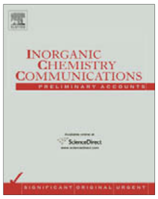
Inorganic Chemistry Communications 12 (2009) 611–614

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche



Novel silver(I) compounds assembled from hybrid ligands based on linear or T-shaped coordination environment

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ARTICLE INFO

Article history:
Received 13 January 2009
Accepted 4 May 2009
Available online 15 May 2009

Keywords:
Coordination polymer
Crystal engineering
Ag–Ag contacts
Fluorescence spectrum

ABSTRACT

Two novel 1D compounds $\{[Ag_3(Hbptc)(bpa)_2]\cdot H_2O\}_n$ (**1**) and $[Ag_2(H_2bptc)(bpp)_2]_n$ (**2**) (H_4bptc = 3,3′,4,4′-benzophenonetetracarboxylic acid, bpa = 1,2-bis(4-pyridyl)ethane and bpp = 1,3-bis(4-pyridyl)propane) were synthesized and structurally characterized. The crystal structures of compounds exhibit two kinds of ladder-like chains based on linear or T-shaped coordination environment of Ag(I). Fluorescence spectra of compounds **1** and **2** indicate the unusual intensity of fluorescent emission upon photoexcitation which may be attributed to ligand-to-metal charge transfer and Ag–Ag interactions.

The rational design and assembly of metal-organic frameworks (MOFs) with well-regulated network structures have received remarkable attention in order to develop new functional materials with potential applications [1]. In principle, the construction of molecular architecture is based upon the sophisticated selection and utilization of suitable metal ions and multifunctional organic ligands. Among various organic ligands, multicarboxylate ligands are often used as multifunctional organic ligands, not only because of their various coordination modes to the metal ions, but also because of their ability to act as H-bond acceptors and donors assembling supramolecular structures [2]. For example, 1,2,4,5-benzenetetracarboxylate, 3,3',4,4'-biphenyltetracarboxylic acid [3–5], 1,1'-biphenyl-2,3',3,4'-tetracarboxylic acid [6] and methylenediisophthalic acid [7] have been extensively used for the synthesis of various coordination polymers. However, coordination polymers built up from H_4bptc ligand (H_4bptc = 3,3′,4,4′-benzophenonetetracarboxylic acid) have been rarely reported [8]. Therefore, we choose H_4bptc and auxiliary ligands (bpa and bpp) to explore some intriguing architectures. The results show that these ligands exhibit a special ability to formulate compounds and play an important role in directing the final structures [8g]. On the other hand, silver(I) salt is often used in crystal engineering because of its ability to form compounds with coordination numbers of 2, 3, or 4 and even more resulting in many different architectures development [9]. Moreover, the potential Ag–Ag interactions also play a crucial role in the structures of coordination polymers formed [10]. Herein, we report the synthesis, crystal structure and luminescent properties of two silver(I) coordination polymeric compounds $\{[Ag_3(Hbptc)(bpa)_2]\cdot H_2O\}_n$ (**1**) and $[Ag_2(H_2bptc)(bpp)_2]_n$ (**2**).

Compound **1** was synthesized hydrothermally by treating AgAc, bpa and H_4bptc at 150 °C. The pH value of the reaction mixture was adjusted to 4 by addition of triethylamine [11]. Compound **2** was obtained at pH value 3 using the same procedure but with bpp instead of bpa [11]. Single-crystal X-ray structural analysis reveals that the structure of **1** contains three crystallographically independent Ag(I) centers (Fig. 1a). The Ag1 ion is coordinated by two carboxylic oxygen atoms (Ag–O 1.954(2) Å) from two different bptc ligands. The Ag2 ion is three-coordinated with a T-shaped coordination geometry binding two nitrogen atoms from two different bpa ligands (Ag–N 2.010(3) and 2.038(3) Å) and one oxygen atom of a carboxylate group from bptc ligand (Ag–O 1.970(4) Å). Ag3 ion coordinational sphere is similar to Ag2. Due to the partial deprotonation, bptc anion in **1** binds to three Ag(I) cations and exhibits a V-shaped geometrical conformation. This can play a decisive role in the formation of fascinating architectures and topologies and it has been demonstrated by previous examples [8e].

