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一维链状银(I)配位聚合物的合成、表征及晶体测定

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摘要:采用水热法合成了 1 个配位聚合物[Ag_2(L)(LH)]NO_3·1.5H_2O(**1**,LH=2-(4-methoxyphenyl)-1*H*-imidazo[4,5-f][1,10]phenanthroline),并对其进行了元素分析、红外光谱、热重表征和 X 射线单晶衍射测定。配位聚合物 **1** 属于单斜晶系,空间群为 *C*2/*c*,晶胞参数为:*a*=2.733 8(6),*b*=1.580 7(3),*c*=1.736 0(4) nm,*β*=107.73(3)°,*V*=7.146(2) nm^3,*Z*=4,293(2) K。在晶体中,2 个 Ag(I)原子与来自于不同 LH 和 L 配体上的 3 个氮原子分别形成三配位的畸变的三角形构型。

关键词:晶体结构;Ag(I)配位聚合物;一维链
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Synthesis, Characterization and Crystal Structure of One-dimensional Chainlike Ag(I) Coordination Polymer

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Abstract: One coordination polymer [Ag_2(L)(LH)]NO_3·1.5H_2O (**1**, LH=2-(4-methoxyphenyl)-1*H*-imidazo[4,5-f][1,10]phenanthroline) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG and single-crystal X-ray diffraction. Complex **1** crystallizes in the monoclinic system, space group *C*2/*c*, with *a*=2.733 8(6), *b*=1.580 7(3), *c*=1.736 0(4) nm, *β*=107.73(3)°, *V*=7.146(2) nm^3, *Z*=4, 293(2) K. In the crystal structure, two Ag(I) ions are three match coordination with three nitrogen atoms from different LH and L ligands, assuming a slightly distorted triangle, respectively. CCDC: 826593.

Key words: crystal structure; Ag(I) coordination polymer; 1D chain

Coordination polymers have attracted increasing interest over the past decade, not only because of their intriguing structural diversity but also because of their tremendous potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics and molecular sensing. The most efficient approach to preparing coordination polymers is via direct chemical combination of functional inorganic and organic components.

Meanwhile, the hydrothermal reaction is often accompanied by many interesting processes such as metal redox, ligand oxidative coupling, hydrolysis, decarboxylation and substitution[1-4]. These reactions provide promising routes and valuable information for the design and synthesis of novel functional building blocks and complexes. Up to date, 1,10-phenanthroline (phen) and its derivatives, as one type of common organic ligand, have been widely used in the construction of coordination polymer[5-9]. 2-(4-Methoxyphenyl)-1*H*-imidazo[4,5-f][1,10]phenanthroline (LH) as a derivative

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of 1,10-phenanthroline and possessing an extended aromatic system, is a planar rigid bidentate chelating reagent which can not only act as a terminal ligand but also potentially provide supramolecular interactions such as aromatic stacking to construct intriguing structures. In the previous paper, we have reported the synthesis of 1,10-phenanthroline and its derivatives[10-14]. However, the investigation for LH ligands is not enough, especially LH ligand and silver(I) constructed polymers have not been reported and they all coordinate with metal by two close adjacent bridging nitrogen atoms. Based on the above reasons, we design and synthesize the complex **1**, namely $[Ag_2(L)(LH)]NO_3 \cdot 1.5H_2O$. In the complex **1** the metal atoms are not only coordinate with two close adjacent bridging nitrogen atoms but also coordinate with nitrogen atoms from pyrazine ring.

1 Experimental

1.1 Materials

The LH ligand was synthesized according to the literature method [12]. Other chemicals from commercial sources were of reagent grade and used without further purification.

1.2 Instruments and measurements

Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; thermogravimetric analysis were performed on a NETZSCH STA 449C analyzer. The Infrared (IR) spectrum was recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a Nicolet FTIR 170SX spectrometer.

