



Photoluminescent metal–organic coordination polymer incorporating one-dimensional silver chains

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ABSTRACT

Solution phase reaction of AgNO_3 with a mixture of benzene-1,3,5-tricarboxylic acid (H_3BTC) and heterocyclic 2-aminopyrimidine (APYM) under the ammoniacal conditions gives rise to a novel metal–organic coordination polymer $\text{Ag}_3(\text{BTC})(\text{APYM})_2$ (**1**). The structure of **1** possesses a unique three-dimensional (3D) framework with one-dimensional channels surrounded by carboxylato-supported Ag–Ag dimers, Ag–Ag chains, fully deprotonated $[\text{BTC}]^{3-}$ and APYM ligands. Moreover, **1** exhibits strong blue photoluminescence maximized at 464 nm at room temperature ($\lambda_{\text{ex}} = 383$ nm) and upon cooling to 77 K, the emission spectrum seems narrowly red-shifted.

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The current interest in coordination polymeric frameworks stems not only from their intriguing variety of architectures and topologies, but also their potential applications in luminescence, nonlinear optics, porous materials, gas storage and catalysis [1–3]. The construction of molecular architecture depends on the combination of several factors, such as the solvent systems, the templates, the temperatures, the counter ions, the ratio of ligands to metal ions, coordination geometries of central metals and organic ligands [4]. In this regard, the organic anions play important roles in directing the final structures and topologies of their coordination polymers. As already known, benzoic multicarboxylate ligands are versatile building blocks for the construction of polymeric structures [5], for example, the use of rigid benzene-1,3,5-tricarboxylic acid (H_3BTC) with a 120° angle between two carboxylic groups can yield many desired networks [6,7] in metal–organic coordination polymers. However, although many benzene multicarboxylate-bridged metal–organic coordination polymers have been reported, those on a silver(I) ion especially containing auxiliary ligands are relatively rare, probably because they often appear as insoluble salts that make structural analyses difficult [8,9].

On the other hand, heterocyclic pyrimidine and its derivatives, in spite of their simplicity, are very versatile systems. Their ability for giving specific H-bonding patterns as a key step in the storage and transmission of genetic information is a well-known process

[10]. Moreover, their efficiency in binding transition metal ions is also well known. Indeed, they are applied to develop polymeric metal–organic hybrid frameworks (MOFs) owing to their demonstrated ability to form very stable hydrogen-bonded chain arrays via their stereochemically associative amino and hetero ring nitrogens to coordinate to the metal centers through various bonding modes [11,12]. In our recent studies, 2-aminopyrimidine and its derivatives have been successfully used to construct a series of Ag^I complexes with dinuclear, tetranuclear, 1D and 2D structures [13,14]. However, we also noticed that it's difficult for us to get high-dimensional structure with interesting luminescence only using 2-aminopyrimidine or its derivatives without other auxiliary ligands. With the principal aim of obtaining novel high-dimensional coordination polymers with interesting luminescence, for the first time, we try to introduce the benzene-1,3,5-tricarboxylate (H_3BTC) as a secondary ligand into previous silver/aminopyrimidine system, and obtain surprisingly a novel 3D metal–organic polymer. Herein, we report the preparation, crystal structure and photoluminescent properties of the 3D metal–organic polymer incorporating 1D silver chains, namely, $[\text{Ag}_3(\text{BTC})(\text{APYM})_2]_n$ (**1**).

In a typical synthesis, the reaction of AgNO_3 , benzene-1,3,5-tricarboxylic acid and 2-aminopyrimidine by using ammoniacal conditions to enhance the solubility of the silver carboxylates gave colorless plate crystals of **1** [15]. Its IR spectrum exhibits the absorptions at $3300\text{--}3400\text{ cm}^{-1}$, corresponding to the N–H stretching vibrations of the amide group, and two strong characteristic bands of carboxylic groups at 1626 and 1555 cm^{-1} for the asymmetric vibrations and at 1430 and 1360 cm^{-1} for symmetric

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vibrations, respectively (see Fig. S1, in the Supplementary material). The separation (Δ) between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ bands show that carboxylate groups coordinate to the metal atoms in a bridging fashion [16]. The absence of the characteristic bands at around 1700 cm^{-1} attributed to the protonated carboxylic groups indicates that the complete deprotonation of BTC ligand upon reaction with Ag ions [17]. Phase purity of **1** is sustained by its powder X-ray diffraction pattern, which is consistent with that simulated on the basis of the single-crystal X-ray diffraction data (see Fig. S2).

The X-ray structural analysis [18] reveals that **1** crystallizes in the triclinic $P\bar{1}$ space group with an asymmetric unit that contains three crystallographically unique Ag^{I} atoms, one deprotonated $[\text{BTC}]^{3-}$ ligand, two APYM ligands, and two lattice water molecules (Fig. 1a). The charge neutrality is achieved by the three deprotonated carboxylate groups of the H_3BTC molecule. Selected bond lengths and angles are listed in Table S1. Ag1 adopts a slightly distorted T-shaped geometry, which is coordinated by two O donors from two $[\text{BTC}]^{3-}$ anions [Ag(1)–O 2.224(9)–2.228(9) Å, O(2A)–Ag(1)–O(3) 165.8(3)°] and one N donor [Ag(1)–N(3A) 2.35(1) Å, O–Ag(1)–N(3A) 95.6(4)–98.4(4)°] from one APYM ligand. Similarly, Ag2 is also coordinated in a distorted T-shaped coordination geometry and is surrounded by two O atoms from two $[\text{BTC}]^{3-}$ anions [Ag(2)–O 2.189(9)–2.217(9) Å, O(2A)–Ag(1)–O(3) 163.5(4)°] and one N atom [Ag(2)–N(6A) 2.39(1) Å, O–Ag(2)–N(6A) 92.0(4)–104.5(4)°] from one APYM ligand. While Ag3 is coordinated to one O atom from one $[\text{BTC}]^{3-}$ anion and two N atoms from two APYM ligands in a slightly distorted Y-shaped geometry [Ag(3)–O 2.42(1) Å; Ag(3)–N 2.28(1) and 2.31(1) Å; N/O–Ag(3)–O/N 87.5(4)–136.1(3)°], as well as forming one weak Ag–O interaction (Ag(3)–O(4) = 2.75(1) Å). It should be noted that there existed two kinds of Ag...Ag interactions in the structures of the complex

