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Syntheses, Structures, and Photoluminescent Properties of Three Silver(I) Cluster-Based Coordination Polymers with Heteroaryldicarboxylate

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Received November 20, 2003

ABSTRACT: Three silver(I) cluster-based coordination polymers, namely, $[\text{Ag}_3(\text{podc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Ag}_2(\text{pidc})]$ (**2**), and $[\text{Ag}_2(\text{pidc})(\text{H}_2\text{O})]$ (**3**) (H_3podc = 3,5-pyrazoledicarboxylic acid and H_2pidc = 2,3-pyrazinedicarboxylic acid) have been synthesized. Among them, **1** consists of stairlike one-dimensional chains with boxlike units as well as the zigzag tetranuclear silver(I) cluster subunits $[\text{Ag} \cdots \text{Ag}$ 2.778(1) and 3.230(1) Å]; **2** features new parallel single-strand silver(I) helices that propagate by the 4_1 -screw symmetry with short $\text{Ag} \cdots \text{Ag}$ contacts $[\text{Ag}2 \cdots \text{Ag}2$ 3.158(1) Å] along the *c*-axis and display the same handedness, while **3** features hexagonal $\text{Ag}_4(\mu_2\text{-O})_2$ cores, in which the $\text{Ag} \cdots \text{Ag}$ separation is 3.150(2) Å. These complexes display room temperature photoluminescence in the blue/green region, which may be assigned to an admixture of ligand-to-metal charge transfer and metal-centered (d-s/d-p) transitions.

Introduction

Recently, the design of polymeric coinage d^{10} metal complexes with fascinating structures and photoluminescent properties has received much attention,^{1–4} and the studies have shown that direct metal–metal interactions are one of the most important factors for the manifestation of such properties. An insight into the phenomenon comes from the observation that the properties of the silver(I) complexes are associated with short $\text{Ag} \cdots \text{Ag}$ separations.^{3,5} On the other hand, it is known that to construct the extended coordination networks with metal cluster-based structures, ligands of various binding sites and shapes, such as nitrogenous aromatic heterocycle carboxylate ligands, have been taken into account. As a part of our efforts toward design and control of the self-assembly of such coordination polymers with specific structures and photoluminescent properties, our attention has been extended to include the assembly of coinage d^{10} metal ions with nitrogen-containing heteroaryldicarboxylate ligands, such as podc and pidc (H_3podc = 3,5-pyrazoledicarboxylic acid and H_2pidc = 2,3-pyrazinedicarboxylic acid), which possess the capability to chelate and bridge metal atoms in various coordination modes using the carboxylate oxygen atoms and nitrogen atoms of the pyrazole or pyrazine ring.^{6–10} Unfortunately, no silver(I) complex with such heterocycle aromatic carboxylate ligands exhibiting short $\text{Ag} \cdots \text{Ag}$ separations was reported.¹⁰ On the other hand, from experience on self-assembly of coordination frameworks, we know that self-assembly of coordination frameworks is highly influenced by factors such as the solvent system, template, pH value of the solution, and steric requirement of the counterion.¹¹ This knowledge has enabled us to synthesize three new silver(I) cluster-based coordination polymers $[\text{Ag}_3(\text{podc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Ag}_2(\text{pidc})]$ (**2**), and $[\text{Ag}_2(\text{pidc})(\text{H}_2\text{O})]$ (**3**) by controlling the solvent system and pH value of the solution. These complexes feature short

$\text{Ag}(\text{I}) \cdots \text{Ag}(\text{I})$ contacts and display photoluminescence in the blue/green region.

Experimental Section

Materials. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet 5DX spectrometer. The emission spectra were recorded on a Perkin-Elmer LS50B fluorescence spectrophotometer, and the excitation source used was the 325 nm line of the He–Cd laser (Kimmon IK5352R-D) with a maximum power of 4 mW. The time-resolved single-photon absorption fluorescence was measured with the third harmonics, 355 nm line of an Nd:YAG laser (Quantel Brilliant B) with a duration of 10 ns as the excitation light.

Synthesis. (a) $[\text{Ag}_3(\text{podc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (1**).** A MeCN solution (5 mL) of H_3podc (0.078 g, 0.5 mmol) was added dropwise to a stirred aqueous solution (5 mL) of AgNO_3 (0.170 g, 1.0 mmol) at 50 °C for 30 min. The mixture was dissolved by dropwise addition of an aqueous NH_3 solution. The resulting colorless solution was allowed to stand in air at room temperature for 2 weeks, yielding pale yellow crystals in a good yield (76%). Anal. calcd for $\text{C}_5\text{H}_9\text{Ag}_3\text{N}_2\text{O}_8$ **1**: C, 12.01; H, 1.01; N, 14.01. Found: C, 11.98; H, 1.10; N, 14.09%. IR (KBr, cm^{-1}): 3325m,br, 2958m, 2875m, 1672m, 1595s, 1553vs, 1453w, 1391s, 1229s, 1173w, 1068w, 1004vs, 835w, 814m, 709s, 681s, 512w, 428w.

