Inorganic Chemistry Communications 46 (2014) 194–197

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Syntheses, structures and properties of silver(I) complexes constructed from nitrogenous aromatic heterocyclic carboxylic acids and N-donor ligands

Hong-Ling Gao [a], Qin-Qin Zhang [a], Chi Wai Cheung [b], Yong-Ling Yi [a], Fang-Fang Li [a], Jing Qu [a], Shu-Xin Jiang [a], Xue-Ying Shi [a], Jian-Zhong Cui [a],*

[a] Department of Chemistry, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China

[b] Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, Ecole Polytecnique Fédérale de Lausanne (EPFL), ISIC-LSCI, BCH 3218, Lausanne 1015, Switzerland

ARTICLE INFO

Article history:
Received 30 March 2014
Accepted 8 May 2014
Available online 24 May 2014

Keywords:
Silver(I) complexes
Nitrogenous aromatic heterocyclic carboxylic acids
N-donor ligands
Ag···O interactions

ABSTRACT

Four new coordination complexes with silver(I) ions and nitrogenous aromatic heterocyclic carboxylic ligands, namely $[Ag_4(pztc)(phen)_4] \cdot 8H_2O$ (**1**), $\{[Ag_4(pztc)(bpe)_3] \cdot 5H_2O\}_n$ (**2**), $[Ag_4(Hmptc)_2(4,4'\text{-bpy})_3] \cdot 4.5H_2O$ (**3**), and $[Ag_2(H_2mptc)_2(2,2'\text{-bpy})_2]$ (**4**) (H_4pztc = pyrazine-2,3,5,6-tetracarboxylic acid, H_3mptc = 6-methyl-2,3,5-pyridine-tricarboxylic acid, phen = 1,10-phenanthroline, bpe = trans-1,2-bis(4-pyridyl)ethylene, 4,4′-bpy = 4,4′-bipyridine, 2,2′-bpy = 2,2′-bipyridine), have been synthesized by the self-assembly reactions and characterized by X-ray diffraction single crystal structure analysis, elemental analysis, IR, PXRD, fluorescence and thermal analysis. In **1**, four crystallographically independent silver(I) atoms are found to coordinate with only one $pztc^{4-}$ ligand. Complex **2** is a 2D grid structure. Complexes **3** and **4** are extended from 0D to 2D or 1D by the Ag···O interactions.

Building blocks play a key role in adjusting the architecture of self-assembled species, in which the selections of metal atoms and ligands are critical factors. Previous works of our group have proved that the rigid nitrogenous aromatic heterocyclic carboxylic ligands, such as pyrazine-2,3,5,6-tetracarboxylic acid (H_4pztc) and 6-methyl-2,3,5-pyridinetricarboxylic acid (H_3mptc), are suitable choices for the constructions of metal organic complexes [1–3], which not only possess the capability to chelate and bridge metal atoms in various coordination modes using the carboxylic oxygen atoms and nitrogen atoms of pyridine and pyrazine rings, but also can provide potential interaction sites to generate non-covalent interactions [4,5]. Although many complexes constructed by H_4pztc and H_3mptc have been reported, most of them focused on the reactions with lanthanide(III) [2,4] and transition metal ions such as Cu(II), Co(II), Zn(II), and Cd(II) [1,3], whereas the reactions based on silver(I) are very rare [6]. Qu reported a complex of silver(I) with H_4pztc and 4,4′-bpy, in which $pztc^{4-}$ and bpy were alternately coordinated to silver to form 2D layers. However, a new phenomenon is observed in this report. Four crystallographically independent Ag(I) atoms are coordinated with one $pztc^{4-}$ ligand in different ways, which is uncommon in Ag-coordinated complexes. As known, silver(I) ion has different electronic configuration compared with other transition metals, such as Cu(II), Co(II), Mn(II), and Ni(II), leading to the various coordination environments [7,8]. Although silver(I) ion has a d^{10} electronic configuration like Zn(II) and Cd(II), it has a tendency to display a highly versatile and irregular coordination number and geometry, which may lead to the formation of new structural motifs. Furthermore, the interactions between Ag(I···Ag(I) and Ag···O also make the complexes exhibit interesting structures and properties. To the best of our knowledge, only a few complexes of silver(I) with H_4pztc have been reported [6] and there is no precedent of silver–H_3mptc complexes. The probable reasons are that (a) silver complexes are sensitive to light, which makes the synthesis of silver complexes more difficult, and (b) silver complexes often appear as insoluble salts under aqueous conditions that would make structural analyses difficult [9,10]. To obtain the silver complexes suitable for analysis, special conditions for crystal growth are necessary, such as the use of gel permeation or ammoniacal conditions [10]. However, the use of H_2O/ethanol/acetonitrile solvent systems to enhance the solubility of the silver carboxylate complexes has been the preferred method employed by our group for preparing crystalline products suitable for X-ray analysis.

