Structural Studies of Silver(I) Coordination Polymers with Aryl Iodide Derived Ligands

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This paper reports novel silver polymers, built with iodine−silver interactions, with interesting structural motifs. Four silver(I) coordination polymers of the aryl iodide derived ligands, triiodobenzoic acid (HL^1), tris(4-iodophenyl)-amine (L^2), and 5,7-diiodo-8-hydroxyquinoline (HL^3), have been synthesized and characterized by X-ray crystallography. Treatment of $Ag(CH_3COO)$ with HL^1 yielded $[Ag(L^1)]$ (**1**), whose structural analysis revealed 2D layers of ladders connected through weak Ag···I interaction. Reactions of $AgClO_4$ and L^2 in benzene and nitrobenzene afforded, respectively, two different products, $[Ag(L^2)(H_2O)]ClO_4 \cdot C_6H_6$ (**2**) and $[Ag(L^2)(ClO_4)]$ (**3**). While the structure of **2** could be described as a 2D layer of square and octagons perpendicular to [100], complex **3** is formed by 2D layers of the same topology of **2** ($8^2 \cdot 4$), alternating as ABAB. In contrast, complex **4**, $[Ag_2(H_2L^3)(CF_3SO_3)_3]$, obtained by reaction of $Ag(CF_3SO_3)$ and HL^3, was found to consist of a 2D layer based on columnar arrays AgH_2L^3−Ag(triflate). The solid-state FT-IR and ^{109}Ag NMR spectra of theses complexes are discussed on the basis of their crystal structures.

Introduction

The design of new functional polymeric coordination complexes consisting of one-, two-, and three-dimensional networks from the assembly of metal ions and suitable multidentate ligands is of intense current interest.[1,2] Halocarbons RX, where R is an alkyl or aryl group and X is a halogen atom, constitute a unique type of ligand in coordination chemistry.[3] They are very weak bases so that the coordination to transition metal centers is labile and the RX−M bonds can be easily broken by nucleophilic attack.[4−7] Recent research results from different research groups have shown that silver(I) is a favorable and fashionable building block for coordination polymers.[8] However, fully characterized examples of coordination complexes of halocarbon ligands with Ag(I) ions are mainly restricted to alkyl halides,[9,10] To date, the utility of the aryl halide ligands in the synthesis of high-nuclearity coinage metal complexes remains virtually unexplored.[10] This is surprising in that aryl halides appear to be equally extremely versatile and easily handled ligands. Compared with other halogen elements in the group, the iodine atom possesses stronger nucleophilic character and is expected to form stable coordination compounds with the soft acid silver(I) ion.[11] In addition, our research into the supramolecular architectures created by self-assembly of copper(I) and silver(I) complexes with multidentate organic ligands[1,12]

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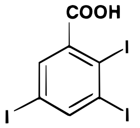
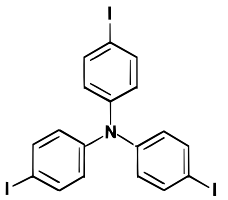
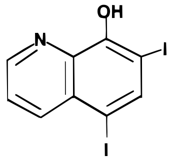
generated a curiosity as to what binding mode an aryl iodide derived ligand with more than two metal coordination sites would adopt when bound to a labile metal center. Here, we describe the preparation and single-crystal structures of four distinct and highly unusual polymeric silver(I) complexes of the aryl iodide derived ligands triiodobenzoic acid (HL^1), tris(4-iodophenyl)amine (L^2), and 5,7-diiodo-8-hydroxyquinoline (HL^3). The versatility of these iodocarbon derived species in complexing metal ions makes them especially interesting candidates for formation of self-assembly of a wide range of infinite frameworks.



triiodobenzoic acid
HL^1



tris(4-iodophenyl)amine
L^2



5,7-diiodo-8-hydroxyquinoline
HL^3

Experimental Section

General Methods. All chemicals were reagent grade. Reactions and manipulations were carried out under an argon atmosphere by using the standard Schlenk vacuum line techniques. Solvents were dried using standard procedures and distilled under an argon atmosphere prior to use. High-purity argon was used to deoxygenate solvents. Triiodobenzoic acid, 5,7-diiodo-8-hydroxyquinoline, silver acetate, and silver perchlorate were purchased from Aldrich. Tris(4-iodophenyl)amine was purchased from Tokyo Chemical Industry Co., Ltd. All chemicals were used as received. The IR spectra were recorded as KBr disks on a JASCO FT-IR-8000 spectrometer, and ESR spectra were recorded on a JEOL JES-TE200 ESR spectrometer. Solid-state ^{109}Ag NMR spectra were obtained with a JEOL GX 500 FT NMR spectrometer at 27 °C.

