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Synthesis and structural characterization of five zinc bisphosphonate compounds



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A R T I C L E I N F O

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ABSTRACT

The hydrothermal reaction of zinc ions with 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) in the presence of additives such as 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,3-propanediamine, imidazole and isonipecotic acid, afforded five metal phosphonates, namely, $[H_2DABCO]{Zn_3[CH_3C(OH)(PO_3)_2]_2}$ (1), $[C_3H_1AN_2]{Zn_3[CH_3C(OH)(PO_3)_2]_2}$ (2), $[C_3H_5N_2]_2{Zn_3[CH_3C(OH)(PO_3)_2]_2}$ (3), ${Zn_2[CH_3C(OH)(PO_3)_2]_2}$ (2), $[C_3H_4N_2]_2{Tn_3[CH_3C(OH)(PO_3)_2]_2}$ (3), ${Zn_2[CH_3C(OH)(PO_3)_2]_2}$ (2), $[C_3H_4N_2]_2$ (4) and ${Zn_2[CH_3C(OH)(PO_3)_2]_2[C_6H_{11}NO_2]_2[H_2O]_2 \cdot H_2O}$ (5). Compounds 1 and 2 are isostructural and adopt a pillar-layered 3D structure. Compound 3 is a 3D framework in which $[ZnO_4]$ tetrahedra are connected by HEDP molecules with tetradentate mode. The $[ZnO_3N]$ tetrahedra in 4 shares corners with the $[CPO_3]$ tetrahedra into a 3D framework with twelve-membered ring. It is also found that 4 displays interesting left-handed helical chains along [100] direction. In 5, HEDP molecules exhibit tetradentate coordination fashion to combine Zn atoms into a complicated 2D hybrid layer, resulting in the coordinated isonipecotic acid rings being sandwiched between the layers. All the compounds have been characterized by infrared spectra (IR), elemental analyses, powder X-ray diffraction (PXRD) and thermogravimetric (TG)

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1. Introduction

Metal phosphonates have been the focus of research due to their structural and compositional diversity, as well as their thermal and chemical stability for potential applications in the field of optics, catalysis, magnetism, gas storage/separation, and so on [1–10]. Compared with the carboxylic, pyridyl, imidazolyl groups broadly used in the generation of functional coordination polymers (CPs) [11–14], the phosphonic group $-PO_3H_2$ has three potential coordinating sites which allows it to bind to metal centers with more flexible coordination modes [1–10]. However, owing to the presence of insoluble phases in the assembly process, it is challenging to prepare crystalline metal phosphonates with high quality for acquiring their precise molecular structures and determining their properties [15–17].

During the past few years, a common strategy has been carried out to improve the solubility and crystallinity of metal

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http://dx.doi.org/10.1016/j.solidstatesciences.2017.06.003 1293-2558/© 2017 Elsevier Masson SAS. All rights reserved. phosphonates by modifying phosphonic acids with functional groups, such as hydroxyl, carboxyl, methyl, amino, pyrazine, sulfonyl and thiophene [18–23]. As a result, many intriguing metal phosphonates have been synthesized and structurally characterized, for instance, two zinc phosphonates containing a potential capability for sensing UV radiation [24], a series of uranyl phosphonates exhibiting typical green-light emission originating from the metal centers [25], as well as two new layered zirconium phosphonates functionalized with amino groups displaying unprecedented topologies [26]. On the other hand, to fabricate new metal phosphonates with novel structures and properties, SDAs (structure-directing agents) or coligands such as aliphatic amine, imidazole, pyridine and their derivatives have usually been used [11,27–29]. Considering the steric and electronic effects together with the differential coordination tendency of the SDAs or coligands for metal centers, the resulting metal phosphonates directed or decorated by SDAs or coligands may present unique structures and/or captivating properties [30-32].

Taking inspiration from the aforementioned points, we decided to extend our research to 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP). Besides one methyl and one hydroxyl, HEDP







contains two -PO₃H₂ coordination groups, which may adopt diverse coordination fashions to construct potential unpredictable multi-dimensional structures. Furthermore, in view of the development of synthesis strategy, the employment of organic amine or acid as SDAs or coligands is an excellent choice for the generation of novel structures. In this work, we introduced 1.4-diazabicvclo [2.2.2]octane (DABCO), 1.3-propanediamine, imidazole and isonipecotic acid as SDA or coligands to the Zn-HEDP system (Scheme 1). Luckily, five new Zn-based phosphonates, namely, [H₂DABCO] $\{Zn_3[CH_3C(OH)(PO_3)_2]_2\}$ (1), $[C_3H_{14}N_2]\{Zn_3[CH_3C(OH)(PO_3)_2]_2\}$ (2), $[C_{3}H_{5}N_{2}]_{2}[Zn_{3}[CH_{3}C(OH)(PO_{3})_{2}]_{2}]$ $\{Zn_2[CH_3C(OH)(PO_3)_2]$ (3), $[C_{3}H_{4}N_{2}]_{2}$ (4) and $[Zn_{2}[CH_{3}C(OH)(PO_{3})_{2}][C_{6}H_{11}NO_{2}]_{2}[H_{2}O]_{2}] \cdot H_{2}O$ (5), with two or three dimensional structures were obtained. Their syntheses, crystal structures, the coordination modes of the HEDP ligand, IR as well as thermal stabilities are described and discussed in detail.

