

A Silver(I) Coordination Polymer Based on a Schiff Base Ligand: Synthesis, Crystal Structure and Luminescence Properties

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A new Ag(I) coordination polymer $[\text{AgL}(\text{NO}_3)]_n$ **1** ($\text{L} = 4\text{-(pyridine-2-yl)methyleneamino-1,2,4-triazole}$) has been synthesized and characterized by IR spectroscopy, elemental analysis, powder and single-crystal X-ray diffraction. The Ag(I) atom has a seesaw environment with an N_3O donor set from three N atoms of two ligands and one O atom of one NO_3^- anion. Each twisted tridentate ligand is bound to two silver centers, and each silver atom is coordinated by two ligands thereby generating a zigzag chain structure. The chains interact with each other featuring a three-dimensional supramolecular network through multiple weak $\text{C-H}\cdots\pi$ interactions and $\text{C-H}\cdots\text{O}$ hydrogen bonds. The luminescence properties of the polymer **1** were investigated in the solid state at room temperature.

Key words: Silver(I), Coordination Polymer, Schiff Base, Luminescence

Introduction

Coordination polymers have attracted much attention due to their multiformity in structure *via* different combinations of various ligands and metal ions, and their potentially useful applications in luminescence, magnetism, catalysis, molecular adsorption and sensing [1–4]. The five-membered N-containing heterocyclic ring of 1,2,4-triazole is regarded as one kind of outstanding coordination groups, and the derived substituted 1,2,4-triazoles as polydentate ligands are intriguing linkers for the generation of structurally versatile metal-organic frameworks [5–11]. In this paper, the chosen ligand **L**, 4-(pyridine-2-yl)methyleneamino-1,2,4-triazole, is an easy-to-prepare Schiff base formed from 4-amino-1,2,4-triazole and 2-pyridinecarboxaldehyde. Different from the reported ligands which were synthesized from 4-amino-1,2,4-triazole and salicylaldehyde or substituted benzaldehyde, the Schiff base ligand **L** affords four potential coordination sites including two $\text{N}_{\text{triazolyl}}$, one N_{imine} and one $\text{N}_{\text{pyridyl}}$ donors. Therefore, the ligand **L** is particularly attractive for making coordination polymer structures, such as the 2D coordination polymers $[\text{Cd}_3\text{L}_2(\text{SCN})_6]_n$ and $[\text{CdLi}_2]_n$ [12].

As a part of our continuing investigations on coordination complexes and their photoluminescence properties [13–16], herein we report the synthesis and crystal structure of a new one-dimensional silver coordination polymer $[\text{AgL}(\text{NO}_3)]_n$ (**1**) displaying fluorescence at room temperature.

Experimental Section

General

Materials: With the exception of the ligand **L** which was prepared according to the previously reported procedure [12], all reagents and solvents for the synthesis were commercially available and used as received.

Instrumentation: Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the $4000\text{--}400\text{ cm}^{-1}$ region. Powder X-ray diffraction patterns were recorded on a D/max- γ A rotating anode X-ray diffractometer with a sealed Cu tube ($\lambda = 1.54178\text{ \AA}$). The luminescence spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer.

Synthesis

6 mL of an ethanol solution of **L** (36 mg, 0.20 mmol) was slowly layered onto 6 mL of an aqueous solution of AgNO_3

(68 mg, 0.40 mmol). The excess of silver salts used here is to improve the yield based on the ligand. The solution was left for several days at room temperature to obtain colorless block-shaped crystals suitable for single-crystal X-ray diffraction. The bulk samples were further purified by recrystallization. The total yield was 53% (36 mg) based on ligand L. – Anal. for $C_8H_7AgN_6O_3$: calcd. C 28.01, H 2.06, N 24.50; found C 28.09, H 2.13, N 24.45. – IR (cm^{-1} , KBr pellet): $\nu = 3115(w)$, $3083(m)$, $3024(w)$, $1587(s)$, $1566(w)$, $1522(s)$, $1484(m)$, $1436(m)$, $1352(vs)$, $1300(s)$, $1183(s)$, $1100(w)$, $1056(s)$, $898(m)$, $825(w)$, $797(m)$, $765(w)$, $638(w)$, $622(s)$, $524(w)$, $414(w)$.

Crystal structure determination

A suitable single crystal of size $0.11 \times 0.08 \times 0.07 \text{ mm}^3$ was mounted on a Bruker Smart APEX II CCD diffractometer, and diffraction intensities were measured in the ω - ϕ scan mode in the range of $2.45 < \theta < 25.05^\circ$. The measurement was performed at room temperature using graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by Direct Methods and refined on F^2 by using full-matrix least-squares methods with the programs SHELXS/L-97 [17, 18]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques, and all hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. Space group, lattice parameters and other relevant information are listed

Table 1. Summary of crystal data and refinement results for **1**.

