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# Construction of a three-dimensional network with open channels via Ag–Ag and π–π interactions between nanoscale sized molecular chains

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**Abstract**

The reaction of $Ag_2O$ with pybz (pybz = 4-(4-pyridyl)benzoate) gave the monomer compound [Ag(pycz)($H_2O$)], **1**. Using 4,4′-bipyridyl (bpy) as a spacer to increase the length of the monomer resulted in the nanosized molecular chain compound [$Ag_2$(pybz)$_2$(bpy)], **2**. In **1**, two monomers [Ag(pycz)($H_2O$)] are combined together through Ag···π, π···π and Ag···(C=C) interactions to form a dimer, with the distances of 3.34, 3.56 and 3.18 Å, respectively. In **2**, the [$Ag_2$(pybz)$_2$(bpy)] units are held together via π···π (3.4–3.5 Å) interactions resulting in a 3D network with 1D open channels.


*Keywords:* Silver(I) complex; 4-(4-Pyridyl)benzoate; 4,4′-Bipyridyl; Crystal structure

## 1. Introduction

In the construction of metal–organic hybrid complexes, the Ag(I) is often used as a metallic synthon due to its high affinity to soft N and S coordination atoms, its flexible coordination number and geometry, as well as for Ag–Ag attractions. By now, many Ag(I) complexes with different frameworks and topologies have been synthesized [1]; some of these show useful conductivity [2] and photoluminescent properties [3].

4-Pyridinecarboxylate (pyca) is useful as a building block because it contains unsymmetrical bifunctional groups and perhaps a chance of producing chiral coordination polymers [4]. However, in most cases, it formed interpenetration coordination polymers without holes [5]. In our previous studies [6], we constructed a 3D non-interpenetration open framework $\{[Cu(pyca)]\cdot 2H_2O\}_\infty$ with 1D channels that can reversibly absorb water molecules, and enlarging the spacers from pyca to 4-(4-pyridyl)benzoate (pybz) resulted in a 6-fold interpenetrating diamondoid framework $[Cu(pybz)_2]_\infty$. One way to avoid interpenetration is to shorten the length of the coordination chain and increase the interactions between the chains. The Ag(I) is expected to coordinate to the N atom rather than an O atom, so using Ag(I) instead of Cu(II) to react with pycz may result in a simple compound of Ag(pycz). However, Ag(pycz) may not be a good choice as monomer to construct a stable high dimensional network as it is very soluble in water. We also decided to explore using 4-4′-bipyridyl (bpy) as a spacer which would increase the length of the monomer and therefore result in the construction of a stable non-interpenetration framework with large channels.

Herein, we reported the syntheses and structures of a Ag(I) monomer: [Ag(pycz)($H_2O$)]·3$H_2O$, **1**·3$H_2O$ and of the larger complex: [$Ag_2$(pybz)$_2$(bpy)]·20$H_2O$ (bpy = 4,4-bipyridyl), **2**·20$H_2O$, which has a 3D network and 1D open channels constructed via Ag–Ag and π–π interactions.

Scheme 1

$$Ag^+ + pycz^- \rightarrow [Ag(pycz)(H_2O)],\ \mathbf{1}$$
$$2Ag^+ + 2pycz^- + bpy \rightarrow \{[Ag(pybz)]_2(bpy)\},\ \mathbf{2}$$

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## 2. Experimental

### 2.1. General data

4-(4-Pyridyl)benzonic acid was synthesized by using a published method of Suzuki reaction of cross coupling of 4-carboxybenzene boronic acid with 4-bromo-pyridine [7]. All other reagents were commercially available and used without further purification. Elemental analyses were determined using an Elementar Vatio EL elemental analyser. IR spectra were taken on a Bruker EQUINOX 55 spectrometer using KBr pellets.

### 2.2. Synthesis

#### 2.2.1. Preparation of $[Ag(pycz)(H_2O)]\cdot 3H_2O$, $\mathbf{1}\cdot 3H_2O$

Ammonia water solution was added to the mixture of $Ag_2O$ (0.116 g, 0.5 mmol) and sodium 4-(4-pyridyl)benzonate (0.221 g, 1 mmol) in 10 mL of $CH_2Cl_2/CH_3OH$ (1:1) resulting in a clear solution. The solution was evaporated slowly under the dark. After about 1 week, slightly yellow crystals were formed from the solution.

#### 2.2.2. Preparation of $[Ag_2(pybz)_2(bpy)]\cdot 20H_2O$), $\mathbf{2}\cdot 20H_2O$

To a mixture of 4,4′-bipyridyl (0.156 g, 1 mmol), sodium 4-(4-pyridyl)benzonate (0.221 g, 1 mmol), and $Ag_2O$ (0.116 g, 0.5 mmol) in $CH_2Cl_2/CH_3OH$ (10 mL, 1:1) was added ammonia water resulting in a clear solution. After heating at 50 °C for 0.5 h, the solution was evaporated slowly under the dark. Two weeks later, slightly yellow crystals were formed from the solution. Yield: 35%. Anal. Found: C, 48.38; H, 3.98; N, 6.56%. Calcd for $C_{34}H_{32}N_4O_8Ag_2$ ($\mathbf{2}\cdot 4H_2O$): C, 48.59; H, 3.84; N, 6.67%. IR (KBr, $cm^{-1}$): 3379(s), 3059(m), 1942(w), 1594(s); 1554(s), 1483(w), 1409(m), 1384(s), 1220(m), 1184(m), 1066(m), 997(w), 779(s), 620(m).

