



Synthesis, structure and effective peroxidase-like activity of a stable polyoxometalate-pillared metal–organic framework with multinuclear cycles

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ABSTRACT

A stable polyoxometalate (POM)-pillared metal–organic framework (MOF) with 6-nuclear Cu-pz and 10-nuclear Cu-pz-Cl cycles, $[\text{Cu}_5(\text{pz})_6\text{Cl}][\text{SiW}_{12}\text{O}_{40}]$ (CuSiW_{12}) (pz = pyrazine), has been hydrothermally synthesized and structurally characterized. Inspired by the reported horseradish peroxidase (HRP) and other enzyme mimics, the peroxidase-like activity of CuSiW_{12} was investigated in detail to catalyze the oxidation of the substrate 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H_2O_2 , which exhibits excellent peroxidase-like activity than that of pristine silicotungstic acid. Moreover, the detection of H_2O_2 was also studied in the TMB/ $\text{CuSiW}_{12}/\text{H}_2\text{O}_2$ system, which exhibits good sensitivity, wide linear range (1–60 μM), the lowest detection limit (0.10 μM) and faster response time towards H_2O_2 (2 min) to date, to the best of our knowledge, maybe due to the maximized synergistic effects of SiW_{12} clusters, pyrazine molecules, Cu ion and the stable structure.

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1. Introduction

Metal–organic frameworks (MOFs), an important class of porous crystalline materials, have caused vast attention originating from their larger surfaces areas, higher tunability and designability [1,2] as well as their potential applications such as catalysis [3,4], gas storage [5,6], sensor [7,8], drug delivery [9] and proton conduction [10,11]. Note that multinuclear cycles, as one kind of subunits with aesthetic characteristics in nature, has captivated the attention to fabricate novel MOFs recently [12,13]. More recently, polyoxometalates (POMs), the all-inorganic metal–oxide cluster species with notable acid/base, redox and photochemical properties in relationship with their unmatched structural variety [14–17], have been employed as valuable building blocks for tailor-made POM-based MOFs (POMOFs) [18–21]. Thanks to the previous work of chemists, many charming POMOFs with multinuclear cycles have been successfully obtained, in which POMs can play three kinds of roles, namely, the template, pillar, or node [22–24]. A case in point is that Keggin anion $[\text{HBW}_{12}\text{O}_{40}]^{4-}$ -templated framework $[\text{Ni}_2(4,4\text{-bpy})_5(\text{H}_2\text{O})_2][\text{HBW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$ with novel hexagon cycles

[25], and Wells–Dawson node-based $[\text{Ag}_3(3\text{-bptzb})_{2.5}(\text{H}_2\text{O})_2[\text{H}_3\text{P}_2\text{W}_{18}\text{O}_{62}]]$ with cycle connecting cycle chains [26]. Compared with template and node, POM-pillared MOFs containing multinuclear cycles are still limited and remain a long-term challenge in the crystal engineering point of view.

In present work, we chose $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ polyanion, Cu ion and pyrazine ligand (pz) to construct new POM-pillared MOFs with multinuclear cycles. The following points are taken into consideration: (i) Cu ions usually behave with changeable oxidation states and versatile coordination geometries under hydrothermal conditions, especially, Cu^{I} ions can adopt ‘seesaw’, T-type, and linear coordination geometries, and so on, which has been widely employed to construct novel multinuclear cycle MOFs recently [27,28]; (ii) pyrazine (pz), as a rigid bridging ligand with small steric hindrance, commonly exhibits the linear coordination mode to combine transition metal ions, which endow it the advantage of constructing multinuclear cycle structures [29,13]; (iii) Keggin POMs possess the Td symmetry and the large number of oxygen atoms (12 terminal and 24 μ_2 -O atoms) as the smart potential sites make the steric orientations of the coordination sites more flexible, which are positive to the construction of the POM-pillared MOFs [30]. Based on the three species mentioned above, herein, we have successfully synthesized a novel POM-pillared MOF, $[\text{Cu}_5(\text{pz})_6\text{Cl}][\text{SiW}_{12}\text{O}_{40}]$ (CuSiW_{12}), which contains 6-nuclear Cu-pz and 10-nuclear Cu-pz-Cl cycles.

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Recently, H₂O₂ detection has attracted much attention and motivated us to develop efficient specific system for detecting and quantifying the amount of H₂O₂ due to its production may affect human health [31–33]. Horseradish peroxidase (HRP), the effective catalytic agent used in optical H₂O₂ detection commonly, can catalyze achromogenic 3,3',5,5'-tetramethylbenzidine (TMB) forming a blue-color product [34]. However, inherent drawbacks of this natural enzyme, including low operational stability as well as time waste and uneconomical consumption, hinder its application in H₂O₂ detection [35,36]. As a result, considerable efforts have been dedicated to design and construct novel compounds with similar functions, such as, POMs [37,38], many carbon-materials [39,40] and nanocomposites [41]. Very recently, POMOFs as novel enzyme mimetic has seen tremendous growth due to their steady crystalline structure [19,42], which exhibits more penitential peroxidase-like activities. But the higher LOD (the limit of detection), less adaptable range and longer discoloration time hinders their application as enzyme mimics around physiological pH conditions. Therefore, the peroxidase-like activity of CuSiW₁₂ used in H₂O₂ detection was explored thoroughly in this work.

