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Syntheses, Structures, and Properties of Intercalation Compounds of Silver(I) Complex with [2.2]Paracyclophane

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Reaction of [2.2]paracyclophane (pcp) with silver(I) trifluoroacetate ($AgCF_3CO_2$) and silver(I) pentafluoroproprionate ($AgC_2F_5CO_2$) has led to isolation of three novel intercalation polymers: $[Ag_4(pcp)(CF_3CO_2)_4](C_6H_6)$ (**1**), $[Ag_4(pcp)(CF_3CO_2)_4](C_6H_3Me_3)$ (**2**), and $[Ag_4(pcp)(C_2F_5CO_2)_4](pcp)$ (**3**). Structure studies using single crystal X-ray diffraction have shown that all compounds contain two-dimensional layered frameworks based on cation–π interactions, in which pcp exhibits an unprecedented μ-tetra-η^2 coordination mode. Guest molecules which weakly interact with the host pcp via C–H···π interactions are intercalated between layers. The guest-eliminated complexes (**1a** and **2a**) and guest-reincorporated ones (**1b** or **1c** and **2b or 2c**), accompanied by small structural changes, were confirmed by ^{1}H NMR, thermogravimetric analysis, mass spectra, and X-ray powder diffraction patterns. The structural changes from **1 → 1a → 1c (=1)** can take place reversibly in the process of exposure of **1a** to benzene vapor. The original framework of complex **2** is also completely recovered by immersing **2a** in mesitylene as well as exposing it to mesitylene vapor.

1. Introduction

Considerable efforts have been devoted to synthesis and characterization of porous coordination polymers because of their versatile applicability to gas separation, shape-selective catalysis, and ion-exchange.[1–19] However, little attention has been paid to intercalation complexes based on the coordination of metal ions and organics. This is because of their unstable frameworks in the absence of guests, though 2-D intercalation chemistry has been widely developed in inorganic compounds such as aluminosilcates, aluminophosphates, pillared clays, and graphite.[20–31] 2-D intercalation

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(1) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428.
(2) Kitaura, R.; Kitagawa, S.; Kubota, Y.; Kobayashi, T. C.; Kindo, K.; Mita, Y.; Matsuo, A.; Kobayashi, M.; Chang, H. C.; Ozawa, T. C.; Suzuki, M.; Sakata, M.; Takata, M. *Science* **2002**, *298*, 2358.
(3) Subramanian, S.; Zaworotko, M. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 2127.
(4) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431.
(5) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2003**, 2781.
(6) Gardner, G. B.; Venkataraman, D. V.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792.
(7) Farell, R. P.; Hambley, T. W.; Lay, P. A. *Inorg. Chem*. **1995**, *34*, 757.
(8) Abrahams, B. F.; Hoskin, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727.
(9) Min, K. S.; Suh, M. P. *J. Am. Chem. Soc*. **2000**, *122*, 6834.
(10) Soldatov, D. V.; Ripmeester, J. A.; Shergina, S. I.; Sokolov, I. E.; Zanina, A. S.; Gromilov, S. A.; Dyadin, Y. A. *J. Am. Chem. Soc.* **1999**, *121*, 4179.
(11) Tabares, L. C.; Navarro, J. A. R.; Salas, J. M. *J. Am. Chem. Soc*. **2001**, *123*, 383.
(12) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 1739.
(13) Ozin, G. A.; Kuperman, A.; Stein, A. *Angew. Chem*. **1989**, *101*, 373; *Angew. Chem., Int. Ed.* **1989**, *28*, 359.
(14) Corma, A. *Chem. Rev*. **1997**, *97*, 2373.
(15) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res*. **2001**, *34*, 319.
(16) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.
(17) Moulton, B.; Zaworotko, M. J. *Chem. Rev*. **2001**, *101*, 1629.
(18) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982.
(19) Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem*. **2000**, *112*, 2162.
(20) *(20) Progress in Intercalation Research*; Müller-Warmuth, W., Schöllhorn, R., Eds.; Kluwer: Dordrecht, 1994.
(21) Jones, W. *In Photochemistry in Organized & Constrained Media*; V. Ramamurthy., Ed.; VCH Publishers: New York, 1991; Chapter 9.
(22) Fitch, A. *Clays Clay Miner*. **1990**, *38*, 391.
(23) Ruiz-Hitzky, E. *Adv. Mater*. **1993**, *5*, 334.
(24) Johnson, J. W. A.; Jacobson, J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowsky, J. T. *J. Am. Chem. Soc*. **1989**, *111*, 381.
(25) Cao, G.; Mallouk, T. E. *Inorg. Chem*. **1991**, *30*, 1434.
(26) Clearfield, A. *Chem. Rev*. **1988**, *88*, 125.
(27) Pinnavaia, T. J. *Science* **1983**, *220*, 4595.
(28) Ohtsuka, K. *Chem. Mater*. **1997**, *9*, 2039.
(29) Kim, R. M.; Pillion, J. E.; Burwell, D. A.; Groves, J. T.; Thompson, M. E. *Inorg. Chem*. **1993**, *32*, 4509.

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frameworks (clay mimics) can complement their 3-D counterparts (zeolite mimics) because they are often capable of varying their interlayer separation in order to accommodate guest molecules, adjusting to the structural and steric requirements of the guest. Recent interest is focused on the metal-organic clay mimics, and several intercalation complexes have been prepared.[32−38] Still lacking are reports on the reversible incorporation of guests in intercalation complexes. In addition, attention has been mainly paid to the synthesis of layered complexes with oxygen or nitrogen ligands, in which the metal ions are directly coordinated to oxygen or nitrogen atoms. To the best of our knowledge, there are no intercalation complexes constructed by η^2-coordination of aromatic compounds to metal ions. In recent years, we have been interested in the silver(I) coordination polymers of polycyclic aromatic hydrocarbons.[39−41] As an extension of these studies, we directed our research interests toward the porous and intercalation complexes of nonplanar ligands to silver(I) through cation$-\pi$ interactions and anticipated opening a new avenue for the synthesis of porous and intercalation polymers. As a result, we recently reported the construction of a porous framework with silver(I) binding to triptycene by η^2/η^1 coordination modes.[42] In this report, we succeeded in the preparation of three intercalation polymers of a new type: $[Ag_4(pcp)(CF_3CO_2)_4](C_6H_6)$ (**1**), $[Ag_4(pcp)(CF_3CO_2)_4](C_6H_3Me_3)$ (**2**), and $[Ag_4(pcp)(C_2F_5CO_2)_4](pcp)$ (**3**). These polymers can reversibly intercalate guest molecules without destruction of the structure, and the pcp ligands adopt an unprecedented μ-tetra-η^2 coordination mode to silver(I) atoms. The reversible incorporation of the guests into the complexes was demonstrated by ^1H NMR spectra, TG analysis, mass spectra, and X-ray powder diffraction (XRPD) patterns.

