



A 4-fold interpenetrated diamondoid metal-organic framework with large channels exhibiting solvent sorption properties and high iodine capture



Gift Mehlana, Gaëlle Ramon, Susan A. Bourne*

Centre for Supramolecular Chemistry Research, Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

ARTICLE INFO

Article history:

Received 11 February 2016

Received in revised form

6 May 2016

Accepted 12 May 2016

Available online 14 May 2016

Keywords:

Interpenetration

Iodine capture

Vapochromism

Desolvation

ABSTRACT

The characterisation of a 4-fold interpenetrated diamondoid metal-organic framework (MOF) $\{[Ni_4(44pba)_8] \cdot sol\}_n$, (**1**) (44pba = 4-(4-pyridyl)benzoate) is reported. The compound was prepared from Ni(II) and 44pba under solvothermal conditions. When activated to give **1d**, the compound absorbs a wide range of solvents which is accompanied by a visible colour change. Sorption of water triggers an irreversible phase transformation, while adsorption of methanol, ethanol, benzene, dimethylformamide and cyclohexanone does not affect the structural integrity of the framework as revealed by powder X-ray diffraction studies. Apart from ethanol, the uptake of polar protic solvents gave rise to an increase in the energy difference between the asymmetric and symmetric carboxylate stretches as confirmed by infrared studies. We attributed this to a change in the binding mode of the carboxylates from chelating to monodentate. The activated phase (**1d**) was found to absorb high levels of iodine into its channels in comparison to other reported MOFs. This is due to the high porosity of the network compound in which aromatic walls allow for the interaction of iodine molecules with the framework walls.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Polymeric coordination compounds and their subset metal-organic frameworks (MOFs) have provided a rich vein of relevance to researchers with interests in solid state functional materials [1,2]. The inherent porosity achievable for 2D and 3D network structures generated from bridging ligands coordinated to metal ions allows for applications as diverse as catalysis, gas storage, separation and extraction [3–6]. A large number of compounds with interesting properties have been synthesised to date but only a few have been put into practical application. This has been attributed to the difficulties associated with synthesising the materials on a large scale. The use of MOFs as chemical sensing material holds great potential since such applications do not require a large amount of sample [7–10]. The 21st century has seen an increasing focus on mesoscopic chemistry, the chemistry at which electrons, photons and neutrons perform. Solvatochromism is one such example and may be defined as a shift in the UV–vis spectrum of a material upon change of solvent in its network [9,11]; the shifts

often correlate with empirical measures of solvent polarity. In addition to solvatochromic behaviour induced by solvent polarity and specific solvent-chromophore interactions, MOFs exhibit solvent dependant colour changes stemming from other mechanisms such as change in the crystal packing induced by hydrogen bonding and changes in the coordination geometry around the metal centre which alters the d–d transitions [12,13].

Interpenetration is sometimes regarded as a hindrance to engineering highly porous materials, because it reduces the void space in a network [14–16]. Nevertheless this phenomenon has advantageous implications for the thermal stability and functionality of porous materials. For example, framework interpenetration can provide structural stabilization of porous networks [17]. Pore size control in MOFs may be achieved by controlling the degree of interpenetration. Ma et al. reported enhanced uptake of hydrogen gas due to the framework stabilizing effect of interpenetration [18]. MOFs containing several channel environments which respond differently to guest molecules are rare [9,11] but are extremely important as they may allow for variable extraction or for the co-existence of several species in a particular chemical environment.

Previous studies have reported structures with mixed functionality pyridyl-carboxylate ligands [19] including those reporting

* Corresponding author.

E-mail address: susan.bourne@uct.ac.za (S.A. Bourne).

the solvatochromic properties of a Co(II) compound assembled from 4-(4-pyridyl)benzoate, 44pba [9,11]. The structure of the compound had a 4-fold interpenetrated **dia** network. The cobalt centre had a distorted octahedral geometry emanating from the chelating binding mode of the two carboxylate groups and two nitrogen atoms of the ligand. In this contribution, we report the chromic properties upon solvent sorption as well as iodine capture of the Ni(II) analogue whose crystal structure was published [9]. This study also provides insight into the role played by interpenetration in response to different supramolecular interactions that prevail along the walls of the channels.

2. Experimental

2.1. Preparation of $\{[Ni_4(44pba)_2] \cdot 2.4H_2O\}_n$ (**1d-water**)

The compound $\{[Ni_4(44pba)_8] \cdot sol\}_n$ (**1**) was prepared as previously reported [9]. When compound **1** is soaked in methanol for 24 h, the guest DMF and ethanol molecules are exchanged for methanol giving the methanol solvate (**1m**) whose cobalt(II) analogue has been reported [10]. Compound **1m** was activated by thermal treatment at 90 °C for 5 h to yield **1d**. Water vapour was allowed to diffuse into **1d** at room temperature to give a partially water load structure **1d-water**.

2.2. Thermal analysis

Thermogravimetric analysis (TG) was carried out using a TA Instrument TA-Q500 instrument. In a typical experiment 1–5 mg of the sample was dried on filter paper, placed in an open aluminium pan and heated in a dry air atmosphere of nitrogen (50 ml min^{-1}) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ within the temperature range of 25–500 °C.

