Inorganic Chemistry

Three Novel Silver Complexes with Ligand-Unsupported Argentophilic Interactions and Their Luminescent Properties

Xi Liu,[†,‡] Guo-Cong Guo,[*,†] Ming-Lai Fu,[†] Xue-Hui Liu,[†] Ming-Sheng Wang,[†] and Jin-Shun Huang[†]

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China, and Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Three novel silver complexes, namely, $[Ag_5(CN)_5(bipy)_2]_n$ (**1**) with a 1-D to 3-D architecture constructed through ligand-unsupported *argentophilic* interactions, $[Ag_5(SCN)_4(CN)(bipy)_2]_n$ (**2**) with a 2-D interesting topology formed by cyanide groups linking $[Ag_5(SCN)_4(bipy)_2]_n^{n+}$ cationic columns, and $[(Me_4N)Ag_3(CN)_4]_n$ (**3**) with 3-fold-interpenetrated 3-D 3-connected (10, 3)-g nets, have been solvothermally synthesized, and all exhibit efficient luminescence.

Introduction

The design and synthesis of topologically appealing architectures with increasing dimensionality is one of the most interesting challenges in supramolecular chemistry and crystal engineering.[1] Apart from using multidentate rigid or flexible ligands as building blocks to form high-dimensional frameworks through strong covalent coordination bonds,[2] weak forces such as H-bonding synthons,[3] $\pi−\pi$ interactions,[4] dipole−dipole attractions,[5] and metal−metal interactions[6] are employed to increase the dimensionalities of the expired products. We have recently endeavored to construct multi-dimensional frameworks with metal−metal interactions especially within monovalent coninage metals, which are viable design elements for the increase of dimensionality or the enrichment of supramolecular topology according to others' and our work.[6e,7] The strengths of the interactions have an order of magnitude comparable to those of H bonds,[8] suggesting useful tools to strengthen the intended frameworks. Compared with gold−gold interactions, silver−silver interactions have been reported as *argentophilicity* and calculated to be relatively weaker.[9] However, there are still many examples of argentophilic interactions; most are ligand-supported,[10] while few are revealed to be ligand-unsupported.[11] The ligand-unsupported $d^{10}−d^{10}$ metal−metal attractions are becoming important elements in the construction

* To whom correspondence should be addressed. E-mail: gcguo@ms.fjirsm.ac.cn. Fax: +86-591-83714946.
† State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.
‡ Graduate School, Chinese Academy of Sciences.

(1) For examples, see: (a) Ouahab, L. *Chem. Mater.* **1997**, *9*, 1909 and references cited therein. (b) Braga, D. *J. Chem. Soc., Dalton Trans.* **2000**, 3705. (c) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313. (d) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (e) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022.
(2) For reviews, see: (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (c) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
(3) For examples, see: (a) Dautel, O. J.; Fourmigué, M.; Canadell, E. *Chem.−Eur. J.* **2001**, *7*, 2635. (b) Beatty, A. M. *CrystEngComm* **2001**, *51*, 1. (c) Liu, X.; Guo, G.-C.; Liu, B.; Chen, W.-T.; Huang, J.-S. *Cryst. Growth Des*. **2005**, *5*, 841.
(4) For examples, see: (a) Noveron, J. C.; Lah, M. S.; Sesto, R. E. D.; Arif, A. M.; Miller, J. S.; Stang, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 6613. (b) Wang, Y.; Hu, X. *J. Am. Chem. Soc.* **2002**, *124*, 8445. (c) Sinnokrot, M. O.; Sherrill, C. D. *J. Am. Chem. Soc.* **2004**, *126*, 7690.
(5) For examples, see: (a) Huang, Z.; Du, M.; Song, H.-B.; Bu, X.-H. *Cryst. Growth Des*. **2004**, *4*, 71. (b) Pickering, A. L.; Long, D.-L.; Cronin, L. *Inorg. Chem*. **2004**, *43*, 4953. (c) King, P.; Clérac, R.; Anson, C. E.; Powell, A. K. *Dalton Trans*. **2004**, 852.

(6) (a) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391. (b) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597. (c) Tzeng, B.-C.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1999**, *38*, 3978. (d) Hollatz, C.; Schier, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1997**, *119*, 8115. (e) Liu, X.; Guo, G.-C.; Wu, A.-Q.; Cai, L.-Z.; Huang, J.-S. *Inorg. Chem.* **2005**, *44*, 4282 and references cited therein. (f) Zheng, S.-L.; Messerschmidt, M.; Coppens, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 4614.
(7) (a) Leznoff, D. B.; Xue, B.-Y.; Batchelor, R. J.; Einstein, F. W. B.; Patrick, B. O. *Inorg. Chem.* **2001**, *40*, 6026. (b) Leznoff, D. B.; Xue, B.-Y.; Patrick, B. O.; Sanchez, V.; Thompson, R. C. *Chem. Commun.* **2001**, 259. (c) Shorrock, C. J.; Xue, B.-Y.; Kim, P. B.; Batchelor, R. J.; Patrick, B. O.; Leznoff, D. B. *Inorg. Chem.* **2002**, *41*, 6743.
(8) Bardaji, M.; Laguna, A. *J. Chem. Educ.* **1999***, 76*, 201.
(9) (a) Fernández, E. J.; López-de-luzuriaga, J. M.; Monge, M.; Rodríguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Inorg. Chem*. **1998**, *37*, 6002. (b) Assefa, Z.; Shankle, G.; Patterson, H. H.; Reynolds, R. *Inorg. Chem.* **1994**, *33*, 2187.
(10) For examples, see: (a) Guo, G.-C.; Zhou, G.-D.; Wang, Q.-G.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 630. (b) Guo, G.-C.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 3183. (c) Guo, G.-C.; Zhou, G.-D.; Mak, T. C. W. *J. Am. Chem. Soc.* **1999**, *121*, 3136. (d) Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001***, 123*, 7594. (e) Wang, Q.-M.; Mak, T. C. W. *Inorg. Chem*. **2003**, *42*, 1637.