In order to enrich the structure, mixed ligands of nitrogenous aromatic heterocyclic carboxylic acid and multi-pyridine have been employed. In this work, we report the details of syntheses [11] and characterizations [12] of four new silver-containing complexes, namely $[Ag_4(pztc)(phen)_4] \cdot 8H_2O$ (**1**), $\{[Ag_4(pztc)(bpe)_3] \cdot 5H_2O\}_n$ (**2**), $[Ag_4(Hmptc)_2(4,4'\text{-bpy})_3] \cdot 4.5H_2O$ (**3**), and $[Ag_2(H_2mptc)_2(2,2'\text{-bpy})_2]$ (**4**).

H_4pztc was synthesized according to the method reported by Wolff [13]. 6-Methyl-2,3,5-pyridine-tricarboxylate acid was prepared from the oxidation of 2,6-dimethyl-3,5-pyridinedicarboxylate, which was

---

* Corresponding author.
E-mail address: cuijianzhong@tju.edu.cn (J.-Z. Cui).

http://dx.doi.org/10.1016/j.inoche.2014.05.017
1387-7003/

reported by our group [4]. Other reagents were purchased from commercial sources. X-ray crystallography reveals that complex **1** crystallizes in orthorhombic system, space group $P2_12_12_1$, which has a two-dimensional supramolecular network connected by the covalent bonds, hydrogen bonds, and π–π weak coordinative interactions. The most intriguing structural feature of **1** is that four crystallographically independent silver(I) atoms coordinate with only one pztc^{4-} ligand: Ag1, Ag2, Ag3 and Ag4, as shown in Fig. 1a. If neglecting the Ag···O contact, Ag1 is coordinated by one nitrogen atom (N1) from pztc^{4-} and two nitrogen atoms (N3 and N4) from phen ligand. Its coordination geometry can be described as a distorted Y-shaped geometry. It is worth noting that Ag2 and Ag4 adopt almost exactly the same geometry, which is coordinated by the two nitrogen atoms (N5, N6) from phen ligand and one oxygen atom (O7) from the pztc^{4-} ligand to form a slightly distorted Y-shaped geometry. Interestingly, the bond lengths and angles around Ag2 are also very similar to that around Ag4. By the way, the phen coordinated to Ag2 is disordered over two positions with site-occupancy factors of 0.5, and one site is present in Fig. 1a for clarity. However, Ag3 is coordinated by the nitrogen atoms (N7 and N8) of phen, as well as one nitrogen atom and one oxygen atom (N2, O1) of the pztc^{4-}, which give the distorted tetrahedron geometry. As in **1**, the hydrogen bonding interactions between pztc^{4-} and free water molecules link the discrete asymmetric structure unit $[Ag_4(pztc)(phen)_4]$ to generate a 1D chain structure. The hydrogen-bonding contacts (Å, °) for complex **1** are shown in Table S3. In addition, the strong π–π interactions (2.701 Å) (Fig. 1a) between the adjacent 1D chains make complex **1** extend to a two-dimensional layer (Fig. 1b).

Compound **2** crystallizes in triclinic system, space group $P\bar{1}$, which has a two-dimensional network. As shown in Fig. 2a, the asymmetric structure unit of **2** consists of two silver(I) atoms which are crystallographically independent, half pztc^{4-} ligand, and 1.5 bpe ligands. Ag1 is coordinated in a slightly distorted tetrahedron geometry by two oxygen atoms (O1, O3B) and a nitrogen atom (N1) from a pztc^{4-} ligand and another nitrogen atom (N2) from a bpe, while Ag2 is coordinated by two nitrogen atoms (N3, N4) from two different bpe ligands and a oxygen atom (O4) from pztc^{4-} ligand to form a slightly distorted T-shaped geometry. In **2**, four silver(I) atoms around pztc^{4-} are connected by two bpe ligands to form a stairlike one-dimensional chain with boxlike units. Furthermore, the adjacent chains are extended to a two dimensional layer connected by another bpe with Ag2-N4, as illustrated in Fig. 2b.