(b) $[\text{Ag}_2(\text{pidc})]$ (2**).** An MeCN solution (5 mL) of H_2pidc (0.084 g, 0.5 mmol) was added dropwise to a stirred MeCN solution (5 mL) of AgNO_3 (0.170 g, 1.0 mmol) at 50 °C for 60 min. The mixture was dissolved by dropwise addition of aqueous NH_3 solution, and the resulting colorless solution was allowed to stand in air at room temperature for 2 weeks, yielding pale yellow crystals in a good yield (72%). Anal. calcd for $\text{C}_6\text{H}_4\text{Ag}_2\text{N}_2\text{O}_4$ **2**: C, 18.87; H, 0.53; N, 7.34. Found: C, 18.82; H, 0.61; N, 7.37%. IR (KBr, cm^{-1}): 3057w, 2966w, 2931w, 1562vs, 1509m, 1439s, 1395vs, 1342m, 1236s, 1046w, 1006vs, 920w, 814m, 738m, 688m, 646m, 625w, 512w.

(c) $[\text{Ag}_2(\text{pidc})(\text{H}_2\text{O})]$ (3**).** It was prepared as for **2** using water in place of MeCN as the solvent. The resulting colorless solution was allowed to stand in air at room temperature for 2 weeks, yielding colorless crystals in a good yield (76%). Anal. calcd for $\text{C}_6\text{H}_4\text{Ag}_2\text{N}_2\text{O}_5$ **3**: C, 18.02; H, 1.01; N, 7.01. Found: C, 18.05; H, 1.07; N, 7.06%. IR (KBr, cm^{-1}): 3396m, 3056w, 1612s, 1591vs, 1429s, 1387s, 1352s, 1199w, 1157m, 1107s, 1065w, 878m, 825m, 738m, 635w, 598w, 417w.

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Table 1. Crystal Data and Structure Refinement for Complexes 1–3

	1	2	3
formula	C ₅ H ₉ Ag ₃ N ₂ O ₈	C ₆ H ₂ Ag ₂ N ₂ O ₄	C ₆ H ₄ Ag ₂ N ₂ O ₅
<i>M_r</i>	548.75	381.84	399.85
crystal size (mm ³)	0.40 × 0.09 × 0.08	0.26 × 0.25 × 0.20	0.16 × 0.12 × 0.10
crystal system	triclinic	orthorhombic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 4 ₃	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> (K)	293(2)	293(2)	293(2)
<i>a</i> (Å)	7.193(1)	7.686(1)	7.705(1)
<i>b</i> (Å)	9.374(2)		16.246(1)
<i>c</i> (Å)	9.900(1)	11.947(1)	7.291(1)
α (deg)	87.55(1)		
β (deg)	68.91(1)		115.19(1)
γ (deg)	78.79(1)		
<i>V</i> (Å ³)	610.7(2)	705.8(1)	825.9(2)
<i>D_c</i> (g cm ⁻³)	2.984	3.594	3.216
<i>F</i> (000)	516	712	752
<i>Z</i>	2	4	4
μ (mm ⁻¹)	4.796	5.531	4.743
reflections collected	3788	4348	4695
independent reflections	2633 (<i>R</i> _{int} = 0.0450)	1487 (0.0233)	1824 (0.0234)
data/parameters	2633/187	1487/127	1824/142
goodness-of-fit on <i>F</i> ²	0.977	1.025	1.247
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0404	0.0197	0.0658
<i>wR</i> ₂ (all data)	0.1027	0.0487	0.1671
largest diff. peak and hole (e Å ⁻³)	1.187/−1.144	0.555/−0.722	1.958/−1.803

Table 2. Selected Bond Lengths (Å) and Angles (°) for Complex 1^a

Ag1–N1	2.124(5)	Ag1–N1	2.124(5)
Ag1–O1 _w	2.135(5)	Ag3–O2	2.222(4)
Ag2–N2	2.111(5)	Ag3–O4	2.428(5)
Ag2–O2 _w	2.129(6)	Ag1–Ag3	3.230(1)
Ag3–O1a	2.223(4)	Ag3–Ag3c	2.778(1)
N1–Ag1–O1 _w	175.0(2)	O1a–Ag3–O4	96.2(2)
N2–Ag2–O2 _w	177.2(2)	O2b–Ag3–O4	109.4(2)
O1a–Ag3–O2b	154.2(2)		

^a Symmetry/translational codes: (a) *x*, *y* + 1, *z*; (b) *−x*, *−y*, *−z* + 1; (c) *−x*, *−y* + 1, *−z* + 1.

