

## Construction of silver–organic framework with silver rods of repeated Ag-triangle units: Synthesis, structure, and properties



Ren-Wu Huang, Yu Zhu, Shuang-Quan Zang\*, Mao-Lin Zhang\*

The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, PR China

### ARTICLE INFO

#### Article history:

Received 26 January 2013

Accepted 8 April 2013

Available online 13 April 2013

#### Keywords:

Coordination polymer

Silver rod

Ag–Ag interaction

### ABSTRACT

A new thick silver rod incorporating repeated  $\text{Ag}_3$  units sustained by 1,3,5-benzenetricarboxylic acid (1,3,5- $\text{H}_3\text{BTC}$ ) and Ag–Ag interactions,  $\{[\text{Ag}_3(\text{BTC})(\text{pyz})] \cdot (\text{H}_2\text{O})_n\}$  (**1**) (pyz = pyrazine), has been synthesized and structurally characterized. Compound **1** displays a three-dimensional coordination framework with infinite 1D Ag rod, and adjacent silver rods bridged by the 1,3,5- $\text{H}_3\text{BTC}$  and pyz ligand. Argentophilicity plays an important role in determining the infinite silver(I) rods. Complex **1** exhibits photoluminescence maximized at 542 nm upon 363 nm excitation at room temperature, which may be mainly assigned to ligand-to-metal charge transfer (LMCT) perturbed by Ag–Ag interactions. Temperature dependent luminescence spectra from 298 to 77 K have been studied. Upon decreasing the temperature from 298 to 77 K, the emission bands grow in intensity. In addition, the thermogravimetric analysis and powder X-ray diffraction (PXRD) of complex **1** have also been investigated.

© 2013 Elsevier B.V. All rights reserved.

In the past few decades, the synthesis of silver(I) complexes has attracted great interest because the silver(I) ion principally exhibits linear, seesaw, trigonal, square-pyramidal, trigonal-bipyramidal, square-planar, tetrahedral, and octahedral coordination geometries and has high affinity for hard donor atoms such as nitrogen or oxygen atoms [1], and is apt to form short Ag–Ag contact. Those have been proved to be two of the most important factors contributing to the formation of such complexes and special properties [2,3]. The argentophilicity, namely the  $d^{10}$ – $d^{10}$  closed-shell attractive interaction that promotes the aggregation of Ag center, plays important role in constructing fascinating structures [4]. Despite the repulsion expected between two closed-shell metal cations, there are numerous examples of Ag(I) coordination compounds with short Ag–Ag contacts that have been structurally characterized, ranging from dimers to intricate high-nuclearity clusters. The thick silver rod occurs widely in silver-ethynide supramolecular synthon [5], which may be due to the diverse coordination modes of the alkynyl moiety and the tendency to form argentophilic interaction. However, the linear ones are rarely documented in silver-organic coordination polymers [6]. One previously known example reported by Kristiansson group is a 1D infinite Ag(I) chain with repeated rhombohedral  $\text{Ag}_4$  units [6b].

On the basis of our previous studies, herein, we focus on the self-assembly of silver(I) and carboxylate incorporating pyrazine as an auxiliary ligand and obtained one new metal–organic framework,

namely,  $\{[\text{Ag}_3(\text{BTC})(\text{pyz})] \cdot (\text{H}_2\text{O})_n\}$  (**1**), in which infinite thick silver rod incorporating diverse Ag–Ag interactions makes its appearance.

Crystals of **1** were obtained using ‘one-pot’ methodology by treatment of  $\text{Ag}_2\text{O}$ , 1,3,5- $\text{H}_3\text{BTC}$ , pyrazine in methanol–water solvent (6 mL, V:V = 5:1) in the presence of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  under ambient conditions in the dark [7]. The solid FT-IR spectrum of **1** shows a very intense peak around  $3422 \text{ cm}^{-1}$  attributed to the O–H stretching vibration of the water molecule. The asymmetric and symmetric stretching vibrations of deprotonated carboxyl group are in  $\sim 1600$  and  $\sim 1330 \text{ cm}^{-1}$ , respectively. These results are in good agreement with solid state crystal structure.

