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Silver(I) Complex Assemblies with Nonplanar Aromatic Compounds

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Reactions of silver(I) perchlorate with the nonplanar aromatic compounds triptycene (L^1), 9,9-bifluorenylidene (L^2), (*R*)-(+)-1,1′-bi-2-naphthol (L^3), and 2,5-norbornadiene (L^4) have isolated four novel hydrocarbon-bridged polymeric complexes: $[Ag_3(L^1)_3(ClO_4)_3]\cdot 2C_6H_5Me$ (**1**), $[Ag_2(L^2)_2(ClO_4)_2]\cdot C_6H_4Me_2$ (**2**), $[Ag_2(L^3)(C_6H_6)_2(ClO_4)_2]$ (**3**), and $[Ag(L^4)(ClO_4)]$ (**4**). Structural studies using single-crystal X-ray diffraction have shown that all compounds contain extended two- or three-dimensional structures based on cation−π interactions. While complex **1** in the solid state contains a three-dimensional architecture in which the triangular molecule triptycene exhibits an unprecedented μ-η^2-η^2 or μ-η^2-η^2-η^1 coordination mode depending on the steric requirements of the network, **3** represents the first example of π coordination of naphthol-containing micropores in its metal complexes. Infinite chains consisting of alternating silver ions and hydrocarbon molecules observed in both **2** and **4** are linked together by perchlorates, affording 2-D frameworks. The potential use of these π complexes for the rational control and synthesis of polymeric organometallic materials is discussed. Crystal data: **1**, $C_{74}H_{58}Ag_3Cl_3O_{12}$, monoclinic, *Cc*, $a = 37.951(4)$ Å, $b = 8.047(4)$ Å, $c = 20.882(5)$ Å, $\beta = 93.72(1)°$, $V = 6363(3)$ Å^3, $Z = 4$; **2**, $C_{60}H_{42}Ag_2Cl_2O_8$, monoclinic, $P2_1/n$, $a = 12.317(4)$ Å, $b = 7.961(1)$ Å, $c = 24.741(1)$ Å, $\beta = 100.015(1)°$, $V = 2389(6)$ Å^3, $Z = 2$; **3**, $C_{32}H_{26}Ag_2Cl_2O_{10}$, tetragonal, $P4_12_12$, $a = 8.759(6)$ Å, $c = 39.967(8)$ Å, $V = 3065(3)$ Å^3, $Z = 4$; **4**, C_7H_8-$AgClO_4$, monoclinic, $P2_1/n$, $a = 9.847(4)$ Å, $b = 9.054(3)$ Å, $c = 10.662(3)$ Å, $\beta = 106.72(2)°$, $V = 910.3(4)$ Å^3, $Z = 4$.

Introduction

Aromatic hydrocarbons have been demonstrated to be a group of versatile ligands for the synthesis of organometallic materials with a variety of structural architectures. By careful control of the synthesis conditions and the organic species employed, it has proven possible to synthesize a vast range of open frameworks and layered materials in which the ionic inorganic species is occluded within an organic framework.$^{1-7}$ Of paramount importance is the ability of the organic molecules to influence profoundly the structures of the synthesized products and to direct their formation with particular structural and physical properties. To date, the vast majority of examples have been derived from planar polycyclic aromatic compounds. Aside from the purely academic interest in these fascinating structures, the new hybrid organic−inorganic layered and chain materials have often shown unique donor−acceptor electronic properties due to the overall planarity of the organic molecules and the extended delocalized π systems.$^{8-11}$

As a part of our recent interest in developing the organosilver(I) chemistry of aromatic hydrocarbons^{1,6,7} and as a consequence of the paucity of known structures of nonplanar aromatic species, we report in this paper the synthesis and characterization of a series of complexes of silver(I) with the nonplanar aromatic compounds L^1−L^4, which might modify the degree of aggregation of the silver complexes. An added impetus for this exploratory study was the metal complexes of the chiral diol of L^3 and the globular molecule of L^4, which are being used experimentally as catalysts and π-delocalized ligands, respectively, in asymmetric activation^{12,13} and photoisomerization processes.^{14,15}

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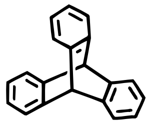
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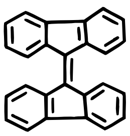
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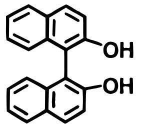
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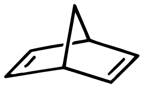
2,5-norbornadiene (L^4)

Experimental Section

General Procedures. All reactions and manipulations were carried out under an argon atmosphere by using standard Schlenk vacuum line techniques. Solvents were dried using standard procedures and distilled under an argon atmosphere prior to use. Reagent grade triptycene, (*R*)-(+)-1,1′-bi-2-naphthol, and 2,5-norbornadiene were purchased from Aldrich, and 9,9-bifluorenylidene was purchased from Tokyo Kasei Kogyo Co., Ltd. All chemicals were used as received. $AgClO_4{\cdot}H_2O$ (Aldrich) was dried at 40 °C under reduced pressure for 5 h before use. All other chemicals were purchased from Wako Pure Chemicals, Inc. IR spectra were recorded as KBr disks on a JASCO 8000 FT-IR spectrometer, and UV−vis spectra were obtained on a Hitachi 150−20 spectrophotometer. All crystallizations of the silver complexes were carried out in the dark.

Caution! Perchlorate salts with organic ligands are potentially explosive and should be handled with the necessary precautions.