1.3 Synthesis and measurement

Complex **1** was prepared from a mixture of $AgNO_3$ (0.10 g, Alfa, 99.5%), LH ligand (0.16 g, 97%), NaOH (Alfa, 99.5%) and H_2O (15 mL) while stirring at room temperature. When the pH value of the mixture was adjusted to about 8.5 with NaOH, the cloudy solution was put into in a 30 mL Teflon-lined autoclave under autogenous pressure at 180 ℃ for six days. After cooling to room temperature at a rate of 5 ℃·h^{-1}, light-yellow block crystals of **1** were collected by filtration and washed with distilled water in 52% yield (based on Ag). Anal. calcd. for $C_{80}H_{60}Ag_4N_{18}O_{13}$(%): C, 52.57; H, 2.75; N, 12.84. Found(%): C, 52.55; H, 2.78; N, 12.79. IR (KBr, cm^{-1}): 1 611.04s, 1 571.82s, 1 1482.53m, 1 452.37 m, 1 438.91m, 1 383.75w, 1 306.90s, 1 249.75m, 1 180.78 m, 1 074.20s, 1 027.09s, 841.01s, 757.36, 732.92s.

1.4 Crystal structure determination and physical measurements

A single crystal with dimension of 0.27 mm×0.24 mm×0.20 mm was mounted on a Rigaku Saturn 724+ CCD X-ray diffractometer with a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm). Cell parameters were refined on all observed reflections by using the program CrystalClear (Rigaku and MSc, Ver. 1.3.5, 2002). The collected data were reduced by the program CrystalClear and an absorption correction (multiscan) was applied. The reflection data for complex **1** was also corrected for Lorentz and polarization effects. The structure was solved by direct methods with SHELXS-97 program[15] and refined by SHELXL97[16] using full-matrix least-squares technique on F^2. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically (C-H 0.093 nm for CH or 0.096 nm for CH_3) and refined as a riding mode, with $U_{iso}(H)=1.2U_{eq}(C)$. All the hydrogen atoms were placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Further crystallographic data and experimental details for structural analyses of the coordination polymer are summarized in Table 1.

CCDC: 826593.

Table 1 Crystallographic data for complex 1

Complex	**1**	Z	4
Empirical formula	$C_{80}H_{60}Ag_4N_{18}O_{13}$	D_c / (g·cm^{-3})	1.769
Crystal system	Monoclinic	Goodness-of-fit on F^2	1.093
Space group	$C2/c$	R, wR ($I>2\sigma(I)$)	0.050 2, 0.114 9
Crystal size / mm	0.25×0.22×0.18	F(000)	3832

Continued Table 1

a / nm	2.733 8(6)	Rflections collected / unique	16 479 / 6 462
b / nm	1.580 7(3)	R_{int}	0.0353
c / nm	1.736 0(4)	θ range / (°)	2.68 to 25.35
β / (°)	107.73(3)	R_1 and wR_2 indices (all data)	0.064 8, 0.124 6
V / nm^3	7.146(2)	Largest diff. peak and hole / (e·nm^{-3})	748, −536

2 Results and discussion

2.1 Description of crystal structures

Single-crystal X-ray diffraction analysis reveals that complex $[Ag_2(L)(LH)]NO_3\cdot 1.5H_2O$ crystallizes in *C*2/*c* space group and consists of a one-dimensional infinite chains structure. There are two Ag(I) ions, one LH ligand, one L ligand, one and a half of free water molecules and one free of nitrate ion in the local coordination environment. The statistical distribution, nitrate ions and water molecules do not exist at the same time, in the complex **1**, the nitrate ions and water molecules (O(1W) and O(2W)) are disordered with refined occupancies and further fixed at 0.5, respectively (Fig.1). Two Ag(I) atoms are bridged by two nitrogen atoms from pyrazine ring. The Ag(1) ion is three match coordination with N(1), N(2) from LH ligand and N(8) from L ligand, the Ag(2) ion is three match coordination with N(5), N(6), N(7) from two different L ligands, assuming a slightly distorted triangle, respectively. The Ag-N bond distances are Ag(1)-N 0.214 6(3)~0.235 9(4) nm and Ag(2)-N 0.213 1(3)~0.233 8(4) nm, respectively, comparable to those of 0.226 3(3)~0.233 0(4) nm for Ag-N in the complex of $[Ag(DICNQ)_2]NO_3$ (DICNQ=6,7-dicyanodipyridoquinoxaline)[17]. The normal Ag-N distance is 0.225 7(2) nm, this distance is similar to the normal Ag-N 0.220 9 nm[18]. The N-Ag-N angles range from 71.75(14)° to 148.62(14)°. The selected important bond parameters are given in Table 2. The interesting feature of complex **1** is that each pyrazine ring links one LH ligand and one L ligand, through N(7) from the L ligand, complex **1** show an infinite one-dimensional chain structure (Fig.2).