The molecular structure of **1** was determined by single-crystal X-ray diffraction analysis [8]. In **1**, the asymmetric unit contains three crystallographically unique Ag(I) atoms, one 1,3,5- $\text{BTC}^{3-}$  ligand, one pyrazine ligand and one lattice water molecule. A view of the local coordination geometries around Ag(I) ions is depicted in Fig. 1a. In complex **1**, the coordination environment of Ag1 and Ag2 can be described as nearly T-shaped and Y-shaped geometries, respectively, and coordinated by two oxygen atoms from two different 1,3,5- $\text{BTC}^{3-}$  ligands and one nitrogen atom from one pyrazine ligand, while Ag3 is in linear geometry and coordinated by two oxygen atoms from two different 1,3,5- $\text{BTC}^{3-}$  ligands. Both Ag–O and Ag–N bonds are within normal ranges [9,10]. In addition, there are weak Ag–O interaction between the Ag(I) cations and carboxyl oxygen atoms, as well as water molecule with the distance in the range of 2.708(7)–3.186(8) Å. Notably, the distance between the silver atoms varies from 2.688(2) to 3.333(2) Å, being shorter than twice the van der Waals radius of silver ions (3.44 Å) [11] and suggesting the presence of significant argentophilic interactions. Then, the versatile Ag–Ag weak interactions assemble these adjacent Ag

\* Corresponding authors. Tel./fax: +86 371 67780136.

E-mail addresses: [zangsqz@zzu.edu.cn](mailto:zangsqz@zzu.edu.cn) (S.-Q. Zang), [mlzhang@zzu.edu.cn](mailto:mlzhang@zzu.edu.cn) (M.-L. Zhang).

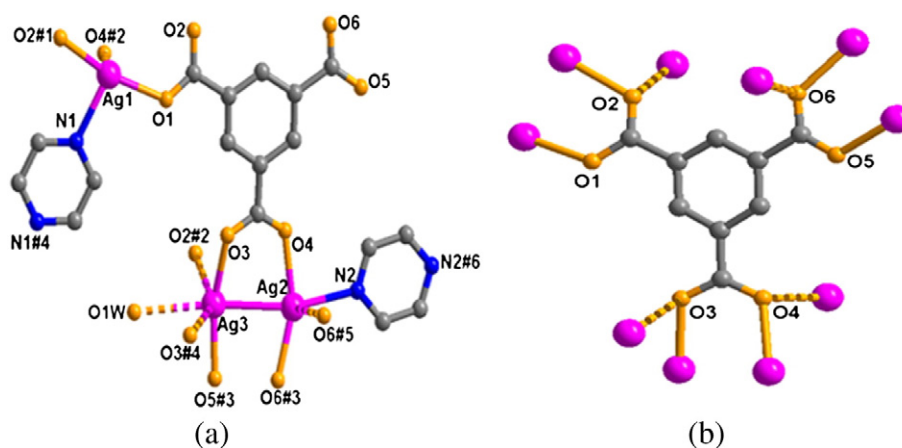


Fig. 1. (a) Metal coordination and atom labeling in complex **1** with hydrogen atoms are omitted for clarity. (b) Coordination modes of ligand 1,3,5-BTC<sup>3-</sup> in complex **1**.

atoms into infinite thick silver rod with repeated Ag-triangle units, consolidated by the weak Ag··O interaction, as shown in Fig. 2. Taking weak Ag··O interactions into account, the coordination mode of 1,3,5-BTC<sup>3-</sup> can be described as  $\mu_{10}(\eta^1, \eta^2):(\eta^1, \eta^2):(\eta^2, \eta^2)$  (Fig. 1b). The  $\mu_{10}$ -BTC<sup>3-</sup> ligands bridge adjacent silver rods to furnish the resulting three-dimensional coordination architecture (Fig. 3a). As displayed in Fig. 3b, such network is also consolidated by pyrazine ligands.

