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Syntheses and crystal structures of four silver(I) complexes based on 2-(4-pyridyl)benzimidazole

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Abstract

Four new silver(I) complexes constructed with 2-(4-pyridyl)benzimidazole, namely, $[Ag(PyBIm) \cdot H_2O] \cdot NO_3$ (**1**), $[Ag(PyBIm) \cdot H_2O] \cdot ClO_4$ (**2**), $[Ag_2(PyBIm)_2] \cdot (SiF_6) \cdot 2H_2O$ (**3**) and $[Ag(PyBIm) \cdot (HBDC)]$ (**4**) (PyBIm = 2-(4-pyridyl)benzimidazole, BDC = 1,3-benzenedicarboxylate) have been synthesized and characterized by X-ray crystallography. All the silver(I) atoms in complexes **1**–**4** are bridged by the different PyBIm ligands via N_{Py} and N_{BIm} into one-dimensional "zigzag" chains. The anions do not coordinate to the silver(I) atoms and only act as counter ions in complexes **1**–**3**. Due to the anions, different hydrogen bonding systems are found in those three compounds, resulting in the different crystal packing. Through hydrogen bonding interactions, the structures of complexes **1**–**3** display a double layer, a three-dimensional framework and a novel double chain, respectively. In complex **4**, the $HBDC^-$ anions act not only as a counter ion but also as bridging ligands, which lead the "zigzag" $[Ag_2(PyBIm)_2]_\infty$ chain into a two-dimensional undulating sheet. The sheets are connected through hydrogen-bonding as well as π–π interactions into a three-dimensional framework. The thermal stabilities of the four complexes and anion exchange properties of complexes **2** and **3** were also studied.

Keywords: Silver complexes; Benzimidazole; Polymer; Coordination complex; Anion influence; Double-layer; Guest molecule

1. Introduction

In inorganic–organic supramolecular architectures derived from building blocks that are linked by coordinate covalent bonds or hydrogen bonds, π–π interactions constitute an active field that impinges on the synthesis of interesting topological structures and potential function materials [1]. However, the influence on coordination polymers is not well understood, although the self-assembly of those architectures has been documented to be heavily influence by various factors such as functionality and denticity of the ligands [2], molar ratio of the reagents, the pH values of the solution [3], and steric requirements of the counter ions [4]. The exploration of synthetic strategies and routines is a long-term challenge, and a great deal of work is required to extend the knowledge of relevant structural types and establish proper synthetic strategies leading to desirable supramolecular species.

Recently, we have focused on the research of silver(I) complexes based on 2-(4-pyridyl)benzimidazole [3c,3d]. Compared with the complexes based on 2,4′-bipyridine [5], the non-coordinating N–H groups of the benzimidazolyl form strong hydrogen-bonding interactions with lattice water and sulfate groups, leading to a wholly different crystal packing. The results also demonstrate that the different pH values result in the sulfate existing in different modes, bringing about crystal structures that are greatly different from each other.

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In this paper, we report four new silver(I) complexes based on PyBIm, namely, [Ag(PyBIm) · H_2O] · NO_3 (**1**), [Ag(PyBIm) · H_2O] · ClO_4 (**2**), [Ag_2(PyBIm)$_2$] · (SiF_6) · $2H_2O$ (**3**) and [Ag(PyBIm) · (HBDC)] (**4**). The Ag(I) atoms are three coordinated in complexes **1** and **2** but two and four coordinated in **3** and **4**, respectively. All the silver(I) atoms of the complexes are bridged by PyBIm via N_{Py} and N_{BIm} into "zigzag" chains. The counter ions have a great effect on the hydrogen bonding systems and coordination spheres, leading to great differences in the crystal packing. Through the hydrogen bonding interactions, the structures of **1**–**3** display a double-layer, a three-dimensional framework and a novel double-chain, respectively. As for complex **4**, the bridging $HBDC^-$ anions connect the $[Ag(PyBIm)]_\infty$ zigzag chain into a two-dimensional coordinate sheet. The counter ions effects and hydrogen-bonding interactions on the polymeric structures represent a new contribution to this active area of study.

2. Experimental

2.1. Materials and methods

The ligand 2-(4-pyridyl)benzimidazole (PyBIm) was synthesized according to the procedure reported by Fieselman [6]. Other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were carried out on an EA1110 CHNS-0 CE element analyzer and the IR spectra (KBr pellets) were recorded at a Nicolet Magna 750 FT-IR spectrometer in the range 400-4000 cm^{-1}. Thermogravimetric analyses (TGA) were performed with a Netzsch STA-499C thermoanalyzer under N_2 (30–800 °C range) at a heating rate of 10 °C/min. X-ray powder diffractions (XRPD) were performed on a Bruker D8 Advanced diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at room temperature.

