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研究简报

一维链状化合物[Ag(L)]·H_2O 的合成、晶体结构和荧光性质

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Synthesis, Crystal Structure and Luminescence of a One-Dimensional Chain-Like Complex [Ag(L)]·H_2O

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Abstract: The title compound, [Ag(L)]·H_2O, **1**, where HL=4-(isonicotinamido)benzoic acid, was synthesized in methanol solution and its crystal structure was determined by X-ray diffraction analysis. The crystal is of monoclinic, space group $P2_1/c$ with a=0.571 8(8) nm, b=1.357 2(18) nm, c=1.558 0(2) nm, β=91.090(2)°, V=1.209 0(3) nm^3, Z=4, D_c=2.009 g·cm^{-3}, F(000)=722, R_{int}=0.042 9, R=0.027 1, wR=0.055 6. In complex **1**, the Ag atoms are linearly coordinated by one O atom and one N atom of two ligand molecules. Each L^- ligand in turn uses its one carboxylate group and one pyridinyl groups to connect two metal centers, then the one-dimensional (1D) chains is formed. On the other hand, the 1D chains are further connected by O1W–H1WB···O2 hydrogen bonds and Ag-O weak interactions to give a two-dimensional (2D) layer, finally, the 2D net extents to three-dimensional (3D) supramolecular framework by O1W–H1WB···O1 as well as N2–H2···O2 interactions. CCDC: 762259.

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

In recent years, the rational design and synthesis of new extended supramolecular frameworks by covalent and weak intra/intermolecular interactions have brought forth architectures with intriguing structure motifs[1-5]. During the past few years, many one-, two-, and three-dimensional coordination polymers have been generated from transition metal templates with rigid and flexible pyridyl-containing bidentate or multidentate organic spacers[6-9]. However, the control of formation of supramolecular complexes is a fascinating challenge for chemists. Our strategy in this approach is using a new multifunctional organic ligand 4-(isonicotinamido) benzoic acid (HL), which was prepared according to the procedure reported by Puddephatt[10], containing different types of binding sites arranged in an unsymmetrical fashion. In this paper, we report herein the synthesis

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and X-ray crystal structure of the novel silver complex, [Ag(L)]·H_2O **1**, which is an infinite 1D chains extended to a 3D supramolecular structures by hydrogen bonds and Ag-O weak interactions.

1 Experimental

1.1 Materials and instruments

All the regents 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. The luminescent spectra for the solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with xenon arc lamp as the light source.

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 HL ligand (0.20 mmol) in the same solvent. Then ammonia was added, the precipitate were dissolved and stirred for another 4 hours. The resulting clear solution was allowed to evaporate slowly at room temperature for three weeks, affording block colorless crystals. The product was collected by filtration, washed with methanol and ether successively, and then dried in air, Yields based on Ag: 38%. Molecular formula is $C_{13}H_{11}AgN_2O_4$. Elemental analysis (%): C, 42.53; H, 3.02; N, 7.63. Found (%): C, 42.57; H, 3.10; N, 7.58. Main IR bands (cm^{-1}): 3 423s, 1 638s, 1 604s, 1 413ms, 1 306ms, 1 244s, 1 087s, 846ms, 725m, 624w.

1.3 X-ray crystallography

A block crystal with dimensions of 0.20 mm×0.18 mm×0.12 mm was selected for the measurement. The diffraction data were collected at 293 (2) K on a Bruker Smart Apex Ⅱ CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ= 0.071 073 nm). A total of 6120 reflections were collected in the range of $1.99° \leqslant \theta \leqslant 25.49°$ by using an ω-scan mode, of which 2 227 were unique with R_{int}=0.042 9, 1 831 were consi-dered to be observed ($I>2\sigma(I)$) and used in the structu-ral analysis and refinement. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL[11]. 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.

CCDC: 762259.

Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$C_{13}H_{11}AgN_2O_4$	Z	4
Formula weight	367.11	Absorption coefficient / mm^{-1}	1.682
Temperature / K	293(2)	F(000)	722
Crystal system	Monoclinic	Crystal size / mm	0.12×0.18×0.20
Space group	$P2_1/c$	θ / (°)	1.99~25.49
a / nm	0.571 8(8)	Limiting indices	$-6 \leqslant h \leqslant 5$, $-16 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$
b / nm	1.357 2(18)	Reflections collected / unique (R_{int})	6 120 / 2 227 (0.042 9)
c / nm	1.558 0(2)	Data / restraints / parameters	2 227 / 0 / 181
β / (°)	91.090(2)	Goodness of fit on F^2	1.009
V / nm^3	1.209 0(3)	final R indices [$I>2\sigma(I)$]	R_1=0.027 1, wR_2=0.055 6
D_c / ($g \cdot cm^{-3}$)	2.009	Largest diff. peak and hole / ($e \cdot nm^{-3}$)	391 and −431

2 Results and discussion

2.1 Crystal structure of the title complex

The single-crystal X-ray diffraction analysis reveals that complex **1** consists of an infinite 1D Ag-L chains. A perspective view of the coordination unit with the atom-labeling scheme is given in Fig.1, the asymmetric unit of **1** contains one Ag(I), one L^- ligand and one free water molecule. As shown in Fig.1, the Ag1 with linear coordination geometry is two-coordinated by one carboxylate oxygen (O1A) atom and one N(N1) atom from two different L^- ligands with Ag1-

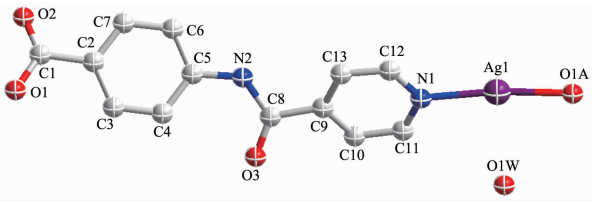
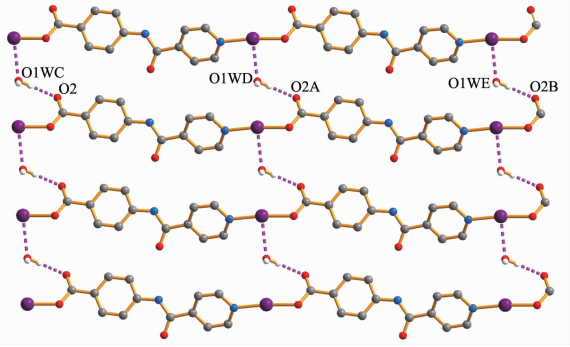


Fig.1　Ortep view of the complex with displacement ellipsoids (30% probability)

O1A=0.212 7(18) nm, Ag1-N1=0.214 3(2) nm and the bond angles O1A-Ag1-N1=173.68(8)°, respectively. Then the silver ions are bridged by L^- ligands to form a 1D infinite polymeric chain structure, alternately.

An interesting feature of this structure is that the 1D chain extended by the Ag1-O1W weak interaction (Ag1-O1W=0.277 8(3) nm) and O1W–H1WB···O2 hydrogen bond interaction to form a 2D layer structure as illustrated in Fig.2, which is different from the alternate Ag chains, 2D layer and 3D Ag complexes in the previous reports[12-16]. Furthermore, the 2D layers of **1** pack together through O1W–H1WB···O1 as well as N2–H2···O2 hydrogen bonding interactions (Table 2) to generate 3D frameworks. These hydrogen bonds interactions thus appear to stabilize the asymmetry molecular disposition around the Ag centers.



Code A: *x*, *y*, 1+*z*; B: *x*, *y*, 2+*z*; C: 1−*x*, 1−*y*, 1−*z*; D: 1−*x*, 1−*y*, 2−*z*; E: 1−*x*, 1−*y*, 3−*z*

Fig.2　Two-dimensional layer structure of the title complex by Ag1-O1W weak interaction and O(1W)–H(1WB)···O(2) hydrogen bond

Table 2　Parameters of hydrogen bonds for the complex

D···H···A	*d*(D-H) / nm	*d*(H-O) / nm	*d*(D-O) / nm	∠D-H-A / (°)
O(1W)···H(1WA)···O(1)	0.085	0.197	0.282 1(3)	174.0
O(1W)···H(1WB)···O(2)[a]	0.085	0.199	0.283 9(3)	174.0
N(2)···H(2)···O(2)[b]	0.086	0.248	0.310 1(3)	130.0

[a] 1−*x*, 1−*y*, 1−*z*; [b] *x*, 1/2−*y*, 1/2+*z*.

2.2　Spectra characteristics

The IR spectrum of the complex exhibits a medium broad band centered at *ca.* 3 423 cm^{-1}, due to the ν(O-H) absorptions of water molecules. One feature of the IR data is the separation between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, which have often been used to diagnose the coordination modes in the carboxylate ligands. The separation for monodentate carboxylate groups is >200 cm^{-1}, whereas it is <200 cm^{-1} in bidentate groups[17]. The separation (Δ) between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is 225 cm^{-1} for **1**, indicating monodentate coordinating modes for the coordinated carboxylate groups, these IR results are coincident with the crystallographic structural analyses.