Chemical formula	$C_8H_7AgN_6O_3$
Formula weight	343.07
Temperature, K	293(2)
Crystal system	monoclinic
Space group	<i>Cc</i>
Unit cell dimensions	
<i>a</i> , Å	9.5151(17)
<i>b</i> , Å	16.613(3)
<i>c</i> , Å	7.1278(13)
β , deg	104.665(4)
Volume, Å ³	1090.0(3)
<i>Z</i>	4
D_{calcd} , g cm ⁻³	2.09
$F(000)$, e	672
μ , mm ⁻¹	1.9
θ range data collection, deg	2.45–25.05
Index ranges	–9/11, ± 19 , –8/7
Reflections collected / unique / R_{int}	2736 / 1328 / 0.0529
Data / restraints / parameters	1328 / 2 / 164
Goodness of fit on F^2	0.994
$R1$ (F) / $wR2$ (F^2) [$I > 2\sigma(I)$]	0.0397 / 0.0803
$R1$ (F) / $wR2$ (F^2) (all data)	0.0481 / 0.0833
Flack (x) parameter	0.04(6)
Largest diff. peak / hole, eÅ ⁻³	0.45 / –0.60

Table 2. Selected bond lengths (Å) and angles (deg) in the crystal structure of **1**^a.

Ag(1)–N(1)	2.185(7)	Ag(1)–N(2)	2.624(7)
Ag(1)–O(1)	2.604(2)	Ag(1)–N(5B)	2.167(7)
N(1)–Ag(1)–N(5B)	168.2(3)	N(2)–Ag(1)–N(5B)	111.0(2)
N(1)–Ag(1)–N(2)	68.9(2)	N(1)–Ag(1)–O(1)	107.2(5)
N(5B)–Ag(1)–O(1)	80.9(5)	O(1)–Ag(1)–N(2)	137.9(1)

^a Symmetry code: B $1/2 + x$, $1/2 - y$, $1/2 + z$.

in Table 1, and selected bond lengths and angles are summarized in Table 2.

CCDC 913854 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

IR spectroscopy

In the IR spectrum of the title complex, the strong absorption band at 1352 cm^{-1} is attributed to a characteristic band of the NO_3^- anion, which agrees well with that of related compounds [16, 19]. The bands at 3115 and 1587 cm^{-1} are attributable to the N–H and C=N stretching frequencies of the ligand L, respectively. The relatively weak absorption band at around 3024 cm^{-1} for **1** is due to the C–H modes involving the aromatic ring hydrogen atoms. The absorption bands with variable intensity in the frequency range 1436 – 1566 cm^{-1} correspond to ring vibrations of the pyridyl rings of the ligand.

Crystal and molecular structure

The single-crystal X-ray structure determination analysis revealed that polymer **1** crystallizes in the monoclinic space group *Cc*. As shown in Fig. 1, Ag(1) is bound to one pyridylimine unit [N(1), N(2)], one terminal triazolyl N-donor [N(5B)] from two ligands and one oxygen atom from one NO_3^- anion to attain a seesaw environment with the value of the topological parameter τ of 0.37 [20]. The average distance Ag(1)–N is 2.33 \AA , similar to previously reported values [21]. The distance Ag(1)–O is 2.604 \AA , thus the nitrate is only weakly coordinated to the silver ion [22, 23]. The four atoms of nitrate are approximately planar with an RMS deviation of the contributing atoms of 0.0029 \AA . The O–N–O band angles are

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)	Symmetry codes of A
C(1)–H(1A)...O(2)	0.93	2.42	3.244(13)	147	
C(3)–H(3A)...O(1)	0.93	2.52	3.385(12)	156	$-1/2+x, 1/2+y, z$
C(4)–H(4A)...O(3)	0.93	2.42	3.238(19)	146	$-1+x, 1-y, -1/2+z$
C(6)–H(6A)...O(3)	0.93	2.37	3.190(15)	147	$-1+x, 1-y, -1/2+z$
C(7)–H(7A)...O(2)	0.93	2.39	3.250(12)	154	$-1+x, 1-y, -1/2+z$
C(8)–H(8A)...N(4)	0.93	2.45	3.352(13)	163	$1/2+x, 1/2-y, 1/2+z$

Table 3. Weak C–H...O hydrogen bond interactions (Å and deg) in the crystal structure of **1**.

