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Construction and Conductivity of W-Type Sandwich Silver(I) Polymers with Pyrene and Perylene

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Introduction

Polycyclic hydrocarbons have been selected as potential donor molecules for preparing metal ion−aromatic π-donor−acceptor complexes with possible applications in electrical conductors and photosensitive devices.[1] This choice probably resulted from the overall planarity of these molecules and the extended delocalized π-system. In this respect silver(I)−aromatic complexes of benzene,[2] cyclophane,[3] indene,[4] acenaphthene,[5] naphthalene,[6] and anthracene[7] have been reported. However, the corresponding compounds of pyrene and perylene have not been structurally defined. Since the first report on an unstable conducting salt of perylene bromide,[8] there have been several publications on molecular metals based on the segregated stacks of perylene or pyrene.[9−11] The physical properties of these solids are mainly due to the existence of the delocalized aromatic conduction electrons. With their unique shape and size and a large number of closely spaced molecular orbitals, pyrene and perylene are expected to produce new materials with the π-electron acceptor silver(I) ion having defined one-, two-, or three-dimensional structures.[2−12] With this goal in mind we conducted a comparative investigation on the structures and electronic properties of the silver(I) complexes of pyrene and perylene. The results of our study are reported herein.

Experimental Section

Preparations were performed under an argon atmosphere using usual Schlenk techniques. All solvents were dried and distilled by standard methods prior to use. Pyrene and perylene (Aldrich Chemical) were used as received. ESR spectra were obtained on a JEOL JES-TE200 ESR spectrometer.

Reaction of pyrene (pyr) or perylene (per) with 2 molar equiv of $AgClO_4 \cdot H_2O$ in 5 mL of benzene yielded a yellow solution, which was transferred to a 6 mm diameter glass tube and layered with *n*-pentane for the pyrene and *n*-hexane for the perylene. The glass tube, sealed under Ar and wrapped with aluminum foil, was left standing at −5 °C for 3 days; pale yellow brick crystals of $[Ag_2(pyr)(ClO_4)_2]$ (**1**) (Anal. Calcd for $C_8H_5ClAgO_4$: C, 31.13; H, 1.63. Found: C, 31.42; H, 1.46.) and orange prisms of $[Ag_2(per)(ClO_4)_2]$ (**2**) (Anal. Calcd for $C_{20}H_{12}Cl_2Ag_2O_8$: C, 36.01; H, 1.80. Found: C, 36.23; H, 1.62.) were isolated.

Crystal data for **1** and **2** are given in Table 1. The crystal, dimensions 0.20 × 0.20 × 0.20 mm for **1** and 0.30 × 0.30 × 0.30 mm for **2**, was mounted in a glass capillary, and room temperature intensity data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation in the $\omega-2\theta$ scanning mode. Each structure was determined by a direct method (MITHRIL)[13] and refined by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all of the non-hydrogen atoms. Hydrogen atoms were located from difference electron density maps but excluded in the refinement. All of the calculations were performed using the TEXSAN package[14] on a micro VAX computer. The selected bond distances and angles are listed in Tables 2 and 3 for **1** and **2**, respectively.

Results and Discussion

X-ray structure determination of the complex **1** with pyrene reveals that it exists in the solid state as an aromatic-linked polymer of dimers lying approximately on the *ab* plane as shown in Figure 1a. Within the dimer, there are two independent Ag(I) ions coupled by one perchlorate oxygen bridging with a Ag(1)···Ag(2) separation of 4.39 Å. Coordination about the silver atom may be described as distorted tetrahedral (taking the C═C group as one ligand). Each metal center is coordinated to two carbon−carbon π bonds from two different pyrene molecules at 2.467(7) and 2.764(6) Å for Ag(1) and 2.507(6) and 2.502(6) Å for Ag(2). These distances are within the limits from 2.47 to 2.92 Å in the reported silver(I)−aromatic complexes.[2−7] The next closest contacts between silver and carbon are 3.038(5) and 3.221(6) Å for Ag(1) and Ag(2), respectively. Furthermore, Ag(1) is chelated by two oxygen atoms of one perchlorate group, O(1) and O(3), at 2.618(7) and 2.576(5) Å, respectively, whereas Ag(2) is bound to one oxygen of two separate perchlorates at distances of 2.562(6) and 2.553(7) Å. Each pyrene moiety exhibits tetra-η^2-coordination, bridging sequentially four metal centers and resulting in a polymeric W-type sandwich of alternating aromatic and silver(I) perchlorate groups running along the *b* axis as shown in Figure 1b.

