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Construction of 2-D multilayer structures: silver(I) complexes with linear aromatic compounds

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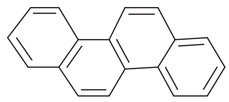
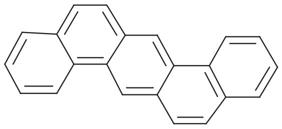
For the purpose of exploring the structural relations of organometallic compounds to their organic components, a series of linear polycyclic aromatic hydrocarbons (PAHs) benzo[*a*]phenanthrene (L^1), dibenz[*a,h*]anthracene (L^2), benz[*a*]anthracene (L^3), and naphtho[2,3-*a*]pyrene (L^4), have been studied towards complexation with silver(I) ion. The crystal structures of $[Ag_3(L^1)(ClO_4)_3(H_2O)_2]$ **1**, $[Ag_2(L^2)(ClO_4)_2]$ **2**, $[Ag_2(L^3)(ClO_4)_2(H_2O)]$ **3**, and $[Ag_2(L^4)(CF_3SO_3)_2]$ **4** have been determined by single-crystal X-ray diffraction. Although each of these complexes exhibits distinct co-ordination behavior and different frameworks, all of them retain or partially keep the herringbone-packing pattern of their metal-free aromatic ligands in the crystalline state, and display similar two-dimensional multilayer architectures on a given plane. The fundamentals of the synthesis, possible formation mechanism of these polymeric networks and some properties are discussed.

Introduction

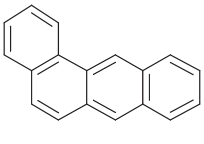
The latest development in polycyclic aromatic chemistry has spurred a renaissance in the use of aromatic units to construct complex molecular structures owing to the fact that cation–π interactions provide a powerful tool for the building of novel molecular architectures and allow the introduction of a wide variety of useful electric and electrochemical properties.[1–3] With the aim to establish whether a favorable combination of cation–π interactions and aromatic stackings might produce functional organometallic materials, we have synthesized several organosilver(I) complexes of polycyclic aromatic hydrocarbons (PAHs) with unique frameworks, such as W-type sandwiches with pyrene and perylene, helical structure with benzo[*a*]pyrene, triple decker with coronene, and multidecker with decacyclene.[4–6] In spite of these achievements, the investigations of structural relevancy of the complex to its "free" ligand in the crystalline state for designing organometallic solid-state materials are very rare. The molecular configuration of the PAH plays a dramatic role in the construction of these novel architectures. In order to seek ways to control the assembly of molecular components into predictable crystal structures, we have targeted on the construction of metal complexes with different types of PAHs. In this paper we describe the co-ordination behaviors of linear PAHs. The aromatics benzo[*a*]phenanthrene (L^1), dibenz[*a,h*]anthracene (L^2), benz[*a*]anthracene (L^3), and naphtho[2,3-*a*]pyrene (L^4) have been selected as organic ligands for some similarities in their molecular structures. On the other hand, crystalline silver(I) complexes with pure linear organic compounds, such as naphthacene and pentacene, were not obtained owing to the low solubility and poor co-ordination ability of the hydrocarbons in solution. It is known that these linear aromatic molecules have the tendency to adopt herringbone packing in the solid state.[7] However, the organometallic networks and their structural dependence on the ligands have never been reported or discussed. Here we present the results of synthetic and structural studies of silver(I) complexes with ligands L^1–L^4 and try to elucidate how the metal ions together with counter anions are assembled in these discrete organic molecules to build up novel polymeric architectures without destroying the herringbone-packing pattern of their "free" ligands. Silver(I) ion is chosen as the metal center due to its diverse and flexible stereochemistry.[8]



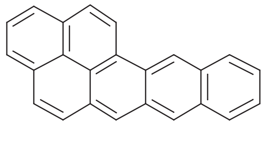
benzo[*a*]phenanthrene (L^1)



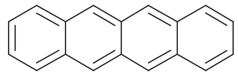
dibenz[*a,h*]anthracene (L^2)



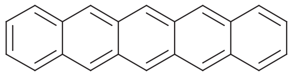
benz[*a*]anthracene (L^3)



naphtho(2,3-*a*)pyrene (L^4)



naphthacene



pentacene

Experimental

General procedures

All reactions and manipulations were carried out under an argon atmosphere using usual Schlenk techniques. Solvents were dried and distilled by using standard methods prior to use. Reagent grade benzo[*a*]phenanthrene, dibenz[*a,h*]anthracene, benz[*a*]anthracene and naphtho[2,3-*a*]pyrene were purchased from Tokyo, Kasei Kogyou Co. Ltd. while silver(I) perchlorate and trifluoromethanesulfonate were from Aldrich. All other chemicals were from Wako Pure Chemical, Inc. and used without further purification. The IR spectra were recorded as KBr disks on a JASCO FT/IR 8000 spectrometer, ESR spectra on a JEOL JES-TE200 ESR spectrometer. The electrical

Table 1 Crystallographic data

	1	**2**	**3**	**4**
Formula	$C_{18}H_{16}Ag_3Cl_3O_{14}$	$C_{22}H_{14}Ag_2Cl_2O_8$	$C_{18}H_{14}Ag_2Cl_2O_9$	$C_{26}H_{14}Ag_2S_2F_6O_6$
M	886.28	692.98	660.95	816.24
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	*Pnma* (no. 62)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
T/°C	23.0	23.0	23.0	23.0
a/Å	5.081(7)	8.304(5)	5.2504(7)	17.976(5)
b/Å	18.497(5)	16.033(7)	12.452(2)	5.010(2)
c/Å	24.310(6)	15.624(4)	15.330(3)	28.242(2)
α/°			99.512(5)	
β/°	93.46(7)		93.871(2)	89.662(3)
γ/°			91.025(3)	
V/Å^3	2280(3)	2080(2)	985.2(2)	2543.3(9)
Z	4	4	2	4
D_c/g cm^{-3}	2.578	2.213	2.227	2.132
μ(Mo-Kα)/cm^{-1}	29.68	21.86	23.04	17.88
No. data collected	5069	2474	4112	6263
No. data refined	All unique	All unique	All unique	3659 [$I > 3.00\sigma(I)$]
$R1$	0.040	0.059	0.069	0.098 (R)
$wR2$	0.107	0.170	0.197	0.159 (R')

conductivity of compacted pellets was measured by the conventional two-probe technique at room temperature employing silver paste coated probes. **CAUTION**: perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared and handled with great care.