of fascinating structures recently, but there is still a long way to go with such systems.[7]

Besides the curiosity in the construction of frameworks with argentophilicity as a design element, an interest in the intriguing properties of silver complexes drives us to explore this system. For instance, the silver thiolate $[Ag(C_5H_4NS)]_n$ exhibits semiconductivity;[12] the silver cyanurate $[Ag_2C_3N_3-HO_3]_n$ possesses anisotropic conductivity;[13] the silver carboxylate $[Ag_3(H_2btc)_2(hbtc)]_n$ shows strong blue photoluminescence.[14] In present work, three kinds of silver salts with small covalent conjugate anions were utilized as reaction precursors to complex with 2,2′-bipy or tetramethylammonium salts under solvothermal conditions and resulted in three novel silver complexes, namely, $[Ag_5(CN)_5(bipy)_2]_n$ (**1**) with a 1-D to 3-D architecture constructed through ligand-unsupported argentophilic interactions, $[Ag_5(SCN)_4(CN)-(bipy)_2]_n$ (**2**) with a 2-D interesting topology formed by cyanide groups linking $[Ag_5(SCN)_4(bipy)_2]_n^{n+}$ cationic columns, and $[Me_4N][Ag_3(CN)_4]$ (**3**) with 3-fold-interpenetrated 3-D 3-connected (10, 3)-g nets, which all exhibit efficient luminescence.

Experimental Section

Materials and Instrumentation. All chemicals except CH_3CN and CH_2Cl_2 solvents were obtained from commercial sources and used without further purification. CH_3CN and CH_2Cl_2 were purified and distilled by conventional methods and stored under nitrogen before use. Elemental analyses were performed on a Vario EL III elemental analyzer. The Fourier transform (FT-IR) spectra were obtained on a Perkin-Elmer Spectrum using KBr disks in the range $4000-400$ cm^{-1}. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. The lifetimes of the emission bands were measured on an Edinburgh LifeSpec-ps system.

Preparation of $[Ag_5(CN)_5(bipy)_2]_n$ (1). A mixture of AgCN (268 mg, 2 mmol) and 2,2′-bipy (125 mg, 0.8 mmol) in 10 mL of dry and distilled acetonitrile was sealed into a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure, heated at 100 °C for 1 day, then heated to 140 °C, and held at this temperature for 5 days, followed by cooling at 0.1 °C/min to room temperature. The resulting orange crystals were collected with ca. 40% yield. Elem anal. Calcd for $C_{25}H_{16}Ag_5N_9$: C, 30.58; H, 1.64; N, 12.84. Found: C, 30.52; H, 1.56; N, 12.57. FT-IR (KBr, cm^{-1}): 3075(w), 2963(w), 2140(s), 1590(s), 1565(w), 1484(m), 1470(m), 1437(s), 1310(m), 1245(w), 1154(m), 1099(w), 1056(w), 1013(m), 811(m), 761(s), 735(m), 645(m), 621(m), 408(m). ν (CN): 2140.

Preparation of $[Ag_5(SCN)_4(CN)(bipy)_2]_n$ (2). Complex **2** can be obtained in a reaction process similar to that of **1** except with

the reactants changed to a mixture of AgCN (67 mg, 0.5 mmol), AgSCN (332 mg, 2 mmol), and 2,2′-bipy (156 mg, 1 mmol) in 10 mL of dry and distilled acetonitrile. The resulting gray crystals were collected with ca. 55% yield. Elem anal. Calcd for $C_{25}H_{16}-Ag_5N_9S_4$: C, 27.05; H, 1.45; N, 11.36. Found: C, 26.98; H, 1.42; N, 11.29. FT-IR (KBr, cm^{-1}): 3055(w), 2813(w), 2113(s), 2092(s), 1589(m), 1566(m), 1482(w), 1470(m), 1435(s), 1311(w), 1245(w), 1170(w), 1151(w), 1055(w), 1007(m), 754(s), 735(m), 642(w), 619(w), 406(w). ν (CN): 2113, 2092.

Preparation of $[(Me_4N)Ag_3(CN)_4]_n$ (3). Complex **3** can be obtained in a reaction process similar to that of **1** except with the reactants changed to a mixture of KAg(CN)$_2$ (200 mg, 1 mmol), Ag_2CO_3 (69 mg, 0.25 mmol), and Me$_4$NBr (77 mg, 0.5 mg) in 10 mL of dry and distilled dichloromethane. The resulting solution was filtered, and the filtrate was left open to air for about 2 days; colorless crystals were obtained in ca. 60% yield. Elem anal. Calcd for $C_8H_{12}Ag_3N_5$: C, 19.15; H, 2.41; N, 13.96. Found: C, 19.18; H, 2.45; N, 13.68. FT-IR (KBr, cm^{-1}): 3035(m), 2957(w), 2749(w), 2578(w), 2131(s), 1734(w), 1480(s), 1415(m), 1285(m), 947(s), 412(m). ν (CN): 2131.

Single-Crystal Structure Determination. Single crystals of **1**−**3** were mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 140 K. The intensity data sets were collected with an ω-scan technique and reduced by *CrystalClear* software.[15] The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-H atoms were located by a difference Fourier map and subjected to anisotropic refinement. H atoms were added according to the theoretical models. All of the calculations were performed by the Siemens *SHELXTL* version 5 package of crystallographic software.[16] Crystallographic data and structural refinements and selected bond distances and angles for the presented three complexes are summarized in Tables 1 and 2, respectively. More details on the crystallographic studies as well as atom displacement parameters are given as Supporting Information. Because the C and N atoms in the bridging cyanide groups cannot be distinguished crystallographically,[17] assignments based on the refinement of their anisotropic thermal parameters have been made in **1** and **3**, while the C and N atoms of cyanide groups in **2** are refined as disordered over two symmetry-related sites due to the cyanide groups in **2** with a crystallographic inversion center.