Safety Note. *Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.*

Synthesis of [Ag(L^1)] (1). An aqueous solution (10 mL) containing 16.6 mg (0.1 mmol) of $AgCH_3COO$ in a glass tube was layered with a methanolic solution (10 mL) of triiodobenzoic acid (50 mg, 0.1 mmol). The glass tube, sealed under Ar and wrapped with aluminum foil, was left standing at room temperature for 1 day; colorless slab crystals of **1** were isolated (38 mg, 57%). Anal. Calcd for $C_7H_2AgI_3O_2$: C, 13.85; H, 0.33. Found: C, 13.68; H, 0.36. Main IR bands (cm^{-1}): 2926(s), 2857(s), 1590(m), 1551(m), 1462(m), 1379(m), 1346(m), 1200(w), 1100(w), and 457(w). ^{109}Ag NMR (ppm): $\delta_{Ag} = 378$.

Synthesis of [Ag(L^2)(H_2O)]ClO_4·C_6H_6 (2). To a benzene solution (5 mL) containing silver perchlorate (22.5 mg, 0.1 mmol) was added tris(4-iodophenyl)amine (62.3 mg, 0.1 mmol). The mixture was stirred for 10 min and filtered. A portion of the filtrate (3 mL) was transferred to a 7 mm diameter glass tube and gently layered with 3 mL of *n*-pentane as a diffusion solvent. After the solution stood for 3 weeks at room-temperature, colorless block crystals of **2** were obtained (33 mg, 39%). Anal. Calcd for $C_{18}H_{14}AgI_3NClO_5$ (the formula without benzene molecule): C, 25.46; H, 1.65; N, 1.65. Found: C, 25.30; H, 1.51; N, 1.59. Main IR bands (cm^{-1}): 3495(m), 2926(w), 2363(w), 1680(s), 1572(s), 1485(s), 1319(s), 1086(s), 1032(s), 828(s), and 625(s).

Synthesis of [Ag(L^2)(ClO_4)] (3). This compound was synthesized by the manner similar to that for **2** with nitrobenzene in place of benzene as the solvent. Anal. Calcd for $C_{18}H_{12}AgI_3NClO_4$: C, 26.01; H, 1.45; N, 1.69. Found: C, 25.88; H, 1.46; N, 1.61. Main IR bands (cm^{-1}): 1572(m), 1485(s), 1319(s), 1292(m), 1271(m), 1120(m), 1099(s), 1030(m), 1003(m), 916(w), 828(m), 808(m), 717(w), 621(m), 525(m), and 451(w).

Synthesis of [Ag_2(H_2L^3)(CF_3SO_3)$_3$] (4). To a toluene solution (5 mL) containing silver triflate (25.7 mg, 0.1 mmol) was added 5,7-diiodo-8-hydroxyquinoline (10 mg, 0.025 mmol). The mixture was stirred for 10 min and filtered. A portion of the filtrate (3 mL) was transferred to a 7 mm diameter glass tube and gently layered with 3 mL of *n*-hexane as a diffusion solvent. After standing for 2 weeks at 5 °C yellow plate crystals of **4** were obtained (11 mg, 48%). Anal. Calcd for $C_{12}H_6Ag_2I_2NS_3F_9O_{10}$: C, 13.57; H, 0.57; N, 1.32. Found: C, 13.81; H, 0.51; N, 1.49. Main IR bands (cm^{-1}): 3061(s), 2498(w), 2375(w), 1557(m), 1483(w), 1455(m), 1389(s), 1331(m), 1267(m), 1134(m), 924(w), 870(w), 806(w), 783(w), 721(w), 650(m), and 548(w).

