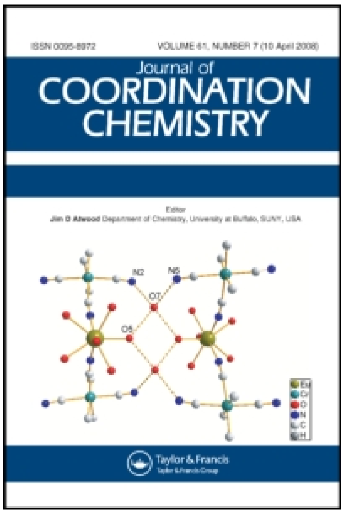

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Solvothermal synthesis and characterization of a new Zn^{II}-PMIDA phosphonate

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Solvothermal synthesis and characterization of a new Zn^{II}-PMIDA phosphonate

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A new Zn(II) phosphonate, $(NH_4)[Zn(HPMIDA)(H_2O)_2]$ (**1**) ($H_4PMIDA = N$-(phosphonomethyl)iminodiacetic acid), has been solvothermally synthesized and characterized by elemental analysis, IR, TGA fluorescence, and X-ray single-crystal diffraction. Compound **1** is an example of a six-coordinate Zn-carboxylate-phosphonate and possesses a 3-D supramolecular structure built from mononuclear anions $[Zn(HPMIDA)(H_2O)_2]_n^-$ through hydrogen bonding. Compound **1** exhibits a solid-state fluorescent emission band at 593 nm under excitation of 413 nm.

Keywords: Zn(II) phosphonate; Solvothermal synthesis; Fluorescence

1. Introduction

A series of metal phosphonates have been synthesized in recent years due to their novel fascinating architectures and potential applications in gas/metal ion adsorption, corrosion control, catalysis, proton conductivity, ion exchange, optical properties, and materials chemistry [1–7]. Phosphonic acids with various kinds of coordination including carboxylic groups provide additional coordination sites, increase solubility of the resulting metal phosphonate, and facilitate crystallization [8]. Phosphonic acid, *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA) with two additional carboxylic groups and one amine, is an appropriate chelating ligand in a less acidic solution [8–11]. A number of metal phosphonates containing H_4PMIDA have been obtained from low-dimensional to 3-D structures [7–17].

A majority of the aforementioned materials were isolated from hydrothermal or conventional solution reaction, only a few of them were prepared by the solvothermal method [17]. Especially, low-dimensional metal phosphonates based on H_4PMIDA were rarely reported. Currently, our research is focused on the synthesis of novel low-dimensional metal phosphonates with interesting properties based on H_4PMIDA and transition metals by using solvothermal methods under weakly acidic

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reaction conditions. Herein, we report the solvothermal synthesis, crystal structure, and characterization of a new metal phosphonate, $(NH_4)[Zn(PMIDA)(H_2O)_2]$ (**1**), from solvothermal reaction using ammonium as structure-directing agent. The fluorescence of **1** is also discussed.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were obtained from commercial sources and used without purification. Elemental analysis was conducted on a Perkin–Elmer 2400 LC II elemental analyzer. IR spectrum was carried out on a Nicolet Impact 410 FT-IR spectrometer with KBr pellets from 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed in air with a heating rate of 10°C min^{-1} on a Perkin–Elmer TGA 7 thermogravimetric analyzer. Emission and excitation spectra were recorded on an Eidingberg FX 900 photoluminescent spectrometer with a 500 W xenon lamp. The emission spectrum was corrected for the sensitivity of the photomultiplier tube, and the excitation spectrum was corrected for the intensity of the xenon lamp. The powder X-ray diffraction (XRD) pattern was collected on a Siemens D 5005 diffractometer using graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å) in the angular range $2\theta = 4$–$40°$ with stepping size of 0.02° and counting time of 4 s per step.