Table 3. Selected Bond Lengths (Å) and Angles (°) for Complex 2^a

Ag1–N1a	2.247(3)	Ag2–N2b	2.366(4)
Ag1–O1c	2.495(3)	Ag2–O1	2.277(3)
Ag1–O3	2.376(4)	Ag2–O2d	2.451(3)
Ag1–O4b	2.345(3)	Ag2–Ag2c	3.158(1)
N1a–Ag1–O1c	129.3(1)	O3–Ag1–O4b	86.2(1)
N1a–Ag1–O3	111.4(1)	N2b–Ag2–O1	149.3(1)
N1a–Ag1–O4b	147.8(1)	N2b–Ag2–O2d	82.1(1)
O1c–Ag1–O3	84.6(1)	O1–Ag2–O2d	127.2(1)
O1c–Ag1–O4b	77.3(1)		

^a Symmetry/translational codes: (a) *x* + 1, *y*, *z*; (b) *−y* + 2, *x*, *z* − 1/4; (c) *y*, *−x* + 1, *z* + 1/4; (d) *−y* + 1, *x*, *z* − 1/4.

X-ray Crystallography. Diffraction intensities for the complexes were collected on a Bruker Smart Apex CCD diffractometer (Mo Kα, λ = 0.71073 Å). Absorption corrections were applied using SADABS.¹² The structures were solved with direct methods and refined with a full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs, respectively.^{13,14} Anisotropic thermal parameters were applied to all nonhydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å); the aqueous hydrogen atoms were located from difference maps and refined with isotropic temperature factors. The absolute structure of **2** was determined with a Flack parameter of 0.02(4).¹⁵ Crystal data as well as details of data collection and refinement for the complexes are summarized in Table 1. Selected bond distances and bond angles are listed in Tables 2–4. Drawings were produced with SHELXTL.¹⁶

Table 4. Selected Bond Lengths (Å) and Angles (°) for Complex 3^a

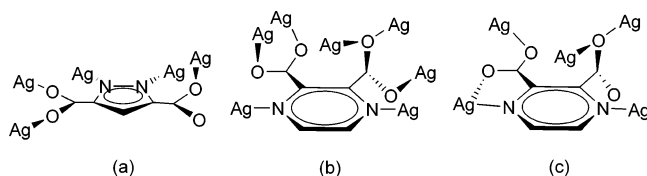
Ag1–N1	2.330(9)	Ag2–N2b	2.262(9)
Ag1–O1	2.43(1)	Ag2–O2d	2.34(1)
Ag1–O3a	2.511(9)	Ag2–O3c	2.280(9)
Ag1–O1 _w	2.23(1)	Ag1–Ag2	3.150(2)
N1–Ag1–O1	70.1(3)	O3a–Ag1–O1 _w	85.6(4)
N1–Ag1–O3a	91.2(3)	N2b–Ag2–O3c	126.1(3)
N1–Ag1–O1 _w	173.3(4)	N2b–Ag2–O2d	136.2(3)
O1–Ag1–O1 _w	116.5(4)	O2d–Ag2–O3c	97.3(3)
O1–Ag1–O3a	125.2(3)		

^a Symmetry/translational codes: (a) *x*, *−y* + 1/2, *z* + 1/2; (b) *x* + 1, *−y* + 1/2, *z* + 1/2; (c) *−x* + 1, *y* − 1/2, *−z* − 1/2; (d) *x*, *−y* + 1/2, *z* − 1/2.