Syntheses

[$Ag_3(L^1)(ClO_4)_3(H_2O)_2$] 1. To a solution of benzo[*a*]phenanthrene (22.8 mg, 0.1 mmol) in 5 mL of benzene was added $AgClO_4·H_2O$ (22.6 mg, 0.1 mmol). After about 30 min of stirring, the resultant light yellow solution was introduced into a 7 mm diameter tube and layered with pentane as a diffusion solvent. The tube was sealed under Ar and wrapped with aluminum foil. After standing at room temperature for one week, yellow needle crystals of complex **1** suitable for single-crystal X-ray analysis were obtained (12 mg). Calc. for $C_{18}H_{16}Ag_3Cl_3O_{14}$: C, 24.37; H, 1.81. Found: C, 23.87; H, 1.75%.

[$Ag_2(L^2)(ClO_4)_2$] 2. This compound was prepared by vapor diffusion. To a solution of dibenz[*a*,*h*]anthracene (14 mg, 0.05 mmol) in 5 mL of toluene was added $AgClO_4·H_2O$ (22.6 mg, 0.1 mmol). The resultant yellow solution was introduced into one compartment of an H-shaped glass tube. The second compartment was filled with *n*-hexane. After standing at room temperature in the dark for 3 days, yellow plate crystals of **2** were obtained (10 mg). Calc. for $C_{11}H_7AgClO_4$: C, 38.10; H, 2.02. Found: C, 37.83; H, 2.10%.

[$Ag_2(L^3)(ClO_4)_2(H_2O)$] 3. Yellow needle crystals of compound **3** were prepared in the same way as **1**, by mixing of benz[*a*]anthracene (46 mg, 0.2 mmol) and $AgClO_4·H_2O$ (22.6 mg, 0.1 mmol) in 3 mL of toluene. Yellow needle crystals of complex **3** were obtained (6 mg). Calc. for $C_{18}H_{14}Ag_2Cl_2O_9$: C, 32.68; H, 2.12. Found: C, 32.84; H, 2.07%.

[$Ag_2(L^4)(CF_3SO_3)_2$] 4. A solution of naphtho[2,3-*a*]pyrene (6 mg, 0.02 mmol) in 4 mL of THF was refluxed for 3 h, to which a toluene solution (4 mL) containing 30 mg of $AgCF_3SO_3$ (0.12 mmol) was added. After stirring for 20 min, the resultant light yellow solution was introduced into a glass tube and layered with *n*-hexane. The tube was sealed and after standing at room temperature in the dark for about 6 months brown brick crystals suitable for X-ray analysis were isolated (4 mg). Calc. for $C_{13}H_7Ag_2F_3O_3S_2$: C, 38.26; H 1.73. Found: C, 37.84; H, 1.77%.

X-Ray crystallography

The single crystals suitable for X-ray measurement was fixed on glass fibres with adhesives. The diffraction data for complexes **2** were collected at room temperature on a Rigaku AFC7R diffractometer and those for **1**, **3** and **4** on a Quantum CCD area detector coupled with a Rigaku AFC7 diffractometer and graphite-monochromated Mo-Kα radiation. Space groups were selected on the basis of systematic absences and intensity statistics. Over the course of data collection no decay correction was applied for all complexes. All intensity data were corrected for Lorentz-polarization effects. The structures were solved by direct methods,[9] expanded using Fourier techniques[10] and refined by a full matrix least-squares analysis on F for **4**, and on F^2 for **1**, **2** and **3**. The positions of all the hydrogen atoms were calculated geometrically and included in the structure factor calculation, but not refined. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[11] All calculations were performed using the TEXSAN package.[12] Details of the X-ray experiments and crystal data are summarized in Table 1, selected bond distances and angles for the four complexes in Table 2.

CCDC reference number 186/1499.

See http://www.rsc.org/suppdata/dt/1999/2529/ for crystallographic files in .cif format.

Results and discussion

Synthesis, IR spectra and properties

Generally, co-ordination of an aromatic ligand to metal ions can be achieved *via* a stoichiometric reaction,[4–6] but sometimes an excess ligand or metal ion has to be implemented. For example, during the preparation of **1** and **3** three to four fold excess stoichiometric amounts of L^1 and L^3 are employed, while for **4** a threefold excess of silver salt is used. The reasons for this are twofold: (i) the solvents benzene and toluene form silver(I) complexes,[13] which consumes silver(I) ions; (ii) when a compound (complex) in solution is "incongruently saturating"[14] its crystals can not be obtained *via* a stoichiometric reaction.

