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Syntheses, crystal structures, thermal stabilities and luminescence of six M(II)-hydroxyphosphonoacetate materials

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Hydrothermal reactions of Zn^{II}, Ba^{II} or Co^{II} ion with 2-hydroxyphosphonoacetic acid (H_3L) afforded six metal phosphonates, namely, $[Zn_5(O_3PCH(OH)CO_2)_4(C_6H_9N_2)_2]$ (**1**), $[(C_4H_{12}N_2)Zn_5(O_3PCH(OH)CO_2)_4(H_2O)_2]$ (**2**), $[(C_3H_{12}N_2)_{0.5}Zn_5(HO_3PCH(OH)CO_2)(O_3PCH(OH)CO_2)_3(H_2O)_2]\cdot 0.75H_2O$ (**3**), $[BaZn_2(O_3PCH(OH)CO_2)_2]$ (**4**), $[Ba(HO_3PCH(OH)CO_2)]$ (**5**) and $[(NH_4)_2Co_7(HO_3PCH(OH)CO_2)_6(HPO_4)_2(H_2O)_6]\cdot 4H_2O$ (**6**). In **1**, zinc tetrahedra ($[ZnO_4]$) and octahedra ($[ZnO_5N]$, $[ZnO_6]$) are bridged by 2-hydroxyphosphonoacetate with penta- and hexadendate modes into a hybrid layer, which is further pillared by the 3-picolylamines to form a 3D structure through Zn–N bonds and hydrogen bondings. Both **2** and **3** are 3D framework encapsulating piperazine and 1,2-propanediamine cations, respectively. In solids **4**–**6**, the cross-linkages of $[ZnO_4]$, $[BaO_{10}]$ and $[CoO_6]$ polyhedral with 2-hydroxyphosphonoacetate form 3D frameworks. Solids **3** and **4** behave thermally stable up to 250 and 300 °C under air atmosphere, respectively. It is interesting that the peak emission of solid **3** displays a 10 nm red-shift after simple heat-treatment.

1. Introduction

Metal phosphonates have attracted considerable attention for their structural diversities and applications as ion-exchangers, catalyst, LB Film, porous materials, small molecular sensors and nonlinear optics [1–3]. During the past five years, many metal phosphonates such as molybdophosphonate clusters [4], "breathing" in adsorbate-responsive calcium tetraphosphonates [5], metal ferrocenylphosphonates with strong third-order nonlinear optical self-focusing effects [6], homochiral phosphonates displaying selective adsorption capacities [7,8] and Fe(III) phosphonate cages [9], have been emerged. In particular, phosphonic acids with additional groups have been used to synthesize interesting solids, including $M_x[Fe(O_2CCH_2)_2NCH_2PO_3]_6\cdot nH_2O$ with maple leaf lattice, as well as $Co(2\text{-pmp})(H_2O)_2$ showing reversible changes of structures and magnetic behaviors upon the dehydration–hydration process [10–16]. In this regard, 2-hydroxyphosphonoacetic acid (H_3L) features a close connection of PO_3H_2, COOH and OH via a carbon atom and adopts 14 modes to afford many coordination polymers, such as a zinc framework with nonlinear optical activity and high thermal stability, 3D heterometal phosphonates displaying the irreversible transformation of luminescent color, pillared manganese phosphonate with metamagnetism and zinc phosphonate exhibiting tunable emissions [17–30]. To expand our studies in this respect, six new metal phosphonates: $[Zn_5(O_3PCH(OH)CO_2)_4(C_6H_9N_2)_2]$ (**1**), $[(C_4H_{12}N_2)Zn_5(O_3PCH(OH)CO_2)_4(H_2O)_2]$ (**2**), $[(C_3H_{12}N_2)_{0.5}Zn_5(HO_3PCH(OH)CO_2)(O_3PCH(OH)CO_2)_3(H_2O)_2]\cdot 0.75H_2O$ (**3**), $[BaZn_2(O_3PCH(OH)CO_2)_2]$ (**4**), $[Ba(HO_3PCH(OH)CO_2)]$ (**5**) and $[(NH_4)_2Co_7(HO_3PCH(OH)CO_2)_6(HPO_4)_2(H_2O)_6]\cdot 4H_2O$ (**6**), have been hydrothermally synthesized and characterized. 2-Hydroxyphosphonoacetate exhibits five new coordination modes through six active oxygen atoms.

2. Experimental

2.1. Materials and instrumentation

H_3L solution (wt%=48.0%) and other chemicals were purchased from commercial sources without further purification. Elemental analyses were carried out with a Vario EL III element analyzer. Infrared spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer. Fluorescent properties were investigated with F-7000 FL spectrophotometer at room temperature. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449C under air gas flow with a heating rate of 10 °C min^{-1} for **3** and nitrogen gas flow with a heating rate of 15 °C min^{-1} for **6**. Powder XRD patterns were acquired on a DMAX-2500 diffractometer using Cu$K\alpha$ radiation (λ=1.54178 Å) under ambient environment. Single crystals of **1**–**5** were obtained in a Parr

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Teflon-lined autoclave (23 mL) as a homogenous phase based on respective powder XRD patterns.

2.2. Synthesis

$[Zn_5(O_3PCH(OH)CO_2)_4(C_6H_9N_2)_2]$ (**1**). A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.2193 g, 0.9991 mmol), H_3L solution (0.5 mL, 2 mmol) and 3-picolylamine (0.7 mL, 6.9 mmol) in 10.0 mL distilled water with pH value adjusted to 3.65, was heated at 160 °C for 120 h. Yield: 0.0500 g (21%). Anal. Calc. for $C_{20}H_{26}N_4O_{24}P_4Zn_5$ (**1**): C 20.76, H 2.26, N 4.84%. Found: C 20.54, H 2.10, N 4.70%. IR (KBr pellet, cm^{-1}): 3378w(υ_{O-H}), 3196w(υ_{N-H}), 3072w(υ_{N-H}), 2932w(υ_{C-H}), 2905w(υ_{C-H}), 1604vs(υas_{CO}), 1577vs(υas_{CO}), 1501w, 1485w, 1422m(δ_{C-H}), 1393w, 1367w, 1201m ($\upsilon_{P=O}$), 1171m, 1142s(υ_{P-O}), 1100s(υ_{P-O}), 1059m, 1047m, 992m(υ_{P-O}), 972m, 897w, 828w, 708w, 672w, 649w, 516m.

$[(C_4H_{12}N_2)Zn_5(O_3PCH(OH)CO_2)_4(H_2O)_2]$ (**2**). A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.2166 g, 0.9871 mmol), H_3L solution (0.6 mL, 2.4 mmol) and $C_4H_{10}N_2\cdot 6H_2O$ (1.0783 g, 5.5517 mmol) in 10.0 mL distilled water with pH value adjusted to 3.74, was heated at 190 °C for 120 h. Yield: 0.0019 g (0.9%). Anal. Calc. for $C_{12}H_{24}N_2O_{26}P_4Zn_5$ (**2**): C 13.56, H 2.28, N 2.64%. Found: C 13.54, H 2.14, N 2.41%. IR (KBr pellet, cm^{-1}): 3435m(υ_{O-H}), 3075w, 2966w(υ_{C-H}), 2804w(υ_{C-H}), 1583s(υas_{CO}), 1385w, 1327w, 1261w, 1202m, 1174m($\upsilon_{P=O}$), 1098vs(υ_{P-O}), 1072m(υ_{P-O}), 996m(υ_{P-O}), 832w, 799w, 656w, 637m, 604w.