2. Experimental Section

2.1. General Procedures. All reactions and manipulations were carried out under an argon atmosphere by using the usual Schlenk techniques. Solvents were dried and distilled by standard methods prior to use and stored under argon. Reagent grade $AgCF_3CO_2$, $AgC_2F_5CO_2$, and pcp were purchased from Aldrich. All chemicals were used as received without further purification. IR spectra were recorded with KBr disks on a JASCO FT/IR 8000 spectrometer. ^1H NMR spectra were measured on a JEOL GSX 270 FT NMR spectrometer at room temperature. Tetramethylsilane was used as an internal reference for ^1H NMR measurement. TG analyses were performed at 1 °C min^{-1} under nitrogen on Rigaku Thermo plus TG 8120. Mass spectra were recorded on a JMS-700T spectrometer. X-ray powder diffraction (XRPD) data were recorded on a Rigaku Rint 2000 diffractometer at 40 kV, 80 mA for Cu Kα ($\lambda = 1.54056$ Å), with a scan speed of 8 deg/min and step size of 0.06° in 2θ at room temperature. XRPD data were reported for the most prominent lines with *d*-spacings in angstroms and the relative intensities placed in parentheses followed by their *hkl* assignments.

2.2. Syntheses. $[Ag_4(pcp)(CF_3CO_2)_4](C_6H_6)$ (1). This complex was prepared by mixing of $AgCF_3CO_2$ (6.6 mg, 0.03 mmol) and pcp (6.2 mg, 0.03 mmol) in 3 mL of benzene. After stirring for 30 min, the resultant solution was introduced into a 7 mm diameter glass tube and layered with tetradecane as a diffusion solvent. The glass tube was sealed under argon and wrapped with aluminum foil. After standing at room temperature for one week, colorless brick crystals of complex **1** suitable for single crystal X-ray analysis were obtained. Yield: 4.1 mg (3.48×10^{-3} mmol, 46.5%). Anal. Calcd for $C_{30}H_{22}O_8F_{12}Ag_4$: C, 30.80; H, 1.90. Found: C, 30.44; H, 1.86%. ^1H NMR (acetone-d_6): δ H 3.09 (CH_2, pcp), 6.54 (pheny, pcp), 7.35 (CH, benzene). IR (KBr, ν/cm^{-1}): 3032(w), 3012(w), 2951(w), 2926(m), 2887(m), 2851(m), 2363(w), 1892(w), 1674(s), 1501(w), 1436(m), 1323(w), 1211(s), 895(w), 840(s), 806(s), 724(s), 623(m), 509(m).

$[Ag_4(pcp)(CF_3CO_2)_4](C_6H_3Me_3)$ (2). The colorless brick crystals of **2** were grown similarly to those of **1** using $AgCF_3CO_2$ (26.4 mg, 0.12 mmol) and mesitylene instead of benzene. Yield: 7.9 mg (6.51×10^{-3}mmol, 21.7%). Anal. Calcd for $C_{33}H_{28}O_8F_{12}Ag_4$: C, 32.70; H, 2.33. Found: C, 32.11; H, 2.25%. ^1H NMR (acetone-d_6): δ H 2.22 (CH_3), 3.08 (CH_2, pcp), 6.54 (pheny, pcp), 6.77 (pheny, mesitylene). IR (KBr, ν/cm^{-1}): 3031(w), 3012(w), 2951(m), 2926(m), 2887(w), 2851(m), 2345(w), 1893(w), 1664(s), 1502(m), 1436(s), 1323(w), 1209(s), 895(m), 840(s), 806(s), 724(s), 623(m), 509(m).

$[Ag_4(pcp)(C_2F_5CO_2)_4](pcp)$ (3). A mesitylene solution (3 mL) was added to 12.2 mg of $AgC_2F_5CO_2$ (0.045 mmol) and 9.4 mg of pcp (0.045 mmol). The solution was treated in the same way as that for **1** and gave colorless brick crystals of **3**. Yield: 5.1 mg (3.41×10^{-3}mmol, 30.3%). Anal. Calcd for $C_{44}H_{32}O_8F_{20}Ag_4$: C, 35.23; H, 2.15. Found: C, 35.16; H, 2.14%. ^1H NMR (THF): δ H 1.73 (THF), 3.04 (CH_2,pcp), 3.58 (THF), 6.45 (pheny, pcp). IR (KBr, ν/cm^{-1}): 3034(w), 2888(w), 2951(m), 2928(m), 2852(m), 2346(w), 1894(w), 1657(s), 1501(m), 1482(m), 1459(w), 1410(s), 1326(s), 1214(s), 1029(s), 895(m), 816(s), 731(s), 624(m), 584(m), 540(m), 509(m).

Complex 1a. By placing complex **1** under nitrogen for 2 h at 110 °C, we can obtain the benzene-eliminated complex **1a**. ^1H NMR (acetone-d_6): δ H 3.08 (CH_2, pcp), 6.54 (pheny, pcp). IR (KBr, ν/cm^{-1}): 2951(w), 2927(w), 2851(w), 2345(w), 1685(s), 1499(w), 1436(m), 1208(s), 895(w), 841(m), 805(m), 722(m), 623(m), 509(w).

Complex 1b. Complex **1a** was immersed in benzene for 7 days at room temperature, filtrated, and dried under an argon atmosphere. Benzene molecules can again fill the space between layers to form complex **1b**. ^1H NMR (acetone-d_6): δ H 3.08 (CH_2, pcp), 6.51 (pheny, pcp), 7.35 (CH, benzene). IR (KBr, ν/cm^{-1}): 3034(w), 3012(w), 2951(m), 2927(m), 2887(m), 2851(w), 2346(w), 1686(s), 1499(w), 1437(m), 1208(s), 895(w), 843(m), 805(m), 723(m), 623(w), 509(w).

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(30) O'Hare, D. *Chem. Soc. Rev.* **1992**, 121.
(31) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995**, *95*, 399.
(32) Kawata, S.; Kitagawa, S.; Kumagai, H.; Kudo, C.; Kamesaki, H.; Ishiyama, T.; Suzuki, R.; Kondo, M.; Katada, M. *Inorg. Chem.* **1996**, *35*, 4449.
(33) Yaghi, O. M.; Li, G. M.; Li, H. L. *Nature* **1995**, *378*, 703.
(34) Kawata, S.; Kitagawa, S.; Kumagai, H.; Tetsuga, T.; Honda, K.; Tobita, H.; Adachi, K.; Katada, M. *Chem. Mater*. **1998**, *10*, 3902.
(35) Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 11600.
(36) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworatko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972.
(37) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.
(38) Shimizu, G. K. H.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A.; Wayner, D. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 1407.
(39) Munakata, M.; Wu, L. P.; Ning, G. L. *Coord. Chem. Rev.* **2000**, *198*, 171.
(40) Munakata, M.; Ning, G. L.; Suenaga, Y.; Sugimoto, K.; Kuroda-Sowa, T.; Maekawa, M. *Chem. Commun*. **1999**, 1545.
(41) Munakata, M.; Wu, L. P.; Sugimoto, K.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N.; Fujita, M. *Inorg. Chem*. **1999**, *38*, 5674.
(42) Wen, M.; Munakata, M.; Suenaga, Y.; Kuroda-Sowa, T.; Maekawa, M. *Inorg. Chim. Acta*. **2002**, *340*, 8.