Results and Discussion

Synthesis. Silver salts with the small covalent conjugate anions such as CN$^-$ and SCN$^-$ anions are good reaction precursors to introduce *argentophilic* interactions in the resulting products because these small anions with little steric hindrance are very helpful for the compact packing of the resulting molecules.[18] On this basis, three kinds of silver salts, AgCN, AgSCN, and KAg(CN)$_2$, are utilized in the preparation of the three complexes. Complexes **1** and **2** were initially

(11) (a) Kim, Y.; Seff, K. J. *J. Am. Chem. Soc.* **1978**, *100*, 175. (b) Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 2942. (c) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, G. E. *Inorg. Chem.* **1998**, *37*, 1380, (d) Tong, M. L.; Chen, X. M.; Ye, B. H.; Ji, L. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2237. (e) Kristiansson, O. *Inorg. Chem.* **2001**, *40*, 5058. (f) Bowmakera, G. A.; Effendy; Junk, P. C.; Skelton, B. W.; White, A. H. *Z. Naturforsch.* **2004**, *59b*, 1277.
(12) Su, W. P.; Hong, M. C.; Weng, J. B.; Cao, R.; Lu, S. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2911.
(13) Rao, C. N. R.; Ranganathan, A.; Pedireddi, V. R.; Raju, A. R. *Chem. Commun.* **2000**, 39.
(14) Sun, D.; Cao, R.; Weng, J.; Hong, M.; Liang, Y. *J. Chem. Soc., Dalton Trans.* **2002**, 291.

(15) Rigaku. *CrystalClear*, version 1.35; Rigaku Corp.: Tokyo, Japan, 2002.
(16) Siemens. *SHELXTL*, version 5; Reference Manual; Siemens Energy & Automation Inc.: Madison, WI, 1994.
(17) Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 839.
(18) For examples, see: (a) Wang, Q.-M.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4135. (b) Lin, Y.-Y.; Lai, S.-W.; Che, C.-M.; Fu, W.-F.; Zhou, Z.-Y.; Zhu, N. *Inorg. Chem.* **2005**, *44*, 1511. (c) Shen, L.; Liu, J. *J. Coord. Chem.* **2003**, *56*, 13. (d) Han, W.; Yi, L.; Liu, Z. Q.; Gu, W.; Yan, S.-P.; Chen, P.; Liao, D.-Z.; Jiang, Z. H. *Eur. J. Inorg. Chem.* **2004**, *6*, 2130. (e) Urban, V.; Pretsch, T.; Hartl, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2794.

Table 1. Crystal Data and Structure Refinements for **1**−**3**

complex	**1**	**2**	**3**
formula	$C_{25}H_{16}Ag_5N_9$	$C_{25}H_{16}Ag_5N_9S_4$	$C_8H_{12}Ag_3N_5$
mol wt	981.82	1110.06	501.84
crystal size (mm^3)	$0.20 \times 0.18 \times 0.12$	$0.20 \times 0.08 \times 0.04$	$0.50 \times 0.20 \times 0.16$
cryst syst	triclinic	triclinic	monoclinic
space group	$P1$	$P\bar{1}$	$P2_1/c$
a (Å)	8.701(5)	4.2953(4)	11.4303(15)
b (Å)	9.057(5)	13.2831(9)	8.8546(8)
c (Å)	9.267(5)	14.0109(8)	15.600(2)
α (deg)	74.079(11)	72.690(11)	90
β (deg)	79.883(11)	88.891(13)	114.810(2)
γ (deg)	80.106(10)	86.327(14)	90
V ($Å^3$)	685.5(6)	761.62(10)	1433.1(3)
D_{calc} (Mg m^{-3})	2.378	2.420	2.326
Z	1	1	4
$F(000)$	464	528	944
abs coeff (mm^{-1})	3.541	3.467	4.041
reflns collected/unique (R_{int})	4487/3215 (0.0154)	5000/2652 (0.019)	8968/2527 (0.0239)
data/param/restraints	2445/304/51	2064/196/0	2295/148/25
R^a	0.0501	0.0492	0.0570
$R_w{}^b$	0.1480	0.1258	0.2118
GOF on F^2	1.002	1.002	1.001
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	0.929 and −1.208	2.569 and −1.045	1.927 and −1.098

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

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**−**3**^{a}

	distance (Å)		angle (deg)
Complex 1			
Ag1−Ag2A	3.276(2)	N1−Ag3−N3	108.3(2)
Ag3−Ag4A	3.314(2)	N1−Ag3−C4	139.9(2)
Ag1−Ag5B	3.373(1)	C4−Ag3−N3	111.8(2)
Ag4−Ag5C	3.342(2)	N4−Ag2−N5	125.8(2)
N1−C1	1.058(7)	N4−Ag2−N2	115.2(2)
N2−C2	1.018(6)	N5−Ag2−N2	112.3(1)
N3−C3	1.182(7)	C3−Ag5−C2	173.8(2)
N4−C4B	1.146(5)	C3−N3−Ag3	164.6(4)
N5−C5	1.116(6)	C2−N2−Ag2	163.0(4)
Complex 2			
Ag1−Ag2	3.3255(4)	N1−C1−S1	178.8(3)
Ag1−S1	2.5011(8)	N2−C2−S2	178.2(3)
Ag3−S2	2.6024(9)	S1−Ag1−S1C	114.69(3)
Ag2−N2	2.161(2)	C(N)3−Ag3−N1	124.7(1)
Ag3−N1	2.296(2)	C(N)3−Ag3−S2	127.21(9)
S1−C1	1.661(2)	N1−Ag3−S2	96.40(7)
N1−C1	1.139(3)	N2−Ag2−N2A	180.0(1)
S2−C2	1.647(2)	C1−S1−Ag1	105.85(9)
N2−C2	1.157(3)	C1−N1−Ag3	154.6(2)
C(N)3−C(N)3B	1.104(5)	C2−N2−Ag2	165.1(2)
Complex 3			
Ag1−Ag3	3.0731(5)	N1−Ag1−N2	132.34(13)
Ag2−Ag4	3.1495(5)	N1−Ag1−N3	123.80(14)
N1−C1	1.109(6)	C3−Ag2−C1	121.40(15)
N2−C2	1.125(5)	C3−Ag2−N4	128.22(14)
N3−C3A	1.028(7)	C4D−Ag3−C4C	180.0(2)
N4−C4	1.139(6)	C2F−Ag4−C2E	180.0(2)