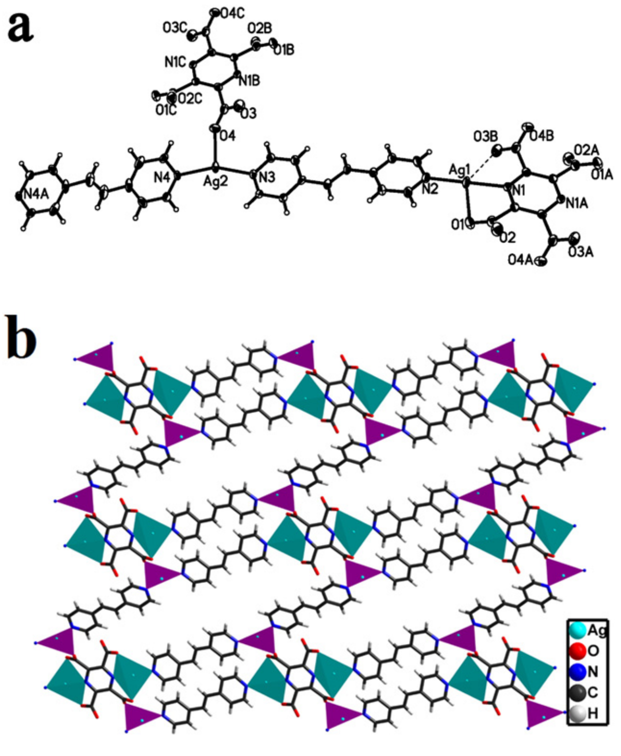

Fig. 2. (a) Coordination environment of Ag(I) in **2** shown with ellipsoids at the 50% probability level. (b) The polyhedral picture of 2D layer structure in **2**.

X-ray crystallography reveals that complex **3** crystallizes in triclinic system, space group $P\bar{1}$, which has a three-dimensional supramolecular network connected by the covalent bonds, hydrogen bonds, and Ag···O coordinative interactions. As shown in Fig. 3a, two crystallographically independent silver(I) atoms are present: Ag1 and Ag2. If the Ag···O interaction is neglected, Ag1 is coordinated with two nitrogen atoms (N3, N4) from two different bpy ligands to form a nearly linear geometry. Ag2 adopts a slightly distorted Y-shaped geometry and is coordinated by one oxygen atom (O1) and one nitrogen atom (N1) from a Hmpdc^{2-} ligand and another nitrogen atom (N2) from bpy ligand. It is worth noting that the discrete asymmetric structure unit of $[Ag_4(Hmptc)_2(4,4'\text{-bpy})_3]$ is extended to a two-dimension grid structure (Fig. 1b) because of the existence of the Ag···O interactions [Ag1···O5B = 2.879 Å, Ag1···O6B = 2.649 Å,

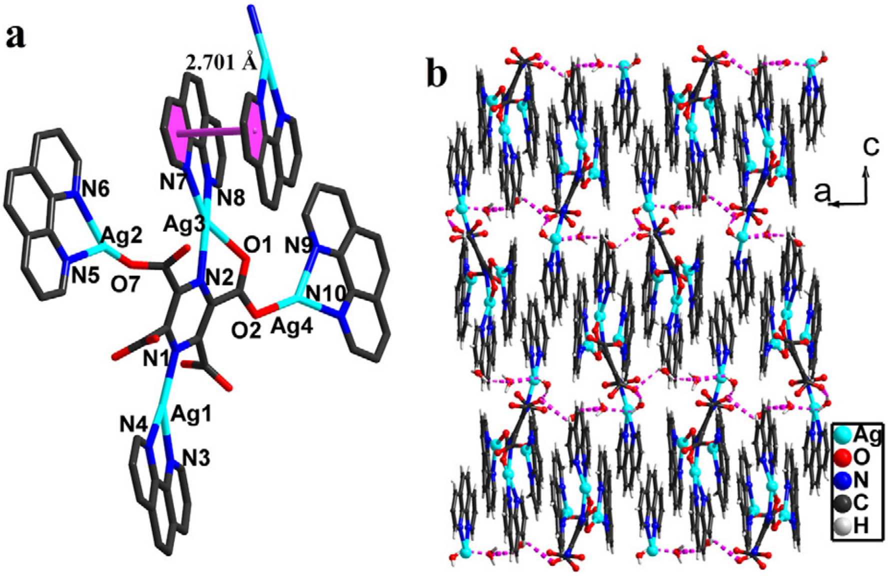

Fig. 1. (a) Coordination environment of the silver ion and the partial π–π interactions in **1**. (b) 2D layer structure of **1** formed by π–π interactions.