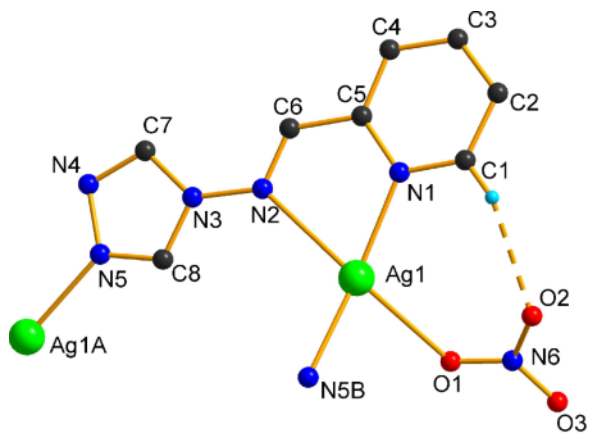


Fig. 1. The diagram of the coordination environment of the Ag atom in **1** showing hydrogen bonding (dashed line). The other hydrogen atoms are omitted for clarity. Symmetry codes: A $-1/2+x, 1/2-y, -1/2+z$; B $1/2+x, 1/2-y, 1/2+z$.

122.6(11), 116.9(9) and 120.5(9)°. These results show that the nitrate structure is only slightly distorted. In addition, a C(1)–H(1A)...O(2) hydrogen bond is found and may play an important role in the molecular structure with a C...O separation of 3.244(13) Å and a C–H...O angle of 171° (Table 3). Adjacent Ag(I) centers are bridged by one twisted tridentate ligand (one pyridylimine bidentate chelate unit and one terminal

N_{triazolyl} monodentate donor) to form a zigzag chain structure with a Ag...Ag separation of 6.80 Å (Fig. 2). Each ligand adopts a slightly twisted conformation with a dihedral angle of 6.4° between the two aromatic rings and a torsion angle of 177.8° for C(5)–C(6)=N(2)–N(3).

In the solid state, the chains further interact with each other forming a three-dimensional supramolecular network through two types of C–H... π interactions and multiform C–H...O hydrogen bonds. Two types of C–H... π interactions are found between C(3), C(4) of pyridyl rings and triazolyl rings from adjacent chains (Fig. 3). The C–H... π interactions are characterized by the C...*M* separation and C–H...*M* angle of 3.702 Å and 112.4° for C(3)–H...*M* (symmetry code: $-1/2+x, -1/2+y, +z$), and 3.553 Å and 102.2° for C(4)–H...*M* (symmetry code: $+x, 1-y, -1/2+z$), respectively (*M*, midpoint of the triazolyl ring). Otherwise, there is one kind of C–H...N hydrogen bond between the C(8) atom of a triazole ring as hydrogen donor and the N(4) atom of an adjacent triazole ring as acceptor with a C...N separation of 3.352(13) Å and a C–H...N angle of 163° (symmetry code: $1/2+x, 1/2-y, 1/2+z$). Four types of C–H...O hydrogen bonds are also observed between the carbon atoms C(3), C(4), C(6), and C(7) and three oxygen atoms of NO₃[−] anions (Table 3). Although these C–H... π interactions and hydrogen bonds are weak compared to the metal–nitrogen

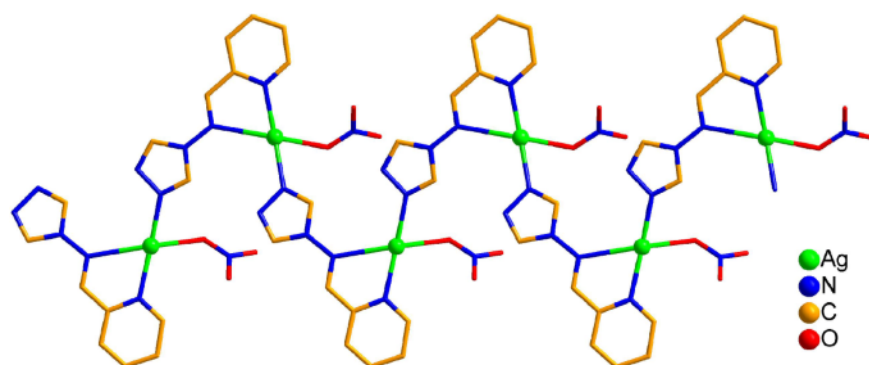


Fig. 2. The illustration of the 1D coordination polymer in the crystal structure of **1**. Hydrogen atoms are omitted for clarity.