$[(C_3H_{12}N_2)_{0.5}Zn_5(HO_3PCH(OH)CO_2)(O_3PCH(OH)CO_2)_3(H_2O)_2]\cdot 0.75H_2O$ (**3**). A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.2193 g, 0.9991 mmol), H_3L solution (0.8 mL, 3.2 mmol) and 1,2-propanediamine (0.9 mL, 10.5 mmol) in 10.0 mL distilled water with pH value adjusted to 3.67, was heated at 150 °C for 120 h. Yield: 0.1826 g (89%). Anal. Calc. for $C_{9.5}H_{20.5}NO_{26.75}P_4Zn_5$ (**3**): C 11.10, H 2.01, N 1.36%. Found: C 11.15, H 2.17, N 1.44%. IR (KBr pellet, cm^{-1}): 3453s(υ_{O-H}), 3109m(υ_{N-H}), 2918w(υ_{C-H}), 2827w, 2735w, 2663w, 1587vs(υas_{CO}), 1435m(δ_{C-H}), 1331w, 1296w, 1168m($\upsilon_{P=O}$), 1187m, 1095vs(υ_{P-O}), 1071m(υ_{P-O}), 991s(υ_{P-O}), 950w, 837m, 780m, 654m, 598m, 515m, 489m.

$[BaZn_2(O_3PCH(OH)CO_2)_2]$ (**4**). A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.2266 g, 1.032 mmol), $Ba(NO_3)_2$ (0.1544 g, 0.5896 mmol), 1,2-diaminocyclohexane (0.5 mL, 4 mmol) and H_3L solution (0.65 mL, 2.7 mmol) in 8.0 mL distilled water with pH value adjusted to 2.46, was heated at 160 °C for 120 h. Yield: 0.27 g (45%). Anal. Calc. for $C_4H_4O_{12}P_2BaZn_2$ (**4**): C 8.40, H 0.71%. Found: C 8.21, H 0.58%. IR (KBr pellet, cm^{-1}): 3412m, 2951m(υ_{C-H}), 2855w(υ_{C-H}), 2340w, 1633m, 1618m(υas_{CO}), 1396m, 1386m, 1325m, 1191m($\upsilon_{P=O}$), 1167m(υ_{P-O}), 1092s(υ_{P-O}), 999m(υ_{P-O}), 931w, 842m, 766w, 666w, 618m, 550m, 522w, 484w.

$[Ba(HO_3PCH(OH)CO_2)]$ (**5**). A mixture of $Ba(OH)_2\cdot 8H_2O$ (0.3103 g, 0.9836 mmol) and H_3L solution (0.65 mL, 2.7 mmol) in 8.0 mL distilled water with pH value adjusted to 1.91, was heated at 170 °C for 120 h. Yield: 0.0970 g (34%). Anal. Calc. for $C_2H_3O_6PBa$ (**5**): C 8.25, H 1.04%. Found: C 7.73, H 0.93%. IR (KBr pellet, cm^{-1}): 3273m(υ_{O-H}), 2965w(υ_{C-H}), 2809w(υ_{C-H}), 2345w, 1613s(υas_{CO}), 1445w, 1384m, 1241m, 1164m($\upsilon_{P=O}$), 1047s(υ_{P-O}), 947m(υ_{P-O}), 926m(υ_{P-O}), 835w, 762m, 621m, 574m, 528m, 474m.

$[(NH_4)_2Co_7(HO_3PCH(OH)CO_2)_6(HPO_4)_2(H_2O)_6]\cdot 4H_2O$ (**6**). A 25 mL PTEE beaker with $Co(CH_3COO)_2\cdot 4H_2O$ (0.1314 g, 0.5276 mmol), H_3L solution (0.5 mL, 2.1 mmol), 1.0 mL ammonia solution (28%), 1.0 mL triethylamine and 4.0 mL distilled water, was sealed into a Parr Teflon-lined autoclave (150 mL) containing 3 mL H_3L solution and 3 mL distilled water, then heated at 120 °C for 96 h. After slow cooling to room temperature, red crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0468 g (35%). Anal. Calc. for $C_{12}H_{48}N_2O_{54}P_8Co_7$ (**6**): C 8.26, H 2.77, N 1.61%. Found: C 8.47, H 3.34, N 2.16%. IR (KBr pellet, cm^{-1}): 3274s(υ_{O-H}), 1618s(υas_{CO}), 1444m, 1399m, 1279m, 1223m, 1197m($\upsilon_{P=O}$), 1075s(υ_{P-O}), 1049m(υ_{P-O}), 975m(υ_{P-O}), 816m, 623m, 537m.

2.3. X-ray crystallography

X-ray data for **1**-**6** were collected on a Rigaku Mercury CCD/AFC diffractometer using graphite-monochromated Mo *K*α radiation (λ(Mo–*K*α)=0.71073 Å). Data were reduced with CrystalClear v1.3. Their structures were solved by direct methods and

Table 1
Crystallographic data for compounds **1**–**6**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{20}H_{26}N_4O_{24}P_4Zn_5$	$C_{12}H_{24}N_2O_{26}P_4Zn_5$	$C_{9.5}H_{20.5}NO_{26.75}P_4Zn_5$	$C_4H_4O_{12}P_2BaZn_2$	$C_2H_3O_6PBa$	$C_{12}H_{48}N_2O_{54}P_8Co_7$
FW	1157.18	1063.06	1027.50	574.09	291.35	1744.79
Space group	P-1	P-1	P-1	Pbca	P-1	P2(1)/n
a/Å	5.2697(15)	5.5512(4)	10.230(8)	9.708(4)	4.764(4)	9.480(2)
b/Å	11.333(4)	9.7858(5)	11.059(8)	8.830(3)	7.471(6)	11.303(3)
c/Å	14.035(5)	12.9382(10)	13.818(10)	12.755(5)	8.389(7)	24.597(6)
α/°	92.279(10)	86.877(10)	69.01(3)	90	83.67(2)	90
β/°	100.779(7)	87.809(10)	78.31(3)	90	86.22(2)	95.747(4)
γ/°	96.214(8)	76.451(9)	72.15(2)	90	78.068(17)	90
V/Å^3	817.0(4)	682.03(8)	1381.7(18)	1093.3(7)	290.0(4)	2622.4(11)
Z	1	1	2	4	2	2
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
D_{calcd}/g cm^3	2.352	2.588	2.470	3.488	3.336	2.210
μ/mm^{-1}	3.922	4.689	4.625	8.279	7.089	2.541
Reflections collected	6306	5259	10,308	7458	2196	19,833
Independent reflections	3488	2901	5859	1249	1224	5997
Observed reflections [$I > 2(I)$]	3125	2675	3855	1171	1168	4996
Parameters refined	263	274	442	105	103	376
Maximum/minimum $\Delta\rho^a$ (e Å^{-3})	1.407/−0.527	0.592/−0.463	2.581/−0.870	0.753/−0.953	1.589/−2.184	2.241/−0.759
GOF on F^2	1.057	1.084	1.118	1.123	1.052	1.052
R_{int}	0.0193	0.0161	0.0238	0.0306	0.0247	0.0387
$R1^a$ [$I > 2\sigma(I)$]	0.0319	0.0273	0.0502	0.0208	0.0297	0.0539
w$R2^b$ [all data]	0.0748	0.0607	0.2016	0.0584	0.0737	0.1581

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

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

Table 2
Selected bond lengths (Å) for compounds **1**–**6**.

