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Syntheses, Structures, and Properties of Three Novel Coordination Polymers of Silver(I) Aromatic Carboxylates with Hexamethylenetetramine Exhibiting Unique Metal−π Interaction

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Three interesting coordination polymers, $[Ag_4(\mu_4\text{-hmt})(\mu_4\text{-}\eta^2\text{-nda})_2]\cdot 2H_2O$ (**1**), $[Ag_2(\mu\text{-hmt})_2(\mu\text{-bi-}\eta^2\text{-bna})]\cdot 2H_2O\cdot MeCN$ (**2**), and $[Ag_2(\mu_4\text{-hmt})(\eta^2\text{-hna})(MeCN)](hna)\cdot H_2O$ (**3**) (hmt = hexamethylenetetramine, nda = 2,6-naphthalenedicarboxylate, bna = 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate, and hna = 1-hydroxy-2-naphthalenecarboxylate), were obtained from the reaction of silver(I) aromatic carboxylates in MeCN solution with hmt in CH_2Cl_2 solution via the liquid diffusion method. In these complexes, the aromatic carboxylates ligate to the metal atoms via a unique η^2-coordination mode involving their aromatic rings, in addition to the normal coordination modes utilizing their carboxylate oxygen atoms. These complexes show interesting electronic properties similar to those reported for the silver(I) complexes of other polycyclic aromatic compounds. Both **1** and **2** exhibit a strong blue photoluminescence at room temperature.

Introduction

Recently, considerable research effort in organometallic chemistry has been focused on organosilver(I) systems containing polycyclic aromatic hydrocarbon ligands with cation−π-ligand interactions, since these polymers might show interesting electrical or magnetic properties associated with electron delocalization and electronic cooperative interactions.[1,2] On the other hand, by careful control of reaction conditions together with the selection of appropriate polycyclic aromatic hydrocarbon ligands, a vast variety of open frameworks and layered materials have been prepared.[2−5] In previous studies of the self-assembly of the potentially tetradentate hexamethylenetetramine (hmt) ligand with the coordinatively flexible silver(I) atoms, attention was devoted to the construction of interesting supramolecular architectures.[6−12] We have recently shown the possible routes for rational organization of 2-D hexagonal Ag(I)−hmt coordination layers into several kinds of 3-D networks with porous structures.[11a] We report herein three novel coordination polymers, namely, $[Ag_4(\mu_4\text{-hmt})(\mu_4\text{-}\eta^2\text{-nda})_2]\cdot 2H_2O$ (**1**), $[Ag_2(\mu\text{-hmt})_2(\mu\text{-bi-}\eta^2\text{-bna})]\cdot 2H_2O\cdot MeCN$ (**2**), and $[Ag_2(\mu_4\text{-hmt})(\eta^2\text{-hna})(MeCN)](hna)\cdot H_2O$ (**3**) (nda = 2,6-naphthalenedicarboxylate, bna = 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate, and hna = 1-hydroxy-2-naphthalenecarboxylate), in which

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the carboxylate ligands exhibit a unique η^2 coordination mode involving their aromatic rings, in addition to their usual carboxylate ligation. All of these complexes are stable toward air and photodegradation and show interesting properties similar to those of other silver(I) complexes of polycyclic aromatic hydrocarbon compounds.[2] Both **1** and **2** exhibit strong blue photoluminescent properties at room temperature.

Results and Discussion

Synthesis and Characterization. Complexes **1**–**3** were synthesized by the reaction of the Ag(I) carboxylates [Ag_2(nda), Ag_2(bna), and Ag(hna)] in MeCN with hmt in CH_2Cl_2 via the liquid diffusion method, which has been extensively employed in the preparation of silver(I) complexes of other polycyclic aromatic compounds.[2] Compared with the synthesis of the related Ag–hmt coordination complexes,[6–12] the present method provides an important route to the construction of frameworks in which the aromatic carboxylates exhibit a unique η^2-coordination mode due to their aromatic rings, in addition to the usual coordination modes via their carboxylate functionality. It should be pointed out that all of the complexes were synthesized in open air, and the products are stable toward air and photodegradation. They are almost insoluble in common organic solvents, a common property of coordination polymers. Thermal analyses showed that the polymeric network of **1** was stable up to ca. 230 °C and started to decompose at this temperature after an exothermic peak. This indicates that the aqua ligand is strongly coordinated to the metal center, in accordance with the relatively short Ag–O bond length as revealed in its crystal structure. The thermal behaviors of **2** and **3** are similar to those of the previously reported Ag–hmt polymeric species with solvated solvent molecules, they lost endothermically the solvated molecules at T <160 °C, and began to decompose above 210 °C after an exothermic peak.[6a,c,7,9,11a] The relatively high thermal stability of **1**–**3**, as compared to other silver(I) complexes of polycyclic aromatic compounds,[2] may be attributed to the normal carboxylate coordination of the naphthalenecarboxylates in these complexes.

Crystal Structures. The structure of **1** consists of staircase-like one-dimensional chains with box-like units (Figure 1). These chains are further extended into a three-dimensional network via the unique [hmt·4Ag(I)] structural units, which are only found in the two silver(I) halide complexes of hmt, viz., [hmt·4AgX] (X = Cl^- and Br^-).[12] As shown in Figure 1b, there are two crystallographically independent Ag(I) atoms. A pair of the Ag(1) atoms, separated at 3.742(4) Å, are bridged by two μ-carboxylate-O groups [Ag(1)–O 2.334(5) and 2.428(5) Å, O(1A)–Ag(1)–O(1B) 76.4(2)°]. Each Ag(1) atom is also ligated by one oxygen atom [Ag(1)–O(3C) 2.598(6) Å] from a carboxylic group of an adjacent dicarboxylate molecule. The other oxygen atom of the same carboxylate group ligates, in turn, to the Ag(2) atom [Ag(2B)–O(4C) 2.413(6) Å], resulting in an unusual non-coplanar *syn*-skew carboxylate-O,O′ bridging mode[10,13] [torsion angle Ag(1)–O(3C)–C(12C)–C(6C) = 54.0(3)°] with the Ag(1)···Ag(2B) distance of 4.452(2) Å.