Counter anions in the synthesis of these co-ordination polymers may also be thought of as the keys to assembling these polymeric architectures. In most cases a perchlorate salt was used to construct silver(I)–aromatic compounds, whereas the reaction of L^4 with $AgClO_4$ in conventional solvents leads to the formation of an oxidized carbon black precipitate. Thus, $AgCF_3SO_3$ is another choice for the preparation of silver(I) complexes due to its high solubility in common organic solvents, although its reactions with aromatics were very slow.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **1**–**4**

1			
Ag(1)–O(7)	2.572(4)	Ag(1)–O(12)	2.590(5)
Ag(1)–O(13)	2.383(3)	Ag(1)–C(10)	2.502(4)
Ag(1)–C(11)	2.408(5)	Ag(2)–O(1)	2.550(4)
Ag(2)–O(6)	2.678(4)	Ag(2)–O(13)	2.367(3)
Ag(2)–C(4)	2.454(4)	Ag(2)–C(5)	2.542(4)
Ag(3)–O(6)	2.647(4)	Ag(3)–O(14)	2.367(4)
Ag(3)–C(1)	2.616(4)	Ag(3)–C(2)	2.584(4)
C(1)–C(2)	1.382(7)	C(4)–C(5)	1.361(6)
C(10)–C(11)	1.387(7)		
O(7)–Ag(1)–O(12)	65.4(1)	O(7)–Ag(1)–O(13)	79.1(1)
O(7)–Ag(1)–C(10)	139.7(1)	O(7)–Ag(1)–C(11)	127.4(2)
O(12)–Ag(1)–O(13)	76.9(1)	O(12)–Ag(1)–C(10)	124.5(1)
O(12)–Ag(1)–C(11)	157.1(2)	O(13)–Ag(1)–C(10)	139.2(1)
O(13)–Ag(1)–C(11)	121.8(1)	O(1)–Ag(2)–O(13)	94.2(1)
O(1)–Ag(2)–C(4)	128.4(1)	O(1)–Ag(2)–C(5)	103.4(1)
O(13)–Ag(2)–C(4)	134.5(1)	O(13)–Ag(2)–C(5)	137.5(1)
O(14)–Ag(3)–C(1)	140.2(1)	O(14)–Ag(3)–C(2)	148.8(1)
2			
Ag(1)–O(1)	2.46(2)	Ag(1)–C(1)	2.599(7)
Ag(1)–C(2)	2.507(7)	Ag(2)–O(3)	2.72(2)
Ag(2)–O(4)	2.383(9)	Ag(2)–C(8)	2.452(7)
Ag(2)–C(9)	2.536(7)	C(1)–C(2)	1.39(1)
C(8)–C(9)	1.350(9)		
O(1)–Ag(1)–C(1)	92.2(4)	O(1)–Ag(1)–C(2)	109.6(2)
C(1)–Ag(1)–C(1)^a	95.0(4)	C(1)–Ag(1)–C(2)^a	118.9(3)
C(2)–Ag(1)–C(2)^a	130.1(4)	O(3)–Ag(2)–O(4)	69.0(6)
O(3)–Ag(2)–C(8)	106.1(2)	O(3)–Ag(2)–C(9)	111.2(4)
O(4)–Ag(2)–C(8)	96.2(2)	O(4)–Ag(2)–C(9)	127.4(2)
C(8)–Ag(2)–C(8)^a	147.8(3)	C(8)–Ag(2)–C(9)^a	130.0(2)
C(9)–Ag(2)–C(9)^a	102.4(3)		
3			
Ag(1)–O(4)^b	2.503(5)	Ag(1)–O(5)	2.495(9)
Ag(1)–O(9)	2.336(5)	Ag(1)–C(3)	2.337(7)
Ag(1)–C(4)^b	2.587(8)	Ag(2)–O(1)	2.360(5)
Ag(2)–O(9)	2.351(6)	Ag(2)–O(2)^c	2.714(6)
Ag(2)–C(13)	2.357(7)	Ag(2)–C(14)	2.507(6)
C(3)–C(4)	1.40(1)	C(13)–C(44)	1.38(1)
O(4)^b–Ag(1)–O(5)^d	93.8(4)	O(4)^b–Ag(1)–O(9)^d	90.2(2)
O(4)^b–Ag(1)–C(3)	133.5(2)	O(4)^b–Ag(1)–C(4)^b	111.1(2)
O(5)^d–Ag(1)–O(9)	82.0(3)	O(5)^d–Ag(1)–C(3)	108.2(5)
O(5)^d–Ag(1)–C(4)^b	139.9(5)	O(9)^d–Ag(1)–C(3)	132.2(3)
O(9)^b–Ag(1)–C(4)	126.8(2)	O(1)–Ag(2)–O(9)	108.7(2)
O(1)–Ag(2)–O(2)^c	84.3(2)	O(1)–Ag(2)–C(13)	123.5(2)
O(1)–Ag(2)–C(14)	125.4(2)	O(9)–Ag(2)–O(2)^c	79.0(2)
O(9)–Ag(2)–C(13)	126.9(3)	O(9)–Ag(2)–C(14)	118.9(2)
O(2)^c–Ag(2)–C(13)	96.1(2)	O(2)^c–Ag(2)–C(14)	128.1(2)
4			
Ag(1)–O(3)	2.391(9)	Ag(1)–O(5)	2.39(1)
Ag(1)–O(6)^b	2.42(1)	Ag(1)–C(1)	2.46(1)
Ag(1)–C(2)	2.42(1)	Ag(2)–O(1)^b	2.440(9)
Ag(2)–O(2)	2.420(8)	Ag(2)–O(4)	2.411(8)
Ag(2)–C(12)	2.41(1)	Ag(2)–C(13)	2.48(1)
C(1)–C(2)	1.37(2)	C(12)–C(13)	1.39(2)
O(3)–Ag(1)–O(5)	84.2(4)	O(3)–Ag(1)–O(6)^b	127.7(4)
O(3)–Ag(1)–C(1)	96.7(4)	O(3)–Ag(1)–C(2)	126.3(5)
O(5)–Ag(1)–O(6)^b	82.2(4)	O(5)–Ag(1)–C(1)	136.7(4)
O(5)–Ag(1)–C(2)	118.7(5)	O(6)–Ag(1)–C(1)	126.6(4)
O(6)^b–Ag(1)–C(2)	104.4(5)	O(1)^b–Ag(2)–O(2)	80.3(3)
O(1)^b–Ag(2)–C(13)^e	104.1(4)	O(2)–Ag(2)–O(4)	84.2(3)
O(2)–Ag(2)–C(12)^e	139.8(4)	O(2)–Ag(2)–C(13)^e	21.6(5)
O(4)–Ag(2)–C(12)^e	98.2(4)	O(4)–Ag(2)–C(13)^e	126.1(4)