### 2.3. X-ray crystallography

The X-ray diffraction intensities were collected at 296(2) K from the crystals of $\mathbf{1}\cdot 3H_2O$ and $\mathbf{2}\cdot 20H_2O$ with dimensions $0.55\times0.10\times0.09$ mm and $0.24\times0.16\times0.12$ mm, respectively. Diffraction measurements were made on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation. The intensities were reduced using the SAINT program [8a]. The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first with isotropic and then with anisotropic thermal parameters to convergence. Hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXL system of computer programs [8b]. The crystal data are listed in Table 1, and selected bond distances and angles are present in Table 2.

Table 1
Crystallographic data for $\mathbf{1}\cdot 3H_2O$ and $\mathbf{2}\cdot 20H_2O$

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{12}H_{16}NO_6Ag$ | $C_{34}H_{44}N_4O_{14}Ag_2$ |
| *M* | 378.13 | 948.47 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *C2/c* | $P2_1/c$ |
| Crystal dimensions/mm | $0.55\times0.10\times0.09$ | $0.24\times0.16\times0.12$ |
| *a* (Å) | 18.868(6) | 24.489(9) |
| *b* (Å) | 6.767(2) | 21.599(8) |
| *c* (Å) | 21.492(7) | 14.989(5) |
| *β* (°) | 90.717(5) | 106.812(7) |
| *U* ($Å^3$) | 2743.9(15) | 7590(5) |
| *Z* | 8 | 8 |
| Linear abs. coeff. ($mm^{-1}$) | 1.489 | 1.104 |
| *Dc* (Mg $m^{-3}$) | 1.792 | 1.660 |
| *F*(000) | 1488 | 3856 |
| GoF | 1.034 | 1.020 |
| Number of reflections (unique) | 8302(3010) | 35,482(9926) |
| $R_{int}$ | 0.0221 | 0.0417 |
| Number of observed reflections [$I>2\sigma(I)$] | 2282 | 6662 |
| Number of refined parameters | 177 | 973 |
| $R_1$ | 0.0338 | 0.0475 |
| $wR_2$ | 0.0895 | 0.1209 |

## 3. Results and discussion

The reaction of $Ag_2O$ with pybz in the molar ratio 1:2 gave compound $[Ag(pycz)(H_2O)]$, **1** (Scheme 1). Compound **1** is very soluble in water, and partly soluble in methanol, acetonitrile and other polar solvents. The results of an X-ray single-crystal analysis indicate that each Ag(I) in **1** is two coordinate consisting of one nitrogen atom from pybz and one water molecule (Fig. 1a).

Table 2
Selected bond distances (Å) and angles (°) for $\mathbf{1}\cdot 3H_2O$ and $\mathbf{2}\cdot 20H_2O$

| | | | |
|---|---|---|---|
| ***1*** | | | |
| Ag–N(1) | 2.145(3) | Ag–O(3) | 2.148(3) |
| N(1)–Ag–O(3) | 177.45(11) | C(10)–N(1)–Ag | 120.8(2) |
| C(12)–N(1)–Ag | 122.2(2) | | |
| ***2*** | | | |
| Ag(1)–N(1) | 2.135(5) | Ag(1)–N(2) | 2.127(5) |
| Ag(2)–N(7) | 2.126(5) | Ag(2)–N(8) | 2.129(5) |
| Ag(3)–N(5) | 2.136(5) | Ag(3)–N(6) | 2.148(5) |
| Ag(4)–N(3) | 2.140(6) | Ag(4)–N(4) | 2.134(6) |
| Ag(1)–Ag(2) | 3.602(2) | Ag(3)–Ag(4) | 3.376(2) |
| N(1)–Ag(1)–N(2) | 171.1(2) | N(7)–Ag(2)–N(8) | 177.2(2) |
| N(5)–Ag(3)–N(6) | 169.7(3) | N(3)–Ag(4)–N(4) | 173.3(3) |
| N(5)–Ag(3)–Ag(4) | 93.96(15) | N(6)–Ag(3)–Ag(4) | 87.63(15) |
| N(4)–Ag(4)–Ag(3) | 93.96(17) | N(3)–Ag(4)–Ag(3) | 90.13(16) |
| C(13)–N(2)–Ag(1) | 119.5(5) | C(15)–N(2)–Ag(1) | 124.6(4) |
| C(10)–N(1)–Ag(1) | 117.6(4) | C(12)–N(1)–Ag(1) | 126.1(4) |
| C(56)–N(7)–Ag(2) | 121.4(5) | C(54)–N(7)–Ag(2) | 121.7(5) |
| C(59)–N(8)–Ag(2) | 126.8(5) | C(57)–N(8)–Ag(2) | 115.9(5) |
| C(46)–N(5)–Ag(3) | 120.1(5) | C(44)–N(5)–Ag(3) | 123.6(5) |
| C(47)–N(6)–Ag(3) | 123.2(5) | C(49)–N(6)–Ag(3) | 119.1(5) |
| C(22)–N(3)–Ag(4) | 123.1(6) | C(20)–N(3)–Ag(4) | 119.6(6) |
| C(23)–N(4)–Ag(4) | 123.8(6) | C(25)–N(4)–Ag(4) | 120.1(6) |