

Construction of Metal Sandwich Systems Derived from Assembly of Silver(I) Complexes with Polycyclic Aromatic Compounds

Megumu Munakata,* Liang Ping Wu, Gui Ling Ning, Takayoshi Kuroda-Sowa, Masahiko Maekawa, Yusaku Suenaga, and Naoto Maeno

Contribution from the Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

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Abstract: A new class of metal sandwich complexes of silver derived from silver(I) perchlorate and fluoranthene (L^1), benzo[ghi]perylene (L^2), [2,2]paracyclophane (L^3), and decacyclene (L^4) was prepared. The idea behind the use of polycyclic aromatic compounds as an alternative approach for construction of organometallic sandwich systems is to combine the plasticity of the metal ion and planarity and coordinative diversity of the hydrocarbons. Structural studies by single-crystal X-ray diffraction have shown that all compounds contain extended one- to three-dimensional structures in which several metal atoms are sandwiched between two fused polycyclic systems. While complex **1**, $[Ag_3(L^1)_2(ClO_4)_3]$, exists in the solid state as a two-dimensional W-type architecture in which $AgClO_4$ layers are separated by two sheets of hydrocarbon, complex **2**, $[Ag(L^2)(ClO_4)]_4$ ·toluene, contains two double-decker polymeric chains coupled via extensive aromatic π - π stackings. Pillared brick sandwiched framework was observed in **3**, $[Ag(L^3)(ClO_4)]$, whereas the multidecker sandwich complex **4**, $[Ag_2(L^4)(ClO_4)_2]$ ·(benzene), is reminiscent of ladder. The structure of L^1 has been redetermined and that of L^2 reported; the structural data are used for discussion of the silver- π interactions. The electrochemical behavior and ESR spectra are consistent with formation of the organic radical species in the system. The present findings may represent an alternative approach for predesigning the multilayered systems in organometallic chemistry.

Introduction

Much of the current interest in the extended polymeric metal sandwich compounds hinges on the design of new solids with structural diversity and desired physical and chemical properties.¹ Since the first report on the synthesis of [2,2]paracyclophane in which two benzene rings are held face to face by methylene bridges,² and the accidental discovery of the epoch-making compound, ferrocene,³ the metal sandwich systems have enjoyed unabated research interest for half a century in organometallic chemistry. These organotransition-metal sandwiches based on either bifacial metal coordination to a single unsaturated ligand or coordination to two such ligands joined in a stack are often highly anisotropic, and thus possess intriguing electrical, electrochemical, and one-dimensional conductive properties.^{4–9}

* To whom correspondence should be addressed. E-mail: munakata@chem.kindai.ac.jp.

(1) Selected references: (a) Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805. (b) Grimes, R. N. *Pure Appl. Chem.* **1987**, *59*, 847. (c) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (d) Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 857. (e) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (f) Amato, I. *Science* **1993**, *260*, 753. (g) Service, R. F. *Science* **1994**, *265*, 316.

(2) (a) Brown, C. J.; Farthing, A. C. *Nature* **1949**, *164*, 915. (b) Cram, D. J.; Steinberg, H. J. *Am. Chem. Soc.* **1951**, *73*, 5691.

(3) (a) Kealy, T. J.; Pauson, P. J. *Nature* **1951**, *168*, 1039. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632.

(4) Staab, H. A.; Zapf, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 757. (5) (a) Plitzko, K.-D.; Rapko, B.; Gollas, B.; Wehrle, G.; Weakley, T.; Pierce, D. T.; Geiger, W. E.; Haddon, R. C.; Boekelheide, V. *J. Am. Chem. Soc.* **1990**, *112*, 6545. (b) Plitzko, K.-D.; Boekelheide, V. *Organometallics* **1988**, *7*, 1573. (c) Edwin, J.; Bochmann, M.; Böhm, M. C.; Brennan, D. E.; Geiger, W. E.; Krüger, C.; Pebler, J.; Pritzkow, H.; Siebert, W.; Swiridoff, W.; Wadepohl, H.; Weiss, J.; Zenneck, U. *J. Am. Chem. Soc.* **1983**, *105*, 2582.

(6) Hopf, H.; Dannheim, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 701.

Further development of the metal sandwich systems in organometallic chemistry requires synthetically accessible versatile ligands and calls for advances in methodology which can lead to a high level of control over molecular interactions. The latest developments in materials science initiated a renaissance in the exploration of polycyclic aromatic compounds as potential donor molecules for preparing donor-acceptor materials,^{10–12} and as building blocks for formation of macromolecules and supramolecular assemblies.^{13–15} Up to now, however, no attempt

(7) Jutzi, P.; Siemeling, U.; Müller, A.; Bögge, H. *Organometallics* **1989**, *8*, 1744.

(8) Foxman, B. M.; Gronbeck, D. A.; Rosenblum, M. *J. Organomet. Chem.* **1991**, *413*, 287.

(9) (a) Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics* **1991**, *10*, 2631. (b) Wang, X.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 4668. (c) Wang, X.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1995**, *34*, 6509. (d) Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 12218. (e) Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 12227.

(10) (a) Janiak, C. *Chem. Ber.* **1993**, *126*, 1603. (b) Janiak, C.; Hemling, H. *Chem. Ber.* **1994**, *127*, 1251.

(11) (a) Bock, H.; Seitz, W.; Sievert, M.; Kleine, M.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2244. (b) Bock, H.; John, A.; Havlas, Z.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 416. (c) Bock, H.; John, A.; Näther, C.; Havlas, Z.; Mihokova, E. *Helv. Chim. Acta* **1994**, *77*, 41. (d) Bock, H.; Gharagozloo-Hubmann, K.; Näther, C.; Nagel, N.; Havlas, Z. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 631.

(12) (a) Ayllón, J. A.; Santos, I. C.; Henriques, R. T.; Almeida, M.; Lopes, E. B.; Morgado, J.; Alcácer, L.; Veiras, L. F.; Duarte, M. T. *J. Chem. Soc., Dalton Trans.* **1995**, 3543. (b) Nakamura, Y.; Tsuihiji, T.; Mita, T.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Am. Chem. Soc.* **1996**, *118*, 1006. (c) Battaglia, L. P.; Bellitto, C.; Cramarossa, M. R.; Vezzosi, I. M. *Inorg. Chem.* **1996**, *35*, 2390.