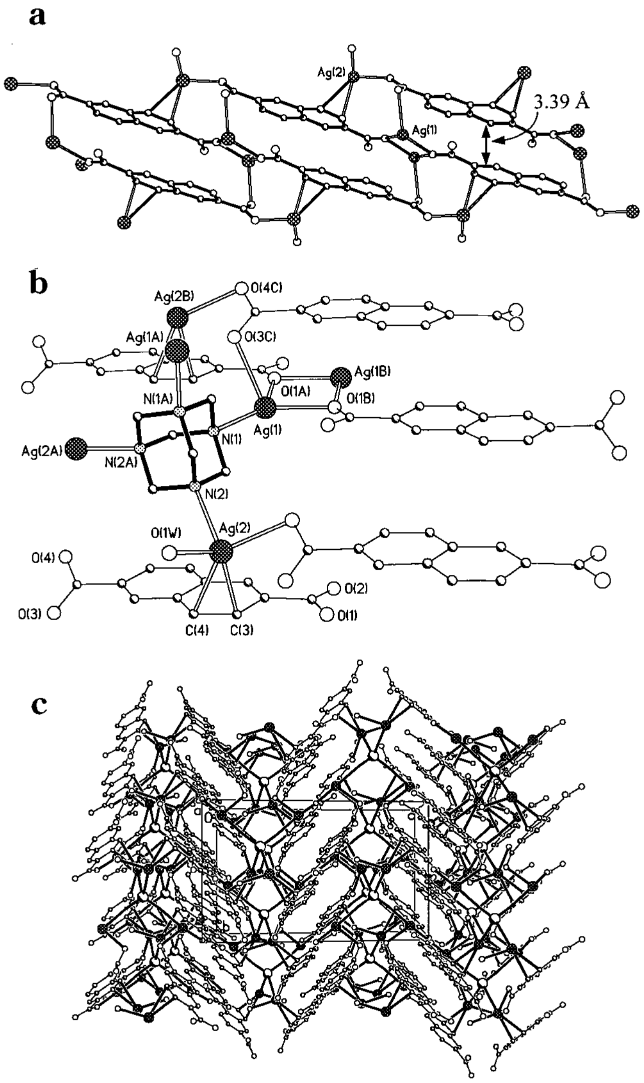
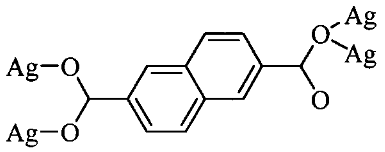


Figure 1. Perspective views showing the staircase-like one-dimensional chain with box-like units (a), coordination environments of the metal atoms and the unique [hmt·4Ag(I)] core (b), and the 3-D network viewed along the *a*-axis (c) in **1**. For clarity, the hmt ligands are simplified as open balls at their centers of mass in (c).

Chart 1. Unique μ-O-Bridging Bidentate Coordination Mode of the Nda Ligand in 1



Each Ag(1) atom is further ligated by one nitrogen atom from the hmt ligand [Ag(1)–N(1) 2.343(5) Å, N(1)–Ag(1)–O 84.4(2)–142.1(2)°], completing a distorted tetrahedral coordination around the metal center. The Ag(2) atom also exhibits a distorted tetrahedral coordination geometry. Besides ligation from a carboxylic oxygen atom, this metal center is coordinated by one hmt nitrogen atom [Ag(2)–N(2) 2.433(6) Å], one aqua ligand [Ag(2)–O(1W) 2.329(6) Å, O(1W)–Ag(1)–O(or N) 92.1(2)–116.8(2)°], and an η^2-bonded aromatic ring of an adjacent nda ligand molecule [Ag(2)–C 2.433(6) and 2.467(6) Å]. To the best of our knowledge, this μ-O-bridging bidentate coordination mode in metal dicar-

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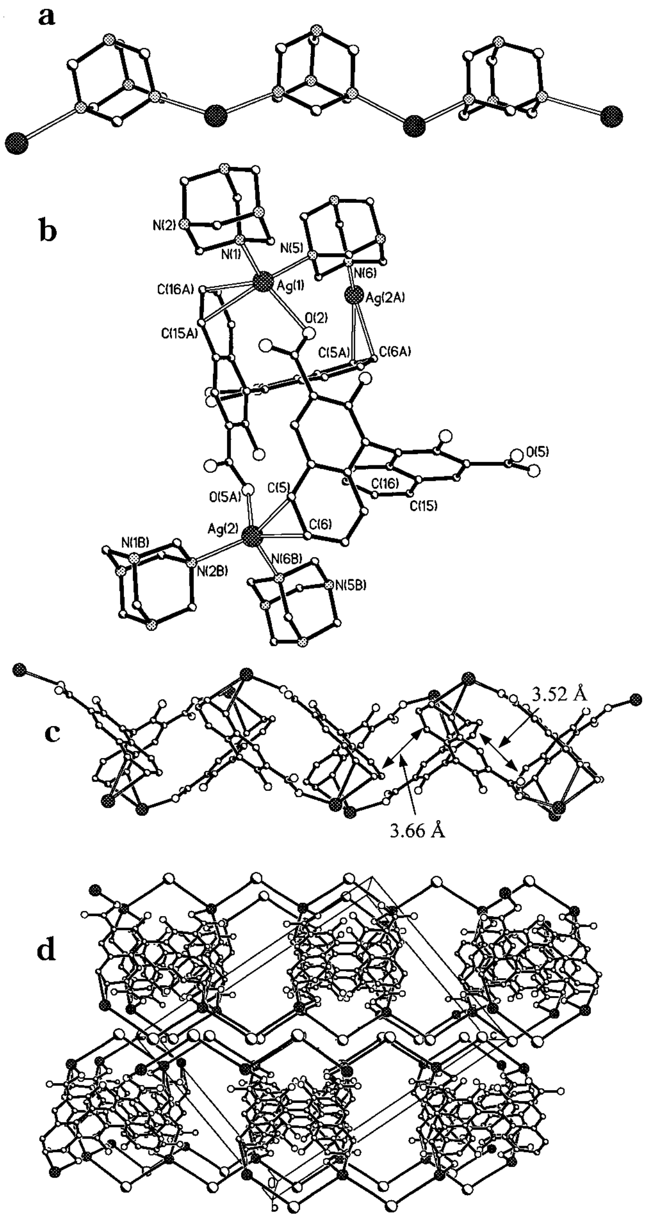

