

三维超分子化合物 $[\text{Ag}_4(\text{L})_4](\text{PMBS})_4 \cdot 2\text{H}_2\text{O}$ 的合成、晶体结构和荧光性质

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Synthesis, Crystal Structure and Luminescence of A 3D Supramolecular Complex $[\text{Ag}_4(\text{L})_4](\text{PMBS})_4 \cdot 2\text{H}_2\text{O}$

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Abstract: The title compound, $[\text{Ag}_4(\text{L})_4](\text{PMBS})_4 \cdot 2\text{H}_2\text{O}$ (**1**), where $\text{L}=2,5\text{-bis}(4\text{-pyridyl})\text{-}3,4\text{-diaz}\text{-}2,4\text{-hexadiene}$, $\text{PMBS}=p\text{-methylbenzenesulfonate}$ was synthesized and its crystal structure was determined by X-ray diffraction structure analysis. The crystal is of triclinic, space group $P1$ with $a=0.820\,3(2)\text{ nm}$, $b=1.322\,7(3)\text{ nm}$, $c=2.061\,0(3)\text{ nm}$, $\alpha=76.155(2)^\circ$, $\beta=78.651(4)^\circ$, $\gamma=89.993(3)^\circ$, $V=2.126\,2(8)\text{ nm}^3$, $Z=2$, $D_c=1.644\text{ g}\cdot\text{cm}^{-3}$, $F(000)=1\,068$, $R=0.052\,4$, $wR=0.113\,6$. The Ag atoms are linear coordinated by two N atoms of two L ligands, while the $p\text{-methylbenzenesulfonate}$ molecules are included in the lattice and connected to $[\text{Ag}(\text{L})]_n$ by hydrogen bonding interactions to form a three-dimensional supramolecular structure. CCDC: 727587.

Key words: Ag(II) complex; crystal structure; hydrogen bond; luminescent property

In recent years, the design, construction, and elucidation of multidimensional supramolecular solid state architectures have attracted considerable attention in the context of crystal engineering and supramolecular chemistry^[1-6]. The drives arise not only from the pragmatic perspective to obtain new technologically relevant materials, but also from the scientists natural interest to reveal the intriguing beauty and diversity of

the architectures that can be assembled and to understand the laws of physics determining the assembly processes. In the last case, the noncovalent interactions may serve as the forces interlinking discrete or low-dimensional coordination motifs (and other components) into higher-dimensional architectures or as additional forces sustaining the coordination networks^[7,8]. During the past few years, many one-, two-,

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and three-dimensional coordination polymers have been generated from transition metal templates with rigid and flexible pyridyl-containing bidentate or multidentate organic spacers^[9–12]. We report herein the synthesis and the crystal structure of the novel silver complex, $[\text{Ag}_4(\text{L})_4](\text{PMBS})_4 \cdot 2\text{H}_2\text{O}$ (**1**), which is formed 3D supra-molecular structures by weak Ag–Ag interactions and hydrogen bonds interactions.

1 Experimental

1.1 Materials and instruments

2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene was prepared according to the literature^[9]. All other reagents and solvents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on FTIR-8700 spectrophotometer using KBr discs.

1.2 Synthesis of the title compound

A methanol solution (5 mL) of AgNO_3 (0.20 mmol) was mixed under stirring with the solution (5 mL) of L ligand (0.40 mmol) in the same solvent. (0.20 mmol) 4-methylbenzenesulfonic acid was added and stirred for about 4 hours. Then, the resulting clear solution was allowed to evaporate slowly at room temperature for three weeks, affording yellow crystals. The product was

collected by filtration, washed with methanol and ether successively, and then dried in air. Yields based on Ag: 38.5%. Elemental analysis Calcd. for $\text{C}_{42}\text{H}_{44}\text{Ag}_2\text{N}_8\text{O}_7\text{S}_2$ (%): C, 47.86; H, 4.18; N, 10.64. Found(%): C, 47.77; H, 4.15; N, 10.58. Main IR bands (cm^{-1}): 3 413s, 1 612s, 1 604s, 1 413ms, 1 306ms, 1 244s, 1 087s, 846 ms, 725m, 624w.

1.3 X-ray crystallography

A yellow needle crystal with dimensions of 0.20 mm×0.18 mm×0.14 mm was selected for the measurement. The diffraction data were collected at 291(2) K on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$). A total of 20 027 reflections were collected in the range of $1.04^\circ \leq \theta \leq 26.00^\circ$ by using an ω -scan mode, of which 15 389 were unique with $R_{\text{int}} = 0.032$, 13 084 with $I > 2\sigma(I)$ were considered as observed and used in the structural solution and refinement. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.0^[14]. The non-hydrogen atoms were refined anisotropically and Hydrogen atoms were localized in their calculation positions and refined by using the riding model. Crystal data and structure refinement parameters are listed in Table 1.