The structure of the complex **2** with perylene consists of a two-dimensional framework of the metal ions on the *bc* plane bridged by the bidentate counterions and the tetra-η^2-arene groups as shown in Figure 2a. As in **1**, each silver(I) ion acquires its usual coordination number of 4 by forming bonds with the π orbitals of two aromatic entities and two perchlorate oxygen atoms. The four Ag−C bond distances range from 2.420(5) to 2.766(4) Å. Each perchlorate ion links two adjacent silver atoms with Ag−O distances of 2.499(5) and 2.497(5) Å,

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Table 1. Crystallographic Data for [Ag_2(pyr)(ClO_4)$_2$] (**1**) and [Ag_2(per)(ClO_4)$_2$] (**2**)

	1	**2**
formula	$C_8H_5ClAgO_4$	$C_{20}H_{12}Cl_2Ag_2O_8$
fw	308.45	666.95
space group	$P2_1/m$	$P2_1/c$
a, Å	7.888(1)	6.269(2)
b, Å	13.002(2)	14.7130(9)
c, Å	8.3009(8)	10.611(1)
b, (deg)	102.375(9)	98.79(1)
V, Å^3	831.6(2)	967.3(3)
Z	4	2
ρ_{calc}, g cm^{-3}	2.463	2.290
T, K	296	296
μ(Mo Ka), cm^{-1}	27.03	23.33
R^a	0.052	0.038
$R_w{}^b$	0.072	0.053

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$, where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ag_2(pyr)(ClO_4)$_2$] (**1**)

Ag(1)−O(1)	2.618(7)	Ag(1)−O(3)	2.576(5)
Ag(1)−C(2)	2.467(7)	Ag(1)−C(3)	2.764(6)
Ag(2)−O(3)	2.562(6)	Ag(2)−O(6)	2.553(7)
Ag(2)−C(6)	2.507(6)	Ag(2)−C(7)	2.502(6)
O(1)−Ag(1)−O(3)	53.2(2)	O(1)−Ag(1)−C(2)	117.2(1)
O(3)−Ag(1)−C(2)	105.5(1)	C(2)−Ag(1)−C(2′)	125.7(3)
O(1)−Ag(1)−C(3)	122.0(1)	O(3)−Ag(1)−C(3)	86.2(1)
C(2)−Ag(1)−C(3′)	112.1(2)	C(3)−Ag(1)−C(3′)	88.7(3)
O(3)−Ag(2)−O(6)	127.0(2)	O(3)−Ag(2)−C(6)	91.4(1)
O(3)−Ag(2)−C(7)	103.9(1)	O(6)−Ag(2)−C(6)	117.5(1)
O(6)−Ag(2)−C(7)	87.4(1)	C(6)−Ag(2)−C(6′)	106.9(3)
C(6)−Ag(2)−C(7′)	133.8(2)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Ag_2(per)(ClO_4)$_2$] (**2**)

Ag−O(2)	2.499(5)	Ag−O(4)	2.497(5)
Ag−C(1)	2.420(5)	Ag−C(6)	2.766(4)
Ag−C(9)	2.426(5)	Ag−C(10)	2.718(5)
O(2)−Ag−O(4)	74.3(2)	O(2)−Ag−C(1)	114.6(2)
O(2)−Ag−C(6)	103.6(1)	O(2)−Ag−C(9)	106.3(2)
O(2)−Ag−C(10)	133.5(1)	O(4)−Ag−C(1)	109.9(2)
O(4)−Ag−C(6)	136.2(1)	O(4)−Ag−C(9)	110.6(2)
O(4)−Ag−C(10)	101.7(1)	C(1)−Ag−C(9)	128.3(2)
C(1)−Ag−C(10)	110.2(1)	C(6)−Ag−C(9)	111.8(1)
C(6)−Ag−C(10)	109.2(1)		