Syntheses. $[Ag_3(L^1)_3(ClO_4)_3]{\cdot}2C_6H_5Me$ (1). A solution of $AgClO_4{\cdot}H_2O$ (22.5 mg, 0.1 mmol) in 5 mL of toluene was added to triptycene (12.7 mg, 0.05 mmol). After 10 min of stirring, the resultant colorless solution was filtered. The filtrate was introduced into a narrow-diameter glass tube and carefully layered with 2 mL of *n*-pentane as a diffusion solvent. The glass tube was sealed under Ar and wrapped with tin foil. The filtrate was allowed to stand at room temperature for 3 days, upon which light colorless prismatic crystals of **1** were obtained. Anal. Calcd for $C_{74}H_{58}Ag_3Cl_3O_{12}$: C, 56.64; H, 3.73. Found: C, 56.59; H, 3.51. IR (KBr, ν/cm^{-1}): 3069 (m), 2969 (m), 1458 (s), 1103 (s), 1086 (s), 750 (s), 627 (s).

$[Ag_2(L^2)_2(ClO_4)_2]{\cdot}C_6H_4Me_2$ (2). A *p*-xylene solution (6 mL) containing 22.5 mg of $AgClO_4{\cdot}H_2O$ (0.1 mmol) was added to 32.8 mg of 9,9-bifluorenylidene (0.1 mmol). The solution was treated in the same way as that for **1** and gave brown needle-like single crystals of **2** after standing for 1 week at room temperature. Anal. Calcd for $C_{60}H_{42}Ag_2Cl_2O_8$: C, 61.14; H, 3.59. Found: C, 60.57; H, 3.68. IR (KBr, ν/cm^{-1}): 3547 (m), 3474 (m), 3057 (w), 1604 (w), 1444 (s), 1350 (m), 1084 (s), 720 (s), 625 (s). 586 (m).

$[Ag_2(L^3)(C_6H_6)_2(ClO_4)_2]$ (3). The colorless brick red crystals of **3** were grown similarly to those of **2** using (*R*)-(+)-1,1′-bi-2-naphthol (16.4 mg, 0.05 mmol) instead of 9,9-bifluorenylidene and benzene instead of *p*-xylene. Anal. Calcd for $C_{32}H_{26}Ag_2Cl_2O_{10}$: C, 44.80; H, 3.03. Found: C, 44.68; H, 2.89. IR (KBr, ν/cm^{-1}): 3510 (s), 3441 (s), 1620 (s), 1597 (s), 1070 (s), 760 (m), 629 (s).

$[Ag(L^4)(ClO_4)]$ (4). The colorless solution of THF (10 mL) containing 45 mg of $AgClO_4{\cdot}H_2O$ (0.2 mmol) was added to 0.2 mL of 2,5-norbornadiene (2 mmol). The mixture was stirred for 20 min and filtered. The filtrate was transferred to a glass tube and layered with *n*-pentane. After the solution was allowed to stand for 3 days at room temperature, colorless prismatic crystals of **4** were isolated. Anal. Calcd for $C_7H_8AgClO_4$: C, 28.08; H, 2.69. Found: C, 28.11; H, 2.63. IR (KBr, ν/cm^{-1}): 3065 (m), 2886 (m), 1485 (m), 1134 (s), 1086 (s), 700 (m), 627 (s). UV−vis (methanol, λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})): 245 (67 900), 265 (5880).

Table 1. Crystallographic Data for Complexes **1**−**4**

	1	2	3	4
formula	$C_{74}H_{58}Ag_3$-Cl_3O_{12}	$C_{60}H_{42}Ag_2$-Cl_2O_8	$C_{32}H_{26}Ag_2$-Cl_2O_{10}	C_7H_8Ag-ClO_4
fw	1569.23	1177.63	857.19	299.46
space group	*Cc*	$P2_1/n$	$P4_12_12$	$P2_1/n$
a, Å	37.951(4)	12.317(4)	8.759(6)	9.847(4)
b, Å	8.047(4)	7.961(1)		9.054(3)
c, Å	20.882(5)	24.741(1)	39.967(8)	10.662(3)
β, deg	93.72(1)	100.015(1)		106.72(2)
V, Å^3	6363(3)	2389(6)	3065(3)	910.3(4)
Z	4	2	4	4
T, °C	23	23	23	23
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69	0.710 69
ρ, g/cm^3	1.638	1.637	1.857	2.185
μ, cm^{-1}	11.03	9.90	15.07	24.78
R^a	0.054	0.056 (R1)	0.062 (R1)	0.043
$R_w{}^b$	0.067	0.155 (wR2^c)	0.177 (wR2^c)	0.055

^{a} R (R1) $= \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} wR2 $= [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^2)^2]^{1/2}$.

X-ray Data Collection and Structure Solution and Refinement. Diffraction data for **1**, **3**, and **4** were collected at room temperature on a Rigaku AFC7R diffractometer, and those for **2**, on a Quantum CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite-monochromated Mo Kα radiation. Periodic remeasurement of three standard reflections revealed no significant crystal decay or electronic instability for all the compounds. Azimuthal scans of several reflections for each compound indicated no need for an absorption correction. Intensities were measured from continuous $\omega-2\theta$ scans. All intensity data were corrected for Lorentz−polarization effects.