2.2. *Synthesis of 1*

A mixture of $ZnCl_2$ (0.109 g, 0.0008 M), H_4PMIDA (0.180 g, 0.0008 M) and NH_4F (0.075 g, 0.002 M) was dissolved in ethanol (10 mL), sealed into an autoclave equipped with a 15 mL PTFE-lined stainless steel vessel, and heated at 160°C for 3 days. Colorless block crystals of **1** were collected by vacuum filtration, washed thoroughly with ethanol, and dried in air (yield 58% based on zinc). Elemental Anal. $C_5H_{15}N_2O_9PZn$ (%): C, 17.52; H, 4.53; N, 8.21. Calcd C, 17.48; H, 4.37; N, 8.15. IR data (cm^{-1}): 3471(s), 3212(s), 3058(w), 2964(w), 2857(w), 1608(s), 1562(s), 1444(s), 1369(s), 1172(m), 1101(m), 1035(m), 1004(w), 875(m), 735(w), 627(m), 577(w), 447(w). The experimental data for **1** are in good agreement with the simulated XRD powder patterns based on single-crystal data XRD analysis, indicating the phase purity of the as-synthesized samples (figures S1 (IR) and S2 (XRD), see Supplementary material).

2.3. *Single-crystal XRD*

A single crystal of **1** was mounted on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensity data were collected at 293 ± 2 K and processed on a PC with the SAINT Plus software package. Structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXTL 97 software. All non-hydrogen atoms of **1** were refined with anisotropic thermal parameters. The positions of hydrogen atoms were either located by difference Fourier maps (H1A, H1B, H2A, H2B, H4A, H4B, H1) or calculated geometrically (H2, H3, H4, H5, H6, H7, H8, H9). Crystallographic data and structural refinements are summarized in table 1, and selected bond lengths (Å) and angles (°) are listed in table 2. Hydrogen bonds (Å) and angles (°) are given in table 3.

3. Results and discussion

3.1. *Description of structure*

Single-crystal XRD analysis reveals that **1** possesses a 3-D supramolecular structure built from mononuclear anions $[Zn(HPMIDA)(H_2O)_2]_n^-$ through hydrogen bonding, in which the asymmetric unit (figure 1) contains one Zn(II), one HPMIDA, two aqua ligands, and one uncoordinated cation NH_4^+. The Zn(1) is six-coordinate with two aqua ligands (O8, O9) and a HPMIDA. Zn(1)–O distances range from 2.024(3) to 2.120(2) Å and the Zn(1)–N bond is 2.120(3) Å. The distances and angles are consistent with those of other Zn(II) phosphonates [8]. The $[HPMIDA]^{3-}$ is tetradentate with two carboxylate oxygens (O4, O6), one N(1), and a phosphonate oxygen (O1), chelating with Zn(II) to form $[Zn(HPMIDA)(H_2O)_2]^{3-}$. H_4PMIDA shows a different coordination from those of reported six-coordinate Zn-carboxylate-phosphonate compounds, in which phosphonate oxygens [8e–g] or carboxylate oxygens [8g] of the carboxylate-phosphonates bind to Zn(II). In **1**, N(1) of H_4PMIDA also participates in chelation with metal. NH_4F was employed during the reaction, and the structure was affected by NH_4^+ as a structure-directing agent. Uncoordinated carboxylate oxygens (O5, O7) and phosphonate oxygens (O2, O3) are involved in hydrogen bonding.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_5H_{15}N_2O_9PZn$
Formula weight	343.53
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.0407(1)
b	7.5372(2)
c	12.273(3)
α	93.65(3)
β	103.13(3)
γ	111.11(3)
Volume (Å^3), Z	584.0(2), 2
Calculated density ($g\,cm^{-3}$)	1.953
Absorption coefficient (mm^{-1})	2.284
θ range for data collection (°)	3.16–27.44
Independent reflection	5789/2651 [$R_{int} = 0.0154$]
Goodness-of-fit on F^2	1.092
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0354$, $wR_2 = 0.1025$
R indices (all data)	$R_1 = 0.0381$, $wR_2 = 0.1069$