Results and Discussion

Syntheses and Characterization. To our knowledge, as a potential polydentate ligand, H₃podc can bridge metal centers together using both the pyrazole nitrogen atoms and the carboxylate oxygen atoms; a variety of coordination complexes of transition, lanthanide, and alkaline earth metal clusters with H₃podc hence have been reported.^{6,7} Moreover, as demonstrated previously, it is possible to control the deprotonation of different labile hydrogen atoms attached to the oxygen or nitrogen atoms at different pH levels and hence tune the coordination mode.⁶ This fact encouraged us to employ such a potential polydentate ligand, by controlling the solution acidity, to obtain a new silver(I) cluster-based coordination polymer, [Ag₃(podc)(H₂O)₂]·2H₂O (**1**), in which the podc ligands act in an unprecedented μ₅-N,N',O,O',O'' coordination mode (Scheme 1a). In light of the above observation, we further chose another similar potential polydentate ligand, H₂pidc, to synthesize two more silver(I) cluster-based complexes, [Ag₂(pidc)] (**2**) and [Ag₂(pidc)(H₂O)] (**3**), under a similar pH value (ca. 8–9), in which the pidc ligands act in unique μ₇-N,N',O,O',O'',O''' and μ₅-(η²-N,O),N',O',O'',O'' coordination modes, respectively (Scheme 1b,c). It should be mentioned that no silver(I) compound with such aromatic heterocycle carboxylate ligands reported before this work contains such metal clusters, which may be

Scheme 1. μ_5 -N,N',O,O',O'' Coordination Mode of podc Ligands in **1** (a) and μ_7 -N,N',O,O',O'',O''' and μ_5 -(η^2 -N,O),N',O',O'' Coordination Modes of podc Ligands in **2** (b) and **3** (c), Respectively



ascribed to the fact that related compounds were produced under a lower reaction pH value (ca. 6).¹⁰ Furthermore, by using different solvent systems, MeCN or water, different coordination frameworks, **2** and **3**, were obtained. This work demonstrates that the appropriate choice of polydentate ligands and reaction condition systems may lead to silver(I) coordination networks featuring metal clusters.

Crystal Structures. The structure of **1** consists of stairlike one-dimensional chains with boxlike units, in which three crystallographically independent Ag(I) atoms have two types of coordination geometries (Figure 1). Both Ag1 and Ag2 atoms are coordinated in a virtually linear geometry by an aqua ligand and a pyrazole nitrogen atom [Ag–O 2.135(5) and 2.129(6) Å, Ag–N 2.124(5) and 2.111(5) Å; N–Ag–O 175.0(2) and 177.2(2)°]. A pair of Ag3 atoms are linked by two bidentate carboxylate bridges [Ag3–O 2.223(4) and 2.222(4) Å] with a Ag...Ag distance of 2.778(1) Å. It is noteworthy that such an extremely short distance is shorter than the Ag...Ag separation of 2.88 Å in the metallic state.¹⁷ Each Ag3 atom is also ligated by one carboxy oxygen atom from an adjacent dicarboxylate ligand in a noncoplanar, highly skew mode [Ag3–O4 2.428(5) Å; torsion angle Ag3–O4–C5–C4 76.7(2)°], completing a triangular coordination geometry around the metal center (Σ_{Ag3} 359.9°). As depicted in Figure 1a, the podc ligand featuring a unique μ_5 -N,N',O,O',O'' coordination mode here plays an important role in the construction of the stairlike chains with boxlike units (size ca. 9.3 Å by 3.3 Å), in which very strong π – π interactions in an offset fashion with a face-to-face stacking distance of 3.28 Å were found. The distance between Ag1 and Ag3 atoms is 3.230(1) Å, which is shorter than the sum of the van der Waals radii of two silver atoms (3.44 Å),^{4,17} resulting in zigzag tetranuclear silver(I) clusters. The podc aromatic rings in the adjacent polymeric chain are significantly staggered without any considerable π – π interaction; however, the weak Ag...O(podc) contacts¹⁸ (Ag...O 3.504 and 3.656 Å) in adjacent chains were observed, resulting in two-dimensional layers along the (001) planes (Figure 1Sa in the Supporting Information). The adjacent layers are further extended to a three-dimensional molecular architecture containing micropores with hydrogen bonds between the aqua ligands and the podc oxygen atoms [O...O 2.999(9) and 3.109(7) Å], as well as the weak Ag...O (podc) contacts (Ag...O 3.654 Å) (Figure 1Sb in the Supporting Information). The lattice water molecules are located in them and hydrogen-bonded to each other and to carboxy or aqueous oxygen atoms of the host network [O...O 2.672(8)–3.239(8) Å].