X-ray Data Collection and Structure Solutions and Refinements. For **1**−**3** a suitable single crystal was mounted on a glass fiber, while that for **4** was enclosed in a glass capillary. Diffraction data were collected at room temperature on a Quantum CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated Mo Kα radiation. Periodic remeasurement of three standard reflections, collected every 150, revealed no significant changes in intensities. 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^2, using the TEXSAN package.[13]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. The counteranions ClO_4^- and $CF_3SO_3^-$ were found to have high thermal motions in **2**−**4**. The highest residual peaks for **4** 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

Structure of [Ag(L^1)] (1). An ORTEP drawing of the complex with the atom numbering scheme is shown in Figure 1. The structure of **1** in the crystalline state features a two-dimensional arrangement of ladders constructed from silver atoms linked by carboxylate anions. Except for the coordination of Ag−I, the coordination environment of each metal atom is almost trigonal planar, comprising three carboxylate oxygen atoms from three different ligand groups. Each $I_3C_6H_2COO^-$ moiety in turn employs its carboxylate group to interact with three metal centers. The unique structural feature of the ligand is its tridentate binding of the carboxylate group to three metal centers with Ag−O bond distances varying widely, ranging from 2.229(3) to 2.518(3) Å. Nevertheless, they are well within the range 2.17−2.61 Å observed in silver(I) carboxylate and oxalate complexes.[11] The two symmetry-related metal centers are coupled by two ligand groups with a Ag···Ag separation of 2.8898(8) Å. This results in an eight-membered macrocycle, which is further linked to its neighboring counterpart by two

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

	1	**2**	**3**	**4**
formula	$C_7H_2AgI_3O_2$	$C_{24}H_{20}AgI_3NClO_5$	$C_{18}H_{12}AgI_3NClO_4$	$C_{12}H_6Ag_2I_2NS_3F_9O_{10}$
fw	606.67	926.46	830.33	1060.89
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, Å	13.33(2)	10.6675(7)	10.854(4)	11.611(1)
b, Å	5.72(2)	10.537(1)	20.176(6)	22.806(3)
c, Å	14.90(3)	25.5279(6)	10.9803(3)	11.9415(1)
β, deg	108.83(4)	93.7476(6)	116.080(2)	110.0051(3)
V, Å^3	1075(4)	2863.3(3)	2159.7(8)	2971.3(3)
Z	4	4	4	4
temp, °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	3.746	2.149	2.553	2.371
μ, cm^{-1}	104.46	40.64	53.69	37.03
R^a	0.028	0.042	0.034	0.075
$R_w{}^b$	0.098	0.130	0.123	0.235

^{a} $\sum(F_o{}^2 - F_c{}^2)/\sum F_o{}^2$. ^{b} $[\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

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

	1		
Ag−I(1)	3.053(4)	Ag−O(1)	2.229(3)
Ag−O(2)	2.518(3)	Ag−O(2′)	2.268(3)
Ag···Ag′	2.8898(8)		
I(1)−Ag−O(1)	99.8(1)	I(1)−Ag−O(2)	74.1(1)
I(1)−Ag−O(2′)	105.7(1)	O(1)−Ag−O(2)	115.0(1)
O(1)−Ag−O(2′)	154.3(1)	O(2)−Ag−O(2′)	75.9(1)
	2		
Ag−I(1)	2.8439(6)	Ag−I(2)	2.7932(6)
Ag−I(3)	3.0103(7)	Ag−O(5)	2.344(4)
I(1)−Ag−I(2)	112.71(2)	I(1)−Ag−I(3)	107.60(2)
I(1)−Ag−O(5)	99.88(9)	I(2)−Ag−I(3)	108.45(2)
I(2)−Ag−O(5)	113.14(10)	I(3)−Ag−O(5)	114.80(9)
	3		
Ag−I(1)	2.7849(5)	Ag−I(2)	2.9119(7)
Ag−I(3)	2.8195(6)	Ag−O(1)	2.483(5)
I(1)−Ag−I(2)	119.18(2)	I(1)−Ag−I(3)	133.03(2)
I(1)−Ag−O(1)	95.1(1)	I(2)−Ag−I(3)	101.42(2)
I(2)−Ag−O(1)	102.2(1)	I(3)−Ag−O(1)	98.6(1)
	4		
Ag−I(1)	2.908(1)	Ag(1)−I(2)	3.046(1)
Ag(1)−O(4)	2.423(7)	Ag(1)−O(9)	2.64(2)
Ag(2)−I(2)	2.946(1)	Ag(2)−O(1)	2.380(9)
Ag(2)−O(3)	2.373(9)	Ag(2)−O(5)	2.501(8)
I(1)−Ag(1)−I(2)	150.76(5)	I(1)−Ag(1)−O(4)	89.3(2)
I(1)−Ag(1)−O(9)	113.3(3)	I(2)−Ag(1)−O(4)	77.2(2)
I(2)−Ag(1)−O(9)	95.0(3)	O(4)−Ag(1)−O(9)	101.9(4)
I(2)−Ag(2)−O(1)	144.8(2)	I(2)−Ag(2)−O(3)	102.1(3)
I(2)−Ag(2)−O(5)	81.4(2)	O(1)−Ag(2)−O(3)	112.1(3)
O(1)−Ag(2)−O(5)	86.7(3)	O(3)−Ag(2)−O(5)	122.9(3)