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Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$\text{C}_{42}\text{H}_{44}\text{Ag}_2\text{N}_8\text{O}_7\text{S}_2$	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.644
Formula weight	1 052.71	Z	2
Temperature / K	291(2)	Absorption coefficient / mm^{-1}	1.080
Crystal system	Triclinic	$F(000)$	1 068
Space group	$P1$	Crystal size / mm	0.14×0.18×0.20
a / nm	0.820 3(2)	θ range for data collection / $^\circ$	1.04~26.00
b / nm	1.322 7(3)	Limiting indices	$-9 \leq h \leq 10, -16 \leq k \leq 16, -25 \leq l \leq 25$
c / nm	2.061 0(3)	Reflections collected / unique (R_{int})	20 027 / 15 389 (0.032)
$\alpha / ^\circ$	76.155(2)	Data / restraints / parameters	15 389 / 3 / 1 111
$\beta / ^\circ$	78.651(4)	Goodness of fit on F^2	1.03
$\gamma / ^\circ$	89.993(3)	final R indices [$I > 2\sigma(I)$]	$R_1=0.052\ 4, wR_2=0.113\ 6$
V / nm^3	2.126 2(8)	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	514 and $-1\ 039$

2 Results and discussion

2.1 Crystal structure of the title complex

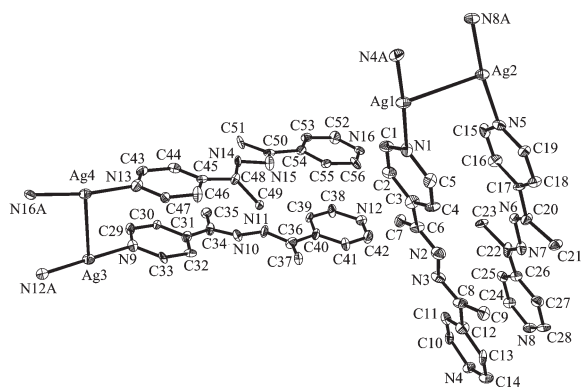
The selected bond lengths and bond angle are given in Table 2, and the molecular structure of the title complex is shown in Fig.1.

The complex **1** consists of infinite 1D cationic Ag–L chains. A perspective view of the coordination unit with the atom-labeling scheme is given in Fig.1, the *p*-methylbenzene sulfonic acid in compound **1** does not show any bonding actions with silver cations; it only

Table 2 Selected bond lengths (nm) and bond angle ($^{\circ}$)

Ag(1)-N(1)	0.217 2(6)	Ag(3)-N(12)#2	0.216 5(7)	Ag(1)-Ag(2)	0.327 9(10)
Ag(1)-N(4)#1	0.219 2(6)	Ag(3)-N(9)	0.218 3(6)	Ag(3)-Ag(4)	0.328 1(9)
Ag(2)-N(8)#1	0.218 3(6)	Ag(4)-N(13)	0.213 9(7)		
Ag(2)-N(5)	0.222 1(6)	Ag(4)-N(16)#2	0.219 6(6)		
N(1)-Ag(1)-N(4)#1	175.2(3)	N(8)#1-Ag(2)-Ag(1)	83.65(18)	N(9)-Ag(3)-Ag(4)	99.91(19)
N(1)-Ag(1)-Ag(2)	83.29(17)	N(5)-Ag(2)-Ag(1)	104.44(16)	N(13)-Ag(4)-N(16)#2	171.8(3)
N(4)#1-Ag(1)-Ag(2)	101.20(18)	N(12)#2-Ag(3)-N(9)	178.2(3)	N(13)-Ag(4)-Ag(3)	84.0(2)
N(8)#1-Ag(2)-N(5)	171.9(2)	N(12)#2-Ag(3)-Ag(4)	81.7(2)	N(16)#2-Ag(4)-Ag(3)	103.53(16)

#1: $x+1, y-1, z$; #2: $x-1, y-1, z$.



All water molecules and *p*-methylbenzenesulfate ions are omitted for clarity

Fig.1 Structure of the title complex with displacement ellipsoids (30% probability)

acts as a counteranion. There are four crystallographically unique silver ions with similar environments in the compound. For example, Ag(1) is coordinated by two pyridyl nitrogen atoms from two different L ligands with Ag(1)-N(1) and Ag(1)-N(4)#1 distances being 0.217 2(6) and 0.219 2(6) nm. These silver cations are bridged by L ligands to form a 1D infinite polymeric chain structure. Ag(2) is also coordinated by two nitrogen atoms from different L ligands with both Ag(2)-N(5) and Ag(2)-N(8)#1 distances being 0.218 3(6), 0.222 1(6) nm, respectively. The other two silver atoms are similar to the Ag(1) and Ag(2), which are all in linear coordinated configuration. Moreover, the Ag(1)-Ag(2), Ag(3)-Ag(4) distance of 0.327 9(10) and 0.328 1(9) nm are shorter than the van der Waals contact distance for Ag-Ag of 0.340 nm; therefore, a Ag-Ag bond exists between two silver cations. Two chains of Ag(1) and Ag(2) cations and L ligands are connected by a Ag-Ag interaction to form 1D ladder

structure as shown in Fig.2, which is different from the alternate Ag chains in the previous reports^[13].