Complex **2** consists of interesting single-strand helical silver(I) chains of 4₁-screw symmetry. As shown in

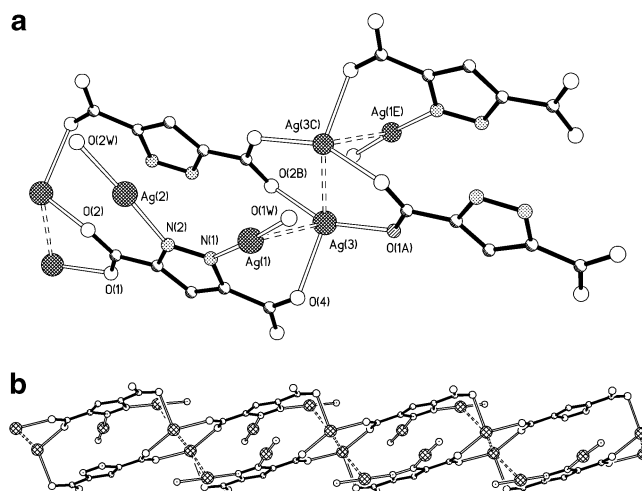


Figure 1. Perspective views showing the coordination environments of the Ag(I) atoms (a) and stairlike one-dimensional chains with boxlike units (b) in **1**.

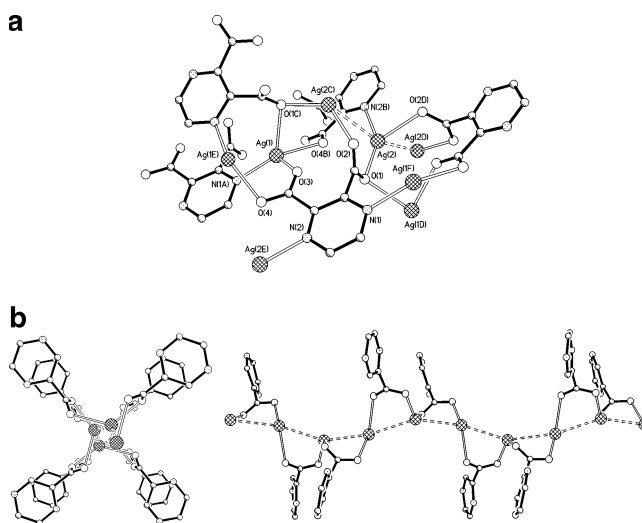


Figure 2. Perspective views showing the coordination environments of the Ag(I) atoms (a) and backbone of the single Ag(I)...Ag(I) helical chain (b) in **2**. For clarity, another carboxylate of the podc ligands is omitted in panel b.

Figure 2a, two crystallographically independent Ag(I) atoms with different types of coordination geometries were observed. Each Ag1 atom is coordinated in a distorted tetrahedral geometry by three different carboxy oxygen atoms and a nitrogen atom from different podc ligands. In other words, each pair of adjacent Ag(1) atoms, separated at 3.406 Å [Ag1...Ag1E], is bridged by the bidentate carboxylate [Ag1–O 2.345(3) and 2.376(4) Å], and μ_2 -N,O [Ag1–N1 2.247(3) Å, N1 atom from pyridyl; and Ag1–O1 2.495(3) Å, O1 atom from a tridentate carboxylate group in a skew mode with a torsion angle Ag1–O1–C1–C 2–62.9(2)°] bridges them from two different podc ligands, resulting in a single-strand helical chain running along a crystallographic 4₁-screw axis (Figure 2Sa,b in the Supporting Information). The tridentate carboxylate group is further linked to a pair of Ag2 atoms [Ag2–O 2.451(3) and 2.277(3) Å], one of them is also in a skew mode [torsion angle Ag2–O2–C1–C 2–129.7(2)°] with a shorter distance [Ag2...Ag2C 3.158(1) Å], resulting in another single-strand helical Ag2 chain running parallel to the Ag1

ones. Each Ag2 atom is further ligated by another pyrazine nitrogen atom [Ag2–N2 2.366(4) Å] from another pidc ligand, completing a triangular coordination around the metal center (Σ_{Ag2} 358.7°). The pidc ligands here act as a unique $\mu_7\text{-N,N',O,O,O',O'',O''}$ bridging mode, resulting in a three-dimensional framework (Figure 2Sc in Supporting Information).

The most intriguing structural feature of **2** is the presence of parallel single-strand helical Ag2 chains of 4₁-screw symmetry featuring the considerably short Ag...Ag contacts and displaying the same right-handedness. The pitch of the helix is equal to the unit length of the crystallographic *c*-axis [11.947(1) Å]. To our best knowledge, only a few previous examples featuring 4₁-screw symmetrical helices in coordination chemistry have been reported,^{19,20} and these in **2** having such short Ag...Ag contacts are even more unusual.