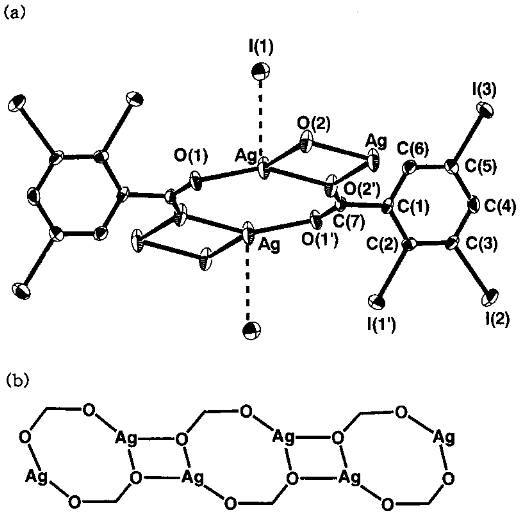

Figure 1. (a) ORTEP view of the structure of **1**, showing 50% thermal ellipsoids. (b) Schematic view of the framework in **1** consisting of square and pentagons.

bridging oxygen atoms O(2) and O(2′), giving rise to a rhombic AgOAgO plane with a negligible Ag···Ag interaction of 3.78 Å. The Ag_2O_2 rhomboid is not coplanar with the eight-membered macrocycle; instead, they are slightly tilted against each other at a dihedral angle of 18.43°. The overall result of this arrangement is a supramolecular ladderlike network virtually based on covalent bonding interactions. The Ag−I(1) bond length of 3.053(4) Å is extra long compared with those in previously reported iodocarbon−silver complexes (2.8−3.0 Å).[10] Thus, we would consider the Ag−I as a weak, nondirectional interaction, and the structure could be described as 2D layers of ladders connected through weak Ag···I interaction running parallel to [010] (Figure 2).

The intramacrocycle Ag···Ag separation (2.8898(8) Å) observed in **1** is very close to the sum of the metallic radii of two Ag atoms (2.884 Å),[14] presumably as a consequence of the requirements of the formation of the dinuclear core. This distance is slightly shorter than those found in disilver(I) complexes $[AgCH_2P(S)Ph_2]_2$ (2.990(2) Å),[15] $[Ag(O_2CCF_3)]_2$ (2.967(3) Å),[16] $[Ag\{CH(COOC_2H_5\}_2PPh_2]_2$ (2.953(1) Å),[17] and $[Ag(O_2CC_6H_5)]_2$ (2.902(3) Å)[18] and recently reported triazopyrimidine complexes (3.089(1)−3.127(1) Å).[19] However, much shorter Ag···Ag interactions have been observed in $[Ag\{o\text{-}(Me_3Si)_2CC_5H_4N\}]_2$ (2.654(1) Å),[20] $[Ag(PhN_3Ph)]_2$ (2.669(1) Å),[21] and $[Ag(p\text{-}CH_3C_6H_4NCHNC_6H_4\text{-}p\text{-}CH_3]_2$ (2.705(1) Å).[22] We

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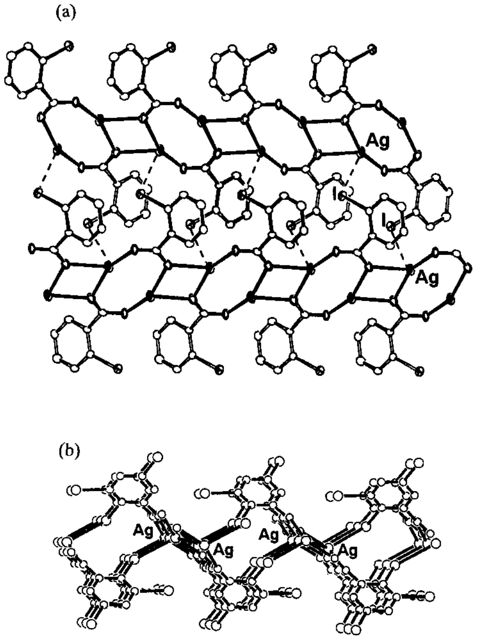

Figure 2. Perspective views of the ladderlike network in **1**: (a) top view and (b) side view.