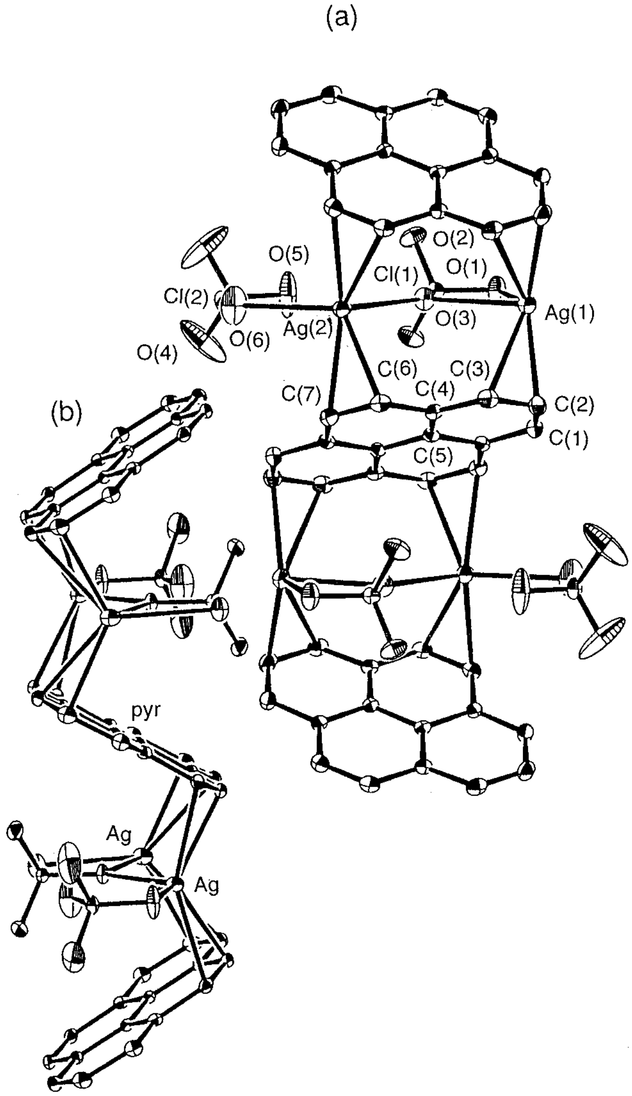

Figure 1. (a) Partial molecular structure of [Ag_2(pyr)(ClO_4)$_2$] and (b) side view showing the W-type sandwich arrangement of the aromatic and silver(I) perchlorate groups (50% probability ellipsoids).

resulting in a two-dimensional W-type sandwich sheet of alternating perylene and silver(I) perchlorate groups. Such 2-D sheets are further connected by the superposed intersheet aromatic $\pi-\pi$ stackings at an average distance of 3.31 Å as illustrated on the *ab* plane in Figure 2b, which generates a three-dimensional network structure.