The most interesting feature of **1** is that the V-shaped bptc ligand and Ag1 ion are acting together as a bridge, linking the adjacent two chains to form a rare 1D double-ladder chain with a T-shaped coordination geometry (AgN_2O). Although three-coordinated Ag atom is not rare in the complexes [12–15], the structure of **1** containing extended N-auxiliary ligands (bpa) is different from the reported Ag complexes with bpy and carboxylate ligands [16]. Usually the carboxylate ligands are not coordinated with Ag ion and Ag–bpy chains are linked into a 1D molecular ladder by

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doi:10.1016/j.inoche.2009.05.004

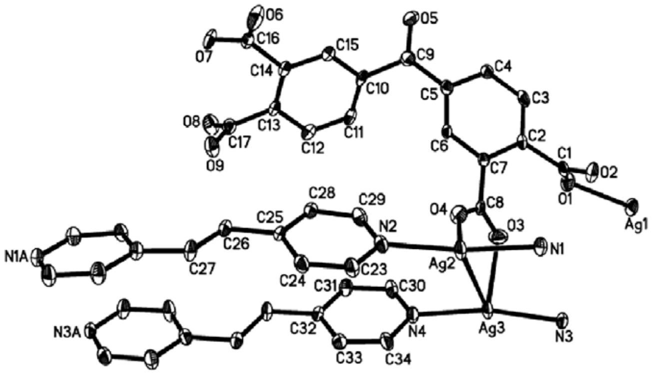

Fig. 1a. ORTEP diagram showing the coordination environments for the Ag(I) ions in **1**.

general Ag–Ag interaction, and only weak Ag···O interactions exist. In contrast, bptc carboxylate oxygen atoms of the compound **1** are directly coordinated with Ag(I) forming a $O_2C–C–C–CO_2$ bridge. In addition, the Ag2···Ag3 distance within the chains is 3.161 Å, which is shorter than the sum of the Van der Waals radii of two silver atoms (3.44 Å) [17]. This is a clear indication of a weak ligand-induced Ag–Ag interaction which could be found in many other Ag(I) coordination polymers with Ag–Ag interatomic distance 3.0–3.3 Å [18]. Hence, ligand-induced Ag–Ag interaction and $O_2C–C–C–CO_2$ bridge play a crucial role in the forming of the 1D double-ladder chain structure (Fig. S1).

Furthermore, there are some other weak interactions between the adjacent chains. The first are hydrogen bonds between the free water molecules and the carboxylate groups (O10–H10 W···O6 2.819(8) and O10–H11 W···O8 2.968(5) Å), which link the 1D double-ladder chains into a 2D layer (Fig. 1b). The second are significant interchain π–π stacking interactions between the bpa ligands. The face-to-face separation of the neighboring phenyl rings of bpa is 3.621 Å. As a result of these weak interactions, the double-ladder chains extend to a novel 3D supramolecular structure (Fig. S2).

The structure of compound **2** is based on Ag–Ag interaction, as shown in Fig. 2a. It is an infinite ladder-like chain arrangement with the $[Ag(bpp)]^+$ unit. The distance of Ag···Ag in **2** is 3.176 Å, which is also a weak Ag–Ag interaction. Due to partial deprotonation of the bptc ligands in compound **2**, they can act as medium H-bond acceptors and donors, resulting in 3D supramolecular structures with channels (hydrogen-bonds: 2.334(2) and 2.509(1) Å). These strong O–H···O hydrogen bonds can play an important role for improving the stability of the 3D architecture (Fig. 2b). The ladder-like chains occupy these channels, and the whole structure is additionally stabilized by the weak Ag···O interactions (2.898(8) and 2.928(1) Å).

Comparing known examples of Ag containing coordination polymers [8] with the compounds **1** and **2**, it is important to note that the fascinating low dimension motifs rely on the following contributions: silver(I) complexes act as bridges and exhibit close Ag–Ag contacts with coordination numbers of 2 and 3 to form 1D chain architectures [9]; the one carboxyl coordinated bptc ligands in **1** are protruding from the both sides of the 1D chain and provide the stable links amongst them, as can be also found in previous literature [8c]; finally, bptc ligands in **2** have sufficient amount of supramolecular recognition sites for hydrogen bond interactions to form unusual supramolecular structure.