1					
Zn(1)–N(1)	2.159(3)	Zn(2)–O(1)	1.986(2)	Zn(3)–O(8)^{c}	2.032(2)
Zn(1)–O(1)	2.238(2)	Zn(2)–O(2)^{a}	1.909(2)	Zn(3)–O(9)^{d}	2.123(2)
Zn(1)–O(5)	2.051(3)	Zn(2)–O(3)^{b}	1.964(2)	Zn(3)–O(9)^{e}	2.123(2)
Zn(1)–O(6)	2.030(2)	Zn(2)–O(7)	1.929(2)	Zn(3)–O(12)	2.145(2)
Zn(1)–O(10)	2.178(2)	Zn(3)–O(8)	2.032(2)	Zn(3)–O(12)^{c}	2.145(2)
Zn(1)–O(11)	2.055(2)				
2					
Zn(1)–O(1)	1.9644(19)	Zn(2)–O(2)^{a}	2.039(2)	Zn(3)–O(6)	2.0139(19)
Zn(1)–O(9)	1.916(2)	Zn(2)–O(3)^{b}	2.159(2)	Zn(3)–O(7)^{c}	2.0305(19)
Zn(1)–O(10)	2.127(2)	Zn(2)–O(5)	2.055(2)	Zn(3)–O(8)	2.0451(18)
Zn(1)–O(12)	2.1238(19)	Zn(2)–O(5)^{a}	2.086(2)	Zn(3)–O(8)^{d}	2.0372(17)
Zn(1)–O(13)	2.030(2)	Zn(3)–O(4)	2.416(2)	Zn(3)–O(11)	2.1474(18)
Zn(2)–O(2)	1.994(2)				
3					
Zn(1)–O(1)	2.054(4)	Zn(2)–O(8)^{b}	2.051(4)	Zn(4)–O(10)	2.106(5)
Zn(1)–O(2)^{a}	2.022(4)	Zn(2)–O(22)	2.301(5)	Zn(4)–O(12)	2.129(4)
Zn(1)–O(8)^{b}	2.034(4)	Zn(2)–O(23)	2.030(4)	Zn(4)–O(19)	1.937(5)
Zn(1)–O(11)	2.188(4)	Zn(3)–O(3)	1.926(5)	Zn(4)–O(26)	2.020(5)
Zn(1)–O(16)	2.313(5)	Zn(3)–O(4)	2.102(5)	Zn(5)–O(15)	2.061(5)
Zn(1)–O(17)	2.015(4)	Zn(3)–O(5)	2.141(4)	Zn(5)–O(18)	2.045(5)
Zn(2)–O(1)	2.038(4)	Zn(3)–O(13)	1.954(4)	Zn(5)–O(20)^{d}	2.053(5)
Zn(2)–O(6)	2.186(4)	Zn(3)–O(25)	2.006(5)	Zn(5)–O(21)	1.992(5)
Zn(2)–O(7)	2.021(4)	Zn(4)–O(9)^{c}	1.923(5)	Zn(5)–O(24)	2.082(5)
4					
Zn(1)–O(1)^{e}	1.9736(18)	Ba(1)–O(1)^{c}	2.900(2)	Ba(1)–O(5)	3.055(2)
Zn(1)–O(2)^{a}	1.894(2)	Ba(1)–O(3)	3.014(2)	Ba(1)–O(5)^{c}	3.055(2)
Zn(1)–O(3)^{d}	1.9497(19)	Ba(1)–O(3)^{c}	3.014(2)	Ba(1)–O(6)^{a}	2.792(2)
Zn(1)–O(5)	2.023(2)	Ba(1)–O(4)^{a}	2.726(2)	Ba(1)–O(6)^{b}	2.792(2)
Ba(1)–O(1)	2.900(2)	Ba(1)–O(4)^{b}	2.726(2)		
5					
Ba(1)–O(1)^{b}	2.784(4)	Ba(1)–O(3)^{f}	3.156(4)	Ba(1)–O(5)^{e}	3.154(4)
Ba(1)–O(1)^{c}	3.100(4)	Ba(1)–O(4)	2.804(4)	Ba(1)–O(6)	2.791(4)
Ba(1)–O(2)^{a}	2.687(4)	Ba(1)–O(5)	2.776(4)	Ba(1)–O(6)^{d}	2.863(4)
Ba(1)–O(2)^{c}	2.843(4)				
6					
Co(1)–O(1)	2.063(3)	Co(2)–O(6)	2.079(3)	Co(3)–O(23)	2.172(4)
Co(1)–O(5)	2.120(3)	Co(2)–O(7)	2.094(3)	Co(3)–O(24)	2.108(4)
Co(1)–O(7)	2.193(3)	Co(2)–O(12)	2.084(3)	Co(4)–O(14)	1.998(4)
Co(1)–O(10)	2.150(3)	Co(2)–O(13)	2.069(4)	Co(4)–O(14)^{b}	1.998(4)
Co(1)–O(11)	2.080(4)	Co(3)–O(2)	2.016(3)	Co(4)–O(18)	2.134(4)
Co(1)–O(20)^{a}	2.017(4)	Co(3)–O(16)	2.145(4)	Co(4)–O(18)^{b}	2.134(4)
Co(2)–O(1)	2.095(3)	Co(3)–O(17)	2.089(4)	Co(4)–O(25)	2.189(6)
Co(2)–O(4)	2.107(3)	Co(3)–O(19)	2.076(4)	Co(4)–O(25)^{b}	2.189(6)

Symmetry codes for **1**: ^{a} $1+x, y, z$. ^{b} $1-x, -y, 1-z$. ^{c} $-x, -y, -z$. ^{d} $1-x, -y, -z$. ^{e} $-1+x, y, z$. for **2**: ^{a} $1-x, -y, 1-z$. ^{b} $-x, -y, 1-z$. ^{c} $1-x, -y, -z$. ^{d} $-x, -y, -z$. for **3**: ^{a} $-x, -y, -z$. ^{b} $-x, -y-1, -z$. ^{c} $-x, -y, -z-1$. ^{d} $-x, -y+1, -z-1$. for **4**: ^{a} $x, 1/2-y, -1/2+z$. ^{b} $-x, -1/2+y, -1/2-z$. ^{c} $-x, -y, -1-z$. ^{d} $-1/2+x, 1/2-y, -1-z$. ^{e} $-1/2-x, -y, -1/2+z$. for **5**: ^{a} $x, -1+y, z$. ^{b} $-x, -y, -z$. ^{c} $1+x, -1+y, z$. ^{d} $1-x, -1-y, -1-z$. ^{e} $-1+x, y, z$; ^{f} $1-x, -y, -z$. for **6**: ^{a} $1/2-x, -1/2+y, 1/2-z$. ^{b} $-x, 1-y, 1-z$.