2. Experimental section

2.1. Materials and general methods

All chemicals purchased commercially were used as received without further purification. Infrared spectra were recorded in the range of 400–4000 cm⁻¹ on an ABB Bomen MB 102 series FT-IR spectrophotometer using KBr pellets. Elemental analyses of carbon, hydrogen and nitrogen atoms were performed using an Elemental Vario EL III instrument. Powder X-ray diffraction (PXRD) measurements for **1–5** were recorded on a Philips X'Pert-MPD diffractometer with Cu-K α_1 radiation ($\lambda = 1.54076$ Å). Thermogravimetric analyses were carried out in the temperature range of 30–800 °C with a heating rate of 10 °C min⁻¹ using a Mettler Toledo TGA/SDTA 851e analyzer.

2.2. Synthesis of [H₂DABCO]{Zn₃[CH₃C(OH)(PO₃)₂]₂} (1)

A mixture of ZnO, HEDP, DABCO and methanol with a molar composition of 1: 1.4: 2.5: 100 was sealed in a Teflon-lined autoclave and heated at 145 °C for 7 days. After cooling to room temperature in 6 h, colorless crystals of **1** were recovered by filtration, washed with distilled water, and dried in air (60.7% yield based on zinc). Anal. calcd for $C_{10}H_{22}N_2O_{14}P_4Zn_3$ (fw 714.41): C, 16.81%; H, 3.10%; N, 3.92%. Found: C, 16.86%; H, 3.21%; N, 3.71%. IR (KBr, cm⁻¹): 3312(m), 2906(w), 1648(w), 1470(w), 1103(s), 969(w), 824(w), 690(w).



Scheme 1. The structural formula of organic constituents in this work.

2.3. Synthesis of $[C_3H_{14}N_2]$ $\{Zn_3[CH_3C(OH)(PO_3)_2]_2\}$ (2)

Compound 2 was prepared using the same procedure as described for 1. The mixture of ZnO, HEDP, 1,3-propanediamine, methanol and H₂O with a molar composition of 1: 1.5: 2.4: 18.6: 125.6 was sealed in a Teflon-lined autoclave and heated at 145 °C for 7 days. After cooling to room temperature in 6 h, colorless crystals formed in 70% yield based on zinc. Anal. calcd for C₇H₂O_N2O₁₄P₄Zn₃ (fw 676.36): C, 12.43%; H, 2.98%; N, 4.14%. Found: C, 12.56%; H, 2.51%; N, 4.31%. IR (KBr, cm⁻¹): 3340(m), 2916(m), 1624(m), 1548(m), 1458(w), 1104(s), 826(w).

2.4. Synthesis of $[C_3H_5N_2]_2\{Zn_3[CH_3C(OH)(PO_3)_2]_2\}$ (3)

A mixture of ZnO, HEDP, imidazole and H₂O with a molar composition of 1: 1.5: 2.5: 223 was sealed in a Teflon-lined autoclave and heated at 160 °C for 7 days. After cooling to room temperature in 6 h, the resulting product, containing colorless crystals of **3**, was recovered by filtration, washed with distilled water, and dried in air (52.6% yield based on zinc). Anal. calcd for C₁₀H₁₈N₄O₁₄P₄Zn₃ (fw 738.39): C, 16.27%; H, 2.46%; N, 7.59%. Found: C, 16.46%; H, 2.51%; N, 7.31%. IR (KBr, cm⁻¹): 3360(m), 2979(w), 1596(w), 1444(w), 1381(w), 1083(m), 812(w).

2.5. Synthesis of $\{Zn_2[CH_3C(OH)(PO_3)_2][C_3H_4N_2]_2\}$ (4)

A mixture of ZnO, HEDP, imidazole and H_2O with a molar composition of 1: 1: 2: 278 was sealed in a Teflon-lined autoclave and heated at 160 °C for 7 days. After cooling to room temperature in 6 h, colorless crystals formed in 61.8% yield based on zinc. Anal. calcd for $C_8H_{12}N_4O_7P_2Zn_2$ (fw 468.97): C, 20.49%; H, 2.58%; N, 11.95%. Found: C, 20.56%; H, 2.51%; N, 11.71%. IR (KBr, cm⁻¹): 3416(m), 2972(w), 1638(w), 1548(w), 1388(w), 1097(s), 1027(w), 812(w).

2.6. Synthesis of $\{Zn_2[CH_3C(OH)(PO_3)_2][C_6H_{11}NO_2]_2[H_2O]_2\} \cdot H_2O(5)$

A mixture of ZnO, HEDP, isonipecotic acid and H₂O with a molar composition of 1: 1: 2: 278 was sealed in a Teflon-lined autoclave and heated at 145 °C for 7 days. After cooling to room temperature in 6 h, colorless crystals of **5** were recovered by filtration, washed with distilled water, and dried in air (76.5% yield based on zinc). Anal. calcd for $C_8H_{21}NO_{12}P_2Zn_2$ (516.02): C, 18.62%; H, 4.10%; N, 2.71%. Found: C, 18.86%; H, 4.02%; N, 2.59%. IR (KBr, cm⁻¹): 3416(s), 2930(w), 1603(w), 1430(w), 1117(s), 999(w), 951(w), 819(w).

2.7. X-ray crystallography

The data for compounds 1–5 were collected using a Siemens SMART CCD diffractometer equipped with graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was resolved by direct methods and refined by full-matrix least-squares fitting on F² by SHELX-97 [33]. All nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms on the organic amine were generated geometrically and refined using a riding model. Because of the high degree of hydration and thermal motion, hydrogen atoms could not be located from their difference Fourier maps for the water molecules in compound 5. Crystallographic data and structure refinement parameters for 1-5 are summarized in Table 1. Selected bond lengths and angles are collated in Table 2. CCDC numbers are 1538033-1538037 for 1-5, respectively.

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