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Notes

A Double-Decker Silver(I) Coordination Polymer of 1-Methylpyrene with Columnar Aromatic Stacks. Effect of Substituting Groups on Structure of Silver(I) Complexes with Polycyclic Aromatic Hydrocarbons

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Introduction

The synthesis and design of supramolecular coordination polymeric architectures has received considerable attention currently and is dominated by the selection of ligand structures and metal ion coordination characteristics[1]. Of these ligands, polycyclic aromatic hydrocarbons (PAHs) represent an important family of organic molecules. PAHs can interact with many transition metal ions to give rise to a wide variety of supramolecular coordination structures by virtue of the fact that they possess multiple ring sites and coordination versatility, such as η^1, η^2, η^3, η^4, and η^6 modes.[2,3] On the other hand, silver(I) also exhibits a coordination diversity when coordinated to organic ligands.[4] The coordination of silver(I) to PAHs demonstrates a unique coordination chemistry, different from those of other transition metals, because silver(I) only interacts with the peripheral carbon atoms of PAHs in η^1 or η^2 coordination.[5] In our previous works, we found that the shape and symmetry of PAH molecules can affect the construction of silver(I) coordination polymers with PAHs; for example, linear PAHs give a herringbone structure, disk PAHs often afford a decker-like structure, while the other types of PAHs give rise to a variety of polymeric motifs, such as W-type, helical, and pseudo triple-decker structures.[6] As is well known, substituting groups on the peripheral carbon atoms of PAH molecules may give rise to a distribution change of electron density of PAH rings and also introduce some steric effects. Therefore, we have recently directed our research interests toward the coordination chemistry of methyl substituted PAHs and silver(I). As a result, we report here on a double-decker silver(I) coordination polymer with 1-methylpyrene.

Experimental Section

General Methods. All preparations and manipulations were carried out under an argon atmosphere, using conventional Schlenk techniques. All chemicals were reagent grade and used as received without further purification. Solvents were dried and distilled by standard methods before use. 1-Methylpyrene was purchased from Tokyo Kasei Kogyou Co. Ltd.; silver perchlorate monohydrate was purchased from Mitsuwa Chem. Co. IR spectra were measured as KBr disks on a JASCO 8000 FT−IR spectrometer.

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

Synthesis of $\{[Ag_2(mpyr)_2(ClO_4)_2]0.5benzene\}_n$ (1). $AgClO_4 \cdot H_2O$ (33.8 mg, 0.15 mmol) was dissolved in 5 mL of benzene at room temperature, and the resultant colorless solution was then transferred to the reactor, where L^1 (97.3 mg, 0.45 mmol) was added in advance. After stirring for a while, the solution was introduced into a 7 mm glass tube and covered by *n*-pentane slowly. The glass tube was sealed under argon and kept at room temperature in the dark. After standing for 3 days, pale yellow block crystals suitable for X-ray analysis were isolated. Anal. Calcd for $C_{37}H_{27}Ag_2Cl_2O_8$: C, 50.14; H, 3.07%. Found: C, 50.01; H, 2.99%. Main IR bands (cm^{-1}): 3040−2924 (m), 1603 (m), 1124 (s), and 627(m).

X-ray Crystallography. A single-crystal suitable for X-ray determination was mounted on a glass fiber with adhesives. All measurements for **1** were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a rotating anode generator at room temperature. Intensity data were measured by continuous $\omega - 2\theta$ scans. The intensities of three representative reflections were measured after every 150 reflections for **1** and remained constant, which is indicative of crystal and electronic stability. Thus, no decay correction was applied. The linear absorption coefficient, μ, for Mo Kα is 14.4 cm^{-1}, and an empirical absorption correction based on azimuthal scans of several reflections was applied. In addition, a correction of secondary extinction was applied. The data for **1** were corrected for Lorentz and polarization effects.

