

A Novel One-dimensional Reduced Molybdenum(V) Decorated with Nickel Coordination Cations:

Ni[Mo₆O₁₂(OH)₃(PO₄)(HPO₄)₃]₂[Ni(H₂O)₂][Ni(H₂O)(bipy)₂]₄•5H₂O

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A novel molybdenum(V) phosphate decorated with nickel complex cations, Ni[Mo₆O₁₂(OH)₃(PO₄)(HPO₄)₃]-[Ni(H₂O)₂][Ni(H₂O)(bipy)₂]₄•5H₂O (bipy = 2,2'-bipyridyl), has been hydrothermally synthesized and characterized by IR, TGA and single-crystal X-ray diffraction. Two {Mo₆P₄} clusters are linked via one Ni cation to form a Ni[Mo₆P₄]₂ dimer unit, which is further connected together by additional nickel coordination complex ions to give 1-D molybdenum(V) phosphate chain-like structure. A probe reaction of the oxidation of benzaldehyde with H₂O₂ using the title compound as catalyst was carried out in a liquid-solid system, showing that the compound had high oxidative catalytic activity to the reaction.

Keywords hydrothermal synthesis, crystal structure, molybdenum phosphate, one-dimensional chain-like, catalytic activity

Introduction

Polyoxometalates continue to be extensively studied due to not only their potential applications to catalysis and medicine, but also to various applied physical sciences because of their optical or magnetic properties.¹⁻⁶ As an important class of the phosphomolybdenum family, the reduced Mo(V)/phosphato compounds with structures ranging from 1-D polymers to 3-D microporous materials have received more and more attention due to their great structural diversity and applications to catalysis, ion exchange and molecular sieves.⁷⁻¹¹ The hydrothermal synthesis techniques, in combination with the organic templates, have been demonstrated to be an effective strategy in the isolation of molybdenum-oxide clusters.¹² The organic-inorganic reduced molybdenum phosphates with a 1-D chain-like structure decorated with transition metal complexes have rarely been reported, although reduced molybdenum phosphates with organic amines and inorganic reduced molybdenum phosphates have been extensively prepared as templating or structure-directing agents in hydrothermal reactions.¹³ As a continuation of our effort on this Mo-P-O system,¹⁴ we attempted to explore the assembly of phosphomolybdates in the presence of Ni²⁺ and 2,2'-bipyridyl under the hydrothermal condition. Herein, we report a novel reduced molybdenum phosphate with the incorporation of nickel coordination cations, Ni[Mo₆O₁₂(OH)₃(PO₄)(HPO₄)₃]-[Ni(H₂O)₂][Ni(H₂O)(bipy)₂]₄•5H₂O (bipy = 2,2'-bipyridyl),

1, which exhibits a one-dimensional chain-like structure.

Experimental

Materials and apparatus

All chemicals were purchased from commercial sources and used without further purification. Infrared spectrum of the title compound was recorded on a Perkin Elmer 2000 FTIR spectrophotometer in a 400—4000 cm⁻¹ region using a powdered sample on a KBr plate. The elemental analysis (C, H and N) was performed using a Vario ELIII elemental analyzer. The contents of Ni and Mo were determined by a Leaman inductively coupled plasma spectrometer. Powder X-ray diffraction data for the as-synthesized compound were collected on a Philips X'pert Pro MPP diffractometer (Cu K α). The TGA curve was obtained on a Netzsch STA 449C thermogravimetric analyzer in the flowing N₂ with a temperature ramp rate of 10 °C•min⁻¹.

Catalytic reaction was carried out in a 50 mL three-necked flask with a reflux condenser. The three-necked flask was charged with 5.1 mL (0.05 mol) of benzaldehyde solution, then 10 mL of 30% H₂O₂ (0.1 mol) were pipetted into the solution. The solution was heated to 348 K and compound 1 (0.1 g) as a powder was added to the solution, and after 4 h at the same temperature, the reaction was stopped and the catalyst separated off. Standard NaOH solution was used to titrate the reactant. The yield of benzoic acid (%) was

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taken to assess the activity of the catalyst.

