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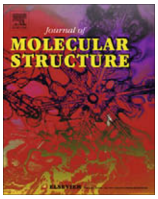

Low dimensional metal–organic frameworks (MOFs) constructed from simple aminopyrimidyl derivatives: From oligomer to single neutral zigzag chain and doubly ionic chains

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ABSTRACT

Three low dimensional silver(I) complexes of the formula $[Ag(L_1)][Ag(L_1)(CF_3SO_3)_2]$ (**1**), $[Ag_2(L_2)_3(CF_3SO_3)_2]$ (**2**), and $[Ag(L_2)(CF_3CO_2)]_n$ (**3**), where L_1 = 2-amino-4-methoxy-6-methylpyrimidine and L_2 = 2-amino-4,6-dimethoxypyrimidine, have been synthesized and structurally characterized by single-crystal X-ray diffraction. Complex **1** is a new rarely reported Ag^I one dimensional (1D) coordination polymer, which consists of independently cationic and anionic doubly chains. The hydrogen bonds and Ag···O weak interactions between chains extend **1** into two dimensional (2D) interlayer networks. Complex **2** is a simple oligomer and two neighbored oligomers interact to produce a supramolecular dimer through hydrogen bonds, weak $Ag\cdots N_{(amino)}$ interactions and anion–π interactions. Complex **3** displays 1D neutral zigzag chain which is structurally very similar to the 1D cationic one in **1**, if neglecting counter anions in the former. The adjacent chains in **3** are further interlinked to generate 1D ladder structure via Ag···O weak interactions and N–H···O intermolecular hydrogen bonds. The results reveal that the nature of the counter anions and organic ligands all has great impact on the structure of the complexes. The luminescence properties of the synthesized silver complexes were also investigated in the solid state at room temperature.

1. Introduction

The programmed self-assembly of coordination networks has attracted intense interest not least because of the intricate structural topologies that can be created [1–4]. As compared to low dimensional frameworks, high dimensional ones were produced more easily due to the high affinity of ligands to metal ions. Low dimensional coordination polymers not only can be found to show highly unusual topologies when additional directional interactions are considered [5–6], but show interesting unique electro-conductive, non-linear optical and magnetic properties which are different from those of high dimensional coordination polymers. Linear bridging ligands such as pyrazine or 4,4′-bipyridine were among the first ligands used in the specific formation of low dimensional coordination polymers because they were simple, readily available, and looked to allow for more predictable formation of network structures [7–9]. On the other hand, the angular-type bridging ligands which are equally simple but can afford 1D chain structures with zigzag, wedge-shaped and helical geometries, were the other ligands considered. One kind of such simple ligands is heterocyclic pyrimidine and its derivatives such as hydroxypyrimidine. When one dimensional coordination polymeric products formed using such ligands are considered, it can be seen that they will usually give rise to zigzag structures as a result of their shape. Many one dimensional metal–organic polymers have been prepared using pyrimidine or its derivatives [10–13]. Recently, we began to concentrate on 2-aminopyrimidine and its derivatives in which the central amino is a hydrogen-bonding synthon, and potential hydrogen-bond acceptors are common in supramolecular systems with other ligands, anions, or solvent molecules all available. We have successfully constructed a series of Ag^I complexes with 2D and 3D structures by using 2-aminopyrimidine and its derivatives [14–16]. As extension of investigation, we will focus on low dimensional metal–organic frameworks (MOFs) with the principal aim to obtain unusual topologies. In this paper, we report the investigation of the effect of counter anions and substituents of aminopyrimidine on the structures of low dimensional Ag^I complexes. The resulting complexes may be divided into 0D oligomer, 1D zigzag chain and 1D doubly ionic chains. For 1D doubly ionic chains, as far as we know, no these structures constructed from simple aminopyrimidine ligands have been reported.

