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Short communication

Synthesis, crystal structure and anti-tumor activity of a novel 3D supramolecular compound constructed from Strandberg-type polyoxometalate and benzimidazole

Xiaoshu Qu *, Hui Feng, Chao Ma, Yanyan Yang, Xiaoyang Yu

Department of Pharmacy, Jilin Institute of Chemical Technology, Jilin City 132073, PR China

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ABSTRACT

A novel 3D supramolecular compound assembled from Strandberg-type polyoxometalate and benzimidazole $[Hbiz]_5[HMo_5P_2O_{23}]\cdot 5H_2O$ (**1**, biz = benzimidazole) was synthesized with a convenient aqueous solution method and structurally characterized through single-crystal X-ray diffraction, elemental analysis, IR and UV–vis spectrum analyses. Single-crystal X-ray analysis revealed that the title compound crystallized in the monoclinic system space group $P2_1/c$ with $a = 11.415(2)$, $b = 33.311(7)$, $c = 13.941(3)$ Å, $\beta = 99.2279(3)°$, $V = 5232.0(18)$ Å^3, and $Z = 4$. Compound **1** was composed of one $[HMo_5P_2O_{23}]^{5-}$ polyanion, five protonated biz cations, and five crystal water molecules; it displayed a 3D supramolecular structure through electrostatic attraction, hydrogen bonding, and π–π interactions. The experiment on anti-tumor activities in vitro showed that compound **1** inhibited human neuroblastoma SHY5Y cells and demonstrated dose dependency and selectivity.

Polyoxometalates (POMs) are aggregates of early transition metal cations, such as the d^0 species tungsten (W), molybdenum (Mo), niobium (Nb), antimony (Sb), and vanadium (V) in their highest oxidation states linked together by sharing oxygen atoms [1]. With the rapid progress of structures, the biological activities of POMs, including antitumor, anti-viral, and anti-bacterial, have been extensively investigated [2]. Research has shown that many POMs are potential anti-tumor drugs and that the therapeutic effects of several POMs on cancer and leukemia are even better than those of certain commercially available drugs [3].

However, many issues still hinder the practical application of POMs as inorganic pharmaceuticals in clinical cancer treatment. The most significant among these issues is the cytotoxicity of POMs when used in normal cells; the side effects of POMs as a medicine need to be addressed by increasing cell specificity [4]. POM-based hybrid complexes, in which electrostatic interaction or covalent bonding links anionic POM clusters and organic ligands, is a versatile method to maximize the synergistic effect of inorganic and organic segments while increasing the anti-tumor efficacy and selectivity of POMs. Many studies have reported that POM-based compounds composed of organic groups, such as cholic acid [5], amino acid [6], peptides [7], and bisphosphonate [8], present the potential to enhance the anti-tumor activity and reduce the toxicity of POMs.

Thus, in the current study, diphosphopentamolybdate $[H_xP_2Mo_5O_{23}]^{-(6-x)}$ (x = 0, 1, 2) (denoted as P_2Mo_5) was selected as the building block, and benzimidazole (denoted as biz) was used as the organic substrate to construct a new supramolecular assembly in an aqueous solution. This study is of interest because of the biological importance of molybdenum(VI) and benzimidazole. Among the various types of POMs, P_2Mo_5 is one of the most well-characterized and well-understood [9]. It is a stable cluster anion occurring in aqueous solutions under self-assembly conditions over a wide range of pH values in the presence of phosphoric acid [10]. A number of supramolecular compounds with P_2Mo_5 as the building blocks have been reported in literature [11].

Meanwhile, biz and its derivatives exhibit pharmacological activities, such as anti-microbial, anti-viral, anti-cancer, anti-inflammatory, and analgesic. Extensive studies have been conducted on biz derivations in the field of medicinal chemistry [12].

In this study, a novel 3D open supramolecular framework, $[Hbiz]_5[HMo_5P_2O_{23}]\cdot 5H_2O$ (**1**), was constructed from P_2Mo_5 and biz through hydrogen bonds, electrostatic interactions, and π-π stacking interactions. Meanwhile, MTT assay was employed to compare the inhibitory effect of **1**, biz and $Na_6(P_2Mo_5O_{23})\cdot 13H_2O$ (abbreviated form: NaP_2Mo_5) against human tumor neuroblastoma cells SHY5Y and human umbilical vein endothelial cells EVC-304 in vitro.

The water-solution compound **1** was prepared by a reaction of $Na_2MoO_4\cdot 2H_2O$ and biz in molar ratio of 1:0.73 in water-alcohol solution [13]. The resulting solution was filtered and allowed to evaporate

* Corresponding author at: Jilin Institute of Chemical Technology, Jilin City, Jilin 132022, PR China.
E-mail address: xiaoshuqu@sina.com (X. Qu).

