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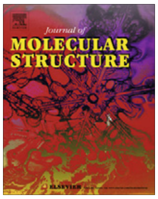

Synthesis, structure and properties of the first organic-templated inorganic-framework Ba(II) perchlorate

Jian-Cheng Zhou *, Bing-Yao Zhou, Xing-Jun Ma, Ting-Ting Cheng, Nai-Xu Li, Hai-Jun Xu *

School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu 211189, PR China

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ABSTRACT

The first organic-templated Ba(II) perchlorate with open architecture, $[(C_6H_8N)_2Ba(ClO_4)_4]_n$ (**1**), has been synthesized in the presence of 3-methylpyridine (3-MP) under hydrothermal conditions. The compound **1** was characterized by single crystal X-ray diffraction, elemental analysis, IR, powder XRD, ^{1}H NMR, TGA and fluorescence spectra. The 12-coordinate Ba(II) ion was located in the center of the irregular icosahedral (BaO_{12}) cage. Then the icosahedral BaO_{12} cages and the ClO_4^- linkers joined together to form a (4, 4) topology. And the protonated amine molecules were residing in the interlamellar space of the inorganic macro-anionic topology layers in the aAa mode (a = amine, A = anionic layer). The N–H···O hydrogen bonds ensure the stability of the structure by mounted the organic molecules to the main body of the inorganic framework. The solid-state fluorescence spectrum of complex **1** exhibits broad emission at 381 nm at room temperature, which is stronger than the free MPP (MPP = 3-methylpyridinium perchlorate). In addition, the two different synthesis methods provide an effectual impetus about applying hydrothermal reaction chemistry to build novel structures.

1. Introduction

Inorganic open-framework compounds involving phosphates [1,2], silicates [3] and carboxylates [4–9] have been synthesized and widely investigated in the past few decades for their novel structure and various properties. And recent studies have found that oxyanions such as sulfate [10,11], selenite [12–14] and selenate [15–17] can also be used to build up open-framework structures. The four O atoms of oxyanions (XO_4, X = P, S, Se and Si) can coordinate to the metal centers in monodentate, chelate or bridged modes to result in the formations of various inorganic frameworks. Therefore, several organic-template silicates, sulfates and phosphates of transition metal, main group metal, uranium and lanthanum have been synthesized [14–26]. However, inorganic-skeleton perchlorates are rarely reported. So far, only the diazabicyclo [2.2.2] octane (DABCO) organic-templated potassium perchlorate has been synthesized [18].

The ClO_4^- has the similar XO_4 structure (here the X is halogen Cl atom). Therefore, the ClO_4^- anion was chosen as inorganic building block to build new open-framework structures. The metal centers are alkaline earth metal ions and transition metal ions. The organic templates are aniline and pyridine derivatives, respectively. However, only single-molecular compounds can be obtained by taking conventional synthesis methods. Finally, one 2D inorganic open-framework barium perchlorate, $[(C_6H_8N)_2Ba(ClO_4)_4]_n$ (**1**), has been successfully prepared when employing 3-methylpyridine (3-MP) as the structure-directing template by taking two different reaction routes (Scheme 1). Then the compound **1** was characterized by single crystal X-ray diffraction, elemental analysis, IR, powder XRD, ^{1}H NMR, TGA and solid state luminescence properties.

2. Experimental section

2.1. Material and instrument

Chemicals and solvents in this work were commercially obtained and used without any further purification. Elemental analysis for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–500 cm^{-1}) were recorded by using KBr pellet on a Bruker Vector 22 spectrophotometer. The X-ray powder diffraction (XRD) data were collected with a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 20 °C/min from ambient temperature to 700 °C. The fluorescent spectra were recorded on a Shimadzu Instrument FL/FS-920 fluorescent spectrometer.

2.2. Preparation of the MPP

The preparation of MPP was shown in Scheme 1, (MPP = anhydrous 3-methylpyridinium perchlorate). 3-MP (100 mmol, 9.3 g)

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* Corresponding authors. Tel./fax: +86 25 52090620.

E-mail addresses: jczhou@seu.edu.cn, zhjcchem@yahoo.com.cn (J.-C. Zhou), xuhaijun_jx@163.com (H.-J. Xu).

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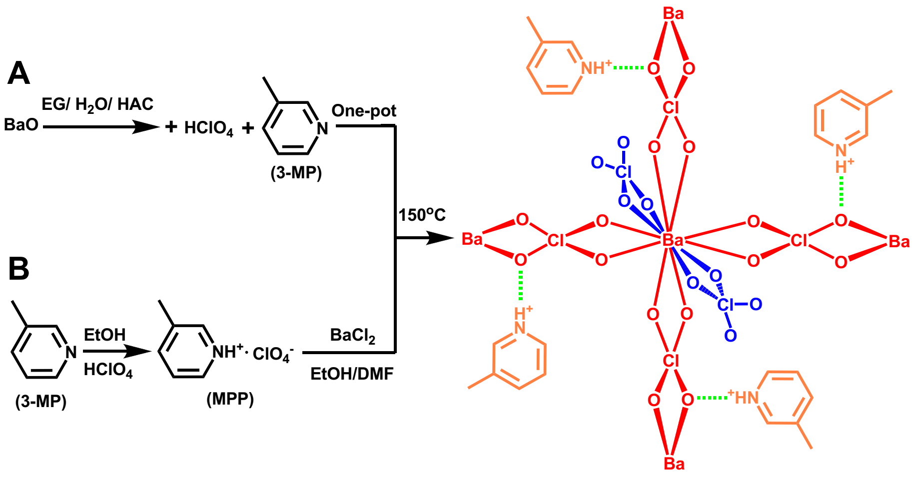

Scheme 1. The synthesis of ligand and complex **1**, and the coordination modes of amine-templated inorganic-framework layer.

was dissolved in 50 ml methanol. And then $HClO_4$ (100 mmol, 10.5 g) was dropped into the above solution. After the solution was evaporated to dry, the solid powder was kept at 120 °C for 6 h in the oven to remove the residual solvent.