(13) (a) Cochran, J. E.; Parrott, T. J.; Whitlock, B. J.; Whitlock, H. W. *J. Am. Chem. Soc.* **1992**, *114*, 2269. (b) Ferguson, S. B.; Sanford, E. M.; Seward, E. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 5410. (c) Marquis-Rigault, A.; Dupont-Gervais, A.; Baxter, P. N. W.; Dorsselaer, A. V.; Lehn, J.-M. *Inorg. Chem.* **1996**, *35*, 2307.

has been made systematically to use polycyclic aromatics as a building block for multilayered metal complexes, whether oligomeric or polymeric.^{16,17} This is surprising, since such hydrocarbons would be very advantageous in respect of combining the synthetic simplicity with the structural versatility and allowing efficient metal–metal communication by connecting metal centers with double-layered organic π -donors. The recent report from Bard's lab that electrochemical oxidation of a nine-ring polyaromatic hydrocarbon produced a new type of conductive ladder polymer with striking electrochromic properties presents an alternative route to layered organic polymers.¹⁸ We are using a building-block approach for the construction of multidimensional coordination polymers through incorporation of coordination bonds, intermolecular forces, and π – π interactions.^{19,20} The possibility that polymers derived from transition-metal complexes of polycyclic aromatic hydrocarbons might show interesting electrical and/or magnetic properties associated with electron delocalization and electronic cooperative interactions has motivated us to prepare various supramolecular silver(I) complexes with diversity of topologies.²⁰ On the basis of cation– π interactions, we have succeeded recently in constructing a new type of air-stable metal sandwich organosilver(I) systems with polycyclic aromatic hydrocarbons fluoranthene (L^1), benzo[ghi]perylene (L^2), [2,2]paracyclophane (L^3), and decacyclene (L^4). These aromatic ligands, unlike the aforementioned centrally π -bonded cyclophane or ferrocene multilayered systems where all the carbon atoms on the delocalized ligand plane participate in coordination, exhibit only η^1 and/or η^2 coordination by peripheral carbon atoms.^{21,22} Such ligands combining good ligating properties and perfect planarity concurrently interacting with metal ions above and below rings give them great promise as an alternative approach to the effective self-assembly of high-nuclearity complexes in a multilayer fashion. The results of our study are reported herein.

(14) (a) Bell, T. W.; Jousselein, H. *J. Am. Chem. Soc.* **1991**, *113*, 6283. (b) Seiders, T. J.; Baldrige, K. K.; O'Connor, J. M.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 4781. (c) Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Terzis, A.; Strouse, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 9480.

(15) (a) Aoyama, Y.; Endo, K.; Anzai, T.; Yamaguchi, Y.; Sawaki, T.; Kobayashi, K.; Kanekisa, N.; Hashimoto, H.; Kai, Y.; Masuda, H. *J. Am. Chem. Soc.* **1996**, *118*, 5562. (b) Swift, J. A.; Pal, R.; McBride, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 96. (c) Wu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 297. (d) Udachin, K. A.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1080.

(16) Oelcker, B.; Chávez, I.; Manríquez, M.; Román, E. *Organometallics* **1993**, *12*, 3396. Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 2039. Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281. Katz, T. J.; Acton, N.; McGinnis, J. *J. Am. Chem. Soc.* **1972**, *94*, 6205.

(17) (a) Bochkarev, M. N.; Fedushkin, I. L. *J. Organomet. Chem.* **1991**, *410*, 321. (b) Bochkarev, M. N.; Fedushkin, I. L.; Cherkasov, V. K.; Nevodchikov, V. I.; Schumann, H.; Görlitz, F. H. *Inorg. Chim. Acta* **1992**, *201*, 69. (c) Bennett, M.; Neumann, H.; Thomas, M.; Wang, X. *Organometallics* **1991**, *10*, 3237. (d) Bush, B. F.; Lagowski, J. J. *Organometallics* **1988**, *7*, 1945.

(18) Debad, J. D.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 2476.

(19) (a) Munakata, M.; Wu, L. P.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Am. Chem. Soc.* **1996**, *118*, 3117. (b) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1727. (c) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173.

(20) (a) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997**, *36*, 4903. (b) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8610.

(21) Fukui, K.; Imamura, A.; Yonezawa, T.; Nagata, C. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1076.

(22) (a) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 743. (b) Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1972**, *11*, 388. (c) Rodesiler, P. F.; Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 761. (d) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 5407.

Experimental Section

General Procedures. All 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. Reagent grade fluoranthene, benzo[ghi]perylene, [2,2]paracyclophane, and decacyclene were purchased from Aldrich and used as received. $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (Aldrich) was dried at 40 °C under reduced pressure for 5 h before use. All other chemicals were purchased from Wako Pure Chemical, Inc. IR spectra were recorded as KBr disks on a JASCO 8000 FT-IR spectrometer. ESR spectra were obtained on JEOL JES-TE200 ESR spectrometer. Cyclic voltammetric measurements were carried out using a polarographic analyzer P-1100 (made in Japan), employing a platinum-disk working electrode, a saturated Ag/AgCl reference electrode (stored in concentrated aqueous KCl when not in use), and a platinum wire as the auxiliary electrode. UV–visible spectra were recorded on a Hitachi 150-20 spectrophotometer. All crystallization of the silver complexes were carried out in the dark. **Caution:** Although no problems were encountered during the preparation of the perchlorate salt described below, suitable care and precautions should be taken when handling such a potentially hazardous compound.

Syntheses. $[\text{Ag}_3(L^1)_2(\text{ClO}_4)_3]$ (**1**). A solution of $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (67.5 mg, 0.3 mmol) in 10 mL of toluene was added fluoranthene (121.4 mg, 0.6 mmol). After stirring for 10 min the resultant colorless solution was filtered. The filtrate was introduced into a 7 mm diameter glass tube and 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 1 month; light yellow prismatic crystals of **1** were obtained. Anal. Calcd. for $\text{C}_{32}\text{H}_{20}\text{Ag}_3\text{Cl}_3\text{O}_{12}$: C, 37.41; H, 1.95. Found: C, 37.15; H, 2.00.

$[\text{Ag}(L^2)(\text{ClO}_4)]_4$ ·Toluene (**2**). The yellow plate crystals of **2** were prepared in the same way as **1** using benzo[ghi]perylene (13.8 mg, 0.05 mmol) instead of fluoranthene. Anal. Calcd. for $\text{C}_{95}\text{H}_{56}\text{Ag}_4\text{Cl}_4\text{O}_{16}$: C, 56.25; H, 2.76. Found: C, 55.20; H, 2.79. The large discrepancy for carbon data is related to partial release of the solvated toluene molecules (the formula without toluene molecules would require C, 54.58; H, 2.48. See the following discussion).

$[\text{Ag}(L^3)(\text{ClO}_4)]$ (**3**). The colorless solution of benzene (4 mL) containing 22.5 mg of $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (0.1 mmol) was introduced into a glass tube and layered with 4 mL of toluene solution of [2,2]-paracyclophane (21 mg, 0.1 mmol). The glass tube was sealed and after standing for 3 days, colorless brick single crystals of **3** were isolated. Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{AgClO}_4$: C, 46.20; H, 3.85. Found: C, 46.64; H, 4.06.