Table 1. Crystallographic Data for Complexes **1**−**3**

	1	**2**	**3**
formula	$C_{30}H_{22}Ag_4F_{12}O_8$	$C_{33}H_{28}Ag_4F_{12}O_8$	$C_{22}H_{16}Ag_2F_{10}O_4$
fw	1169.95	1212.03	750.09
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$C2/c$
a, Å	10.995(2)	16.541(1)	28.738(4)
b, Å	9.635(2)	10.230(7)	9.723(1)
c, Å	17.432(4)	22.382(1)	17.378(3)
β, deg	111.243(8)	101.358(10)	111.135(7)
V, Å^3	1721.3(6)	3713(4)	4529(1)
Z	2	4	8
ρ, g/cm^3	2.257	2.168	2.200
μ, cm^{-1}	23.49	21.82	18.37
measd reflns (unique)	3904	4211	5192
obsd reflns ($I > 2\sigma(I)$)	3216	3257	4110
params	278	260	391
$R_1{}^a$ ($I > 2\sigma(I)$)	0.056	0.072	0.044
$R_w{}^b$ (all data)	0.087	0.164	0.074

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**−**3**

Complex **1**			
Ag(1)−O(1)	2.530(3)	Ag(1)−O(2′)	2.382(4)
Ag(1)−O(3)	2.233(5)	Ag(1)−C(1)	2.504(7)
Ag(1)−C(6)	2.412(7)	Ag(2)−O(1′)	2.379(4)
Ag(2)−O(2)	2.428(4)	Ag(2)−O(4)	2.250(6)
Ag(2)−C(4)	2.612(7)	Ag(2)−C(5)	2.377(7)
O(1)−Ag(1)−O(2′)	80.5(1)	O(1)−Ag(1)−O(3)	91.0(1)
O(1)−Ag(1)−C(1)	95.1(2)	O(2)−Ag(1)−C(6)	115.7(2)
O(2′)−Ag(1)−O(3)	99.3(2)	O(2′)−Ag(1)−C(1)	90.5(2)
O(2′)−Ag(1)−C(6)	118.1(2)	O(3)−Ag(1)−C(1)	169.2(2)
O(3)−Ag(1)−C(6)	136.2(2)	C(1)−Ag(1)−C(6)	33.1(2)
O(1′)−Ag(2)−O(2)	82.7(1)	O(1′)−Ag(2)−O(4)	99.4(2)
O(1′)−Ag(2)−C(4)	91.2(2)	O(1′)−Ag(2)−C(5)	110.8(2)
O(2)−Ag(2)−O(4)	95.1(2)	O(2)−Ag(2)−C(4)	88.4(2)
O(2)−Ag(2)−C(5)	114.7(2)	O(4)−Ag(2)−C(4)	169.2(2)
O(4)−Ag(2)−C(5)	139.3(2)	C(4)−Ag(2)−C(5)	31.7(2)
Complex **2**			
Ag(1)−O(1)	2.515(5)	Ag(1)−O(2′)	2.394(5)
Ag(1)−O(3)	2.227(6)	Ag(1)−C(1)	2.512(7)
Ag(1)−C(6)	2.425(7)	Ag(2)−O(2)	2.432(5)
Ag(2)−O(1′)	2.389(5)	Ag(2)−O(4)	2.236(6)
Ag(2)−C(4)	2.505(7)	Ag(2)−C(5)	2.384(7)
O(1)−Ag(1)−O(2′)	82.4(2)	O(1)−Ag(1)−O(3)	93.0(2)
O(1)−Ag(1)−C(1)	92.8(2)	O(1)−Ag(1)−C(6)	114.6(2)
O(2′)−Ag(1)−O(3)	101.6(2)	O(2′)−Ag(1)−C(1)	88.5(2)
O(2′)−Ag(1)−C(6)	114.6(2)	O(3)−Ag(1)−C(1)	168.9(2)
O(3)−Ag(1)−C(6)	136.3(2)	C(1)−Ag(1)−C(6)	32.8(2)
O(2)−Ag(2)−O(1′)	80.5(2)	O(2)−Ag(2)−O(4)	89.3(2)
O(2)−Ag(2)−C(4)	95.7(2)	O(2)−Ag(2)−C(5)	121.6(2)
O(1′)−Ag(2)−O(4)	96.7(2)	O(1′)−Ag(2)−C(4)	95.4(2)
O(1′)−Ag(2)−C(5)	117.8(2)	O(4)−Ag(2)−C(4)	167.5(2)
O(4)−Ag(2)−C(5)	135.6(2)	C(4)−Ag(2)−C(5)	33.2(3)
Complex **3**			
Ag(1)−O(1′)	2.458(3)	Ag(1)−O(2)	2.399(3)
Ag(1)−O(3)	2.232(2)	Ag(1)−C(1)	2.391(4)
Ag(1)−C(6)	2.549(3)	Ag(2)−O(1)	2.377(2)
Ag(2)−O(2′)	2.498(3)	Ag(2)−O(4)	2.246(2)
Ag(2)−C(2)	2.387(4)	Ag(2)−C(3)	2.637(3)
O(1′)−Ag(1)−O(2)	83.70(9)	O(1′)−Ag(1)−O(3)	98.1(1)
O(1′)−Ag(1)−C(1)	113.5(1)	O(1′)−Ag(1)−C(6)	89.4(1)
O(2)−Ag(1)−O(3)	97.38(9)	O(2)−Ag(1)−C(1)	116.5(1)
O(2)−Ag(1)−C(6)	93.59(10)	O(3)−Ag(1)−C(1)	135.0(1)
O(3)−Ag(1)−C(6)	167.3(1)	C(1)−Ag(1)−C(6)	32.6(1)
O(1)−Ag(2)−O(2′)	83.30(9)	O(1)−Ag(2)−O(4)	101.68(9)
O(1)−Ag(2)−C(2)	111.1(1)	O(1)−Ag(2)−C(3)	87.96(10)
O(2′)−Ag(2)−O(4)	97.7(1)	O(2′)−Ag(2)−C(2)	113.1(1)
O(2′)−Ag(2)−C(3)	89.8(1)	O(4)−Ag(2)−C(2)	136.7(1)
O(4)−Ag(2)−C(3)	168.4(1)	C(2)−Ag(2)−C(3)	31.8(1)

Complex 1c. Complex **1a** was exposed to benzene vapor for 3 days under reduced pressure at room temperature. Similarly, benzene molecules can occupy the space between layers to afford complex **1c**. ^{1}H NMR (acetone-d_6): δ H 3.08 (CH_2, pcp), 6.51 (pheny, pcp), 7.35 (CH, benzene). IR (KBr, ν/cm^{-1}): 3031(w), 3012(w), 2951(m), 2927(m), 2886(w), 2851(w), 2346(w), 1686(s), 1495(w), 1437(m), 1208(s), 895(w), 843(m), 805(m), 723(m), 623(w), 509(w).

Complex 2a. The mesitylene-eliminated complex **2a** was obtained by placing complex **2** under nitrogen for 1 h at 100 °C. ^{1}H NMR (acetone-d_6): δ H 3.09 (CH_2, pcp), 6.55 (pheny, pcp). IR (KBr, ν/cm^{-1}): 2927(w), 2851(w), 1661(s), 1542(w), 1508(w), 1436(m), 1212(s), 895(w), 840(m), 807(m), 725(m), 624(w), 509(w).