The structure was solved by direct methods, expanded using Fourier techniques, and refined by full matrix least-squares analysis on F^2. All calculations were performed using the teXsan package. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Details of the X-ray experiments and crystal data are summarized in Table 1. The selected bond distances and angles for the complex are given in Table 2.

Results and Discussion

Double-Decker Structure of $\{[Ag_2(mpyr)_2(ClO_4)_2]0.5benzene\}_n$ (1). The structure study shows that complex **1**

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Table 1. Crystallographic Data for Complex **1**

chemical formula	$C_{37}H_{27}Ag_2Cl_2O_8$
formula weight	886.26
space group	$P\bar{1}$ (No. 2)
a, Å	11.451(3)
b, Å	14.796(2)
c, Å	11.029(2)
α, deg	91.15(2)
β, deg	112.95(2)
γ, deg	108.93(2)
V, Å^3	1604.4(7)
Z	1
T (°C)	23.0
λ (Mo Kα), Å	14.40
D_{calcd}, g/cm^3	1.834
μ, cm^{-1}	14.40
R^a	0.058
$R_w{}^b$	0.186

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

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **1**

Bond Distances			
Ag(1)−C(2)	2.421(9)	Ag(1)−C(3)	2.523(7)
Ag(1)−C(22)	2.471(7)	Ag(1)−C(23)	2.487(7)
Ag(1)−O(1)	2.45(1)	Ag(1)−O(5)	2.519(5)
Ag(2)−C(5)	2.424(9)	Ag(2)−C(6)	2.468(9)
Ag(2)−C(19)	2.460(9)	Ag(2)−C(20)	2.568(8)
Ag(2)−O(2)	2.424(9)	Ag(2)−O(7)	2.532(8)

Bond Angles			
O(1)−Ag(1)−O(5)	85.0(3)	O(1)−Ag(1)−C(2)	117.2(3)
O(1)−Ag(1)−C(3)	91.3(3)	O(1)−Ag(1)−C(22)	85.7(3)
O(1)−Ag(1)−C(23)	113.6(4)	O(5)−Ag(1)−C(2)	95.5(2)
O(5)−Ag(1)−C(3)	114.7(2)	O(5)−Ag(1)−C(22)	109.3(2)
O(5)−Ag(1)−C(23)	96.3(2)	C(2)−Ag(1)−C(3)	32.8(3)
C(2)−Ag(1)−C(23)	128.5(4)	C(3)−Ag(1)−C(22)	135.5(2)
C(22)−Ag(1)−C(23)	31.6(4)	O(2)−Ag(2)−O(7)	84.2(3)
O(2)−Ag(2)−C(5)	91.1(4)	O(2)−Ag(2)−C(6)	119.0(4)
O(2)−Ag(2)−C(19)	113.5(5)	O(2)−Ag(2)−C(20)	89.4(4)
O(7)−Ag(2)−C(5)	108.3(3)	O(7)−Ag(2)−C(6)	93.9(3)
O(7)−Ag(2)−C(19)	97.0(5)	O(7)−Ag(2)−C(20)	116.7(4)
C(5)−Ag(2)−C(6)	32.2(2)	C(5)−Ag(2)−C(19)	146.5(6)
C(5)−Ag(2)−C(20)	134.9(4)	C(6)−Ag(2)−C(19)	127.2(4)
C(6)−Ag(2)−C(20)	140.9(3)	C(19)−Ag(2)−C(20)	32.0(4)