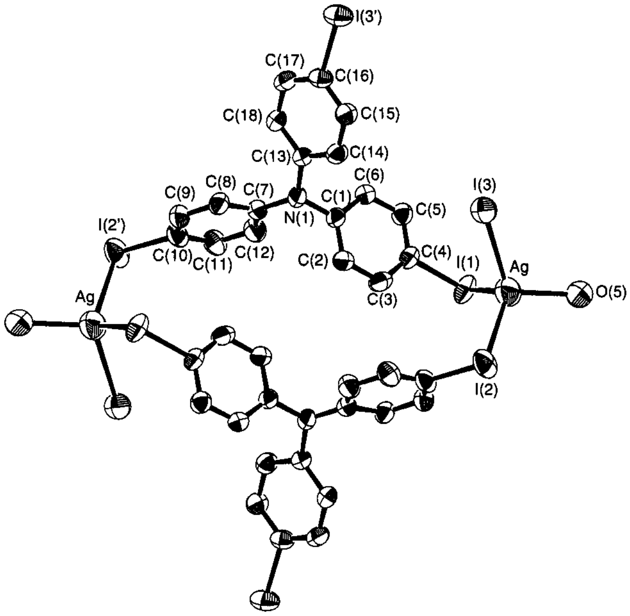

Figure 3. ORTEP view of the structure of **2**, showing 50% thermal ellipsoids.

conclude that **1**, like those dinuclear silver compounds with very short Ag···Ag separations,[20−22] has little or no formal metal−metal bonding, and hence, no special physicochemical properties derived from metal−metal interactions have been detected.

Structure of [Ag(L^2)(H$_2$O)]ClO$_4$·C$_6$H$_6$ (2). The structure determination of **2** reveals an infinite cationic lattice of formula $[\mathrm{Ag(C_{18}H_{12}I_3N)(H_2O)}]_n^{n+}$ and noninteracting perchlorate anions. The cation comprises a dimeric unit as shown in Figure 3, in which each metal center is tetrahedrally coordinated to one iodine atom of three distinct ligand groups and the fourth coordination is accomplished by interaction with one crystallized water molecule. Half of the molecule is related to the other half by a center of symmetry. Each ligand molecule exhibits tridentate coordination, employing all three iodine binding sites to link three metal centers. Here, all the Ag−I interactions are comparable and the topology of the network is easily described as a 2D layer of square and octagons (8^2·4) perpendicular to [100]. A two-dimensional porous structure is formed in which the larger cavity consisting of four metal ions and four ligand groups incorporates one solvated benzene molecule as shown in Figure 4. Discrete ClO$_4^-$ anions maintain electroneutrality.

