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Crystal Structure and Luminescent Property of 2D Hybrid Silver Chloride with 1,2-Bis(4-pyridyl) Ethane

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Abstract: Using the flexible dipyridyl ligand 1,2-bis(4-pyridyl) ethane (bpe), a hybrid silver chloride $[Ag_3Cl_3(bpe)_2]_n$(1) has been synthesized by ultrasonic method. The experimental results indicate that it belongs to triclinic system with space group $P\bar{1}$. The structure of complex **1** features 1D $(Ag_6Cl_6)_n$ chains, which are further linked by bipodal spacers bpe to form a 2D bilayer structure. In addition, the complex 1 shows a strong yellow emission band that peaks at 525 nm (λ_{ex} = 385 nm) in the solid state at room temperature, and it is thermally stable below 170 ℃.

Key words: coordination polymer; 1,2-bis(4-pyridyl) ethane; ultrasonic reaction; fluorescent spectrum; thermal analysis

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以AgCl和1,2-二(4-吡啶)乙烷为原料合成的二维无机-有机杂化聚合物的晶体结构及荧光性质

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摘要: 以AgCl与柔性配体1,2-二(4-吡啶)乙烷(bpe)为原料,在1∶1的甲醇-水混合溶剂中超声反应合成了一个新的无机-有机杂化聚合物$[Ag_3Cl_3(BPE)_2]_n$(**1**),并对该配合物进行了元素分析、红外光谱分析、热重分析、发光测试以及晶体结构研究。配合物属于三斜晶系,$P\bar{1}$空间群,$a = 0.998\,8(2)$ nm, $b = 1.115\,1(2)$ nm, $c = 1.269\,5(3)$ nm, $\alpha = 64.27(3)°$, $\beta = 85.71(3)°$, $\gamma = 86.70(3)°$, $V = 1.269\,7(5)$ nm^3, $Z = 2$。单晶结构分析表明,该化合物**1**含有一维的$(Ag_6Cl_6)_n$链,双氮配体BPE进一步连接该一维链形成了二维双层结构。固体发光性能测试表明,该化合物在385 nm光激发下能发出峰值为525 nm的黄光。此外,热分析表明,该化合物热稳定性可达到170 ℃。

关　键　词: 配位聚合物; 1,2-二(4-吡啶)乙烷; 超声合成; 发光性质

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1　Introduction

The design and synthesis of coordination polymers have provided exciting new prospects for its novel structures and properties[1-5]. As an important class of coordination polymers, hybrid organic-inorganic materials, especially metal halides, have attracted increasing attention[6-7]. Recently, some hybrid copper halides constructed by N-donor ligands have been reported[8-10]. However, Ag-*X* skeletons have rarely participated in constructing this kind of hybrid material, maybe due to the strong depositing trend of silver and halogens[11-13]. In fact, besides their intriguing topologies, these hybrid silver halides have attracted wide interest for their rich photophysical properties. The presence of direct Ag⋯Ag interactions has been proved to be one of the crucial causes to the luminescent properties in such species.

1,2-bis(4-pyridyl)ethane (bpe) and its analogues are neutral linear ligands and previously used by us[14-16] as excellent spacers in the construction of novel metal-organic compounds including diverse motifs. In an attempt to exploit AgCl-bpe hybrid materials, we successfully obtained the title complex, $[Ag_3Cl_3(BPE)_2]_n$ (**1**, bpe: 1,2-bis(4-pyridyl)-ethane), by the solution-phase ultrasonic synthesis technique, and report its crystal structure and properties here.

2　Experiments

2.1　Materials and General Methods

All reagents and solvents for synthesis were purchased commercially and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE instruments EA 1110 analyzer. FTIR spectrum (KBr pellets) was taken on a Nicolet Nexus 470 spectrometer in the range 4 000 ~ 400 cm^{-1}. TG curve was performed from 25 ~ 700 ℃ on a TA5200/MDSC2910 instrument at a heating rate of 5° · min^{-1} under N_2 atmosphere. Fluorescent spectrum was recorded on a Hitachi F-4500 fluorescence spectrophotometer (slit width, 5 nm; sensitivity, high) with solid powder on a 1 cm quartz round plate.