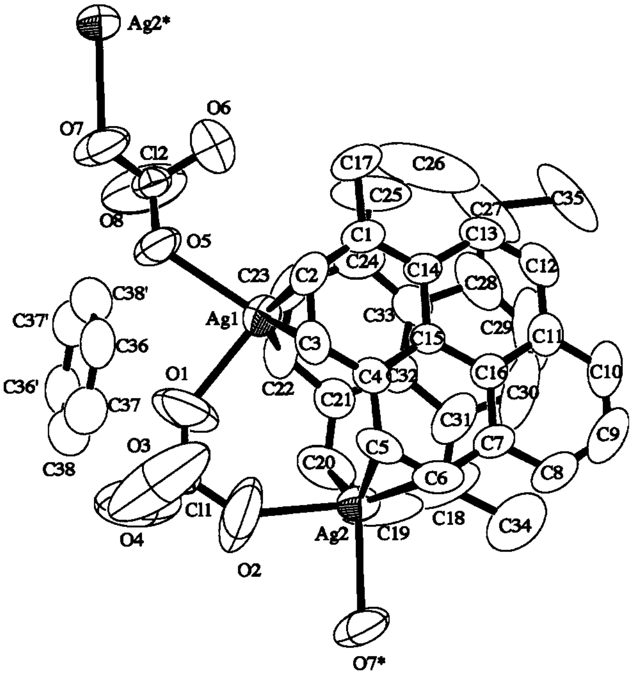

Figure 1. ORTEP view of molecular structure of **1** (50% thermal ellipsoids).

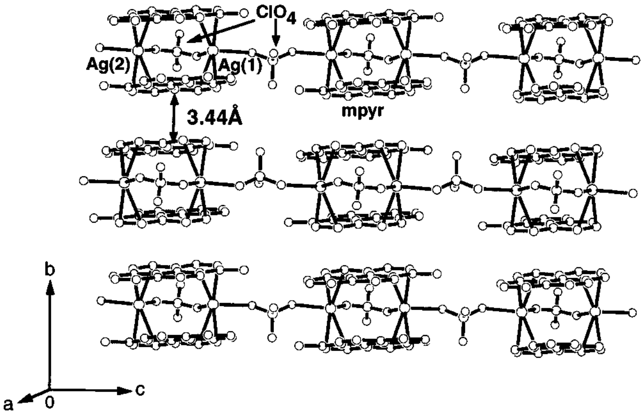

Figure 2. 1-D chain structure with double-decker motifs for **1**.

comprises 1-D chains, with double-decker motifs and molecules of solvent distributed between these chains. A perspective view of the molecular structure with the atom numbering for **1** is given in Figure 1. The basic unit of the structure is a dimeric double-decker moiety, $[Ag(mpyr)(ClO_4)]_2$, which is linked by the perchlorate groups to give rise to a 1-D chain (Figure 2). There exist two crystallographically independent silver(I) atoms in this structure, and both of them have a similar distorted tetrahedral coordination in which the silver(I) atoms interact with two independent ligand molecules via η^2 coordination, and the other sites are occupied by two perchlorate oxygen atoms. Within the double-decker unit, the two silver ions are sandwiched by two μ-di-η^2 crystallographically independent ligand molecules, with Ag−C distance ranging from 2.421(9) to 2.568(8) Å. The intradimeric and interdimeric metal−metal distances between Ag(1) and Ag(2) are 4.2634(9) and 6.7684(9) Å, respectively. It is noted that these 1-D chains are held together via intermolecular face to face $\pi-\pi$ interactions with an interplanar separation of 3.44 Å to construct a 2-D stacking polymer. In addition, the shortest carbon−carbon distance between the two ligands within the dimeric double-decker unit is 3.39 Å (Figure 3), which is indicative of existing intramolecular $\pi-\pi$ interactions. The overall result affords $\pi-\pi$ column stacks (Figure 3). The intermolecular overlaps of **1** possess two different types resulting from the two existing independent ligand molecules, and thus, these dimeric units are stacked in an alternate manner of head-to-head and tail-to-tail.

