

**The hydrothermal synthesis and X-ray crystal structure of  
Ag (I)-4, 4'-bipyridine-based coordination polymer**

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**ABSTRACT**

Hydrothermal synthetic were studied for the preparation of coordination polymeric material based on Ag (I) and 4, 4'-bipy. A polymeric compound [Ag (4, 4'-bipy)].NO<sub>3</sub> (I), was prepared and structurally characterized by single crystal X-ray diffraction. Compound I (91% yield) was isolated from the reaction of AgNO<sub>3</sub> with 4, 4'-bipy in 2:1 molar ratio. In compound I, each silver (I) is linked to two nitrogens of different but symmetry-equivalent 4, 4'-bipy units in a nearly linear coordination to form extended chains.

**Keywords:** Hydrothermal synthesis; Crystal structure; Ag (I) complexes; 4, 4'-bipy

**INTRODUCTION**

The significant interest in crystal engineering of composite organic/inorganic solid-state materials reflects their diverse properties, with applications to catalysis, sorption, electrical conductivity, magnetism and photochemistry [1, 2]. One approach has exploited appropriate metal centers that are linked through suitable polydentate ligands for the self-assembly of extended networks [3]. Rod-like ligands such as 4, 4'-bipyridine are effective for construction of extended solids [4-9]. The incorporation of organic subunits in the structure of inorganic phases provides an efficient method for the structural modification and synthesis of novel organo-inorganic hybrid compounds. The prototypical materials of this class are polymeric coordination complexes cations constructed from Cu(I), Ag(I), Cu(II), Zn(II) and Cd(II) centers and organodimine bridging ligands [10,11]. In the reaction of

metal halide with 4, 4'-bipy, the products are normally obtained through conventional synthetic methods [12] and are typically insoluble in all organic solvents, so their structures are difficult to characterize. The present work reports out attempts to the hydrothermal synthesis and prepare single crystal of Ag (I)-4, 4'-bipy based coordination polymer with suitable quality for structural characterization.

**EXPRIMENTAL**

Synthesis was carried out in Parr acid digestion bombs with 23 ml polytetrafluoroethylene-lined stainless steel containers under autogenously pressure. All starting materials were purchased from Merck and used without further purification.

**Synthesis of [Ag (4, 4'-bipy)].NO<sub>3</sub> I**

A mixture of 4, 4'-bipyridine (0.16 gr, 1.02

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mmol) and  $\text{AgNO}_3$  (0.35 gr, 2 mmol) and  $\text{H}_2\text{O}$  (30 gr, 1660 mmol) in the molar ratio 1:2:1660 was heated at  $200^\circ\text{C}$  for 96 h under autogenous pressure. The mixtures were then cooled to room temperature either at a slow cooling rate  $10^\circ\text{C h}^{-1}$ . The yellow crystals were recovered by filtration and washed with deionized water before being left to dry in air.

### Structural characterization

The X-ray diffraction measurements were made on a STOE IPDS 2T diffractometer with graphite monochromated Mo- $K_\alpha$  radiation. The yellow block crystal was mounted on a glass fiber and used for data collection. The data collection and reduction were performed by X-Area 1.52 [13] program. The multi-scan absorption correction was performed by MULABS routine [14]. The structures were solved by direct methods using SHELXS97 and

subsequent difference Fourier map and then refined by a full-matrix least-squares on  $F^2$  by SHELXL97 in SHELXTL package [15]. The non-hydrogen atoms were refined anisotropically. All of the H atoms were positioned geometrically and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . All refinements were performed using the SHELXTL crystallographic software package. All calculations were done using PLATON [16]. A summary of the crystal data, collection parameters, and refinement criteria are given in Table 1.

### RESULTS AND DISCUSSION

The yellow crystals of I with suitable quality for further structural characterization, could be obtained as the only exclusive solid when the molar ratio of  $\text{AgNO}_3$ , 4,4'-bipy,  $\text{H}_2\text{O}$  of the reaction mixture were adjusted to be precisely 2.0:1.0: 1660 respectively.