refined by full-matrix least-squares techniques on F^2 using SHELXTL-97 [31]. All non-hydrogen atoms were treated anisotropically. Zn2 in **2** and Zn5 in **3** disorder over two sites. H1, H2 and H4–H13 in **1**, H1–H4 in **3** and H1–H7 in **6** were generated geometrically. While the positions of H3 in **1** and hydrogen atoms in **2**, **4** and **5**, were located from difference Fourier map and assigned with fixed isotropic thermal parameter. No attempts were performed to locate other hydrogen atoms in **3** and **6**. Crystallographic data and selected bond lengths for **1**–**6** are summarized in Tables 1 and 2, respectively. CCDC 798790–798795 for **1**–**6**, respectively.

3. Results and discussion

3.1. Structural descriptions

The asymmetric unit of **1** consists of three Zn(II) ions, two L^{3-} groups and one 3-picolylamine cation (Fig. 1). Zn1, Zn2 and Zn3 are in distorted $[ZnO_5N]$ octahedral, $[ZnO_4]$ tetrahedral and $[ZnO_6]$ octahedral coordination geometries, respectively. Two L^{3-} groups are chelated to Zn1 via carboxylate groups (O5, O11) along with phosphonate (O1) or hydroxyl (O10) groups to form Zn–O–C–C–P–O or Zn–O–C–C–O rings. As a result, the bond angle of O10–Zn1–O11 is only 76.18(9)°, which deviates from 90° for octahedral angle. This is similar to those in reported compounds [26,28,30]. The other two sites of $[Zn(1)O_5N]$ octahedron are occupied by a phosphonate oxygen atom (O6) from the third L^{3-} group and a nitrogen donor from the 3-picolylamine cation. Each L^{3-} group interacts with Zn2 through one phosphonate oxygen atom. The basal plane of $[Zn(3)O_6]$ octahedron is defined by two equivalent L^{3-} groups through two Zn–O–C–C–P–O chelating rings, while the apical sites are occupied by two phosphonate oxygen atoms (O9d, O9e) from another two equivalent L^{3-} groups. 2-Hydroxyphosphonoacetate displays a new μ_5:η_1:η_1:η_2:η_1:η_1 pentadentate and a known μ_4:η_1:η_1:η_1:η_1:η_1:η_1 hexadentate modes (Scheme 1a,b). Thus, L^{3-} groups bridge zinc tetrahedra ($[ZnO_4]$) and octahedra ($[ZnO_5N]$, $[ZnO_6]$) to form a hybrid layer. The layers are further pillared by 3-picolylamine cations through Zn–O bonds and hydrogen bondings into 3D

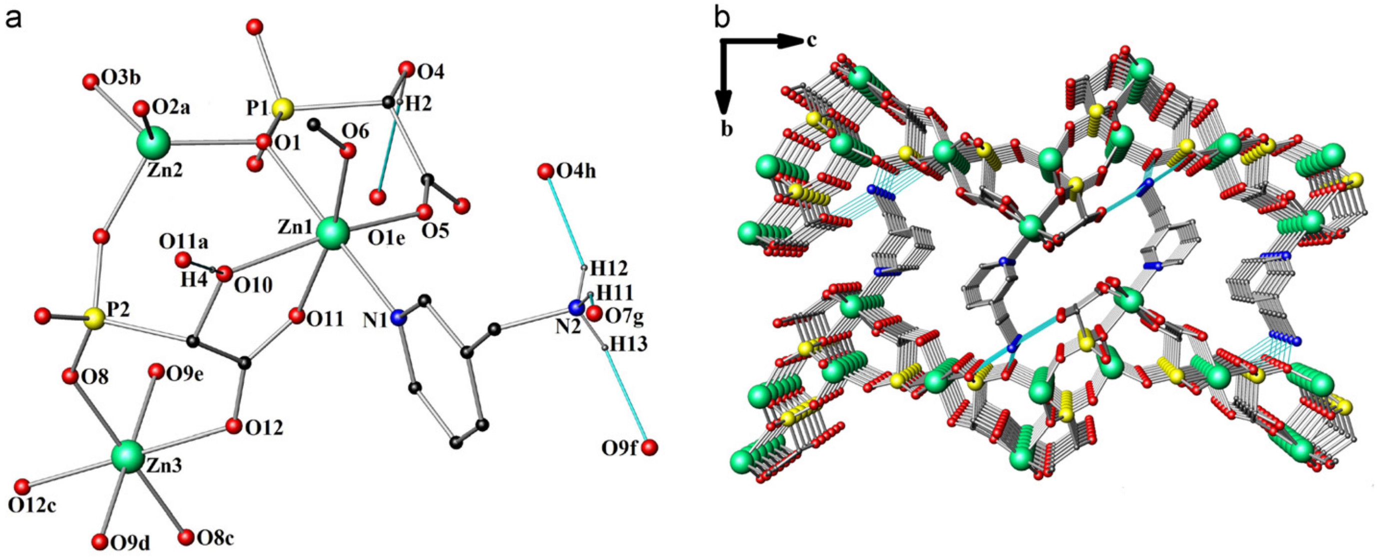
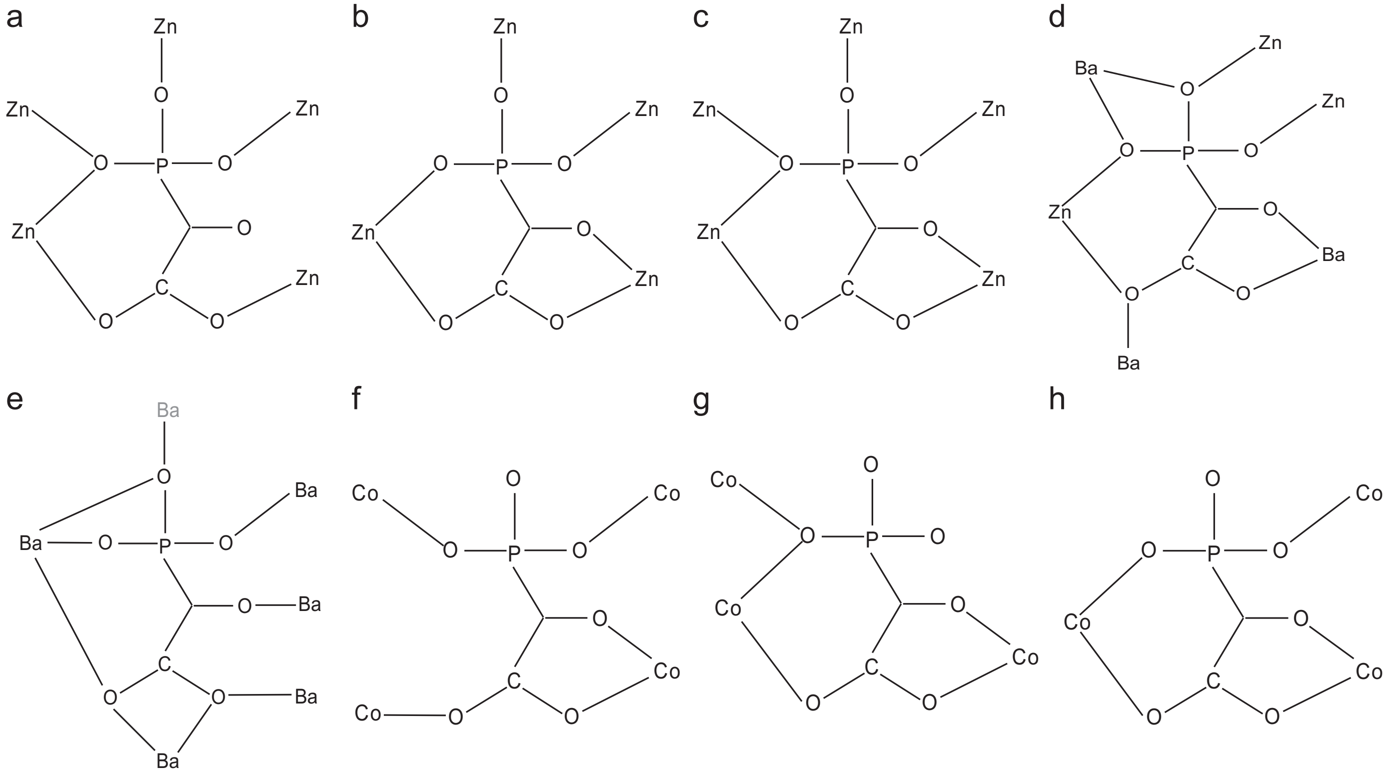