The thermal weight measurement for the compound was carried out in the range of 31–800 °C (Fig. 4). The TG curve of compound **1** shows a weight loss of 2.97% (calc. 2.86%) from room temperature to 62 °C which corresponded to the removal of the water molecule. The anhydrous composition begins to decompose at 62 °C and ends above 542 °C, which corresponds to the loss of organic components. Phase purity of **1** is sustained by the powder X-ray diffraction pattern (Fig. 5). The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

Taking into account the excellent luminescent properties of d<sup>10</sup> metal-organic polymers, the solid-state photoluminescent properties of compound **1** and H<sub>3</sub>BTC ligand were investigated at room temperature. The photoluminescent spectrum of H<sub>3</sub>BTC ligand has been investigated and shows the emission maximum at 395 nm ( $\lambda_{\text{ex}} = 363$  nm) [12]. At 298 K, the emission spectrum is centered around 542 nm when excited at 363 nm, roughly 147 nm red-shifted. Fig. 6 shows the emission spectra of **1** recorded at different temperature. Temperature dependent luminescence spectra between 298 and 77 K are shown in Fig. 6. With a temperature decrease from 298 to 77 K, the emission intensity of **1** sharply increases and the band maximum red-shifts. The presence of the red shift (about 6 nm) upon lowering the temperature appears to result from the stronger self-association of the Ag(I) ions through argentophilic interactions and is consistent with what have been observed in other photoluminescent polynuclear silver compounds with Ag··Ag interactions [13]. Therefore, the emissions may be assigned

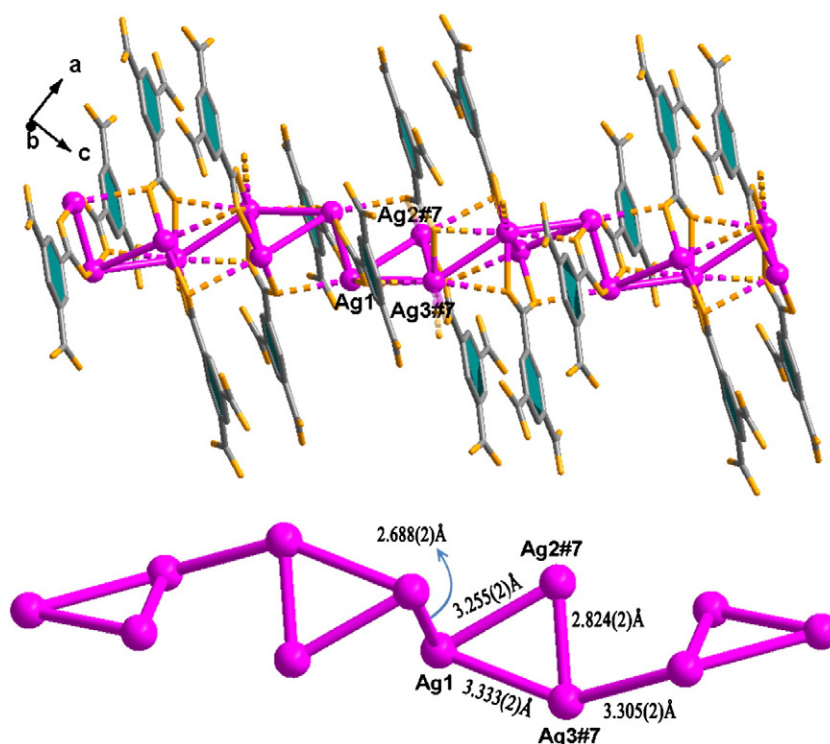


Fig. 2. View of the infinite Ag chain.

Download English Version:

<https://daneshyari.com/en/article/7749753>

Download Persian Version:

<https://daneshyari.com/article/7749753>

[Daneshyari.com](https://daneshyari.com)