The structures were solved by direct methods followed by subsequent Fourier-difference calculation and refined by a full-matrix least-squares analysis on F for **1** and **4** and on F^2 for **2** and **3**, using the TEXSAN package.[16] All the full-occupancy non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the four structures were introduced in their calculated positions; they were included, but not refined, in the refinement. In **2**, the hydrogen atoms for the *p*-xylene molecule were excluded. The counteranions ClO_4^- were found to have high thermal motions in each case. The low accuracy of the bond lengths for **1** and **3** resulted from this disorder. Details of the X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Results and Discussion

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, but sometimes an excess of ligands or metal ions has to be used to obtain coordinated complexes. For example, during the preparation of **1** in toluene, a 2-fold excess of the stoichiometric amount of the silver salt is used, while for the preparation of complex **4** in THF, an excess of ligand L^4 is employed. Reasons for the use of such excesses are a follows: (i) The solvent benzene or toluene may form metal complexes in solution with silver ions,[17] which consumes partial metal salt. Thus, the preparation of silver(I) complexes in benzene or toluene sometimes requires an excess of the silver salts.[7] (ii) When a compound (complex) in solution is “incongruently saturating”, its crystal cannot be obtained via a stoichiometric reaction.[18] We examined the effect of a different molar ratio on the nature of the final product. The reactivity of $AgClO_4$ with hydrocarbon L^4 was systematically studied in THF

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **1**−**4**

Complex **1**							
Ag(1)−O(1)	2.42(1)	Ag(1)−O(8)	2.43(1)	Ag(3)−O(9)	2.45(1)	Ag(3)−C(33)	2.76(1)
Ag(1)−C(1)	2.42(1)	Ag(1)−C(2)	2.66(1)	Ag(3)−C(34)	2.43(1)	Ag(3)−C(42)	2.56(1)
Ag(1)−C(55)	2.58(1)	Ag(1)−C(56)	2.44(1)	Ag(3)−C(43)	2.61(1)	Ag(3)−C(48)	2.47(1)
Ag(2)−O(5)	2.42(1)	Ag(2)−C(8)	2.46(1)	C(1)−C(2)	1.40(2)	C(14)−C(15)	1.42(2)
Ag(2)−C(14)	2.49(1)	Ag(2)−C(15)	2.62(1)	C(21)−C(22)	1.42(2)	C(33)−C(34)	1.42(2)
Ag(2)−C(21)	2.75(1)	Ag(2)−C(22)	2.49(1)	C(42)−C(43)	1.36(2)	C(55)−C(56)	1.41(2)
O(1)−Ag(1)−O(8)	107.2(5)	O(1)−Ag(1)−C(1)	114.4(5)	C(14)−Ag(2)−C(15)	32.0(4)	C(14)−Ag−C(21)	100.8(4)
O(1)−Ag(1)−C(2)	97.5(5)	O(1)−Ag(1)−C(55)	114.9(5)	C(14)−Ag(2)−C(22)	127.9(4)	C(15)−Ag−C(21)	96.4(3)
O(1)−Ag(1)−C(56)	83.1(5)	O(8)−Ag(1)−C(1)	91.2(5)	C(15)−Ag(2)−C(22)	111.4(4)	C(21)−Ag−C(22)	31.0(4)
O(8)−Ag(1)−C(2)	122.4(6)	O(8)−Ag(1)−C(55)	92.5(6)	O(9)−Ag(3)−C(33)	85.1(5)	O(9)−Ag(3)−C(34)	99.8(5)
O(8)−Ag(1)−C(56)	108.4(6)	C(1)−Ag(1)−C(2)	31.6(4)	O(9)−Ag(3)−C(42)	82.2(5)	O(9)−Ag(3)−C(43)	112.4(5)
C(1)−Ag(1)−C(55)	126.8(4)	C(1)−Ag(1)−C(56)	149.0(4)	O(9)−Ag(3)−C(48)	98.6(6)	C(33)−Ag(3)−C(34)	30.8(4)
C(2)−Ag(1)−C(55)	122.7(5)	C(2)−Ag(1)−C(56)	125.8(4)	C(33)−Ag(3)−C(42)	97.3(4)	C(33)−Ag(3)−C(43)	95.0(3)
C(55)−Ag(1)−C(56)	32.4(4)	O(5)−Ag(2)−C(8)	105.7(6)	C(33)−Ag(3)−C(48)	150.4(4)	C(34)−Ag(3)−C(42)	126.0(4)
O(5)−Ag(2)−C(14)	87.4(6)	O(5)−Ag(2)−C(15)	118.3(6)	C(34)−Ag(3)−C(43)	113.4(4)	C(34)−Ag(3)−C(48)	120.6(4)
O(5)−Ag(2)−C(21)	81.3(5)	O(5)−Ag(2)−C(22)	97.4(6)	C(42)−Ag(3)−C(43)	30.6(4)	C(42)−Ag(3)−C(48)	112.3(4)
C(8)−Ag(2)−C(14)	113.1(4)	C(8)−Ag(2)−C(15)	108.7(4)	C(43)−Ag(3)−C(48)	110.3(4)		
C(8)−Ag(2)−C(21)	145.5(4)	C(8)−Ag(2)−C(22)	115.1(4)				
Complex **2**							
Ag−O(1)	2.574(5)	Ag−O(1′)	2.633(5)	Ag−C(19)	2.342(5)	Ag−C(20)	2.743(6)
Ag−C(2)	2.626(5)	Ag−C(3)	2.371(7)	C(2)−C(3)	1.370(9)	C(19)−C(20)	1.374(9)
O(1)−Ag−O(1′)	67.5(2)	O(1)−Ag−C(2)	115.5(2)	O(1′)−Ag−C(20)	124.4(2)	C(2)−Ag−C(3)	31.3(2)
O(1)−Ag−C(3)	101.4(2)	O(1)−Ag−C(19)	91.3(2)	C(2)−Ag−C(19)	152.6(2)	C(2)−Ag−C(20)	154.9(2)
O(1)−Ag−C(20)	79.1(2)	O(1′)−Ag−C(2)	80.7(2)	C(3)−Ag−C(19)	153.4(2)	C(3)−Ag−C(20)	129.9(2)
O(1′)−Ag−C(3)	100.3(2)	O(1′)−Ag−C(19)	106.1(2)	C(19)−Ag−C(20)	30.0(2)		
Complex **3**							
Ag−O(1)	2.48(1)	Ag−O(2)	2.65(1)	Ag−C(11)	2.69(3)	Ag−C(12)	2.42(2)
Ag−C(1)	2.58(1)	Ag−C(2)	2.51(1)	C(1)−C(2)	1.38(2)	C(11)−C(12)	1.36(3)
O(1)−Ag−O(2)	92.0(6)	O(1)−Ag−C(1)	128.7(5)	O(2)−Ag−C(12)	135.3(9)	C(1)−Ag−C(2)	31.5(4)
O(1)−Ag−C(2)	98.8(5)	O(1)−Ag−C(11)	101.3(8)	C(1)−Ag−C(11)	129.2(6)	C(1)−Ag−C(12)	107.9(6)
O(1)−Ag−C(12)	113.6(7)	O(2)−Ag−C(1)	78.3(3)	C(2)−Ag−C(11)	151.4(7)	C(2)−Ag−C(12)	121.6(8)
O(2)−Ag−C(2)	87.2(4)	O(2)−Ag−C(11)	112.2(6)				
Complex **4**							
Ag−O(1)	2.453(8)	Ag−O(1′)	2.664(7)	Ag−C(3)	2.472(7)	Ag−C(4)	2.415(6)
Ag−C(1)	2.423(6)	Ag−C(2)	2.424(5)	C(1)−C(2)	1.321(9)	C(3)−C(4)	1.33(1)
O(1)−Ag−O(1′)	62.3(3)	O(1)−Ag−C(1)	123.7(2)	O(1′)−Ag−C(4)	123.2(2)	C(1)−Ag−C(2)	31.6(2)
O(1)−Ag−C(2)	94.1(2)	O(1)−Ag−C(3)	123.7(2)	C(1)−Ag−C(3)	110.7(2)	C(1)−Ag−C(4)	121.9(2)
O(1)−Ag−C(4)	100.2(2)	O(1′)−Ag−C(1)	110.9(2)	C(2)−Ag−C(3)	141.9(2)	C(2)−Ag−C(4)	148.7(2)
O(1′)−Ag−C(2)	88.1(2)	O(1′)−Ag−C(3)	112.1(2)				

