



Fe(III) and Cu(II) coordination polymers assembled from di/tris-phosphonic acid and auxiliary ligands : Structure, SOD-like activity and magnetic behavior



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ABSTRACT

Hydrothermal reactions of (benzylazanediy)bis(methylene)-diphosphonic acid (H_4L^1) or (benzene-1,3,5-triyltris(methylene))triphosphonic acid (H_6L^2) with Fe(III)/Cu(II) nitrate and 4, 4'-bipy or 2, 2'-bipy result in five new phosphonates, namely, $[FeHL^1(H_2O)]_n$ (**1**), $\{[Cu_2L^1(4, 4'-bipy)_{0.5}(H_2O)] \cdot 0.25H_2O\}_n$ (**2**), $[Cu_2H_2L^2(4, 4'-bipy)(H_2O)_2]_n$ (**3**), $[CuH_4L^2(2, 2'-bipy)]_n$ (**4**) and $[Cu_2(H_4L^2)_2(2, 2'-bipy)_2(H_2O)_4]$ (**5**), respectively. X-ray structural analysis indicates that **2** and **3** feature 3D framework structures with 3, 3, 3, 4-connected and 4, 5-connected topology; **1** and **4** display 1D chain structures, while **5** has a dimer structure. The di- or trisphosphonate ligands (H_4L^1 and H_6L^2) in the five complexes adopt different coordination modes and auxiliary ligands (4, 4'-bipy and 2, 2'-bipy) control the dimensionality of the final complexes. The superoxide dismutase (SOD) activities of **2–5** were assessed by modified nitrobluetetrazolium (NBT) assay. The IC_{50} values required to yield 50% inhibition of the reduction of NBT are 1.84, 2.02, 6.95 and 1.70 μM for **2–5**, respectively, demonstrating better SOD-like activity than most of the Cu-SOD mimic enzymes reported in literatures. Among them, **2** and **3** have good stability and reusability under the simulative physiological conditions. The dismutation of **4** and **5** toward superoxide anion radicals can be attributed to the synergistic effect of the decomposition products of **4** and **5** containing Cu(II) and $[H_4L^2]^{2-}$ with or without 2, 2'-bipy or Cu(II) and 2, 2'-bipy, which were identified by liquid mass spectrometry (LC/MS). The magnetic properties of complexes **1–4** were also investigated, indicating the presence of magnetic exchange between metal ions. The results show that **1** and **3** exhibit antiferromagnetic interactions, while **2** and **4** show ferromagnetic interactions between metal centres.

1. Introduction

In recent years, there has been increasing interests in the development of metal organic frameworks or coordination polymers due to their versatile architectures [1–3], design construction principles [4,5] and their potential applications in catalytic field [6,7], photoluminescence [8], magnetism [9], medicine [10], absorption [11–13] and proton conductivity [14]. Among the inorganic–organic hybrid materials, metal phosphonates are still less developed because of their poor crystallinity in water and other organic solvents. However, the syntheses toward metal phosphonates are attractive for their higher thermal stability than carboxylate complexes and diversity of metal connectivity derived from multifarious coordination modes [15,16]. The structures of this kind of complexes change with various conditions such as molar ratio, pH, reaction temperature and solvent even with same reactants. The use of ancillary ligands with phosphonic acids has been proved to

be a reasonable synthetic control to isolate metal phosphonate complexes [17]. It is well known that Cu, Zn-superoxide dismutase (Cu, Zn-SOD) is a ubiquitous enzyme with an essential role in a defence through catalysis of the disproportionation of $O_2^{\cdot -}$ under physiological conditions [18–21]. Natural enzyme is very sensitive to the environment, hard to extract and store, leading to high cost and low usability. To overcome these shortcomings, many works have been done on the development of Cu, Zn-SOD mimics. Some complexes have been proved to show high SOD-like activity, for example, dinuclear Cu(II) complexes involving 6-(benzylamino)purine derivatives [22,23]. The results show that the complexes have similar coordination environment with that of Cu(II) in Cu, Zn-SOD exhibit higher SOD-like activity. Currently, the SOD-like activity studies of the mimics mainly concentrate on nitrogen or carboxylic based complexes. However, the Cu(II) phosphonates have not been explored so far.