Figure 2. Perspective views showing the infinite zigzag $[Ag(\mu\text{-hmt})]_\infty$ chains (a), the coordination environments of the metal atoms (b), the double-helical chain (c), and the 3-D network viewed along the *a*-axis (d) in **2**. For clarity, the lattice water and acetonitrile molecules are omitted and the hmt ligands are simplified as open balls at their centers of mass in (d).

boxylates (Chart 1) has not been reported so far. This dicarboxylate coordination mode plus the η^2-coordination of the nda ligand in **1** plays an important role in the construction of the staircase-like one-dimensional chains with box-like units (size ca. 11 by 3.4 Å). The aromatic rings of the nda ligands in each box-like subunit of the polmeric chain show strong $\pi-\pi$ interactions in an offset fashion with a face-to-face stacking distance of 3.39 Å. The staircase-like chains are interconnected by the μ_4-hmt ligands to form a three-dimensional network (Figure 1c), featuring the uncommon [hmt·4Ag(I)] cores (Figure 1b).

The structure of **2** features a two-dimensional framework with channels constructed from infinite zigzag $[Ag(\mu\text{-hmt})]_\infty$ chains (Figure 2a), in which the hmt ligands act in an unusual μ-bridging coordination mode.[10] As shown in Figure 2b, two crystallographically independent Ag(I) atoms, having a similar distorted tetrahedral environment, have been identified. Each of the Ag(I) atoms is coordinated by one C=C π-bond of a bna ligand [Ag(1)−C 2.639(9) and 2.710(9) Å, and Ag(2)−C 2.633(9) and 2.647(9) Å] (taking a C=C group as one ligand), one carboxylate oxygen atom of an adjacent bna ligand [Ag(1)−O(2) 2.402(6) Å, and Ag(2)−O(5A) 2.463(6) Å], and two nitrogen atoms from two hmt ligand molecules [Ag(1)−N 2.405(6) and 2.433(7) Å, N−Ag(1)−N(or O) 84.0(2)−123.2(2)°, and Ag(2)−N 2.392(7) and 2.408(7) Å, N−Ag(2)−N(or O) 85.3(2)−117.9(2)°]. On the other hand, as shown in Figure 2c, each bna ligand displays the unique bis-monodentate-bi-η^2-coordination mode to ligate four metal centers. Furthermore, two naphthyl rings of each bna ligand are not coplanar to each other. A dihedral angle of 89.4° between two naphthyl rings is observed. This may be responsible for the formation of a double-helical chain, featuring an offset intermolecular $\pi-\pi$ interaction with face-to-face stacking distances of 3.52 and 3.66 Å between naphthyl groups on adjacent bna ligands. The period of the helix is equal to the length of the crystallographic *b*-axis (12.461(7) Å). In addition, each hmt ligand functions as a linkage bridging two adjacent double-helical chains via the Ag(I) atoms, giving rise to a two-dimensional framework with channels (effective size[14] of ca. 4 × 5 Å) along the *b*-axis (Figure 2d). The free dimensions of these channels occupy 13.3% of the crystal volume.[15] The lattice water molecules and acetonitrile molecules are clathrated in these channels, and the former form donor hydrogen bonds [O(1w)···O(2) 2.895(10)−3.042(11) Å] with the uncoordinated carboxylic oxygen atoms.

As shown in Figure 3, the structure of **3** consists of two-dimensional infinite wavy cationic layers of square units, which are similar to those reported for the related complexes $[Ag_2(\mu_4\text{-hmt})X]$ (X = SO_4^{2-}, NO_2^-, oxalate, and *p*-toluenesulfonate).[7,9] Each square unit of **3** consists of four Ag(I) atoms (which exhibit two different types of coordination geometries) and four hmt molecules, each of which is located at the corner and the midpoint of each side of the square. The Ag(1) atom is bound by two nitrogen atoms from two different hmt ligands [Ag(1)−N 2.329(4) and 2.476(4) Å, N−Ag(1)−N 148.3(2)°] and one MeCN nitrogen atom [Ag(1)−N 2.264(6) Å, N−Ag(1)−N 97.1(2)° and 112.9(1)°], resulting in a *T*-shaped geometry. The Ag(2) atom exhibits a distorted tetrahedral geometry, being coordinated by two nitrogen atoms from two different hmt ligands [Ag(2)−N 2.368(4) and 2.426(4) Å, N−Ag(2)−N 110.2(1)°], one oxygen from a hna ligand [Ag(2)−O 2.324(5) Å, O−Ag(2)−N 90.8(2)° and 103.2(2)°], and a strongly η^2-bonded aromatic ring of an adjacent hna ligand [Ag(2)−C 2.480(5) and 2.522(5) Å]. In other words, the hna ligands here interlink the Ag(2) atoms on the opposite edges of the two-dimensional infinite wavy neutral layers in a unique η^2-coordination fashion (Figure 3b). As shown in Figure 3c, an equivalent amount of hna ligands and lattice water molecules are clathrated between the two-dimensional layers with weak Ag···O contacts [Ag(1)···

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[14] The channel dimensions are estimated from the van der Waals radii for carbon (1.70 Å), nitrogen (1.55 Å), and oxygen (1.40 Å).