Complex 2b. The mesitylene-reincorporated complex **2b** was formed by immersing complex **2a** into mesitylene for two weeks at room temperature. ^{1}H NMR (acetone-d_6): δ H 2.22 (CH_3), 3.08 (CH_2, pcp), 6.52 (pheny, pcp), 6.77 (pheny, mesitylene). IR (KBr, ν/cm^{-1}): 3032(w), 3012(w), 2951(w), 2887(m), 2851(m), 2346(w), 1892(w), 1685(s), 1500(m), 1436(m), 1207(s), 895(w), 841(m), 805(m), 722(m), 623(m), 509(m).

Complex 2c. Complex **2a** was exposed to mesitylene vapor for 20 days under reduced pressure at room temperature to give complex **2c**. ^{1}H NMR (acetone-d_6): δ H 2.23 (CH_3), 3.07 (CH_2, pcp), 6.54 (pheny, pcp), 6.77 (pheny, mesitylene). IR (KBr, ν/cm^{-1}): 3034(w), 3012(w), 2951(w), 2887(m), 2851(m), 2346(w), 1895(w), 1685(s), 1500(m), 1438(m), 1207(s), 895(w), 843(m), 805(m), 722(m), 623(m), 509(m).

The pcp-eliminated complex cannot be obtained from complex **3** mainly owing to the higher boiling point of pcp so that the structural decomposition occurs at about 195 °C before pcp is completely eliminated.

2.3. X-ray Data Collection and Structure Solutions and Refinements. A suitable single crystal was fixed on a glass fiber, and diffraction data were collected at −123 °C on a Quantum charge-coupled device area detector coupled with a Rigaku AFC7 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) and a rotating mode generator. The intensities of three reflections were monitored regularly after the measurement of 150 reflections and indicated crystal stability in all cases. An empirical absorption correction based on azimuthal scans was applied which resulted in transmission factors ranging from 0.85 to 0.93 for **1**, from 0.72 to 0.80 for **2**, and from 0.73 to 0.83 for **3**, respectively. All intensity data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods,[43] expanded using Fourier techniques,[44] and refined by full-matrix least-squares analysis on F using the TEXSAN package.[45] All the full-occupancy non-hydrogen atoms were refined anisotropically. Hydrogen atoms of all the structure were introduced in their calculated positions. They were included but not refined in the refinement. Details of X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

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(43) Gilmore, C. J. *J. Appl. Crystallogr*. **1984**, *17*, 42.

(44) Beurskens, P. T. *DIRDIF94: Direct Methods for Different Structures: an automatic procedure for phase extension and refinement of different structure factors*; Technical Report; Crystallographic Laboratory: University of Nijimegen, The Netherlands, 1994; Vol.1

(45) *TEXSAN-TEXRAY: Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1999.

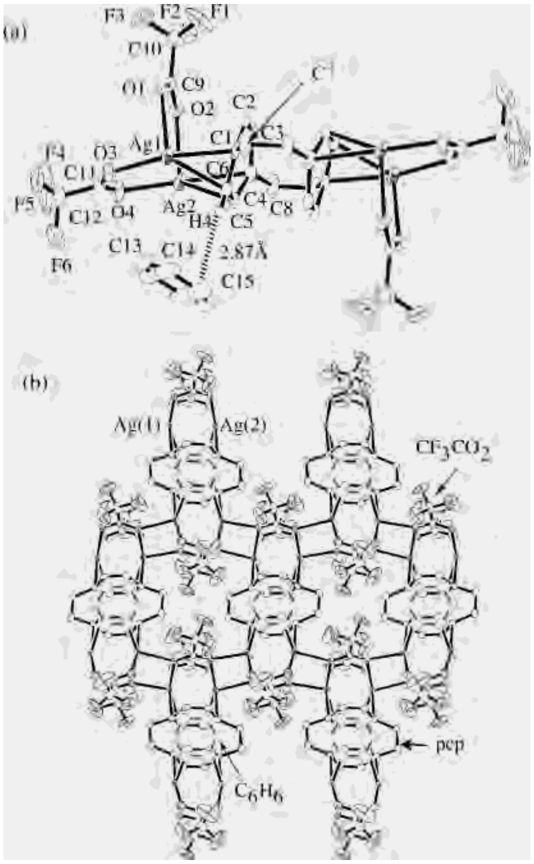


Figure 1. (a) Structure and labeling of **1**, all hydrogen atoms except H4 are omitted for clarity. (b) View down the crystallographic *a*-axis showing the extended 2-D network of **1**.

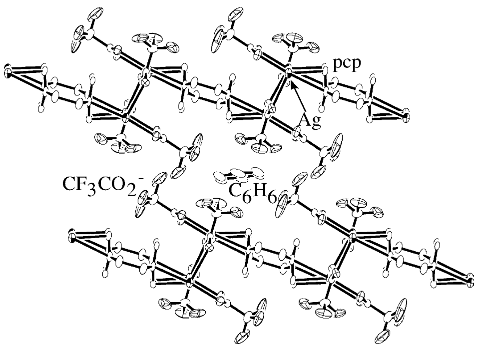
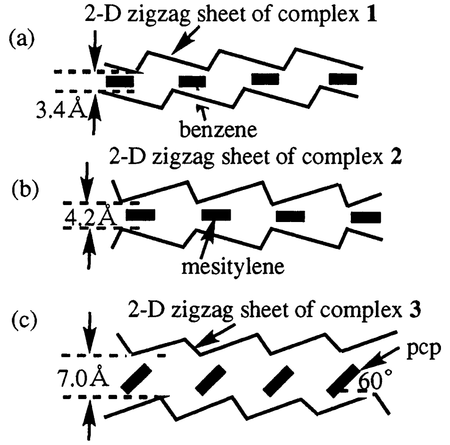


Figure 2. Side view of the packed structure of **1**, showing benzene intercalated between layers.

Scheme 1. Schematic Representation of Intercalation Mode of (a) Benzene in **1**, (b) Mesitylene in **2**, and (c) pcp in **3**



3. Results and Discussion

3.1. Description of the Structures. $[Ag_4(pcp)(CF_3CO_2)_4]$-(C_6H_6) (1). The molecular structure and atom numbering scheme of complex **1** are given in Figure 1a. The crystallographic studies reveal that complex **1** contains a two-dimensional network of $[Ag_4(pcp)]$ units in which the two crystallographically independent silver(I) ions are coupled in pairs through Ag−O−C−O−Ag bonds. Each metal center is coordinated to one C═C moiety of the pcp ligand at Ag−C distances of 2.412(7) and 2.504(7) Å for Ag(1) and 2.377(7) and 2.612(7) Å for Ag(2), respectively, well within the limits from 2.36 to 2.77 Å of reported silver(I)−aromatic complexes.[46−49] Furthermore, each Ag(1) and Ag(2) is bridged by one oxygen of three different $CF_3CO_2^-$ groups, one of which comes from an adjacent unit. Thus, the environment of the silver atom can be described as tetrahedral. The Ag−O distances range from 2.233(5) to 2.530(3) Å. Each pcp moiety exhibits μ-tetra-η^2 coordination mode symmetrically bridging four metal centers with two on the upper and lower decks of the pcp ligand and linking two $-Ag-CF_3CO_2-Ag-$ chains to form a weblike 2-D sheet that spreads out along the *bc*-plane as shown in Figure 1b. The 2-D sheets are in a zigzag fashion and cavities of 6.4 Å × 7.6 Å surrounded by six $CF_3CO_2^-$ species are formed up and down the 2-D sheet, respectively. The pcp ligands in the two adjacent sheets are arranged in the same direction. The nearest distance between the adjacent sheets is 3.4 Å, which represents the approximate interlayer separation. Thus, a space of 6.4 Å × 7.6 Å × 3.4 Å is formed between the layers, in which the benzene molecule is intercalated with the plane parallel to the extending direction of host layers as shown in Figure 2 and Scheme 1a. The resulting alternating arrangement of host layer and guest layer gives weak C−H···π interactions[50,51] since the shortest distance between a hydrogen of pcp and a carbon of benzene is 2.87 Å (Figure 1a).

