Research paper

Synthesis, structure and adsorption studies of a nickel coordination polymer with selective removal on methyl orange

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ABSTRACT

A new coordination network based on 5-(1H-benzoimidazol-2-ylsulfanylmethyl)-isophthalic acid (H_2bismip) along with 4,4-bis(1-imidazolyl)bibenzene (bimb), formulated as $[Ni_2(bismip)_2(bimb)_2(H_2O)]_n$ (**1**) has been synthesized under solvothermal condition. Compound **1** has been structurally characterized by elemental analysis, IR spectroscopy, powder X-ray diffraction (PXRD). Single crystal X-ray diffraction analysis shows compound **1** is a 2D network with a Schläfli symbol of 4^4. The layer framework exhibits effective adsorption on organic dye. The kinetic of the adsorption process was analyzed by the pseudo-first-order and pseudo-second-order model equations and the data was fitted well with the pseudo-second-order kinetic model (R > 0.99). The compound was found to be an excellent selective absorbent for the removal of methyl orange (MO) from the mixture solution of methyl orange - methylene blue (MO-MB).

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1. Introduction

Recent years, the destructive results brought by the industry have aroused human being's serious concern about the ecosystem and environment, among which water contamination is especially severely. Therefore, great efforts have been made for the removal of organic pollutant from polluted water utilizing various kinds of coordination polymers (CPs) by adsorption [1] or degradation [2]. In the presence of CPs, the organic dyes, such as Methylene Blue (MB) [3], Rhodamine B (RhB) [4], Methyl Orange (MO) [5] and Congo red (CR) [6], could be degraded into less toxic molecules under the irradiation of UV or visible light. Although this kind of photocatalyst is superior to the homogeneous catalyst for their renewability, it is still a great challenge for the designations of water-stable CPs with semiconductor characteristics which rely on the rational combinations between ligands and metals. Compared to the traditional biological and physical treatment methods, CPs employed as simple and convenient adsorbents have the potential to improve water quality [7]. Some specific interactions facilitate the adsorption, electrostatic interaction, hydrogen-bonding and π...π stacking, for example [8]. Thus, a CP which is capable of selective adsorption on dye should be satisfied the followed two points simultaneously: (1) a stable and flexible framework which adapts to adopt the dye; (2) specific interactions existed between

the CP and dye, which stimulate the former to discriminate different types of dyes. Sun group reported a negatively charged CP for the remarkable capability to selectively adsorb and separate the cationic dye MB over neutral dye MO [9]. Furthermore, Wu et al. developed a 1D polyoxometalated-based material with the use of high selectivity toward the cationic dye CR with superior adsorption capacity [10]. We convinced that the conjugated system and certain flexible framework in a CP benefited the formation of π...π stacking between the dye and adsorbent.

Considering the reasons mentioned above, we used the flexible ligand based on benzimidazole carboxylate (H_2bismip, 5-(1H-benzoimidazol-2-ylsulfanylmethyl)-isophthalic acid) and semi-rigid N-donor ligand (bimb, 4,4′-bis(1-imidazolyl)bibenzene) to construct CPs. Herein, the synthesis and crystal structure of a new coordination polymer $[Ni_2(bismip)_2(bimb)_2(H_2O)]_n$ (**1**) was reported. Moreover, the diffuse reflectance spectrum of the compound **1** was recorded and the band-gap of the compound was calculated using Kubelka-Munk function. The property of selective adsorption on MO and the kinetic study were also investigated.

2. Experimental

2.1. Materials and physical measurements

The ligand H_2bismip and bimb were prepared as reported previously [11]. All other chemical reagents were obtained from commercial sources and used without further purification. Infrared (IR) sample was prepared as KBr pellets, and spectrum was obtained in

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the 4000–400 cm^{-1} range on a Nicolet 380 spectrophotometer. The elemental analyses for C, H and N were performed on a Perkin Elmer240C elemental analyzer. The powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku D/max-2200/PC system. The solution UV–Vis absorbance spectra were collected on a Cary-300 UV–Vis spectrophotometer. The UV–vis diffusion reflectance spectrum was obtained with a Shimadzu UV-3600 spectrophotometer, where an integrating sphere was used in diffusion reflectance absorption analysis. The field-emission scanning electron microscopy (SEM) images were obtained by using a JEOL JSM-6700F scanning electron microscope.

2.2. Preparation of compound [Ni$_2$(bismip)$_2$(bimb)$_2$(H$_2$O)]$_n$ (1)

To a 10 mL Pyrex glass tube was loaded NiCl$_2$·6H$_2$O (24 mg, 0.1 mmol), H$_2$bismip (33 mg, 0.1 mmol), bimb (29 mg, 0.1 mmol), 2 mL of DMF and 1 mL H$_2$O. The glass tube was sealed and heated in an oven to 120 °C for 1 d, and then cooled to ambient temperature at the rate of 5 °C h^{-1}. Green block crystals were collected and washed with H$_2$O/DMF (1:1 v/v). Yield: 12.4 mg (18% yield based on Ni). Anal. calcd for C$_{68}$H$_{54}$N$_{12}$O$_{11}$S$_2$Ni$_2$: C 58.47; H 3.90; N 12.04. Found: C 58.91H 3.72; N 11.94. IR (KBr, cm^{-1}): 3130 s, 1606 s, 1550 s, 1516 s, 1428 m, 1370 s, 1303 m, 1258 m, 1122w, 1062 m, 1002w, 961w, 814 m, 785w, 738 m, 654w, 519w, 440w.