Complex **3** consists of a hexagonal Ag₄($\mu_2\text{-O}$)₂ core organized by four Ag(I) atoms and two μ_2 -oxygen atoms from pidc ligands each at the corner. As shown in Figure 3a, each Ag(I) atom adopts a distorted tetrahedral geometry coordinated by an aqua ligand [Ag1–O1w 2.23(1) Å], the $\eta_2\text{-N,O}$ chelate from a pyrazine nitrogen atom [Ag1–N1 2.330(9) Å], and an adjacent bidentate carboxy oxygen atom [Ag1–O1 2.43(1) Å] of same pidc ligand, and a carboxy μ_2 -oxygen atom from another pidc ligand [Ag1–O3 2.511(9) Å], which also ligates to the Ag2 atom [Ag2–O3 2.280(9) Å]. Each Ag2 atom is further ligated to the other bidentate carboxy oxygen atoms [Ag2–O2 2.34(1) Å] and a pyrazine nitrogen atom [Ag2–N2 2.262(9) Å] from different pidc ligands, completing a triangular coordination around the metal center (Σ_{Ag2} 359.7°). As depicted in Figure 3b, two pairs of such crystallographically independent Ag(I) atoms with μ_2 -oxygen atoms bridges are connected by the Ag...Ag interaction [Ag1...Ag2 3.150(2) Å], resulting in a cyclic hexagonal subunit. When only the carboxylate bidentate/tridentate coordination modes are considered, the adjacent Ag₄($\mu_2\text{-O}$)₂ cores are interlinked to a wavy sheet along the (100) planes (Figure 3b), and the offset π - π stacking interactions between the aromatic rings of the adjacent pidc ligands with a face-to-face distance of 3.65 Å were observed. However, the pidc ligand here, in fact, acts as an unprecedented $\mu_5\text{-(}\eta_2\text{-N,O),N',O',O'',O''}$ bridging mode, and the additional ligation from the pyrazine nitrogen atom results in an infinite three-dimensional coordination framework (Figure 3S in the Supporting Information).

As mentioned above, pidc has demonstrated versatile coordination modes including μ_n -bridging ($n = 2, 3, 4$, or 6) modes in ligation to metal ions, hence generating a large amount of coordination frameworks (Scheme 2);^{6,7} however, no silver(I) compound with it has been reported. Moreover, the $\mu_5\text{-N,N',O,O',O'',O''}$ coordination mode of pidc found in **1** (Figure 1a and Scheme 1a) is also different from the other modes reported in the literature. On the other hand, although some different coordination modes of pidc, such as μ_n -bridging ($n = 2$ or 3) modes,^{8–10} have been observed in a series of coinage d¹⁰ metal coordination complexes previously (Scheme 3), no silver(I) cluster-based coordination complex has been reported. It should be pointed out that the pidc ligands here have more coordination sites than those reported, either binding seven metal atoms in the

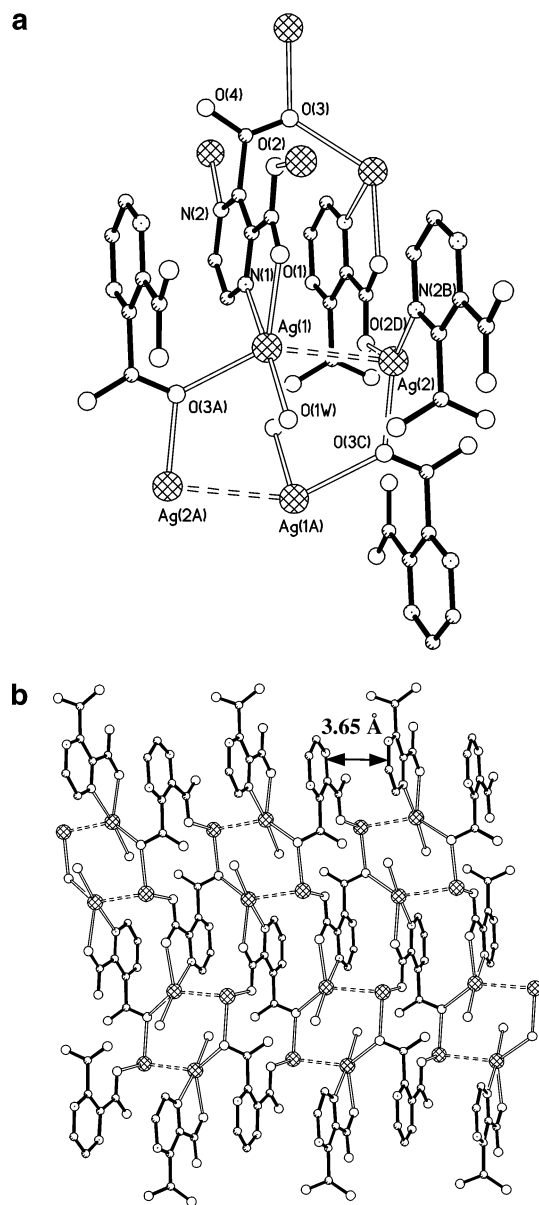
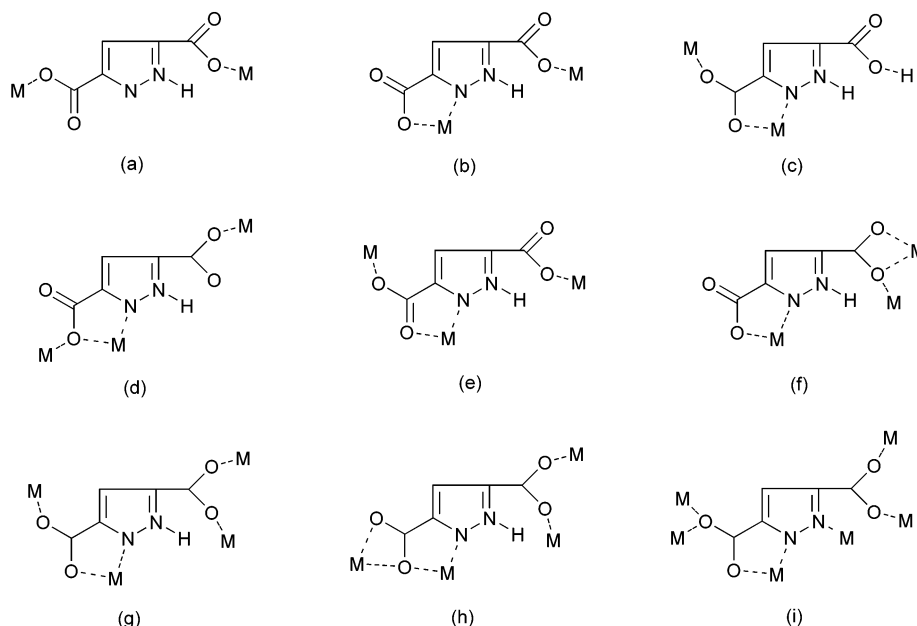