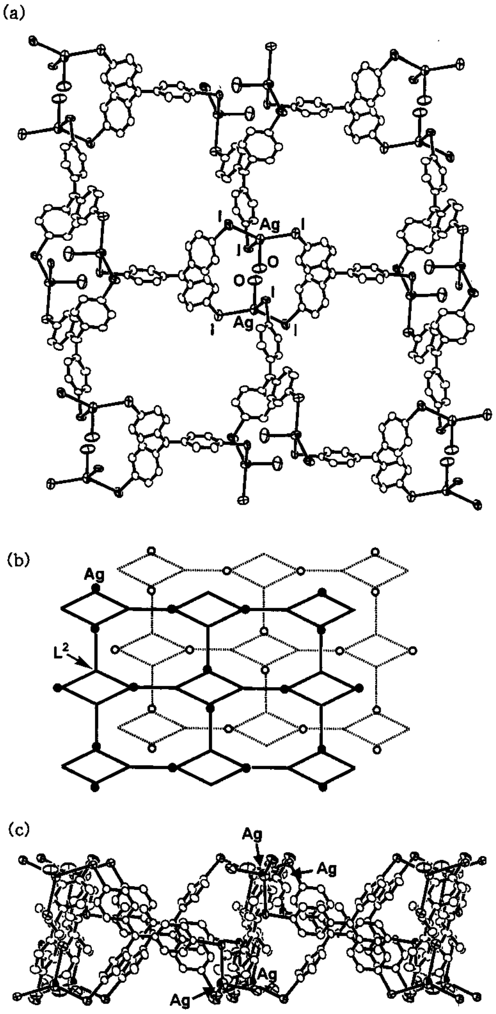

Figure 4. Perspective views of the packing of **2**: (a) top view, (b) schematic view of the framework (solid line is for upper layer and dotted line for lower layer), and (c) side view.

Complex **2** was found to be unstable under atmosphere possibly because of release of the solvated benzene molecule from the lattice. Therefore, the theoretical value for elemental analysis is based on the formula without benzene molecules. The colorless crystals were also very sensitive to light and readily changed to black color under light irradiation.

Structure of [Ag(L^2)(ClO$_4$)] (3). Although colorless single crystals of **3** were synthesized by the manner similar to that for **2**, employment of nitrobenzene as the solvent gave a different compound involving coordination of the perchlorate anions, which was confirmed by X-ray analysis and infrared spectrum. A view of the molecular structure with atom numbering scheme is shown in Figure 5. The formation of the macrocyclic dinuclear unit is directly analogous to that in **2**. Each metal center basically involves a trigonal pyramidal coordination geometry rather than a tetrahedron as observed in **2**, comprising one iodine atom of three distinct ligand groups to form the base, and the apex site is occupied by one ClO$_4^-$ ion. The three I−Ag−I angles range from 101.42(2)° to 133.03(2)° and the three I−Ag−O angles from 95.1(1)° to 102.2(1)°. As in **2**, each ligand group uses all three iodine binding sites to link three silver atoms with Ag−I

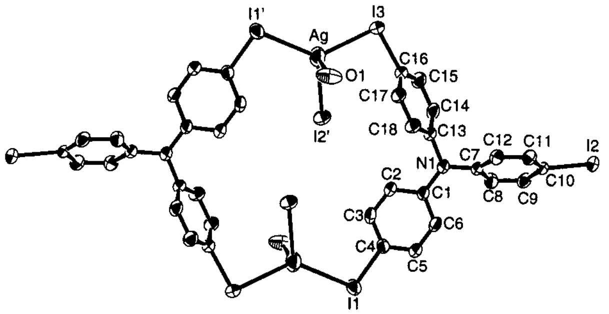

Figure 5. ORTEP view of the structure of **3**, showing 50% thermal ellipsoids.

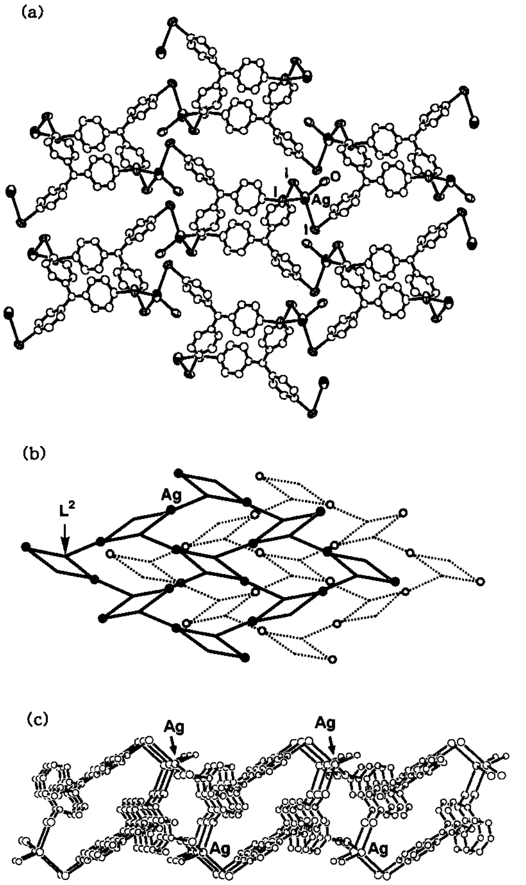

Figure 6. Perspective views of the packing of **3**: (a) top view, (b) schematic view of the framework (solid line is for upper layer and dotted line for lower layer), and (c) side view.

bond lengths varying from 2.7849(5) to 2.9119(7) Å. Following the above description of **2**, the relation with **3** is straightforward. Indeed, **3** is formed by 2D layers of the same topology of **2** ($8^2 \cdot 4$), running perpendicular to [101] and alternating as ABAB. This again deprives the possibility of formation of the channel structure. The layers have a different corrugation compared to **2** and are interdigitated as shown in Figure 6. In contrast to clathration of solvent molecules in **2**, the octagon consisting of four metal ions and four ligand groups includes the coordinated perchlorate ion as guest species.