$[Ag_4(pcp)(CF_3CO_2)_4](C_6H_3Me_3)$ (2). Figure 3a depicts the local coordination around the silver(I) ions together with the atom-numbering scheme. Similar to complex **1**, each tetrahedral metal center is coordinated to one C═C bond from pcp at Ag−C distances ranging from 2.384(7) to 2.512(7) Å. Both Ag(1) and Ag(2) ions are bonded to three different $CF_3CO_2^-$ groups, although they share two of them. The Ag−O distances range from 2.227(6) to 2.515(5) Å. The tetra-η^2-pcp groups virtually act as a linkage between the two $-Ag-CF_3CO_2-Ag-$ chains, affording an extended 2-D

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(46) Ning, G. L.; Wu, L. P.; Sugimoto, K.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Chem. Soc., Dalton Trans.* **1999**, 2529.

(47) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8610.

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

(49) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 743.

(50) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/pi Interaction*; Wiley-VCH: New York, 1998.

(51) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23.

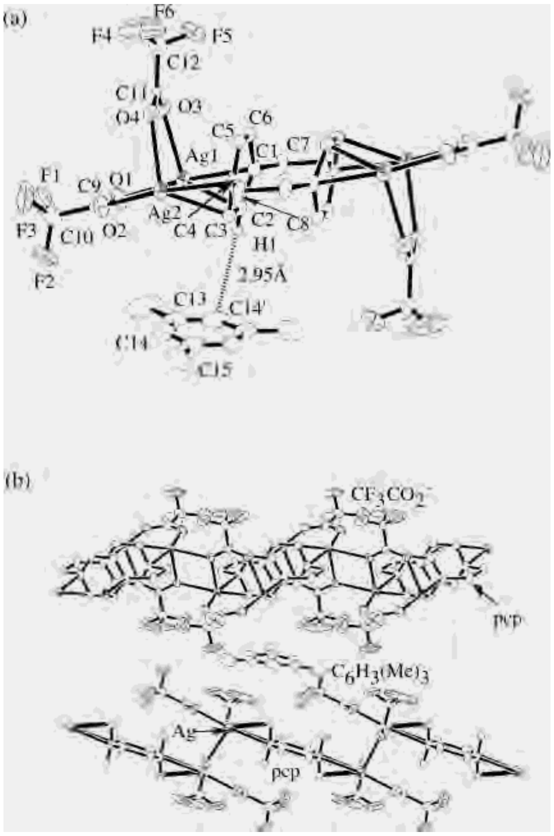

Figure 3. (a) Molecular structure and labeling of **2**, all hydrogen atoms except H1 are omitted for clarity. (b) Side view of packed structure of **2**, showing mesitylene intercalated between sheets.

sheet network with cavities of 5.9 Å × 9.0 Å. Mesitylenes are intercalated between layers with the benzene ring parallel to the extending direction of host layers as shown in Figure 3b and Scheme 1b. It is interesting that the pcp ligands in the two adjacent sheets are arranged in different directions forming an angle of 58.3°. There also exist weak C−H⋯π interactions between the guest mesitylene and the host pcp (Figure 3a). The bigger mesitylene makes it possible for these 2-D sheets to sit loosely and provides a larger separation of 4.2 Å (the shortest distance) between interlayers compared with that of complex **1** to give a space of 5.9 Å × 9.0 Å × 4.2 Å. This observation shows that the structures of **1** and **2** are so flexible that mesitylene may occupy the space between the sheets instead of benzene.

[Ag$_4$(pcp)(C$_2$F$_5$CO$_2$)$_4$](pcp) (3). The molecular structure and atom numbering scheme of complex **3** are illustrated in Figure 4a. The Ag−C and Ag−O distances and bond angles are listed in Table 2. Similar to complex **1** and **2**, each tetrahedral silver(I) center has a five-coordinate environment, and C−H⋯π interactions also exist between guest pcp and host pcp (Figure 4a). There are, however, two most remarkable features in **3** in comparison with **1** and **2**. Pcp molecules are intercalated between the corrugated sheets with the benzene plane of pcp tilting 60° to the stacking direction and parellel to each other (Figure 4b and Scheme 1c). The shortest separation between the 2-D sheets is 7.0 Å, over two times longer than that of complex **1**, which is mainly attributable to the larger guest pcp.

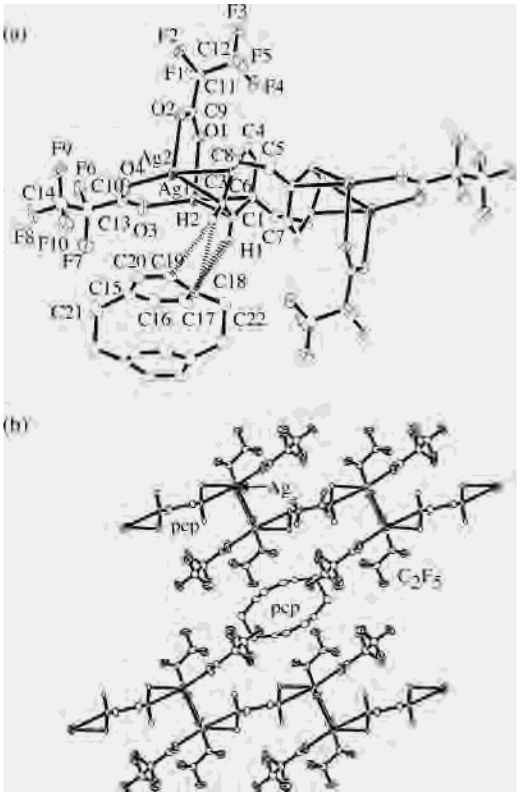

Figure 4. (a) Structure and labeling of **3**, all hydrogen atoms except H1 and H2 are omitted for clarity (C17−H1 = 2.91 Å, C18−H1 = 2.82 Å, C18−H2 = 2.91 Å, C19−H2 = 2.80 Å). (b) Guest pcp between layers.

The η^6- or di-η^6-bonded transition metal complexes of pcp have been widely studied,[52] and the synthesis and phosphorescent properties of pcp complexes of silver perchlorate were reported.[53,54] On the other hand, the pcp molecules of the present three silver(I) pcp complexes display an unusual symmetric tetra-η^2-coordination, which, to our knowledge, has never been characterized in pcp coordination complexes. The present structures differ from [Ag(pcp)(GaCl$_4$)] and [Ag(pcp)(ClO$_4$)], where the two-dimensional networks are based on chains of metal ions cross-linked hydrocarbons by μ-η^2/η^3 fashion and aromatic sandwiched metal units by μ-di-η^2 fashion, respectively.