In general, 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)[18-19]. Therefore, the photoluminescence properties of **1** and NaL were investigated in the solid state at room temperature. As shown in Fig.3, intense emission bands were observed at 409 nm (λ_{ex}=380 nm) for NaL ligand, 411 nm (λ_{ex}=380 nm) for **1**, respectively. These emissions can be attributed to neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT)

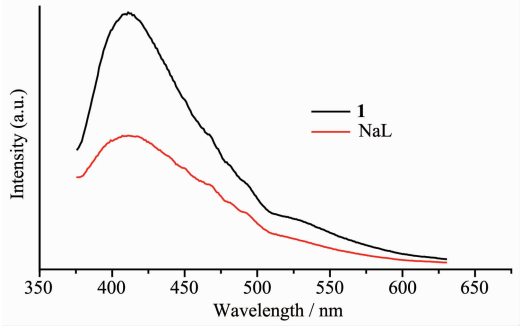


Fig.3　Flourscence spectra of the NaL and the title complex

because the Ag(I) ions are in d^{10} configuration and difficult to oxidize or to reduce. Therefore the emission observed in **1** is attributed to the π-π* intraligand photoluminescence due to its resemblance to that of NaL ligand, and the enhancement and slight red-shift of **1** compared to that of the NaL ligand probably result from the fact that the coordination of Ag(I) ions increases the ligand conformational rigidity and thus reduces the loss of energy by thermal vibrational decay[20-21].

References:

[1] Cheng D P, Khan M A, Houser R P. *J. Chem. Soc. Dalton Trans.*, **2002**:4555-4560

[2] Zhang L Y, Liu G F, Zheng S L, et al. *Eur. J. Inorg. Chem.*, **2003**:2965-2971

[3] Go Y B, Wang X Q, Anokhina E V, et al. *Inorg. Chem.*, **2004**, **43**:5360-5367

[4] Awaleh M O, Badia A, Brisse F. *Cryst. Growth Des.*, **2005**,**5**: 1897-1906

[5] Hong C S, Yoon J H, Lim J H, et al. *Eur. J. Inorg. Chem.*, **2005**:4818-4821

[6] Dong Y B, Smith M D, Layland R C, et al. *Chem. Mater.*, **2000**,**12**:1156-1161

[7] Dong Y B, Smith M D, zur Loye H C. *Inorg. Chem.*, **2000**,**39**: 4927-4935

[8] Dong Y B, Zhao X, Huang R Q. *Inorg. Chem.*, **2004**,**43**:5603-5612

[9] Ciurtin D M, Dong Y B, Smith M D, et al. *Inorg. Chem.*, **2001**, **40**:2825-2834

[10]Burchell T J, Eisler D J, Puddephatt R J. *Inorg. Chem.*, **2004**, **43**:5550-5557

[11]Sheldrick G M. *SHELXTL, Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

[12]CHEN Man-Sheng(陈满生), HE Chun-Mei(何春梅), DENG Yi-Fang(邓奕芳), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2009**,**25**:1312-1315

[13]YAN Ze-Qun(严泽群). *Chinese J. Struct. Chem.* (*Jiegou Xuebao*), **2005**,**24**:315-318

[14]TIAN Ge(田 戈), YUAN Hong-Ming(袁宏明), CHEN Yan(陈 岩), et al. *Chem. J. Chinese Universities* (*Gaodeng Xuexiao Huaxue Xuebao*), **2006**,**27**:2405-2407

[15]Liu B, Yuan Q. *Inorg. Chem. Commun.*, **2005**,**8**:1022-1024

[16]Liu Z, Liu P, Chen Y, et al. *New J. Chem.*, **2005**,**29**:474-478

[17]Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. New York: John Wiley & Sons, **1986**.

[18]Vogler A, Kunkely H. *Coord. Chem. Rev.*, **2006**,**250**:1622-1626

[19]Wen L L, Li Y Z, Lu Z D, et al. *Cryst. Growth Des.*, **2006**,**6**: 530-537

[20]Bunz U H F. *Chem. Rev.*, **2000**,**100**:1605-1644

[21]Yang W Y, Schmider H, Wu Q G, et al. *Inorg. Chem.*, **2000**, **39**:2397-2404