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Hydrothermal synthesis and characterization of $\{[Ni_2(NA)_4(\mu\text{-}H_2O)]\cdot 2H_2O\}_n$ (HNA = nicotinic acid) and its heterogeneous catalytic effect

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ABSTRACT

A carboxylate-bridged metal–organic coordination polymer $\{[Ni_2(NA)_4(\mu\text{-}H_2O)]\cdot 2H_2O\}_n$ (**1**, HNA = nicotinic acid) has been synthesized under hydrothermal conditions and characterized by FT-IR, TG/DTA, micro analysis and single-crystal X-ray diffraction. **1** has an interesting 3D network structure and adjacent networks are further connected together via strong π–π packing interactions. The thermal behavior and catalytic performance of **1** were investigated and its selectivity was measured as 100% for the oxidation of thymol (T) to thymoquinone (TQ).

1. Introduction

Metal–organic frameworks (MOFs) including multifunctional carboxylic acid ligands have attracted considerable attention because of their interesting structural motifs and potential applications in different areas [1,2]. Additionally, MOFs containing nickel are widely used in several catalytic reactions, such as oxidation, hydrogen production, isomerization and dehydrogenation reactions [3]. Carboxylic acid ligands bearing oxygen and nitrogen donor atoms are the most widely used compounds for the synthesis of MOFs [4–6]. All kinds of rigid pyridinedicarboxylic (pydc) acids (2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-) are good choices for constructing MOFs due to the coexistence of reliable pyridyl groups as well as carboxylate moieties with rich coordination modes [7–13]. With these ligands, a large number of beautiful networks of ingenious design have been constructed [14–20]. However, compared with other pyridinedicarboxylic acids, the use of the 2,3-pydc^{2-} ligand in heterometal–organic frameworks chemistry has been very limited [21,22]. The first reason for this is that this ligand prefers decarboxylation of the 2-position carboxylate group which transforms it to nicotinic acid under the hydrothermal conditions. Secondly, it often behaves like picolinic acid (Scheme 1), acting as a chelating bidentate ligand through the nitrogen atom and one oxygen atom of the 2-position carboxylate group, and the 3-position carboxyl group remains idle [23–25].

The hydrothermal method has been a promising technique in preparing novel coordination polymers [26]. In particular, pyridinedicarboxylic acids have been proven to be interesting and versatile ligands and may exhibit various coordination modes to build different structures with higher dimensions [27,28]. Factors such as solvent, pH and reaction temperature appear to control the dimensionality, though the different coordination compounds of the metal ions also play an important role in determining the crystal structures of the corresponding metal–organic polymers [29].

One of the potential applications of MOFs including carboxylic acid ligands is the oxidation of organic compounds. Monoterpenes are extensively used in industrial and medical areas as a starting agent. Thymol (T) is an important component of monoterpenes and its oxidation product TQ is commercially important [30–32]. In this sense, TQ can be obtained from T using convenient catalysts (see Scheme 2). TQ is the main constituent of the volatile oil of *Nigella sativa* (black seed). Black seed belongs to the family *Ranunculaceae* and is an annual herb of the Mediterranean region, South and Central Asia, and now is also cultivated in Eastern Europe. The main active components of black seed include TQ, thymohydroquinone, dithymoquinone, thymol and carvacrol, which are important pharmacologically active substances. TQ demonstrates anticancer [33], antifungal [34], antioxidant [35–37], antinociceptive [38]

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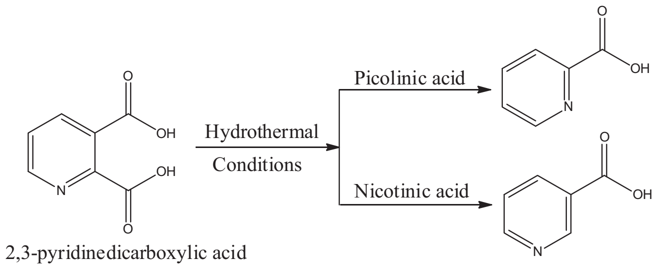
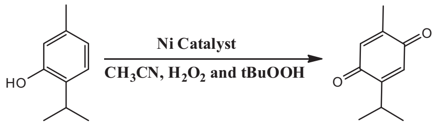


Scheme 1. The behavior of the 2,3-pydc^{2-} ligand under hydrothermal conditions.



Scheme 2. Oxidation of T to TQ using a Ni(II) catalyst.

and neuropharmacological activities [39]. TQ, representing 18.4–24% of the essential oil of black seed, possesses antibacterial, antihistaminic and anti-inflammatory activities [40]. The oxidation product TQ is a crucial compound for research, such as for treatment of cancer and other diseases. Especially in the last three years, it has been proven to be effective in the treatment of cancer of the pancreas [41], breast [42,43], prostate [44] and colon [45]. Also, it has anti-microbial [46], anti-histamine [47], anti-inflammatory [48] activities and oxidative stress [49] properties.

In this article, we chose 2,3-pyridinedicarboxylic acid as a ligand because of its interesting behavior under hydrothermal conditions, and have synthesized and structurally characterized a dinuclear coordination polymer, $\{[Ni_2(NA)_4(\mu\text{-}H_2O)]\cdot 2H_2O\}_n$ (**1**). The complex was obtained with higher yield and under different conditions, such as starting materials, reaction temperature and reaction time, than complexes of similar empirical formulas [50]. The thermal property and catalytic activity of complex **1** were studied. The polymer showed high thermal stability and high selectivity in the catalytic oxidation reaction of T to TQ (Scheme 2).