$[\text{Ag}_2(L^4)(\text{ClO}_4)_2(\text{benzene})]$ (**4**). On gentle heating, decacyclene (18.2 mg, 0.04 mmol) was dissolved in a mixed solution of benzene (8 mL) and nitrobenzene (4 mL). The clear solution was cooled to room temperature and then $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (42 mg, 0.2 mmol) was added. The mixture was stirred for 20 min and filtered. The filtrate was transferred to a glass tube and layered with *n*-hexane. After the solution was allowed to stand for 4 weeks at room-temperature, brown needle crystals of **4** were isolated. Anal. Calcd. for $\text{C}_{42}\text{H}_{24}\text{Ag}_2\text{Cl}_2\text{O}_8$: C, 53.43; H, 2.54. Found: C, 53.28; H, 2.26.

X-ray Data Collection, Structure Solution, and Refinement. All measurements were carried out at room temperature on a Rigaku AFC7R diffractometer. Periodic remeasurement of three standard reflections revealed no significant crystal decay or electronic instability for all the compounds except **3**. Over the course of data collection for **3**, the standards decreased by 2.8%. A linear correction factor was applied to the data to account for this phenomenon. Intensities were measured from continuous ω – 2θ scans. All intensity data were corrected for Lorentz polarization effects. All the full-occupancy non-hydrogen atoms were refined anisotropically. The counteranions ClO_4^- were found to have high thermal motions in each case. The highest residual peaks for **4** resulted from this disorder. Hydrogen atoms of the six structures were introduced in their calculated positions; they are included, but not refined, in the refinement. In **2**, the hydrogen atoms for toluene molecules are excluded. The structures were solved by direct methods followed by subsequent Fourier-difference calculation and refined by a full-matrix least-squares analysis on F using the

Table 1. Crystallographic Data

	L ¹	L ²	1	2	3	4
formula	C ₃₂ H ₂₀	C ₂₂ H ₁₂	C ₃₂ H ₂₀ Ag ₃ Cl ₃ O ₁₂	C ₉₅ H ₅₆ Ag ₄ Cl ₄ O ₁₆	C ₁₆ H ₁₆ AgClO ₄	C ₄₂ H ₂₄ Ag ₂ Cl ₂ O ₈
fw	404.51	276.34	1026.47	2026.76	415.62	943.29
cryst color, habit	colorless, prismatic	yellow, prismatic	yellow, prismatic	yellow, plate	colorless, brick	brown, prismatic
cryst dimens, mm	0.20 × 0.20 × 0.30	0.20 × 0.25 × 0.35	0.25 × 0.15 × 0.35	0.40 × 0.40 × 0.20	0.15 × 0.15 × 0.20	0.20 × 0.10 × 0.20
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	18.398(4)	9.837(5)	15.789(2)	29.538(3)	7.934(1)	13.290(4)
<i>b</i> , Å	6.232(3)	11.874(6)	6.188(4)	10.882(1)	17.932(1)	31.599(5)
<i>c</i> , Å	19.902(3)	11.658(2)	16.816(2)	24.084(2)	10.6046(9)	7.774(3)
β, deg	109.88(1)	98.35(3)	111.115(7)	110.275(6)	92.097(9)	92.46(3)
<i>V</i> , Å ³	2145(1)	1347.3(8)	1532.7(9)	7262(1)	1507.7(2)	3261(1)
<i>Z</i>	4	4	2	4	4	4
<i>d</i> (calcd), g cm ⁻³	1.252	1.362	2.224	1.854	1.831	1.921
<i>F</i> (000)	848	576	1000	4040	832	1872
μ, cm ⁻¹	0.71	0.77	22.23	12.85	15.25	14.23
no. of reflns measd	3203	3263	3634	17100	3702	8025
no. of obsd data	957	1109	2665	8236	2093	3794
(<i>I</i> > 3.00σ(<i>I</i>))	(<i>I</i> > -10.00σ(<i>I</i>))					
no. of parameters	289	199	231	1072	199	487
<i>R</i> ^a , <i>R</i> _w ^b	0.043, 0.046	0.058, 0.065	0.030, 0.040	0.051, 0.060	0.046, 0.055	0.056, 0.064
goodness of fit	1.27	1.90	1.51	1.78	1.57	1.73
max, min peaks in final difference map/e Å ⁻³	0.12, -0.15	0.16, -0.18	0.60, -0.74	0.88, -0.75	0.70, -0.69	1.33, -0.99

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

TEXSAN package.²³ Details of the X-ray experiments and crystal data are summarized in Table 1. Final atomic coordinates, bond lengths, and bond angles for all structures are given in the Supporting Information.

Results and Discussion

Syntheses and Infrared Spectroscopy. The reactions of the four commercially available aromatics, L¹–L⁴ with silver(I) perchlorate carried out at ambient temperature afforded the complexes **1**–**4** in high yields. These salts once isolated are reasonably stable in the open laboratory environment, but they show moisture sensitivity at room temperature. Their solubilities in standard organic solvents are very low, suggesting coordination polymers. The synthesis of these organometallics can be thought of as a type of dynamic combinatorial chemistry, achieved by combining the appropriate metal salt and a large planar ligand in a suitable solvent. It seems that large coordinating oxyanions such as ClO₄⁻ and CF₃SO₃⁻ play a key role in stabilizing the silver(I) π complexes.^{20,22} Among the silver(I) salts in hand, both the nitrate and acetate have low solubility in organic solvents such as benzene, toluene, and xylene. Although silver(I) triflate is soluble in toluene, its reaction with the aromatics was very slow. The reactivity of AgClO₄ with the aromatic hydrocarbons was systematically examined in solvents with different polarity. Similar reactions to that described in the Experimental Section but performed in other solvents such as methanol, acetone, and diethyl ether lead to no evidence for formation of an isolable complex, although the variation of the ¹H NMR spectra line widths in these solvents suggests that some interaction may occur. Silver(I) perchlorate does react with decacyclene in tetrahydrofuran, but the crystals isolated are in cubic rather than in needle shape as obtained in benzene. In addition, the product is soluble in most organic solvents. Its structure, which will be reported in a separate paper, has been shown by X-ray analysis to be another complex containing coordinated THF molecules. Since decacyclene is sparingly soluble in benzene or toluene, hot nitrobenzene was employed

in preparation of **4** to assist dissolution of the aromatic. These facts indicate that polymeric aromatic structures containing silver(I) ions are strongly solvent dependent. In general, we have found both benzene and toluene to be the most favorable solvents to isolate the compounds in solution in the majority of cases.

Characterization of the compounds was mainly based on X-ray diffraction studies. Nevertheless, infrared spectroscopy is a good indicator of incorporation of metal ions into the polymeric aromatic system. The infrared spectra were recorded in the region 4000–400 cm⁻¹ on KBr disks. The four aromatic ligands have several distinctive signals, including an aromatic CH stretching at 3046–3052 cm⁻¹. A second region, from 1304 to 1614 cm⁻¹, consists of three or four quite intense signals, corresponding to the in-plane vibrations of the C=C bonds. All of these are present in the infrared spectra of **1**–**4**. In addition, each complex exhibits a strong split absorption of ν(OCI) at 1086–1142 cm⁻¹, consistent with the general trend that the unidentate or bidentate coordination of the perchlorate ion to the metal occurs in the complexes prepared in nonaqueous solvents.