Table 2. Bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(6)	2.024(3)	Zn(1)–N(1)	2.120(3)
Zn(1)–O(8)	2.057(3)	P(1)–O(1)	1.505(2)
Zn(1)–O(4)	2.067(2)	P(1)–O(2)	1.509(2)
Zn(1)–O(9)	2.096(3)	P(1)–O(3)	1.577(3)
Zn(1)–O(1)	2.120(2)	P(1)–C(1)	1.821(3)
O(6)–Zn(1)–O(8)	91.31(1)	O(6)–Zn(1)–O(1)	91.46(1)
O(6)–Zn(1)–O(4)	89.70(1)	O(8)–Zn(1)–O(1)	98.97(1)
O(8)–Zn(1)–O(4)	95.76(1)	O(4)–Zn(1)–O(1)	165.19(9)
O(6)–Zn(1)–O(9)	177.45(1)	O(9)–Zn(1)–O(1)	89.21(1)
O(8)–Zn(1)–O(9)	86.15(1)	N(1)–Zn(1)–O(1)	84.29(9)
O(4)–Zn(1)–O(9)	90.28(1)	O(1)–P(1)–C(1)	106.63(1)
O(6)–Zn(1)–N(1)	83.58(1)	O(2)–P(1)–C(1)	108.44(1)
O(8)–Zn(1)–N(1)	174.03(1)	O(3)–P(1)–C(1)	105.76(1)
O(4)–Zn(1)–N(1)	81.16(9)	N(1)–C(1)–P(1)	110.7(2)
O(9)–Zn(1)–N(1)	98.94(1)		

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(2)–H(1)···O(9)#1	0.82	2.14	2.746(4)	131.2
O(8)–H(2)···O(7)#4	0.90(5)	2.22(5)	3.060(4)	155(4)
O(8)–H(3)···O(5)#3	1.00(6)	2.18(6)	3.066(4)	147(5)
O(9)–H(4)···O(2)#1	0.786(2)	1.99(2)	2.746(4)	161(5)
O(9)–H(5)···O(5)#3	0.813(2)	1.96(2)	2.750(4)	163(5)
N(2)–H(6)···O(7)#2	0.86(5)	1.92(5)	2.772(4)	171(4)
N(2)–H(7)···O(6)#5	0.79(6)	2.05(6)	2.839(4)	177(5)
N(2)–H(8)···O(1)#6	0.72(5)	2.16(5)	2.874(4)	170(5)
N(2)–H(9)···O(4)	0.83(5)	2.05(5)	2.876(4)	176(4)

Symmetry transformations used to generate equivalent atoms: #1: $-x, -y+1, -z+1$; #2: $x-1, y-1, z$; #3: $x-1, y, z$; #4: $-x+1, -y+2, -z+2$; #5: $-x+1, -y+1, -z+2$; #6: $x, y-1, z$.

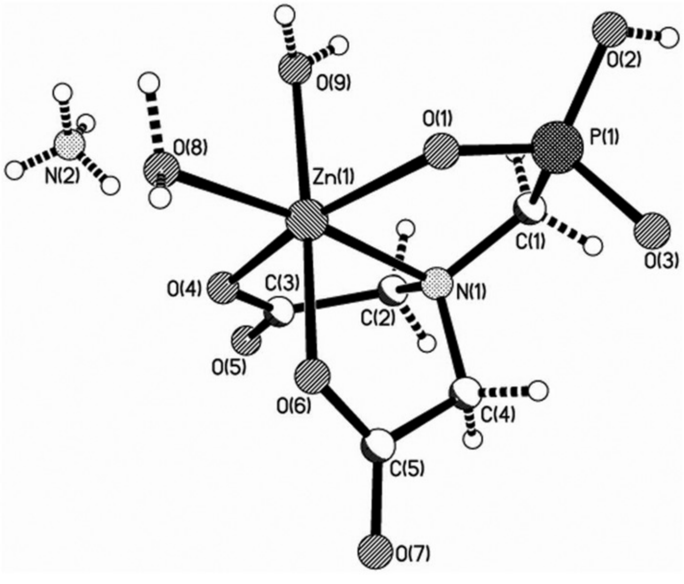

Figure 1. ORTEP view of **1** showing the atom-labeling scheme (50% thermal ellipsoids).