Discussion

Interestingly, the 1-D double-decker chain structure presented here is similar to that of the silver(I) coordination polymer with benzo[*ghi*]perylene.[7] Despite some resemblances between them, the latter has four crystallographically independent silver(I) atoms and thus comprises two different double-decker chains, while the former involves two crystallographically independent silver(I) atoms and consists of one kind of chain. Compared with pyrene, which coordinates to silver(I) in μ-tetra-η^2 coordination, leading to a 1-D W-type sandwich complex,[8] 1-methylpyrene exhibits a different coordination chemistry in which 1-methylpyrene only μ-di-η^2 bonds to silver(I), resulting in a 1-D double-decker structure. Although both of them exhibit a 1-D chain structure, the chain of complex **1** is formed via perchlorate ion linkage, while the chain of the silver(I) polymer

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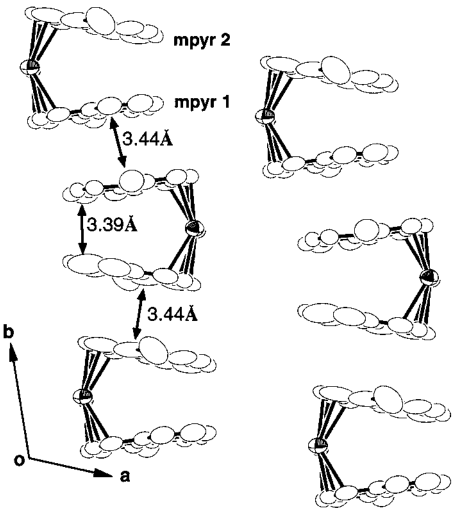
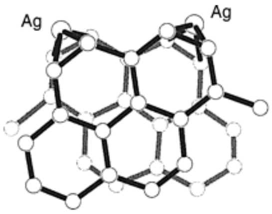
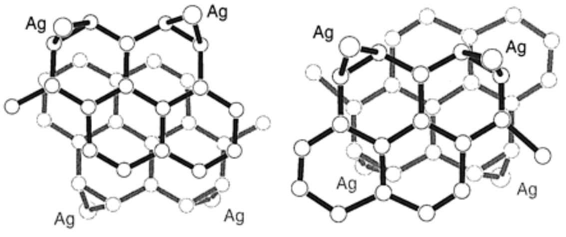


Figure 3. Stacking view of dimeric units with column $\pi-\pi$ stacks in **1** (50% thermal ellipsoids).



Overlap of molecules 1 and 2

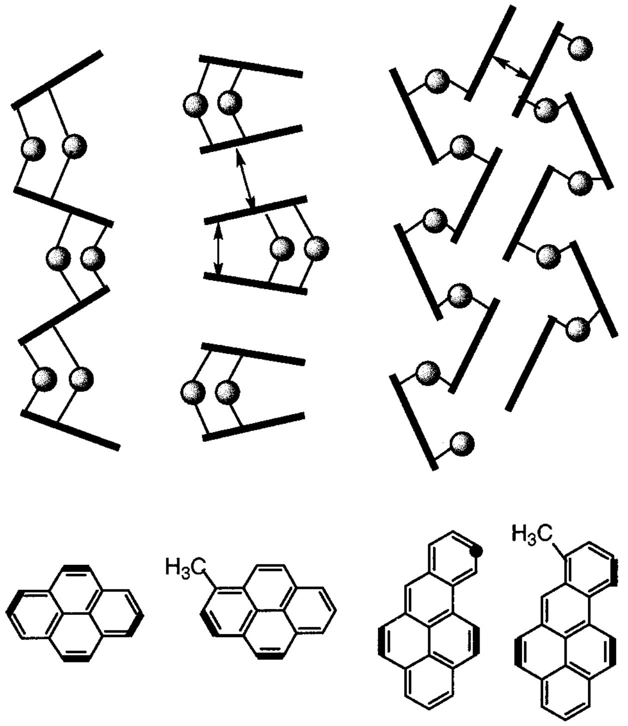


Overlap of molecules 1 and 1 Overlap of molecules 2 and 2

Figure 4. Intradimeric and interdimeric overlaps of 1-methylpyrene molecules in **1**.