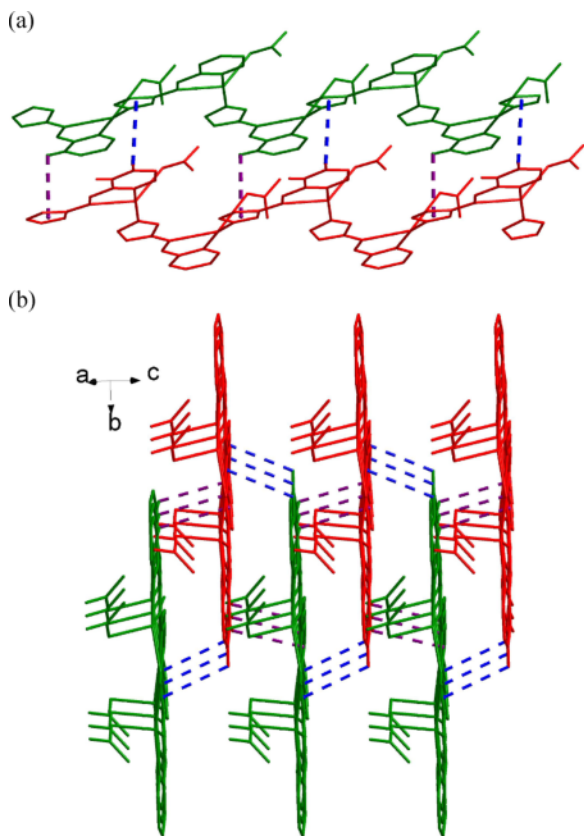


Fig. 3. Packing diagram of two chains (a) and the 3D supramolecular framework (b) in the crystal structure of **1** with C–H \cdots π interactions shown as dashed lines.

and metal-oxygen coordination bonds, it is suggested that these kinds of interactions are important in the packing of the molecules.

Powder X-ray diffraction

The powder X-ray diffraction measurement of polymer **1** was performed to check the phase purity of the samples. As shown in Fig. 4, most peak positions of the simulated and experimental patterns correspond approximately to each other.

Luminescence properties

The luminescence properties of some metal-organic compounds based on Schiff base ligands and d^{10} metal ions have been investigated previously [24, 25]. Herein, the properties of **1** were studied in the solid

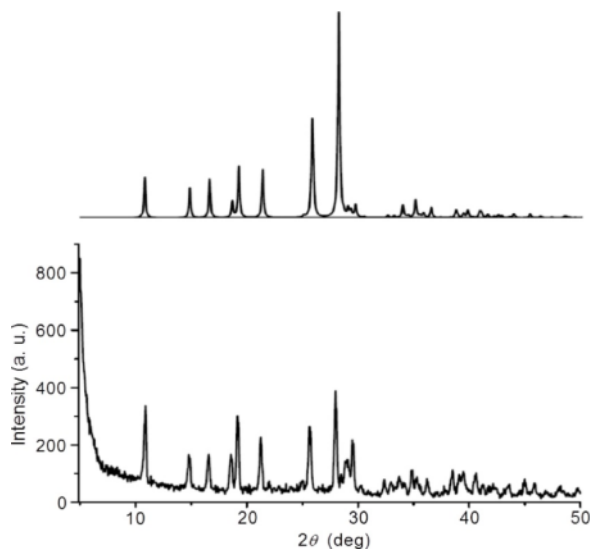


Fig. 4. The powder X-ray diffraction patterns calculated from the single-crystal data (top) and that obtained from the experiments (bottom) for polymer **1**.

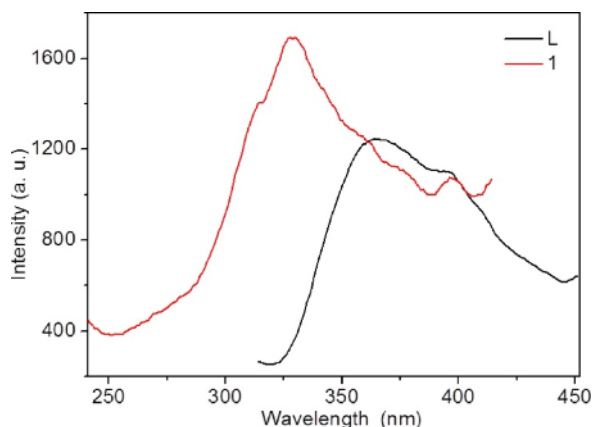


Fig. 5. The emission spectra of ligand **L** and polymer **1** in the solid state at room temperature.

state at room temperature. The spectrum of **1** and that of the corresponding ligand **L** reported in ref. [12] are both depicted in Fig. 5. Compared to the main emission peak at 364 nm and a shoulder emission at 396 nm for **L**, polymer **1** shows a similar luminescence emission peak at 397 nm, while the emission band at 328 nm is blue-shifted by 36 nm from 364 nm due to the coordination effect between **L** and the metal center. This is commonly observed in other Schiff base compounds [26, 27].

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