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2. Experimental procedure

2.1. Materials and methods

All chemicals and solvents used in the syntheses were analytical grade and used without further purification. Infrared spectra were recorded with a Nicolet AVATAR FT-IR 360 spectrometer using the KBr pellet technique. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. Photoluminescence measurements were performed on a Hitachi F-4500 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate at room temperature.

2.2. Syntheses of complexes **1**, **2** and **3**

2.2.1. Synthesis of complex $[Ag(L_1)][Ag(L_1)(CF_3SO_3)_2]$ (**1**)

A methanol solution (5 ml) of L_1 (70 mg, 0.5 mmol) was slowly diffused into an aqueous solution (5 ml) of $AgCF_3SO_3$ (128 mg, 0.5 mmol) in a test tube. Colorless crystals of **1** were formed at the interface of the solvent in two weeks and were obtained in 46% yield. Anal. Calcd (found) for $Ag_2C_{14}H_{18}N_6O_8F_6S_2$: C, 21.25 (21.23); H, 2.34 (2.29); N, 10.68 (10.61)%. IR (cm^{-1}): 3420 (s), 3333 (m), 1654 (m), 1595 (m), 1467 (m), 1391 (m), 1356 (w), 1205 (m), 1134 (m), 1039 (m), 937 (w), 838 (m), 834 (m), 793 (m), 580 (m), 557 (m).

2.2.2. Synthesis of complex $[Ag_2(L_2)_3(CF_3SO_3)_2]$ (**2**)

The synthesis of **2** was similar to that of **1**, but with ligand L_2 (78 mg, 0.5 mmol) in place of ligand L_1. Colorless crystals of **2** were obtained in 53% yield. Anal. Calcd (found) for $Ag_2C_{20}H_{27}N_9O_{12}F_6S_2$: C, 24.44 (24.53); H, 2.87 (2.78); N, 12.75 (12.87)%. IR (cm^{-1}): 3415 (m), 3314 (m), 3192 (m), 3020 (m), 1656 (m), 1585 (m), 1457 (m), 1386 (m), 1214(s), 1164 (m), 1043 (m), 930 (m), 790 (m), 678 (m), 559 (m), 514 (m).

2.2.3. Synthesis of complex $[Ag(L_2)(CF_3CO_2)]_n$ (**3**)

The synthesis of **3** was similar to that of **2**, but with silver salt $AgCF_3CO_2$ (110 mg, 0.5 mmol) in place of $AgCF_3SO_3$. Colorless crystals were obtained in 44% yield. Anal. Calcd (found) for $AgC_8H_9N_3O_4F_3$: C, 25.59 (25.55); H, 2.35 (2.41); N, 11.25 (11.17)%. IR (cm^{-1}): 3418 (m), 3311 (m), 3190 (m), 1685 (s), 1634 (m), 1591 (m), 1457 (m), 1430 (m), 1390 (m), 1212 (s), 1144 (m), 1049 (m), 985(w), 927 (w), 838 (m), 775 (m), 562 (m), 549 (m).

2.3. X-ray crystallography

Data collections were performed on Bruker SMART Apex CCD diffractometer with graphite monochromated Mo Kα radiation at 173 K for **1**, **2** and **3**. Absorption corrections were applied by using the multi-scan program SADABS [17a]. Structural solutions and full-matrix least-square refinements based on F^2 were performed with the SHELXS 97 [17b] and SHELXL 97 [17c] program packages, respectively. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated positions and included in the refinement in the riding model approximation. Crystal data as well as details of data collection and refinement for the complexes **1**–**3** are summarized in Table 1, and selected bond lengths and angles are shown in Table 2.