It is noteworthy that the intercalation mode of guest molecules in the present three polymers is different from that of the reported copper(II) intercalation compounds, {[Cu(CA)(H$_2$O)](G)}$_n$ (H$_2$CA = chloranilic acid, G = 2,5-

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(52) (a) Maekawa, M.; Hashimoto, N.; Sugimoto, K.; Kuroda-Sowa, T.; Suenaga, Y.; Munakata, M. *Inorg. Chem. Acta*. **2003**, *344*, 143. (b) Kai, Y.; Yasuoka, N.; Kasai, N. *Acta Crystallogr*. **1978**, *B34*, 2840. (c) Hanson, A. W. *Cryst. Struct. Commun*. **1982**, *11*, 901. (d) Elsegood, M. R. J.; Tocher, D. A. *J. Organomet. Chem*. **1988**, *C29*, 356. (e) Benn, R.; Blank, N. E.; Haenel, M. W.; Klein, J.; Koray, A. R.; Weidenhammer, K.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl*. **1980**, *19*, 44. (f) Elschenbroich, C.; Hurley, J.; Massa, W.; Baum, G. *Angew. Chem., Int. Ed. Engl*. **1988**, *27*, 684. (g) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc*. **1989**, *111*, 1698. (h) Schmidbour, H.; Bublak, W.; Huber, B.; Hofmann, J.; Müller, G. *Angew. Chem., Int. Ed. Engl*. **1989**, *122*, 265.

(53) (a) Schmidbour, H.; Bublak, W.; Huber, B.; Reber, G.; Müller, G. *Angew. Chem., Int. Ed. Engl*. **1986**, *25*, 1089. (b) Munakata, M.; Wu, L. P.; Ning, G. L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N. *J. Am. Chem. Soc*. **1999**, *121*, 4968.

(54) Zander, M. *Z. Naturforsch*. **1984**, *A39*, 1009.

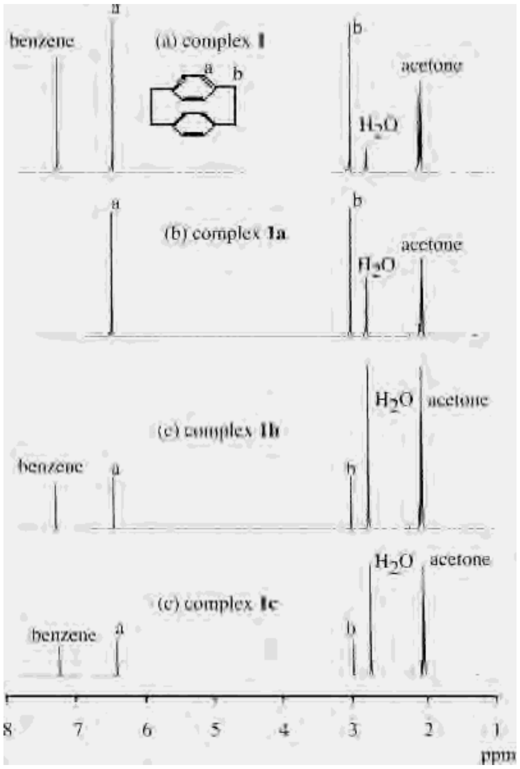

Figure 5. ^1H NMR spectra of complex **1** and its derivatives in acetone-d_6 at room temperature: (a) **1**, (b) **1a**, (c) **1b**, (d) **1c**.

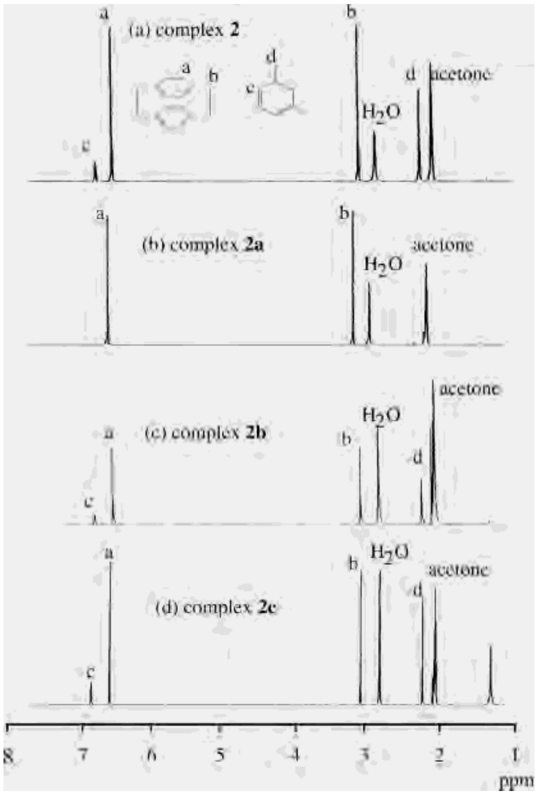

Figure 6. ^1H NMR spectra of complex **2** and its derivatives in acetone-d_6 at room temperature: (a) **2**, (b) **2a**, (c) **2b**, (d) **2c**.

dimethylpyrazine or phenazine),[32] in which the guests are included by hydrogen bonds between the guest and coordinated water. On the other hand, $C-H\cdots\pi$ interactions are observed between the guest and the host pcp in complexes **1**−**3**. It is well-known that hydrogen bonds are widely used to govern the crystal packing,[36,55−59] and some hydrogen-bonded networks can rapidly exchange inclusions or counterions while maintaining crystal integrity.[32,60−62] Even so, removal of guest species especially in the 2-D sheet systems apparently leads to destruction of the host lattice.[32,36] The present complexes **1** and **2**, however, can reversibly lose and reincorporate guests without collapse of layered structure as described below.

3.2 Elimination of Guests. To examine the liberation of guests within the layered frameworks, thermogravimetric (TG) analysis for **1** and **2** was carried out and showed the release of guest molecules with increasing temperature up to 110 °C for **1** and 100 °C for **2**. A weight loss of 6.27% for **1** (calcd 6.67%) and 10.04% for **2** (calcd 9.99%) indicates the elimination of one benzene and one mesitylene molecule per formula unit, respectively. No further weight loss was observed between 110 and 150 °C for **1a** and from 100 to 150 °C for **2a**, respectively. ^1H NMR resonances of benzene were observed in acetone-d_6 of **1** (Figure 5a) but were not observed in **1a** (Figure 5b). Similarly, the resonances of mesitylene were observed in **2** but not observed in **2a** (Figure 6). Furthermore, the mass spectrum of **1** measured at 110 °C indicates a peak ($M = 78$) corresponding to benzene's molecule weight, but that of **1a** does not exist (Figure 7). The same phenomena were observed for **2** and **2a** (Figure 8). These results support complete elimination of benzene in **1** and mesitylene in **2**. Figures 9 and 10 show the X-ray powder diffraction (XRPD) patterns of **1** and **2** and their derivatives, respectively. Sharp diffraction peaks of the XRPD patterns of **1a** and **2a** indicate that the layered structures are not essentially collapsed even without guests, although the initial structures of **1** and **2** are slightly different from those of **1a** and **2a**. Peaks corresponding to the relative position of the layer motifs shift to the larger angle region, and the intensity of XRPD patterns decreases. These findings indicate shrinking of the layer gap, which is attributable to the absence of the guest molecules. Interestingly, the guest molecules in complexes **1** and **2** are completely liberated to give complexes **1a** and **2a**, respectively, accompanied by little structural changes.