Considering the charge balance of the coordination environment, the P–O distance of phosphonate group and acidic environment, one of the three phosphonate oxygens (O2) is protonated.

The [ZnO_5N] octahedron is attached by hydrogen bonds to each other along the *a*-axis, forming a 1-D chain (figure 2). The O(9) $\cdots$ O(2), O(9) $\cdots$ O(5), and O(8) $\cdots$ O(5) distances are 2.746(4) Å, 2.75(4) Å, and 3.066(4) Å, and the bond angles are 161(5)°, 163(5)°, and 147(5)°, respectively. In the *ac* plane, 2-D layers (figure 3) are constructed from 1-D chains *via* O–H $\cdots$ O(N) hydrogen bonds, between uncoordinated carboxylate oxygens (O5, O7), phosphonate oxygens (O2, O3), aqua oxygens (O8, O9), and N(2) from NH_4^+. As shown in figure 4, O–H $\cdots$ O(N) hydrogen bonds further extend the 2-D layer structure into a 3-D supramolecular network, with NH_4^+ cations located in the 3-D structure. The O(8) $\cdots$ O(7) and O(2) $\cdots$ O(9) distances and angles are 3.06(4) Å, 2.746(4) Å, 155(4)° and 131(2)°, respectively. Hydrogen bond interactions formed by N(2) $\cdots$ O(7), N(2) $\cdots$ O(6), N(2) $\cdots$ O(1), and N(2) $\cdots$ O(4) further reinforce the stability of this 3-D supramolecular network.

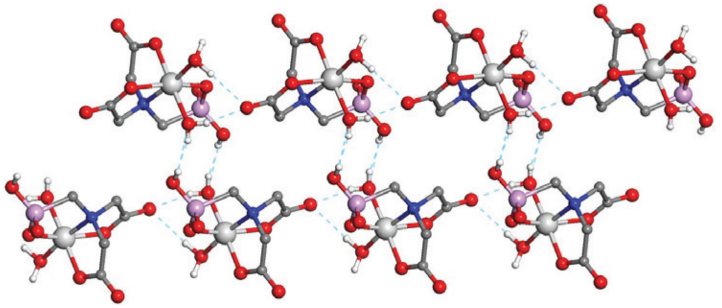

Figure 2. 1-D O–H $\cdots$ O hydrogen-bond network of **1** along the *a*-axis. Hydrogen bonds are drawn as dotted blue lines. Color code: Zn, light gray; N, blue; O, red.

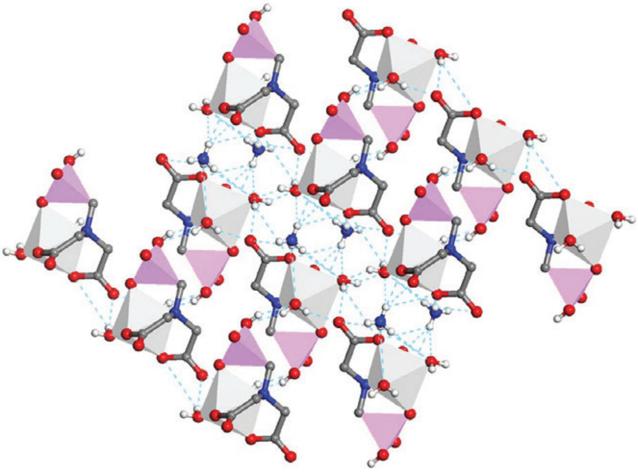

Figure 3. 2-D O–H $\cdots$ O(N) hydrogen-bond network of **1** in the *ac* plane. Hydrogen bonds are drawn as dotted blue lines.