with different metal:ligand ratios. Reactions similar to that described in the Experimental Section but performed with metal: ligand ratios of 1:1 lead to no evidence for formation of an isolable complex. On the other hand, the product obtained with a ratio of 1:10 was identical to that obtained with a ratio of 1:5 as determined by comparison of ^{1}H NMR spectra and powder X-ray diffractions data. However, the former reaction offered better quality crystals.

3-D Network Structure of [$Ag_3(L^1)_3(ClO_4)_3$]·$2C_6H_5Me$ (1). The crystallographic studies revealed that complex **1** contains a two-dimensional network of [$Ag_3(L^1)_3$] units in which the three crystallographically independent metal ions are bridged by the aromatic groups. The structure of the trimeric molecular unit of the crystals is shown in Figure 1 with the atomic numbering scheme employed. The environment of the silver atom can be described as distorted tetrahedral. The Ag(1) ion is bonded to two perchlorate groups at Ag−O distances of 2.42(1) and 2.43(1) Å, and the four-coordinate polyhedron of the metal ion is completed by interaction with two C−C moieties from two different aromatics. In contrast, the tetrahedral coordination geometry of Ag(2) or Ag(3) comprises one perchlorate anion and three aromatic groups. The Ag−O bond lengths are 2.42(1) Å for Ag(2) and 2.45(1) Å for Ag(3), whereas Ag−C bond distances range from 2.46(1) to 2.75(1) Å and from 2.43(1) to 2.76(1) Å, respectively. It is noteworthy that the Ag−O bond distances do not involve significant variations in this complex and those for bridging, Ag(2)−O(5), and terminal, Ag(1)−O(1), perchlorates, in particular, are virtually the same. This suggests that a conformationally rigid triangular molecule bonded complex does not involve significant molecular constraints, which will be discussed later.

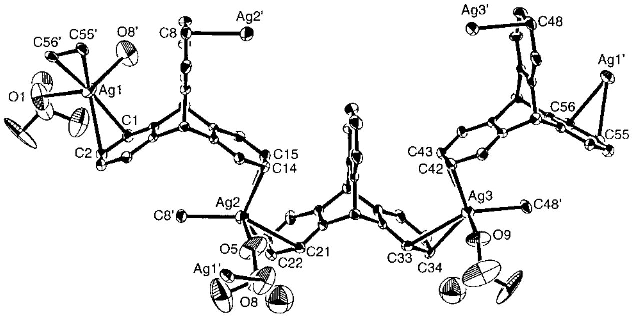


Figure 1. Molecular structure and partial labeling of **1**.

The molecule also contains three crystallographically independent aromatic moieties with distinctly different coordination modes, one with a μ-η^2-η^2 mode bridging Ag(2) and Ag(3) ions and the other two involving a μ-η^2-η^2-η^1 mode bridging three metal centers. A 2-D sheet network of metal ions is thus formed in which the aromatic groups are arranged alternately such that