Fig. 1. Ball-stick views of coordinated environment of Zn ions (a) and 3D structure (b) in **1**. Blue-green lines represent hydrogen bondings. Unrelated hydrogen atoms are omitted for clarity. Symmetry codes: $a\,1+x, y, z$; $b\,1-x, -y, 1-z$; $c\,-x, -y, -z$; $d\,1-x, -y, -z$; $e\,-1+x, y, z$; $f\,x, y+1, z$; $g\,x+1, y+1, z$; $h\,1-x, 1-y, 1-z$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 1

structure (Table 3) [32–43]. It worth to note the 3-picolylamine cation serves as not only a second ligand, but also a structure-directing agent.

The asymmetric unit of **2** contains three Zn(II) ions, two L^{3-} groups, one coordinated water molecule and half piperazine cation (Fig. 2). The τ value (0.52) reveals that the geometry around Zn1 is nearly in between square pyramidal and trigonal–bipyramidal geometry [44]. Beside a Zn–O–C–C–O chelating ring and the coordinated water molecule, the Zn1 geometry is also defined by two phosphonate oxygen atom (O1, O9) from another two L^{3-} groups. Zn2 is in a $[ZnO_5]$ square–pyramidal coordination geometry with τ value of 0.007. The basal plane of $[Zn(2)O_5]$ square–pyramid is surrounded by two equivalent L^{3-} groups through two Zn–O–C–C–P–O chelating rings, which is similar to that of Zn3 in **1**. The apical site is occupied by a phosphonate oxygen atom (O3b) from the third L^{3-} group. Two L^{3-} groups are chelated to Zn3 via carboxylate groups (O11, O6) along with phosphonate (O8d) or hydroxyl (O4) groups to form Zn–O–C–C–P–O or Zn–O–C–C–O rings. As a result, the bond angle of O4–Zn3–O6 is only 70.31(7)°, which is obvious smaller than

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

D–H···A	D–H	H···A	D···A	D–H···A
O4–H2···O1^e	0.82(6)	2.21(6)	3.029(4)	174.4
O10–H4···O11^a	0.81(5)	1.91(5)	2.723(4)	180(6)
N2–H12···O4^h	0.89	2.05	2.862(4)	151.3
N2–H11···O7^g	0.89	1.95	2.766(4)	151.7
N2–H13···O9^f	0.89	1.95	2.766(4)	151.7

Symmetry codes: ^{a} $x+1, y, z$. ^{e} $x-1, y, z$. ^{f} $x, y+1, z$. ^{h} $-x+1, -y+1, -z+1$. ^{g} $x+1, y+1, z$.

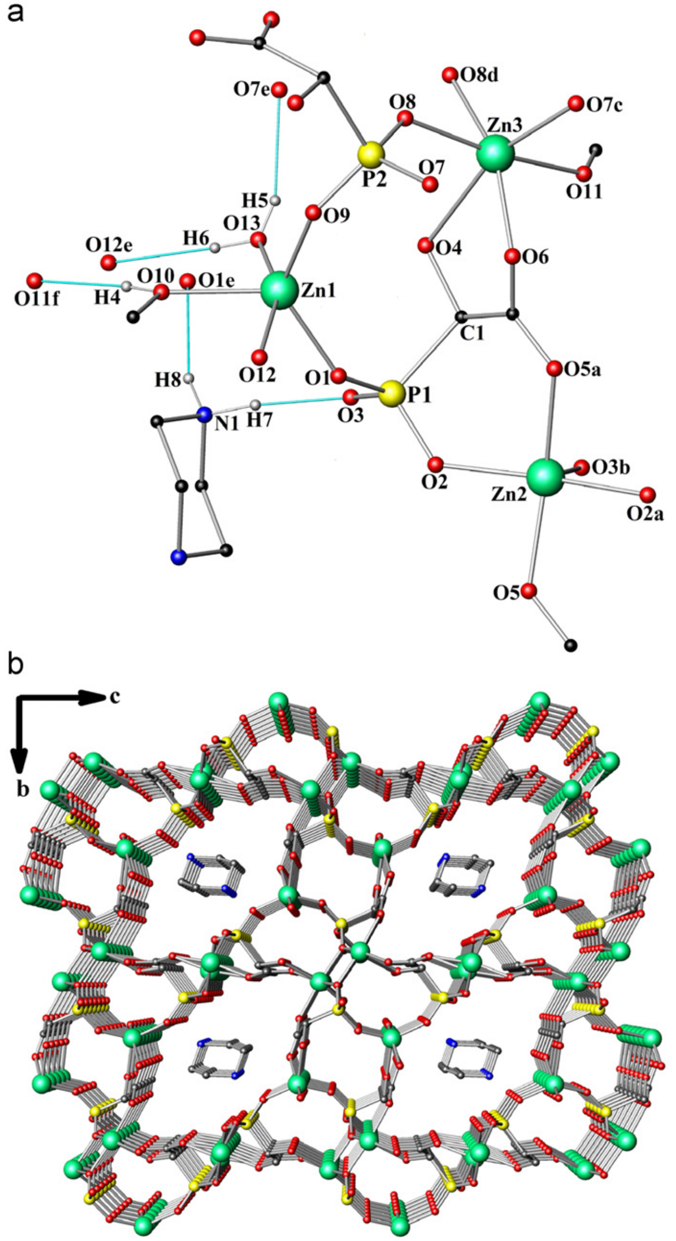


Fig. 2. Ball-stick views of coordinated environment of Zn ions (a) and 3D framework in **2**. Blue-green lines represent hydrogen bondings. Unrelated hydrogen atoms are omitted for clarity. Symmetry codes: $a\,1-x, -y, -z$; $b\,-x, -y, 1-z$; $c\,1-x, -y, -z$; $d\,-x, -y, -z$; $e\,-1+x, y, z$; $f\,-1+x, 1+y, z$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