Crystal Structures of Free Ligands L¹ and L². In order to gain an insight into cation–π interactions, the crystal structure of the metal free ligand L² was determined by X-ray analysis. Along with that, the structural redetermination of L¹ was carried out in an attempt to obtain more accurate data since the results from the previous study of fluoranthene based on X-ray and neutron diffraction show some discrepancies.²⁴ Single crystals for both L¹ and L² were obtained by diffusion of *n*-pentane into benzene (or toluene) solution containing fluoranthene or benzo-[ghi]perylene. Both compounds crystallized in monoclinic system and the segregated molecules in the cell do not involve significant intermolecular interactions. We do not deal with any detailed structures here since their structural data are presented in the Supporting Information. The results from X-ray analysis of L¹, apart from giving better *R* values, are in good agreement

(23) TEXSAN: Crystal Structural Analysis Package. Molecular Structure Corp.: Houston, TX, 1985 and 1992.

(24) Hazell, A. C.; Jones, D. W.; Sowden, J. M. *Acta Crystallogr.* **1977**, *B33*, 1516.

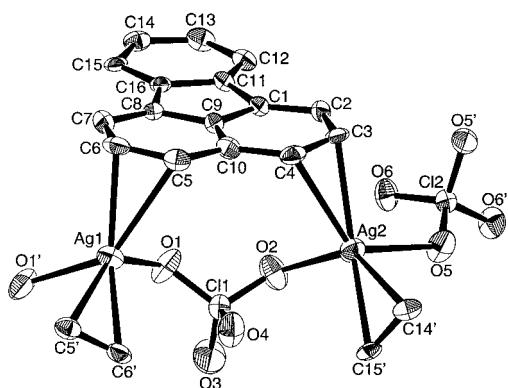


Figure 1. Structure and labeling of 1.

with the previously reported data including crystal parameters and little distortion of the ligand from planarity.²⁴

W-type Metal Sandwich [Ag₃(L¹)₂(ClO₄)₃] (1). The molecular structure of complex 1 together with numbering scheme is shown in Figure 1. The crystallographic studies revealed that complex 1 exists in the solid state as a two-dimensional polymer of silver(I) sandwiched by the aromatic groups. The crystallographically independent Ag(1) and Ag(2) lie in a mirror plane along with two oxygens of each perchlorate group. Each silver is bonded to two oxygen atoms of different perchlorate groups at Ag–O distances ranging from 2.447(3) to 2.477(3) Å. The coordination polyhedron of the metal ion is completed to four (taking the C=C group as one ligand) by interaction with the π orbitals of the aromatics on either side of the mirror plane. The Ag–C bond distances range from 2.410(4) to 2.655(4) Å for Ag(1), and 2.479(3) to 2.686(4) Å for Ag(2), well within the limits from 2.47 to 2.77 Å in the reported silver(I)–aromatic complexes.^{20–22} The next closest contacts between silver and carbon are 3.04 and 3.22 Å for Ag(1) and Ag(2), respectively. Each aromatic group asymmetrically tri- η^2 interacts with three metal ions below and above the ligand plane, linking two –Ag–O₂ClO₂–Ag– chains. The overall result of this arrangement is that the AgClO₄ chains lie in sheets with aromatics on either side such that the packing consists of a sequence of sheets: \cdots aromatic \cdots ionic \cdots aromatic \cdots in a W-type fashion as shown in Figure 2. This type of 2-D framework has been observed previously in pyrene and perylene complexes where each aromatic molecule involves a tetra- η^2 -coordination mode interacting symmetrically with four Ag(I) ions above and below the ligand plane.^{20a} Complex 1 is unusual in a sense that all the fluoranthene molecules are arranged alternately in two different orientations in order to give an overall equal number of π interactions (three) on both sides of the plane for every two neighboring aromatics despite asymmetric bonding of each individual group.

Double-Decker Metal Sandwich [Ag(L²)(ClO₄)₄·Toluene] (2). The unit-cell contents, as determined by the structural study, showed that the stoichiometry of the complex was a 1:1:1 metal-to-ligand-to-anion tertiary system; however, molecules of solvent also exist independently of the complex in lattice interstices. The molecular structure of 2 together with the atomic numbering scheme is given in Figure 3. This compound can be regarded as both a coordination polymer and a stacking polymer. The two-dimensional network shows two types of cationic chains, Ag(1)/Ag(2) and Ag(3)/Ag(4). The basic unit of the well-defined portion of the structure is a dimeric double-decker [Ag(L²)(ClO₄)₂] species with the two silver atoms bridged by one perchlorate group [Ag(1)–O(1) = 2.430(9) Å, Ag(2)–O(2) = 2.425(7) Å, Ag(3)–O(11) = 2.52(1) Å, and Ag(4)–O(9) =

2.470(7) Å]. The metal–metal distance between Ag(1) and Ag(2) is 4.08 Å and that between Ag(3) and Ag(4) is 4.20 Å. Within each double-decker unit the two silver ions are sandwiched by two μ -di- η^2 -benzo[ghi]perylene moieties with Ag–C distances ranging from 2.407(7) to 2.578(8) Å. Each aromatic is planar within experimental error, and the bond distances and angles are not too dissimilar from that of the free molecule. The average interplanar separation between the two benzo[ghi]perylene molecules within the double-decker unit is 3.51 Å, suggesting presence of aromatic interactions.²⁵ The overlap between the two aromatics at the end part opposite to metal coordination site is very small. Due to lack of strong π – π interactions within the double-decker, the two aromatic planes are not significantly deviated from planarity with the mean deviation from the aromatic plane being 0.04 Å. This is in sharp contrast with the observation in the triple-decker coronene complex where the unique interplanar aromatic interactions cause the outer metallomacrocyclic to bend by 0.25 Å.^{20b} Each double-decker unit is linked to its two nearby counterparts via the coordination of a second perchlorate group to each polyhedral metal ion [Ag(1)–O(6) = 2.530(5) Å, Ag(2)–O(5) = 2.543(5) Å, Ag(3)–O(14) = 2.492(7) Å, and Ag(4)–O(16) = 2.528(5) Å]. This gives a pair of independent infinite one-dimensional AgClO₄ chains sandwiched by the hydrocarbons (Figure 4). These two chains are held together via extensive face to face interchain π – π interactions between the two adjacent aromatic planes. The interplanar separations are within 3.36–3.51 Å range, and the complexes are thus linked in a columnar fashion to generate a supramolecular architecture of an infinite two-dimensional sheet. The solvate toluene molecules occupy the void space between the chains and are not involved in intermolecular contacts. These molecules can be partially removed from the lattice with a slow stream of dry argon. Therefore, the calculated values and the observed values for elemental analysis of 2 show large discrepancies.