Preparation of compound 1

The title compound was synthesized from the reaction mixture of MoO_3 (1.1 mmol), H_3PO_4 (3.5 mmol), NiSO_4 (1.5 mmol), 2,2'-bipyridyl (1.6 mmol) and distilled water (21 mL) in a 30 mL Teflon-lined reactor, under an autogenous pressure at 448 K for 5 d, which was then cooled to room temperature. Brown block crystals of the title compound were isolated, washed with water, and dried at ambient temperature to be afforded in a good yield (65.6%, based on Mo). Anal. calcd for $\text{C}_{80}\text{H}_{98}\text{Mo}_{12}\text{Ni}_6\text{N}_{16}\text{P}_8\text{O}_{73}$: C 22.84, H 2.33, N 5.33, Ni 8.38, Mo 27.39; found C 22.60, H 2.41, N 5.39, Ni 8.45, Mo 27.51.

Single crystal X-ray diffraction

Single crystal X-ray data of the compound 1 with dimensions 0.28 mm \times 0.21 mm \times 0.16 mm were collected on a Rigaku Mercury CCD diffractometer equipped with graphite monochromatized Mo K α ($\lambda = 0.071070$ nm) by Crystal Clear software.¹⁵ Empirical absorption corrections were applied to each case. All calculations were conducted using SHELXS-97 and SHELXL-97 programs,¹⁶ while the structures were solved by the direct methods. All the nonhydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL via a full-matrix least-square procedure. The hydrogen atom positions

were fixed geometrically at calculated distances and rode on the parent carbon atoms, but the hydrogen atoms attached on hydroxy groups and water molecules were not found. The crystallographic data of the complex are summarized in Table 1 and the selected bond distances and bond angles in Table 2. Crystallographic data for compounds 1 was deposited with the Cambridge Crystallographic Data Center by the deposition number of CCDC 640049.

Results and discussion

Structure of compound 1

As shown in Figure 1, the compound 1 consists of $\{\text{Ni}[\text{Mo}_6\text{O}_{12}(\text{OH})_3(\text{PO}_4)(\text{HPO}_4)_3]_2\}$ ($\text{Ni}[\text{Mo}_6\text{P}_4]_2$) cluster anions, $[\text{Ni}(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{H}_2\text{O})(\text{bipy})_2]$ polyhedra and lattice water molecules. The $[\text{Mo}_6\text{P}_4]$ subunits of compound 1 have been often observed in similar reduced molybdenum phosphate derivatives.^{13,14} Each $[\text{Mo}_6\text{P}_4]$ cluster (Figure 2a) consists of a ring of six edge-sharing MoO_6 octahedra with alternating long (0.350 nm) and short (0.259 nm) Mo—Mo contacts, with the latter suggesting direct Mo—Mo single bonds. Each Mo site in compound 1 has a distorted octahedral configuration with an apical Mo—O bond at a length of about 0.168 nm and five other Mo—O bonds at lengths ranging from 0.193 to 0.234 nm. The phosphate groups decorate these clusters: three groups are around the periphery of the ring and the other one group is at the $[\text{Mo}_6\text{P}_4]$ center,

Table 1 Crystallographic data for complex 1

Empirical formula	$\text{C}_{80}\text{H}_{98}\text{Mo}_{12}\text{N}_{16}\text{Ni}_6\text{O}_{73}\text{P}_8$
Formula weight	4203.04
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 1.40680(6)$ nm, $\alpha = 110.690(4)^\circ$ $b = 1.56808(5)$ nm, $\beta = 107.529(3)^\circ$ $c = 1.58088(6)$ nm, $\gamma = 91.616(5)^\circ$
Volume	$3.0753(2)$ nm ³
Z, Calculated density	1, 2.269 Mg/m ³
Absorption coefficient	2.288 mm ⁻¹
$F(000)$	2066
Crystal size	0.28 mm \times 0.21 mm \times 0.16 mm
θ range for data collection	2.99° — 27.48°
Limiting indices	$-18 \leq h \leq 16$, $-20 \leq k \leq 20$, $-19 \leq l \leq 20$
Reflections collected/unique	29126/13454 [$R_{\text{int}} = 0.0558$]
Data/restraints/parameters	13454/0/871
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0463$, $wR_2 = 0.1380$
R indices (all data)	$R_1 = 0.0551$, $wR_2 = 0.1466$
Largest diff. peak and hole	1318 and -1657 e \cdot nm ⁻³