^{a} Symmetry codes for **1**: A, −1 + x, 1 + y, −1 + z; B, 1 + x, −1 + y, 1 + z; C, x, y, z + 1. Symmetry codes for **2**: A, −x, −y, −z; B, 1 − x, 1 − y, −1 − z; C, −1 + x, y, z. Symmetry codes for **3**: A, x, ¹/₂ − y, ¹/₂ + z; C, −x, 1 − y, −z; D, x, −1 + y, z; E, x, 1 + y, z; F, 1 − x, −y, −z.

synthesized in a one-pot reaction with AgCN, AgSCN, and 2,2′-bipy in a 1:3:4 molar ratio in a distilled CH$_3$CN solvent, which can be obtained separately as pure phases under similar reaction conditions when the reactants are in the same molar ratios as the resulting components in the products (see the Experimental Section). Complex **3** was synthesized and segregated by utilizing the insolubilities of its coproducts KBr and K$_2$CO$_3$ in a distilled CH$_2$Cl$_2$ solvent, which was proven by the reaction of KAg(CN)$_2$, Ag$_2$CO$_3$, and Me$_4$NI

in a 4:1:2 molar ratio in a distilled CH$_2$Cl$_2$ solvent also leading to **3** (KI is insoluble in a distilled CH$_2$Cl$_2$ solvent also).

Crystal Structure Description of 1. The structure of **1** crystallizes in the noncentrosymmetric space group $P1$ and features a 1-D to 3-D structure constructed through ligand-unsupported argentophilic interactions. As shown in Figure 1, the asymmetric unit contains five crystallographically unique Ag atoms, five cyanide groups, and two 2,2′-bipy ligands. Each Ag1 and Ag4 atom is in a distorted trigonal-planar coordination environment and is coordinated by one cyanide C atom and two N atoms of one 2,2′-bipy ligand to form a [(CN)Ag(bipy)] moiety, while each Ag2 and Ag3 atom is in an approximate trigonal-planar coordination geometry and is coordinated by three cyanide groups. Ag1, Ag2, Ag3, and Ag4 atoms are approximately coplanar with no crystallographic inversion center because Ag2 is linked by three cyanide N atoms while Ag3 is connected by one cyanide C atom and two cyanide N atoms. The two-coordinate Ag5 atom is approximately linearly connected by two cyanide C atoms to form a subunit of [Ag(CN)$_2$]$^-$ with the C−Ag−C bond angle of 174.7(2)°. The Ag−C bond distances vary from 1.989(4) to 2.173(4) Å, and the Ag−N$_{cyanide}$ bond lengths range between 2.148(4) and 2.304(5) Å, which are comparable with those in Ag$_x$(CN)$_y$-based complexes.[19] The C2N2, C3N3, and C4N4 cyanide groups bridge the Ag2, Ag3, and Ag5 atoms to form a 1-D zigzag chain extending along the [1, −1, 1] direction, with

(19) (a) Geiser, U.; Wang, H. H.; Gerdom, L. E.; Firestone, M. A.; Sowa, L. M.; Williams, J. M.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1985**, *107*, 8305. (b) Soma, T.; Iwamoto, T. *Chem. Lett.* **1994**, 821. (c) Schwarten, M.; Chomic, J.; Cernak, J.; Babel, D. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1449. (d) Golhen, S.; Ouahab, L.; Lebeuze, A.; Bouayed, M.; Delhaes, P.; Kashimura, Y.; Kato, R.; Binet, L.; Fabre, J.-M. *J. Mater. Chem.* **1999**, *9*, 387. (e) Brunner, H.; Hollman, A.; Nuber, B.; Zabel, M. *J. Organomet. Chem.* **2001**, *633*, 1. (f) Shorrock, C. J.; Xue, B.-Y.; Kim, P. B.; Batchelor, R. J.; Patrick, B. O.; Leznoff, D. B. *Inorg. Chem.* **2002**, *41*, 6743. (g) Zhou, H.-B.; Dong, W.; Liang, M.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Cheng, P. Z. *Anorg. Allg. Chem.* **2004**, *630*, 498.
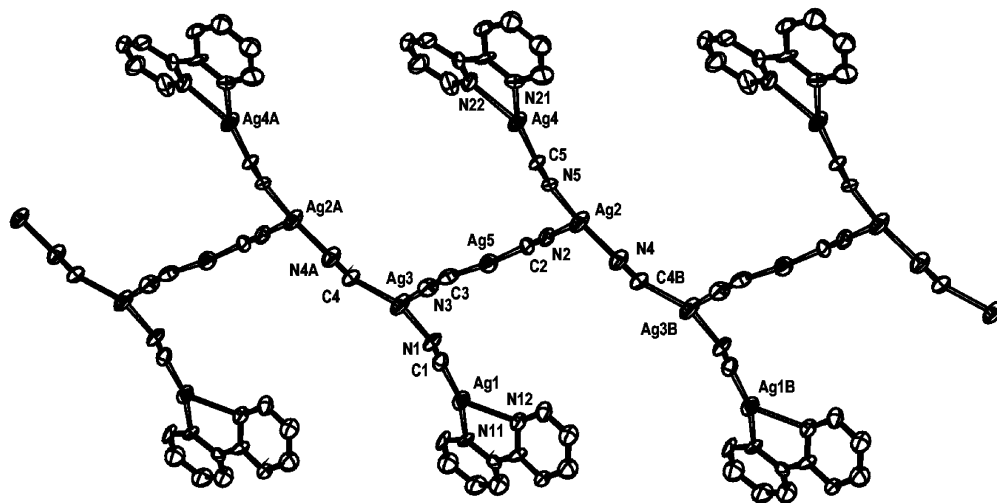
Figure 1. Coordination environments of Ag atoms in **1** with 30% thermal ellipsoids. All H atoms are omitted for clarity. Symmetry codes: A, $-1 + x$, $1 + y$, $-1 + z$; B, $1 + x$, $-1 + y$, $1 + z$.
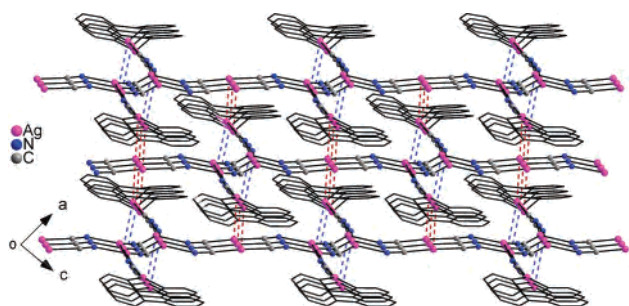