Pillared Brick Metal Sandwich [Ag(L³)(ClO₄)₄] (3). Figure 5 depicts a perspective view with atom numbering of the molecule. Complex 3 is also a 1:1:1 metal-to-ligand-to-anion tertiary system, but without participation of molecules of solvent in lattice. The structure contains a dinuclear core, Ag₂O₂, in which each silver(I) ion is tetrahedrally coordinated to one oxygen atom of the two symmetry related perchlorate anions and sandwiched by two distinct paracyclophane ligands. The rhombic ring formed by bridging of the two oxygen atoms between pairs of silver atoms leads to a Ag \cdots Ag distance of 4.29 Å and Ag–O(1)–Ag bond angle of 115.7(2)°. Each paracyclophane group is acting as a linkage between the two dinuclear units by a μ -di- η^2 -coordination fashion. The four Ag–C distances are unequal ranging from 2.412(7) to 2.719(7) Å. It is surprising that the bond length Ag–C(1) is as much as 0.3 Å shorter than Ag–C(2), while the rest of the bond distances for the silver atom are comparable. The two paracyclophanes bonded to the same metal ion face up to each other, not stacked one above the other but slightly slipped, and are associated together by weak π – π interactions with an intermolecular separation ranging from 3.47 to 4.20 Å. A two-dimensional pillared brick arrangement of the aromatic sandwiched metal units results which spreads out along the diagonal axis of the *ac* plane. Previously the synthesis and phosphorescent property of the [2,2]paracyclophane complex of silver perchlorate was reported, but its structure remains unknown until this work.^{26,27} On the other hand, the present structure differs significantly from that of [2,2]paracyclophane(tetrachlorogal-

(25) (a) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101. (b) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, 112, 5525.

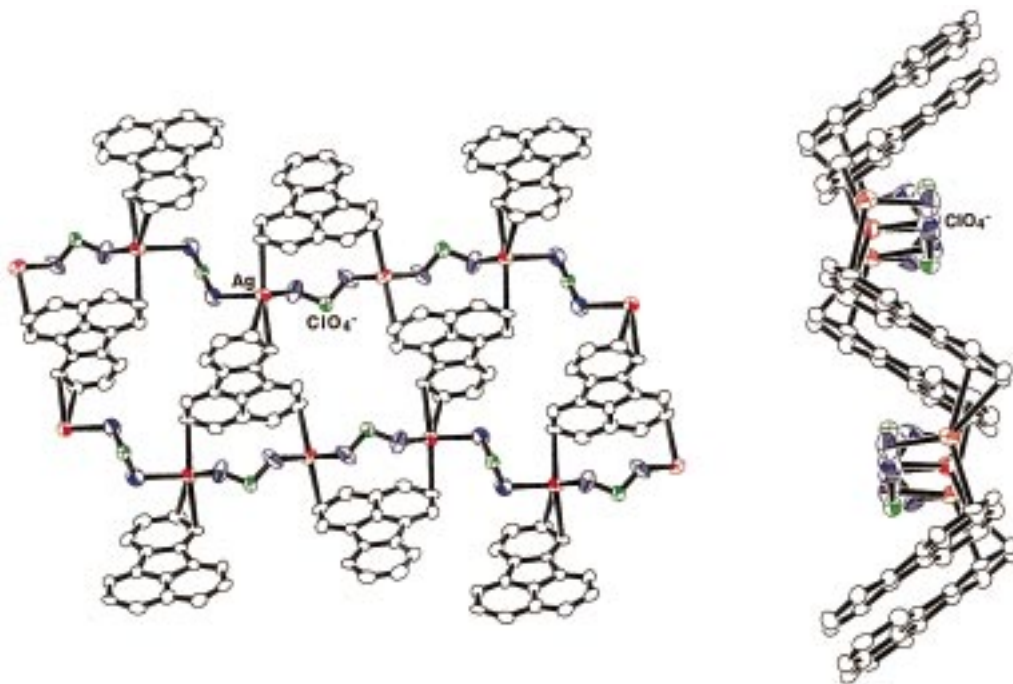


Figure 2. Perspective views of the packing of **1** down the crystallographic *b* axis (left) and *a* axis (right).

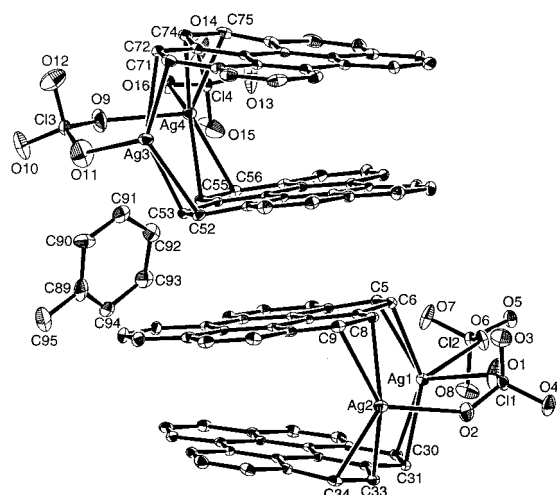


Figure 3. Structure and partial labeling of **2**.

lato)silver, $[\text{AgL}^3(\text{GaCl}_4)]$, where the two-dimensional network is based on chains of metal ions cross-linked by $\mu\text{-}\eta^2/\eta^3$ hydrocarbons and $\mu\text{-GaCl}_4^-$ anions.²⁶

Multidecker Metal Sandwich $[\text{Ag}_2(\text{L}^4)(\text{ClO}_4)_2(\text{benzene})]$ (4**).** The molecular structure and atom numbering scheme of **4** is given in Figure 6. The neutral complex exists in the solid state as an aromatic-linked polymeric multidecker lying approximately on the *ab* plane as shown in Figure 7. The multilayered structure is formed by the cationic $[\text{Ag}_2(\text{L}^4)]$ building blocks while the ClO_4^- anions and solvate benzene molecules reside on the side of the parallel layers. The decacyclene molecules are arranged alternately in two orientations and adopt staggered conformation within a pair. The cationic layers lie perpendicular to the crystallographic *c* axis with an interlayer separation ranging from 3.33 to 3.51 Å, suggesting the presence of strong $\pi\text{-}\pi$ interactions between the adjacent layers. The coordination geometry about the Ag ions

is a distorted tetrahedron comprising one crystallized solvate benzene molecule, one oxygen atom from the perchlorate ion, and two carbon-carbon π interactions from decacyclene. Each aromatic ligand exhibits a $\mu\text{-tetra-}\eta^2$ -coordination bound to four metal centers with two on each side of the ring. Remarkably, in order to achieve such a structure, it is necessary for the highly symmetric decacyclene (D_{3h}) to be asymmetrically coordinated to four Ag(I) ions at irregular positions. In addition, the deviation from ideal planar geometry is most readily seen by inspecting the dihedral angles between the acenaphthene plane and the central benzene ring. Although each of the three acenaphthene moieties of the decacyclene group is essentially planar, it deviates from the mean plane of the central benzene ring by $7.25^\circ\text{--}13.73^\circ$. Nevertheless, the Ag-C bond lengths fall within the expected range and are similar to those in **1-3**.

