), O(1), O(4), and O(10), and with an oxygen of counter-anion, O(31). Although thiazole-functionalized arms were confirmed to play important roles in these two binuclear complexes, the size of the crown ring significantly influenced complex structure. These double armed crown ethers can organize their conformations to wrap two Ag$^+$ ions nicely, and their unique inclusion is able to overcome the substantial electrostatic repulsion of the two Ag$^+$ ions.

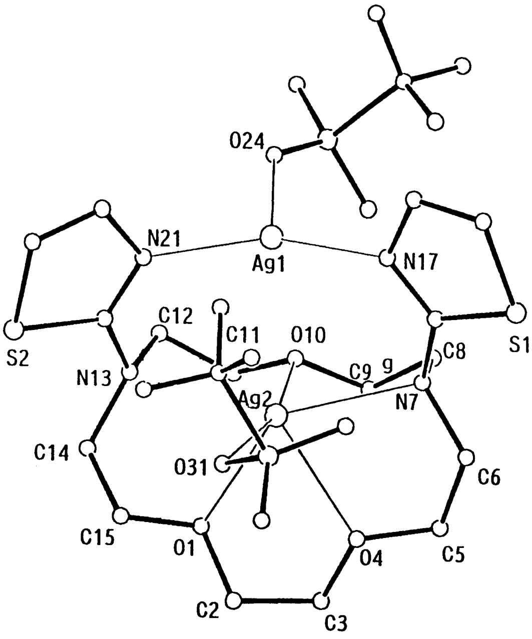


Fig. 2. Perspective drawing of **2**-(AgOSO$_2$CF$_3$)$_2$ complex. Selected distances (Å) and angles (deg): Ag(1)-O(10), 2.809(5); Ag(1)-N(17), 2.211(7); Ag(1)-N(21), 2.219(7); Ag(1)-O(24), 2.488(7); Ag(2)-N(7), 2.577(6); Ag(2)-O(1), 2.568(6); Ag(2)-O(4), 2.509(6); Ag(2)-O(10), 2.435(5); Ag(2)-O(31), 2.304(8); O(10)-Ag(1)-N(17), 93.8(2); O(10)-Ag(1)-N(21), 95.9(2); O(10)-Ag(1)-O(24), 78.6(2); N(17)-Ag(1)-N(21), 144.2(3); N(17)-Ag(1)-O(24), 115.1(2); N(21)-Ag(1)-O(24), 100.6(2); O(1)-Ag(2)-O(4), 66.2(2); O(1)-Ag(2)-N(7), 125.2(2); O(1)-Ag(2)-O(10), 85.4(2); O(1)-Ag(2)-O(31), 87.5(2); O(4)-Ag(2)-N(7), 68.4(2); O(4)-Ag(2)-O(10), 95.5(2); O(4)-Ag(2)-O(31), 94.0(3); N(7)-Ag(2)-O(10), 70.0(2); N(7)-Ag(2)-O(31), 124.9(2); O(10)-Ag(2)-O(31), 164.7(2).

^{1}H-NMR spectrum of the binuclear **2**-Ag$^+$ complex was recorded at ambient temperature in CD$_2$Cl$_2$.9) Both aromatic and aliphatic signals shifted and broadened; large low field shifts of thiazole protons (0.4–0.5 ppm) were observed, whereas crown ring protons were broadened and slightly shifted (≈0.1 ppm). Although its low solubility has prevented further investigation, cooperative binding of side arm and diaza-crown ring was supported in homogeneous solution.

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5) **1**-$(AgOSO_2CF_3)_2$: dec. 156-160 °C (Found: C, 25.21; H, 2.87; N, 6.03%. Calcd for $C_{20}H_{28}N_4O_{10}F_6S_4Ag_2$: C, 25.49; H, 2.99; N, 5.94%); M, 942.32, monoclinic, space group $P2_1/a$, a=16.266(1), b=12.604(1), c=8.206(1) Å, β=104.918(8)°, U=1626.6(3) $Å^3$, Z=2, Dc=1.932 g cm^{-3}, μ=15.3 cm^{-1}. 2618 Reflections with $2\theta \leq 50°$ were recorded on a four circle diffractometer using graphite-monochromated Mo-Kα radiation. Of these 2083 [with $I > 3\sigma(I)$] were judged observed. The structure was solved using Patterson methods. All hydrogen atoms could be located on a difference Fourier synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic hydrogens converged to R=0.034 and Rw=0.069. **2**-$(AgOSO_2CF_3)_2$: dec. 180-183 °C (Found: C, 23.88; H, 2.57; N, 6.06%. Calcd for $C_{18}H_{24}N_4O_9F_6S_4Ag_2$: C, 24.06; H, 2.69; N, 6.28%); M, 898.43, monoclinic, space group $P2_1$, a=10.577(6), b=14.490(9), c=9.801(4) Å, β=90.07(4)°, U=1502(3) $Å^3$, Z=2, Dc=1.993 g cm^{-3}, μ=16.5 cm^{-1}. 2758 Reflections with $2\theta \leq 50°$ were recorded, and 2609 [with $I > 3\sigma(I)$] were judged observed (R=0.036 and Rw=0.048).

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9) NMR studies were performed at the SC-NMR Laboratory of Okayama University.

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