Table 2 Selected bond distances (nm) and angles (°) for compound **1**^a

Mo(1)—O(23)	0.1688(3)	Mo(5)—O(14)	0.1670(4)	Ni(2)—O(29)#2	0.1991(4)
Mo(1)—O(4)	0.1930(3)	Mo(5)—O(5)	0.1946(4)	Ni(2)—O(32)	0.2103(4)
Mo(1)—O(13)	0.2294(3)	Mo(5)—O(6)	0.1981(3)	Ni(2)—O(15)	0.2118(3)
Mo(2)—O(21)	0.1676(4)	Mo(5)—O(11)	0.2047(3)	Ni(2)—O(15)#2	0.2118(3)
Mo(2)—O(2)	0.1937(3)	Mo(5)—O(19)	0.2111(4)	Ni(3)—O(26)	0.2065(4)
Mo(2)—O(1)	0.1986(3)	Mo(5)—O(18)	0.2290(3)	Ni(3)—N(4)	0.2070(5)
Mo(2)—O(12)	0.2071(3)	Mo(6)—O(6)	0.1976(3)	Ni(3)—N(2)	0.2081(4)
Mo(3)—O(8)	0.1683(3)	Mo(6)—O(9)	0.2109(3)	Ni(3)—N(1)	0.2082(5)
Mo(3)—O(4)	0.1932(3)	Mo(6)—O(13)	0.2245(3)	Ni(3)—O(33)	0.2098(4)
Mo(3)—O(7)	0.1991(3)	Ni(1)—O(1)	0.2137(3)	Ni(3)—N(3)	0.2112(5)
Mo(3)—O(20)	0.2060(3)	Ni(1)—O(1)#1	0.2137(3)	Ni(4)—O(30)	0.2041(4)
Mo(3)—O(3)	0.2096(3)	Ni(1)—O(7)	0.2156(3)	Ni(4)—N(8)	0.2073(5)
Mo(3)—O(10)	0.2257(3)	Ni(1)—O(7)#1	0.2156(3)	Ni(4)—N(6)	0.2081(5)
Mo(4)—O(24)	0.1684(4)	Ni(1)—O(6)#1	0.2175(3)	Ni(4)—N(5)	0.2091(5)
Mo(4)—O(2)	0.1931(3)	Ni(1)—O(6)	0.2175(3)	Ni(4)—N(7)	0.2094(5)
Mo(4)—O(18)	0.2342(3)	Ni(2)—O(29)	0.1991(4)	Ni(4)—O(34)	0.2120(5)
O(23)-Mo(1)-O(4)	105.70(17)	O(5)-Mo(6)-O(6)	95.61(14)	O(15)-Ni(2)-O(15)#2	180.0
O(23)-Mo(1)-O(7)	103.34(16)	O(6)-Mo(6)-O(22)	158.46(15)	O(26)-Ni(3)-N(4)	95.2(2)
O(4)-Mo(1)-O(7)	95.34(14)	O(27)-Mo(6)-O(9)	96.84(17)	O(26)-Ni(3)-N(2)	90.45(16)
O(1)-Mo(2)-O(12)	159.03(15)	O(1)-Ni(1)-O(1)#1	180.00(15)	N(4)-Ni(3)-N(2)	96.96(19)
O(21)-Mo(2)-O(3)	96.29(15)	O(1)-Ni(1)-O(7)	95.79(13)	O(33)-Ni(3)-N(3)	85.50(16)
O(2)-Mo(2)-O(3)	157.17(14)	O(1)#1-Ni(1)-O(7)	84.21(13)	O(30)-Ni(4)-N(8)	93.70(18)
O(4)-Mo(3)-O(20)	85.75(15)	O(7)-Ni(1)-O(7)#1	180.00(14)	O(30)-Ni(4)-N(6)	93.71(16)
O(7)-Mo(3)-O(20)	157.88(13)	O(7)#1-Ni(1)-O(6)#1	96.80(12)	N(8)-Ni(4)-N(6)	90.46(19)
O(8)-Mo(3)-O(3)	96.15(15)	O(1)-Ni(1)-O(6)	96.85(12)	O(30)-Ni(4)-N(5)	96.15(17)
O(16)-Mo(4)-O(19)	83.74(14)	O(1)#1-Ni(1)-O(6)	83.15(12)	N(8)-Ni(4)-N(5)	166.00(19)
O(24)-Mo(4)-O(18)	170.98(16)	O(7)-Ni(1)-O(6)	96.80(12)	N(7)-Ni(4)-O(34)	88.4(2)
O(2)-Mo(4)-O(18)	82.24(14)	O(7)#1-Ni(1)-O(6)	83.20(12)	O(15)-P(1)-O(13)	112.1(2)
O(1)-Mo(4)-O(18)	80.42(12)	O(6)#1-Ni(1)-O(6)	180.0	O(15)-P(1)-O(10)	107.94(19)
O(14)-Mo(5)-O(6)	102.27(16)	O(29)-Ni(2)-O(29)#2	180.0(3)	O(30)-P(2)-O(25)	105.3(2)
O(5)-Mo(5)-O(6)	95.72(14)	O(29)-Ni(2)-O(32)#2	90.71(17)	O(12)-P(2)-O(25)	109.4(2)
O(14)-Mo(5)-O(11)	96.09(17)	O(32)#2-Ni(2)-O(32)	180.000(1)	O(29)-P(3)-O(17)	110.6(2)
O(5)-Mo(5)-O(11)	88.09(15)	O(32)#2-Ni(2)-O(15)#2	88.08(14)	O(26)-P(4)-O(11)	113.8(3)