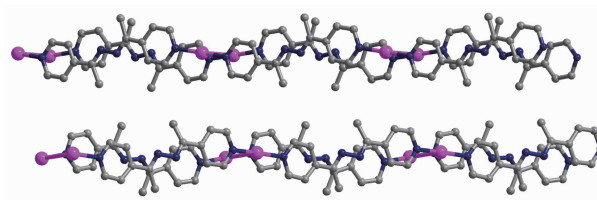
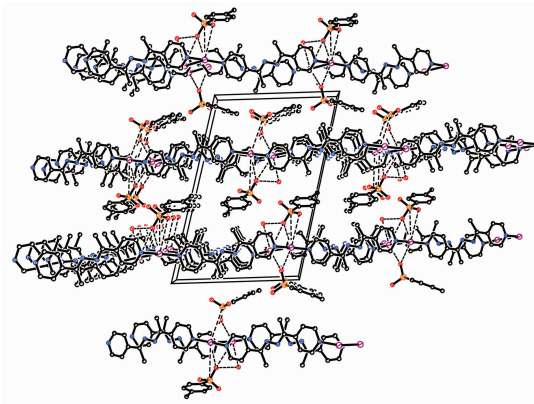


Fig.2 One-dimensional ladder structure of the title complex by Ag-Ag weak interaction

An interesting feature of this structure is that the 1D ladder was formed to 2D structure by the weak π - π interaction with the distance of 0.368 2 (6)~0.379 8(6) nm and weak O-Ag interaction from the *p*-methylbenzenesulfonate oxygen atoms with the distance of 0.279 0(6)~0.286 6(4) nm. Furthermore, the polymeric double ladders are bridged through the hydrogen-bonding interactions between the water molecules and the sulfonate oxygen atoms to form an overall three-dimensional supramolecular structure, as shown in Fig.3. There are other C-H \cdots N and C-H \cdots O hydrogen bonds within the 3D network, which further consolidate the



Hydrogen bonds are shown as dotted lines

Fig.3 Packing of structure 1 viewed along the *a*-axis

structure.

2.2 Spectra characteristics

The IR spectrum of the complex exhibits a medium broad band centered at *ca.* $3\,413\text{ cm}^{-1}$, due to the $\nu(\text{O-H})$ absorptions of water molecules. The strong absorption at $1\,612\text{ cm}^{-1}$ is attributable to the $\nu(\text{C=N})$ vibration of the ligand, and the very strong absorptions at $1\,306$ and $1\,244\text{ cm}^{-1}$ indicate the presence of the *p*-methylbenzenesulfonate ion. These IR results are coincident with the crystallographic structural analyses.

Inorganic-organic hybrid coordination compounds, especially with d^{10} metal centers, have been investigated for fluorescence properties owing to their potential applications as luminescent materials, such as light-emitting diodes (LEDs)^[15]. Therefore, the photoluminescence property of **1** was investigated in the solid state at room temperature. As shown in Fig.4, intense emission bands were observed at 439.9 nm for **1**, (Ligand= 380 nm) respectively. These emissions can be attributed to metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT).

It is known that only the non-centrosymmetric structure may have the second-order non-linear optical

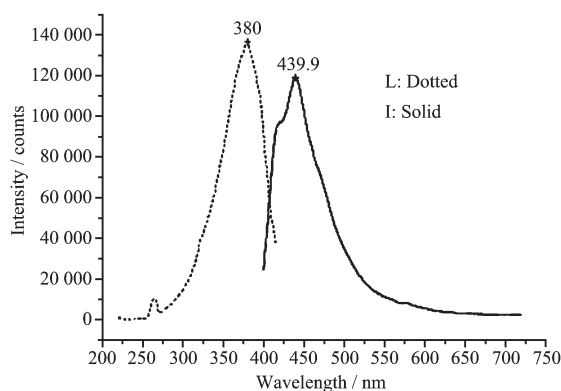


Fig.4 Fluorescence spectra of the ligand and the title complex

effect. Approximate estimations were carried out on a pulsed Q-switched Nd:YAG laser at a wavelength of $1\,064\text{ nm}$. Comparison of the results was obtained from a powdered sample ($80\sim150\text{ }\mu\text{m}$ diameter) in the form of a pellet (Kurtz powder test) with those obtained for urea^[16]. The preliminary experimental results revealed that complex **1** exhibits modest powder SHG intensity with a response 0.4 times that for urea, which means that this complex can be used as a potential optical material.

Table 3 Parameters of hydrogen bonds for the complex

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H-A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H-A} / (^\circ)$
O(13)-H(13A)...O(4) ^a	0.085	0.195	0.259 4(8)	132.0
O(13)-H(13B)...O(1) ^b	0.085	0.257	0.306 9(8)	118.0
O(14)-H(14A)...O(5) ^c	0.085	0.221	0.294 7(8)	144.0
O(14)-H(14B)...O(2) ^c	0.085	0.236	0.271 0(8)	105.0

^a $x, 1+y, z$; ^b $-1+x, 1+y, z$; ^c $-1+x, y, z$.

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