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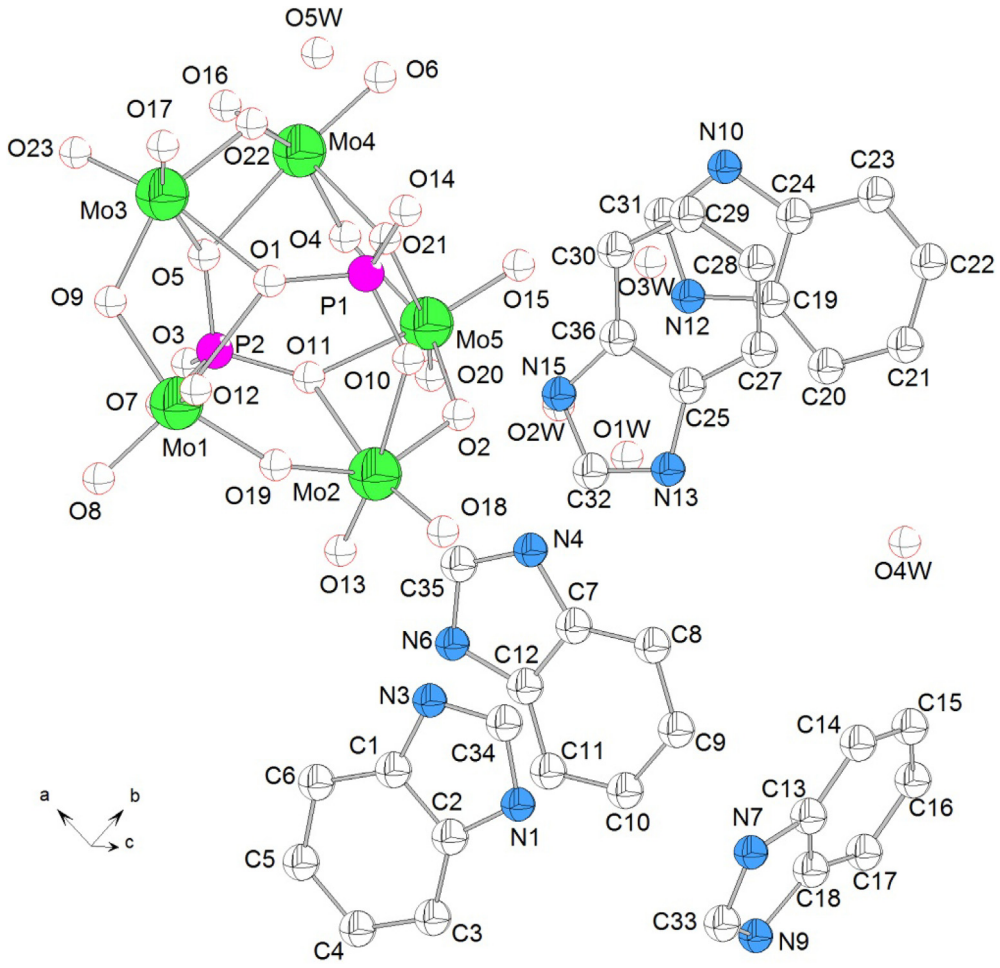

Fig. 1. Asymmetric unit of **1**.

at room temperature after one day to obtain colorless block crystals of compound **1**. Single-crystal X-diffraction showed that compound **1** consists of one $[HMo_5P_2O_{23}]^{5-}$ polyanion, five protonated biz cations $[C_7H_7N_2]^+$, and five crystal water molecules (Fig. 1). The $[HMo_5P_2O_{23}]^{5-}$ cluster can be described as a ring of five distorted MoO_6 octahedra with two PO_4 tetrahedra capped on each side. Each phosphate subunit shares three oxo-groups with the molybdate ring. One of these oxo-groups adopts the μ_2-bridging mode (linking one molybdenum site and phosphorus), and the other two adopt the μ_3-bridging mode (linking two molybdenum sites and phosphorus). In the compound, the Mo—O distances are 1.707(3) Å for terminal oxygen, 1.927(3) Å for O bonded to two Mo atoms, 2.314(3) Å for O bonded to

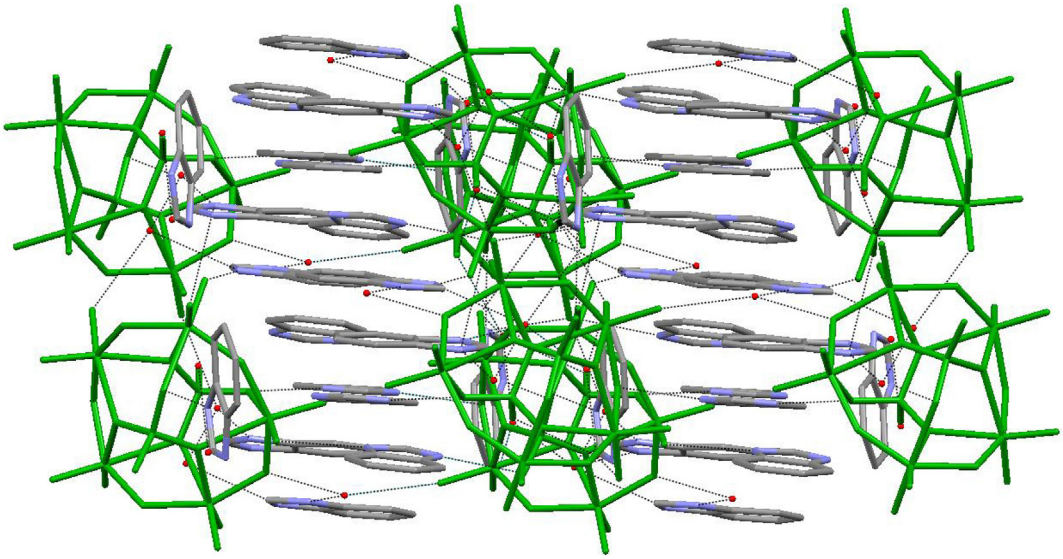

Fig. 2. View of the hydrogen-bonded 3D network in **1** along the b-axis.