To study the thermal stabilities of these complexes, thermal gravimetric analysis (TGA) of compounds **1**–**2** was carried out (Fig. S3). Compound **1** first loses its free water molecules below 160 °C; the weight loss found of 1.54% is consistent with that calculated (1.68%). When the temperature is in the 180–620 °C, the product begins to decompose. The weight loss is owed to the release of ligands, the final residual weight is 30.74% (calc. 30.35%) corresponding to Ag. For complex **2**, TGA results show that the weight loss in the range of 190–750 °C, which corresponds to the release of ligands, the residual percentage weight (observed 20.23%) at the end of the decomposition of the complex is consistent with the formation of Ag (expected 21.91%).

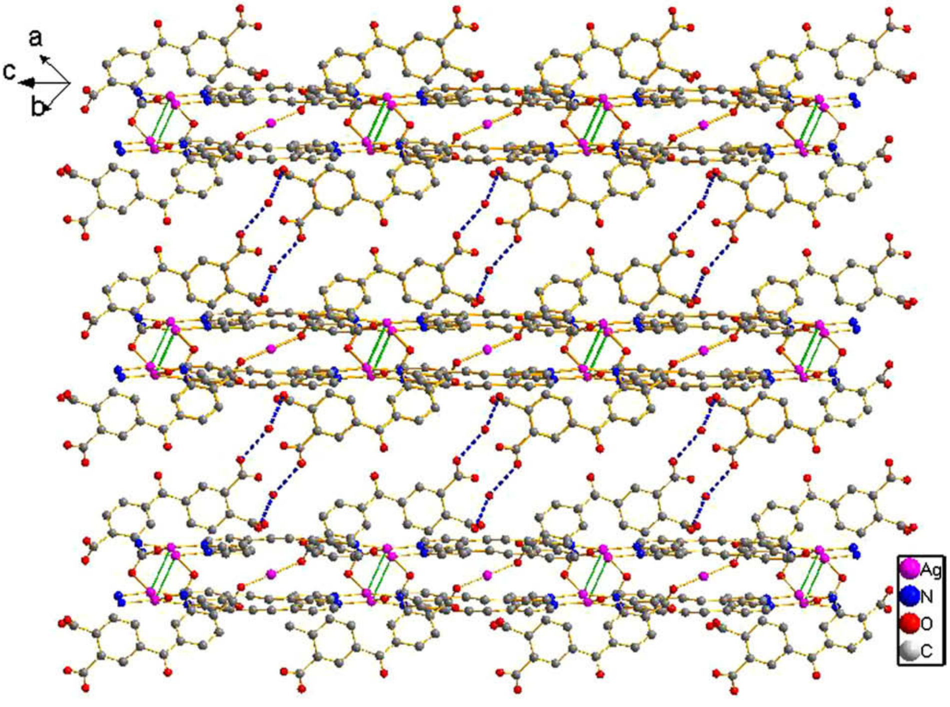

Fig. 1b. 1D double-ladder chains linked by hydrogen-bonding interactions into a 2D layer in **1.** Hydrogen bonds are shown as dashed lines.