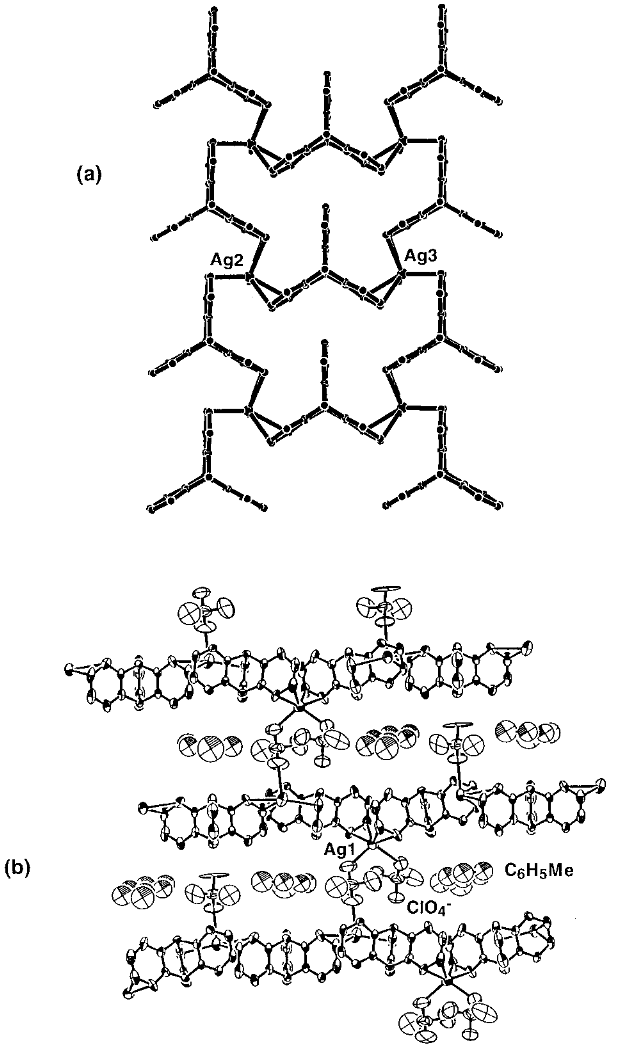


Figure 2. Perspective views of the packing of **1**: (a) view down the crystallographic *c*-axis showing the aromatic bridged 2-D sheet of metal ions; (b) view down the *b*-axis showing the 2-D sheets connected by perchlorate ions.

three line up in one direction and the next three stand in the reverse direction. The two adjacent sheets are connected by bridging of the perchlorate groups between Ag(1) and Ag(2) ions, giving rise to a three-dimensional supramolecular network where the solvate toluene molecules occupy the space between the sheets, Figure 2.

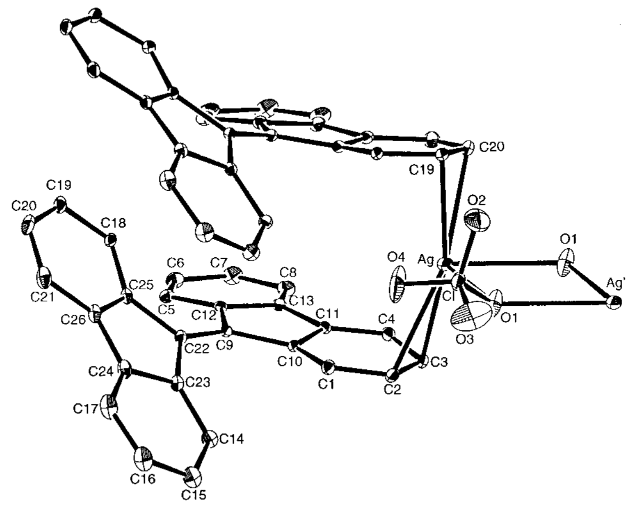
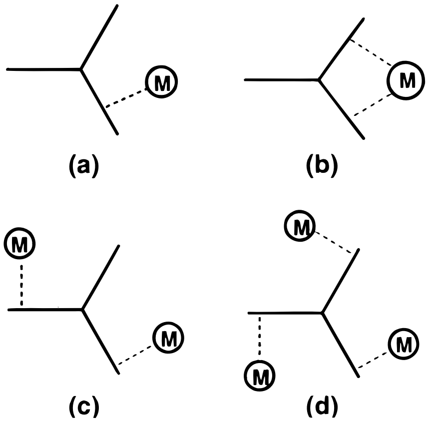


Figure 3. Structure and labeling of **2**.

Chart 1



The triangular molecule triptycene is a very special hydrocarbon with relatively rigid molecular geometry, having three equivalent benzene rings mutually inclined by 120°.[19] Prior to the present work, only few X-ray structures of triptycene π complexes have been reported, such as $[(L^1)Cr(CO)_3]$,[20] $[(L^1)Co_4(CO)_9]$,[20] $[(L^1)SnCl(AlCl_4)]_2$,[21] $[(L^1)Cr_2(CO)_6]$,[22a] and $[(Cp^*Ru)_3(L^1)](CF_3SO_3)_3$.[22b]. In these complexes, triptycene exhibits only η^6 coordination by one to three benzene rings; η^2 is never observed. For smaller metal atoms such as chromium, it tends to interact with one metal atom by one arene ring with small widening of the inter-arene angles[20] (Chart 1a), while with the larger metal atom tin it offers bis(arene) coordination (Chart 1b), sandwiching the cation with the angle between the two arene rings contracted to 108.2° and the remaining inter-arene angles widened accordingly to 125.8 and 126.0°.[21] In this work triptycene exhibits an unprecedented μ-η^2-η^2 or μ-η^2-η^2-η^1 coordination bridging two Chart 1c) or three (Chart 1d) silver atoms, affording polymeric material. Surprisingly, the triptycene framework was found to involve relatively little deformation as compared to the metal-free hydrocarbon and the variation of the three inter-arene angles (115.6−124.4°) is relatively small regardless of bis- or tris(arene) coordination. Such an eased conformation of the aromatic may in part be the contributing factor for the stable three-dimensional complex network formed and the relatively similar Ag−O bond distances observed.