Figure 2. 1-D zigzag chains linking with each other through the ligand-unsupported Ag1···Ag2A and Ag3···Ag4A argentophilic interactions (represented as blue dashed lines) to form 2-D wavelike layers, which are further stacked together to form a 3-D framework through the ligand-unsupported Ag1···Ag5B and Ag4···Ag5C argentophilic interactions (represented as red dashed lines). Symmetry codes: A, $x - 1$, y, $z - 1$; B, x, y, $z - 1$; C, x, y, $z + 1$.

the [(CN)Ag(bipy)] moieties anchoring to the Ag2 and Ag3 atoms on both sides of the chain (Figure 1). The 1-D chains link each other to form a 2-D wavelike layer extending along the [0, 1, 0] and [1, 0, 1] directions through the ligand-unsupported Ag1···Ag2A [3.276(2) Å; A, $x - 1$, y, $z - 1$] and Ag3···Ag4A [3.314(1) Å] argentophilic interactions (Figure S1 in the Supporting Information). These layers stack together tightly to form a 3-D framework through the ligand-unsupported Ag1···Ag5B [3.373(1) Å; B, x, y, $z - 1$] and Ag4···Ag5C [3.342(2) Å; C, x, y, $z + 1$] argentophilic interactions (Figure 2).

Crystal Structure Description of 2. The structure of **2** features a 2-D framework formed by cyanide groups linking the $[Ag_5(SCN)_4(bipy)_2]_n^{n+}$ cationic columns. As shown in Figure 3, there are five Ag atoms in the repeating unit, with Ag2 atom located on the crystallographic inversion center, so there are only three crystallographically independent Ag atoms in the asymmetric unit of **2**. The four-coordinate Ag1 atom is in a slight distorted tetrahedron and is coordinated by two thiocyanate anions through S atoms and one 2,2′-bipy ligand; the four-coordinate Ag3 atom is approximately tetrahedrally coordinated by two thiocyanate S atoms, one thiocyanate N atom, and one symmetry-related disordered μ-cyanide C(N)3 atom, while two-coordinate Ag2 is linearly
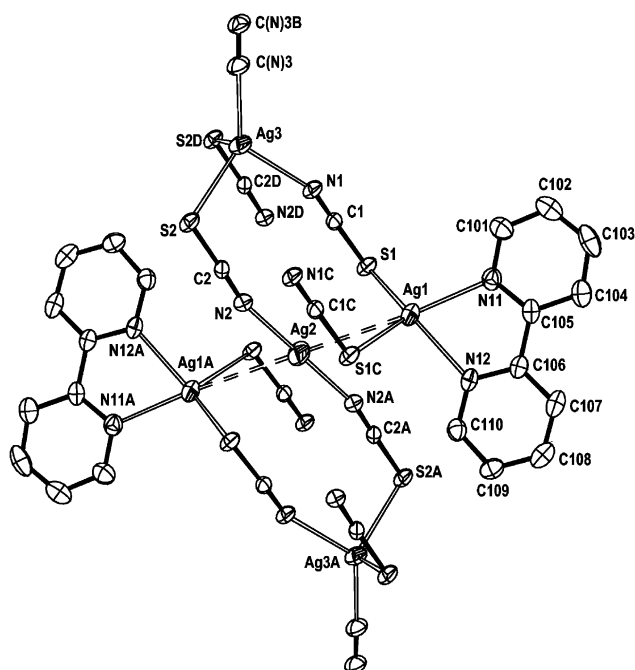

Figure 3. Coordination environments of Ag atoms in **2** with 30% thermal ellipsoids. All H atoms are omitted for clarity. The double-dashed lines represent the ligand-unsupported argentophilic interactions. Symmetry codes: A, $-x$, $-y$, $-z$; B, $1 - x$, $1 - y$, $-1 - z$; C, $-1 + x$, y, z; D, $1 + x$, y, z.

