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Crystal structure, microbiological activity and theoretical studies of Ag(I) and Cu(I) coordination polymers with 1,1′-(butane-1,4-diyl)bis (3-methylimidazoline-2-thione) ligand

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ABSTRACT

Reaction of 1,1′-(butane-1,4-diyl)bis(3-methylimidazoline-2-thione) (bbit) with appropriate silver(I) and copper(I) salts at room temperature leads to the formation of $\{[Ag(\mu_2\text{-bbit})](BF_4)\}_n$ (**1**) and $\{[Cu_2(\mu\text{-bbit})_3](PF_6)_2\}_n$ (**2**) coordination polymers. These compounds have been fully characterized by using the single crystal X-ray diffraction, XRPD, TGA, elemental analysis, infrared spectroscopy, antibacterial activity and molecular docking studies. Crystal structure of (bbit) shows that the molecule has a center of symmetry lies at the mid-point of the $-(CH_2)_4-$ spacer between the two imidazole-2-thione rings. In the cationic 3D structure of **1**, silver atom has a distorted tetrahedral coordination geometry and each of the centrosymmetric μ_2-bbit ligands with an anticonformation bridging two crystallographically related silver atoms to form a double-bridged $Ag(\mu_2\text{-}S)_2Ag$ core as a basic building block. Coordination mode of the bbit ligands and geometry around the metal ions in polymers **1** and **2** are different. Each of the copper atoms in **2** has a trigonal planar CuS_3 environment and μ-bbit act as a bridging bidentate ligand, so that two of the CuS_3 motifs are interconnected by a pair of μ-bbit ligands through the thione sulfur atoms to generate a 22-membered $[Cu_2(\mu\text{-bbit})_2]^{2+}$ ring. The adjacent $[Cu_2(\mu\text{-bbit})_2]^{2+}$ cores are linked by a single μ-bbit ligand to form a 1D chain structure. Additionally, the adjacent 1D chains are extended into a non-covalent 3D network structure by the intermolecular P—F...H hydrogen bonds. The in vitro antibacterial studies of bbit, polymers **1** and **2** showed that, polymer **1** was able to inhibit growth of the tested bacteria, whereas the bbit ligand has a weak and polymer **2** showed no antibacterial activity against these bacteria.

1. Introduction

In coordination chemistry, silver(I) and copper(I) ions with variable coordination numbers and versatile coordination geometries are widely used for the construction of one, two- or three-dimensions coordination polymers [1–9]. The chemistry of these ions is largely based upon coordination to ligands with S or N donor atoms. Among the S, N donor ligands heterocyclic thioamides with a variety of coordination modes are of particular interest. Thus, in the past two decades or so, a great deal of research has been done on the synthesis and structural characterization of metal complexes containing heterocyclic thiones as ligands [10–18]. The chemical interest of these thiones lies in the fact that they are potentially ambidentate or multi-functional donors with the exocyclic S and heterocyclic N atoms available for coordination. Their biological interest arises from their structural analogy to thiolated nucleosides. In this context, our research has been focused for some time on coordination compounds of Cu(I), Ag(I), Cd(II) and Zn(II) ions with a range of heterocyclic thiones such as 1-methylimidazoline-2(3H)-thione (Hmimt) [19,20], imidazolidine-2-thione (Imt) [21] and 1,3-diazepane-2-thione (Diap) [22]. On the other hand, in recent years many researchers have focused their attention on the synthesis and investigation of new metal-based antibacterial agents in order to design complexes with better biological activity and lower toxicity [23–44]. In addition, molecular docking analysis is a useful approach for understanding the way in which a drug interacts with a protein and evaluate the factors which have a direct influence on the drug-binding affinity [45–57]. Herein, we describe the synthesis and characterization of

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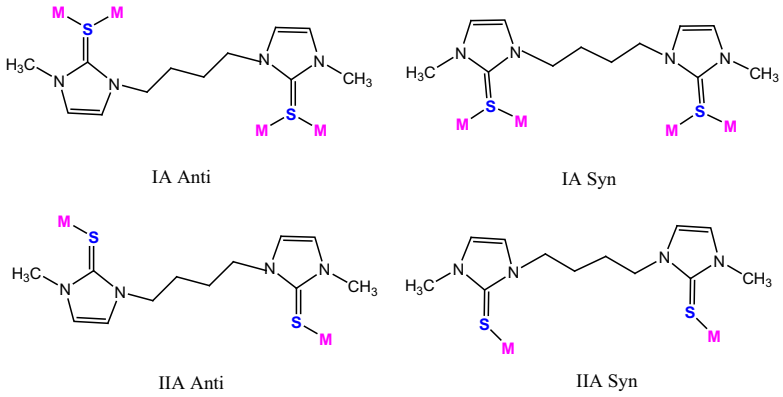

Scheme 1. The conformation and coordination modes of 1,1′-(butane-1,4-diyl)bis(3-methylimidazoline-2-thione).

two new silver(I) and copper(I) coordination polymers with different topologies formed by the 1,1′-(butane-1,4-diyl)bis(3-methylimidazoline-2-thione) (bbit) ligand and appropriate silver (I) and copper(I) salts; in order to investigate the effect of the variation of metal ions, size of BF_4^- and PF_6^- anions and coordination modes of bbit (Scheme 1) on the structural topology of the coordination polymers and study their antibacterial activity and molecular docking.

