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Synthesis, crystal structures and luminescence properties of two metal carboxyphosphonates

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ABSTRACT

Two metal carboxyphosphonates, $[Co_2(OOCC_5H_3NPO_3)_2.(H_2O)_3]$ (Compound1) and $Zn_3[OOCC_6H_3CH(OH)PO_3]_2.2H_2O$ (Compound2) were successfully synthesized under the hydrothermal reactions. In compound 1, two $\{Co1\text{-}NO_5\}$ octahedra link the $\{CPO_3\}$ by sharing the corner, which link the two $\{Co2\text{-}O_6\}$ octahedra. From a-axis the six clusters form the layer. Each layer is linked through hydrogen bond. In compound 2, the $\{Zn\text{-}O_4\}$ tetrahedron and $\{CPO_3\}$ tetrahedron are corner-shared, which arrange in line. From a-axis, each line forms the columnar. The thermal and luminescence properties of these compounds were investigated.

1. Introduction

Metal-organic frameworks(MOFs) are attracting enormous amount of research due to their applications in proton conductivity [1,2], catalysts activity [3], gas sorption ability [4], magnetism property [5], photovoltage [6], antibacterial activity [7,8], nonlinear optical property [9], ion exchangers capability [10] and luminescence. However, there are difficulties in controlling the structures and the pore size of the MOFs [11]. Selecting the suitable organic ligands is an effective way to adjust the structures and the pore size. In the last decades, metal phosphonates have attracted much attention. As the ligands in metal phosphonate coordination polymers, phosphonic acids can be prepared by relatively mild methods and display relatively high stability in cruel chemical and thermal environment. For each phosphonic acid molecule, there are three O atoms from phosphonic acid, which can form three coordination bonds at least. However, there are some disadvantages. Three oxygen atoms in the phosphonate ligands tend to form more condensed structures and the growth of single crystals is difficult as the phosphonate phases precipitate is much more complex because of different states of deprotonation. So it is necessary to add some functional groups to overcome the weaknesses. To date, diverse functional groups were designed and involved in the phosphonate based MOFs, such as amino [12], carboxylate [13,14], pyridyl [15,16], hydroxyl triazole [17], imidazole [18,19] etc. The R groups may play an important role. First, adding different R groups can enrich the coordination modes thus improving the crystallinity and forming different structures. Carboxylate is easier to coordinate than phosphonate and can supply more oxygen atoms to participate in linking to the metal ions, which can provide more opportunities to form new structures and can apply into many fields. For example, only metal phosphonates were rarely used for sensing applications because of their preference to form condensed structures and lack of secondary building units with metal ions. A paper that called a highly stable indium phosphonocarboxylate frameworks as a multifunctional sensor for Cu^{2+} was reported by Wenyan Dan [20]. In this work, they use the functional groups which combine the carboxylate and the phosphonate and can reach the target. Second, the functional R groups which contained amines may be acted as the template in growth of single crystals with phosphonates, like 4,4′-bipyridine [21]. Third, the R groups that are rigid or flexible may influence the structures of the MOFs. Rigid organic groups attend to produce extended frameworks of high structural stability [22]. Compared to the rigid R groups, the flexible groups have more advantages, because their flexibility and conformational freedom allow them to form various MOFs with interesting structures and functional properties. Sun had reported a series of MOFs based on several flexible multicarboxylate ligands [23]. So it is worth noting that the property of the R groups can play an important role in constructing the MOFs.

Now, we choose two multifunctional ligands, namely 5-phosphononicotinic acid (5-H_3PN) and 4-(hydroxy(phosphono)methyl) benzoic acid(4-HPMB) as the organic ligands. 5-H_3PN consists of pyridyl, carboxyl and phosphonyl groups in one ligand. 4-HPMB is made of benzene ring, carboxyl, hydroxy and phosphonyl groups. Herein, we prepared two MOFs based on the 5-H_3PN and 4-HPMB, respectively. The compound1 $[Co_2(OOCC_5H_3NPO_3)_2\cdot(H_2O)_3]$ and compound2 $Zn_3[OOCC_6H_3CH(OH)PO_3]_2\cdot 2H_2O$ were successfully synthesized and characterized by single-crystal X-ray diffraction and luminescence spectroscopy.

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2. Experiments

2.1. Materials and instruments

All starting materials were of reagent quality and were obtained from commercial sources without further purification. The 5-phosphononicotinic acid(5-H_3PN) and 4-(hydroxy(phosphono)methyl)benzoic acid(4-HPMB) were synthesized according to the literature [24,25]. Elemental analyses for C, H, and N were preformed on a Vario EL III elemental analyzer. The powder X-ray diffraction patterns of samples were carried out by Bruker-Axs D8 Advance X-ray diffractometer with a Cu K_α radiation (λ=0.15406 nm), operating at 40 kV and 40 mA. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC (1517148-1517149) reference numbers for compound 1 and compound 2, respectively. The FT-IR absorption spectra of the complexes were recorded in the range 400–4000 cm^{-1} using a Nicolet IS10 spectrometer with KBr pellets. The thermal behavior of samples were studied by thermogravimetry (Netzsch STA 449 F3 Jupiter, Germany) from 30 °C to 800 °C in nitrogen atmosphere at the heating rate of 10 °C/min (Fig. S2). The emission and excitation spectra were recorded in the solid state at room temperature with a Fluromax-4 fluorescence spectrophotometer.