connected by two centric symmetry-related thiocyanate N atoms. The five Ag atoms in the repeating unit are coplanar and bridge four thiocyanate anions to form a centric S-type pattern without considering the coordination of the cyanide groups, which extend along the a direction to form an $[Ag_5(SCN)_4(bipy)_2]_n^{n+}$ cationic column through the thiocyanate anions, further coordinating to the Ag atoms of the adjacent units (Figure 4). Within the cationic column, there exist significant ligand-unsupoerted argentophilic interactions between the Ag1 and Ag2 atoms with the Ag···Ag distance of 3.3255(4) Å, which have an important role in forming the S-type topology, and the adjacent pyridine rings of 2,2′-bipy ligands are parallel to each other, with their centroid-to-centroid distances ranging from 3.9252(6) to
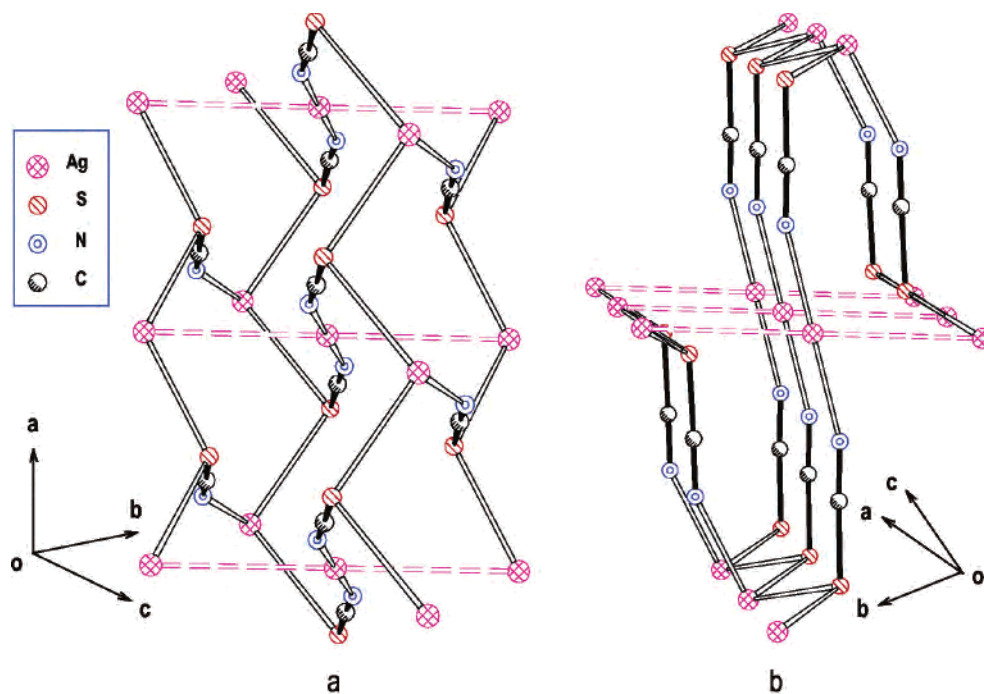
Figure 4. View of a $[Ag_5(SCN)_4(bipy)_2]_n^{n+}$ cationic column in **2** from the side face (a) and underside (b). The pink double-dashed lines represent the ligand-unsupported argentophilic interactions, and the 2,2′-bipy ligands are omitted for clarity.
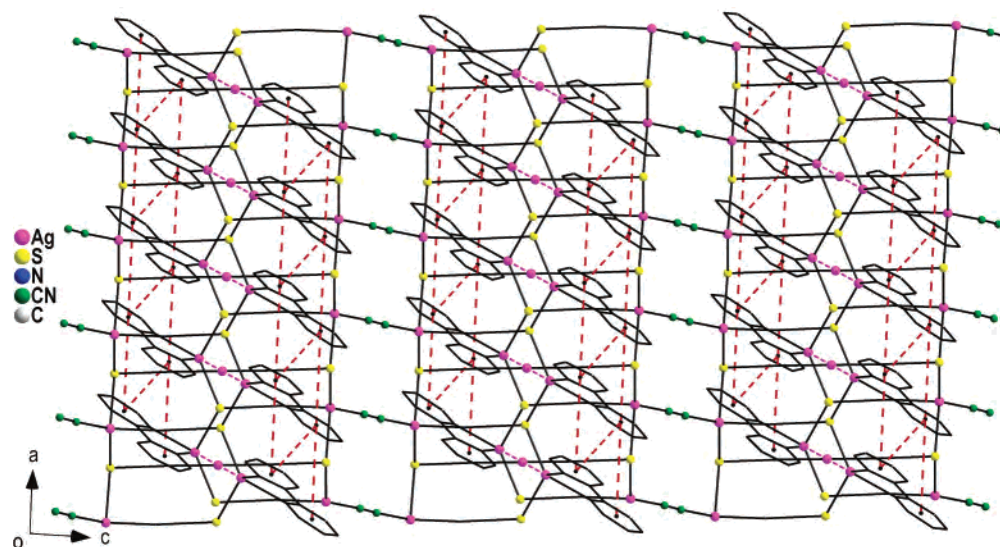

Figure 5. View of a 2-D layer in **2** constructed by symmetry-related disordered cyanide groups bridging 1-D $[Ag_5(bipy)_2(SCN)_4]_n^{n+}$ cationic columns. The red dashed lines represent the $\pi\cdots\pi$ stacking interactions, and the pink dashed lines represent the ligand-unsupported argentophilic interactions.

4.2953(4) Å and plane-to-plane distances varying between 3.403(4) and 3.493 (4) Å, indicating that there exist abundant $\pi\cdots\pi$ stacking interactions.[20] These robust cationic columns are further bridged by symmetry-related disordered μ-cyanide groups to form a 2-D framework (Figure 5).

Crystal Structure Description of 3. Complex **3** features 3-fold-interpenetrated 3-D 3-connected (10, 3)-g nets in