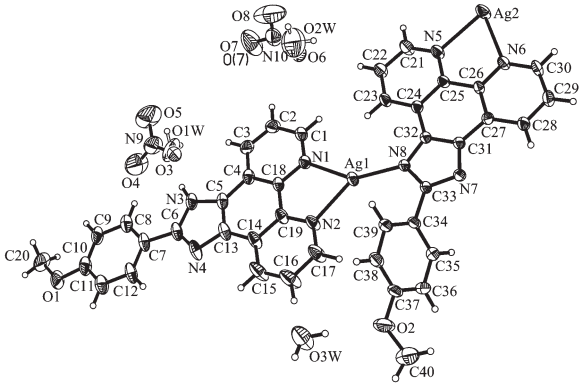

Fig.1 ORTEP drawing of **1** showing the local coordination environment of Ag(I) with thermal ellipsoids at 30% probability

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architectures[19]. There are persistent strong O–H···O hydrogen bonding interactions between crystal molecules, free water molecule and free nitrate ion, the hydrogen bonds of the complex **1** are shown in Table 3. The shortest intersheet Ag···Ag distance is 0.617 9 nm, which play an important role in stabilizing the network structure and controlling the orientation of ligands. At the same time, There are π-π interactions in coordination complex **1**, aromatic ring of the ligands and symmetry of the two adjacent equivalent of aromatic ring have π-π interactions with the centroid distance between 0.354 2(3) and 0.384 1(4) nm (Table 4). Through these noncovalent bonds, coordination complex **1** is extended

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

Ag(1)-N(1)	0.235 9(4)	Ag(1)-N(2)	0.228 2(4)	Ag(1)-N(8)	0.214 6(3)
Ag(2)-N(5)	0.233 8(4)	Ag(2)-N(6)	0.228 5(4)	Ag(2)-N(7)	0.213 1(3)
N(2)-Ag(1)-N(1)	71.75(14)	N(8)-Ag(1)-N(1)	147.00(13)	N(8)-Ag(1)-N(2)	141.25(13)
N(6)-Ag(2)-N(5)	72.52(13)	N(7)-Ag(2)-N(5)	148.62(14)	N(7)-Ag(2)-N(6)	138.81(13)

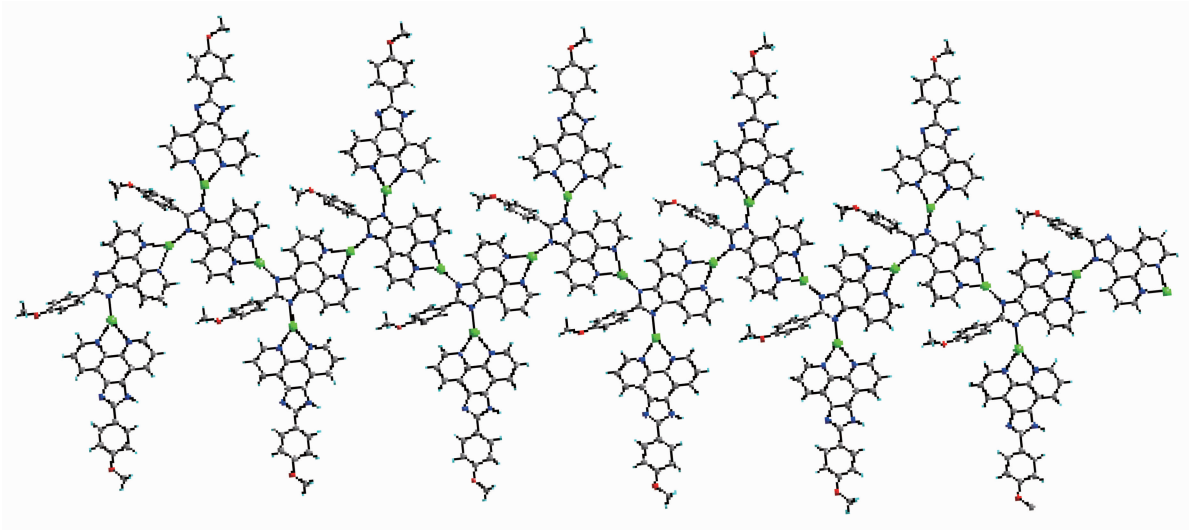

Fig.2 View of one-dimensional chain structure of **1**

Table 3 Hydrogen bond lengths and bond angles for complex 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
N(3)–H(3A)···O(1W)	0.094(5)	0.210(5)	0.303(3)	167(5)
N(3)–H(3A)···O(3)	0.094(5)	0.187(5)	0.279 6(15)	165(5)
O(3W)–H(3C)···O(2)	0.085	0.214	2.970(11)	165
O(3W)–H(3D)···O(7) i	0.085	0.195	2.693(16)	146

Symmetry codes: i : *x*, 1+*y*, *z*.