^{a} $x, \frac{1}{2} - y, z$. ^{b} $x, y - 1, z$. ^{c} $x + 1, y, 1 - z$. ^{d} $x - 1, y - 1, z$. ^{e} $x, \frac{5}{2} - y, 1 - z$.

Characterization of the complexes was mainly based on X-ray diffraction studies. Nevertheless, IR spectroscopy is a good supplementary means to confirm incorporation of metal ions into the polymeric aromatic system. The four aromatic ligands have several distinctive signals, including a CH stretching at 3040 to 3055 cm^{-1} and three or four quite intense signals from 1338 to 1608 cm^{-1} corresponding to the in-plane vibrations of the C=C bonds. All of these are present in the IR spectra of **1**–**4**. In addition, **1**–**3** exhibit a strong split absorption of ν(OCl) at 1103–1120 cm^{-1}, consistent with co-ordination of the perchlorate ion. Complex **4** shows three strong resolved absorptions at 1172–1269 cm^{-1}, indicative of bound $CF_3SO_3^-$.[15] The bridging water molecules of **1** and **3** are also confirmed by the IR spectra.

At room temperature no ESR spectrum was observed for complex **3** or **4**. However, **1** and **2** exhibit a well resolved intense resonance with $g = 2.0058$ and 2.0072, respectively, typical of aromatic hydrocarbon radicals.[16] However, the formation of silver-(0) and -(II) species accompanied by electron transfer was not observed probably due to the low sensitivity. All of the complexes showed semiconducting behavior at room temperature with $\sigma = 1.65 \times 10^{-3}$–$6.9 \times 10^{-2}$ S cm^{-1}.

Description of the structures

[Ag$_3$(L^1)(ClO$_4$)$_3$(H$_2$O)$_2$] 1. The molecular structure of complex **1** together with the atom-numbering scheme is shown in Fig. 1(a). The single-crystal X-ray analysis reveals an aromatic-linked chain structure propagating along the *c* axis. There exists a trinuclear unit comprised of three crystallographically independent metal centers, in which each metal ion interacts with one aromatic group through a C=C π bond at Ag–C distances ranging from 2.408(5) to 2.616(4) Å, well within the limits from 2.36 to 2.77 Å of reported silver(I)–aromatic complexes.[4–6,18] The next closest contact between silver and carbon is 3.08 Å. In addition, each Ag(1) and Ag(2), co-ordinates with three oxygen atoms (two perchlorate ions and one bridging water) to exhibit a distorted tetrahedral geometry (taking the C=C group as one ligand), while Ag(3) co-ordinates with one perchlorate ion and one terminal water to give a three-co-ordinate environment. The Ag–O distances range from 2.367(4) to 2.678(4) Å. The aromatic ligand involves two different co-ordination modes, μ-di-η^2 bridging two metal ions and μ-tetra-η^2 linking four metal centers. Thus, an alternating arrangement of aromatics and trinuclear moieties forms a chain structure. Furthermore, such chains are connected by interchain π–π stacking of aromatics (spacing 3.40–3.52 Å) and hydrogen bonding of the inorganic groups to create a two-dimensional sheet framework in which a twisted herringbone arrangement of aromatic groups on the *ac* plane is retained, Fig. 1(b).

[Ag$_2$(L^2)(ClO$_4$)$_2$] 2. Fig. 2(a) depicts the local co-ordination around silver(I) ions together with the atom-numbering scheme. Complex **2** exists in the solid state as an infinite chain of silver(I) ions joined by double bridging by L^2 C=C π bonds. There exists a dinuclear unit in the structure made up by two crystallographically independent silver(I) ions with a Ag(1)···Ag(2) separation of 4.34 Å. Each metal center is co-ordinated to two C=C π bonds from two different L^2 molecules at Ag–C distances ranging from 2.452(7) to 2.599(7) Å. The next closest contact between silver and carbon is 3.10 Å. Furthermore, the distorted tetrahedral Ag(2) ion is co-ordinated by two oxygen atoms from one terminal and one bidentate perchlorate at Ag–O distances of 2.383(9) and 2.72(2) Å, respectively, whereas the three-co-ordinate Ag(1) is only bonded to one oxygen of the bidentate perchlorate, O(1), at 2.46(2) Å. The next closest distance is 2.77(3) Å of Ag(2)···O(1), being hardly considered as an effective interaction.[4–6,19] Thus, each L^2 moiety exhibits a tetra-η^2 co-ordination, bridging sequentially four metal centers and resulting in a polymeric W-type sandwich of alternating aromatic and AgClO$_4$ groups running along the *b* axis. Despite the similar co-ordination mode of L^2 to that of pyrene in metal complexes,[4] the linear L^2 molecule provides a larger space to overcome the steric effect of perchlorate anions and makes it