(20) For examples, see: (a) Reger, D. L.; Gardinier, J. R.; Smith, M. D.; Pellechia, P. J. *Inorg. Chem.* **2003**, *42*, 482. (b) Gorp, J. J. V.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2002**, *124*, 14759. (c) Nagayoshi, K.; Kabir, M. K.; Tobita, H.; Honda, K.; Kawahara, M.; Katada, M.; Adachi, K.; Nishikawa, H.; Ikemoto, I.; Kumagai, H.; Hosokoshi, Y.; Inoue, K.; Kitagawa, S.; Kawata, S. *J. Am. Chem. Soc.* **2003**, *125*, 221.
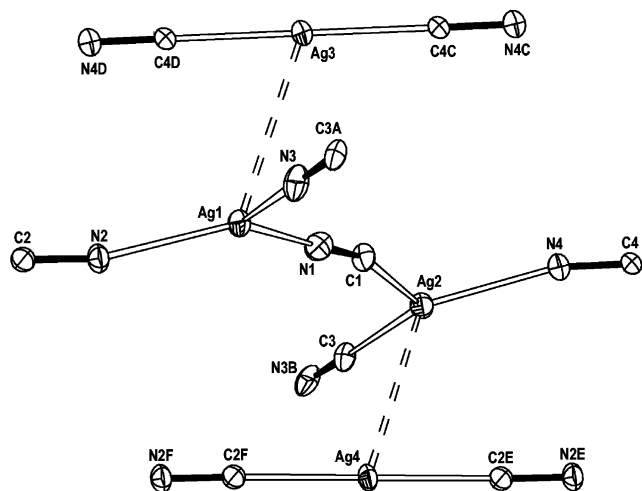
which there are four unique Ag atoms in the asymmetric unit (Figure 6). The three-coordinate Ag1 and Ag2 atoms are both in distorted trigonal-planar coordination environments and are coordinated by three cyanide groups, while the two-coordinate Ag3 and Ag4 atoms are both linearly coordinated by two cyanide groups. The Ag−C bond distances vary from 2.062(4) to 2.221(4) Å, and the Ag−N bond lengths range between 2.111(4) and 2.307(5) Å, which are comparable with those in $Ag_x(CN)_y$-based complexes.[19] The cyanide groups bridge the Ag atoms in a μ_2 fashion to form a peculiar 3-D 3-connected (10, 3)-g net when the three-coordinate Ag atoms are treated as nodes and CN− and

Figure 6. Coordination environments of Ag atoms in **3** with 30% thermal ellipsoids. The double-dashed lines represent the ligand-unsupported argentophilic interactions. Symmetry codes: A, x, $^1/_2 - y$, $^1/_2 + z$; B, x, $^1/_2 - y$, $-^1/_2 + z$; C, $-x$, $1 - y$, $-z$; D, x, $-1 + y$, z; E, x, $1 + y$, z; F, $1 - x$, $-y$, $-z$.
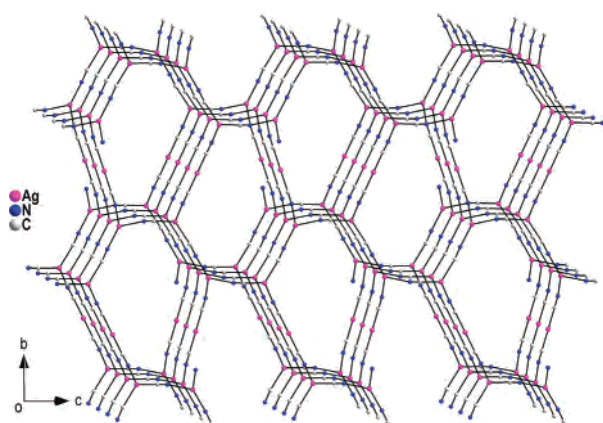
Figure 7. View of a 3-D 3-connected (10, 3)-g net in **3** with three-coordinate Ag atoms as nodes and CN^- and $[Ag(CN)_2]^-$ as links.

$[Ag(CN)_2]^-$ (the Ag is in two-coordinate mode) as links (Figure 7 and Figure S2 in the Supporting Information). This net[21] has short and long Schläfli vertical symbols of 10^3 and $10_410_410_4$, which contain pseudo-6-fold helices. Each pseudo-6-fold helix has an opposite handedness relative to the adjacent four helices along the c axis and the same handedness relative to the adjacent two helices along the b axis (Figure S2 in the Supporting Information). Adjacent three kinds of these nets interpenetrate each other to form a complex structure of **3** with 3-fold-interpenetrated 3-D 3-connected (10, 3)-g nets (Figure 8), which possess two kinds of approximately hexagonal channels along the [1, 1, 0] direction with an effective size of ca. 5 × 5 Å^2 and along the [1, 0, 1] direction with an effective size of ca. 3 × 3 Å^2 (Figure S3 in the Supporting Information), and the tetramethylammonium cations locate in the cross section of the two kinds of channels. More interestingly, between the adjacent 3-D 3-connected (10, 3)-g nets, there exist the ligand-unsupported Ag1···Ag3 [3.0731(5) Å] and Ag2···Ag4

(21) (a) Wells, A. F. *Three-dimensional nets, polyhedra*; John Wiley & Sons: New York, 1977. (b) Öhrström, L.; Larsson, K. *Dalton Trans.* **2004**, 347.
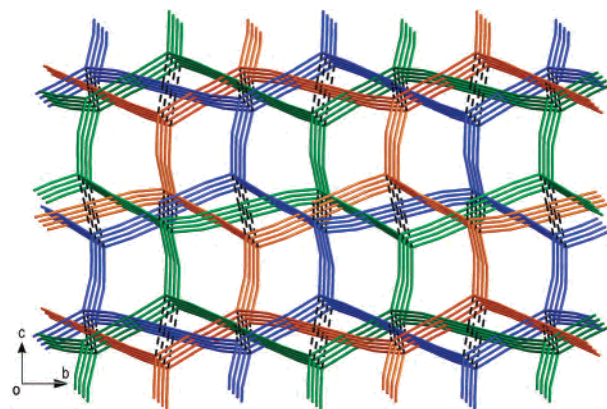
Figure 8. View of 3-fold-interpenetrated 3-connected (10, 3)-g nets in **3**, which are drawn in blue, green, and orange, respectively. The black dashed lines represent the ligand-unsupported argentophilic interactions between the (10, 3)-g nets.
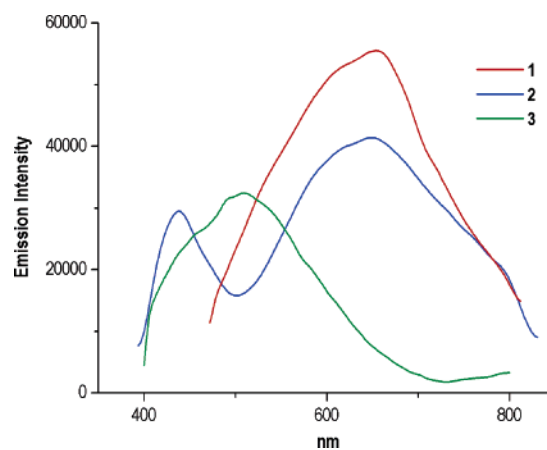

Figure 9. Solid-state electronic emission spectra of **1** ($\lambda_{ex} = 450$ nm), **2** ($\lambda_{ex} = 380$ nm), and **3** ($\lambda_{ex} = 398$ nm) at room temperature.