^a Symmetry codes: #1 $-x+2, -y+1, -z$; #2 $-x+1, -y+1, -z$.

forming a hexamer structure [Mo₆P₄]. The phosphorous atoms have P—O bond lengths in the range 0.1487(4)—0.1592(4) nm, while the O—P—O bond angles are in the range 104.2(3)°—116.6(2)°. The two [Mo₆P₄] moieties are combined by a Ni(1)O₆ octahedron linked by six O atoms from two hexamer ring units, resulting in a [Ni(Mo₆P₄)₂] dimer (Figure 2b), in which the Ni—O bond lengths and O—Ni—O bond angles range in 0.2137(3)—0.2175(3) nm and 83.1(1)°—180.0 (0)°, respectively.

The bond valence sums(BVS)¹⁷ for **1** suggest that the bond valence values for all the molybdenum and phosphorous atoms are in the ranges 5.20—5.25 and 4.80—4.90, respectively, indicating that all Mo and P atoms have a +5 oxidation state. In addition, the appearance of brown crystals of the compound **1** is the typical color of an oxide cluster containing Mo⁵⁺ cation. In this heavy atom structure, it is difficult to find the H atoms from hydroxy groups and water molecules in a difference

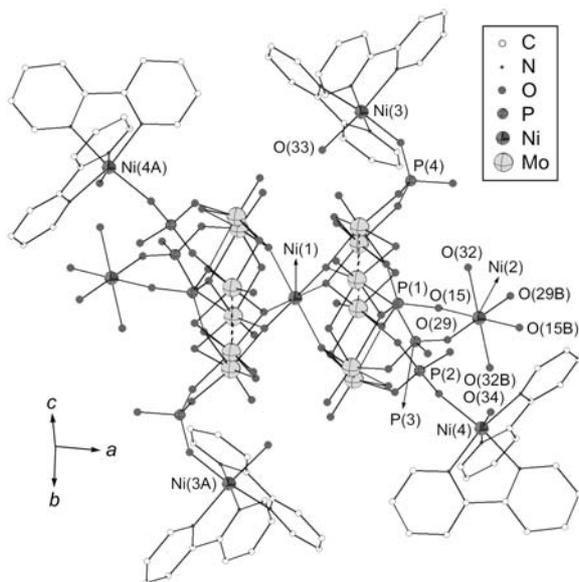


Figure 1 The structure of compound **1** (all H atoms and lattice water are omitted for clarity).