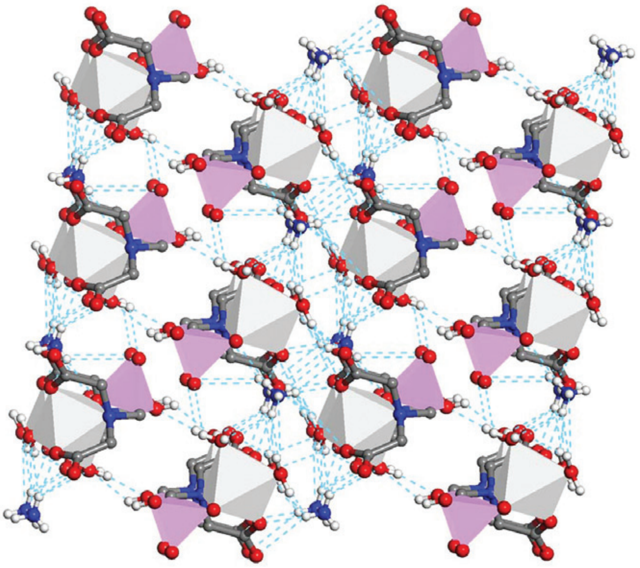

Figure 4. 3-D O–H ··· O(N) hydrogen-bond network of **1**. Hydrogen bonds are drawn as dotted blue lines.

3.2. *Thermogravimetric study*

Combined TGA-DTA curves for **1** are shown in Supplementary material, figure S3. Three weak endothermic peaks centered at 90°C, 237°C and 317°C are due to loss of two aqua ligands, one water molecule from the condensation of phosphonate group and one NH_3 molecule. The observed weight loss of 20.60% is consistent with the calculated value 20.67%. From 380°C to 600°C, the DTA curve shows a stronger exothermic peak at 477°C. TGA curve shows a weight loss in this temperature range, which corresponds to the pyrolysis of the organic ligand. The total weight loss is 76.64%, consistent with the calculated value 76.31%, and the final thermal decomposition product at 800°C is amorphous ZnO.

3.3. *Fluorescence*

The fluorescence of **1** is shown in Supplementary material, figure S4. The free H_4PMIDA ligand does not emit intense fluorescence at room temperature in the visible region, whereas the zinc(II) phosphonate exhibits a strong fluorescent emission at 593 nm under the excitation of 413 nm. The emission band may be attributed to the formation of the mononuclear unit and/or ligand-to-metal charge transfer (LMCT). To the best of our knowledge, the emission band has not been reported on zinc(II)-PMIDA.

4. Conclusions

We have successfully obtained a new phosphonate, $(NH_4)[Zn(HPMIDA)(H_2O)_2]$, based on zinc(II), and H_4PMIDA under solvothermal conditions. The zinc(II) is six-coordinate. Compound **1** displays a strong fluorescent emission band at 593 nm under the excitation of 413 nm at room temperature.

Supplementary material

CCDC 643502 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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References

[1] (a) J.A. Groves, S.R. Miller, S.J. Warrender, C. Mellot-Draznieks, P. Lightfoot, P.A. Wright. *Chem. Commun.*, 3305 (2006); (b) K.D. Demadis, M. Papadaki, R.G. Raptis, H. Zhao. *Chem. Mater.*, **20**, 4835 (2008); (c) A. Popa, C.M. Davidescu, N. Petru, I. Gheorghe, A. Katsaros, K.D. Demadis. *Ind. Eng. Chem. Res.*, **47**, 2010 (2008).

[2] E.W. Stein Sr., A. Clearfield, M.A. Subramanian. *Solid State Ionics*, **83**, 113 (1996).