[3.1495(5) Å] argentophilic interactions, which play an important role in forming the stable framework.

In the three complexes, the adjacent ligand-unsupported Ag···Ag distances range from 3.073 to 3.373 Å, which are shorter than the sum of the van der Waals radii for Ag (3.44 Å). Along these Ag···Ag vectors, there is no coulombic interaction[22] or evident ligand-packing effects,[11b,23] such as H-bonding and π-stacking interactions, suggesting the existence of ligand-unsupported argentophilic interactions in the present three complexes.

Luminescent Properties. Complex **1** exhibits a very strong and broad red emission band in the solid state at 650 nm upon photoexcitation at 450 nm, and complex **2** displays two strong fluorescent emission bands in the solid state at 438 and 650 nm upon photoexcitation at 380 nm, while complex **3** emits green luminescence in the solid state at 510 nm upon photoexcitation at 398 nm (Figure 9). Their lifetimes were measured to be 0.25 μs of the 650-nm peak for **1**, 1.6 ns of the 438-nm peak and 0.26 μs of the 650-nm peak for **2**, and 1.36 ns of the 510-nm peak for **3**, suggesting that all three complexes are potential candidates for lumi-

(22) Bowmaker, G. A.; Harris, R. K.; Assadollahzadeh, B.; Apperley, D. C.; Hodgkinson, P.; Amornsakchai, P. *Magn. Reson. Chem.* **2004**, *42*, 819.
(23) Pretsch, T.; Hartl, H. *Inorg. Chim. Acta* **2005**, *358*, 1179.

nescent materials. Time-dependent density functional theory calculations[24] using the B3LYP functional were performed on the three complexes with their ground-state geometries adapted from the truncated X-ray data. The results indicate that the lowest singlet excitation for **1** is dominated by the approximately degenerate combination of HOMO → LUMO and HOMO → LUMO+1 transitions, in which HOMO is mostly composed of ds/dp orbitals of Ag^I and both LUMO and LUMO+1 mainly consist of π* orbitals of pyridine rings of the 2,2′-bipy ligands, and for **2** the lowest singlet excitation is also dominated by the approximately degenerate combination of HOMO → LUMO and HOMO → LUMO+1 transitions, in which HOMO is mostly composed of ds/dp orbitals of Ag^I and π orbitals of thiocyanate groups and both LUMO and LUMO+1 mainly consist of π* orbitals of pyridine rings of the 2,2′-bipy ligands, while for **3** the lowest singlet excitation is dominated by the degenerate combination of HOMO → LUMO and HOMO → LUMO+1 transitions, in which HOMO is mostly composed of ds/dp orbitals of Ag^I and both LUMO and LUMO+1 consist of π* orbitals of cyanide groups and ds/dp orbitals of Ag^I accompanied by obvious bonding interactions between the adjacent Ag atoms (Figure S4 and Table S1 in the Supporting Information). As a result, the origin of the fluorescence at 650 nm of **1** can be ascribed to metal-to-ligand charge transfer (MLCT), where the electron is transferred from the Ag^I centers to an unoccupied π* orbital of the 2,2′-bipy ligands, which is also consistent with the fluorescent ascription of the simple Ag complex [Ag$_2$(L$_2$)(ClO$_4$)$_2$] (L = 4,5-diazo-spirobifluorene, bipyridine-like ligand);[24c] the origin of the fluorescence at 510 nm of **3** can be attributed to the coupling

of a MLCT (Ag → CN$^-$) transition and a metal-centered transition (Ag^I, ds/dp) modified by argentophilic interactions. Considering the structural characteristics and the similar emission bands around 650 nm in **1** and **2**, the low-energy emission of **2** may be assigned to originate from the single state of MLCT (Ag → bipy) character, whereas the origin of the high-energy emission at 438 nm of **2** is tentatively attributed to ligand-to-ligand charge transfer, where the electron is transferred from the π orbital of thiocyanate groups to an unoccupied π* orbital of the 2,2′-bipy ligands.

Conclusion

In summary, we have demonstrated the preparation and characterization of three novel Ag complexes, with ligand-unsupported argentophilic interactions being employed to increase their dimensionalities or to enrich their topologies. Through the ligand-unsupported argentophilic interactions, complex **1** exhibits a 1-D to 3-D architecture, complex **2** presents a 2-D interesting topology containing the S-type [Ag$_5$(SCN)$_4$(bipy)$_2$]$_n^{n+}$ cationic columns, and complex **3** features a complex framework with 3-fold-interpenetrated 3-D 3-connected (10, 3)-g nets. The results provide a rational route to generating high-dimensional frameworks by using Ag-containing species. Besides, these three complexes are revealed to be potential luminescent materials.

Supporting Information Available: Theoretical approach methodology, X-ray crystallographic files for **1**−**3** in CIF format, additional plots of the structures, and a detailed luminescent lifetime analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0601539

(24) For latest examples, see: (a) Yong, L.; Hoffmann, S. D.; Fässler, T. F.; Riedel, S.; Kaupp, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 2092. (b) Zheng, S.-L.; Yang, J.-H.; Yu, X.-L.; Chen, X.-M.; Wong, W.-T. *Inorg. Chem.* **2004**, *43*, 830. (c) Wang, C.-C.; Yang, C.-H.; Tseng, S.-M.; Lin, S.-Y.; Wu, T.-Y.; Fuh, M.-R.; Lee, G.-H.; Wong, K.-T.; Chen, R.-T.; Cheng, Y.-M.; Chou, P.-T. *Inorg. Chem.* **2004**, *43*, 4781.