



Effect of the synthesis temperature on the dimensionality of hybrid fluorozincates



Vanessa Pimenta, Quang Hoang Hanh Le, Annie Hemon-Ribaud, Marc Leblanc, Vincent Maisonneuve, Jérôme Lhoste*

LUNAM Université, Université du Maine, CNRS UMR 6283, Institut des Molécules et Matériaux du Mans (IMMM), Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

ARTICLE INFO

Article history:

Received 26 May 2016

Received in revised form 4 July 2016

Accepted 7 July 2016

Available online 11 July 2016

Keywords:

Hybrid fluoride

Tetrazole

MOF

Solvothermal synthesis

Microwave heating

ABSTRACT

A series of new hybrid fluorozincates incorporating 5-aminotetrazole (*Hamtetraz*) is obtained from a same starting mixture of ZnF_2 , HF solution and *Hamtetraz* in acetonitrile at different synthesis temperatures. The structures, determined by single crystal X-ray diffraction, exhibit various networks with dimensionalities that increase as a function of the synthesis temperature. At 120 °C, two phases, $ZnF_2(H_2O)(Hamtetraz)$ (**1**) and $ZnF_2(Hamtetraz)_2$ (**2**), coexist and display 1D infinite chains. $\infty[ZnN_2F_2O]$ chains are built up from $ZnN_2F_3(H_2O)$ octahedra linked by opposite fluorine corners in **1**, while $\infty[ZnN_2F_2]$ chains of edge sharing ZnN_2F_4 octahedra are found in **2**. At 130 °C, dense layers appear in $Zn_3F_5(H_2O)_2(amtetraz)$ (**3**); they result from the condensation of $\infty[ZnF_3N_2]$ and $\infty[ZnF_2NO]$ chains by fluorine corners to form a neutral 2D network. At 140 °C, $[NH_4] \cdot (Zn_4F_5(amtetraz)_4) \cdot 3H_2O$ (**4**) presents an anionic 3D network containing small cavities in which water molecules and ammonium cations are inserted. The thermal behavior of the coordination polymers **3** and **4** is studied by TGA analysis and X-ray thermodiffraction; an intermediate phase is observed during the decomposition of **4**.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Hybrid inorganic–organic porous materials, also called porous coordination polymers (PCPs) or metal–organic frameworks (MOFs), represent a new generation of crystalline multifunctional porous materials with potential applications in numerous fields, such as energy or health [1,2]. The PCPs, considered as supramolecular compounds with zeolite-like architectures, are built up from inorganic units and organic linkers that lead eventually to 3D frameworks with large cavities giving high surface area. Consequently, these porous materials can show exceptional catalytic and gas storage properties [3,4]. The first explored properties of MOFs were focused on adsorption of H_2 or CH_4 which could be used as future energy sources [5,6]. Nonetheless, CO_2 capture [7] and gas separation [8] are also seen as promising applications. The adsorption properties of these architectures are strongly influenced by numerous parameters such as the size and the topology of the organic linkers [9] or the presence of unsaturated metal sites known to be a key factor in gas adsorption [10]. To tune the network's topology, the most common approach consists to modify the

chemical nature of the precursors: organic linkers, metal cations or counterions [11]. Depending on the transition metal ions and its oxidation states, numerous coordination numbers from 2 to 7 give multiple geometries leading to original network topologies. The coordination numbers and the orientation of linker binding sites can also modify the network topologies and influence the size and shape of pores. The influence of metal cations and linkers has been largely demonstrated for MOFs containing carboxylate ligands [12]. As examples, MIL-53 [13] and MOF-5 [14] are prepared with benzenedicarboxylate ligands and Cr^{3+} and Zn^{2+} cations respectively. Ouellette et al. reported six new structures in the Cd(II)-1,2,4-triazolate system by changing the counterion nature only (F^- , Cl^- , Br^- , I^- , SO_4^{2-} and NO_3^-) [15]. It must be noted that the metal complexes with azoles as organic ligands are called Metal Azolate Frameworks (MAFs).