3.3 Reincorporation of Guests. It is of interest to note whether guest molecules of benzene or mesitylene can again take up the layer space in **1a** or **2a**, so that the original structure is recovered. We obtained the benzene-reincorpo-

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(55) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.
(56) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc*. **1991**, *113*, 4696.
(57) Ermer, O. *J. Am. Chem. Soc*. **1988**, *110*, 3747.
(58) MacNicol, D. D.; McKendrick J. J.; Wilson, D. R.*Chem. Soc. Rev.* **1978**, *7*, 65.
(59) MacNicol, D. D. *Inclusion Compounds*; Academic: London, 1984; Vol. 2, pp 1−45.
(60) Mahdyarfar, A.; Harris, K. D. M. *J. Chem. Soc. Chem. Commun*. **1993**, 51.
(61) Wang, X.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc*. **1994**, *116*, 12119.
(62) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341.

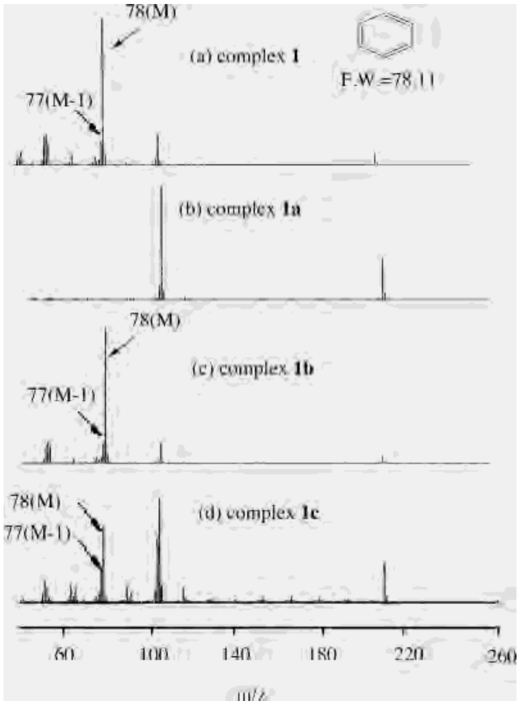

Figure 7. Mass spectra of complex **1** and its derivatives (a) **1**, (b) **1a**, (c) **1b**, (d) **1c**.

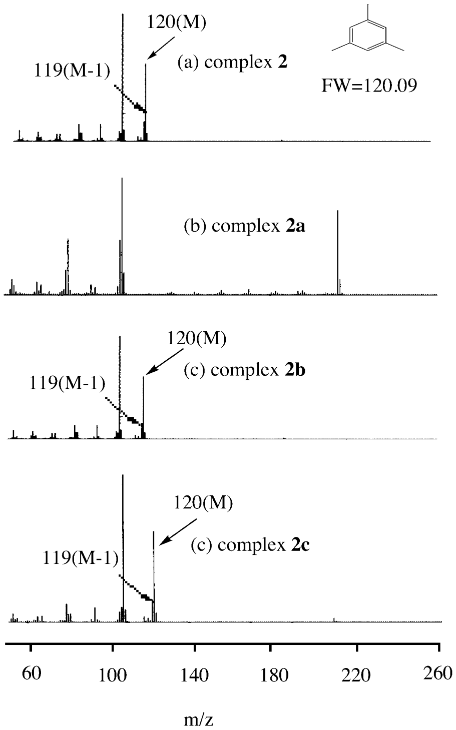

Figure 8. Mass spectra of complex **2** and its derivatives (a) **2**, (b) **2a**, (c) **2b**, (d) **2c**.

rated complexes **1b** and **1c** and mesitylene-reincorporated complexes **2b** and **2c** as shown in the Experimental Section.

TG analysis of **1b** shows the release of the benzene molecule at 110 °C with a weight loss of 6.35%, which is similar to the calculated value of 6.67%. ^{1}H NMR resonances of benzene were observed in acetone-d_6 solution of **1b**, indicating that benzenes are incorporated in **1a** to give **1b** (Figure 5c). The mass spectrum of **1b** (Figure 7c) demonstrates the existence of benzene in **1b**. In the case of **2b**, similar behaviors are observed (Figures 6c and 8c), and subsequently, mesitylenes can be intercalated in **2a** to give **2b**. This is supported by the 9.85% weight loss of **2b** in TG analysis. The XRPD pattern of **2b** is essentially the same as that of **2** (Figure 10c), which indicates that the original layered structures are recovered after reincorporation of mesitylene. But the XRPD pattern of **1b** is different from those of **1**, which indicates the original structure of **1** is not completely recovered by immersing **1a** in benzene (Figure 9c). However, the XRPD pattern of complex **1c** (Figure 9d), obtained on exposing **1a** to benzene vapor for 3 days under reduced pressure at room temperature, is virtually identical to that of **1**. This is supported by ^{1}H NMR and mass spectra as shown in Figures 5d and 7d, respectively. In addition, the attempts to convert **2a** to **2c (=2b = 2)** in the presence of mesitylene vapor for 20 days under reduced pressure at room temperature was also successful, which is confirmed by ^{1}H NMR spectra, mass spectra, and XRPD patterns shown in Figures 6, 8, and 10. The process of adsorption of mesitylene in the presence of mesitylene vapor needs much longer time (20 days) than that of benzene (3 days) mainly because of the higher steric hindrance of mesitylene as well as the lower pressure. The reversible structural changes of **1** → **1a** → **1** (=**1c**) and **2** → **2a** → **2**(=**2b** = **2c**) can take place, showing the flexibility of the layered structure. It is noted that the XRPD patterns of **1a** and **2a** are complete identical, indicative of isostructure. Furthermore, they can incorporate guest molecules with different size (benzene and mesitylene) accompanied by the adjustment of the interlayer

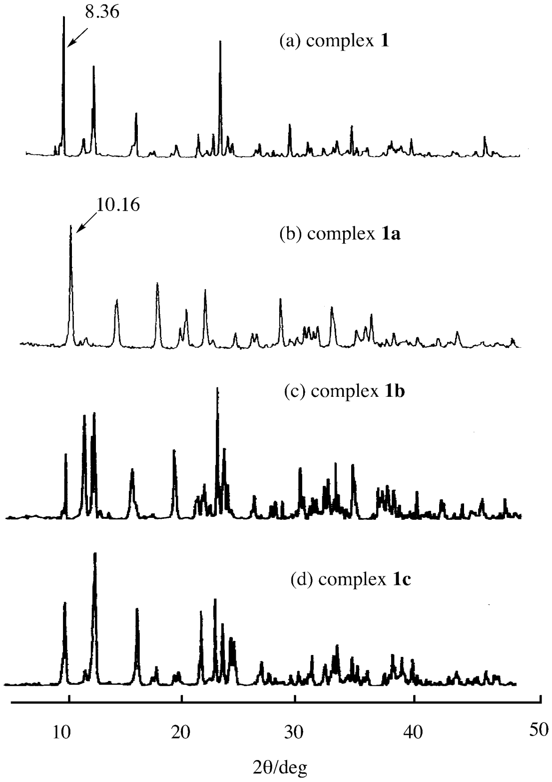

Figure 9. XRPD patterns of (a) **1**, (b) **1a**, (c) **1b**, and (d) **1c**.

