



Syntheses, structures, thermal stabilities and luminescence of two new 3D zinc phosphonates

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ABSTRACT

A 1,4-Butanediamine has been introduced as a structure-directing agent to synthesize two 3D zinc phosphonates under hydrothermal conditions, $[(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)_2\text{Zn}_2(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}(\text{Cl})]$ (**1**) and $[(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)_3\text{Zn}_3(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3)_2]$ (**2**). Compounds **1**–**2** were characterized by single-crystal X-ray diffraction along with powder XRD, EA, IR and TGA. Compound **1** is a 3D open-framework consisting of tetranuclear units and 16-membered-ring channel. In compound **2**, each trinuclear unit contacts with surrounding six trinuclear units through O–P–O groups into a single hybrid layer, which is further pillared by $\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3$ groups to form a 3D open-framework with 1D channel. In both compounds, 1,4-butanediamines are protonated and encapsulated into the channel through hydrogen bondings. Solids **1** and **2** are thermally stable up to 300 and 350 °C under air atmosphere, respectively. The luminescent properties of solids **1** and **2** are also studied in detail.

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1. Introduction

Metal phosphonates have attracted extensive interest for their structural diversities and applications as porous materials, catalyst, ion-exchangers, Langmuir–Blodgett Film (LB), sensors and non-linear optics [1]. During the last five years, metal phosphonates with fascinating structures and properties have continuously emerged as follows [2,3]. Phosphonic acids with additional functional groups like NH_2 , OH, COOH, pyridyl, imidazole, triazole, thienyl and benzimidazol exhibit many coordination modes to form numerous solids, such as layered calcium tetrakisphosphonates undergoing a swelling upon $\text{NH}_3/\text{H}_2\text{O}$ uptake, $\text{Co}(2\text{-pmp})(\text{H}_2\text{O})_2$ showing reversible changes of structures and magnetic behaviors upon the dehydration–hydration process, as well as porous heterometal phosphonate with helical channels and hydrogen sorption ability [4–13]. The combination of copper-bipyrimidine and molybdophosphonate clusters results in many hybrid materials [14]. Pillared metal diphosphonates have been exploited as meso/micro-porous materials [15–17]. Phosphonate clusters with manganese, iron, cobalt and copper, show interesting magnetism and strong third-order nonlinear optical (NLO) self-focusing effects [18–20]. Homochiral zinc and lanthanide phosphonates display 1D triple-strand helical chains and selective adsorption capacities for N_2 , H_2O and CH_3OH molecules [21,22]. Furthermore, an important subject is to introduce organic amines as structure-directing agents to achieve various phosphonates, like mixed-valence vanadium

phosphonoacetates with 16MR channels, and zinc phosphonates with tunable emission [23–28]. In this regard, Zheng et al. have successfully exploited 1,4-butanediamine as a structure-directing agent to tune the structures and properties of metal 1-hydroxyethylidenediphosphonates [29–35]. However, 1,4-butanediamine has not been introduced into metal nitrilotris (methylenephosphonates) and 1,2-ethylenediphosphonates. In this paper, we report syntheses, crystal structures, thermal stabilities and luminescence of two new 3D zinc phosphonates: $[(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)_2\text{Zn}_2((\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}(\text{Cl}))]$ (**1**) and $[(\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3)_3\text{Zn}_3(\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3)_2]$ (**2**).

2. Experimental

2.1. Materials and characterizations

$\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3\text{H}_2$ was prepared according to the previously reported method [36,37]. Other chemicals were obtained from commercial sources without further purification. Compounds **1**–**2** were synthesized in 25 mL Teflon-lined stainless steel vessels under autogenous pressure. The reactants were stirred homogeneously before heating. Elemental analyses were carried out with a Vario EL III element analyzer. Infrared spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer. Photoluminescence properties for solids **1**–**2** were investigated under room temperature with FLS920 and LifeSpec-ps. While luminescent properties for 1,4-diaminobutane and acidified 1,4-diaminobutane solution were performed under room temperature with a F-7000 FL spectrophotometer. The diffuse reflectance spectra of solids **1**–**2** and 1,4-diaminobutane dihydrochloride were recorded on

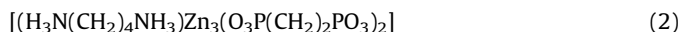
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a Perkin-Elmer Lambda 900 UV–vis-NIR spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449C at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $800\text{ }^{\circ}\text{C}$ under air gas flow. Powder XRD patterns were acquired on a DMAX-2500 diffractometer using $\text{CuK}\alpha$ radiation at an ambient environment.