Table 1. Crystal data and refinement parameters

Empirical formula	$\text{C}_{20}\text{H}_{16}\text{Ag}_2\text{N}_6\text{O}_8$
Formula weight	684.13
Temperature	291(2) K
Wavelength	0.71069
Crystal system	Orthorhombic
Space group	F ddd
Unit cell dimensions	a = 9.915(5) Å b = 12.981(5) Å c = 34.498(5) Å
Volume	4440(3) Å <sup>3</sup>
Z	8
Density (calculated)	2.047 Mg/m <sup>3</sup>
Absorption coefficient	1.827 mm <sup>-1</sup>
F(000)	2688
Index ranges	-12 ≤ h ≤ 12, -8 ≤ k ≤ 17, -47 ≤ l ≤ 47
Reflections collected	4863
Independent reflections	1463 [R(int) = 0.0314]
Goodness-of-fit on $F^2$	1.033
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0389, wR2 = 0.1018
Largest diff. peak and hole	0.772 and -0.918 e.Å <sup>-3</sup>

**Table 2.** Selected bond lengths (Å) and angles [°]

Ag(1)-N(1)	2.156(3)
Ag(1)-N(1)#1	2.156(3)
Ag(1)-Ag(1)#2	2.9820(15)
C(4)-C(5)	1.381(4)
C(4)-C(3)	1.393(5)
C(3)-C(2)	1.380(5)
C(3)-C(3)#3	1.488(5)
C(2)-C(1)	1.392(5)
C(5)-N(1)	1.344(5)
N(1)-C(1)	1.330(5)
N(1)-Ag(1)-N(1)#1	173.68(19)
N(1)-Ag(1)-Ag(1)#2	86.84(10)
N(1)#1-Ag(1)-Ag(1)#2	86.84(10)
C(5)-C(4)-C(3)	119.5(3)
C(2)-C(3)-C(4)	117.0(3)
C(2)-C(3)-C(3)#3	121.4(4)
C(4)-C(3)-C(3)#3	121.6(4)
C(3)-C(2)-C(1)	119.9(3)
N(1)-C(5)-C(4)	123.2(3)
C(5)-N(1)-Ag(1)	121.2(2)

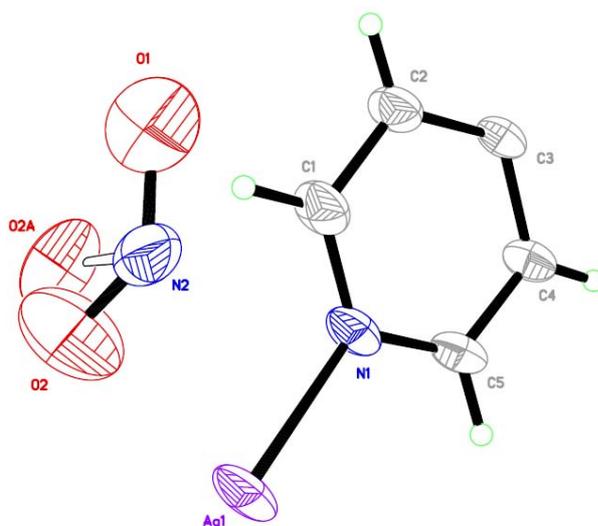
Symmetry transformations used to generate equivalent atoms:

#1  $-x+1/4, y, -z+5/4$  #2  $-x+1/4, -y+1/4, z$  #3  $-x-1/2, -y, -z+3/2$ , #4  $-x-1/4, -y-1/4, z$

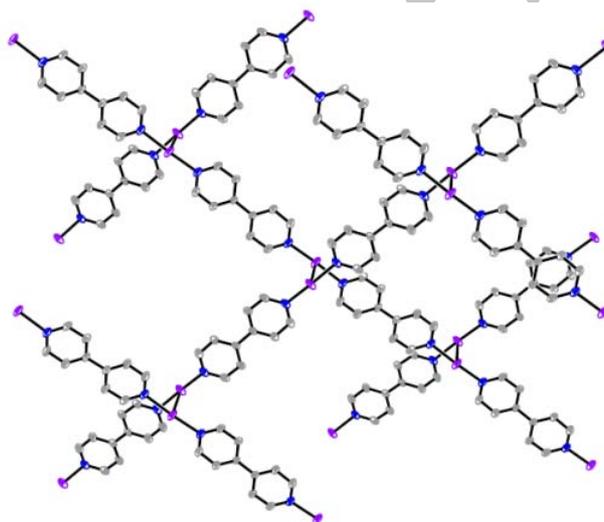
The asymmetric unit of the complex comprises half of the 4,4'-bipy ligand which is coordinated to Ag(I) and a nitrate anion in which one of its oxygen atoms is disordered over two position with a refined site occupancies ratio of 0.52(4)/0.48(4). The ORTEP view of the molecular structure is shown in Figure 1. The selected bond lengths and angles are listed in (Table 2).