Examination of the cell-packing diagram revealed the polymeric nature of **4**. The infinite multideckers run parallel to one another and do not form any short interdecker contacts. Thus, the multidecker network of **4** is reminiscent of a ladder in which the decacyclene molecules constitute the rungs, and the silver atoms sequence the legs. The cavity generated between the individual rungs of the ladder approximately resembles a rectangular space of 11.9×3.5 Å. The benzene molecules do not penetrate the cavity to be involved in short host-guest contacts; instead, they are positioned halfway between the rungs and oriented outward the ladder. The center of the benzene molecule lies on the 2-fold axis and interacts with two metal centers from two paralleled multideckers. Thus, each multidecker column is linked to four neighboring multideckers through $\mu\text{-di-}\eta^1$ -coordination of the benzene molecules to form three-dimensional multidecker networks.

Electronic Structure of Hydrocarbon Radicals. Typically, aromatic hydrocarbons in their transition metal complexes can form charge transfer species or even organic radicals depending on the degree of charge transfer in the ground state.^{28,29} The electronic structures of radicals were first studied by electronic absorption spectroscopy. The UV-visible spectra of the double-

(26) Schmidbauer, H.; Bublak, W.; Huber, B.; Reber, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1089.

(27) Zander, M. *Z. Naturforsch. A* **1984**, *39*, 1009.

(28) Schmitt, R. D.; Wing, R. M.; Maki, A. H. *J. Am. Chem. Soc.* **1969**, *91*, 4394.

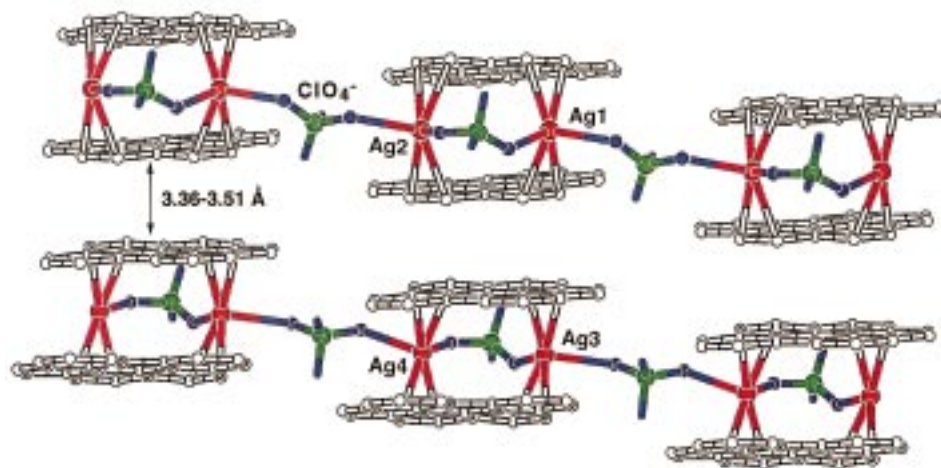


Figure 4. Double-decker polymeric structure of **2**.

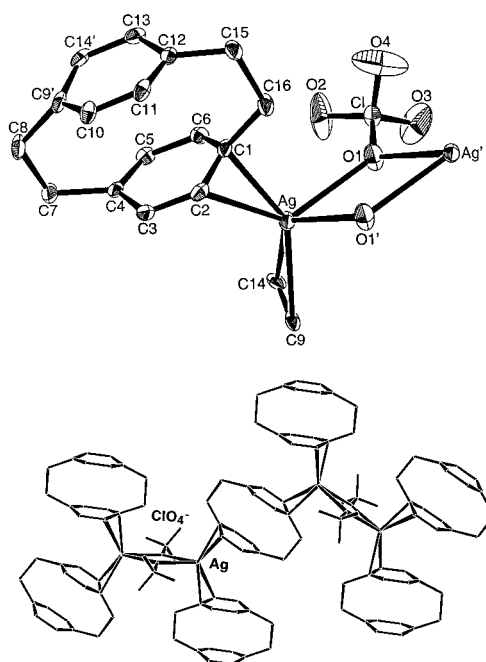


Figure 5. View of the molecular structure of **3**.

decker **2** and mutidecker **4** in solution exhibit one major and one or more small bands, with the dominant band having maximum absorbance between 400 and 420 nm. This falls within the range of maxima in the spectra of donor–acceptor complexes of the highly conjugated aromatic molecules pyrene and perylene.²⁸ In addition, the high extinction coefficients are strongly suggestive of charge-transfer excitations.

The redox behavior of compounds **1**, **2**, and **4** was probed by solution electrochemistry. The solutions of up to approximately 1 mM were prepared in THF and proved adequate for electrochemical measurements. The resulting cyclic voltammograms are shown in Figure 8. The CV for **1** and **2** are very similar, except for the potential at which the redox process occurs. For this reason only those for **1** and **4** are shown in the figure. Each voltammogram shows two distinct redox processes, related respectively to one aromatic-based and one metal-based electrochemical reactions. In support of this, the CV of the free ligands L¹, L², and L⁴ were recorded in the same conditions

(29) Davies, A. G.; McGuchan, D. C. *Organometallics* **1991**, *10*, 329. Courtneidge, J. L.; Davies, A. G. *Acc. Chem. Res.* **1987**, *20*, 90. Davies, A. G.; Shields, C. J. *Chem. Soc., Perkin Trans. 2* **1989**, 1001.

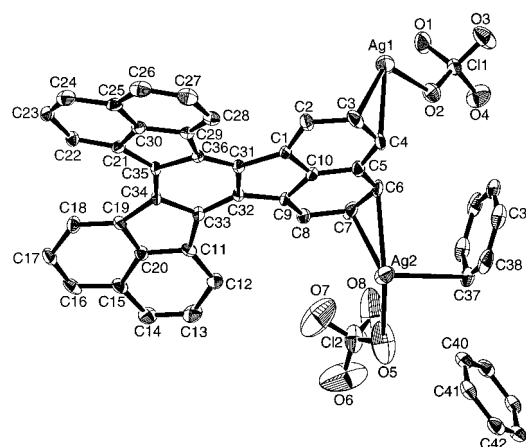


Figure 6. Structure and labeling of **4**.

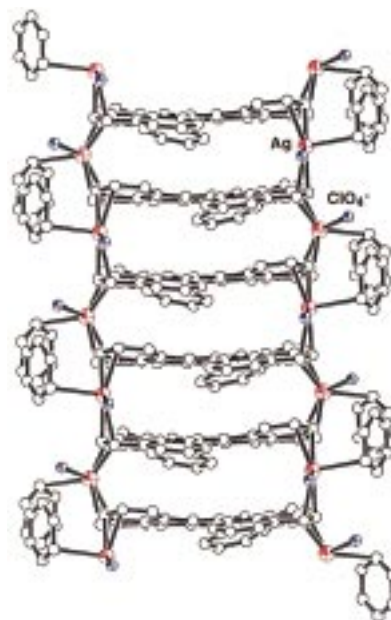


Figure 7. Multidecker unit in **4**.

which showed only one redox process in each case in the region of -1.35 – 0.24 V. Each of the reduction peaks and oxidation peaks was accompanied by a corresponding oxidation peak and reduction peak. The waves generally showed poor electrochemical reversibility with anodic to cathodic peak potential separated widely.