2.2. Synthesis



A mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.3468 g, 1.580 mmol), $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2 \cdot 2\text{HCl}$ (0.6346 g, 3.625 mmol), $(\text{C}_2\text{H}_5)_4\text{NBr}$ (1.5134 g, 7.201 mmol) and H_6L solution (wt% = 50%, 0.4 mL), with the pH value was adjusted to in the range 2–3, and then heated at $160\text{ }^{\circ}\text{C}$ for 120 h. After slow cooling to room temperature, colorless prismatic crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.2576 g (59%). Anal. Calc. for $\text{C}_7\text{H}_{21}\text{ClN}_3\text{O}_9\text{P}_3\text{Zn}_2$: C 15.28, H 3.85, N 7.63%. Found: C 15.31, H 3.76, N 7.62%. IR (KBr pellet, cm^{-1}): 3099 m($\nu_{\text{N-H}}$), 2941 w($\nu_{\text{C-H}}$), 2896 w, 1631 m, 1509 m, 1468 w, 1436 m, 1236 m, 1227 m, 1174 w($\nu_{\text{P=O}}$), 1113 s($\nu_{\text{P-O}}$), 1081 s($\nu_{\text{P-O}}$), 1051 s($\nu_{\text{P-O}}$), 999 m($\nu_{\text{P-O}}$), 981 m, 908 m, 775 m, 591 s and 576 m.



A mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.1149 g, 0.5235 mmol), $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2 \cdot 2\text{HCl}$ (0.3507, 2.003 mmol), $(\text{C}_2\text{H}_5)_4\text{NBr}$ (1.2821 g, 6.100 mmol), $\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3\text{H}_2$ (0.1645 g, 0.8657 mmol) and H_2O (8.0 mL, 444 mmol), with the pH value was adjusted to 5.4, and then heated at $180\text{ }^{\circ}\text{C}$ for 144 h. After slow cooling to room temperature, colorless prismatic crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0884 g (77%). Anal. Calc. for $\text{C}_8\text{H}_{22}\text{N}_2\text{O}_{12}\text{P}_4\text{Zn}_3$: C 14.60%, H 3.37%, N 4.26%. Found: C 14.45%, H 3.06%, N 4.25%. IR (KBr pellet, cm^{-1}): 3005 w($\nu_{\text{N-H}}$), 2931 m($\nu_{\text{C-H}}$), 2970 w, 2806 w, 2632 w, 2112 w, 1526 m, 1652 m, 1452 w, 1298 w, 1263 w, 1196 m($\nu_{\text{P=O}}$), 1124 s($\nu_{\text{P-O}}$), 1108 s($\nu_{\text{P-O}}$), 1071 s($\nu_{\text{P-O}}$), 1047 s($\nu_{\text{P-O}}$), 1013 s($\nu_{\text{P-O}}$), 986 s, 807 w, 758 m and 537 m.

2.3. X-ray crystallography

X-ray data for **1–2** were collected at 293(2) K on a Rigaku Mercury CCD/AFC diffractometer, using graphite-monochromated

Table 1
Crystallographic data for compounds **1** and **2**.

Compound	1	2
Formula	$\text{C}_7\text{H}_{21}\text{ClN}_3\text{O}_9\text{P}_3\text{Zn}_2$	$\text{C}_8\text{H}_{22}\text{N}_2\text{O}_{12}\text{P}_4\text{Zn}_3$
FW	550.37	658.27
Space group	$P2(1)/n$	$P-1$
<i>a</i> (Å)	8.130(3)	9.0800(17)
<i>b</i> (Å)	22.358(7)	14.939(6)
<i>c</i> (Å)	10.538(3)	28.994(12)
α (deg.)	90	78.18(2)
β (deg.)	112.357(3)	88.974(9)
γ (deg.)	90	89.72(2)
<i>V</i> (Å ³)	1771.5(10)	3849(2)
<i>Z</i>	4	8
<i>T</i> (K)	293(2)	293(2)
Measured/unique/ observed reflections	13,523/4036/3545	28,866/17,104/7558
<i>D</i> _{calcd} (g cm ⁻³)	2.064	2.272
μ (mm ⁻¹)	3.178	4.106
GOF on <i>F</i> ²	1.076	1.039
<i>R</i> _{int}	0.0419	0.0959
<i>R</i> ¹ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0556	0.1441
w <i>R</i> ² ^b [all data]	0.1660	0.4351

^a $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$.