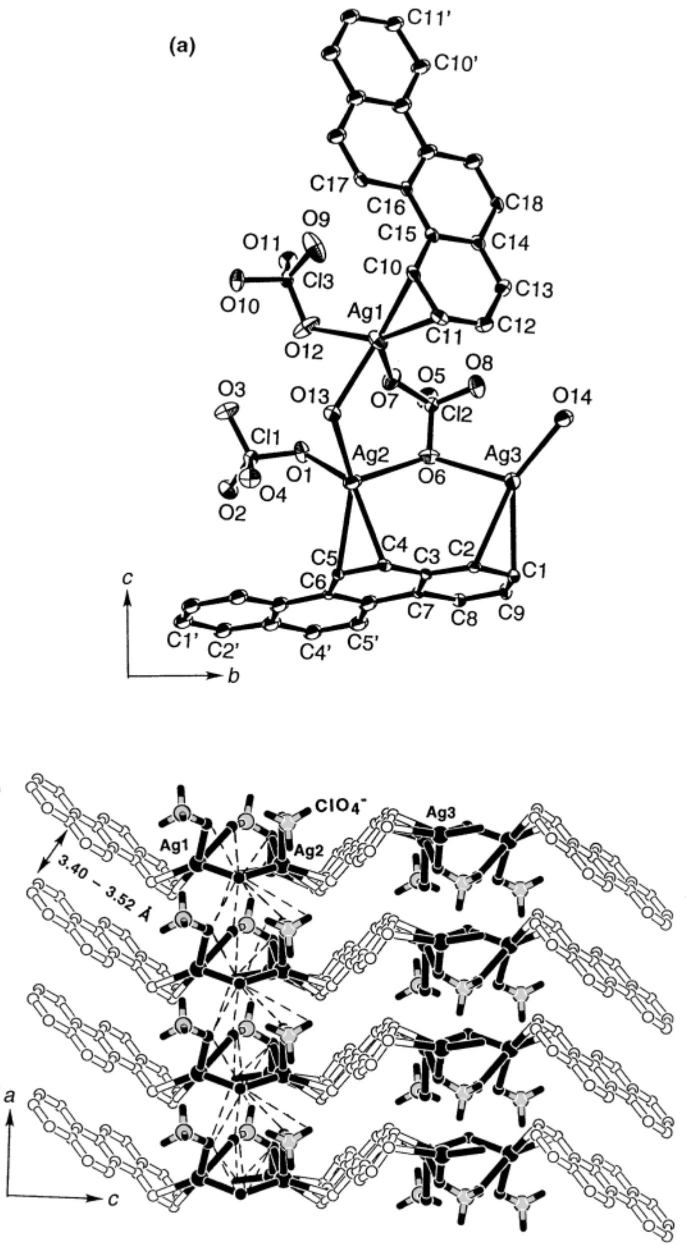


Fig. 1 Crystal structure of compound **1**: (a) labeling scheme (ORTEP,[17] 30% probability); (b) view of the 2-D multilayer structure on the *ac* plane.

possible for these chains to sit closely through the superposed interchain aromatic π–π stacking interactions. The distances between the adjacent chains range from 3.47 to 3.66 Å. As a result, the strong π–π interactions in discrete chains generate a two-dimensional sheet network on the *ab* plane with the herringbone arrangement of the aromatic moiety maintained, Fig. 2(b).

$[Ag_2(L^3)(ClO_4)_2(H_2O)]$ 3. The molecular structure and atom numbering scheme of compound **3** are given in Fig. 3(a). The neutral complex in the crystalline state exhibits a polymeric sheet framework built up of multilayer aromatic ligands suspended between two infinite inorganic chains through co-ordinated silver(I) ions as shown in Fig. 3(b). The inorganic chain is composed of $AgClO_4$ and H_2O propagating along the *a* axis, in which the two independent Ag(1) and Ag(2) are coupled in pairs through Ag–O–Cl–O–Ag and Ag–O–Ag bonds with a separation of 4.01 Å. Both Ag(1) and Ag(2) ions are bonded to two perchlorates and one bridging water although the two metal centers (together with an adjacent Ag(2′)) share one tridentate perchlorate anion. The Ag–O distances range from 2.336(5) to 2.714(6) Å. The tridentate perchlorate ions virtually act as a linkage between two dinuclear units to construct the inorganic ionic chain. All Ag(1) atoms sit on one side of the chain co-ordinated to the head of L^3, whereas Ag(2) atoms sit on the other side connected to the tail of L^3. The Ag–C distances range from 2.337(7) to 2.587(8) Å. The metal–metal distances between Ag(1) ions are surprisingly equal to that of Ag(2) ions, being 5.23 Å. Such co-ordination also results in strong π–π interactions between two aromatic molecules with the interplane distances ranging from 3.39 to 3.62 Å. In addition, like complex **1**, the co-ordinated water molecules in the structure have a hydrogen-bonding effect in the ionic chains. Interestingly, although L^3 shows some structural similarity with L^2, complex **3** displays a stair-like 2-D multilayer architecture, in which the herringbone packing of free L^3 was only partially kept.

