Bull. Chem. Soc. Jpn. Vol. 83, No. 2, 173–175 (2010)

A Novel 3D Photoluminescent Silver(I) Coordination Polymer Featuring Unusual μ_4-Bonded and Usual μ_2-Bonded 2-Aminopyrazine

Di Sun, Geng-Geng Luo, Na Zhang, Qin-Juan Xu, Zhan-Hua Wei, Cheng-Feng Yang, Li-Rong Lin, Rong-Bin Huang,* and Lan-Sun Zheng

State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

Received September 17, 2009
E-mail: rbhuang@xmu.edu.cn

The coexistence of unusual μ_4- and usual μ_2-bonding modes of 2-aminopyrazine (NH_2pyz) is observed for the first time in a novel 3D Ag^I coordination polymer $[Ag_4(NHpyz)_2(NH_2pyz)_3(PF_6)_2]_n$ (**1**). The structure of **1** possesses 1D $\{[Ag_4(\mu_4\text{-}NHpyz)_2]^{2+}\}_n$ cylinders which are further extended by μ_2-NH_2pyz into a 3D framework.

The synthesis and design of transition metal coordination polymers by exploiting the knowledge of crystal engineering have drawn enormous interest in recent years due to their intriguing coordination architectures and potential applications in various fields, including catalysis, photophysics, photochemistry, fluorescence, magnetism, and biological properties.[1,2] Compared to pyrazine or alkyl-substituted pyrazine,[3] 2-aminopyrazine (NH_2pyz) not only demonstrates the ability to coordinate to metal centers through usual linear μ_2-bonding modes with $N_{pyrazinyl}$, but also introduces the possibility that coordination and hydrogen bonding might act cooperatively to stabilize the resulting structure through the amino group of NH_2pyz. Although sporadic reports about Mn^{II}, Cu^I, and Cu^{II} complexes with NH_2pyz have appeared in the literature,[4] only two silver(I) complexes containing NH_2pyz have been documented until now.[5] In our current study, as an ongoing research interest in a previous silver/2-aminopyrimidine system,[6] we successfully obtained a novel photoluminescent Ag^I coordination polymer $[Ag_4(NHpyz)_2(NH_2pyz)_3(PF_6)_2]_n$ (**1**), which consists of infinite 1D $\{[Ag_4(\mu_4\text{-}NHpyz)_2]^{2+}\}_n$ cylinders incorporating diverse Ag···Ag interactions and shows unusual μ_4-NHpyz and usual μ_2-NH_2pyz ligands simultaneously.

$[Ag_4(NHpyz)_2(NH_2pyz)_3(PF_6)_2]_n$ (**1**) was obtained as yellow crystals by the reaction of Ag_2O, NH_2pyz, and NH_4PF_6 in $H_2O/CH_3OH/NH_3$ media under ultrasonic treatment. The compositions of **1** were further deduced from X-ray single crystal diffraction, elemental analyses, and IR spectrum. Its IR spectrum exhibits the N–H stretching band at ca. 3360 cm^{-1} which proves the existence of aromatic amino groups.[7] Two infrared bands at 558 and 832 cm^{-1} clearly show the existence of PF_6^-.[8] Phase purity of **1** is sustained by its powder X-ray diffraction pattern, which is consistent with that simulated on the basis of the single-crystal X-ray diffraction data (Figure S2).

Table 1. Crystal Data of Complex **1**

	1
Formula	$Ag_4C_{20}H_{22}F_{12}N_{15}P_2$
M_r	709.55
Crystal system	Orthorhombic
Space group	*Pbcn*
a/Å	21.1071(16)
b/Å	10.5494(6)
c/Å	14.9173(9)
α/°	90
β/°	90
γ/°	90
Z	4
V/Å^3	3321.6(4)
D_{calcd}/g cm^{-3}	2.388
μ/mm^{-1}	2.531
F(000)	2292
Unique reflns	3188
Obsd reflns [$I > 2\sigma(I)$]	1698
Parameters	246
GOF	0.843
R indices [$I > 2\sigma(I)$][a),b)]	$R_1 = 0.0473$, $wR_2 = 0.1000$
R indices (all data)	$R_1 = 0.1001$, $wR_2 = 0.1092$
$\Delta\rho$ (e Å^{-3})	1.290 and −0.745

a) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. b) $wR_2 = \sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