^b $wR2 = \{ \sum w[(F_o^2 - F_c^2)^2] / \sum w[F_o^2] \}^{0.5}$.

Mo- $K\alpha$ radiation ($\lambda(\text{Mo-}K\alpha) = 0.71073\text{ \AA}$). Data of **1–2** were reduced with CrystalClear v1.3. Their structures were solved by direct methods and refined by full-matrix least-squares techniques on *F*² using SHELXTL-97 [38]. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were generated geometrically. Crystallographic data for **1–2** are summarized in Table 1. CCDC 782688 (**1**) and 782689 (**2**).

3. Results and discussion

3.1. Structural descriptions

The asymmetric unit of **1** includes two crystallographically independent Zn(II) ions, one $(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}$ group, one Cl^- anion and a protonated 1,4-butanedi-amine cation. As shown in Fig. 1, Zn1 ion is surrounded by two $(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}$ groups into a distorted $[\text{ZnO}_4\text{N}]$ trigonal bipyramidal coordination geometry. It is attractive that one $(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}$ group is chelated to the Zn1 ion via three phosphonate oxygen atoms (O3, O5 and O8a) on the basal plane, along with a nitrogen donor (N1) occupying one polar site. To the best of our knowledge, the chelating mode is rare and only reported in $[\text{Hpy}][\text{Cu}(\text{N}(\text{CH}_2)_3\text{PO}_3\text{H})_3(\text{H}_2\text{O})]$, due to the nitrogen atom in other compounds is protonated [39–47]. And the other polar site of $[\text{ZnO}_4\text{N}]$ trigonal bipyramid is occupied by the fourth phosphonate oxygen atom (O9) from another $(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}$ group. While the Zn2 ion is in a distorted $[\text{ZnO}_3\text{Cl}]$ tetrahedral coordination geometry defined by three oxygen atoms from three different $(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}$ groups and one Cl^- anion. The bond lengths of Zn–O lie in the range 1.915(4)–2.034(4) Å, which match with those of zinc phosphonates [27]. The bond lengths of Zn1–N1 and Zn2–Cl1 are 2.304(4) and 2.3021(13) Å, respectively, which are longer than those of zinc phosphonates [7,22,48–49]. On the other hand, the $(\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{PO}_3\text{H}$ group exhibits a new octadentate mode to combine five Zn ions through seven phosphonate oxygen atoms along with one nitrogen donor. It is worth to mention that the nitrogen atom is not protonated and takes part in coordination. This is different from those in the reported compounds [40–47]. In addition, there are four hydrogen bondings in this structure: (1) the protonated 1,4-butanedi-amine provides three hydrogen atoms to form hydrogen bondings with adjacent phosphonate groups (N2...O5, 2.816(6) Å; N3...O3, 2.816(6) Å; N3...O8d, 2.892(7) Å); (2) the protonated phosphonate oxygen atom (O7) interacts with the neighboring phosphonate oxygen atom (O2e) through a strong hydrogen bonding (O7...O2e, 2.460(6) Å).

Thus, adjacent two Zn2 ions are bridged by two O4–P2–O6 into a binuclear unit. And the binuclear unit contacts with neighboring two Zn1 ions via O5 atoms to form a tetranuclear unit. On the *bc* plane, each tetranuclear unit contacts with surrounding four tetranuclear units through O9 to form a 2D hybrid layer. While along an *a* axis, adjacent tetranuclear units interact each other with O1 to form a chain. Thus, each tetranuclear unit contacts with surrounding six tetranuclear units to form a 3D framework with 16 MR channel along an *a* axis. The Cl^- ion points to the channel. And the channel is occupied by the protonated 1,4-butanedi-amine cations, which interacts to the 3D framework with hydrogen bonding.

Suitable single-crystal XRD reveals that solid **2** crystallize in the central space group $P-1$ with 3D pillared framework (Fig. 2). All Zn ions are in $[\text{ZnO}_4]$ distorted tetrahedral coordination geometries, which are surrounded by four oxygen atoms from four different $\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3$ groups. The bond lengths of Zn–O are in the range 1.881(14)–2.043(4) Å, which match with those in **1**. On the other hand, each $\text{O}_3\text{P}(\text{CH}_2)_2\text{PO}_3$ group exhibits a hexadentate mode to combine six Zn ions through all deprotonated oxygen atoms, which

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