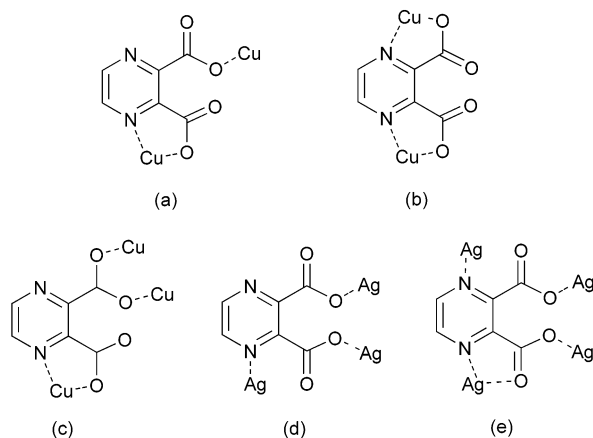
Figure 3. Perspective views showing the coordination environments of the Ag(I) atoms and hexagonal Ag₄($\mu_2\text{-O}$)₂ core (a) and the layer containing the Ag₄($\mu_2\text{-O}$)₂ cores (b) in **3**.

$\mu_7\text{-N,N',O,O,O',O'',O''}$ bridging mode in **2** or ligating five Ag(I) atoms through the $\mu_5\text{-(}\eta_2\text{-N,O),N',O',O'',O''}$ bridging mode in **3**, which is somewhat unprecedented (Figures 2a and 3a and Scheme 1b,c). Because of this higher connectivity, the versatile coordination modes of pidc and pidc ligands play an important role in the formation of numerous different coordination frameworks, and it becomes possible to find the short Ag(I)...Ag(I) contacts in these complexes.

Luminescent Properties. As we mentioned above, the presence of direct metal–metal interactions may be one of the important factors contributing to the photoluminescent properties of coinage d¹⁰ metal coordination compounds.^{1,3,5} It is shown that all of the silver(I) cluster-based complexes in this work are even more luminescent than we had expected. To our knowledge, Ag(I) complexes usually emit weak photoluminescence at low temperatures, and only a few silver(I) complexes exhibiting luminescent properties at room temperature

Scheme 2. Known Coordination Modes^{6a,b} of H₃podc in the Literature^a

^a (a) μ_2 -O,O''; (b) μ_2 -(η_2 -N,O),O''; (c) μ_2 -(η_2 -N,O),O'; (d) μ_3 -(η_2 -N,O),O,O''; (e) μ_3 -(η_2 -N,O),O',O''; (f) μ_3 -(η_2 -N,O), (η_2 -O'',O'''),O'; (g) μ_4 -(η_2 -N,O),O',O'',O'''; (h) μ_4 -(η_2 -N,O), (η_2 -O',O'',O'''),O'; and (i) μ_6 -(η_2 -N,O),N,O',O',O'',O''' (M = La, Ce, Er, Lu, or Cd therein).