$[Ag_2(L^4)(CF_3SO_3)_2]$ 4. The local co-ordination around silver(I) ions together with the atom-numbering scheme of compound **4** is shown in Fig. 4(a). Similar to **3**, complex **4** in the solid state also exhibits a polymeric sheet framework with multilayer aromatic ligands suspended between two infinite ionic chains through co-ordinated silver(I) ions, Fig. 4(b). How-

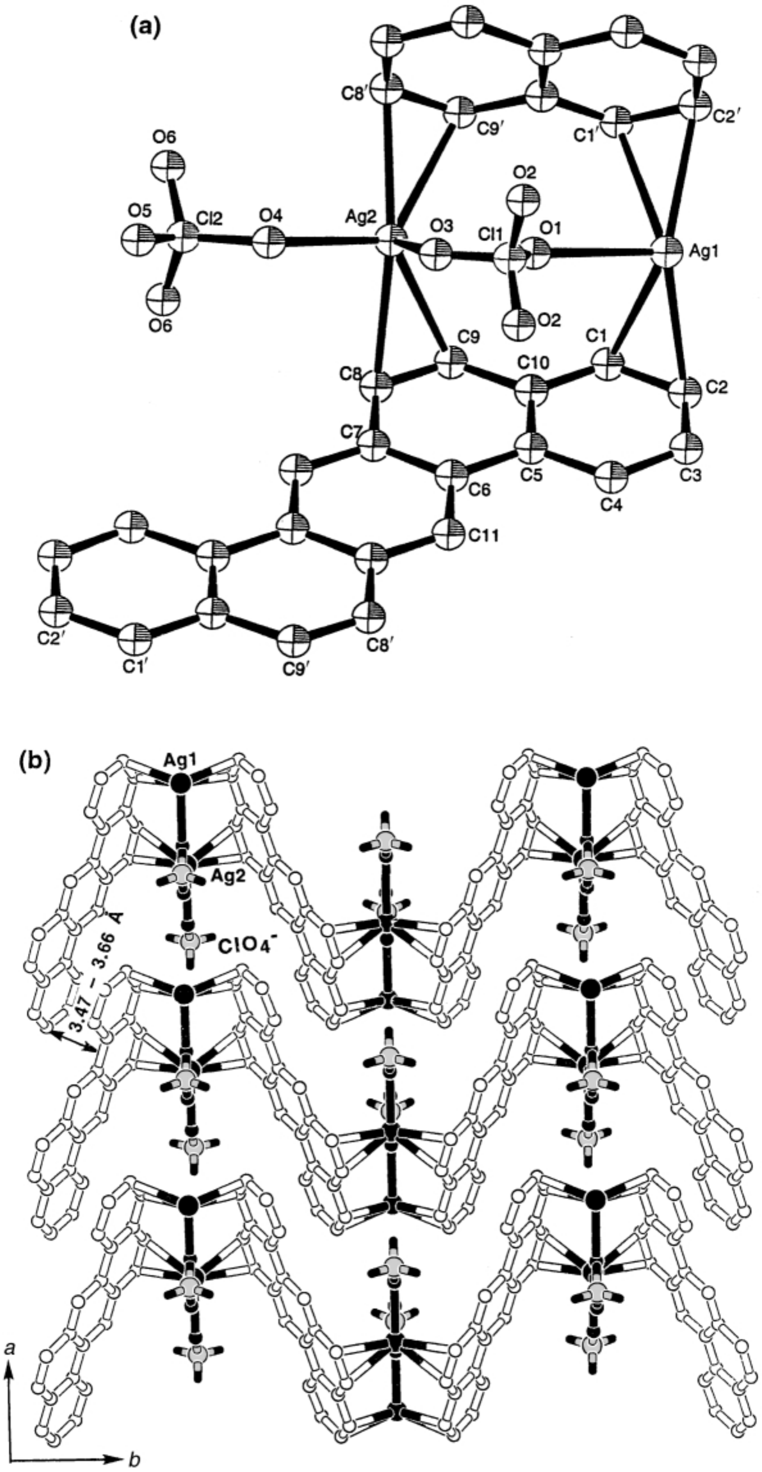


Fig. 2 Crystal structure of compound **2**: (a) local co-ordination around silver(I) ions with labeling scheme (ORTEP, 30% probability) and (b) 2-D multilayer structure on the *ab* plane.

ever, the chain in **4** is constructed by silver(I) ions together with the poorly co-ordinating anions $CF_3SO_3^-$ [15,20] extending along the *b* axis, in which each silver(I) atom is bonded to an oxygen of three distinct tridentate triflate groups above and below it, at Ag–O distances ranging from 2.39(1) to 2.440(9) Å. The two independent Ag(1) and Ag(2) ions with a separation of 3.35 Å in the chain are coupled in pairs by Ag–O–S–O–Ag bonds from the tridentate bridging anion to yield a two stranded ribbon having a tube-like appearance. The metal–metal distances for these two strands are also equal, being 5.01 Å. The L^4 molecules are stacked in the channels formed by two tubes, such that each μ-di-η^2 L^4 molecule π interacts with Ag(1) of one tube at the head and with Ag(2) of the other tube at the tail with Ag–C distances ranging from 2.41(1) to 2.48(1) Å. The interplane distances between two aromatic molecules range from 3.42 to 3.56 Å, indicative of strong π–π interactions. Like complex **2**, here again the herringbone packing of L^4 ligands is retained. However, these aromatic molecules are held together not only by π–π interactions but also by the infinite tube-like ionic chains. The overall result of such connection is a two-dimensional multilayer network.

Discussion

As described above, complexes **1** and **3** involve co-ordinating water molecules, which result in the formation of intra- and inter-molecular hydrogen-bonding networks. These hydrogen bonds contribute, respectively, to the construction of continu-