Perhaps the most significant structure feature of the two silver(I)−aromatic complexes is that both pyrene and perylene, owing to the unique aromatic shape and highly conjugated molecular orbitals, display an unusual symmetric tetra-η^2-coordination, linking four metal atoms and forming W-type sandwich polymeric chain and sheets, which, to the best of our knowledge, has never been characterized in aromatic coordination chemistry. Whereas benzene and other aromatics form the most widely studied section of η^6-ligand transition metal chemistry,[2,15] η^1-, η^2-, or η^3-coordinated arene silver complexes are reported in cyclophane, acenaphthene, and indene.[3−5] In the previously reported naphthalene and anthracene complexes with silver perchlorate, although each aromatic is found to be associated with four silver atoms, it serves essentially as a guest, rather than a linkage, in the water and $AgClO_4$ host lattice.[6,7] In the pyrene-coordinated complex [$(Os(NH_3)_5)_2$(μ-Pyr)](O_3SCF_3)$_4$ the aromatic shows the capacity of a ligand in a di-η^2 fashion to link two $Os(NH_3)_5{}^{2+}$ cations,[16] while in $2BiCl_3$·pyr[17] and (per)$_3$[Bi_4Br_{12}][11b] both pyrene and perylene exhibit a very weak η^6 interaction with bismuth halides.

At room temperature no strong ESR spectrum was observed for either complex. However, the fine crystals of complexes **1** (pale yellow) and **2** (orange) turned black on the surface upon irradiation for 2 days using a 400 W mercury lamp (the interior of the crystals remains the initial color probably because of insufficient irradiation time). The irradiated pyrene complex exhibits an ESR signal with $g = 2.003$ as shown in Figure 3a. The same spectrum was obtained with the perylene (Figure 3b). The characteristic g value of 2.003 for both organometallic complexes may be attributable to the aromatic hydrocarbon radicals.[18] Pyrene has a reduction potential of −2.078 V [V vs

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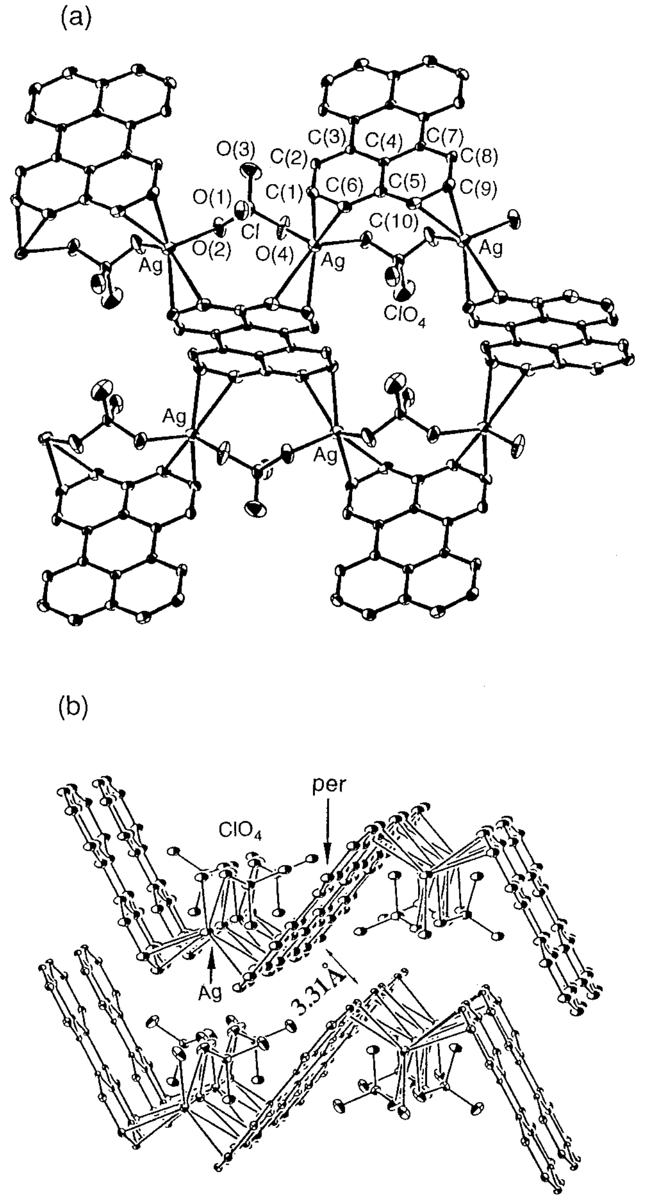