2.2　Synthesis of $[Ag_3(bpe)_2Cl_3]_n$ (1)

A mixture of AgCl (143 mg, 1 mmol) and bpe (184 mg, 1 mmol) was stirred in $V(CH_3OH):V(H_2O)=1:1$ mixed solvent (10 mL) under ultrasonic treatment at ambient temperature for 20 min. Then, an aqueous NH_3 solution (25%) was added dropwise until a clear solution was obtained. The formation of the product is not affected by changes in the reaction mole ratio of organic ligands to metal ions. The resultant solution was allowed to evaporate slowly in darkness at room temperature for one week to give colorless block-shaped crystals of **1** (yield ca. 49%, based on Ag). They were washed with small volumes of cold CH_3OH and diethyl ether. Analyse calculate (%) for $C_{24}H_{24}Ag_3Cl_3N_3$: C, 36.75; H, 3.08; N, 5.36. Found: C, 36.43; H, 3.18; N, 5.48. FT-IR (KBr, cm^{-1}) ν: 2 932(w), 2 846(w), 1 609(s), 1 554(m), 1 502(w), 1 427(m), 1 220(m), 1 075 (w), 825 (s), 668 (w), 625(w), 543(m), 487(w).

2.3　X-ray Crystallography and Structural Refinement

Structure measurement of **1** was performed on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer with graphite-monochromated Mo Kα radiation source ($\lambda=0.071\ 073$ nm) operating at 50 kV and 90 mA in ω scan mode for **1**. A total of 44° × 5.00° oscillation images was collected, each being exposed for 5.0 min. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program[17]. The highest possible space group was chosen. The structure was solved by direct methods using SHELXS-97[18] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97[19]. All non-hydrogen atoms were finally refined with anisotropic displacement parameters. Hydrogen atoms of organic ligands were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2 times U_{eq} of the attached C atoms. The structure was examined using the Addsym subroutine PLATON[20] to assure that no additional symmetry could be applied to the model. Crystal structure views were obtained using Diamond v3.1f. The crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2, respectively. CCDC: 837535.

Table 1 The crystallographic data for complex 1

Formula	$C_{24}H_{24}Ag_3Cl_3N_4$	Formula	$C_{24}H_{24}Ag_3Cl_3N_4$
M_r	798.43	Dcalcd	2.088 g cm^3
Crystal size	0.18 mm × 0.15 mm × 0.11 mm	μ(Mo Kα),	2.63 cm^{-1}
Crystal system	triclinic	$F(000)$	776 e
Space group	$P\bar{1}$	hkl range	±11, ±12, ±13
a	0.998 8(2) nm	Refl. measured	9 908
b	1.115 1(2) nm	Refl. unique	4 441
c	1.269 5(3) nm	R_{int}	0.070 5
α	64.27(3)°	Param. refined	307
β	85.71(3)°	R_1(F)/wR_2(F^2)^a(all refl.)	0.049 1/0.113 7
γ	86.70(3)°	GoF(F^2)^b	1.036
V	1.269 7(5) nm^3	$\Delta\rho_{fin}$(max/min),	840/ −910 e · nm^{-3}
Z	2		

$^aR_1(F) = \sum \| F_o| - |F_c \| / \sum |F_o|,\ wR_2(F^2) = [\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$

$w = [\sigma^2(F_o^2) + (0.0502P)^2 + 0.0789P]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

$^b\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2]/(n_{obs} - n_{param})]^{1/2}$.

Table 2 Selected bond lengths (nm), and angles (°) for complex 1^a

Ag1—N1	2.316(4)	Ag1—Cl1	2.539(1)	Ag1—Cl2	2.736(1)
Ag1—Cl3	2.587(1)	Ag2—N3	2.305(4)	Ag2—Cl1	2.516(2)
Ag2—Cl2^{i}	2.591(1)	Ag2—Cl2	2.663(1)	Ag3—N2^{ii}	2.278(4)
Ag3—N4^{iii}	2.291(4)	Ag3—Cl3^{iv}	2.712(1)	Ag3—Cl2^{iv}	3.023(1)
Ag3—Cl3	2.945(1)	Ag1—Ag2	3.084(1)	Ag3—Ag3^{iv}	3.318(2)
N1—Ag1—Cl1	115.06(11)	N1—Ag1—Cl3	97.70(10)	Cl1—Ag1—Cl3	128.86(5)
N1—Ag1—Cl2	109.15(10)	Cl1—Ag1—Cl2	106.13(5)	Cl3—Ag1—Cl2	97.93(5)
N3—Ag2—Cl1	110.29(10)	N3—Ag2—Cl2^{i}	100.09(10)	Cl1—Ag2— Cl2^{i}	130.75(5)
N3—Ag2—Cl2	110.37(10)	Cl1—Ag2—Cl2	109.01(5)	Cl2—Ag2— Cl2^{i}	94.68(4)
N2^{ii}—Ag3—N4^{iii}	155.29(13)	N2^{ii}—Ag3—Cl3^{iv}	107.56(10)	N4^{iii}—Ag3—Cl3^{iv}	95.78(10)
Cl3—Ag3—Cl2^{iv}	161.73(4)	Cl3—Ag3—Cl3^{iv}	108.30(4)		