Scheme 3. Known Coordination Modes of pidc in Coinage d¹⁰ Metal Coordination Frameworks in the Literature^a

^a (a) μ_2 -(η_2 -N,O),O'';^{9a} (b) μ_2 -(η_2 -N,O), (η_2 -N',O'');^{9b} (c) μ_3 -(η_2 -N,O),O',O'',O''';^{9c} (d) μ_3 -N,O,O',O'';^{10a} and (e) μ_3 -(η_2 -N,O),N,O',O'',O'';^{10b}

have been reported. Interestingly, as depicted in Figure 4, solids **1–3** exhibit the blue/green photoluminescence at room temperature with the emission maximum at ca. 458, 518, and 502 nm, respectively, upon excitation at 325 nm. Noting that both free H₃podc and H₂pidc display very weak luminescence in the solid state at ambient temperature,²¹ the enhancement of luminescence in complexes **1–3** may be attributed to the silver(I) cluster-based centers therein.^{1,3,5} To our knowledge, because of the impact of the relativistic effect, as well as the coordination structures, the (*n* + 1)s orbitals of d¹⁰ metal are contracted and hereby have lower energy.^{1d,4,22,23} A possible assignment for the origin of the emission involves emissive states derived from ligand-to-metal charge transfer (LMCT) transition mixed with d-s character. Presumably, in these complexes, the highest occupied molecular orbital (HOMO) is associated with the silver(I) 4d orbital and the carboxy-

late group σ orbital, while the lowest unoccupied molecular orbitals (LUMOs) are mainly associated with silver(I) unoccupied hybrid orbital based on 4d, 5s, and 5p, which is similar to the related silver(I) cluster-based coordination complexes reported previously.^{1c-f} It is noteworthy that a band with higher emission energy is observed for **1**, which can be attributed to the smaller π -conjugated system in the podc ligand, resulting in a larger HOMO–LUMO gap. On the other hand, both **2** and **3** are based on silver(I) and the pidc ligand; hence, the different emission bands may be attributed to the different three-dimensional architectures featuring different intensities of supramolecular interactions (such as π - π interaction, Ag...Ag interaction), which may result in the different HOMO–LUMO gaps.²⁴ What is more, the lifetimes of solids **1–3** at room temperature are 0.8, 1.6, and 1.2 μ s, respectively, being significant longer than those of the free ligands.²¹ This fact means that the emissions of these silver(I) cluster-based coordination complexes are associated with a spin-forbidden

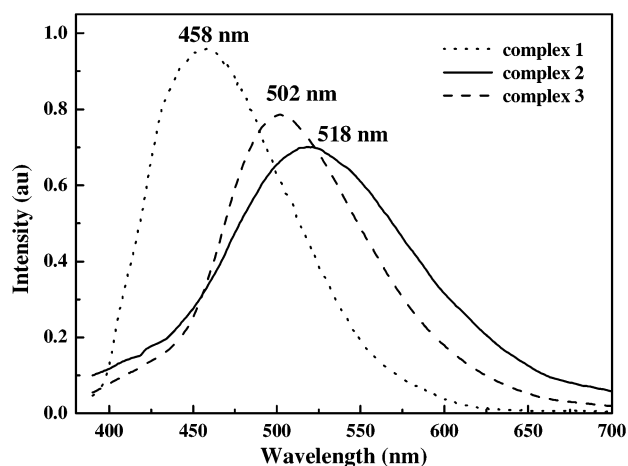


Figure 4. Fluorescent emission spectra of **1–3** in the solid state upon excitation at 325 nm at room temperature.

transition, which further supports the previous photoluminescence mechanism analysis suggesting inclusion of a metal-centered (d–s/d–p) transition ingredient.^{1c–f}

In summary, we have synthesized three silver(I) cluster-based coordination complexes featuring short Ag(I)···Ag(I) contacts based on the aromatic heterocycle carboxylate ligands by an appropriate choice of the solvent system and the pH value of the solution. All of these complexes display photoluminescent properties in the blue/green region at room temperature, which may be assigned to be an admixture of LMCT and metal-centered (d–s/d–p) transitions.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (20001008) and the Ministry of Education of China (01134).

Supporting Information Available: Three X-ray crystallographic files in CIF format. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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CG0342258