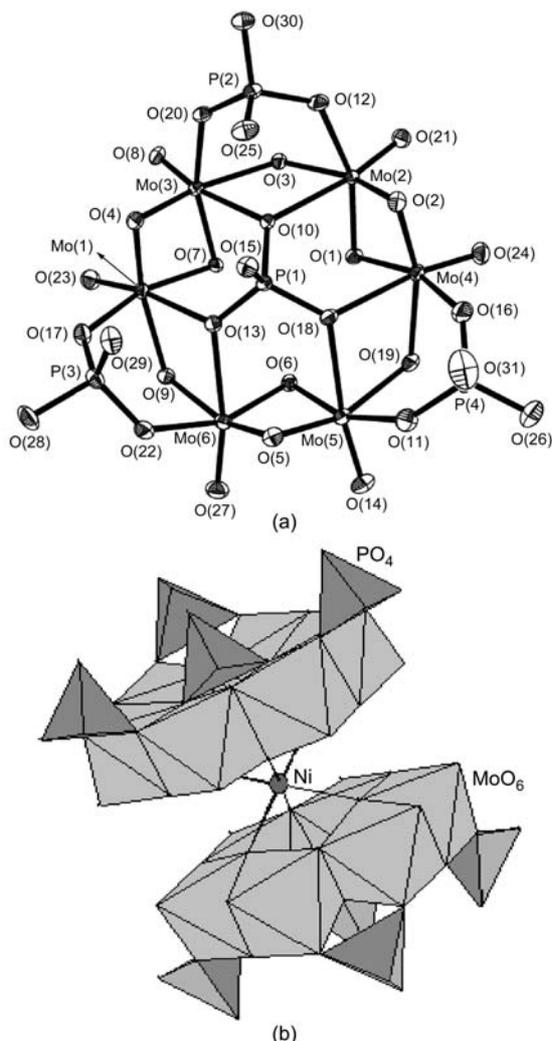


Figure 2 Ball and stick representation of $[\text{Mo}_6\text{P}_4]$ hexamer with labeling (a) and View of $[\text{Ni}(\text{Mo}_6\text{P}_4)_2]$ dimer (b).

Fourier transform. So the H atoms were also validated by BVS. The bond valence values for O(3), O(9), O(19), O(25), O(28) and O(31) are in the range 1.03–1.20, indicating that these oxygen atoms are in hydroxy groups; those for O(32), O(33), and O(34) linked to Ni atoms are 0.59, 0.30 and 0.28, respectively, indicating that these oxygen atoms are from water molecules; and those for all other oxygen atoms are very close to 2. Therefore, the molybdenum hexamer and the nickel coordination cations bonded with the $\text{Ni}[\text{Mo}_6\text{P}_4]_2$ unit should be formulated as $[\text{Mo}_6\text{O}_{12}(\text{OH})_3(\text{PO}_4)(\text{HPO}_4)_3]^{6-}$ and $\{[\text{Ni}(\text{H}_2\text{O})_2][\text{Ni}(\text{H}_2\text{O})(\text{bipy})]_4\}^{10+}$, respectively.

There are three distinct Ni environments in the asymmetric unit of compound **1**: (1) Ni(1) bridges two $\{\text{Mo}_6\text{P}_4\}$ units via six μ_3 -O atoms of the two $\{\text{Mo}_6\text{P}_4\}$ units to produce a centrosymmetric $[\text{Ni}(\text{Mo}_6\text{P}_4)_2]$ dimer. The Ni(1) site lies at a center of symmetry and accordingly only half of the molecule is independent; (2) Ni(3) and Ni(4) are both coordinated by four N atoms from two 2,2'-bipy ligand [$\text{Ni}-\text{N}$: 0.2070(5)–0.2094(5) nm] and two O atoms to form a distorted octahedral geometric configuration, in which one oxygen atom is from one PO_4 group [$\text{Ni}(3)-\text{O}(26)$: 0.2065(4) nm, $\text{Ni}(4)-\text{O}(30)$: 0.2041(4) nm], while the other oxygen atom from a water molecule [$\text{Ni}(3)-\text{O}(33)$: 0.2098(4) nm, $\text{Ni}(4)-\text{O}(34)$: 0.2120(5) nm]; (3) Ni(2) site links the adjacent $[\text{Ni}(\text{Mo}_6\text{P}_4)_2]$ dimers through four O atoms from four different PO_4 groups, and is coordinated by two terminal coordinated water molecules to finish a distorted octahedron with Ni–O bond lengths of 0.1991(4)–0.2175(3) nm and the O–Ni–O bond angles of $82(1)^\circ$ – $180.0(3)^\circ$.

Each $[\text{Ni}(1)(\text{Mo}_6\text{P}_4)_2]$ dimer in the title compound is decorated with two $[\text{Ni}(3)\text{O}_2\text{N}_4]$ and two $[\text{Ni}(4)\text{O}_2\text{N}_4]$ polyhedra, and then the adjacent polyanions are linked by a $[\text{NiO}_4(\text{H}_2\text{O})_2]$ octahedron, forming a one-dimensional chain-like structure (Figure 3). The 1-D structure can be also viewed as that the $\text{Ni}[\text{Mo}_6\text{P}_4]_2$ cluster unit and the $[\text{Ni}(2)(\text{H}_2\text{O})_2]^{2+}$ coordinated cations are connected together one by one to generate an unusual one-dimensional chain-like along the *a*-axis.