Structure of [$Ag_2(H_2L^3)(CF_3SO_3)_3$] (4). Yellow plate single crystals of **4** were obtained by the reaction of HL^3 with an excess of $Ag(CF_3SO_3)$. The compound was formulated on the basis of the IR spectrum as well the elemental analysis and single-crystal X-ray structure determination. The infrared spectrum shows the strong ν(NH) stretching frequency at 3061 cm^{-1}, indicating that the ligand exists as a monocation $^+H_2L_3$ rather than the neutral

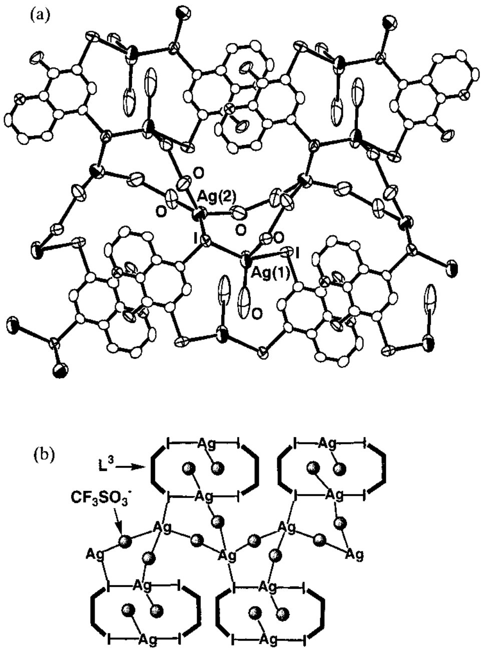

Figure 7. (a) Overall view of the extended structure of **4** where $CF_3SO_3^-$ is represented as O–O for clarity. (b) Schematic view of 2D layer structure in **4**.

HL^3 moiety, consistent with the stoichiometry decided by structure analysis.

The structure is based on columnar arrays of two crystallographically independent silver(I) ions bridged by $^+H_2L_3$ groups and CF_3SO_3 anions (Figure 7). On the Ag(1) column the two symmetry-related ligand groups each bind two metal atoms with two iodine atoms, giving a dinuclear core in which each Ag(1) atom is coordinated to two H_2L^3 groups, one bridging and one terminal $CF_3SO_3^-$ ions. In contrast, on the Ag(2) column the two adjacent metal atoms are linked together by $CF_3SO_3^-$ ions, affording a zigzag chain. The one-atom bridging of I(2) between Ag(1) and Ag(2) connects the columnar arrays of metal ions together, leading to an alternate arrangement of 2D layers of $Ag_2(H_2L^3)_2$ and $Ag_2(CF_3SO_3)_2$. The packing diagram shows that there is no interaction between the adjacent columns in the cell, suggestive of a stronger interaction between the molecules stacked within a chain than between chains. Such a columnar structure may have larger electrical or magnetic interactions along the column than perpendicular to the column, leading to anisotropic (one-dimensional) properties.[23]

ESR, Conductivity, and Solid-State Multinuclear NMR Studies. At ambient temperature complexes **1**, **2**, and **4** show an isotropic ESR signal with $g = 2.005-2.007$, whose origin is not immediately clear. In contrast, **3** did not exhibit such strong ESR resonance. The electrical conductivity of compacted pellets was measured by the conventional two-probe technique employing gold or silver paste coated probes. All the compounds are electrically nonconducting, whereas the light-irradiated samples display semiconducting behavior at ambient temperature with a σ_{300} value ranging from 6.3×10^{-5} to 2.1×10^{-4} S cm^{-1}. This behavior clearly implies that electron transfer between the Ag(I) ion and the ligand in the solid state is enhanced by irradiation of light.