2.2. Preparations

2.2.1. $[Co_2(OOCC_5H_3NPO_3)_{2\cdot}(H_2O)_3]$

A mixture of 5-H_3PN (0.10 mmol,0.0203 g) and $CoSO_4.7H_2O$ (0.10 mmol,0.0281 g) in 10 mL of distill water, adjusted to pH about 3.0–4.0 with 2 mol/L ammonium hydroxide was kept in a Teflon-lined autoclave at 140 °C for 2 days. After slowly cooling to room temperature, pink blocky crystals were obtained as a monophasic product, judged by PXRD measurements. (Fig. S3). Yield:81% based on Co. Anal.found(calcd): C,25.09(25.17); H,2.11(2.09);N,4.95(4.89)%. IR(KBr, cm^{-1}):3447(vs),3119(v),3081(m),1716(w),1616(vs),1548(w),1423(w),1385(w),1336(w),1303(w),1266(w),1180(vs),1130(m),994(vs),928(-w),857(w),766(m),691(m),672(m),660(w), 584(s),536(s),444(w) (Fig. S1).

2.2.2. $Zn_3[OOCC_6H_3CH(OH)PO_3]_2.2H_2O$

A mixture of 4-HPMB (0.10 mmol,0.0235 g) and $ZnSO_4.7H_2O$ (0.10 mmol,0.0287 g) in 8 mL of distill water and 2 mL of C_2H_5OH were stirred till dissolved. The pH value of solution was adjusted to 5.0 with NaOH (2 mol/L), and then the mixture was transferred to a Teflon-lined stainless steel vessel(25 mL) and heated at 160 °C for 2 days. After slowly cooling to room temperature, colorless blocky crystals were obtained as a monophasic product, judged by PXRD measurements. (Fig. S3) Yield:74%, based on Zn. Anal.found(calcd): C,27.88(27.95); H,2.11(2.04)%. FT-IR: (KBr, cm^{-1}):3431(vs),1651(w),1590(w),1545(m),1435(w),1186(w), 1096(vs),999(m), 869(w), 793(w),749(w), 547(w), 483(w), 446(w) (Fig. S1).

2.3. Crystallographic studies

Single crystals of dimensions 0.15×0.14×0.07 mm^3 for compound 1 and 0.34×0.30×0.29 mm^3 for compound 2 were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Ka radiation (λ=0.071073 nm) at 173 ± 2 K and 273 ± 2 K, respectively. A hemisphere of data was collected in the θ range 2.78–25.37° for 1 and 2.95–23.37° for 2 using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5 s/frame. Numbers of observed and unique [I > 2σ(I)] reflections are 3257 and 2624 (R_{int}=0.0410) for compound 1 and 3015 and 2876 (R_{int}=0.0480) for compound 2, respectively. The data were integrated using the Siemens SAINT program with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption corrections were applied. The structures were solved by direct methods and were refined on F2 by full matrix least squares using SHELXTL [26]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystallographic and refinement details of 1 and 2 are listed in Table 1. Selected bond lengths and angles are given in Tables S1 and S2.

Table 1
Crystal data and refinement details for compounds 1 and 2.

Complex	Compound 1	Compound 2
Formula	$C_{12}H_{14}O_{13}N_2P_2Co_2$	$C_{16}H_{16}O_{14}P_2Zn_3$
Formula weight	574.05	690.34
T(K)	173	273
Space group	*P*-1	*P*-1
a(Å)	5.0863(3)	8.093(4)
b(Å)	13.6215(10)	11.551(6)
c(Å)	14.6061(10)	12.407(6)
α(deg)	62.638(2)	69.409(7)
β(deg)	83.865(2)	83.441(8)
γ(deg)	84.883(2)	73.976(8)
V(Å^3)	892.67(10)	1043.4(9)
Z	2	2
F(0 0 0)	576	688
Min and max transmission	0.6663 and 0.7452	0.3699 and 0.4173
GOF on F^2	1.053	1.135
R1, wR2 [I > 2σ(I)][a]	0410, 0.1178	0.0480, 0.1293
R1, wR2 (All data)[a]	0.0550, 0.1255	0.0500, 0.1312
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (eÅ^{-3})	−1.052, 0.875	−0.882, 0.855

[a] $R_1=\sum(||Fo|-|Fc||)/\sum|Fo|$, $wR_2=\{\sum w(Fo^2-Fc^2)^2/\sum w(Fo^2)^2\}^{1/2}$

3. Results and discussion

3.1. Description of structure

Single crystal X-ray diffraction reveals that compound 1 belongs to *P*-1 space group with Z=2. Each unit contains five Co atoms, two 5-PN^{2-}, five coordinated water molecules and three lattice water molecules (Fig. 1). There are two crystallographically distinguishable Co atoms. The Co(1) atom is coordinated with two phosphonate oxygen atoms and one nitrogen atom (O(1),O(2A),N(1B)) from three equivalent phosphonate ligands. The remaining three sites are occupied by the fourth phosphonate oxygen (O(8)) and two water (O(11),O(12)). The Co(2) atom is filled with six oxygen atoms. Three sites are occupied by three oxygen atoms (O(6),O(6C),O(7D)) from three equivalent phosphonate ligands. The two sites are coordinated with the fourth phosphonate oxygen atoms (O(3),O(1)). The remaining site is linked with one water (O(13)).

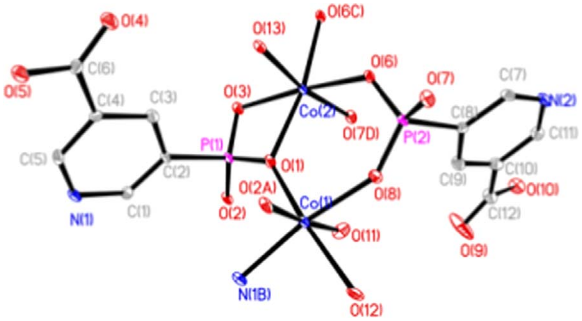

Fig. 1. Building unit of compound 1 with atomic labelling scheme.All H atoms are omitted for clarity.Symmetry codes are the same as those given in Table S1.