

Synthesis, characterization and crystal structure of a copper molybdate coordination polymer as an epoxidation catalyst



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ABSTRACT

Through exploitation of hydrothermal synthesis, a mixture of crystals containing blue $[\text{CuMoO}_4(\text{N}_2\text{C}_{12}\text{H}_8)] \cdot \text{H}_2\text{O}$ (**1**) and yellow $[\text{Cu}_3\text{Cl}(4,4'\text{-bipy})_4][\text{Cu}^{\text{II}}(1,10\text{-phen})_2\text{Mo}_8\text{O}_{26}]$ ($4,4'\text{-bipy}$ = 4,4'-bipyridine and 1,10-phen = 1,10-phenanthroline) (**2**) were obtained. Single crystal X-ray diffraction analysis revealed that compound **1** is a new 1-D coordination polymer while compound **2** is a known metal-organic framework. The obtained crystals have been further characterized by means of powder X-ray diffraction (PXRD), FT-IR and inductive coupled plasma optical emission spectroscopy (ICP-OES). The catalytic properties of the prepared mixture were investigated in the epoxidation of some olefins and allylic alcohols using *tert*-butyl hydroperoxide (TBHP) or cumene hydroperoxide (CHP) as oxidants. It was found that the crystals could serve as an active and selective catalyst for the epoxidation of the olefins and allylic alcohols. The catalyst can be recovered easily and reused in the reaction without considerable decrease in activity or selectivity. Moreover, the influence of the type of oxidant and solvent on the conversion of the olefins was studied.

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1. Introduction

The synthesis, design and characterization of coordination polymers, based on the assembly of metal ions and functional organic ligands, have been rapidly developed owing to their special physical properties and potential applications in functional materials, for molecular adsorption, and ion exchange [1–6]. Besides these applications, coordination polymers have emerged as catalysts for epoxidation of olefins [7–9].

In the area of catalysis, epoxidation of olefins is important in organic synthesis since epoxides are synthetic intermediates widely utilized for the manufacturing of chemicals such as surfactants, unsaturated resins, paints and other useful substances [10,11].

A lot of research is directed to the heterogeneous catalytic processes owing to easier work-up and better recyclability and stability of the heterogeneous catalysts. A number of approaches have been developed for heterogenization of homogeneous catalysts using various supports such as silica [12–15], carbon [16–19], polymers [20,21], metal-organic frameworks [22,23] and metal

oxide nanoparticles [24–26] or performing the reactions in unconventional media such as ionic liquids [27,28].

Utilization of inorganic-organic hybrid materials and coordination polymers as self-supported catalysts is another development in this regard. Depending on the coordination geometry of the metals and the bonding preference of donating atoms as well as the geometry of organic linkers, coordination polymers with one, two or three dimensions can be constructed. These metal organic assemblies formed via coordinate bonds, hydrogen bonds and aromatic π - π interactions can be insoluble in the conventional reaction media and can be utilized as heterogeneous catalysts. Coordination polymers with extended structures do not suffer from negative effects of some pre-synthesized supports such as random anchoring, reduced catalytic activity and/or selectivity of catalysts due to poor accessibility, or disturbed geometry of active sites in the solid supports [29,30]. Inorganic-organic hybrids and coordination polymers such as $\{[\text{Co}^{\text{II}}\text{Cl}_3](\text{tptz})\{[\text{Co}^{\text{II}}\text{Cl}(\text{H}_2\text{O})]\} \cdot 0.25\text{H}_2\text{O}$ (tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine), [7] $[\text{Cu}(\text{H}_4\text{bttec})(\text{bipy})]_{\infty}$ (H_4bttec = 1,2,4,5-benzenetetracarboxylic acid) [31,32], $\{[\text{Ni}(\text{L})_2(\text{H}_2\text{O})][\gamma\text{-Mo}_8\text{O}_{26}] \cdot 0.5 \text{H}_2\text{O}\}_n$ (L = 1,4-bis(1,2,4-triazol-yl)-butane) [33], and $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{dipy-pra})\text{Cl}_2$ (dipy-pra = 1,3-bis(4-pyridyl)propane) [34] were prepared and used as self-supported catalysts for the epoxidation of olefins.