X-ray single-crystal diffraction analysis reveals that **1** crystallizes in an orthorhombic *Pbcn* space group with an asymmetric unit that contains three crystallographically unique Ag^I ions, one NHpyz, one and half NH_2pyz, and one PF_6^-. Crystallographic data are listed in Table 1. As shown in Figure 1, Ag1 adopts a tetrahedral coordination geometry in which bond angles around Ag1 opened up to 132.7(2)° from the ideal tetrahedral angle while the remaining angles are in the range from 92.1(3) to 118.7(3)°. In the AgN_4 tetrahedron, Ag1 is bonded by three $N_{pyrazinyl}$ atoms and one unusual μ_2-N_{imino} atom. Analysis of the local symmetry of the Ag2 and Ag3 showed that they reside on a twofold axis (site occupancy factor (SOF) = 0.5). They adopt slightly distorted T-shaped coordination geometries completed by three N atoms, in detail, Ag2 is coordinated by three usual $N_{pyrazinyl}$ atoms, but Ag3 is bonded by one $N_{pyrazinyl}$ atom and two unusual μ_2-N_{imine} atoms. The Ag–N_{imino} and Ag–$N_{pyrazinyl}$ distances range from 2.238(7) to 2.303(7) Å and 2.166(7) to 2.374(12) Å, respectively. It is noteworthy that the configuration of N_{imine} atom (N3) is entirely different from that of the other two N_{amino} atoms (N6 and N7) where the μ_2-N_{imino} atom holds a tetrahedral geometry [$\angle$C3–N3–$Ag3^{iii}$ = 117.2(6), C3–N3–H3B = 112.2, $Ag1^{vi}$–N3–H3B = 118.5(6)°] and affords a pair of lone electrons and one negative charge to two Ag^I ions respectively. Although some reports about Ag^I coordinated with deprotonated aromatic amino-containing ligands have been presented in the literature,[9]

Published on the web January 29, 2010; doi:10.1246/bcsj.20090251

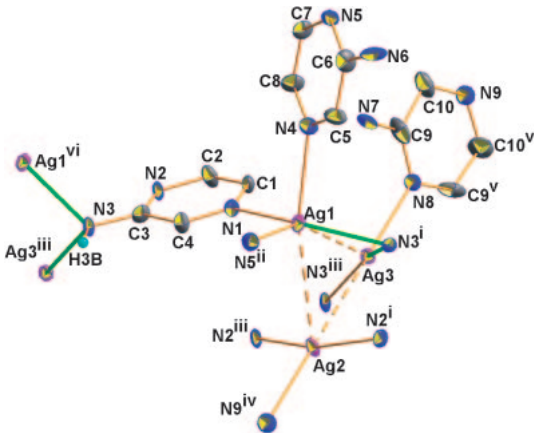

Figure 1. Part of the molecular structure and atom labeling of **1**, showing the coordination environments of the silver centers and Ag···Ag interactions (dashed lines). PF_6^- is omitted for clarity (symmetry codes: (i) x, $2-y$, $0.5+z$; (ii) $1.5-x$, $0.5+y$, z; (iii) $1-x$, $2-y$, $-z$; (iv) x, $1+y$, z; (v) $1-x$, y, $0.5-z$; (vi) x, $2-y$, $-0.5+z$).