^{a}Symmetry codes: i $-x, -y+2, -z$; ii $x-1, y-1, z$; iii $+1, y, z+1$; iv $-x, -y+1, -z+1$.

3 Results and Discussion

3.1 Synthesis

It is well known that silver compounds are not stable in the light. So the synthesis of the compound **1** was carried out in darkness to avoid photodecomposition and described in the experiment section. During the synthesis, precipitates were quickly formed when mixing the starting reactants. Therefore, ammonia solution (25%) was introduced into the reaction mixture under ultrasonic treatment until it was almost completely dissolved, and then filtering to get a clear solution to evaporate in air. Good crystalline of **1** for structural data collection can be easily obtained after one week later. The reproducibility for the present complex is very nice and the formation of **1** is found to be not so sensitive by variations in the molar ratio of organic to metal ions. The resultant crystals are insoluble in water and common organic solvents. The composition of $[Ag_3(bpe)_2Cl_3]_n$ (**1**) was characterized by single-crystal X-ray crystallography, and further confirmed by elemental analysis, IR spectrum and thermogravimetric analysis.

3.2 Structure Description

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the triclinic system with space group $P\overline{1}$ and is a 2D inorganic-organic hybrid coordination network. Within the asymmetric unit of **1**, there are three crystallographically independent Ag (Ⅰ) ions, two bpe ligands, and three Cl^- anions. As depicted in Fig. 1, the Ag1 and Ag2 have similar tetrahedron geometries and surrounded by three Cl^- anions and one N-donor of one bpe ligand. The bond lengths of Ag—N and Ag—Cl are in the range 0.230 5 ~ 0.231 5 nm and 0.251 6 ~ 0.273 6 nm, respectively, which are well matched to those observed in several related species[13]. The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser[21] to describe the geometry of a four-coordinate metal system. The τ_4 parameter is 0.98 (for Ag1) and 0.84 (for Ag2) (for perfect tetrahedral geometry $\tau_4 = 1$), respectively, which indicate Ag1 is the least distorted one in **1**. The Ag3 is located in a square-pyramidal geometry and coordinated by three Cl^- anions (Ag3—Cl3 = 0.294 5(1), Ag3—$Cl2^{iv}$ = 0.302 3(1) and Ag3—$Cl3^{iv}$ = 0.271 2(1) nm) and two N atoms (Ag3—$N2^{ii}$ = 0.227 8(4) and Ag3—$N4^{iii}$ = 0.229 1(4) nm) from two different bpe ligands. Addison[22] also defined a geometric parameter τ_5 ($\tau_5 = [(\theta - \varphi)/60]$), where θ and φ are the angles between the donor atoms forming the basal plane in square-pyramidal geometry to five-coordinate metal system as an index of the degree of distortion. The τ_5 parameter for Ag3 is 0.11 (for ideal square-pyramidal geometry, $\tau_5 = 0$).