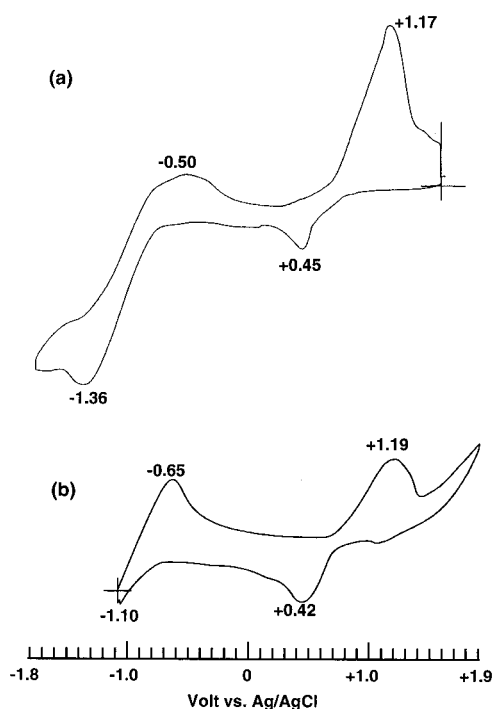


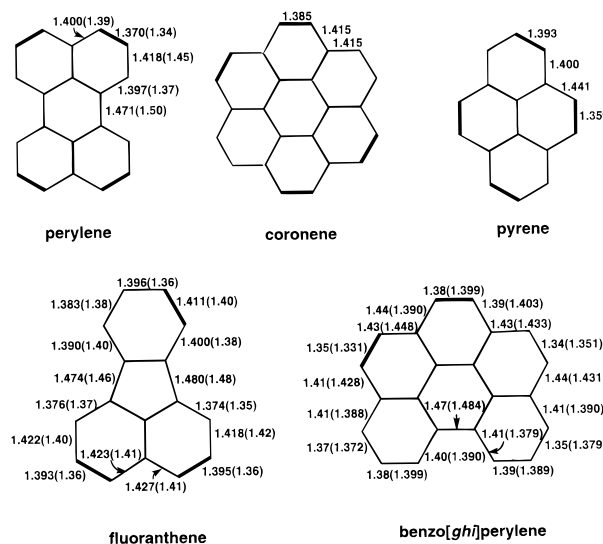
Figure 8. Cyclic voltammograms of **1** (a) and **4** (b) recorded in THF at room temperature, 0.1 M tetrabutylammonium perchlorate, 100 mV/s scan rate.

At room temperature no strong ESR spectrum was observed for **1** and **3**. However, both **2** and **4** exhibit a well-resolved intense resonance with $g = 2.003$ and 2.0047 , respectively, typical of aromatic hydrocarbon radicals.²⁹ However, the formation of Ag(0) or Ag(II) species accompanied by the electron transfer was not observed because of the low sensitivity. The spin densities for the organic radicals, estimated from the comparison with the DPPH (diphenylpicrylhydrazyl) standard, were low, being 0.004% for **2** and 0.0072% for **4**.

Silver- π Interactions. Silver is known to have a remarkable high affinity for some aromatic π -donor systems.^{21,22} The propensity of AgClO₄ to form adducts with a variety of aromatic compounds appears to be unparalleled by any other transition-metal salt. This may in part due to the diversity and flexibility of the silver(I) stereochemistry. As we have observed previously in other silver(I)/aromatic compounds,²⁰ the aromatics in the present four silver(I) complexes are always found η^2 interacting with the silver ions; η^4 or η^6 coordination is never observed. As shown in Table 2, the Ag-C interaction varies over wide limits, 2.403(8)–2.764(6) Å, and the next closest contacts between silver and carbon atoms are all above 3.0 Å. Here we tend to view the bond length of 2.9 Å as the upper limit for effective π interactions between Ag(I) and carbon atom.^{20–22} It seems unlikely that the individual Ag-C interactions greater than 3.0 Å have an appreciable effect in stabilizing the complex, but the cumulative effect of the Ag-C interactions should not be ruled out. It is significant that all the known silver(I)-aromatic complexes, with the exception of naphthalenetetrakis(silver perchlorate) tetrahydrate,^{22a} 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 [2,2]paracyclophane where the two Ag-C distances differ by 0.3 Å.

As an important component in the sandwich system, each aromatic group always interacts with two or four metal ions equally divided below and above the ring. The only exception

Chart 1. π -Coordination Sites (Bold Line) in Ag(I) Complexes of Aromatic Compounds^a


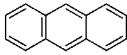
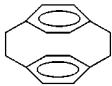
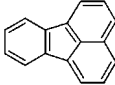
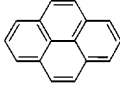
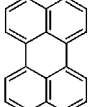
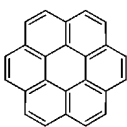
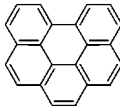
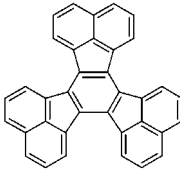


^a The bond lengths are in Å and those in parentheses are for the free ligands.

is found in **1** where each fluoroanthene molecule is μ -tri- η^2 -coordinated to three metal centers; but the alternate arrangement of the aromatic groups in two different orientations gives an overall equal number of linkages on both sides of the aromatic plane. In all silver(I) complexes with aromatic compounds, silver(I) ions are found to be inclined to bond at the short carbon-carbon bond portion, indicative of large electron density accumulated on the π -bonded carbon atoms. We have demonstrated that for the highly symmetric aromatics such as pyrene, perylene, and coronene, the metal- π interaction always takes place at symmetric positions.²⁰ The carbon-carbon atoms with the shortest and the second shortest C-C bonds are most vulnerable to the cation attacking (Chart 1). In contrast, the π interaction occurs at unsymmetric positions for less symmetric aromatics such as fluoroanthene and benzo[ghi]perylene. Here the coordination sites are not necessarily the shortest C-C bonded carbon atoms because the size and geometry of the aromatic, steric hindrance, molecular packing energy, and other structural details can affect the coordinating positions on the aromatic plane. For example, fluoroanthene interacts with Ag(I) ions at the fourth (1.393 Å) and fifth (1.395 Å) shortest C-C moieties while benzo[ghi]perylene is coordinated to the metal center at the second (1.35 Å) and the fourth (1.38 Å) shortest C-C bonded carbon atoms. The symmetry of the aromatic compounds not only affects the coordination positions but also controls the self-assembling of the sandwich components as we have seen that the highly symmetric coronene complex gives a triple-decker structure whereas less symmetric benzo[ghi]perylene gives a double-decker structure.