2. Experimental

2.1. Materials

All experiments were carried out in air. Starting materials were purchased from commercial sources and used without further purification. The bbit ligand was prepared from them by the published method with some modification [58].

2.2. Preparation of $\{[Ag(\mu_2\text{-bbit})](BF_4)\}_n$ (**1**)

$NaBF_4$ (0.055 g, 0.5 mmol) and $AgNO_3$ (0.084 g, 0.5 mmol) were added to a mixture of methanol–water solution (3:1, 20 mL) and the mixture was stirred at room temperature for 20 min. To this solution, bbit (0.141 g, 0.5 mmol) was added and the mixture was stirred for 30 min. The reaction mixture was filtered off and the colorless supernatant was decanted. The precipitate was washed with methanol (2 × 10 mL) and chloroform (2 × 10 mL) and dried in vacuo to give the required product as a white powder (0.250 g, yield: 80% based on Ag). Colorless needle single crystals suitable for X-ray crystallography were obtained by adding a stoichiometric amount of $NaBF_4$, $AgNO_3$ and bbit in the main arm of a branched tube. A mixture of methanol–water solution (3:1 v/v) was added to fill the arms. The tube was sealed and the arm containing the reagents immersed in an oil bath at 60 °C, while the other arm was kept at ambient temperature (Fig. 1). After four days, the colorless crystals of **1** were deposited in the cooler arm. Mp = 230 °C. *Anal.* Calc. for $C_{12}H_{18}AgBF_4N_4S_2$: C, 30.20; H, 3.80; N, 11.74; S, 13.44. Found: C, 29.30; H, 3.173; N, 11.54; S, 13.55. Selected IR (KBr, cm^{-1}): *v* —CH_2— of spacer) 3183–2920 (m), 1570 (s), 1477 (s), 1418 (s), 1237 (s), 1181 (m), *v* (BF_4^-) 1006–1084 (vs), 788 (m), 732 (s), 674 (m), *v*(C=S) 519 (m), 478 (m).

2.3. Preparation of $\{[Cu_2(\mu\text{-bbit})_3](PF_6)_2\}_n$ (**2**)

$Cu(CH_3CN)_4PF_6$ (0.100 g, 2 mmol) in acetonitrile (15 mL) was added to bbit (0.135 g, 3 mmol) in dichloromethane (10 mL). The mixture was stirred for 3 h and then filter to remove any insoluble material. The cubic shaped crystals of **2** were obtained by slow evaporation of the solvent after one day. Mp = 250 °C. *Anal.* Calc. for $C_{36}H_{54}Cu_2P_2F_{12}N_{12}S_6$: C, 34.19; H, 4.30; N, 13.29; S, 15.21. Found: C, 34.40; H, 4.541; N, 13.53; S, 15.71. Selected IR (KBr, cm^{-1}): *v* —CH_2— of spacer) 3183–2920 (m), 1566 (m), 1476 (s), 1415 (s), 1252 (m), 1225 (m), 1188 (m), *v* (PF_6^-) 842 (vs) and 557 (s), 724 (m), 679 (m), *v*(C=S) 517 (m), 478 (m).

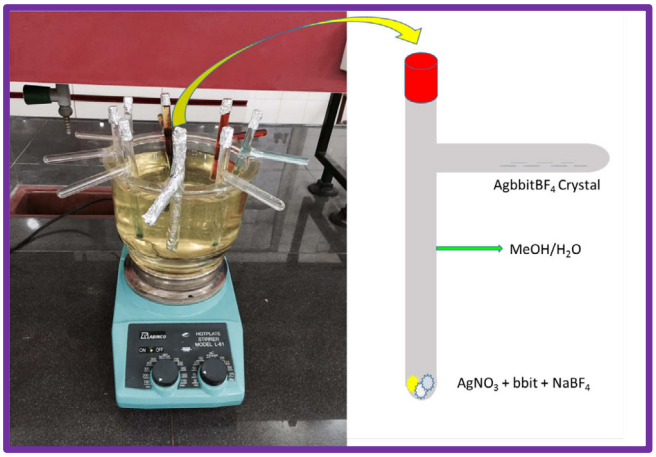

Fig. 1. Apparatus for the preparation of suitable crystals of **1**.

2.4. Measurements

Infrared spectra (4000–400 cm^{-1}) were recorded from KBr disks with a BOMEN MB102 FT-IR spectrometer. Elemental analysis for C, H and N were performed on a Thermo Finigan Flash EA 1120 CHN analyzer. Thermal analysis were performed on a Bahr-STA 503 TG/DTA thermal analyzer under dynamic nitrogen. A ramp rate of 10 °C·min^{-1} in the range of 50–1200 °C was used. X-ray powder diffraction patterns were recorded on a Philips X'Pert Pro diffractometer (Cu Kα radiation, λ = 1.54184 Å) in the 2θ range 5–50°.

2.5. X-ray crystallography

Single crystal data collections and corrections for bbit ligand and compounds **1** and **2** were done at 100(2) K with Bruker D8Venture diffractometer using graphite mono chromated Mo Ka (λ = 0.71073 Å). The structures were solved by direct methods with SIR97 [59] and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [60]. The molecular structure plot was prepared using ORTEPIII, DIAMOND and MERCURRY [61].