with pyrene is constructed by ligand bridging. The structural difference between them arises from the substitution of a methyl group on pyrene. It is noteworthy that two 1-methylpyrene molecules in the dimeric unit exhibit an interesting relationship in which the two ligand molecules are enantiomorphous with respect to each other, owing to the molecular unsymmetry of 1-methylpyrene (Figure 4). Albeit silver(I) is inclined to interact with the peripheral carbon atoms of PAHs, such an arrangement of the ligand molecules directly results in two ligand molecules adopting the face to face ring sites to sandwich silver(I) ions. The intermolecular stacks in **1** show a so-called ring-over-bond overlap mode (Figure 4); therefore, it is more difficult for the 1-methylpyrene molecules to effectively interact with silver(I) despite their rotating 180° relative to each other in order to preclude the mutual repulsion between the two methyl groups. The difference between intermolecular and intramolecular overlaps was also observed in the silver(I) coordination polymer of coronene, which consists of 1-D chains with triple-decker motifs.[9] The effect of substituting groups on the self-assembly of silver(I) coordination polymeric structures was also observed in the silver(I) complexes of benzo[*a*]pyrene[9] and 7-methyl benzo[*a*]pyrene.[6] However, it is worth mentioning that the substitution of a methyl group only results in a tiny alternation of the coordination ring sites for 7-methyl benzo[*a*]pyrene relative to benzo[*a*]pyrene, which mainly arises from the methyl induction effect and does not change the basic packing manner of PAHs (Scheme 1). By contrast, alternation of the ligand coordination mode in complex **1** results from the methyl steric effect, which induces the difference of the packing modes between 1-methylpyrene and pyrene in their silver(I) complexes. In addition, the disklike molecules are inclined to face-to-face overlap to a larger extent than linear molecules due to their higher ratios of core carbon atoms to rim carbon atoms. Core carbon atoms and part (50%) of the rim carbon atoms help stacking, while the other part (50%) of the rim carbon atoms and all hydrogen atoms promote glide (or herringbone) stacking in the free PAH crystals.[10] The packing alternation of 1-methylpyrene in its silver(I) complex with respect to pyrene can be ascribed to strong intermolecular and intramolecular $\pi-\pi$ interactions in complex **1**, besides the methyl steric effect, compared with that of 7-methylbenzo[*a*]pyrene relative to benzo[*a*]pyrene. Therefore, the packing modes of substituted PAH molecules in their silver(I) coordination polymers depends on the synergic effect of the aforementioned factors.

Scheme 1. Structural Comparison of Several Silver(I) Complexes with Methyl Substituted PAHs. Bold Lines and a Black Circle of Organic Compounds Represent the Coordination Sites to Silver(I) Ions



It is noted that one of the 1-methylpyrene molecules in the dimeric unit shows disorder in the position of the methyl group, with site occupancy factors of 0.65(C34) and 0.35(C35). The reasons for this can be ascribed to: (i) the repulsion effect of the methyl groups of the ligand molecules in the dimeric unit, which results in the molecular reorientation between the face-to-face ligand molecules; (ii) the rotational rearrangements of flat molecules in the crystal;[11] and (iii) the hindered rotation of

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the 1-methylpyrene molecule in the crystal structure.[11,12] Generally, ligands with protruding groups, such as toluene, xylene, mesitylene, and substituted cyclopentadieneyl ligands, are more easily blocked in place by the surrounding molecules than ligands with discoid shape, such as cyclopentadieneyl and benzene ligands.[12] The similar disorder phenomenon was also observed in some crystal structures such as 2-fluoronaphalene.[13] In addition, another reason for the rotation hindrance can be attributed to the sandwich structure of complex **1**, in which the disorder of the 1-methylpyrene molecule is similar to that of the cyclopentadiene units in ferrocene[14] and the benzene rings in dibenzenechromium.[11]

In conclusion, the construction of the silver(I) coordination polymer with methyl substituted PAHs depends not only on the methyl induction and steric effects, but also on other factors, such as the molecular shape of PAHs and the intramolecular and intermolecular interactions. Consequently, the self-assembly of silver(I) and the methyl substituted PAHs is more complicated than that of silver(I) and unsubstituted PAHs.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $\{[Ag_2(mpyr)_2(ClO_4)_2]0.5benzene\}_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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