In the present work, we focus on the synthesis of hybrid fluorides with Zn^{2+} cation and aminotetrazole (*Hamtetraz*) as linker. The deprotonated form of aminotetrazole (*amtetraz*)⁻, that presents an aromatic cycle with four nitrogen donor atoms to form N–M bonds, is preferred in order to promote high network dimensionality. The values of deprotonation acidic constants of *Hamtetraz/amtetraz*⁻ couple ($pK_A = 4.6$) and the HF/F^- couple ($pK_A = 3.2$) are very close; this feature favours the crystallization of fluorinated MAFs. Zn^{2+} cation is selected for its aptitude to accept

* Corresponding author.

E-mail address: jerome.lhoste@univ-lemans.fr (J. Lhoste).

different coordination geometries, from a tetrahedral environment to an octahedral geometry. Suh et al. have reported the synthesis of Zn-based networks in which the Zn²⁺ coordination reversibly changes from trigonal bipyramidal to tetrahedral geometry by a desolvation/solvation mechanism [16]. Therefore, it is expected that the association of tetrazole cycles, fluoride ions and unsaturated metal sites in porous materials will be propitious to the gas uptake. While the literature is rich in terms of azole compounds, the presence of fluoride counterions is sparse. Thirteen metalate hybrids with fluorinated 2D or 3D networks are reported to date; six phases integrate only Zn²⁺ cations [17–21] and seven others combine divalent cations (Fe²⁺, Zn²⁺, Ni²⁺) associated to trivalent cations (A = Al³⁺, Fe³⁺) [17,22,23–25]. Most of the reported compounds are elaborated from 1,2,4-triazole or derivatives and they are generally obtained by solvothermal synthesis. While it is well known that the choice of the solvent or the reaction temperature allows the control of the network dimensionalities and topologies of metal carboxylates [26,27], the effects of the synthesis parameters are rarely described for fluorinated hybrids with nitrogen ligands. We have recently evidenced 3D networks that are obtained in acidic conditions and low azole concentrations [17,22,23]. Following an equivalent synthesis strategy, this paper reports on four new compounds with *Hamtetraz* and Zn²⁺ cations obtained by changing the synthesis temperature only: ZnF₂(H₂O)(*Hamtetraz*) (**1**) and ZnF₂(*Hamtetraz*)₂ (**2**) at 120 °C, Zn₃F₅(H₂O)₂(*amtetraz*) (**3**) at 130 °C and [NH₄](Zn₄F₅(*amtetraz*)₄)·3H₂O (**4**) at 140 °C. It is demonstrated that the increase of the synthesis temperature results in increased network dimensionality. We first describe the structures and the entities condensation. Then, the thermal behavior of **3** and **4** is studied and it is evidenced that **4** presents a crystalline intermediate with possible unsaturated metal sites.

2. Results and discussion

2.1. Crystal structure description

Four new hybrid fluorozincates are obtained by solvothermal synthesis at different temperature: ZnF₂(H₂O)(*Hamtetraz*) (**1**) and ZnF₂(*Hamtetraz*)₂ (**2**) at 120 °C, Zn₃F₅(H₂O)₂(*amtetraz*) (**3**) at 130 °C and [NH₄](Zn₄F₅(*amtetraz*)₄)·3H₂O (**4**) at 140 °C. The structures are determined from single crystal X-ray diffraction data. Details of the structure determinations are given in Table 1. Selected interatomic distances of zincate and organic groups are gathered in Table 2.

The structure of **1** is built up from neutral *trans*-chains ∞[ZnF₂N₂O] oriented along the *b* axis (Fig. 1 left). These chains contain ZnF₃N₂O octahedra connected by fluorine atoms F(2) and by *Hamtetraz* in the N1,N2-bridging mode [17] (Scheme S1). The presence of water molecule is confirmed by a long distance to Zn²⁺ (2.16 Å) compared to Zn–F(1) (2.10 Å). Fluoride ions, hydrogen atoms of –NH₂ of *Hamtetraz* and coordinated water molecules ensure the stability of the structure (Fig. 1 right) via hydrogen bonds (2.61–2.98 Å).