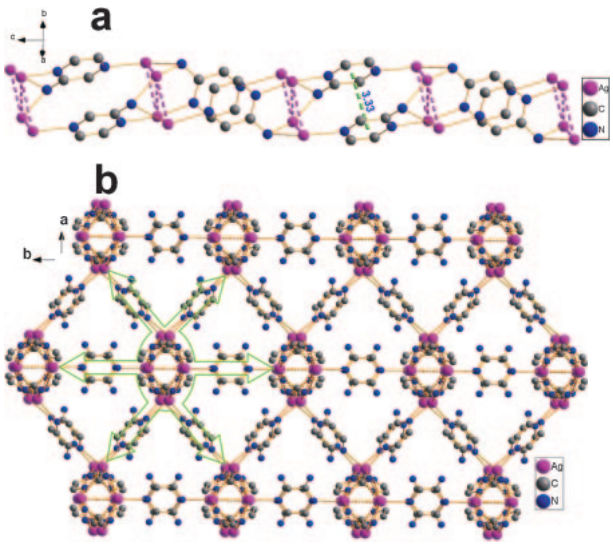

Figure 2. (a) 1D infinite $\{[Ag_4(\mu_4\text{-NHpyz})_2]^{2+}\}_n$ cylinder constructed by μ_4-NHpyz ligands with different Ag···Ag distances. (b) A 3D framework constructed by 1D infinite cylinder subunits and μ_2-NH_2pyz ligands.

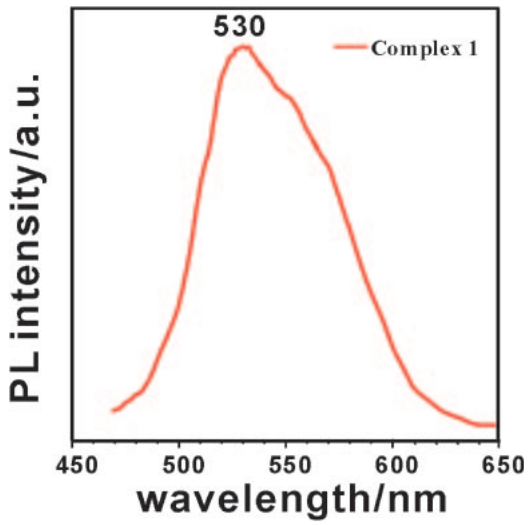

Figure 3. Solid-state emission spectrum for **1** at room temperature.

silver(I) complex with deprotonated NH_2pyz ligand has not been documented to date. Therefore, complex **1** is the first example containing unusual μ_4-NHpyz and usual μ_2-NH_2pyz ligands simultaneously.

The crystal packing behavior of **1** is also particularly intriguing. As displayed in Figure 2a, two Ag1, one Ag2, and one Ag3 form a diamond-shaped cross-section through diverse Ag···Ag interactions with the distances spanning from 2.9387(13) to 3.1605(8) Å which are shorter than twice the van der Waals radii of silver (3.44 Å),[10] and indicate ligand-supported Ag···Ag interactions.[11] The μ_4-NHpyz ligands further link the Ag_4 cross-sections to build 1D $\{[Ag_4(\mu_4\text{-NHpyz})_2]^{2+}\}_n$ cylinders in which strong $\pi\cdots\pi$ interaction exists in the adjacent pyrazinyl rings [$Cg1\cdots Cg1^{iii} = 3.334(5)$ Å, $Cg1$ is the centroid of the N1/C1/C2/N2/C3/C4 ring]. The cylinders are extended into a 3D framework by μ_2-NH_2pyz ligands (Figure 2b). Interestingly, remarkable anion···π interactions involving the pyrazinyl ring and PF_6^- anion are observed.[12] Both F3 and F6 atoms of the PF_6^- anion are engaged in anion···π interactions. [P1–F3···$Cg2^{ii} = 3.256(11)$ Å, P1–F6···$Cg2^{vi} = 3.510(12)$ Å; $Cg2$ is the centroid of the N4/C5/C6/N5/C7/C8 ring]. These noncovalent interactions cooperatively contribute to the stability of the resulting 3D framework. (symmetry codes: (ii) $1.5-x$, $0.5+y$, z; (iii) $1-x$, $2-y$, $-z$; (vi) x, $2-y$, $-0.5+z$).