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It has been proved that molybdenum complexes are excellent epoxidation catalysts [35]. Therefore, several research groups including us have studied molybdenum oxide-based inorganic–organic hybrid materials, oxomolybdenum complexes as well as polyoxomolybdate compounds [36–40].

As a part of our continuing interest in oxidation reactions, we report the hydrothermal synthesis, characterization and catalytic behavior of a mixture of blue $[\text{CuMoO}_4(\text{N}_2\text{C}_{12}\text{H}_8)]\cdot\text{H}_2\text{O}$ (**1**) and yellow $[(\text{Cu}_3\text{Cl}(4,4'\text{-bipy})_4)[\text{Cu}^{\text{II}}(1,10\text{-phen})_2\text{Mo}_8\text{O}_{26}]]$ (**2**) crystals in the epoxidation of olefins and allylic alcohols.

2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased from commercial sources and used as received. Powder X-ray diffraction (PXRD) patterns were obtained using a Philips PW1800 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra of the samples were recorded with Bruker Enquinox 55 spectrometer equipped with a single reflection diamond ATR system. The metal content of the sample was measured using inductive coupled plasma optical emission spectroscopy (ICP) analysis on ICP-OES Optima 8000. Oxidation products were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a flame ionization detector (FID). Gas chromatography-mass spectrometry (GC-MS) was recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25).

2.2. Synthesis of the catalyst

A mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.1 mmol, 0.124 g), $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.3 mmol, 0.052 g), 4,4'-bipy (0.3 mmol, 0.047 g), 1,10-phenanthroline (0.2 mmol, 0.036 g), KF (0.3 mmol, 0.017 g) and H_2O (10 ml) was stirred for 30 min in air. The starting pH value of the mixture was adjusted to 5.5 by the addition of diluted ethylenediamine solution followed by transferring it to a Teflon-lined stainless steel autoclave and keeping it at 165°C for 4 days. After slow cooling to room temperature, the resulting product

Table 1
Crystal and structure refinement data for $[\text{CuMoO}_4(\text{N}_2\text{C}_{12}\text{H}_8)]\cdot\text{H}_2\text{O}$ (**1**).

Compound	1
Empirical formula	$\text{C}_{12}\text{H}_{10}\text{CuMoN}_2\text{O}_5$
Molecular weight	421.70
Crystal system	Monoclinic
Space group	$P_{21/n}$
T (K)	295(2)
Wavelength, $\text{MoK}\alpha$ (\AA)	0.71073
a (\AA)	14.1533(7)
b (\AA)	5.8810(3)
c (\AA)	16.2510(8)
α ($^\circ$)	90.00
β ($^\circ$)	103.244(4)
Cell volume (\AA^3)	1316.68(11)
Z	4
ρ (g cm^{-3})	2.127
μ (mm^{-1})	2.590
$T_{\text{min}}/T_{\text{max}}$	0.855/1.000
Total reflections	28393
Unique reflections	3170
Observed reflections [$F^2 > 2\sigma(F^2)$]	2514
R_{int}	0.0490
Data/restraints/parameters	3170/3/197
Goodness-of-fit (GOF) on F^2	1.058
R [$F^2 > 2\sigma(F^2)$] (R_1, wR_2)	0.0275, 0.0612
R (all data) (R_1, wR_2)	0.0417, 0.0660
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.460, -0.469

containing 0.162 g of a mixture of blue (**1**) and yellow $[(\text{Cu}_3\text{Cl}(4,4'\text{-bipy})_4)[\text{Cu}^{\text{II}}(1,10\text{-phen})_2\text{Mo}_8\text{O}_{26}]]$ (4,4'-bipy = 4,4'-bipyridine and 1,10-phen = 1,10-phenanthroline) (**2**) [41] crystals, was filtered off, washed with distilled water and dried in air.