[3] (a) A. Clearfield. *Curr. Opin. Solid State Mater. Sci.*, **1**, 268 (1996); (b) A. Clearfield. In *Metal Phosphonate Chemistry*, K.D. Karlin (Ed.), Vol. 47, p. 371, John Wiley & Sons, New York (1998).

[4] D.A. Burwell, K.G. Valentine, J.H. Timmermans, M.E. Thompson. *J. Am. Chem. Soc.*, **114**, 4144 (1992).

[5] P. Hubert Mutin, G. Guerrero, A. Vioux. *C. R. Chimie*, **6**, 1153 (2003).

[6] F.A. Almeida Paz, J. Rocha, J. Klinowski, T. Trindade, F.N. Shi, L. Mafra. *Prog. Solid State Chem.*, **33**, 113 (2005).

[7] J.G. Mao. *Coord. Chem. Rev.*, **251**, 1493 (2007).

[8] (a) J.G. Mao, A. Clearfield. *Inorg. Chem.*, **41**, 2319 (2002); (b) J.G. Mao, Z. Wang, A. Clearfield. *Inorg. Chem.*, **41**, 6106 (2002); (c) J.L. Song, H.H. Zhao, J.G. Mao, K.R. Dunbar. *Chem. Mater.*, **16**, 1884 (2004); (d) J.G. Mao, Z.K. Wang, A. Clearfield. *New J. Chem.*, **26**, 1010 (2002); (e) D.M. Poojary, A. Clearfield. *J. Am. Chem. Soc.*, **117**, 11278 (1995); (f) C. Lei, J.G. Mao, Y.Q. Sun, H.Y. Zeng, A. Clearfield. *Inorg. Chem.*, **42**, 6157 (2003); (g) Y.Q. Guo, B.P. Yang, J.L. Song, J.G. Mao. *Cryst. Growth Des.*, **8**, 600 (2008).

[9] D.C. Crans, F.L. Jiang, O.P. Anderson, S.M. Miller. *Inorg. Chem.*, **37**, 6645 (1998).

[10] (a) B. Zhang, D.M. Poojary, A. Clearfield, G.Z. Peng. *Chem. Mater.*, **8**, 1333 (1996); (b) D.M. Poojary, A. Clearfield. *J. Organomet. Chem.*, **512**, 237 (1996); (c) D.M. Poojary, B. Zhang, A. Clearfield. *Angew. Chem. Int. Ed. Engl.*, **33**, 2324 (1994); (d) B. Zhang, D.M. Poojary, A. Clearfield, G.Z. Peng. *Inorg. Chem.*, **37**, 249 (1998).

[11] H.X. Pei, S.M. Lu, Y.X. Ke, J.M. Li, S.B. Qin, S.X. Zhou, X.T. Wu, W.X. Du. *Struct. Chem.*, **15**, 207 (2004).

[12] A. Mateescu, C.P. Raptopoulou, A. Terzis, V. Tangoulis, A. Salifoglou. *Eur. J. Inorg. Chem.*, 1945 (2006).

[13] A. Mateescu, C. Gabriel, R.G. Raptis, P. Baran, A. Salifoglou. *Inorg. Chim. Acta*, **360**, 638 (2007).

[14] Y. Fan, G.H. Li, W.P. Jian, M. Yu, L. Wang, Z.F. Tian, T.Y. Song, S.H. Feng. *J. Solid State Chem.*, **178**, 2267 (2005).

[15] S.F. Tang, J.L. Song, X.L. Li, J.G. Mao. *Cryst. Growth Des.*, **6**, 2322 (2006).

[16] F.H. Allen. *Acta Crystallogr.*, **B58**, 380 (2002).

[17] S.O.H. Gutschke, D.J. Price, A.K. Powell, P.T. Wood. *Angew. Chem. Int. Ed.*, **38**, 1088 (1999).