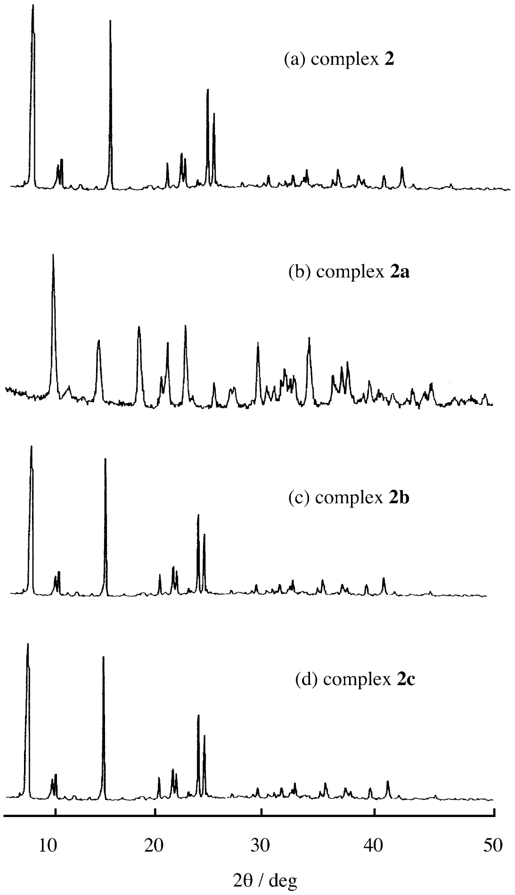

Figure 10. XRPD patterns of (a) **2**, (b) **2a**, (c) **2b**, (d) **2c**.

distance. These observations also illustrate the flexibility of the sheet packing as well as the 2-D sheet structures.

Complex **3** was synthesized in mesitylene with a molar ratio of 1:1 between $AgC_2F_5CO_2$ and pcp. The result of ^1H NMR resonances of **3** in THF shows that there are no other peaks except those of pcp (δ H, 3.04 and 6.45) and THF (δ H, 1.73 and 3.58), indicating the presence of pcp in **3**. Elemental analysis and X-ray structure determination demonstrate that there exist two molecules of pcp per formula unit, one as a ligand and the other as a guest molecule. Pcp elimination of complex **3** cannot be obtained mainly due to the higher boiling point of pcp. TG analysis for **3** reveals that weight loss occurs at 140 °C and the structure decomposition occurs at 195 °C (Figure 11). The weight loss of 4.8% between 140 and 195 °C (calcd 13.87%) indicates liberation of a small fraction of guests in **3** before decomposition.

3.4 Incorporation of Other Guests. We select complex **2a** as samples to confirm its adsorption of other guests because the structures of complexes **2a** and **1a** are completely the same according to the above results. Further, it is very difficult to collect a large amount of complex **1** mainly because the crystals are very tiny. It is surprising that complex **2a** has high selectivity of the linear aromatic hydrocarbons of benzene, naphalene, and anthracene, which were evidenced by their ^1H NMR spectra. When complex **2a** was immersed in benzene/mesitylene (volume ratio, 1:1) for one week, ^1H NMR spectra of the resulting complex indicated that only benzene was incorporated in **2a**. The same phenomena were observed when **2a** was immersed in naphthalene/mesitylene for two weeks or anthracene/mesitylene for two weeks. That is, only naphthalene or anthracene was included in **2a**. Further, there is a selectivity of toluene over mesitylene if both are present in solution. Compound **2a** can also selectively adsorb benzene and toluene when a mixture of benzene, toluene, mesitylene, and anthracene is present in solution. On the basis of these findings, it seems reasonable to assert that the lower steric hindrance of linear atomatic hydrocarbons (including toluene) makes them the priority to other aromatic hydrocarbons to be incorporated.

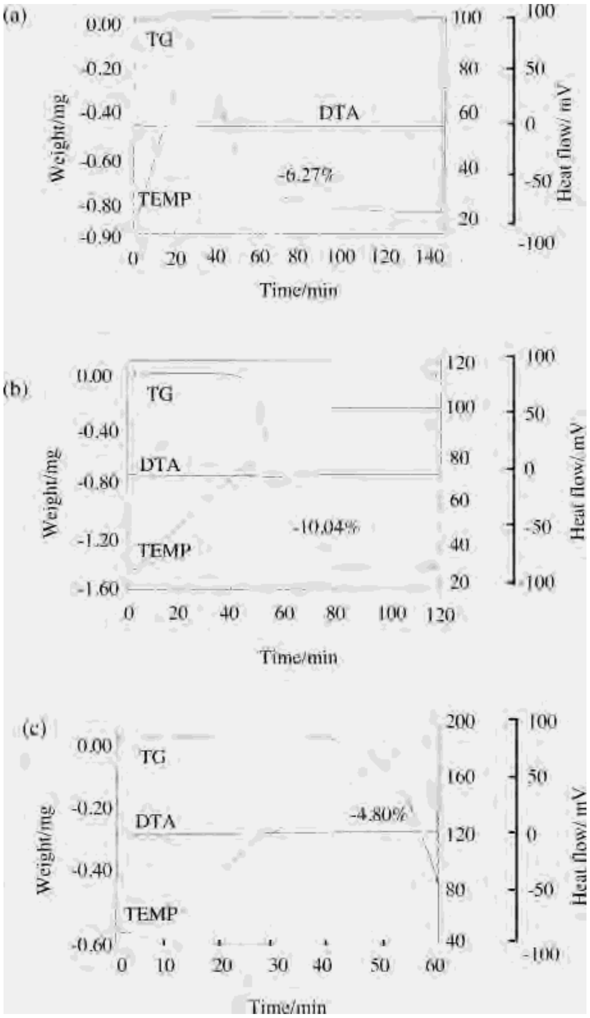

Figure 11. TG curves of complex (a) **1**, (b) **2**, and (c) **3**.

4. Conclusion

We succeeded in synthesizing a series of intercalation compounds ($[Ag_4(pcp)(CF_3CO_2)_4](C_6H_6)$ (**1**), $[Ag_4(pcp)(CF_3CO_2)_4](C_6H_3Me_3)$ (**2**), and $[Ag_4(pcp)(C_2F_5CO_2)_4](pcp)$ (**3**)) with 2-D sheet structures. The interlayer distances of these compounds are adjusted to the size of guest molecules, indicative of flexibility of the 2-D sheet packing. The guests (benzene and mesitylene) in complexes **1** and **2** can be easily eliminated by heating to give isostructral complexes **1a** and **2a**, respectively, accompanied by small structural changes, and subsequently the original layered structures of **1** and **2** can be completely recovered by reincorporation of benzenes for **1a** and mesitylenes for **2a**, respectively. Complex **2a** has a high selectivity of linear aromatic hydrocarbon over mesitylene. It may be possible to create new functional intercalation compounds by replacing the guests which have potential functions such as fluorescence or magnetic properties. Thus, organometallic complexes are potentially a very rich field in the study on intercalation network, and the flexible coordination network opens up a new field in intercalation compounds.

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Supporting Information Available: Additional details of crystal structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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