Sodium templated formation of a unique tetradecanuclear \( \{ \text{Zn}_{12}(\mu_3\text{-OH})_6\text{Na}_2(\mu_2\text{-O}) \}^{18+} \) hetero-metal cluster core having an auxiliary bithiazole dibenzoate ligand

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A R T I C L E   I N F O

Article history:
Received 11 February 2013
Accepted 13 March 2013
Available online 22 March 2013

Keywords:
Hetero-metal cluster
Sodium(I) template
Zinc(II) complex
Crystal structure
Fluorescence spectrum

A B S T R A C T

A three-dimensional (3D) metal-organic framework having a unique tetradecanuclear \( \{ \text{Zn}_{12}(\mu_3\text{-OH})_6\text{Na}_2(\mu_2\text{-O}) \}^{18+} \) hetero-metal cluster core, formulated as \( \{ \text{Zn}_{12}\text{(BTDA)}_{10}\text{Na}_2(\mu_2\text{-O}) \} \) \( \{ \text{H}_2\text{BTDA} = 4,4'-(4,4'-\text{dibutyl-2,2'}-\text{bithiazole-5,5'}-\text{diyl})\text{dibenzoic acid} \} \), has been described herein. The tetradecanuclear hetero-metal cluster core is composed of two heptanuclear \( \{ \text{Zn}_6(\mu_2\text{-OH})_3\text{Na} \}^{10+} \) trifolium-shaped subunits where the axle sodium(I) ion is connected with three pairs of zinc(II) ions by three \( \mu_3\text{-OH} \) ions and the two sodium(I) ions are further linked by a \( \mu_2\text{-O} \) bridge. Besides, the auxiliary BTDA ligand serves as a multi-dentate bridging mode linking adjacent tetradecanuclear hetero-metal clusters into a 3D coordination polymer where a rhombohedral array with a new \( (4^8 \cdot 8^3 \cdot 1^2)^{12} \cdot 4 \) topology is observed.

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Research on the metal-organic frameworks (MOFs) has attracted considerable attention in the field of molecule-based materials in recent years [1–3]. Recently, the syntheses and assemblies of versatile MOFs have a rocketed growth in coordination chemistry and crystal engineering, not only because of their various and intriguing molecular structures, but also owing to their interesting optical, electronic, ferroelectric, catalytic and magnetic properties [4–8]. One of the most important problems is how to design and select suitable organic functional building blocks with fixed geometry and variable coordination modes in order to rationally produce MOFs on the basis of self-assembly [9,10]. In addition, the presence of suitable metal ions is vital in constituting certain functional MOFs. For example, many high-performance luminescent materials have been reported, where simple d¹⁰ metal ions, such as Cu(I), Ag(I), Zn(II) and Cd(II), are commonly involved [11,12]. However, metal clusters can also serve as the nodes instead of simple metal ions to produce fluorescent MOFs. Compared with the simple metal ions, the metal clusters have the advantage to hold more directional information by predestined bridging ligands, and then to control the overall coordination networks [13].

Based upon the above-mentioned considerations, we think 4,4'-(4,4'-dibutyl-2,2'-bithiazole-5,5'-diyl)dibenzoic acid (H₂BTDA) is a good candidate for assembling luminescent MOFs because its large π-conjugated aromatic heterocyclic system can afford both ligand based luminescence and ligand-to-metal (or metal-to-ligand) charge transfer based luminescence [14,15]. Besides, it is a multi-dentate chelating ligand in the deprotonated form which can link different metal ions to form rigid polymeric frameworks. In our previous work, we have described a series of coplanar bithiazole-centered heterocyclic aromatic fluorescent compounds having different donor/acceptor terminal groups including the single-crystal structure of H₂BTDA [16]. However, BTDA-based metal complexes have not been reported up until now.

Herein, we report the synthesis [17] and single-crystal structure [18] of a new 3D zinc(II)/Na(I) hetero-metal coordination polymer formulated as \( \{ \text{Zn}_{12}\text{(BTDA)}_{10}\text{Na}_2(\mu_2\text{-O}) \} \). Our synthetic strategy is based on the sodium templated method, in which the starting material H₂BTDA was prepared according to the previously reported approaches [16]. A solvothermal reaction of Zn(ClO₄)₂ · 6H₂O, H₂BTDA and NaOH in a mole ratio of 1:1:2 in EtOH (10 mL) sealed in a 20 mL Teflon lined stainless steel autoclave yields complex I at 120 °C for 3 days, where the Na⁺ ion in this case acts as a template instead of the self-assembly of the tetradecanuclear hetero-metal cluster.

The molecular structure of I with the atom-numbering schemes is shown in Fig. 1, and the selected bond distances and bond angles are listed in Table 1. As shown in Fig. 1a, it has a unique tetradecanuclear \( \{ \text{Zn}_{12}(\mu_3\text{-OH})_6\text{Na}_2(\mu_2\text{-O}) \}^{18+} \) hetero-metal cluster core where two heptanuclear trifolium-shaped \( \{ \text{Zn}_6(\mu_2\text{-OH})_3\text{Na} \}^{10+} \) subunits are bridged by one \( \mu_2\text{-O} \) linkage with the \( \mu_2\text{-O} \)–Na bond length of 1.645(5) Å. The tetradecanuclear \( \{ \text{Zn}_{12}(\mu_3\text{-OH})_6\text{Na}_2(\mu_2\text{-O}) \}^{18+} \) unit consists of two four-coordinate sodium(I) ions, six four-coordinate and six five-coordinate zinc(II) ions where every OH¹⁻ group links adjacent two zinc(II) and one sodium(I) ions in a \( \mu_2 \) fashion, as can be seen in Fig. 1b. The coordination geometry of two central Na(I) ions is slightly distorted tetrahedral, where four oxygen atoms from one \( \mu_2\text{-O} \) and...
three μ₃-OH bridges occupy the coordination sites. The three symmetrically related μ₃-OH–Na bond distances are longer (1.649(5) Å) than that of μ₁-O–Na one, indicative of the right assignment of the OH⁻ groups instead of the oxo units in this structure in addition to the charge equilib-ration consideration. The coordination geometry of six four-coordinate Zn(II) ions is tetrahedral with the mean Zn–O coordination bond length of 1.934(6) Å. In contrast, the coordination spheres for six five-coordinate Zn(II) ions are severely distorted trigonal bipyramidal (τ = 0.596) [19] due to the presence of a weak Zn–O coordinative bond (Zn2–O8 = 2.831(6) Å) and the mean Zn–O coordinative bond length for the other four is 1.947(5) Å.