Table 4 Relative parameters of intermolecular *π*-*π* interactions in complex 1

Cg(I) Cg(J)	Dist. centroids / nm	CgI_Perp / nm	CgJ_Perp / nm
Cg(3) → Cg(8) iii	0.372 0(3)	0.346 6(2)	0.333 55(18)
Cg(3) → Cg(11) iii	0.372 4(3)	0.344 8(2)	0.341 32(18)
Cg(4) → Cg(5) iii	0.371 2(3)	0.337 13(19)	0.340 1(2)
Cg(4) → Cg(10) ii	0.359 1(3)	0.337 64(18)	0.342 1(2)
Cg(5) → Cg(5) ii	0.356 2(3)	0.351 4(2)	0.351 4(2)
Cg(6) → Cg(6) ii	0.384 1(4)	0.382 1(2)	0.382 1(2)
Cg(6) → Cg(7) iii	0.375 7(3)	0.352 0(2)	0.352 7(2)
Cg(7) → Cg(9) iii	0.369 2(3)	0.351 9(2)	0.344 0(2)
Cg(9) → Cg(11) iii	0.370 6(3)	0.345 6(2)	0.341 9(18)
Cg(10) → Cg(11) ii	0.354 2(3)	0.342 2(2)	0.340 48(18)

Defined rings and symbol explanations Cg(3): N(3) → C(5) → C(13) → N(4) → C(6); Cg(4): N(7) → C(31) → C(32) → N(8) → C(33); Cg(5): N(1) → C(1) → C(2) → C(3) → C(4) → C(18); Cg(6): N(2) → C(17) → C(16) → C(15) → C(14) → C(19); Cg(7): N(5) → C(21) → C(22) → C(23) → C(24) →C(25); Cg(8): N(6) → C(26) → C(27) → C(28) → C(29) → C(30); Cg(9): C(4) → C(5) → C(13) → C(14) → C(19) → C(18); Cg(10): C(7) → C(8) → C(9) → C(10) → C(11) → C(12); Cg(11): C(24) → C(25) → C(26) → C(27) → C(31) → C(32); Cg(I)= plane number I (= ring number in () above); Dist. centroids=Distance between ring centroids (nm); CgI_Perp=perpendicular distance of Cg(I) on ring J (nm); CgJ_Perp=perpendicular distance of Cg(J) on ring I (nm); Symmetry codes: ii : 1–*x*, *y*, 3/2–*z*; iii: 1–*x*, 1–*y*, 1–*z*.

into a three-dimensional supramolecular framework.

2.2 Thermal analysis

The stability of the complex **1** was investigated by thermogravimetric analysis (Fig.3). The first weight loss of 8.74 % for **1** is in the range from 24.2 to 143.3 ℃ corresponding to the removal of H_2O and nitrate ion (calcd. 9.30%). Upon further heating, an obvious weight loss (68.26%) occurs in the temperature range of 127.6 ~772.9 ℃, corresponding to the release of ligands (calcd. 66.45%). After 772.9 ℃ no weight loss is observed, indicating the complete decomposition of **1**. The residual weight 23.01% (calcd. 24.25%) corresponds to Ag_2O.

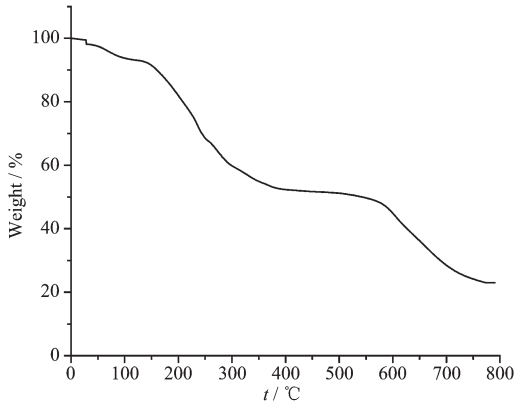

Fig.3　TG of the complex **1**

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