3. Results and discussion

3.1. Construction

The syntheses of complexes **1**–**3** are summarized in Scheme S1. The formation of the products is not significantly affected by changes of the reaction mole ratio of ligands to metal ions, and the resultant crystals are insoluble in water and common organic solvents. The reaction of $AgCF_3SO_3$ with L_1 generates one new rarely reported 1D coordination polymer (**1**) consisting of independently cationic and anionic doubly chains. The hydrogen bonds and Ag···O weak interactions between chains extend **1** into 2D interlayer network. On the other hand, the reactions of L_2 with $AgCF_3SO_3$ and $AgCF_3CO_2$ yield 0D oligomer (**2**), 1D neutral zigzag chain (**3**), respectively. In complexes **1**–**2**, 2-aminopyrimidine and its derivatives adopt similar coordination modes, bidentate N,N′-donor ligands binding with silver atoms, while the different substitutions of 2-aminopyrimidyl ligands in the same substitutional positions in these complexes result in distinct structural motifs. The different structures of complexes **2**–**3** are caused by the difference in coordination ability and geometry of the counter anions. In addition, the secondary forces such as intra- and intermolecular hydrogen bonds, anion–π interactions and π–π interactions also play important role in the overall architecture and stabilization of the complexes.

3.2. Crystal structures of complexes **1**–**3**

Single-crystal X-ray diffraction analysis reveals that **1** is a one dimensional (1D) chain, and the local coordination environment around Ag(I) is shown in Fig. 1a and b. Different from other 1D chain complexes, **1** is made up of independently cationic chain $[Ag(L_1)]^+$ and anionic chain $[Ag(L_1)(CF_3SO_3)_2]^-$. In the anion chain $[Ag(L_1)(CF_3SO_3)_2]^-$, the central silver is coordinated by two oxygen atoms from two triflate anions and two nitrogen atoms from two L_1 ligands in a distorted tetrahedral geometry, with an average Ag–O bond length of 2.550(4) Å and an average Ag–N bond length of 2.260(3) Å. Intramolecular hydrogen bonds are observed in the anionic chain, involving the amino groups of L_1 with the oxygen atoms on the coordinated $CF_3SO_3^-$ anions [2.845(5) and 2.872(5) Å for N(5)···O(3) and N(5)···O(6A), symmetry for A: x, $-y + 3/2$, $z + 1/2$]. The charge balance comes from another 1D cationic chain, $[Ag(L_1)]^+$. In this $[Ag(L_1)]^+$ unit, the silver ion is coordinated by two pyrimidyl nitrogen atoms of two L_1 ligands in a distorted linear geometry, with the bond angles of N(3)–Ag(2)–N(4) being 163.3(1)° and the bond lengths of Ag(2)–N(3) and Ag(2)–N(4) being 2.160(3) and 2.171(3) Å, respectively. The average Ag–N distance being 2.166(3) Å, shorter than that in the $[Ag(L_1)(CF_3SO_3)_2]^-$ unit. Each L_1 ligand bridges two silver atoms in a "μ_2–η^1–η^1"mode to form a 1D cationic zigzag polymeric chain motif wherein the closest Ag. . .Ag separation is 6.172 Å. (Fig. 1b).

The unusual structural feature of **1** is the independence of the cationic and anionic chains. To the best of our knowledge, most of the reported 1D chains are single neutral ones and some polymeric complexes containing two kinds of chains have been reported, however, the chains are usually not independent and are connected by coordination bonds [18,19]. In **1**, there is no direct bonding interaction between the two chains, only N–H···O intermolecular hydrogen bonds are observed, where the amino groups of L_1 ligands from cation chains serve as donors while the oxygen atoms of triflate anions from anionic chains act as acceptors [2.968(5) and 2.897(5) Å for N(6)···O(1) and N(6)···O(4)]. Aside from the hydrogen bonds between the chains, there are also weak Ag–O interactions between the layers: the oxygen atoms of triflate anions from anionic chains coordinate weakly to the silver ions of cationic chains with Ag···O distances in the range of 2.892–2.931 Å, which are a bit longer but still fall in the 'secondary bonding' range (the sum of Van der Waals radii of Ag and O is 3.20 Å) [20]. Through non-covalent interactions mentioned above, the cationic and anionic double chains assembly into two dimensional (2D) interlayer network along *b*-axis (Fig. 1c). To the best of our knowledge, **1** is the first example consisting of independently cationic and anionic chains in a