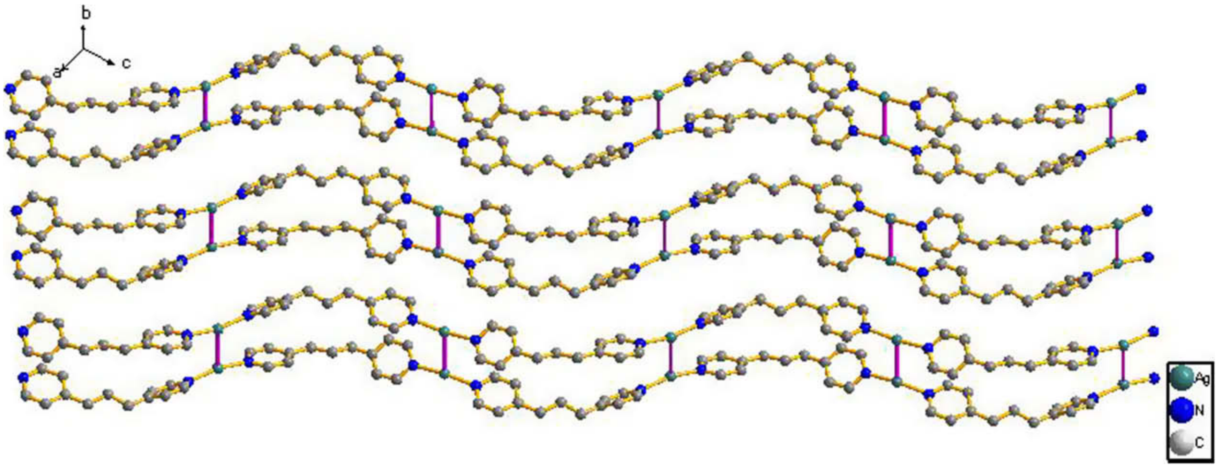

Fig. 2a. Infinite ladder-like chains arrangement based on Ag—Ag contacts with the $[Ag(bpp)]^+$ unit in **2**.

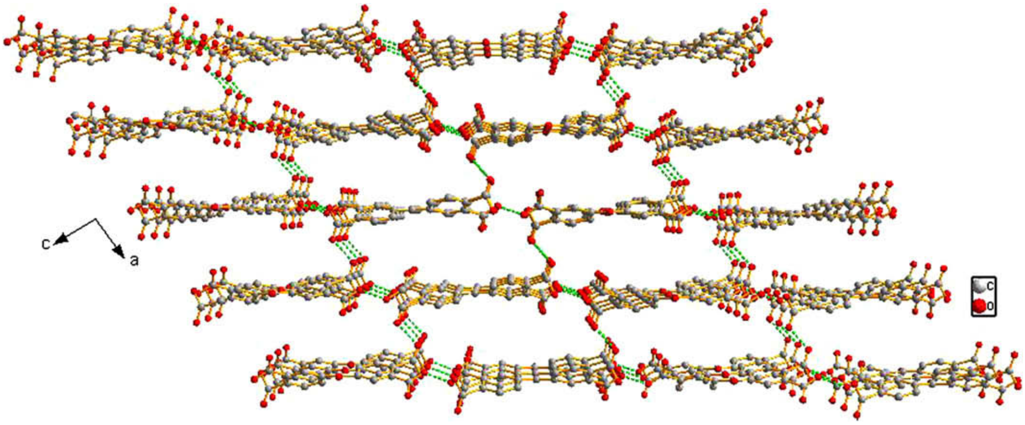

Fig. 2b. bptc Ligands as medium H-bond acceptors and donors forming 3D supramolecular structure with channels along *b* axis in **2**. Hydrogen bonds are shown as dashed lines.

The solid-state emission spectra of compounds **1** and **2** have been investigated at room-temperature (Fig. 3). The intense bands in the emission spectra were observed at 398 nm and 460 nm (λ_{ex} = 230 nm) for **1,** 415 nm and 462 nm (λ_{ex} = 260 nm) for **2.** It could be found that one weak emission at 462 nm (λ_{ex} = 280 nm) could be observed for free H_4bptc ligand (*Fig.* S5). According to the literature [3,19], the luminescent properties of **1** (398 nm) and **2** (415 nm) can be attributed to ligand-to-metal charge transfer and Ag—Ag interactions. Compounds with Ag—Ag interactions show emission with similar energy [20–23]. Experimental and theoretical results have proved that Ag—Ag interactions are significant for the formation of luminescent species, which has been also discussed in our previous work [24]. Moreover, the peak of 458 nm for **1** and 462 nm for **2** may be assigned to the intraligand (π–π^*) fluorescence.