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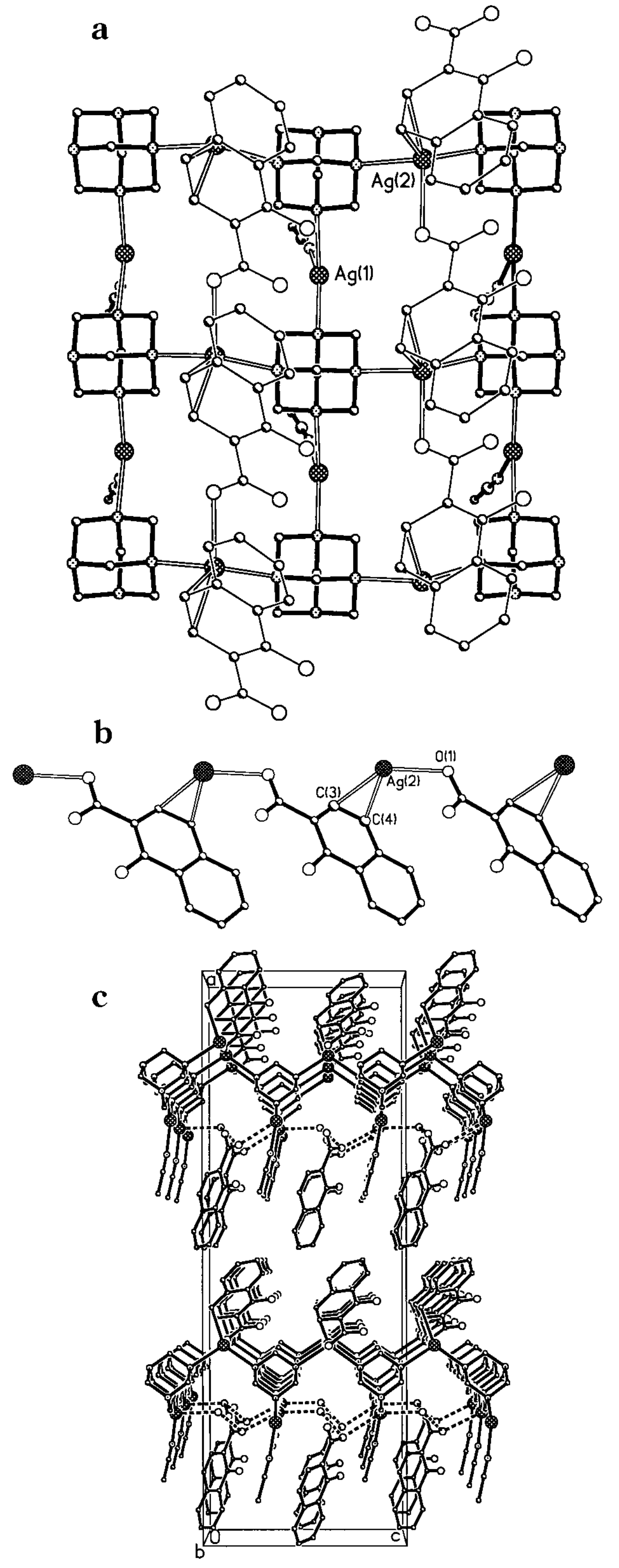

Figure 3. Perspective views showing the layer (a), the unique monodentate-η^2-coordination fashion of the hna ligands (b), and the 3-D network viewed along the *b*-axis (c) in **3**.

Table 1. Crystal Data and Structure Refinement for 1, 2, and 3

empirical formula	$C_{30}H_{28}Ag_4N_4O_{10}$	$C_{36}H_{43}Ag_2N_9O_8$	$C_{30}H_{31}Ag_2N_5O_7$
fw	1036.04	945.53	789.34
space group	*C*2/*c* (No.15)	*P*2$_1$/*n* (No.14)	*Cc* (No.9)
a (Å)	15.460(7)	14.855(11)	36.35(2)
b (Å)	10.902(5)	12.461(7)	6.473(3)
c (Å)	17.884(11)	19.860(18)	12.711(7)
β (deg)	102.60(6)	95.12(8)	90.12(2)
V (Å^3)	2942(3)	3662(5)	2991(3)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	2.339	1.715	1.753
T (°C)	20(2)	20(2)	20(2)
μ (mm^{-1})	2.693	1.136	1.366
λ (Å) (Mo Kα)	0.71073	0.71073	0.71073
R_1 ($I > 2\sigma(I)$)^a	0.0675	0.0662	0.0309
wR_2 (all data)^b	0.1853	0.1874	0.0775

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (0.1(\max(0,F_o^2) + 2F_c^2)/3)^2]^{-1}$.

O(5) 3.056(8) Å and Ag(1)···O(1w) 2.629(3) Å]. Hydrogen bonds between these clathrated molecules were observed, as evidenced by the O(1w)···O distances of 2.739(6) and 2.819(7) Å. A face-to-face stacking distance of 3.65 Å is observed between aromatic rings of adjacent uncoordinated hna anions, which are oriented in an offset fashion, suggesting the presence of $\pi-\pi$ stacking interactions.

The most significant structural feature presented here is the unique η^2-coordination fashion of the aromatic rings of the naphthalenecarboxylates. Despite the demonstrated coordination ability of the naphthalenecarboxylates in chelating and/or bridging metal atoms, studies on the unique silver$-\pi$ bonding interaction involving naphthalene carboxylates have never been documented. To our knowledge, compounds **1**−**3** represent the first structurally characterized metal$-\pi$ bonding complexes of aromatic carboxylates, although a similar η^1 Ag$-\pi$ interaction [Ag−C 2.688(8) Å] had been recently reported for [$Ag_2(\mu_4$-hmt)(tos)] (tos = *p*-toluenesulfonate)[7] as well as for the silver(I) complexes of other polycyclic aromatic compounds.[2]