Powder diffraction, IR spectra and TGA analysis of compound **1**

The experimental and simulated XRPD patterns of compound **1** are shown in Figure 4. Their peak positions are in good agreement with each other, indicating the high phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

The IR spectrum of **1** exhibits an intense band at 964 cm^{-1} , characteristic of $\nu(\text{Mo}=\text{O})$ and features at 1042 , 1177 cm^{-1} associated with $\nu(\text{P}-\text{O})$, respectively. The peaks at 1473 , 1492 , 1575 and 1635 cm^{-1} are characteristic of a 2,2'-bipy group, while the broad band in 3435 – 3290 cm^{-1} is ascribed to water molecules.

Thermogravimetric analysis (TGA) of compound **1** showed a first weight loss of 7.2% in the temperature

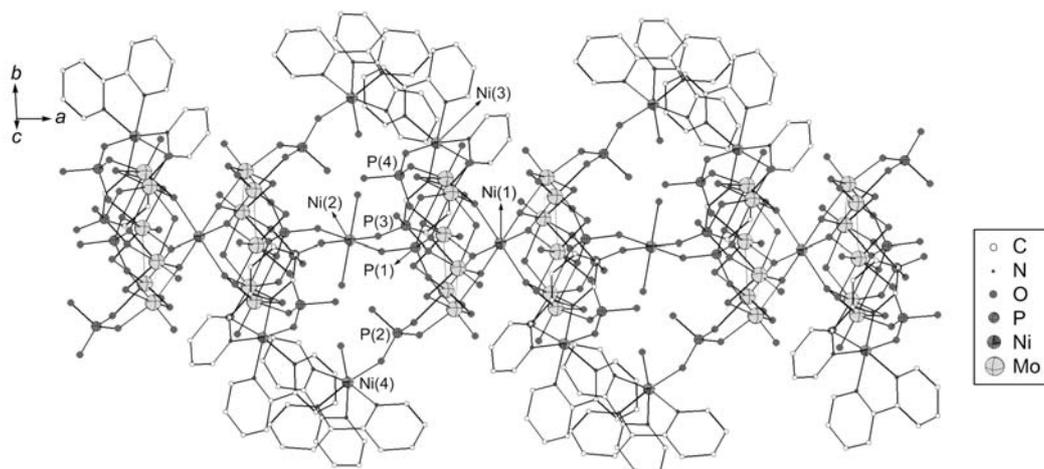


Figure 3 View of the one-dimensional structure along the *a*-axis.

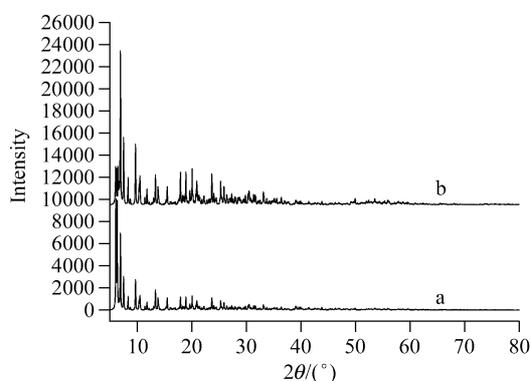


Figure 4 Powder XRD patterns (Cu $K\alpha$ radiation), simulated from crystal structure data (a) and as-synthesized compound (b).

range 80–195 °C and a second weight loss of 41.5% in the range 395–580 °C. These two weight losses correspond to the release of crystal and coordinated water molecules (calculated value of 6.4%) and the 2,2'-bipy (calculated value of 40.6%), respectively. Compound **1** continued to lose weight gradually up to 650 °C, the highest temperature measured.

Catalytic properties of compound **1**

To investigate the oxidative catalytic activity of the compound **1**, we performed a probe reaction of the oxidation of benzaldehyde with H_2O_2 using compound **1** as a catalyst. Under the above-mentioned experimental conditions, the overall oxidative conversion of benzaldehyde was 88.6%, yielding benzoic acid. In a comparative experiment, where no catalyst was added, the oxidative formation of benzoic acid was observed only in a small amount (less than 8%). This suggests that compound **1** may be useful as an oxidative catalyst for some organic syntheses.

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