The photoluminescent properties of **1** as well as free ligand were examined in the solid state at room temperature. The free NH_2pyz ligand is photoluminescent with a main emission band at 394 nm (Figure S4). As shown in Figure 3, when excited at 330 nm, **1** has an emission band centered at 530 nm. This emission band may be attributed to an intraligand (IL) phosphorescence of the NH_2pyz ligand which is induced by silver. The manifestation of this IL triplet emission of the silver complex at room temperature is suggestive of the presence of a strong heavy-atom effect of silver.[13] In addition, the optical absorption spectrum of **1** was also measured by the diffuse reflectance experiment showing absorption edge at ca. 500 nm (Figure S3).

In summary, we represented the first example of coexistence of unusual μ_4- and usual μ_2-bonding modes of 2-aminopyrazine in a 3D cylinder-based Ag^I coordination polymer featuring diverse Ag···Ag interactions. Additionally, absorption and emission properties of **1** were also measured.

Experimental

Structure Determination. Crystal structure of **1** was determined using a BRUKER APEX SMART CCD area detector diffractometer with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The diffraction data were treated using SMART and SAINT, and absorption correction was performed using SADABS.[14a] The structure was solved by using direct methods with SHELXTL.[14b] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically.

Pertinent and selected metric parameters for **1** are presented in Table S1 (see Supporting Information). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-743534 for complex **1**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis. Reaction of Ag_2O (116 mg, 0.5 mmol), 2-aminopyrazine (94 mg, 1 mmol), and NH_4PF_6 (163 mg, 1 mmol) in H_2O/CH_3OH/NH_3 media under ultrasonic treatment gave a clear solution. The resultant solution was allowed slowly to evaporate in darkness at room temperature for several weeks to give yellow block crystals of **1**. The crystals were washed with deionized water and dried in air. Yield: ca. 62% based on Ag. Elemental analysis: Anal. Calcd for $Ag_4C_{20}H_{22}F_{12}N_{15}P_2$: C, 20.12; H, 1.86; N, 17.60%. Found: C, 20.18; H, 1.79; N, 17.67%. Selected IR peaks (cm^{-1}): 3372 (s), 3356 (s), 1625 (m), 1530 (m), 1430 (m), 1384 (w), 1259 (w), 1210 (w), 832 (s, PF_6^-), 558 (s, PF_6^-).

This work was financially supported by the National Natural Science Foundation of China (No. 20721001), 973 Project (Grant 2007CB815301) from MSTC and The National Science Fund of China for Fostering Talents in Basic Science (No. J0630429).

Supporting Information

Figures S1–S4 are IR, XRD, diffuse reflectance spectra of **1**, and emission and excitation spectra of NH_2pyz respectively. Selected bond lengths and angles for **1** were placed into Table S1. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

References

1 a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319. b) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. c) X.-M. Zhang, M.-L. Tong, X.-M. Chen, *Angew. Chem., Int. Ed.* **2002**, *41*, 1029. d) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853. e) S. R. Batten, R. Robson, *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. f) R. Wang, M. Hong, J. Luo, R. Cao, J. Weng, *Chem. Commun.* **2003**, 1018. g) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117. h) A. J. Blake, N. R. Champness, P. A. Cooke, J. E. B. Nicolson, C. Wilson, *J. Chem. Soc., Dalton Trans.* **2000**, 3811. i) N. S. Oxtoby, A. J. Blake, N. R. Champness, C. Wilson, *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4905.

2 a) C. Yan, L. Chen, R. Feng, F. Jiang, M. Hong, *CrystEngComm* **2009**, *11*, 2529. b) W. Su, M. Hong, J. Weng, R. Cao, S. Lu, *Angew. Chem., Int. Ed.* **2000**, *39*, 2911. c) S.-L. Zheng, J.-P. Zhang, W.-T. Wong, X.-M. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 6882.

3 a) F. Würthner, C.-C. You, C. R. Saha-Möller, *Chem. Soc. Rev.* **2004**, *33*, 133. b) C. Janiak, *Dalton Trans.* **2003**, 2781. c) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. d) P. J. Steel, C. M. Fitchett, *Coord. Chem. Rev.* **2008**, *252*, 990.