those in **1** and the reported solids [26–30]. Another two L^{3-} groups interact with Zn3 through phosphonate oxygen atom (O7, O8). [ZnO_5] and [ZnO_6] polyhedra are bridged by 2-hydroxyphosphonoacetate with two known hexadentate modes (Scheme 1b,c), resulting in a 3D framework with 1D channel encapsulating piperazine cations through hydrogen bondings (Table 4). In addition, the hydroxyl group and coordinated water molecule interact with the framework through hydrogen bondings.

Single crystal X-ray diffraction reveals that **3** is a 3D framework with 1D 24-atom channels encapsulating 1,2-propanediamine cations (Fig. 3). Except for the 1,2-propanediamine, the structure is same to that of [$(C_5H_{14}N_2)_{0.5}Zn_5(HO_3PCH(OH)\,CO_2)(O_3PCH(OH)CO_2)_3\cdot 2H_2O]\cdot 2H_2O$ [30].

In **4**, Zn1 is in a distorted [ZnO_4] tetrahedral coordination geometry defined by four oxygen atoms from three L^{3-} groups (Fig. 4). It worth to note that one L^{3-} group is chelated to Zn1 via phosphonate (O1e) and carboxylate (O5) groups to form a Zn–O–P–C–C–O ring. Such chelating mode for [ZnO_4] tetrahedron has not been reported previously [27]. As a result, the bond angle of O1e–Zn1–O5 is only 98.45(8)°, which deviates from 109.47° for tetrahedral angle. The central Ba is coordinated by ten oxygen atoms from three pairs of L^{3-} groups. Beside Ba–O–C–C–O chelating rings, L^{3-} groups can also be chelated to Ba1 through two phosphonate oxygen atoms (O1/O3, O1c/O3c) into Ba–O–P–O rings. On the *ab* plane, [ZnO_4] tetrahedron shares corners with [PO_3C] tetrahedron to form a 6^3 hybrid layer. Ba ions lie between the layers and pack the layers into 3D structure through coordination bonds. In the structure, hydroxyl group provides a hydrogen atom to form hydrogen bonding with carboxylate group (O4···O6g, 2.743(3) Å). In addition, 2-hydroxylphosphonoacetate exhibits a new $\mu_6{:}\eta_1{:}\eta_2{:}\eta_2{:}\eta_1{:}\eta_1{:}\eta_2$ hexadentate mode and bridges three Zn along with three Ba ions (Scheme 1d).

Ba(II) ion in **5** is also coordinated by ten oxygen atoms from seven HL^{2-} groups (Fig. 5(a)). It is interesting that one HL^{2-}

Table 4
Hydrogen bond lengths (Å) and angles (deg.) for solid **2**.

D–H··· A	D–H	H···A	D···A	D–H···A
O4–H4···O11^f	0.75(4)	1.90(4)	2.651(3)	174(4)
O13–H5···O7^e	0.76(5)	1.99(5)	2.717(3)	159(5)
O13–H6···O12^e	0.81(10)	3.10(10)	2.905(4)	169(9)
N1–H7···O3	0.96(5)	1.71(5)	2.638(3)	160(4)
N1–H8···O1^e	0.89(4)	2.21(4)	3.068(3)	162(4)

Symmetry codes: ^{e} $-1+x, y, z$. ^{f} $-1+x, 1+y, z$.

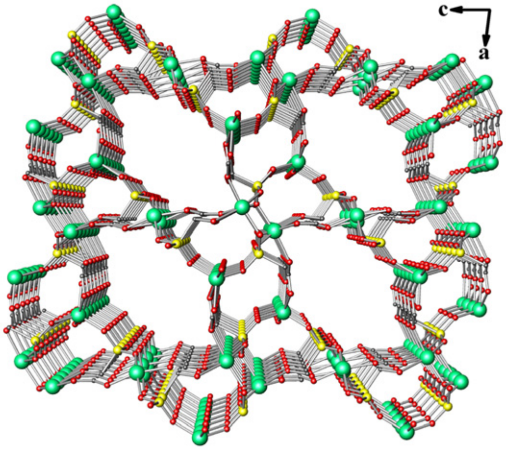


Fig. 3. Ball-stick view of 3D framework in **3**. 1,2-Propanediamine cations are omitted for clarity.