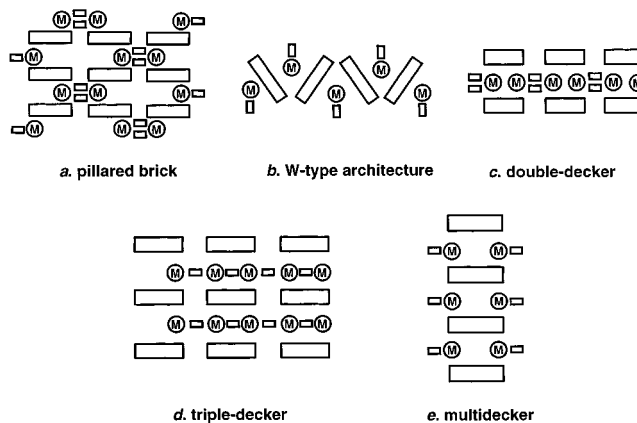
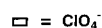
Construction of Metal Sandwich Systems by Polycyclic Aromatic Compounds. Study of transition-metal oligomers and polymers having sandwich structures is a conceptual extension of metallocene chemistry.^{1–3} In recent years many research groups have applied the stepwise approach to the preparation of numerous carborane-bridged or hydrocarbon ring (Cp, Cp*, or arene)-bridged sandwich metal complexes.^{4–9} Such study has already extended from double- and triple-decker to penta- and hexa-decker systems. For construction of even larger systems, an alternative approach to use synthetically accessible materials, that is, reasonably air-stable and soluble in common organic solvents such as polycyclic aromatic hydrocarbons, and to

Table 2. Polycyclic Aromatic Compounds Having Sandwich Structures

aromatic	metal	metal–C bond distance (Å)	bonding mode	frameworks	ref
	Ag(I)	2.44(1)–2.51(1)	μ -tetra- η^2	stairlike chain	22b
	Ag(I)	2.454(8)–2.552(8)	μ -tetra- η^2	multidecker	22d
	V(0)	2.137(3)–2.277(3)	μ -di- η^6	triple-decker	17a
	V(0)	2.10(1)–2.28(1)	μ - η^6, η^2	triple-decker	17b
	Yb(0)	2.63(1)–3.068(2)			
	Ag(I)	2.412(7)–2.719(7)	μ -di- η^2	pillared brick	this work
	Ag(I)	2.410(4)–2.686(4)	μ -tri- η^2	W-type architecture	this work
	Ag(I)	2.467(7)–2.764(6)	μ -tetra- η^2	W-type architecture	20a
	Ag(I)	2.420(5)–2.766(4)	μ -tetra- η^2	W-type architecture	20a
	Ag(I)	2.402(4)–2.517(4)	μ -tetra- η^2	triple-decker	20b
	Ag(I)	2.407(7)–2.578(8)	μ -di- η^2 μ -tetra- η^2	double-decker	this work
	Ag(I)	2.403(8)–2.754(7)	μ -tetra- η^2	multidecker	this work

control predictably the arrangement of crystalline material's constituents would greatly aid in the design of infinite solid-state arrays. There are a few reports of staggered transition-metal sandwich structures containing bicyclic or polycyclic bridging ligands such as naphthalene or pentalene whose individual rings are facially coordinated to only one metal atoms.^{16,17} We have so far systematically examined seven extended silver(I) sandwich complexes with polycyclic aromatic compounds, which constitute five different frameworks, Chart 2. It seems that the energetic differences between the different species should be very small and make the final stereochemistry and the framework of such system nearly unpredictable.

Perhaps the most striking feature of this chemistry is the ability of these aromatics to stabilize unusual or novel organosilver molecular systems, including multidecker sandwiches. Ligands that form the extended sandwich compounds must be planar and flexible enough to interact with metal ions on both sides of the plane. In contrast with centrally π -bonded ferrocene or carborane multilayered systems where all the carbon and boron atoms on the delocalized ligand plane participate in coordination, the π interaction for the polycyclic aromatic compounds only involves the peripheral carbon atoms regardless of stereochemistry, or nature of aromatic. The aromatic hydro-

Chart 2

carbons employed in this work tend to align in linear chains due to their planarity and intermolecular π - π interactions.²⁵ In order to achieve such a structure, the highly symmetric polycyclic plane may deviate significantly from planarity as we

have observed in perylene,^{20a} benzo[ghi]perylene, and decacyclene. In an extreme case as coronene, even a bent conformation might occur owing to both intramolecular and intermolecular π - π interactions involved.^{20b} The aromatic π - π stacking sometimes can affect the self-assembling process of the metal sandwich system. As we have noticed in this work, the ligands having strong aromatic π - π interactions may give a decker structure with coordination of the counteranions to the metal centers outward the decker. However, the aromatics with negligible π - π interactions may give a W-type structure in which the hydrocarbon groups sandwich the ionic sheet containing both cationic and anionic species.

The metal centers in these coordination polymers may be thought of as the keys to assembling and templating the aromatic groups. Although copper(I) is also a preferred ligand linker because of its coordination flexibility, our efforts to synthesize the corresponding copper(I) complexes containing polycyclic aromatic compounds have been unsuccessful due to the sensitivity of Cu(I) species toward moisture and air oxidation. Apart from metal ions and the hydrocarbons, the final structures and frameworks of these aromatic sandwich compounds may well depend on a variety of factors such as nature of anion. All the compounds we have studied contain perchlorate ions coordinated in a variety of ways to the silver ions, such as terminal bonding to one metal, or bridging two metal centers by one or two oxygen atoms of the ion. Due to the large size of the polycyclic aromatics, the unique functions of the perchlorate ion as spacers and linkers between aromatic π -sandwiched metal units seem to be even more profound in the stabilization of the complex and in construction of the extended multilayered systems.

Concluding Remarks

Our study provides detailed insight into structural aspects of a number of metal sandwich systems. This work demonstrates

that the polycyclic aromatic compounds, which offer π -electron delocalization combined with two sides for metal complexation, may open the way to a rich and diverse chemistry in the multilayered metal sandwich systems. Different metal salts, various coordination geometries, and numerous aromatic ligands to choose may provide a wide range of possibilities for connecting metal ions together to construct many other metal sandwich architectures. These polymeric organometallic sandwiches are of importance in materials science and technology associated with electron delocalization and electronic cooperative interactions, but the requirements for the desired physical and chemical properties are as yet hardly well-defined. Furthermore, analyzing these polymeric materials, which are frequently insoluble, is fraught with problems. Further investigations in this area of chemistry including different metal ions and aromatics are clearly warranted.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Science Research [Nos. 09554041, 10440201, and 10016743 (priority areas "Metal-assembled Complexes")] from the Ministry of Education, Science, Culture and Sports in Japan. We thank H. Ohta and K. Sugimoto for their assistance in experiment.

Supporting Information Available: Tables of crystal data, intensity measurements, structure solution and refinement, atomic coordinates and thermal parameters, intramolecular bond lengths and angles, and least-squares planes for L¹, L², and **1-4**. An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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