As listed in Table 2, the Ag−C separations range from 2.433(6) to 2.710(9) Å. The next closest contacts between the silver and carbon atoms are all above 3.13 Å, well beyond the values reported for the silver(I) complexes of other polycyclic aromatic compounds.[2] Thus, each naphthalenecarboxylate in **1**−**3** displays the unique η^2-coordination mode which involves their aromatic rings, apart from the usual coordination via their carboxylate functionality. It should be pointed out that, being similar to the silver(I) complexes of other polycyclic aromatic compounds,[2] coordination polymers **1**−**3** demonstrate a common feature of asymmetric η^2 Ag$-\pi$ interaction, in which the two Ag−C distances differ significantly from each other. Furthermore, in the previously reported silver(I) complexes of aromatic compounds, silver(I) atoms are found to be inclined to bond at the shortest carbon−carbon bond portion,[2] and this tendency is generally maintained in the present coordination polymers, indicative of the large electron density accumulated on the π-bonded carbon atoms. Although the naphthalenecarboxylate ligands in **1**−**3** display the normal coordination mode via their carboxylate functionalities, they also display their coordination ability utilizing their aromatic π-bonds to ligate to Ag(I) atoms. Therefore, **1**−**3** may exhibit physical properties

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 1, 2, and 3[a]

Complex **1**			
Ag(1)−O(1a)	2.334(5)	Ag(2)−N(2)	2.433(6)
Ag(1)−N(1)	2.343(5)	Ag(2)−C(3)	2.467(6)
Ag(1)−O(1b)	2.428(5)	Ag(2)−C(4)	2.669(7)
Ag(1)−O(3c)	2.598(6)	O(1w)···O(2e)	2.721(8)
Ag(2)−O(1w)	2.329(6)	O(1w)···O(4f)	2.741(9)
Ag(2)−O(4d)	2.413(6)		
O(1a)−Ag(1)−N(1)	141.3(2)	O(4d)−Ag(2)−N(2)	92.1(2)
O(1a)−Ag(1)−O(1b)	76.4(2)	O(1W)−Ag(2)−C(3)	122.9(2)
N(1)−Ag(1)−O(1b)	142.1(2)	O(4d)−Ag(2)−C(3)	104.2(2)
O(1a)−Ag(1)−O(3c)	113.5(2)	N(2)−Ag(2)−C(3)	122.1(2)
N(1)−Ag(1)−O(3c)	84.4(2)	O(1w)−Ag(2)−C(4)	103.0(2)
O(1b)−Ag(1)−O(3c)	80.3(2)	O(4d)−Ag(2)−C(4)	134.2(2)
O(1w)−Ag(2)−O(4d)	116.8(2)	N(2)−Ag(2)−C(4)	106.6(2)
O(1w)−Ag(2)−N(2)	95.3(2)	C(3)−Ag(2)−C(4)	30.8(2)
Complex **2**			
Ag(1)−O(2)	2.402(6)	Ag(2)−C(6)	2.633(9)
Ag(1)−N(1)	2.405(6)	Ag(2)−C(5)	2.647(9)
Ag(1)−N(5)	2.433(7)	O(1)···O(1w)	2.895(10)
Ag(1)−C(16a)	2.639(9)	O(2)···O(3)	2.550(8)
Ag(1)−C(15a)	2.710(9)	O(5)···O(6)	2.545(8)
Ag(2)−N(2b)	2.392(7)	O(1w)···O(4d)	3.042(11)
Ag(2)−N(6c)	2.408(7)	O(2w)···O(4d)	2.821(10)
Ag(2)−O(5a)	2.463(6)	O(2w)···O(2wb)	3.138(18)
O(2)−Ag(1)−N(1)	123.2(2)	N(2b)−Ag(2)−N(6c)	111.5(2)
O(2)−Ag(1)−N(5)	84.0(2)	N(2b)−Ag(2)−O(5a)	117.9(2)
N(1)−Ag(1)−N(5)	115.2(2)	N(6c)−Ag(2)−O(5a)	85.3(2)
O(2)−Ag(1)−C(16a)	122.1(3)	N(2b)−Ag(2)−C(6)	108.3(2)
N(1)−Ag(1)−C(16a)	102.7(3)	N(6c)−Ag(2)−C(6)	103.9(3)
N(5)−Ag(1)−C(16a)	108.0(3)	O(5a)−Ag(2)−C(6)	125.4(3)
O(2)−Ag(1)−C(15a)	99.7(3)	N(2b)−Ag(2)−C(5)	108.5(2)
N(1)−Ag(1)−C(15a)	104.4(3)	N(6c)−Ag(2)−C(5)	128.0(3)
N(5)−Ag(1)−C(15a)	129.6(3)	O(5a)−Ag(2)−C(5)	104.0(3)
C(16a)−Ag(1)−C(15a)	30.1(3)	C(6)−Ag(2)−C(5)	30.5(3)
Complex **3**			
Ag(1)−N(5)	2.264(6)	Ag(2)−C(3)	2.480(5)
Ag(1)−N(3)	2.329(4)	Ag(2)−C(4)	2.522(5)
Ag(1)−N(4a)	2.476(4)	O(4)···O(1w)	2.739(6)
Ag(2)−O(1b)	2.324(5)	O(5)···O(6)	2.504(6)
Ag(2)−N(1c)	2.368(4)	O(1w)···O(5a)	2.819(7)
Ag(2)−N(2)	2.426(4)		
N(5)−Ag(1)−N(3)	148.3(2)	N(1c)−Ag(2)−C(3)	115.0(2)
N(5)−Ag(1)−N(4a)	97.1(2)	N(2)−Ag(2)−C(3)	100.6(1)
N(3)−Ag(1)−N(4a)	112.9(1)	O(1b)−Ag(2)−C(4)	101.1(2)
O(1b)−Ag(2)−N(1c)	103.2(2)	N(1c)−Ag(2)−C(4)	136.5(2)
O(1b)−Ag(2)−N(2)	90.8(2)	N(2)−Ag(2)−C(4)	105.0(2)
N(1c)−Ag(2)−N(2)	110.2(1)	C(3)−Ag(2)−C(4)	31.7(2)
O(1b)−Ag(2)−C(3)	132.8(2)		