It is noted that every tetradecanuclear cluster core cation in 1 is coordinated by thirty-six oxygen atoms from eighteen BTDA ligands. There are one and a half BTDA ligands in the asymmetric unit of 1, indicative of the rigidity of the Zn(II) cations towards the charge equilib-ration consideration. The coordination geometry of Zn(II) ions is tetrahedral with the mean Zn–O coordinative bond length of 1.934(6) Å. In contrast, the coordination spheres for six five-coordinate Zn(II) ions are severely distorted trigonal bipyramidal (τ = 0.596) [19] due to the presence of a weak Zn–O coordinative bond (Zn2–O8 = 2.831(6) Å) and the mean Zn–O coordinative bond length for the other four is 1.947(5) Å.

### Table 1

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond angles (°)</th>
</tr>
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<tr>
<td>Zn1–O2</td>
<td>O2–Zn1–O1</td>
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<tr>
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</tr>
<tr>
<td>Na1 · · · Na1b</td>
<td>Na1–Na1–Na1b</td>
</tr>
</tbody>
</table>

Symmetry codes: *x, y + 1, z; *x, 1/3–x, 2/3–y, 5/3–z; *x, y, x, 1–z; *y, 1, y, 1–x, *z; -1/3 + x, -2/3 + y, -2/3 + z; *x, 1/3 + x, -1/3 + y, 5/3–z; *x, 2/3–x, 4/3–y, 7/3–z.

To further study the sodium template effect, the alterations of molar ratios and alkali metal ions have been carried out. The control experiments were performed by using LiOH, KOH as the metal sources and different molar ratios of three starting materials. However, powder X-ray diffraction (XRD) and FT-IR spectral results demonstrate that those obtained powder samples are only impurities or even H₂BTDA. That is to say, Li⁺ and K⁺ templated formation of similar hetero-metal cluster was not successful mainly because of the size effect [22] of alkali metal ions. That is to say, the ion size of Li⁺ is too...
small and the shape of K⁺ is too big for this self-assembly reaction. In addition, BTDA ligand is suggested to play an important role in forming this 3D supramolecular framework.

The solid-state fluorescence spectra of H₂BTDA and its hetero-metal complex 1 at room temperature are depicted in Fig. 3. Compared with 4,4’-dibutyl-2,2’-bithiazole, in which the fluorescence emission band is observed at λmax = 389 nm upon excitation at 350 nm, H₂BTDA exhibits a strong yellow fluorescence emission peak at 458 nm upon excitation at the same wavelength [16]. The several tens of bathochromic shift for H₂BTDA arises from the presence of a large conjugated π-system of the molecule. After the metal-ion complexation, different color luminescence is observed for 1. Complex 1 displays two strong blue emission peaks at 366 and 386 nm with the excitation at 350 nm. The observation of blue-shifts in the solid-state fluorescence emission after metal-ion complexation is mainly because of the aforementioned distortions of adjacent aromatic ring in ligand BTDA (Fig. 2), which will reduce the planarity and the delocalization of conjugated π-system of the whole ligand.

In conclusion, a new 3D tetradecanuclear \{Zn₁₂(μ₃-OH)₆Na₂(μ₂-O)\}⁺⁺ hetero-metal cluster has been successfully synthesized by using the sodium templated method. In complex 1, two heptanuclear \{Zn₆(μ₃-OH)₃Na\}⁺⁺ trifolium-shaped subunits are found where the axle sodium(I) ion is connected with three pairs of zinc(II) ions by three μ₃-OH ions and the two sodium(I) ions are further linked by a μ₂-oxo bridge. The auxiliary BTDA ligand with a molecular length of 1.8 nm serves as a multi-dentate bridging ligand to coordinate adjacent tetradecanuclear hetero-metal clusters into a 3D puck-type MOF, where a new topology is observed with the Schlafli symbol of (4₁⁸ · s¹₀⁸ · 1₂²⁷ · 4₉). In addition, sodium templated effect and photoluminescence property of 1 have been studied.

To the best of our knowledge, the tetradecanuclear \{Zn₁₂Na₂\} hetero-metal cluster is still unexplored and ligand BTDA is firstly involved in the study of metal complex. We believe this work can provide an informative example in preparing functional multi-dimensional hybrid complexes based upon the alkali/transition metal ions and the carboxylate ligands. Thus, further investigations on other type of alkali metal ions and polynuclear transition-metal complexes are being underway.

Acknowledgment

This work was financially supported by the Major State Basic Research Development Programs (Nos. 2013CB922101 and 2011CB933300), the National Natural Science Foundation of China (No. 21171088) and Qing Lan Project.

Appendix A. Supplementary material

CCDC number 923377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.03.009.

References