2-D Sheet Network Structure of $[Ag_2(L^2)_2(ClO_4)_2]\cdot C_6H_4Me_2$ (2). The molecular structure and numbering scheme for complex **2** are given in Figure 3. The complex exists in the solid state as an aromatic-linked zigzag chain structure propagating along the *b*-axis. The chain is formed by the cationic $[Ag_2(L^2)_2]$ building blocks having an alternate −Ag−aromatic−Ag-aromatic- sequential arrangement, while each ClO_4^- anion bridging between the two metal centers connects the two adjacent chains. The double-bridged dinuclear core Ag_2O_2 is thus formed with an Ag···Ag separation of 4.33 Å. The bifluorenylidene molecules are arranged alternately in two orientations and adopt a staggered conformation within a pair such that the intermolecular π−π interactions between the

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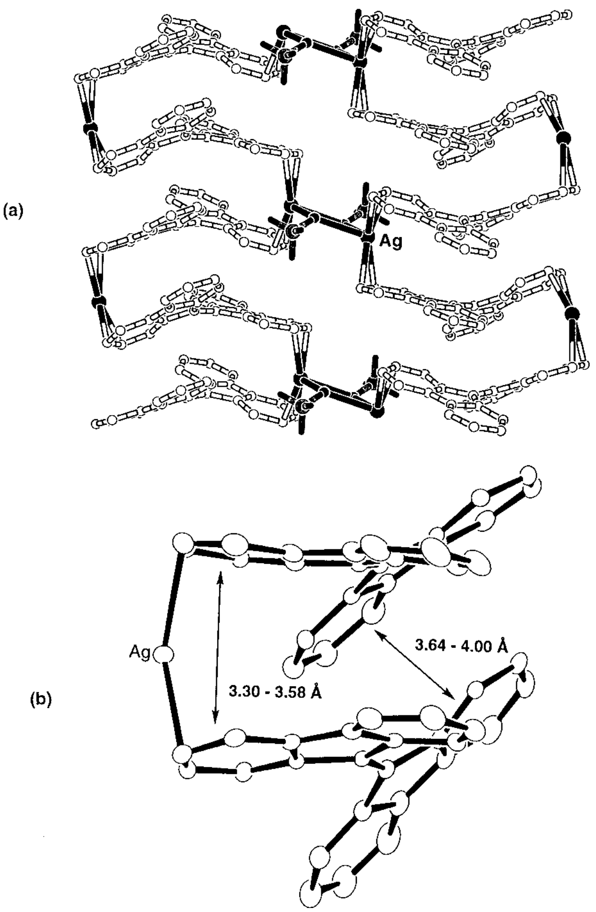

Figure 4. Views of the 2-D sheet network in **2** (a) and the intermolecular $\pi-\pi$ interactions between the fluorenyl moieties (b).

fluorenyl moieties (3.30−3.58 and 3.64−4.00 Å) form a columnar aromatic stacking on the *bc* plane, Figure 4.

The crystal structure of the free aromatic ligand[23] shows a substantial intramolecular torsion of the two fluorenyl moieties around the C(9)=C(9′) bond of 39.3°. This conformation is maintained in its silver complex, as the dihedral angle between the molecular half-fragments is 39.6°. This twist results in a significant elongation of the C=C bond at 1.36 Å. Extensive Chemical Abstracts Service (CAS) and Cambridge Structural Database searches gave no hint of known 9,9-bifluorenylidene structures of π-hydrocarbon coordination compounds except $[\{\eta^5\text{-}C_5Me_5)Ru\}(L^2)](OSO_2CF_3)$, in which the metal center is sandwiched by an η^6-aromatic ring and the C_5Me_5 group.[24]

3-D Porous Network Structure of $[Ag_2(L^3)(C_6H_6)_2(ClO_4)_2]$ (3). The molecular structure of **3** together with the atomic numbering scheme is given in Figure 5. In this compound, the coordination geometry about silver is best described as a highly distorted tetrahedron comprising one ligand group, one benzene molecule, and two ClO_4^- ions. The hydroxyl groups of the ligand do not participate in coordination; instead, each aromatic group symmetrically interacts with two metal ions in a $\mu\text{-}\eta^2\text{-}\eta^2$ fashion, linking two $-Ag-O_2ClO_2-Ag-$ chains. The overall result of this arrangement is that the $AgClO_4$ chains lie in sheets with aromatics on either side such that the packing consists of a sequence of sheets, −aromatic−ionic−aromatic−, affording an extended microporous network in which Ag atoms are rallied along the wall and each bridging perchlorate ion interacts with two Ag atoms belonging to two different layers, Figure 6. The interplane distance between the two aromatic molecules is 8.76 Å. The ligand molecule is not planar and the dihedral angle between the two naphthyl rings of 68.3° is not unusual because of the easier rotation of the two portions against a single C−C bond.

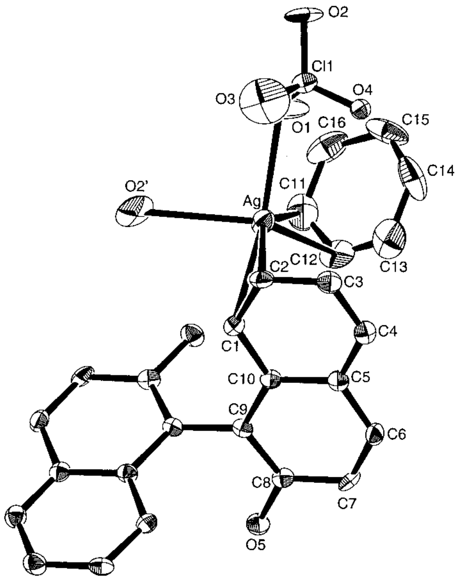

Figure 5. Molecular structure and labeling of **3**.