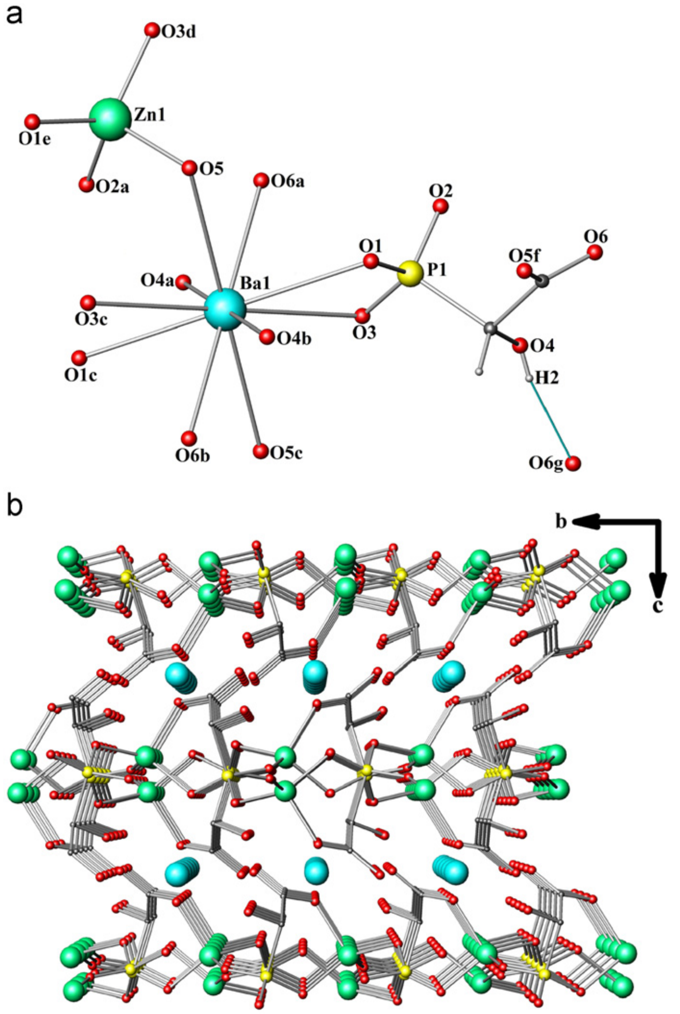


Fig. 4. Ball-stick views of coordinated environment of Zn and Ba ions (a) and 3D framework (b) in **4**. Blue-green line represents hydrogen bondings. Unrelated hydrogen atoms are omitted for clarity. Symmetry codes: *a*x, 1/2−*y*, −1/2+*z*; *b*−*x*, −1/2+*y*, −1/2−*z*; *c*−*x*, −*y*, −1−*z*; *d*−1/2+*x*, 1/2−*y*, −1−*z*; *e*–1/2−*x*, −*y*, 1/2+*z*; *f*−1/2−*x*, −*y*, 1/2+*z*; *g*1/2+*x*, 1/2−*y*, −*z*. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

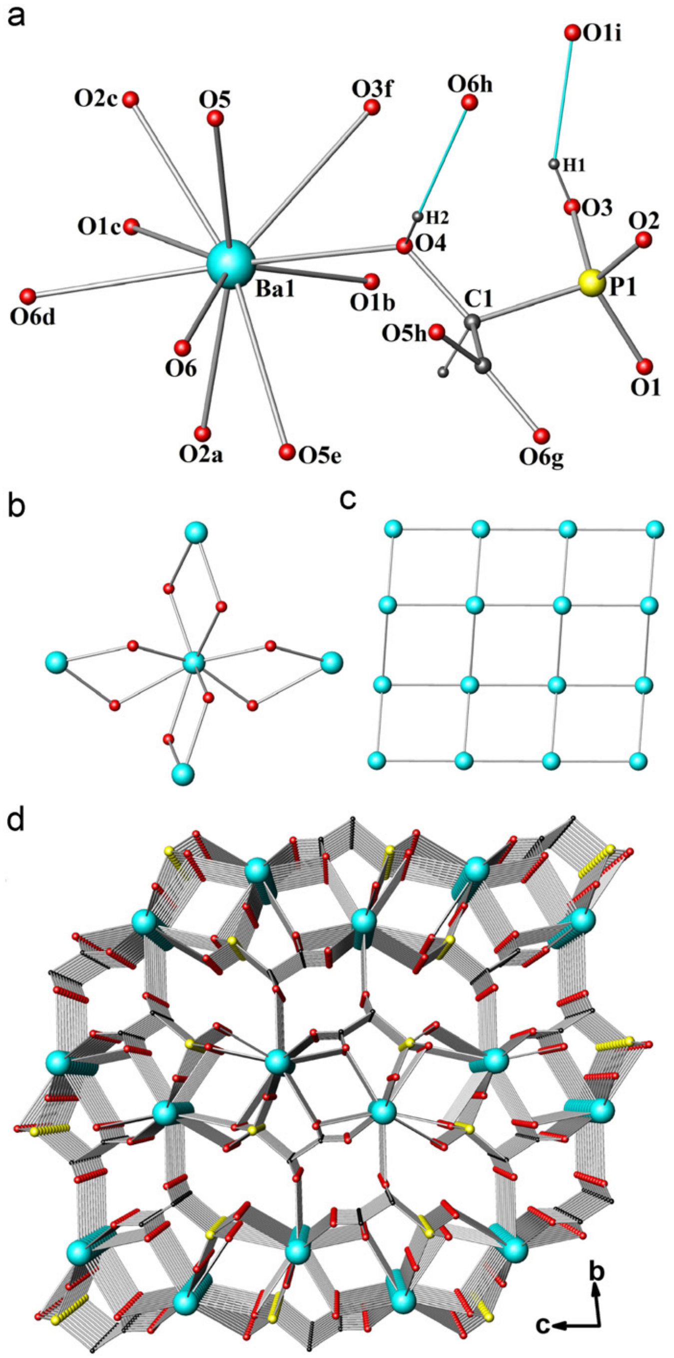


Fig. 5. Ball-stick views of coordinated environment of Ba ion (a), the interaction of Ba ions (b), Ba···Ba net (c) and 3D structure (d) in **5**. Blue-green lines represent hydrogen bondings. Symmetry codes: *a*x, −1+*y*, *z*; *b*−*x*, −*y*, −*z*; *c*1+*x*, −1+*y*, *z*; *d*1−*x*, −1−*y*, −1−*z*; *e*−1+*x*, *y*, *z*; *f*1−*x*, −*y*, −*z*; *g*−*x*, −*y*, −1−*z*; *h*1−*x*, −*y*, −1−*z*; *i*1+*x*, *y*, *z*. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

group is chelated to Ba1 through two phosphonate oxygen atoms (O1c, O2c) along with one carboxylate oxygen atom (O6d), which has not been reported previously. Another HL^{2-} group is chelated to Ba1 through two carboxylate oxygen atoms (O5e, O6). The remaining five HL^{2-} groups interact with Ba1 through five oxygen atoms, including three phosphonate (O1b, O2a, O3f), one carboxylate (O5) and one hydroxyl (O4) oxygen atom. The interaction between neighboring Ba ions is through a pair of oxygen atoms (Fig. 5(b)). Thus, each Ba ion interacts with four surrounding Ba ions to form 4^4 Ba···Ba net (Fig. 5(c)). As shown in Fig. 5(d), these nets are further linked by 2-hydroxyphosphonoacetates with a new μ_6:η_1:η_2:η_1:η_1:η_2:η_2 hexadentate mode to form 3D structure (Scheme 1e). In addition, there are two hydrogen bondings (O4···O6h, 2.853(5) Å; O3···O1i, 2.560(5) Å) in the structure.

The asymmetric unit of **6** contains four Co(II) ions, three HL^{2-} groups, one HPO_4^{2-}, one NH_4^+, three coordinated and two free water molecules (Fig. 6). The HPO_4^{2-} comes from H_3L solution which contains a small amount of H_3PO_4. Co1–Co3 are in distorted [CoO_6] octahedral coordination geometries. HL^{2-} group can be chelated to Co1–Co3 *via* hydroxyl and carboxylate groups to form Co–O–C–C–O ring. As a result, bond angles of O10–Co1–O11, O10–Co2–O11 and O16–Co3–O17 are 75.58(13), 76.84(13) and 75.64(14)°, respectively, which deviate from 90° for octahedral angle. Both Co1 and Co2 are also surrounded by a Co–O–P–C–C–O ring. The remaining four sites of [$Co(3)O_6$] octahedron are occupied by the other HL^{2-} group, one HPO_4^{2-} and two coordinated water molecules. Different from those of Co1–Co3, Co4 is in a slightly distorted [$Co(4)O_6$] octahedral coordination geometry defined by six oxygen atoms from two equivalent HL^{2-} groups and two equivalent water molecules. The HL^{2-} group is also chelated to Co4 via phosphonate (O14) and carboxylate (O18)