2.3. Catalytic epoxidation process

In a typical procedure for the epoxidation reaction, to a mixture of catalyst (100 mg) and substrate (8 mmol) in chloroform (10 ml), *tert*-butyl hydroperoxide (TBHP, 14.4 mmol) as oxidant was added. TBHP (70% in H_2O) was dried prior to use according to the procedure described in the literature [42]. The mixture was refluxed for appropriate time and the final products were quantified with isooctane (8.75 mmol) as internal standard.

2.4. Single crystal X-ray data collection and refinement

The data were recorded on a Bruker APEX-II diffractometer using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 295 K. Cell refinement and data reduction were carried out using the algorithms implemented in SAINT Bruker (Bruker AXS Inc. 2007, Madison, Wisconsin, USA). The structure was solved by direct methods using SHELXS-97 and the obtained model refined with SHELXL-97 [43]. The data were deposited in Cambridge Crystallographic Data Centre, with deposition number CCDC-970134 for **1** and 970133 for **2**.

3. Results and discussion

3.1. Structure of $[\text{CuMoO}_4(\text{N}_2\text{C}_{12}\text{H}_8)]\cdot\text{H}_2\text{O}$ (**1**)

The crystallographic details for **1** are provided in Table 1. The asymmetric unit of **1** consists of a Cu^{2+} cation, a molybdate anion, 1,10-phen ligand and one free water molecule (Fig. 1). The coordination environment of Cu1 ion exhibits a $\{\text{CuN}_2\text{O}_3\}$ distorted square pyramidal geometry. The Cu1 ion is coordinated to two nitrogen atoms from 1,10-phen (with the bond distances of $\text{Cu1-N1} = 2.038(2) \text{ \AA}$ and $\text{Cu1-N2} = 2.005(2) \text{ \AA}$ and bond angles of $\text{N1-Cu1-N2} = 81.67(9)^\circ$), two $\mu_2\text{-O}$ groups at basal position ($\text{Cu1-O1} = 1.927(2) \text{ \AA}$; $\text{Cu1-O3} = 1.906(2) \text{ \AA}$) and one $\mu_2\text{-O}$ group at apical position ($\text{Cu1-O2} = 2.269(2) \text{ \AA}$). Each Mo1 site has a distorted tetrahedral geometry and is surrounded by three $\mu_2\text{-O}$

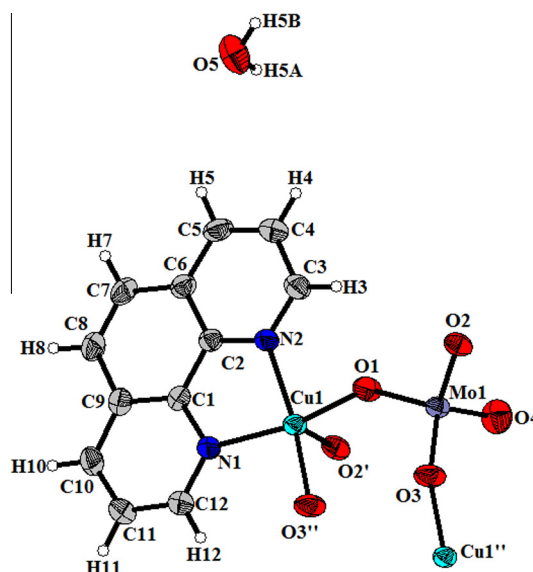


Fig. 1. View of the asymmetric unit of $[\text{CuMoO}_4(\text{N}_2\text{C}_{12}\text{H}_8)]\cdot\text{H}_2\text{O}$ (**1**) with 50% probability ellipsoids. Symmetry code: (') : $x, -1 + y, z$ ("); $1 - x, -y, 2 - z$.

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