2.3. Infrared analysis

IR (Infrared) studies were carried out on a Bruker Alpha spectrometer equipped with an ATR platinum Diamond reflectance for solid samples. Samples were scanned over a range of 450–4000 cm^{-1} .

2.4. PXRD studies

Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D8 Advance X-ray diffractometer operating in a DaVinci geometry equipped with a Lynxeye detector using a $\text{CuK}\alpha$ -radiation ($\lambda = 1.5406 \text{ \AA}$). X-rays were generated by an accelerating voltage of 30 kV and a current of 40 mA. A receiving slit of 0.6 mm and a primary and secondary slits of 2.5 mm were used. Samples were placed on a zero background sample holder and scanned over a range of 4 to 40 θ with a step size of 0.01° per second.

2.5. Single crystal X-ray diffraction analysis

Structure determination was performed by single crystal X-ray diffraction using a Bruker KAPPA APEX II DUO diffractometer equipped with a graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collections were performed at room temperature. The program SAINT [20] was used for unit cell refinement and data reduction. Data were corrected for Lorentz-polarization effects and for absorption (program SADABS) [21]. Structure solutions were achieved by direct methods program SHELXS and refined by full-matrix least-squares on F^2 using SHELXL [22] within the XSEED [23] interface. The non-hydrogen atoms for the framework were located in the difference electron density maps and

were refined anisotropically while all the hydrogen atoms were placed with geometric constraints and refined with isotropic temperature factors. Crystallographic parameters are given in Table S1. The structures were deposited at the Cambridge Crystallographic Data Centre and allocated the refcodes CAXZOS and CAXZUY.

3. Results and discussion

3.1. Structural description

Compound **1** was reported in a previous publication [9]. The crystal structure of **1** could not be refined to an acceptable level owing to the massive solvent disorder present in the channels. Due to the large channels present in this compound, it was noted that the solvent content may vary from crystal to crystal. Compound **1** is an analogue of the cobalt structure which was fully described [9]; the full structural description is not given here. **1** crystallized in the tetragonal crystal system and space group *I4*. Four independent nickel centres were modelled in the asymmetric unit. Each metal centre is coordinated to four 44pba ligands via four oxygen atoms and two nitrogen atoms to furnish a distorted octahedral geometry. The overall network is 4-fold **dia** network which possess large channels running along the *c*-axis accounting for 47% of the unit cell volume. The adjacent **dia**-networks are stabilized by hydrogen bonding interactions. Fig. 1 depicts the structural features of the network found in both compound **1** and **1d-water**.

Single crystal X-ray diffraction data show that the compound **1d-water** crystallizes in the tetragonal crystal system and non-centrosymmetric space group *P42₁2*. The four nickel centres found in **1** merge into one centre and the eight 44pba ligand merge into two ligands in the asymmetric unit of **1d-water**. The unit cell parameters in compound **1d-water** can be transformed into the unit cell of **1** by the matrix $\begin{bmatrix} 1 & -1 & 0 & 1 & 1 & 0 & 0 & 0 & 2 \end{bmatrix}$. The nickel ion is coordinated to two carboxylate groups of the ligand which bind in a chelating fashion and two nitrogen atoms from the two pyridyl moieties to give the same geometry as that in compound **1**. As in compound **1**, compound **1d-water** exhibits the same **dia** network which is 4-fold interpenetrated. Despite this interpenetration, channels with the same volume as those found in **1** are present with pore sizes of $11.9 \times 11.9 \text{ \AA}$ taking into account the van der Waals radii. These channels (A and B) are not crystallographically equivalent (Fig. 2). Channel A and B forms about a 2 and 4 fold-fold rotation axis respectively. This gives rise to different geometries of the channels as illustrated in Fig.S1.

Furthermore, examination of the packing of **1d-water** found a putative $\pi \cdots \pi$ interaction that is present only along the walls of channel A (Fig. 2) suggesting that there are different electrostatic interactions which prevail in the two channels. Each **dia**-network is positioned in such a way that the Ni \cdots Ni distance between adjacent nets is 6.00 Å while the centroid to centroid distance of the pyridyl rings is 3.90 Å in nets related by translational symmetry. The $\pi \cdots \pi$ interactions observed in the **1d-water** structure are longer than those reported by Janiak [24] and the pyridyl rings are tilted relative to one another. However this interaction if present would be consistent with other reports which suggest that π interactions can assist or induce interpenetration [25,26]. Analysis of the frameworks shows that the presence of these $\pi \cdots \pi$ interactions on adjacent walls in A give rise to the Class IIIa ($Z = 4[2^*2]$) interpenetration. Thus the four interpenetrated nets can be considered as two sets of 2-fold nets, as first described by Zaworotko and co-workers [27].

The solvent in **1d-water** could not be modelled accurately owing to the solvent disorder. The unmodelled electron density was found to constitute 2.4 water molecules per formula unit

Download English Version:

<https://daneshyari.com/en/article/71976>

Download Persian Version:

<https://daneshyari.com/article/71976>

[Daneshyari.com](https://daneshyari.com)