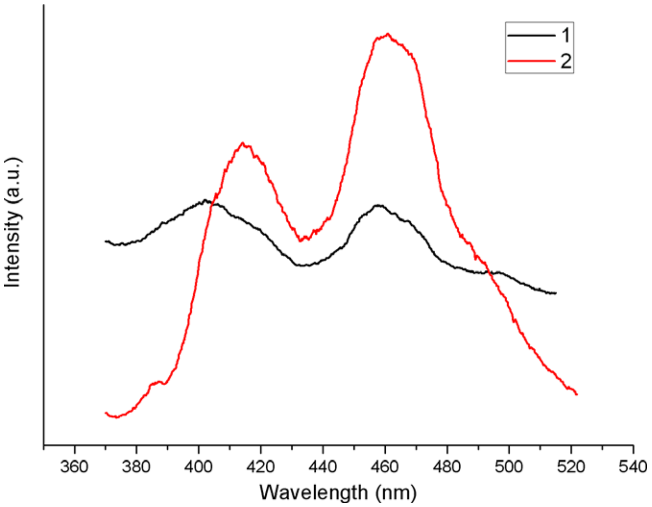

Fig. 3. Solid-state emission spectra of compounds **1** and **2** at room temperature.

In order to confirm the phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiments were carried out on **1** and **2**. The XRPD experimental and computer-simulated patterns of them are shown in *Fig.* S4. Although minor differences can be seen in the positions, intensities, and widths of some peaks, it can also be considered that the as-synthesized materials are homogeneous (*Fig.* S4).

In conclusion, we have developed two novel luminescent silver(I) compounds with H_4bptc and extended N-auxiliary ligands. Analysis of the silver compounds **1** and **2** crystal structures indicates that ligand-induced and ordinary Ag–Ag interactions can link Ag(I) ions into two kinds of ladder-like chains.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20771090) and TRAPOYT, and Specialized

Research Found for the Doctoral Program of Higher Education (No. 20050697005).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.05.004.

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[11] *Preparation of* $\{[Ag_3(Hbptc)(bpa)_2]\cdot H_2O\}_n$ (**1**) and $[Ag_2(H_2bptc)(bpp)_2]_n$ (**2**): compound **1** was obtained by the reaction of AgAc, bpa and H_4bptc in molar ratio of 4:1:1 mixed with 15 mL of aqua and 1 mL of triethylamine under hydrothermal conditions (at 150 °C for 6 days and cooled to room temperature with a 5 °C h^{-1} rate). Colorless crystals of **1** were collected in 55% yield. Anal. Calcd. for $C_{41}H_{34}Ag_3N_4O_{10}$: C 46.18, H 3.21, N 5.25. Found C 46.48, H 3.31, N 5.16. IR data (KBr, cm^{-1}): 3407 s, 3213 s, 2927 m, 2821 w, 1653 w, 1551 vs, 1414 vs, 1083 m, 980 w. *Crystal data for compound* **1**: fw = 710.23, Triclinic, $P-1$, $a = 12.2609(14)$ Å, $b = 13.1835(14)$ Å, $c = 13.6532(15)$ Å, $\alpha = 71.692(2)^\circ$, $\beta = 69.016(2)^\circ$, $\gamma = 65.056(2)^\circ$, $V = 1833.4(3)$ Å^3, $Z = 1$, $D_{Calcd} = 1.826$ g cm^{-3}; $R_1/wR_2 = 0.0375/0.1107$ $(I > 2\sigma)$ and 0.0558/0.1428 (all data); GOF = 1.061. When bpa was replaced by bpp and pH was adjusted to 3, compound **2** was gained. Anal. Calcd. for $C_{43}H_{36}Ag_2N_4O_{10}$: C 52.46, H 3.69, N 5.69. Found C 52.36, H 3.75, N 5.66. IR data (KBr, cm^{-1}): 3304 s, 3221 s, 2914 m, 1673 w, 1541 vs, 1314 vs, 1043 m, 991 w. *Crystal data for compound* **2**: fw = 984.50, Monoclinic, C2/c, $a = 14.683(6)$ Å, $b = 11.736(6)$ Å, $c = 22.187(9)$ Å, $\beta = 94.849(13)^\circ$, $V = 3810(3)$ Å^3, $Z = 4$, $D_{Calcd} = 1.698$ g cm^{-3}; $R_1/wR_2 = 0.0632/0.1482$ $(I > 2\sigma)$ and 0.2026/0.1908 (all data) ; GOF = 0.920. The carboxylate group hydrogen atoms were refined at half site occupancy in **2**. 26% of the data were observed in **2**, which may be attributed to the small measurable crystals and the relatively bad quality of data.

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