On the other hand, molecular magnetism is also a significant area

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for transition metal complexes that has been considered interest. The proper choice of bridging groups between metal centres has a prominent influence on the magnetic strength and behavior of the molecules when constructs magnetism materials. The magnetic exchange coupling in phosphonate is mainly through O-P-O and/or μ -O bridge. In most cases, the O-P-O bridge mediates weak antiferromagnetic interactions between metal centres [24,25]. However, stronger antiferromagnetic or even a ferromagnetic interaction is also observed [26,27]. For example, $[\text{Cu}\{(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H})_2\}]_n$ [24], $[\text{Cu}(\text{C}_6\text{H}_{10}(\text{OH})\text{PO}_3)]_n$ and $[\text{Cu}(\text{C}_6\text{H}_9\text{PO}_3)(\text{H}_2\text{O})]_n$ [26], exhibit antiferromagnetic properties, while $[\text{Cu}(\text{C}_6\text{H}_{10}(\text{OH})\text{PO}_3)(\text{H}_2\text{O})_2]$ [26] and $[\text{Cu}_2(\text{H}_2\text{O})_2\{\text{O}_3\text{PCH}_2\text{N}(\text{C}_2\text{H}_4)_2\text{NCH}_2\text{PO}_3\}]_n$ [27] show dominant ferromagnetic interactions. The results show that the structural difference can result in obvious magnetic discrepancy. Zheng and coworkers found that the magnetic nature of phosphonates depends on the distance between metal centres and M-O...O-M torsion angle [28–30].

Herein, we reported five new transition metal phosphonates that assembled from H_4L^1 or H_6L^2 and auxiliary ligands, namely, $[\text{FeHL}^1(\text{H}_2\text{O})]_n$ (**1**), $\{[\text{Cu}_2\text{L}^1(4, 4'\text{-bipy})_{0.5}(\text{H}_2\text{O})]\cdot 0.25\text{H}_2\text{O}\}_n$ (**2**), $[\text{Cu}_2\text{H}_2\text{L}^2(4, 4'\text{-bipy})(\text{H}_2\text{O})_2]_n$ (**3**), $[\text{CuH}_4\text{L}^2(2, 2'\text{-bipy})]_n$ (**4**) and $[\text{Cu}_2(\text{H}_4\text{L}^2)_2(2, 2'\text{-bipy})_2(\text{H}_2\text{O})_4]$ (**5**). These complexes exhibit structural polytrope with different dimensionality. Considering that the similar structural character of Cu(II) centre in the complexes **2–5** with the active site of native enzyme (bovine erythrocyte), the SOD-like activity was first investigated for metal phosphonates. The results show that these complexes exhibit good SOD-like activity, among them, **2** and **3** have better stability and reusability. Moreover, the stabilities of the complexes were investigated both in temperature programming and in buffer solution. The magnetic properties of complexes **1–4** were also investigated.

2. Experimental

2.1. Materials

Chemical reagents were purchased commercially from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification. The ligands (benzylazanediy)bis(methylene)-diphosphonic acid (H_4L^1) and (benzene-1,3,5-triyltris(methylene)triphosphonic acid (H_6L^2) were prepared according to the literature methods [31,32].

2.2. Physical measurements

Elemental analyses (C, H and N) were performed by using a Perkin-Elmer 2400 series II CHN analyzer. Infrared (IR) spectrum was recorded in the range of 4000–400 cm^{-1} on a FT-IR analyzer (1601, shimadzu Co., Japan) by using KBr-pellet method. The powder X-ray diffraction measurements were conducted on a Bruker D8 ADVANCE X-ray diffractometer. Thermogravimetric analyses were carried out on a NETZSCH STA 449 C unit at a heating rate of 10 $^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. Liquid mass spectrometry (LC/MS) was conducted by using LC/MS6120. Magnetic susceptibility measurement was measured over the temperature range 2–300 K with a MPMS SQUID VSM magnetometer with applied magnetic field of 1000 Oe.

2.3. Synthesis of complex $[\text{FeHL}^1(\text{H}_2\text{O})]_n$ (**1**)

H_4L^1 (0.1 m mol, 0.0292 g), 4, 4'-bipy (0.1 m mol, 0.0156 g), $\text{Fe}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.1 m mol, 0.0404 g) and 3 mL of water were mixed in 10 mL vial. Then, 35 μL triethylamine was added, the vial was kept in an autoclave at 140 $^\circ\text{C}$ for three days. Red crystals were collected and washed with deionized water. Yield: 30.7 mg (36%, based on Fe). Anal. Calcd. For $\text{C}_9\text{H}_{14}\text{FeNO}_7\text{P}_2$: C, 29.53; H, 3.86; N, 3.827%. Found: C, 29.3; H, 3.5; N, 3.4%. Main IR data (KBr, cm^{-1}): 3386 (s), 2987 (w), 2781 (w), 2722 (w), 1160 (s), 941 (m).