[a] Symmetry codes: (a) −*x*+1/2, −*y*+1/2, −*z*+1; (b) *x*−1/2, *y*−1/2, *z*; (c) *x*, *y*−1, *z*; (d) *x*+1/2, *y*−1/2, *z*; (e) *x*, −*y*+1, *z*−1/2; (f) −*x*, *y*, −*z*+1/2 for **1**; (a) −*x*+3/2, *y*−1/2, −*z*+3/2; (b) −*x*+2, −*y*, −*z*+1; (c) −*x*+3/2, *y*+1/2, −*z*+3/2; (d) *x*+1/2, −*y*+1/2, *z*−1/2 for **2**; (a) *x*, *y*−1, *z*; (b) *x*, *y*+1, *z*; (c) *x*, −*y*+2, *z*+1/2 for **3**.

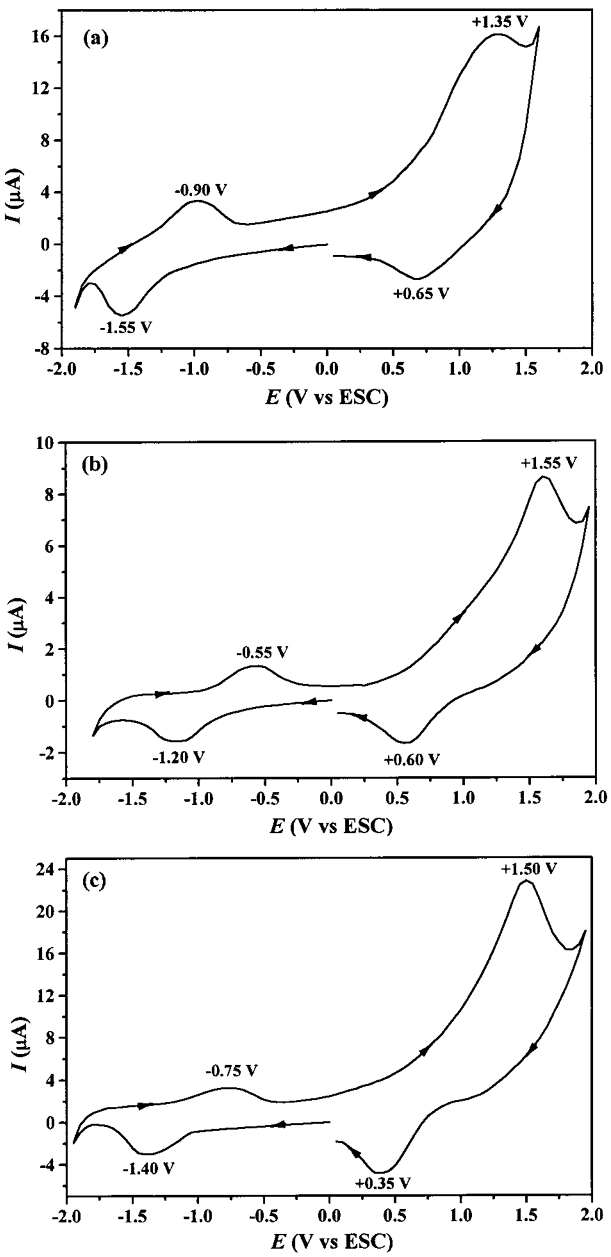

Figure 4. Cyclic voltammograms of **1** (a), **2** (b), and **3** (c) in DMF at room temperature with 0.1 mol·L^{-1} of Bu$^n{}_4$NPF$_6$ as electrolyte at the Pt electrode and SCE reference electrode. Condition: 1.0 × 10^{-4} mol·L^{-1}, v = 100 mV·s^{-1}.

similar to those observed in the silver(I) complexes of other polycyclic aromatic compounds.[2]

Physical Properties. Typically, aromatic hydrocarbon ligands of transition metal complexes can form charge transfer species or even organic radicals, depending on the degree of charge transfer in their ground states.[2b,c,16,17] The UV−vis absorption spectra of the free ligands ndaH$_2$, bnaH$_2$, and hnaH in DMF (5.0 × 10^{-5} M) displayed an intense absorption at around 360 nm, indicative of $\pi^* \leftarrow \pi$ transitions.[2b,c,16] Compared with this, the spectra of **1**, **2**, and **3** in solution exhibit one major absorption band at around 400−420 nm, which are consistent with those of donor−acceptor complexes of highly conjugated aromatic molecules.[2b,c,16] This fact indicates that although disaggregation of these coordination polymers should occur, similar to some silver(I) complexes of polycyclic aromatic compounds,[2] oligomeric species are retained in solution, resulting in some degree of Ag−π interaction. In addition, the high extinction coefficients strongly suggest that these transitions are charge-transfer in nature. It is noteworthy that the spectrum of **3** also displays an intense absorption around 375 nm, which may be ascribed to the uncoordinated hna anions in the complex.

The redox behaviors of **1**−**3** in solution were studied by cyclic voltammetry. Solutions of the complexes in DMF with concentrations up to approximately 1 mM

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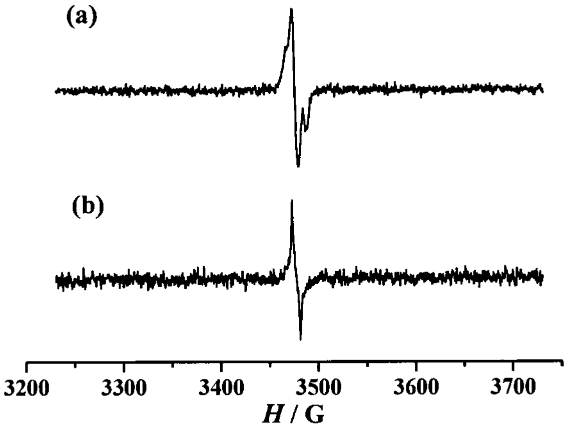