2. Experimental

2.1. Materials and methods

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400 CHN Elemental Analyzer. The IR spectra were obtained on an Alpha Centaur FT/IR spectrometer with KBr pellet in the 400–4000 cm⁻¹ region. XRD patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu K α radiation (λ = 0.154 nm) and 2 θ ranging from 5 to 50°. XPS analyses were performed on thermo ESCALAB 250 spectrometer with an Mg-K α achromatic X-ray source. All the reactions were monitored in time scan mode at 634 nm using a Hitachi UV2010 spectrophotometer.

2.2. Synthesis of [Cu₅(pz)₆Cl] [SiW₁₂O₄₀] (CuSiW₁₂)

A mixture of H₄SiW₁₂O₄₀ (0.300 g, 0.10 mmol), CuCl₂ (0.130 g, 1.00 mmol), pz (0.100 g, 1.25 mmol), NH₄VO₃ (0.036 g, 0.31 mmol) and H₂O (8 mL) was stirred for 30 min in air until it was homogeneous. When the pH value of the mixture was adjusted to about 2.16 with 1 M HCl, the solution was transferred and sealed in a 23 mL Teflon-lined stainless steel autoclave, which was heated at 180 °C under autogenous pressure for 4 days. The black block crystals were isolated and collected by filtration, washed thoroughly with distilled water, and dried at room temperature (45% yield based on Cu). Elemental analysis: C₂₄H₂₇Cu₅ClN₁₂O₄₀SiW₁₂ (3710.89). Anal. Calc. H, 0.73; C, 7.76; N, 4.53. Found: H, 0.81; C, 7.75; N, 4.51 (%).

2.3. X-ray crystallographic study

The crystal structure of the title compound was determined from single-crystal X-ray diffraction data. Intensity data were collected on a Bruker SMART CCD diffractometer equipped with a graphite monochromatized Mo K α radiation (λ = 0.71073 Å). The structure was solved by direct methods and difference Fourier map with the WINGX and SHELXTL software package [43,44], and refined by full-matrix least-squares techniques on F². Semiempirical absorption corrections were applied using the SADABS program. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms on carbon atoms of organic ligands were included at calculated positions and refined with a riding

Table 1

Crystal data and structure refinements for CuSiW₁₂.

Chemical formula	C ₂₄ H ₂₇ Cu ₅ ClN ₁₂ O ₄₀ SiW ₁₂
Formula weight	3710.89
CCDC	1815968
T (K)	296(2)
λ (Å)	0.71073 Å
Crystal system	triclinic
Space group	P $\bar{1}$
a (Å)	11.7181(8)
b (Å)	13.5286(10)
c (Å)	20.6568(14)
α (°)	89.302(1)
β (°)	76.772(1)
γ (°)	66.742(1)
V (Å ³)/Z	2917.6(4)/2
Density (g cm ⁻³)	4.294
Absorption coefficient (mm ⁻¹)	25.503
F(000)	3336.0
Data collect θ range	1.645–25.000°
Reflections collected	14679
Independent reflections	10179
R _{int}	0.0385
Refinement method on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	10179/306/890
Goodness-of-fit (GOF) on F ²	1.117
Final R indices [I > 2 σ (I)]	R ₁ = 0.1090, wR ₂ = 0.2349
R indices (all data)	R ₁ = 0.1214, wR ₂ = 0.2411
Largest difference peak and hole (e Å ⁻³)	3.807 and -4.601

$$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|, wR_2 = \Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w(|F_o|^2)^{1/2}.$$

model. The crystal data and refinement parameters of CuSiW₁₂ are summarized in Table 1. The selected bond lengths and bond angles of CuSiW₁₂ are listed in Table S1.

2.4. Peroxidase-like activity of CuSiW₁₂

To investigate the peroxidase-like activity of CuSiW₁₂, the catalytic oxidation of the peroxidase substrate TMB in the presence of H₂O₂ was tested by monitoring the absorbance change of TMB at 634 nm. In a typical experiment, the reaction solution consists of TMB (83 μ M), of H₂O₂ (97.8 μ M), and 0.4 mg/mL dispersion stock solution of CuSiW₁₂ in pH 4.0 acetate buffer solution at 25 °C. To examine the influence of reaction buffer pH value and the reaction temperature on the activity of CuSiW₁₂, the acidity of the acetate buffer solutions from pH 3.5 to 7.0 and the reaction temperature from 25 to 55 °C were investigated. In final, various concentrations of H₂O₂ was added into the mixed solution and incubated at 25 °C for 10 min for standard curve measurement.

3. Results and discussion

3.1. Structure description of CuSiW₁₂

Valence sum calculations [45] ($S = \exp[\Sigma - (R - R_o)/B]$) (S = bond valence, R = bond length) shows that all Cu ions are in +I oxidation state (1.138 for S_{Cu1}, 0.8923 for S_{Cu2}, 0.960 for S_{Cu3}, 0.8455 for S_{Cu4}, 0.8659 for S_{Cu5}), and all twelve W atoms are located at the full oxidation state (+VI) (6.3590, 6.2141, 6.3962, 5.8295, 5.7286, 5.9845, 5.8947, 5.7889, 5.9287, 5.8934, 6.1857, 6.1957 for S_{w1}–S_{w12}, respectively). It is noteworthy that Cu^{II} ions are reduced into Cu^I due to organonitrogen species in the reaction system, which is usual in the organonitrogen/Cu/POM systems. The black color of compound should be caused by Cu^I ions and the stacking mode (Fig. S2). Crystal structure analysis reveals that CuSiW₁₂ consists of two crystallographically independent half of [SiW₁₂O₄₀]⁴⁻ (SiW₁₂) anion, hereafter labeled SiW₁₂-A and SiW₁₂-B, five Cu^I ions, one Cl atom and six pz ligands as shown in

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