2.4. Synthesis of complex $\{[\text{Cu}_2\text{L}^1(4, 4'\text{-bipy})_{0.5}(\text{H}_2\text{O})]\cdot 0.25\text{H}_2\text{O}\}_n$ (**2**)

H_4L^1 (0.05 m mol, 0.0146 g), 4, 4'-bipy (0.15 m mol, 0.0235 g), $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.102 m mol, 0.0247 g) and 3 mL of water were mixed in 10 mL vial and the hydrothermal reaction conditions are same with that of **1**. Blue crystals were collected and washed with deionized water. Yield: 26.38 mg (42%, based on Cu). Anal. Calcd. For $\text{C}_{14}\text{H}_{17.5}\text{N}_2\text{O}_{7.25}\text{P}_2\text{Cu}_2$: C, 32.41; H, 3.4; N, 5.4%. Found: C, 32.81; H, 3.17; N, 5.22%. Main IR data (KBr, cm^{-1}): 3363 (s), 2918 (w), 1611 (s), 1492 (m), 1418 (w), 1223 (m), 1148 (m), 1024 (m), 977 (m).

2.5. Synthesis of complex $[\text{Cu}_2\text{H}_2\text{L}^2(4, 4'\text{-bipy})(\text{H}_2\text{O})_2]_n$ (**3**)

H_6L^2 (0.05 m mol, 0.0176 g), 4, 4'-bipy (0.158 m mol, 0.0246 g), $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.1 m mol, 0.0240 g) and 3 mL of water were mixed in 10 mL vial. Then, 50 μL 1 mol/L NaOH was added. The hydrothermal reaction was performed on the same conditions with **1**. Blue crystals were collected and washed with deionized water. Yield: 29.8 mg (45%, based on Cu). Anal. Calcd. For $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_{11}\text{P}_3\text{Cu}_2$: C, 33.79; H, 3.43; N, 4.15%. Found: C, 33.46; H, 3.72; N, 4.48%. Main IR data (KBr, cm^{-1}): 3386 (s), 3099 (w), 2903 (w), 1611 (s), 1492 (m), 1417 (w), 1222 (m), 1148 (w), 1070 (s), 927 (s).

2.6. Synthesis of complex $[\text{CuH}_4\text{L}^2(2, 2'\text{-bipy})]_n$ (**4**)

The preparation of **4** was similar to that of **3** except the displacement of 4, 4'-bipy with 2, 2'-bipy. Blue crystals were obtained and washed with deionized water. Yield: 27.1 mg (41%, based on Cu). Anal. Calcd. For $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_9\text{P}_3\text{Cu}$: C, 39.492; H, 3.663; N, 4.848%. Found: C, 39.60; H, 3.32; N, 4.52%. Main IR data (KBr, cm^{-1}): 3424 (s), 3116 (w), 2912 (w), 1651 (w), 1603 (s), 1495 (w), 1410 (w), 1235 (s), 1171 (m), 1137 (w), 1035 (m), 991 (m), 932 (m).

2.7. Synthesis of complex $[\text{Cu}_2(\text{H}_4\text{L}^2)_2(2, 2'\text{-bipy})_2(\text{H}_2\text{O})_4]$ (**5**)

H_6L^2 (0.05 m mol, 0.018 g), 2, 2'-bipy (0.155 m mol, 0.0242 g), $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.048 m mol, 0.0117 g), $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.051 m mol, 0.019 g) and 3 mL of water were mixed in 10 mL vial. Then, 50 μL 1 mol/L NaOH was added. The hydrothermal reaction was conducted under the conditions of **1**. Blue crystals were obtained and washed with deionized water. Yield: 16 mg (22%, based on Cu). Anal. Calcd. For $\text{C}_{38}\text{H}_{50}\text{N}_4\text{O}_{22}\text{P}_6\text{Cu}_2$: C, 37.17; H, 4.11; N, 4.56%. Found: C, 37.51; H, 4.41; N, 4.15%. Main IR data (KBr, cm^{-1}): 3443 (m), 3081 (m), 1605 (s), 1475 (m), 1445 (s), 1254 (w), 1088 (s).

2.8. SOD activity study of **2–5**

The SOD activity of **2–5** were assayed by using a modified NBT-reduction method [33,34].

2.9. X-ray crystallography

Single-crystal X-ray diffraction data for **1–5** were collected on a Bruker Smart CCD area-detector diffractometer with graphite-monochromatic Mo/K α radiation ($\lambda = 0.71073 \text{ \AA}$) in ω -scan mode. The collected data were reduced using the software package SAINT [35], and semi-empirical absorption correction was applied to the intensity data using SADABS program [36]. The structures of **1–5** were solved using direct methods, and all nonhydrogen atoms were refined anisotropically by least squares on F^2 using the SHELXTL-2014 program [37]. Hydrogen atoms were placed in calculated positions and refined isotropically using the riding model. Details of the crystallographic data of **1–5** are summarized in Table 1. Selected bond lengths (\AA) and angles ($^\circ$) for **1–5** are listed in Table 2.

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