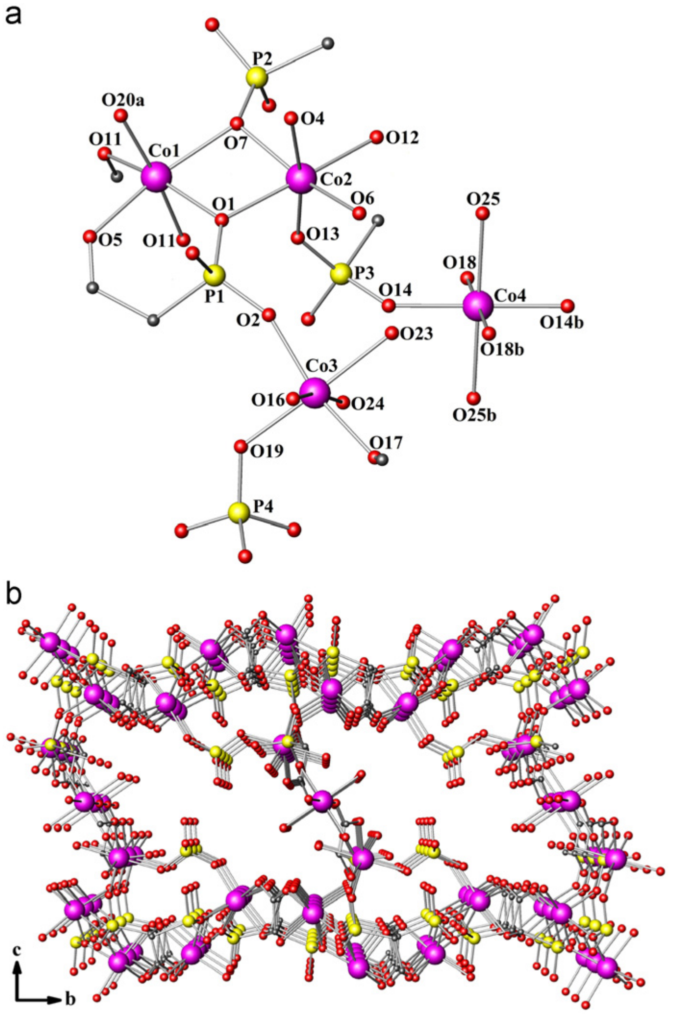


Fig. 6. Ball-stick views of coordinated environment of Co ions (a) and 3D structure (b) in **6**. Unrelated atoms are omitted for clarity. Symmetry codes: a $-x+1/2, y-1/2, -z+1/2$; b $-x, y+1, -z+1$.

groups into a Co–O–P–C–C–O ring. On the other hand, 2-hydroxyphosphonoacetates display a new μ_4:η_1:η_1:η_1:η_1:η_1 pentadentate, a new μ_3:η_2:η_1:η_1:η_1 tetradentate and a known μ_3:η_1:η_1:η_1:η_1:η_1 pentadentate modes (Scheme 1f–h) [17–25]. And HPO_4^{2-} group serves as a bridge to link Co1 and Co3. Thus, the cross-linkage of $[CoO_6]$ octahedra by HL^{2-} and HPO_4^{2-} groups is to form a complicated 3D framework with ellipsoid-like channels along *a* axis.

3.2. Thermal stability

TGA curve of **3** indicates a stage occurs from room temperature to 200 °C with 5.0% weight loss, corresponding to the loss of all water molecules (calculated 4.8%). Thereupon, a sharp stage appears from 300 °C due to the collapse of the framework. TGA curve of **6** indicates a stage occurs from 80 to 270 °C with 10.0% weight loss attributing the loss of all water molecules (calculated 10.3%). Furthermore, as-prepared **3** and **4** were heated at 250 and 300 °C for 2 h under air atmosphere, respectively, and cooled to room temperature. Both powder XRD patterns are in agreement with those of respective as-prepared solids. These results demonstrate that the structures of solids **3** and **4** behave thermally stable up to 250–300 °C under air atmosphere, respectively.

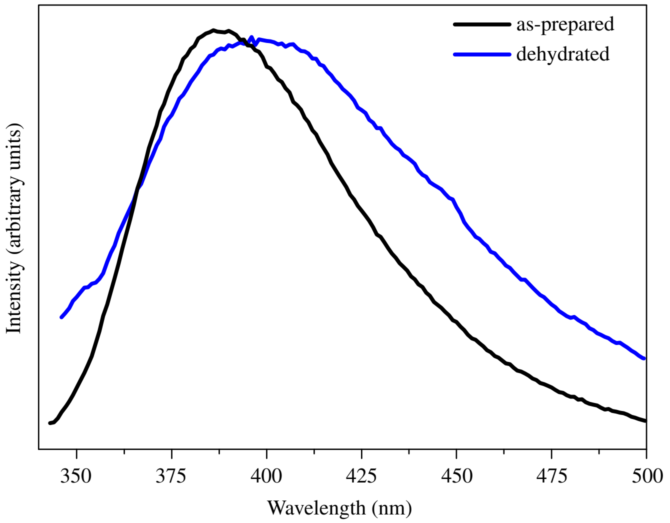


Fig. 7. Fluorescent emissions for as-prepared **3** ($\lambda_{ex}=328$ nm) and dehydrated **3** ($\lambda_{ex}=331$ nm).

3.3. Luminescent properties

No luminescent emissions for **1** and **4–6** can be detected under our experimental conditions. As-prepared **3** displays near UV emission with a peak band around 386 nm upon excitation at 328 nm (Fig. 7). Upon excitation at 258 nm, as-prepared **3** also displays near UV emission with a peak band around 389 nm. This is in accord with the excitation spectrum containing two peaks centered at 330 and 256 nm. And dehydrated **3** which has been heated at 250 °C for 2 h under air atmosphere and cooled to room temperature, displays purple light with a peak band around 396 nm. It is interesting that the peak emission of solid **3** displays a 10 nm red-shift after simply heat-treatment [45].

4. Conclusions

In summary, six new metal phosphonates with layered or 3D frameworks have been synthesized and fully characterized. As expected, 2-hydroxyphosphonoacetate displays five new coordination modes in these compounds. Beside common M–O–P–C–C–O and M–O–C–C–O chelating rings, 2-hydroxyphosphonoacetate can also be chelated to metal centers with two phosphonate oxygen atoms to form M–O–P–O ring, as well as with two phosphonate and one carboxylate oxygen atoms. It is worth to mention that there is a M–O–P–C–C–O chelating ring around $[ZnO_4]$ tetrahedron. The frameworks of **3** and **4** behave thermally stable up to 250 and 300 °C under air atmosphere, respectively. And the emission of solid **3** exhibits a 10 nm red-shift after simply heat-treatment. Future efforts are focused on introducing other structure-directing agents and secondary ligands to explore new metal phosphonates with attractive structures and properties.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.02.023.

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