Figure 2. (a) Portion of an infinite 2-D sheet framework in $[Ag_2(per)(ClO_4)_2]$. (b) Overlapping of intersheet perylene molecules at a distance of 3.31 Å resulting in a 3-D network (50% probability ellipsoids).

a saturated calomel electrode (SCE)],[19] which suggests that it can be oxidized to the cation radical along with the light-induced reduction of the silver(I) ion [$E°(Ag^+/Ag^0) = +0.799$ V]. We therefore propose that, upon irradiation of **1** and **2** with light, electron transfer partially takes place from the aromatic donor to the silver(I) ion, giving organic radical cation and silver(0). However, no ESR signal of silver(0) was observed because of its low intensity. In addition, the I_2-doped samples of **1** and **2** also turned black and exhibited even stronger ESR spectra of cation radicals, Figure 3. This suggests that both Per and Pyr can be more effectively oxidized by iodine doping than light irradiation.

The electrical conductivity measurements of compacted pellets were measured by the conventional two-probe technique. Both compounds are electrically nonconducting, whereas their I_2-doped complexes display semiconducting behavior at ambient temperature with σ_{300} values of 1.7×10^{-5} and 4.4×10^{-5} S cm^{-1} for the pyrene and perylene, respectively. The electrical conductivity observed here is presumed to connect mainly with the nonintegral formal oxidation state of the crystallized organic radicals.

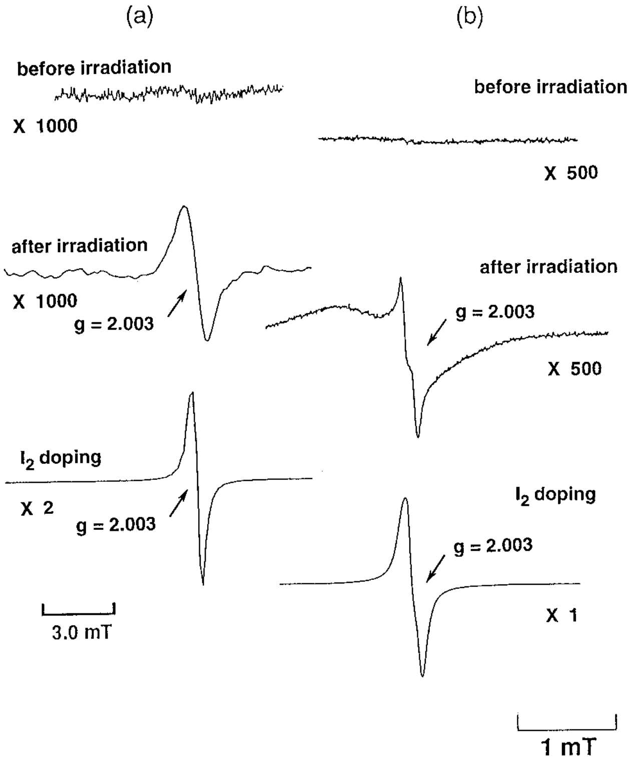

Figure 3. ESR spectra of (a) $[Ag_2(pyr)(ClO_4)_2]$ and (b) $[Ag_2(per)(ClO_4)_2]$ upon irradiation and with I_2 doping.

In conclusion, we have described the first crystallographically characterized silver(I) complexes of pyrene and perylene, which, in addition to providing an unusual tetra-η^2-coordination and the resultant one- and three-dimensional network structures in organometallic chemistry, display typical radical cation ESR spectra and become conducting upon iodination. These conducting radical cation complexes might constitute new functional materials among low-dimensional molecular solids similar to polymetallocenes and multidecker metallacarboranes.[1,20]

We also found that η^2-coordinating C=C bond distances in **1** (C_1-C_3 = 1.375(8) and C_6-C_7 = 1.356(7) Å) are shorter than those of free Pyr (1.395 and 1.367 Å), respectively. Theoretical study on the bond shortening is underway.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters and intramolecular bond lengths and angles for **1** and **2** (14 pages). Ordering information is given on any current masthead page.

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