X-ray structure determination on a single crystal isolated from the reaction mixture was performed to reveal an extended open cationic network composed of the building unit shown in Figure 2. Each silver (I) is linked to two nitrogens of different but symmetry-equivalent 4, 4'-bipy units in a nearly linear coordination [ $N1-Ag-N1A=173.68(19)^\circ$ ] to form extended chains.

Adjacent chains are cross-linked in an almost perpendicular fashion [ $N1-Ag-AgF-N1F=81.47(19)^\circ$ ] by Ag-Ag bonds leading to a three dimensional open network as represented in Figure 3. The overall structure is composed of three such networks that interpenetrate to give an open framework having  $23 \times 6 \text{ \AA}$  channels running along the [100] crystallographic axis where the nitrate ions reside. The T-shaped silver coordination leaves an open coordination site pointing toward the center of the channels. The nitrate guests from very weak interactions to the silver by binding to the vacant site (through the oxygens) in a trans fashion to the Ag-Ag bonds with Ag-O=2.78(1) and 2.83(2) Å, which are typical of ionic interactions in metal nitrates.



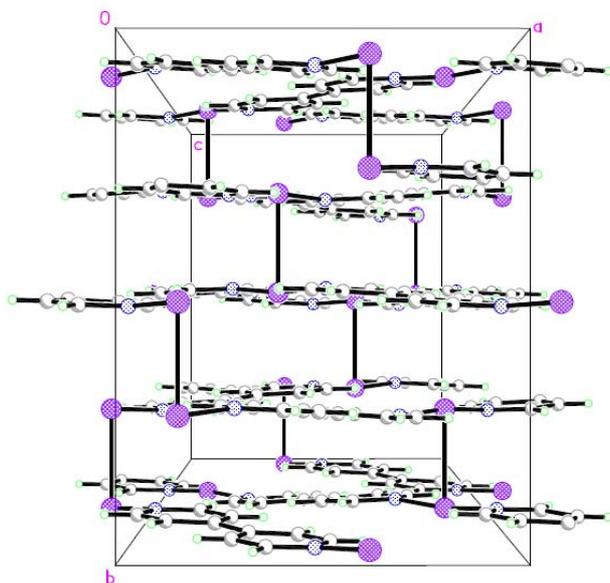
**Fig. 1.** The asymmetric unit of the title complex with atom labeling. One of the O atoms of the nitrate anion is disordered.



**Fig. 2.** The grow structure of the title compound showing extended open networks. The nitrate group and H atoms were removed for clarity.

At the outset of this study interpenetration had precluded the formation of open frameworks with accessible channels that are amenable to reversible inclusion chemistry. This work demonstrates the feasibility of achieving large channels having shapes yet unobserved in zeolites and other metal-organic porous frameworks in spite of the presence of interpenetrating frameworks. The T-shaped building unit which is responsible for the assembly of this

3-D open framework has the unique character of providing a vacant coordination site on the metal, a desirable property which has been implicated as the key structural feature causing activation of small molecules over metal oxides. Current investigations take into account the rarity of T-shaped coordination in porous materials and focus on accessing other solids that are based on this motif.



**Fig. 3.** The crystal packing of the complex viewed down the c-axis showing 3-D open network in [1 0 0] direction.

## CONCLUSION

Hydrothermal techniques have been exploited in the synthesis of polymeric compounds. Coordination of the metal and organic ligand has an important impact on the structures of the products. In this work each silver(I) linked to two nitrogens of different but symmetry-equivalent 4,4'-bipy units in a nearly linear coordination to form extended chains.

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