In **2**, the condensation of (ZnF₄N₂) units by the connection of F–F edges gives infinite ∞[ZnF₂(*Hamtetraz*)₂] chains oriented along *a* axis (Fig. 2 left). Nitrogen atoms of neutral tetrazole cycles, in N1-bridging mode, occupy the axial positions of the octahedra. Hydrogen bonds contribute to the stability of the structure with N–H···F(1) (2.58 and 2.89 Å) and N–H···N (3.16 Å) intra- and inter-chain interactions (Fig. 2 right).

The crystal system of **3** is orthorhombic with *Fmmm* space group. The architecture results from the stacking of (001) sheets linked by interlayer bonds Ow–H···Ow (2.58 Å) along the *c* axis (Fig. 3 left). The sheet can be described from inorganic 1D [100] columns (Fig. 3 right) connected by deprotonated aminotetrazole

Table 1

Crystallographic data of ZnF₂(H₂O)(*Hamtetraz*) (**1**), ZnF₂(*Hamtetraz*)₂ (**2**), Zn₃F₅(H₂O)₂(*amtetraz*) (**3**) and [NH₄](Zn₄F₅(*amtetraz*)₄)·3H₂O (**4**) at room temperature.

Formula	1 ZnF ₂ ON ₅ CH ₅	2 ZnF ₂ N ₁₀ C ₂ H ₆	3 Zn ₃ F ₅ O ₂ N ₅ CH ₆	4 Zn ₄ F ₅ O ₃ N ₂₁ C ₄ H ₁₂
<i>M</i>	206.47	273.52	411.25	758.83
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
ρ _{calc} (g cm ⁻³)	2.331	2.222	3.098	2.260
Space group	<i>P2₁2₁2₁</i>	<i>P2₁/n</i>	<i>Fmmm</i>	<i>P2₁/c</i>
<i>a</i> (Å)	6.2611(6)	3.2988(1)	3.9732(18)	6.5873(1)
<i>b</i> (Å)	6.9066(5)	12.2103(4)	17.551(7)	12.9396(3)
<i>c</i> (Å)	13.6068(13)	10.2295(3)	25.28(2)	13.0141(3)
β (°)	–	97.205(2)	–	90.023(1)
<i>V</i> (Å ³)	588.4(1)	408.8(1)	1762.8(13)	1109.3(1)
<i>Z</i>	4	2	8	2
μ(Mo, Kα) (mm ⁻¹)	4.152	3.026	8.175	4.374
<i>F</i> (000)	408	272	1552	730
No. of unique reflns	1712	2476	1171	2542
No. of obsd reflns [<i>I</i> > 2σ(<i>I</i>)]	1130	2157	956	2469
Refined parameters	98	70	53	162
GOF	0.999	1.266	1.257	1.250
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.0428 wR ₂ = 0.0771	R ₁ = 0.0632 wR ₂ = 0.1737	R ₁ = 0.0486 wR ₂ = 0.1431	R ₁ = 0.0513 wR ₂ = 0.1428
R indices (all data)	R ₁ = 0.0738 wR ₂ = 0.0881	R ₁ = 0.0685 wR ₂ = 0.1767	R ₁ = 0.0660 wR ₂ = 0.1675	R ₁ = 0.0523 wR ₂ = 0.1441
Largest diff. peak and hole (e ⁻ /Å ³)	–0.496, 0.510	–1.025, 4.708	–1.614, 1.559	–0.863, 4.026

Crystallographic data (excluding structure factors) for all structures have been deposited at the Cambridge Crystallographic Data Centre, CCDC 1446241 (ZnF₂(H₂O)(*Hamtetraz*) (**1**)), 1044011 (ZnF₂(*Hamtetraz*)₂ (**2**)), 1044009 (Zn₃F₅(H₂O)₂(*amtetraz*) (**3**)) and 1044010 ([NH₄](Zn₄F₅(*amtetraz*)₄)·3H₂O (**4**)). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Download English Version:

<https://daneshyari.com/en/article/1313534>

Download Persian Version:

<https://daneshyari.com/article/1313534>

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