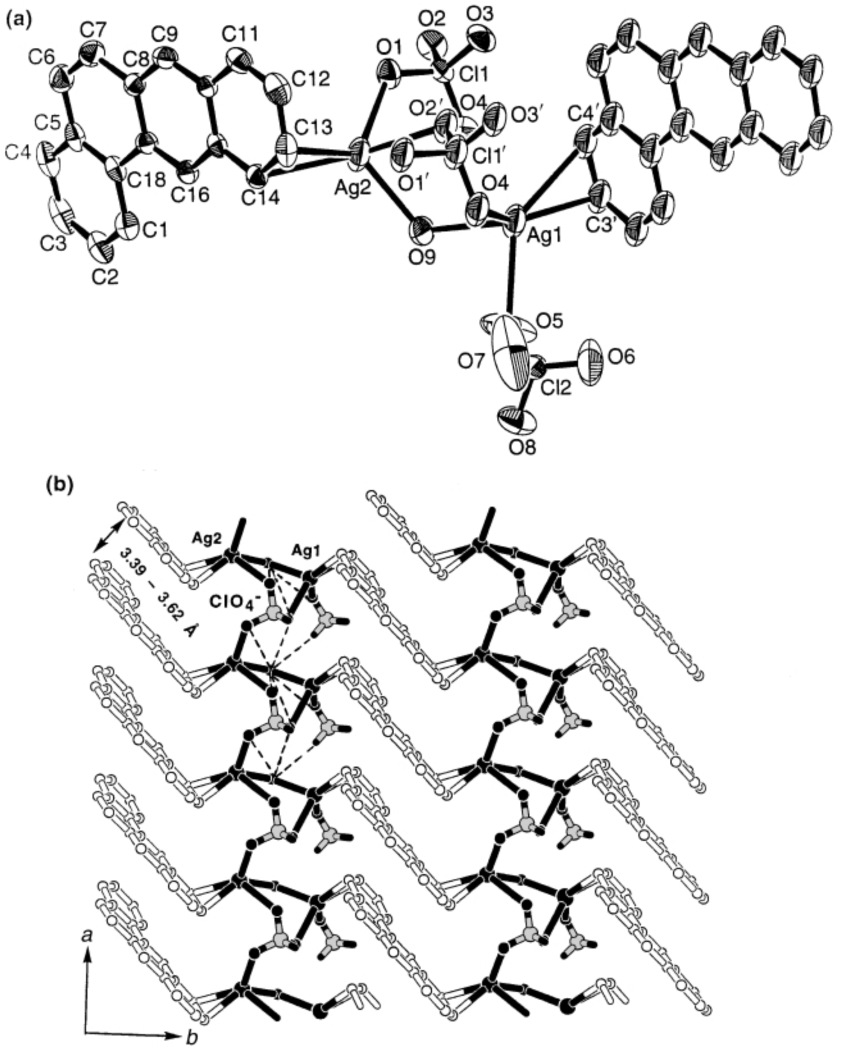


Fig. 3 Crystal structure of compound **3**: (a) labeling scheme (ORTEP, 30% probability) and (b) stair-like 2-D multilayer framework on the *ab* plane.

ous ionic chains in **1** and the modification of established chains in **3**. Although the presence of such molecules in silver(I) complexes is well established,[21] bridging water ligands are much less commonly encountered in silver(I)–aromatic complexes. In addition, complex **3** includes unusual tridentate perchlorate ions, through which the ionic chain structure along the *a* axis is established. To the best of our knowledge, very few co-ordination compounds have been found thus far to contain tridentate perchlorate anions. Furthermore, it is noteworthy that the triflate ions in complex **4** display another unique tridentate co-ordination mode. Very often $CF_3SO_3^-$ anion acts as a good leaving group.[15] Its low degree of nucleophilicity and big steric effect, indicative of poor co-ordination ability, explain the very rare occurrence of its tridentate bonding in co-ordination chemistry. There is only one report describing tridentate $CF_3SO_3^-$ in the copper(I) complex $[Cu(OSO_2CF_3]\cdot C_6H_{10}$.[22] In related silver(I) complexes, $CF_3SO_3^-$ often acts as an unco-ordinated or unidentate group,[20,23] and sometimes shows bidentate behavior.[15,24] This work presents the first example of a silver(I) complex involving tridentate bridging triflate anions. It can be seen from Figs. 3(b) and 4(b) that both tridentate ClO_4^- in **3** and $CF_3SO_3^-$ in **4** form inorganic chain networks bound to the linear aromatics to support or maintain the herringbone packing of the "free" ligands. Of paramount importance is the ability of such anions to influence profoundly the structures and stability of the synthesized products, and to direct the packing of the aromatics with particular conformation and physical properties.

Generally, silver(I) ions are inclined to bond at the short carbon–carbon bond portion,[1–6] indicative of large electron density accumulated on the π-bonded carbon atoms. However, this does not always apply for the present silver(I) complexes, although the aromatics adopt the same η^2 co-ordination as that reported previously. For example, in **2** the silver(I) ions are bound to the shortest (1.348 Å) C=C bonds of L^2,[25] whereas in **3** the metal centers do not interact with the shortest C=C bonds,[26] Chart 1. This phenomenon may be attributable to the geometry of the aromatics, the molecular packing energy and other structural details which determine the co-ordination positions.

The most remarkable feature of this study is the herringbone or twisted herringbone multilayer arrangement of the aromatic hydrocarbons hinging upon counter anions (ClO_4^- or $CF_3SO_3^-$) through silver(I) ions. It is obvious that all the complexes still keep the tendency for herringbone packing of their metal-free aromatic ligands, although L^3 in **3** underwent a reorientational motion. The counter anions look like pillars, inserted into the gaps of aromatic herringbone packings, whereas silver(I) ions just play a role of linkage, sequentially binding these linear multilayer organic components to the two adjacent pillars, leading to strong π–π interactions between the aromatics. Such a structural feature or configuration tendency has never been revealed in aromatic co-ordination chemistry. In our previous report[4] the silver(I) complex with perylene exhibits a similar W-type framework to that of **2**. However, the molecular packing pattern of perylene has changed.[7] The ease of keeping the organic fragment packing in the crystalline complex is basically a function of the shape of the fragment.[27] The more