Figure 5. EPR spectra of **1** (a) and **2** (b) upon irradiation.

were prepared for electrochemical measurements. The resulting cyclic voltammograms (CVs) are shown in Figure 4. Each CV shows two distinct redox processes, which have been assigned to ligand-based and metal-based electrochemical reactions, respectively. The CVs of the free ligands ndaH$_2$, bnaH$_2$, and hnaH were recorded under the same conditions. Each shows only one redox process in the region of -1.35 to $+0.24$ V. The waves generally show poor electrochemical reversibility. Similar electrochemical response has been observed previously.[2b,c] Since the polarization potential is governed by the coordination state of a complex: the stronger the donor-coordination ability, the more negative the polarization potential will result.[18] The cathodic waves of **1**, **2**, and **3** occur with the reduction peaks at -1.50, -1.20, and -1.40 V, respectively, which indicates the reduction process. The results of the electoreduction directly correlated to the Ag$-$C bond lengths of **1**, **2**, and **3**. This fact also implies that although disaggregation of the coordination polymers occurs in dissolution, oligomeric species with Ag$-\pi$ interactions in solution similar to those in the solid state are also retained.

Both solid **1** and **2** are EPR silent at room temperature. However, upon irradiation with a 50 W mercury lamp for 2 h, both complexes elicit a well-resolved intense resonance signal centered at $g = 2.00$ (Figure 5), which can be ascribed to the corresponding aromatic hydrocarbon radicals.[2,17] We therefore suggest that, upon irradiation of **1** and **2** with light, electron transfer partially takes place from the aromatic donor to the silver(I) ion, resulting in the formation of an organic radical cation and a silver(0) species. Similar to those silver(I) complexes of polycyclic aromatic compounds,[2] no EPR signal due to the silver(0) species was observed for our compounds probably due to their low sensitivity.

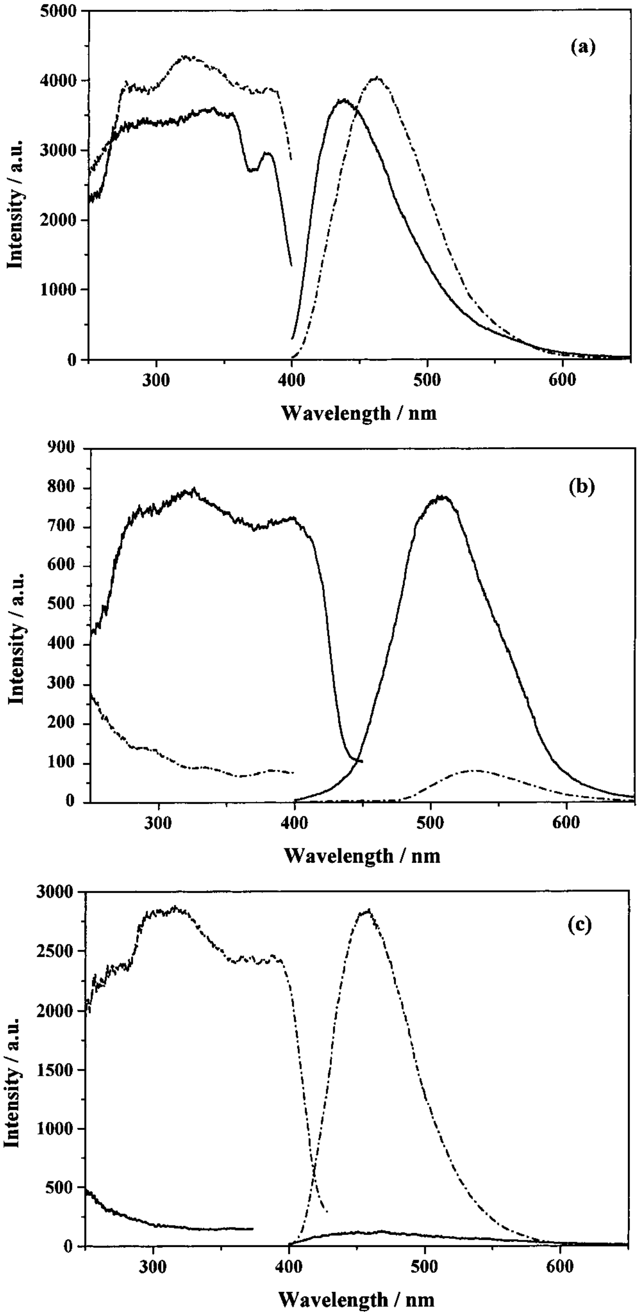

Figure 6. Photoluminescent spectra of **1**$-$**3** and the free ligands (ndaH$_2$, dnaH$_2$, and hnaH) in solid state at room temperature (a$-$c, respectively). The solid lines represent those of complexes, and the dash$-$dot lines represent those of the free ligands.

The solid state photoluminescent spectra of **1**, **2**, **3**, and the free ligands (ndaH$_2$, bnaH$_2$, and hnaH) are depicted in Figure 6. Complex **1** exhibits an intense blue photoluminescence with an emission maximum at ca. 439 nm upon excitation at 312 nm at room temperature, representing a rare example of blue luminescent organometallic compounds.[19] Complex **2** shows an emission with a maximum at ca. 508 nm upon excitation at 334 nm. Although both the free ligand hnaH and its deprotonated form hna$^-$ are strongly photoluminescent, surprisingly, **3** does not display any significant photoluminescent behavior. The quenching phenomenon observed for **3** is in contrast to the observations for **1** and **2**, which are unexpected. Compared with the emission of the free ligand ndaH$_2$, a red shift of ca. 24 nm has been observed upon the coordination of the nda ligand to Ag(I) atoms in **1**. It is noteworthy that the free bnaH$_2$ ligand displays a very weak luminescence in the solid state at ambient temperature, while **2** emits a moderately strong greenish blue luminescence. The enhancement of luminescence in **2** may be attributed to the chelation of the ligand to the metal center. This enhances the "rigidity"

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of the ligand and thus reduces the loss of the energy via a radiationless pathway, facilitating the $\pi^* \rightarrow \pi$ transitions.[20] It should be noted that luminescent silver(I) compounds, usually exhibiting emission at low temperature, are unstable organometallic compounds containing chalcogenides and acetylides as bridging ligands.[21] Only a few monomeric[22] and polymeric[23] silver(I) complexes that exhibited luminescent properties at room temperature have been reported. However, both of our current complexes, **1** and **2**, are strongly luminescent at ambient temperature.