MPP: Anal. Calcd. for $C_6H_8NO_4Cl$: C, 37.21; H, 4.13; N, 7.24. Found: C, 37.09; H, 4.06; N, 7.11. ESI-MS m/z (%): $[M^-] = 99.63$ (ClO_4^- anion); $[M^+] = 94.11$ (3-methylpyridinium cation). Main IR (cm^{-1}, KBr): 3287(s), 3091(w), 2981(m), 2856(m), 1557(s), 1467(m), 1338(w), 1203(m), 1101(s), 938(s), 778(m), 729(w), 704(m), 667(w)), 650(m), 628(m)), 595(w), 557(w), 511(w), 472(w), 422(w).

2.3. Preparation of complex $[(C_6H_8N)_2Ba(ClO_4)_4]_n$ (**1**)

The title complex has been synthesized by the following two methods from different starting materials under hydrothermal conditions (Scheme 1) [27–34]. Complex **1** is air-stable and insoluble in common organic solvents.

2.3.1. Method A

Compound **1** was synthesized by employing mild solvothermal methods in the presence of organic amine. BaO (1 mmol, 0.153 g) was dissolved in a mixture solution under constant stirring, (ethylene glycol (EG)/H_2O/acetic acid are 5.0, 1.0 and 0.5 mL, respectively). To this solution, 0.22 g (2 mmol) of $HClO_4$ (98%) was slowly added. Finally, 0.186 g (2 mmol) of 3-methylpyridine was added to the mixture, and the mixture was stirred for 1 h to obtain a homogeneous gel. The final mixture with the molar composition of BaO/$HClO_4$/3-MP (1:2:2) was transferred into a 20 mL Teflon-lined acid digestion bomb and heated at 150 °C for 3 days under autogenous pressure. Then the reaction was slowly cooled to room temperature at a rate of 5 °C/h. Colorless block crystals suitable for X-ray diffraction were obtained in 73% yield (based on BaO).

2.3.2. Method B

Method B was performed by employing anhydrous 3-methylpyridinium perchlorate (MPP) as the source of the perchlorate anions and the amine. In a typical synthesis, 0.208 g (1 mmol) of $BaCl_2$ was dispersed in an ethanol/DMF mixture under constant stirring. To this mixture, 0.483 g (2.5 mmol) of MPP was added and the mixture was stirred for 1 h. The final mixture with the molar composition of $BaCl_2$/MPP/DMF/ethanol (1:2.5:40:40) was transferred into a 10 mL Teflon-lined acid digestion bomb and heated at 150 °C for 3 days. The reaction solution was slowly cooled and left to stand at room temperature. Colorless block crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate within one month (Yield: 54%, based on $BaCl_2$).

Elemental analysis for **1**, $C_{12}H_{16}BaCl_4N_2O_{16}$ (723.41): Anal. (%) calcd. C 19.91, H 2.21, N 3.87; found C 19.78, H 2.15, N 3.73. ^1H NMR (300 MHz, DMF, TMS, 298 K): δ (ppm): 8.85 (s, 1 H, aromatic-H), 9.02 (d, $J_{HH} = 5.7$ Hz, 1 H, aromatic-H), 8.29 (t, $J_{HH} = 5.7$ Hz, 1 H, aromatic-H), 8.65 (d, $J_{HH} = 5.7$ Hz, 1 H, aromatic-H) and 2.28 (s, 3H, methyl-H). IR spectrum (cm^{-1}, KBr): 3306(s), 3163(w), 3012(m), 2897(m), 1568(s), 1456(m), 1354(w), 1201(m), 1085(s), 925(s), 778(m), 729(w), 704(m), 667(w)), 650(m), 632(w), 619(m)), 594(w), 555(w).

2.4. Crystal structure determination

Single-crystal X-ray diffraction measurement for complex **1** was carried out on a Bruker SMART APEX CCD based on diffractometer operating at room temperature. Intensities were collected with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 35 mA, using ψ-ω scans technique. The data reduction was made with the Bruker SAINT package [35]. Absorption corrections were performed using the SADABS program [36]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms in the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to the C and N atoms were placed in calculated positions and refined as riding mode, with N–H = 0.86 Å (N), C–H = 0.93 Å (aromatic) and 0.96 Å (methyl), with U_{iso} (H) = 1.2 U_{eq}(aromatic C and N) and 1.5 U_{eq} (methyl). All computations were carried out using the SHELXTL-97 program package [37]. Detailed data collection and refinement of the compound **1** are summarized in Table 1, and the selected bond distances, angles and H-bonding are listed in Table 2. CCDC: 819564 contains the supplementary crystallographic data for this paper. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

3. Results and discussion

3.1. IR, UV/Vis spectra and powder XRD

The IR spectrum shows a series of peaks at 1568, 1456, 1201, 778 and 704 cm^{-1} are the characteristic of aromatic ring. The bands at 1085, 925, 650, 619 cm^{-1} are attributed to the ClO_4^- group.