Safety notes. Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.

*Synthesis of [Ag(PyBIm) · H_2O] · NO_3 (**1**).* An acetonitrile (5 mL) solution of $AgNO_3$ (0.085 g, 0.50 mmol) was slowly diffused into an ethanol (5 mL) solution of PyBIm (0.097 g, 0.50 mmol). Colorless crystals formed in about two weeks (80% yield) *Anal.* Calc. for $C_{12}H_{11}AgN_4O_4$: C, 37.62; H, 2.89; N, 14.62. Found: C, 37.15; H, 3.12; N, 14.13%. IR (KBr pellet, cm^{-1}): 3434s, 1613s, 1559w, 1537w, 1495m, 1480w, 1443, 1414, 1385s, 1357s, 1229m, 1072m, 1041m, 1017w, 838m, 821m, 782s, 700m, 556m, 502w.

*Synthesis of [Ag(PyBIm) · H_2O] · ClO_4 (**2**).* An ethanol solution (5 mL) of $AgClO_4$ (0.06 g, 0.30 mmol) was slowly diffused into an ethanol solution of PyBIm (0.06 g, 0.30 mmol). Colorless crystals formed in about three weeks (75% yield). *Anal.* Calc. for $C_{12}H_{11}AgClN_3O_5$: C, 34.27; H, 2.64; N, 9.99. Found: C, 34.15; H, 3.12; N, 10.13%. IR (KBr pellet, cm^{-1}): 3496s, 1612s, 1537w, 1494m, 1481w, 1436s, 1319m, 1285w, 1226m, 1120vs, 1085vs, 969w, 932w, 838m, 816m, 775s, 744w, 672w, 624s, 557w, 500w.

*Synthesis of [Ag_2(PyBIm)$_2$] · (SiF_6) · $2H_2O$ (**3**).* A solution of Ag_2SiF_6 (0.22 g, 0.61 mmol), PyBIm (0.24 g, 1.22 mmol), NaF (0.025 g, 0.61 mmol) and H_2O (15 ml) was stirred under ambient conditions, then sealed in a Teflon-lined stainless steel vessel, heated at 150 °C for 5 days and cooled to room temperature. The resulting product was recovered by filtration, washed with distilled water and dried in air (65% yield). *Anal.* Calc. for $C_{24}H_{22}Ag_2F_6N_6O_2Si$: C, 36.75; H, 2.83; N, 10.72. Found: C, 36.54; H, 3.09; N, 10.79%. IR (KBr pellet, cm^{-1}): 3445s, 1614s, 1560w, 1541m, 1496w, 1481w, 1439s, 1384w, 1319m, 1287w, 1227m, 1118s, 1084s, 1065s, 1022s, 839m, 818m, 775s, 745s, 558m, 500w, 473m.

*Synthesis of [Ag(PyBIm)(HBDC)] (**4**).* A solution of Ag_2O (0.069 g, 0.30 mmol), PyBIm (0.24 g, 1.22 mmol), H_2BDC (0.101 g, 0.61 mmol) and H_2O (15 ml) was stirred under ambient conditions, then sealed in a Teflon-lined stainless steel vessel, heated at 150 °C for 5 days and cooled to room temperature. The resulting product was recovered by filtration, washed with distilled water and dried in air (60% yield). *Anal.* Calc. for $C_{20}H_{14}AgN_3O_4$: C, 51.31; H, 3.01; N, 8.97. Found: C, 51.52; H, 3.26; N, 9.06%. IR (KBr pellet, cm^{-1}): 3433s, 1416s, 1566m, 1778w, 1438m, 1384s, 1319m, 1283w, 1228w, 1095w, 1069m, 936m, 839m, 751s, 687m, 539w, 507w.

2.2. X-ray crystallography

Suitable single crystals of **1**–**4** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. An empirical absorption correction was applied using the SADABS program [7]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELXTL-97 program package [8]. Attempts to locate the hydrogen atoms of water in complex **3** failed; the other hydrogen atoms on carbon and nitrogen atoms were generated geometrically. The crystallography details for the structure determination of complexes **1**–**4** are presented in Table 1. Selected bond lengths and bond angles are listed in Table 2.

2.3. Result and discussion

2.3.1. Syntheses and general characterization

Complex **1** can also be obtained by hydrothermal methods, but the crystals obtained were not suitable for X-ray diffraction. As for complex **2**, it can be obtained by hydrothermal methods (the reaction temperature might be better less than 120 °C for security considerations) with the