Since many silver compounds are light-sensitive and quite labile in solution, solid-state ^{109}Ag NMR spectroscopy seems to be an especially attractive method in chemical structure

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[23] Miller, J. S.; Spstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1.

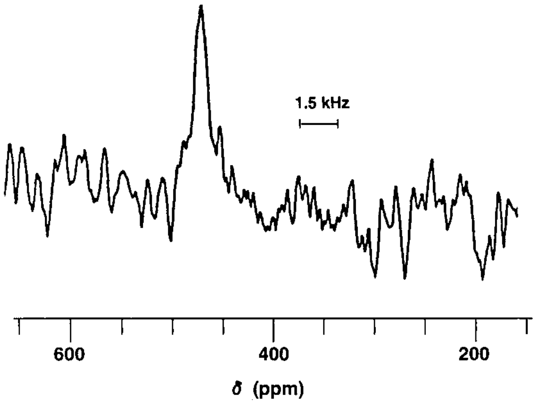

Figure 8. Solid-state ^{109}Ag spectrum of complex **1** at 300 K and 23.28 MHz.

analysis, especially for polymeric complexes. Unfortunately, while the solid-state ^{109}Ag chemical shift data for several simple silver(I) salts have been measured,[24] those for silver(I) complexes have not been extensively studied yet. NMR spectra of complexes **2** and **3** are not possible for safety reasons, whereas complex **4** was unstable upon extended exposure to light and gradually decomposed, which also prevented a ^{109}Ag spectrum from being obtained. Therefore, in this work only complex **1** was selected for a tentative study.

Silver-109 has $I = {}^{1}/_{2}$, but direct observation of the solid ^{109}Ag NMR resonance is difficult because of its low magnetogyric ratio, low receptivity, and long relaxation times. However, in this work we measured the solid ^{109}Ag NMR of **1** at 300 K and 23.28 MHz in natural abundance and were able to obtain the resonance by operating the Fourier transfer of the free induction decay (FID) by the window function with a broadening factor of 300 MHz (Figure 8). The spectrum consists of a peak and a much broader line, suggestive of only one metal coordination environment present in the compound. The ^{109}Ag resonance at $\delta = 378$ ppm is referenced to aqueous Ag(ClO$_4$) solution ($\delta \equiv 0$ ppm.) It is well-known that the silver chemical shifts are ligand-dependent and that the ^{109}Ag resonance substantially shifts downfield with coordination to soft ligands,[24] for example, Ag[CH$_3$CHC(OH)CO$_2$] (345.9, 320.2, 219.7, and 210.7 ppm), Ag(CH$_3$CO$_2$) (401.2 and 382.7 ppm), AgCl (370 ppm), AgBr (350 ppm), AgI (710 ppm), and KAg$_4$I$_5$ (810 ppm). The chemical shift observed in **1** conforms to this pattern when the four-coordinate silver ion in the complex bonding to one iodine and three carboxylate oxygen atoms is taken into consideration. The single peak and the δ value observed for **1** are both consistent with the structural data determined by X-ray analysis.

Conclusions

Of all the common organic functional groups, halocarbons have been by far the least studied in coordination chemistry. To our knowledge, this work represents the first structural characterization of silver(I) polymers with simple aryl iodide derived ligands, triiodobenzoic acid, tris(4-iodophenyl)amine, and 5,7-diiodo-8-hydroxyquinoline. The average Ag−I bond distances of 3.053, 2.882, 2.839, and 2.967 Å observed in **1**, **2**, **3**, and **4**, respectively, are slightly longer or shorter than those found in inorganic silver(I) iodide compounds such as $[\mathrm{Ag_2I_3}]_n^{-}$ (2.851 Å) and $[\mathrm{AgI_3}]_n^{2-}$ (2.847 Å),[25] indicating that the interaction of the aryl iodide with the silver(I) ion is almost of the same extent as those of the inorganic iodide species. The study demonstrates that the iodocarbon-derived ligands may have a rich coordination chemistry, possessing unique coordinative versatility and diversity and bridging the metal centers to form a supramolecular architecture brought about by covalent bonding interactions. Further studies are directed toward the development of various self-assembly process involving other aryl halide derivatives such as 2,4,6-triiodophenol and 3,5-diiodosalicylic acid, as well as the elucidation of spectroscopic and conductive properties observed in such systems.

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

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[25] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, 1993; p 1109 and the references therein.