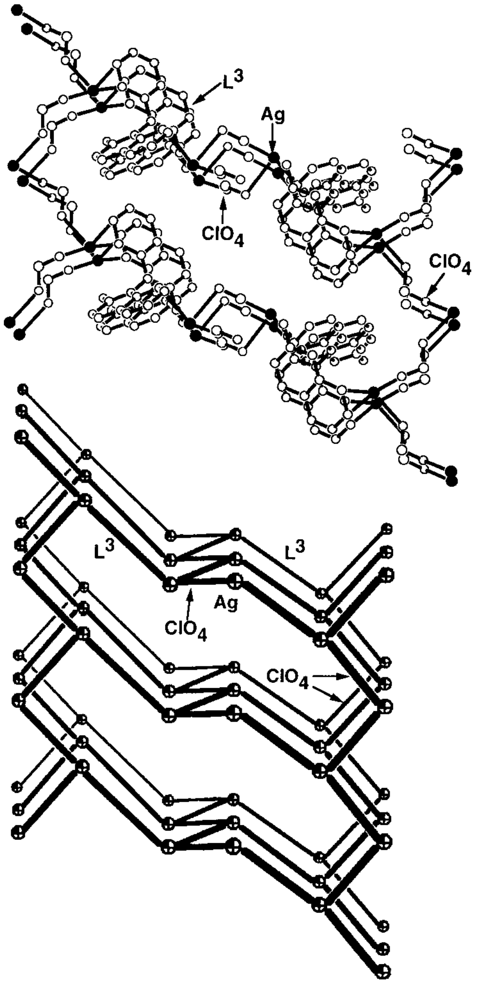

Figure 6. View of the 3-D porous network in **3**. Noncoordinating oxygen atoms of the perchlorate ions are omitted for clarity.

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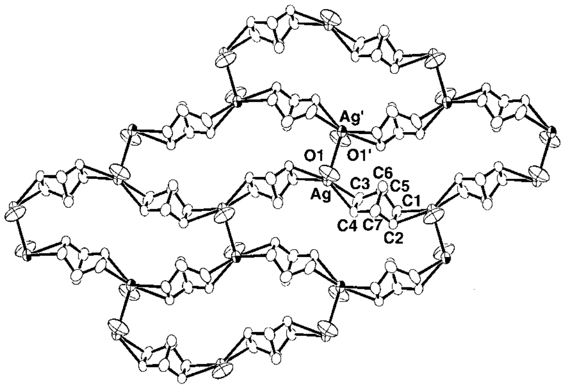


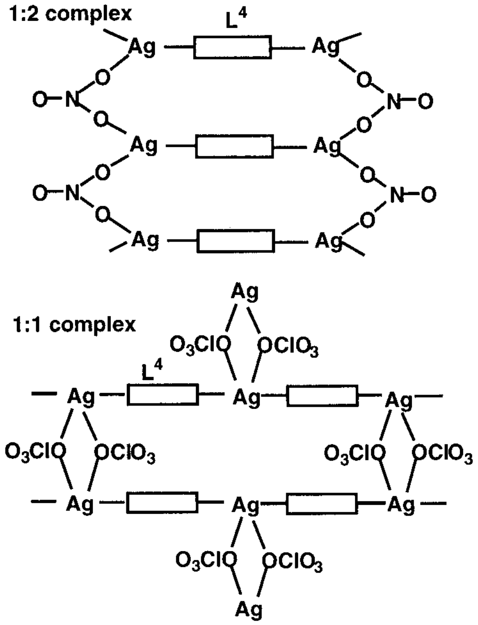
Figure 7. Structure and labeling of **4**. Noncoordinating oxygen atoms of the perchlorate ions are omitted for clarity.

The ligand 1,1′-bi-2-naphthol has potential uses as a chiral auxiliary in oxidation catalysis.[12,13,25] It has also been widely used as a chelating and bridging ligand through coordination of the two hydroxyl groups for synthesis of high-valent transition metal and optically active rare earth metal complexes.[25,26] The significance of the present study is two-fold: First, to our knowledge, it presents the first structurally characterized silver(I) complex of naphthol. Despite the demonstrated ability of naphthol to chelate and bridge metal atoms, no study has been conducted on naphthol complexes with the univalent coinage metal ions before this work. Second, this study presents the first example of π coordination of naphthol in its metal complexes. The study further demonstrates that the silver(I) ion has a remarkablly high affinity for aromatic π-donor systems. Apart from its aforementioned catalytic and covalent bonding ability, naphthol may also represent a potential wide-ranging class of useful ligands capable of holding two or more metal ions in close proximity, highly relevant to the formation of multilayered organometallic systems.

2-D Sheet Network Structure of $[Ag(L^4)(ClO_4)]$ (4). The solid-state structure of **4** consists of polymeric chains of $[Ag(L^4)]^+$ units in which norbornadiene molecules and silver(I) ions are interconnected by cation−π interactions. Each norbornadiene group interacts with two metal centers via two double bonds of the olefin, with the Ag−C bond distances varying in a narrow range, 2.415(6)−2.472(7) Å. The fact that the coordinated double bonds in **4** having C═C bond distances of 1.321(9) and 1.33(1) Å, much the same [1.337(1) Å] as found in the free ligand,[14] is probably due to the high symmetry of the molecule and the absence of ligands with high steric demands.

A view of the symmetry-related fragment with the atom-labeling scheme is depicted in Figure 7. The polymeric chains are cross-linked by two symmetry-related perchlorate anions bridging between the two tetrahedral metal centers with Ag−O(1) and Ag−O(1′) bond lengths of 2.453(8) and 2.664(7) Å, respectively, giving a two-dimensional arrangement of the metal ions. The basic motif contains a rhombic Ag_2O_2 core with an O−Ag−O bond angle of 62.3(3)°.