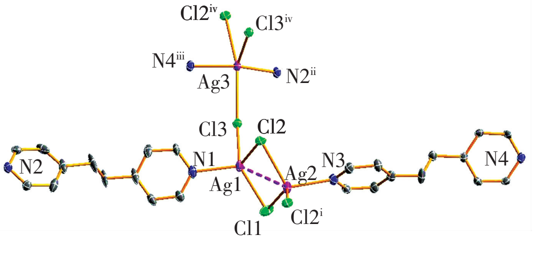
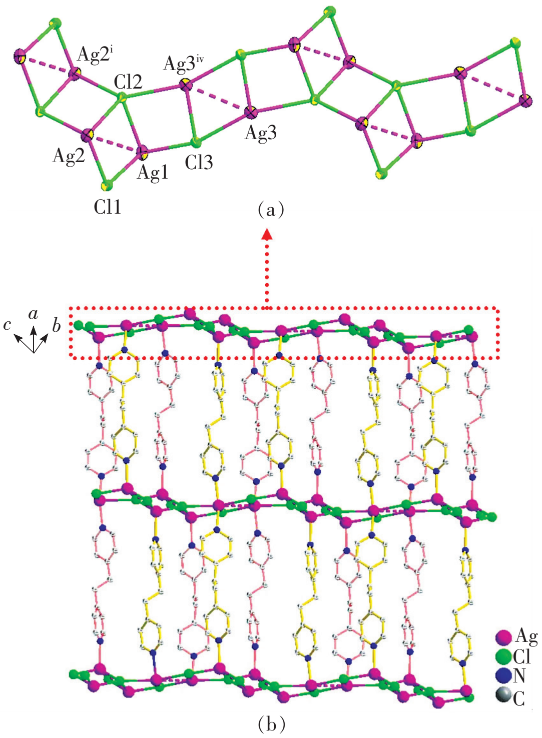


Fig. 1　ORTEP plot showing the coordination environments of Ag(Ⅰ) ions in 1 with the thermal ellipsoids at the 50% probability level (symmetry codes: ⅰ -*x*, -*y* + 2, -*z*; ⅱ *x*-1, *y*-1, *z*; ⅲ *x* + 1, *y*, *z* + 1; ⅳ -*x*, -*y* + 1, -*z* + 1). Hydrogen atoms are omitted for clarity.

The most interesting feature of this structure is the existence of the unusual $(Ag_6Cl_6)_n$ skeletons (Fig. 2(a)). The core can be described as two Ag3Cl3 ladder-like structures of alternating silver and chlorine atoms linked by Ag—Cl interactions (Ag1—Cl3). The Cl^- anions take on three types of bridging arrangements. Cl1 is involved in a μ_2 bridging ligand that links Ag1 and Ag2; Cl2 acting as μ_3 coordinates to Ag1, Ag2, $Ag2^{i}$ and $Ag3^{iv}$, while Cl3 serves as a μ_4 bridging ligand to connect three neighboring Ag1, Ag3 and $Ag3^{iv}$ atoms. Because of the different coordinated geometry for silver atoms, the Ag⋯Ag distances within the $(Ag_6Cl_6)_n$ skeletons are very different. The shortest intracluster Ag⋯Ag distance was in the coupling bi-ladder structure of Ag1⋯Ag2 of 0.308 4 nm, and the longest Ag⋯Ag



(a)

(b)

Fig. 2　(a) The one-dimensional $(Ag_6Cl_6)_n$ polymer chain structure, where Cl as bridging ligand connects neighboring silver(Ⅰ) centers to form a 1D chain. (b) Perspective view of the 2D layered coordination network. Symmetry codes: ⅰ -*x*, -*y* + 2, -*z*; ⅳ -*x*, -*y* + 1, -*z* + 1.

distance was Ag1···Ag3^{iv} 0.376 3 nm. The $(Ag_6Cl_6)_n$ skeletons are further connected by bpe ligands which take on bis-monodentate bridging modes with anti-conformations, resulting in the overall 2D undulated bi-layered net (Fig. 2b).

3.3 Thermogravimetric Analysis and Photoluminescence

Thermogravimetric analysis (TGA) for complex **1** was performed in a flowing N_2 atmosphere over the temperature range 25 ~ 700 ℃ and depicted in Fig. 3. The molecular architecture remained stable up to 170 ℃. A dramatic weight loss of 45.6% occurred between 170 ~ 240 ℃, in good agreement with a process involving the loss of organic ligands (calcd 46.1%) and the decomposition of the title compound.