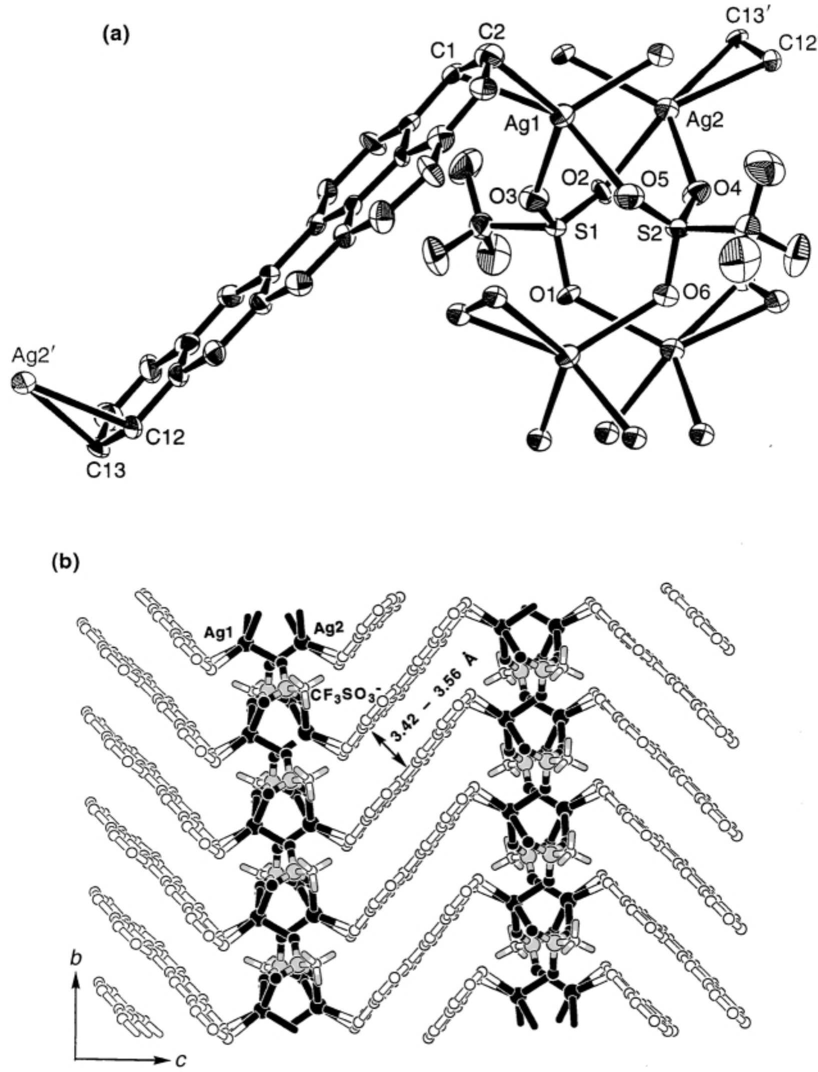
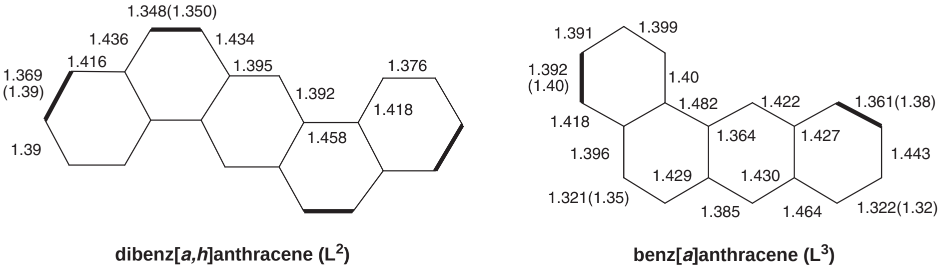


Fig. 4 Crystal structure of compound **4**: (a) labeling scheme (ORTEP, 30% probability) and (b) 2-D multilayer network on the *bc* plane.



dibenz[*a,h*]anthracene (L^2)

benz[*a*]anthracene (L^3)

Chart 1 π-Co-ordination sites (bold lines) in silver(I) complexes of aromatic compounds. The bond lengths are in Å and those in parentheses are for the complexes.

the molecular shape approximates that of a disc, an ellipsoid, or a sphere, which can not be efficiently blocked in the crystal structure, the easier it is for the reorientational motion to take place.[28] Organic molecules, such as benzene, hexamethylbenzene, or larger aromatic carbocyclic compounds, undergo reorientational motions in the solid state with low or very low activation energies or potential barriers,[27,28] while these linear organic ligands are easily blocked in place.

As reported previously,[1,29] delocalized π-electron interaction is a significant structural characteristic of PAHs. An understanding of the relationship between the molecular structure of the "free" ligand and that of its complex would provide insight into the design of solid materials with properties that depend on the arrangement of molecules in crystals. One approach would be to construct organometallic supramolecular compounds by introducing some functional metal groups or ionic chains into the aromatic system without destroying the aromatic packing patterns.

Conclusion

This work demonstrates an interesting wave-like multilayer structure feature of a group of organosilver(I) complexes with linear polycyclic aromatic ligands. Despite the different anions, various co-ordination geometries, distinct bridging modes, and changed aromatic ligands, all the four polymeric complexes retained or partially kept the herringbone packing pattern of their "free" ligands in the solid state. It is believed from this study that the shape of an aromatic ligand is a key factor to dictate the crystal construction and control the structural features in the sophisticated process of molecular self-recognition and self-assembling crystal engineering. The revealing of the structural relation of the complex to its "free" ligand may open the way to the design of solid-state materials and organization of molecules into predictable arrays. On the other hand, these multilayer polymers are of importance in materials science and technology associated with electron delocalization and electronic co-operative interactions. Further investigations in this area including different metal ions and different types of aromatics are clearly warranted.

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