Conclusions

Three unprecedented organosilver(I) complexes with aromatic carboxylate ligands based on Ag−hmt coordination networks were synthesized and characterized. The aromatic carboxylates in these complexes exhibit the unique η^2-coordination mode of the aromatic rings, in addition to the normal carboxylate coordination modes. The complexes show interesting properties analogous to those of silver(I) complexes of polycyclic aromatic compounds reported previously. This work provides a new strategy to the preparation of air-stable multidimensional metallorganic coordination polymers with metal−aromatic interaction, which may exhibit a strong blue photoluminescent behavior at room temperature.

Experimental Section

The free ligand bnaH_2 was obtained by the hydrolytic reaction of its dimethyl ester, which was prepared according to a literature method.[24] The salts Ag_2(nda), Ag_2(bna), and Ag(hna) were also prepared according to a literature procedure.[25] Other reagents and solvents employed were commercially available and used as received without further purification. C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Nicolet 5DX spectrometer. EPR and emission/excitation spectra were recorded on a Bruker EMX spectrometer operating at X-band and a Hitachi F-4500 fluorescence spectrophotometer with solid samples, respectively. Thermogravimetric data were collected on a Perkin-Elmer TGS-2 analyzer in flowing dinitrogen at a heating rate of 10 °C/min.

Synthesis of $[Ag_4(\mu_4\text{-hmt})(\mu_4\text{-}\eta^2\text{-nda})_2]\cdot 2H_2O$ (1). On a solution of hmt (0.070 g, 0.50 mmol) in CH_2Cl_2 (5 mL) was carefully layered a solution of Ag_2(nda) (0.430 g, 1.00 mmol) in the MeCN solution (5 cm^3). After standing of the mixture for three weeks in the dark, pale yellow crystals [ca. 64% yield based on silver] were yielded. Anal. Calcd for $C_{30}H_{28}Ag_2N_4O_{10}$, **1**: C, 43.93; H, 3.44; N, 6.83. Found: C, 44.01; H, 3.41; N, 6.89. IR (KBr, cm^{-1}) for **1**: 3463m, br, 2923m, 2879m, 2017w, 1649w, 1460m, 1371m, 1239s, 1146s, 1113vs, 1087vs, 1006s, 930w, 813s, 688m, 630s, 510m. TGA analysis of **1** shows a weight loss starting at 230 °C.

Synthesis of $[Ag_2(\mu_2\text{-hmt})_2(\mu\text{-bi-}\eta^2\text{-bna})]\cdot 2H_2O\cdot$MeCN (2). The compound was prepared according to an analogous procedure as for **1** (yield ca. 62%). Anal. Calcd for $C_{36}H_{43}Ag_2N_9O_8$, **2**: C, 45.73; H, 4.58; N, 13.33. Found: C, 45.91; H, 4.61; N, 13.41. IR (KBr, cm^{-1}) for **2**: 3417s, br, 3056 m, 2958 m, 2879m, 1953 w, 1832 w, 1643s, 1570s, 1506s, 1459vs, 1395s, 1347vs, 1310s, 1236vs, 1151m, 1085w, 1070w, 1005vs, 941m, 876m, 812s, 748m, 687m, 622m, 595m, 517m, 442w, 410w. The TGA curve for **2** shows that the first weight loss of 8.4% between 70 and 140 °C corresponds to the loss of the two lattice water molecules and one acetonitrile molecule (calculated: 8.2%). Decomposition of the polymeric framework of **2** began at >210 °C.

Synthesis of $[Ag_2(\mu_4\text{-hmt})(\eta^2\text{-hna})(\text{MeCN})](\text{hna})\cdot H_2O$ (3). The compound was prepared according to an analogous procedure as for **1** (yield ca. 68%). Anal. Calcd for $C_{30}H_{31}Ag_2N_5O_7$, **2**: C, 45.65; H, 3.96; N, 8.87. Found: C, 46.01; H, 3.91; N, 8.91. IR (KBr, cm^{-1}) for **3**: 3382m, br, 3056w, 2990w, 2948w, 2924w, 2880w, 1621m, 1680vs, 1503m, 1466s, 1432s, 1402vs, 1369m, 1309s, 1233s, 1173w, 1148w, 1081m, 1052w, 1006vs, 925m, 871w, 807s, 778s, 724w, 688m, 657w, 60w, 525w, 533w, 505w, 448w. The TGA curve for **3** shows that the first weight loss of 2.6% between 100 and 156 °C corresponds to the loss of one lattice water molecules (calculated: 2.3%). The second weight loss of 28.4% between 170 and 210 °C corresponds to the loss of one uncoordinated hna anion and one coordinated acetonitrile molecule (calculated: 28.9%). Decomposition of the polymeric framework of **3** began at >210 °C.

X-ray Crystallography. Diffraction intensities were collected at 21 °C on a Siemens *R*3*m* diffractometer using the ω-scan technique. Lorentz−polarization and absorption corrections were applied.[26] The structures were solved with direct methods and refined with full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively.[27,28] Non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C−H = 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[29] The absolute structure for **3** has been determined with a Flack parameter of 0.00(3).[30] The crystallographic data for **1**−**3** are listed in Table 1. Selected bond lengths (Å) and bond angles (deg) for **1**−**3** are given in Table 2. Drawings were produced with SHELXTL.[31]

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Supporting Information Available: An X-ray crystallographic file, in PDF and CIF formats, for the structure determinations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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