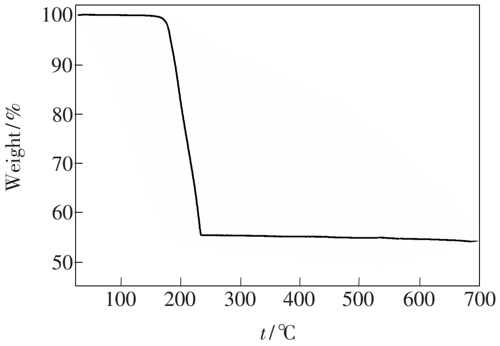


Fig. 3 The TGA curve for **1**

The luminescence of **1** has been investigated in the solid state at room temperature, as shown in Fig. 4(a). Upon excitation at 385 nm, complex **1** exhibits strong photoluminescence with an emission maximum at about 525 nm. When compared to the photoluminescence spectrum of the free bpe ligand[14], the emission band of complex **1** is red-shifted by more than 90 nm, which may come from the electronic transition between p orbitals (filled orbitals) of coordinated N atoms and the 5s orbital (empty orbital) of Ag(Ⅰ) ion, *i.e.*, ligand-to-metal charge transfer (LMCT), admixed with the chlorine-to-ligand charge transfer (XLCT). This phenomenon has already been observed for some hybrid silver halides supported by dipyridyl ligand bridges[13]. As displayed in Fig. 4(b), the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of the emission excited by 385 nm light are approximately (0.36, 0.52), which yellow light. Therefore, the complex **1** may find applications in the field of solvent-resistant photoactive materials owing to its strong yellow emission and insolubility in the common solvents.

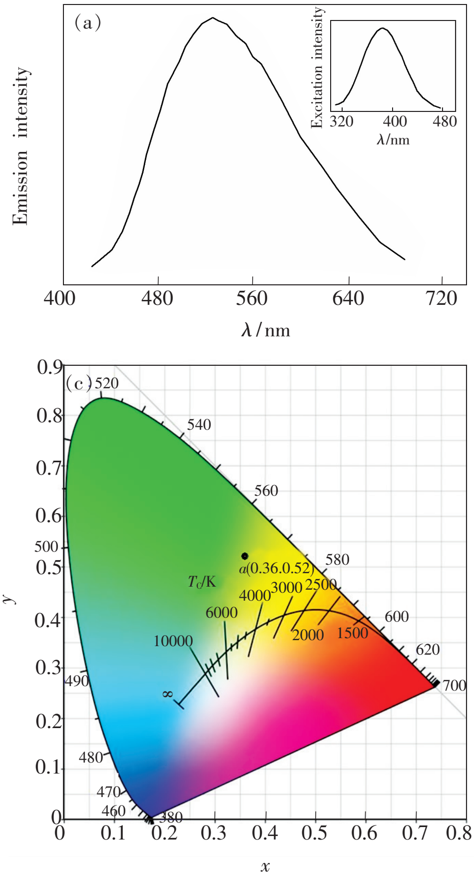


Fig. 4 (a) Photoluminescence (PL) spectrum and excitation spectrum (insert) of complex **1** in the solid state at room temperature. (b) CIE-1931 chromaticity diagram showing the yellow PL of complex **1**.

4 Conclusion

In summary, we synthesized and characterized an interesting 2-D undulated bilayer hybrid silver(Ⅰ) chlorine $[Ag_3(bpe)_2Cl_3]_n$(**1**). Complex **1** is fascinating for the next two reasons: (i) this molecular structure is constructed by the first reported $(Ag_6Cl_6)_n$ skeletons, giving a new strategy for the design of hybrid materials; (ii) it exhibits a yellow photoluminescence maximized at 525 nm at room temperature.

References:

[1] Ding B, Chuang R N, Wu X X, *et al*. Synthesis and characterization of one novel 1D double-chain copper(Ⅱ) complex with 1,2-bis(1,2,4-triazole-1-yl)ethane [J]. *Chin. J. Inorg. Chem.* (无机化学学报), 2011, 27(1):189-192 (in English).

[2] Gu L Y, Tu H, Zhu L, *et al*. Synthesis and luminescent properties of novel metal-organic coordination polymers based on bisphenol A [J]. *Chin. J. Lumin.* (发光学报), 2011, 32(2):127-133 (in Chinese).

[3] Wang C C, Song Y X, Wang Y L, *et al*. Syntheses, crystal structure and optical property of two bis-ligand silver(Ⅰ) complexes containing diphenic acid and bidentate N-donor ligands [J]. *Chin. J. Inorg. Chem.* (无机化学学报), 2011, 27(2):361-366 (in English).

[4] Luo G G, Wu D L, Liu L, *et al*. A novel 1D T5(0)A(2) water tape incorporated in the channel of the first 3D silver-suberate framework [J]. *J. Mol. Struct.*, 2012, 1014(1):92-96.

[5] Luo G G, Li D X, Wu D L, *et al*. Characterization of a well-resolved acyclic methanol(water)$_5$ heterohexamer in the solid state [J]. *Inorg. Chem. Commun.*, 2012, 17(1):108-112.