1: the first sort of Ag–Ag distances [Ag(1)–Ag(1A) 2.786(2) and Ag(2)–Ag(2B) 2.809(2) Å] are comparable to the Ag...Ag separation (2.89 Å) in metallic silver [19], which provides supporting evidence for the significance of argentophilicity [20]. Similar Ag...Ag distances could be found in silver cyclohexanhexacarboxylate (2.916 Å) [21a], silver benzenetricarboxylate (2.859 Å) [21b] and silver benzenesulfonate (2.915 Å) [21c]. The second sort of Ag–Ag distances [Ag(1)–Ag(2A) 3.176(2) and Ag(3)–Ag(3A) 3.253(3) Å] are shorter than the sum of van der Waal' radii of Ag ($r_{\text{vdw}}(\text{Ag}) = 1.72$ Å) [22], which is suggestive of a weak interaction between the two metal silver centers. Each $[\text{BTC}]^{3-}$ anion connects five Ag^{I} atoms through three fully deprotonated carboxylate groups with $\mu_2:\eta^1:\eta^1$, $\mu_2:\eta^1:\eta^1$, $\mu_1:\eta^2$ coordination modes, respectively (Fig. 1b). It's noteworthy that each APYM ligand, taking N,N'-bidentate coordination mode, connects each pair of adjacent silver atoms *via* pyrimidyl nitrogen atoms to form 1D wavy pattern chains, which are further linked by $[\text{BTC}]^{3-}$ anions to generate a 2D structure (Fig. 1c and Fig. S3). The most striking feature of complex **1** is that two types of cluster units of Ag...Ag interactions exist: the carboxylate-supported Ag3...Ag3 dimer and the 1D carboxylate-supported infinite zigzag $(\text{Ag}1\cdots\text{Ag}2\cdots\text{Ag}2\cdots\text{Ag}1)_{\infty}$ chain unit (Fig. 2a and b). Such robust Ag...Ag interactions make the silver(I) ions form a one-dimensional chain running along the *a* axis direction supported by μ_2 -carboxylate bridges. It should be noted that most Ag...Ag interactions in the reported complexes are ligand-supported, *i.e.* the two concerning silver(I) ions are also maintained by bridging or capping atoms or ligands. The complexes containing ligand-unsupported Ag...Ag interactions are scarce, only a few examples have been reported [21b,23]. As shown in Fig. 2c, these dimeric motifs and 1D Ag...Ag chains are further linked by the $[\text{BTC}]^{3-}$ and APYM ligands to form 3D infinite network. We believe

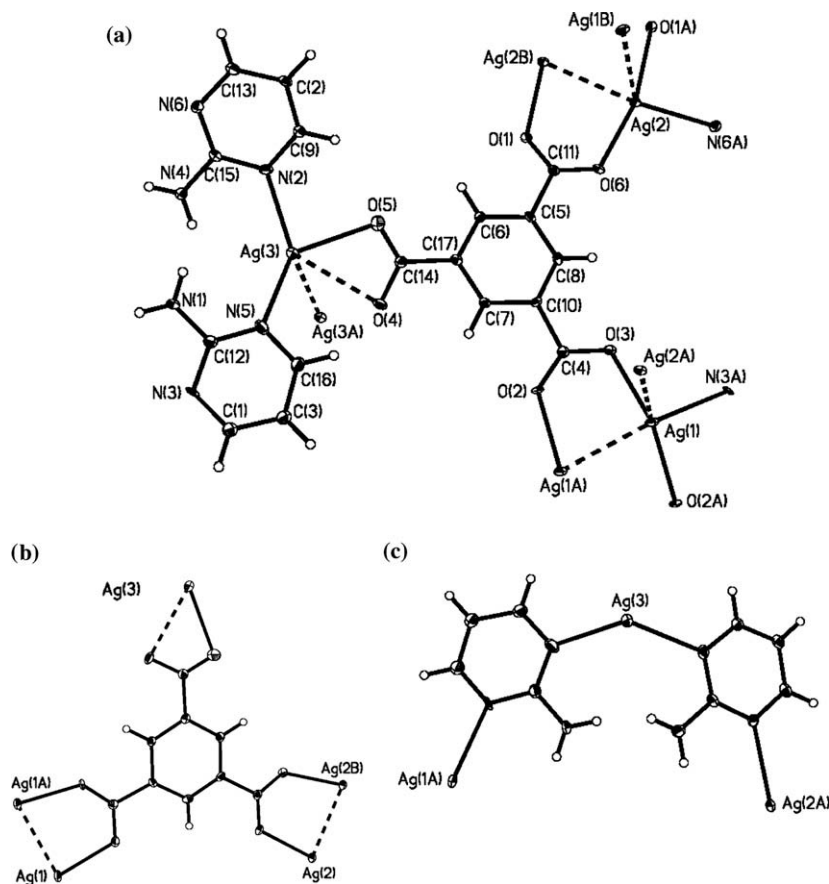


Fig. 1. (a) Perspective views showing the coordination environments of silver atoms, and the coordination mode of the $[\text{BTC}]^{3-}$ anion (b) and APYM ligand (c) in **1**.

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