2. Experimental

2.1. Materials and methods

$NiCl_2\cdot 6H_2O$, 2,3-pyridinedicarboxylic acid, NaOH, T, TQ, acetonitrile, *tert*-butyl hydroperoxide (~80%) and hydrogen peroxide (30%) were purchased from commercial sources and used as received. Hydrothermal synthesis was carried out in 23 mL PTFE-lined stainless steel containers under autogenous pressure. Infrared spectra were recorded with KBr pellets on a Perkin-Elmer RX-1 FT-IR spectrometer in the range 4000–400 cm^{-1}. Thermogravimetric analyses (TGA) were conducted in a nitrogen atmosphere with a Perkin Elmer Pyris Diamond TG/DTA equipment at a heating rate of 10 °C min^{-1}. HPLC and headspace GC/MS were used for the characterization of TQ, determination of the percentage conversion and selectivity values. The GC/MS was measured on a Thermo Brand chromatograph with TR5MS capillary columns (60 m × 0.25 mm i.d.; 25 μm film thickness). The chromatographic conditions were injector temperature: 240 °C, beginning temperature: 50 °C, final temperature: 250 °C and heating rate: 3 °C min^{-1}. For the HPLC analysis a Shimadzu HPLC system equipped with a reversed phase C8 column (250 cm × 4.6 mm column dimensions, 5 μm particle sizes, Ascentis® was used. $CH_3OH:CH_3CN:H_2O$ (50:20:30, v/v) was used for the separation as the mobile phase. The column temperature was 35 °C, the detection wavelength was 254 nm, the flow rate was 1.0 mL min^{-1} and the retention time was 15 min. Before injection of a sample, the column was equilibrated with the mobile phase at a flow-rate of 1.0 mL min^{-1} for at least 30 min or until a steady baseline was obtained. Calibration curves of T and TQ were used for determination of the conversion and yield values.

2.2. Synthesis of the coordination polymer 1

All starting materials were used directly without further purification. A mixture of $NiCl_2\cdot 6H_2O$ (0.192 g, 0.8 mmol), pyridine 2,3-dicarboxylic acid (0.134 g, 0.8 mmol), NaOH (0.064 g, 1.6 mmol) and H_2O (5 mL, 278 mmol) in the mole ratio 1.00:1.00:2.00:348 was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 160 °C for 96 h. The mixture was cooled to room temperature at a rate of 20 °C h^{-1} and turquoise colored crystals were obtained. The heterogeneous solution mixture was separated from the solid phase and the crystals were washed with water and then dried at room temperature. Yield: 92.8% based on Ni. Initial pH: 3.60, final pH: 2.00. The coordination polymer is insoluble in common solvents (ethanol, methanol, acetonitrile etc) and water. *Anal.* Calc. for $C_{24}H_{22}N_4Ni_2O_{11}$: C, 43.64; H, 3.33; N, 8.49. Found: C, 43.12; H, 3.32; N, 8.19%. IR data (KBr pellet, cm^{-1}): 3436(w), 3103(m), 2952(m), 1605(s), 1584(s), 1491(m), 1364(s), 1006(m), 779(s), 763(s), 588(s), 516(m).

2.3. X-ray structure determination

The crystallographic data collection for **1** was performed using a Bruker AXS SMART CCD diffractometer with Mo Kα radiation at 100 K. The APEX2 Crystallographic Suite was used for determination of the unit-cell parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package. Crystal data and structure refinement for **1** are summarized in Table 1 and selected bond lengths and angles are given in Table 2. Anisotropic displacement parameters, hydrogen coordinates and other crystallographic data are available in the Supporting Information (SI) (Tables S1–S4). A BRUKER AXS D8 model diffractometer was used for the powder X-ray diffraction of the catalyst.

2.4. Oxidation of thymol (T)

T oxidation was carried out at room temperature and at 60 °C in a three-necked flask (250 mL) equipped with a magnetic stirrer, a reflux condenser and a temperature controller in an oil bath. T (3.0 g, 20 mmol) and 20 mL acetonitrile were added successively into the flask. The appropriate amount of oxidant, 30 wt.% of aqueous H_2O_2 (7.0 mL, 69.80 mmol) and 80 wt.% aqueous of the *tert*-butyl hydroperoxide (6.0 mL, 48 mmol), were then added to the reaction mixture. After heating this mixture to 25 and 60 °C, the metal complex (0.1, 0.2 and 0.3 g) was added to start the reaction and stirred incessantly for 2, 5, 8 and 24 h. The mixture of the reactions was collected at given time intervals and was analyzed by HPLC.

3. Results and discussion

3.1. Crystal structure of $\{[Ni_2(NA)_4(\mu\text{-}H_2O)]\cdot 2H_2O\}_n$ (1)

The coordination polymer was synthesized hydrothermally. It is interesting to note that when the temperature was 160 °C, decarboxylation occurred and the pyridine-2,3-dicarboxylic acid was transformed into nicotinic acid in the process of the hydrothermal reaction [51,52]. Single crystal X-ray analysis showed that the