[6] Engelhardt L M, Gotsis S, Healy P C, *et al*. Lewis-base adducts of group 11 metal(I) compounds. XLV. conformational systematics of $[(\text{N-base})_1(\text{AgX})_1]_N$ complexes [J]. *Aust. J. Chem.*, 1989, 42(1):149-176.

[7] Zhang L, Zhang J, Li Z J, *et al*. New coordination motifs of melamine directed by N-H center dot center dot center dot *X* (*X* = Cl or Br) hydrogen bonds [J]. *Inorg. Chem.*, 2007, 46(15):5838-5840.

[8] Graham P M, Pike R D, Sabat M, *et al*. Coordination polymers of copper(Ⅰ) halides [J]. *Inorg. Chem.*, 2000, 39 (22):5121-5132.

[9] Place H, Scott B, Willett R D. A new one-dimensional copper(Ⅰ) halide lattice: (paraquat)Cu_4Cl_6[J]. *Inorg. Chim. Acta*, 2001, 319(1):43-48.

[10] Xu X X, Ma Y, Wang E B. Synthesis, structure, and luminescent property of the first mixed-valence Cu-halide complex constructed from novel D6R Cu_6Cl_6 cores [J]. *Inorg. Chem. Commun.*, 2007, 10(9):1113-1116.

[11] Bowmaker G A, Effendy, Skelton B W, *et al*. Syntheses, structures and vibrational spectroscopy of some unusual silver (I) (pseudo-) halide/unidentate nitrogen base polymers [J]. *Inorg. Chim. Acta*, 2005, 358(14):4307-4326.

[12] Zartilas S, Kourkoumelis N, Hadjikakou S K, *et al*. A new silver(Ⅰ) aggregate having an octagonal Ag_4S_4 Core where μ_3-S bonding interactions lead to a nanotube assembly that exhibits quasiaromaticity [J]. *Eur. J. Inorg. Chem.*, 2007, (9):1219-1224.

[13] Zhang L, Li Z J, Qin Y Y, *et al*. Homochiral moganite-type metal-organic framework based on unusual $(Ag_2Cl)_n$ skeletons [J]. *Cryst. Eng. Comm.*, 2008, 10(6):655-657.

[14] Luo G G, Xiong H B, Sun D, *et al*. A discrete spirocyclic $(H_2O)_9$ cluster and 1D novel water chain with tetrameric and octameric clusters in cationic hosts [J]. *Cryst. Growth & Des.*, 2011, 11(5):1948-1956.

[15] Luo G G, Sun D, Xu Q J, *et al*. Photoluminescent metal-organic coordination polymer incorporating one-dimensional silver chains [J]. *Inorg. Chem. Commun.*, 2009, 12(5):436-439.

[16] Luo G G, Wu D L, Liu L, *et al*. A discrete water hexamer with a new planar tetrameric water moiety trapped in the crystal host of [Ag(azelate)(4,4′-bipyridine)]·$(H_2O)_3$[J]. *J. Mol. Struct.*, 2011, 1005(1):172-177.

[17] Luo K J, Jiang S P, Wang X, *et al*. Efficient green phosphorescent polymer light-emitting diodes based on cyclometalated iridium complex [J]. *Chin. J. Lumin.* (发光学报), 2011, 32(4):368-373 (in English).

[18] Sheldrick G M, Phase annealing in SHELX-90: Direct methods for larger structures [J]. *Acta Crystallogr.*, 1990, A46 (6):467-473.

[19] Sheldrick G M. A short history of SHELX [J]. *Acta Crystallogr.*, 2008, A64(1):112-122.

[20] Spek A L. *Implemented as The PLATON Procedure*, *A Multi-purpose Crystallographic Tool* [M]. Ultrecht, Netherlands: Utrecht University, 1998.

[21] Yang L, Powell D R, Houser R P. Structural variation in copper(Ⅰ) complexes with pyridylmethylamide ligands: Structural analysis with a new four-coordinate geometry index, τ_4[J]. *Dalton Trans.*, 2007, (9):955-964.

[22] Addison A W, Rao T N, Reedijk J, *et al*. Synthesis, structure, and spectroscopic properties of copper(Ⅱ) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2′-yl)-2,6-dithiaheptane]copper(Ⅱ) perchlorate [J]. *J. Chem. Soc.*, *Dalton Trans.*, 1984, (7):1349-1356.