4 a) T. A. Tronic, K. E. de Krafft, M. J. Lim, A. N. Ley, R. D. Pike, *Inorg. Chem.* **2007**, *46*, 8897. b) J. K. Clegg, K. Gloe, M. J. Hayter, O. Kataeva, L. F. Lindoy, B. Moubaraki, J. C. McMurtrie, K. S. Murray, D. Schilter, *Dalton Trans.* **2006**, 3977. c) J. L. Manson, J. A. Schlueter, U. Geiser, M. B. Stone, D. H. Reich, *Polyhedron* **2001**, *20*, 1423. d) J. R. Allan, A. D. Paton, K. Turvey, H. J. Bowley, D. L. Gerrard, *Inorg. Chim. Acta* **1987**, *134*, 259. e) S. Pagola, R. D. Pike, K. deKrafft, T. A. Tronic, *Acta Crystallogr., Sect. C* **2009**, *64*, m134.

5 a) D. Sun, G.-G. Luo, Q.-J. Xu, N. Zhang, Y.-C. Jin, H.-X. Zhao, L.-R. Lin, R.-B. Huang, L.-S. Zheng, *Inorg. Chem. Commun.* **2009**, *12*, 782. b) A. A. Massoud, A. Hefnawy, V. Langer, M. A. Khatab, L. Öhrstrom, M. A. M. Abu-Youssef, *Polyhedron* **2009**, *28*, 2794.

6 a) G.-G. Luo, R.-B. Huang, J.-H. Chen, L.-R. Lin, L.-S. Zheng, *Polyhedron* **2008**, *27*, 2791. b) G.-G. Luo, R.-B. Huang, N. Zhang, L.-R. Lin, L.-S. Zheng, *Polyhedron* **2008**, *27*, 3231. c) G.-G. Luo, D. Sun, Q.-J. Xu, N. Zhang, R.-B. Huang, L.-R. Lin, L.-S. Zheng, *Inorg. Chem. Commun.* **2009**, *12*, 436. d) D. Sun, G.-G. Luo, N. Zhang, J.-H. Chen, R.-B. Huang, L.-R. Lin, L.-S. Zheng, *Polyhedron* **2009**, *28*, 2983. e) D. Sun, G.-G. Luo, R.-B. Huang, N. Zhang, L.-S. Zheng, *Acta Crystallogr., Sect. C* **2009**, *65*, m305.

7 B. H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Wiley, New York, **2004**.

8 O.-S. Jung, Y. J. Kim, Y.-A. Lee, K.-M. Park, S. S. Lee, *Inorg. Chem.* **2003**, *42*, 844.

9 a) R. S. Rarig, Jr., J. Zubieta, *Inorg. Chim. Acta* **2002**, *340*, 211. b) W.-Z. Shen, B. Costisella, B. Lippert, *Dalton Trans.* **2007**, 851. c) H. Hou, Y. Wei, Y. Song, L. Mi, M. Tang, L. Li, Y. Fan, *Angew. Chem., Int. Ed.* **2005**, *44*, 6067.

10 A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

11 M. Jansen, *Angew. Chem., Int. Ed.* **2002**, *41*, 3746.

12 a) P. Gamez, T. J. Mooibroek, S. J. Teat, J. Reedijk, *Acc. Chem. Res.* **2007**, *40*, 435. b) P. de Hoog, P. Gamez, I. Mutikainen, U. Turpeinen, J. Reedijk, *Angew. Chem., Int. Ed.* **2004**, *43*, 5815.

13 H. Kunkely, A. Vogler, *Inorg. Chem. Commun.* **2006**, *9*, 866.

14 a) G. M. Sheldrick, *SADABS-Program for Empirical Absorption Correction for Area Detector Data*, University of Göttingen, Göttingen, Germany, **1996**. b) G. M. Sheldrick, *SHELXS 97-Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1998**.