Chart 2



Norbornadiene is a molecule of globular shape, and its single-crystal structure has been determined recently.[14] While the photoisomerization of norbornadiene to quadricyclane is promising as a potential solar energy storage system,[15] its coordinative versatility as either a monodentate or bidentate or even a tridentate ligand has yielded a great number of mono- or diolefin metal complexes.[15,27−31] At least three silver(I) complexes of norbornadiene are known crystallographically. In the tetrameric compound $[\{Ag(hfacac)\}_2(L^4)]$, where hfacac = 1,1,1,5,5,5-hexafluoroacetylacetonate, only one carbon−carbon double bond of the norbornadiene interacts strongly with silver, the bond lengths of Ag−C being 2.356(9) and 2.373(8) Å.[29] In the silver(I) complex of 7-*tert*-Bu-butoxynorbornadiene, the tetrahedral metal centers are bridged by the ligand molecules with one C═C moiety chelating the first silver and another C═C group together with one oxygen atom bonded to the second metal atom, resulting in an infinite polymeric species.[28] Perhaps the silver nitrate complex of norbornadiene is most relevant to this work. There has been a long-time debate over the description of norbornadiene−silver nitrate complexes.[32] Different preparations isolated the products with different compositions, i.e., 1:1 or 1:2 diene-metal species. The crystal structure of the 1:2 complex $L^4 \cdot 2AgNO_3$ was reported over 30 years ago.[27] The structure revealed a cross-linkage of the norbornadiene molecule between the two $Ag-NO_3$ chains, Chart 2. Nevertheless, the structure of the 1:1 complex remained unknown prior to this

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work. The present work offers the first example of the 1:1 diene-silver complex. Now it is clear that these two species exhibit several structural differences including those seen in the molecular packing diagrams and in the stereochemistries of the metal ions.

Silver(I) Complexes of the Nonplanar Aromatic Compounds. In previous studies of the silver(I) complexes of aromatic compounds, attention was devoted to the planar hydrocarbon species.[1−7] Such ligands combining good ligating properties and perfect planarity concurrently interacting with metal ions above and below rings have great promise as building blocks for self-assembly of high-nuclearity complexes in a multilayer fashion. Thus, the structures in most cases feature two aromatic planes sandwiching the inorganic chain on both sides, resulting in double-decker, triple-decker, multidecker, or W-type sandwich frameworks. In this work, we have turned out attention to silver(I) complexes with nonplanar aromatic ligands. Like those of the planar aromatics, the silver(I) complexes of the nonplanar aromatics also exist as infinite metal−π polymeric species, indicative of the high affinity of the silver(I) ion for aromatic π interactions. However, due to the conformation of the aromatic hydrocarbons, a multilayered system is not possible; instead, the aromatics employed in this work tend to act as linear bidentate ligands (e.g., in **2** and **4**) interacting with silver ions alternately in an infinite-chain fashion. The final structures resulting from further connection of the chains by the bridging anions could have 2-D network architectures, as we have found in **2** and **4**, or 3-D and porous structures as observed in **1** and **3**, respectively, well dependent on a variety of factors, such as the detailed conformation of the hydrocarbon and the presence of the third component, the solvent molecule of crystallization in the system. Further investigations in this area of chemistry including different metal ions and aromatics to clarify this point are clearly warranted. Furthermore, in the previously reported silver(I) complexes of aromatic compounds, silver(I) ions are found to be inclined to bond at the short carbon−carbon bond portion.[1−7] This tendency is generally maintained in the present work, indicative of the large electron density accumulated on the π-bonded carbon atoms. For example, in the case of **2**, the two silver(I) ions are found to bond to the shortest C═C bonds (1.371(4) Å) of the bifluorenylidene.[23] However, unavailability of structural data for L^3 precludes a similar comparison.

The propensity of $AgClO_4$ to form adducts with a variety of aromatic compounds appears to be unparalleled by any other transition metal salt.[1−7] As we have observed previously in other silver(I)/aromatic compounds, the aromatics in the present four silver(I) complexes are found η^2 interacting with the silver ions and the η^2 bonds are quite asymmetrical in most cases. It is significant that all the known silver(I)−aromatic complexes, with the exception of naphthalenetetrakis(silver perchlorate) tetrahydrate,[3a] have as a common feature an asymmetric Ag−C interaction with the aromatic; that is, the silver atom η^2-coordinates to two carbon−carbon π bonds at unequal distances. The most surprising example was found in the [2.2]paracyclophane complex, where the two Ag−C distances differ by 0.3 Å.[33] A similar phenomenon was observed in the present work; for example, the two Ag−C distances in complexes **2** and **3** differ by 0.4 and 0.27 Å, respectively (Table 2).

Among structurally characterized silver(I) complexes of aromatic compounds the Ag−C interactions vary over wide limits,[1] ranging from 2.36(2) Å observed in the indene complex to 2.921(9) Å in the paracyclophane complex. As shown in Table 2, the Ag−C bond lengths observed in this work range from 2.342(5) to 2.75(1) Å. It is noted that the Ag−C(19) distance of 2.342(5) Å found in **2** is the shortest silver−carbon bond in silver−arene complexes reported thus far. As in previously reported silver(I) arene compounds, all the complexes we have studied here contain perchlorate ions coordinated in a variety of ways to the silver ions. The observed Ag−O bond distances ranging from 2.42(1) Å in **1** to 2.664(7) Å in **4** are normal[1] and comparable with those of 2.27(3) Å and 2.67(3) Å reported for complexes of the planar aromatics rubrene and 9,-10-diphenylanthracene, respectively.[7a]

In conclusion, we have reported several unprecedented organosilver(I) complexes with nonplanar aromatic compounds. The work affords a new strategy to build multidimensional coordination polymers, which is based on the use of the silver−aromatic units as building blocks and the unique functions of the counteranions as linkages between the building blocks. The preliminary results obtained here open an avenue to future rational design of many novel architectures of organometallic chemistry with specific geometric shapes and arrangements of molecular packing. In particular, further research on functional hydrocarbon ligands such as L^3 and L^4 holds the promise of providing interesting inorganic materials.

Acknowledgment. This work was partially supported by Grants-in-Aid for Science Research [Nos. 09554041, 10440201, and 10016743 (priority area: metal-assembled complexes)] from the Ministry of Education, Science, Culture, and Sports of Japan.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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