2.3. X-Ray crytallography

Single-crystal X-ray diffraction data for **1** was collected on a Bruker APEX II CCD diffractometer equipped with graphite-monochromated Mo-Kα (λ = 0.71073 Å) by using the Φ/ω scan technique. Absorption correction was based on symmetry equivalent reflections using the SADABS program [12]. The crystal structure of compound **1** was solved by direct methods and refined on F^2 by full-matrix least-squares methods using *SHELXL* program [13]. All non-hydrogen atoms refined anisotropically. All H atoms were introduced at the calculated positions and included in the structure-factor calculations. A summary of key crystallographic information for **1** was given in Table 1. Selected bond lengths and angles for **1** were listed in Table 2.

Table 1
Summary of crystallographic data for **1**.

Compounds	**1**
Chemical formula	C$_{68}$H$_{54}$N$_{12}$O$_{11}$S$_2$Ni$_2$
Formula weight	1396.73
Crystal system	Monoclinic
a/Å	34.145(4)
b/Å	10.2845(13)
c/Å	25.033(3)
α/°	90.00
β/°	131.353(2)
γ/°	90.00
Unit cell volume/Å^3	6598.8(14)
Temperature/K	291(2)
Space group	$C2/c$
Z	4
No. of reflections measured	22,714
No. of independent reflections	5809
R$_{int}$	0.0538
Final R_I values ($I > 2\sigma(I)$)	0.0545
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.1520
Final R_I values (all data)	0.0702
Final w$R(F^2)$ values (all data)	0.1628
Goodness of fit on F^2	1.099

Table 2
Selected bond lengths (Å) and angles (deg) for **1**.

Compound **1**			
Ni(1)-O(1)	2.179(3)	Ni(1)-N(3)	2.058(3)
Ni(1)-O(2)	2.127(3)	Ni(1)-O(4A)	2.0634(19)
Ni(1)-O(5)	2.0740(19)	Ni(1)-N(6B)	2.076(3)
O(1)-Ni(1)-O(2)	61.29(10)	O(2)-Ni(1)-N(6B)	88.30(13)
O(1)-Ni(1)-O(5)	101.49(9)	O(5)-Ni(1)-O(4A)	94.63(8)
O(1)-Ni(1)-O(4A)	163.88(9)	O(5)-Ni(1)-N(3)	92.39(11)
O(1)-Ni(1)-N(3)	90.73(11)	O(5)- Ni(1)-N(6B)	89.03(12)
O(1)-Ni(1)-N(6B)	88.30(13)	O(4A)-Ni(1)-N(3)	89.21(10)
O(2)-Ni(1)-O(5)	162.67(9)	O(4A)-Ni(1)-N(6B)	92.05(12)
O(2)-Ni(1)-O(4A)	102.58(9)	N(3)-Ni(1)-N(6B)	178.02(13)
O(2)-Ni(1)-N(3)	89.93(12)		

Symmetry codes for **1**: (A) $x, y + 1, z$; (B) $x - 1/2, y + 1/2, z$

2.4. Dye adsorption experiments

To investigate the adsorption kinetic, 10 mg microcrystal sample as synthesized which have been grinded before was immersed in 20 mL methyl orange (MO) aqueous solution with the concentration of 30 mg/L. The beakers were sealed, continuously stirred at room temperature. 100μL solutions were taken out at different time intervals and diluted into 2 mL with water. The concentrations of MO in the solutions were then measured by UV spectrophotometry. The amount of MO adsorption at time t, q_t was calculated using the following equation [14]:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where q_t is the uptake of MO (mg/g), C_0 and C_t (mg/L) are the concentrations of MO in the solution at initial and any time t, respectively, V is the volume of the solution (L) and W is the total mass of sorbent (g) used in MO sorption.

3. Results and discussion

3.1. Synthesis

Green blocks of complex **1** were isolated through hydrothermal reaction of NiCl$_2$, H$_2$bismip and bimb in water/DMF (1:2 v/v) at 120 °C. In this process, temperature played an important role in producing the single phase of title compound. Upon lowering the reaction temperature to 100 °C, the title compound formed together with an unknown light green precipitate which was not characterized. Increasing the reaction temperature to 150 °C, green precipitate was formed in the system. Furthermore, attempts to prepare crystalline complex by using MeOH, EtOH, or CH$_3$CN instead of DMF were not successful. It is supposed that some DMF molecules act as Lewis base to accept the protons from ligands which facilitates the self-assembly between the nickel cations and ligand anions. However, the metal salts and reaction time have little influence on the formation of the final product except the yields.

3.2. Crystal structure of compound 1

The X-ray crystallographic analysis reveals that compound **1** crystallizes in the monoclinic space group $C2/c$ and features a two-dimensional (2D) network. As shown in Fig. 1a, Ni1 atom shows octahedral geometry, with three oxygen atoms from two different bismip ligands, one oxygen atom from one water molecule and two nitrogen atoms from two equivalent bimb ligands. In **1**, each bidentate bismip ligand connects two Ni atoms with μ_2-η_1:η_2 mode affording an infinite chain running along the b axis (Fig. 1b). Notably, the benzimidazole groups derived from bismip