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ORIGINAL PAPER

Two Novel Cationic Frameworks Based on Cadmium(II) Vinylphosphonate with 4,4′-Bipyridine as Coligand

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Abstract The reaction of cadmium nitrate and vinylphosphonic acid (H_2L) with 4,4′-bipyridine (bipy) as coligand led to two novel cadmium(II) vinylphosphonates, namely, $[Cd_4(L)_3(NO_3)(bipy)_4(H_2O)_3]\cdot(NO_3)\cdot3(H_2O)$ (**1**) and $[Cd_3(HL)_3(L)(bipy)_3(H_2O)_4]\cdot(NO_3)\cdot3.5(H_2O)$ (**2**). Both compounds feature a cationic framework which encloses charge-balanced nitrate anions as well as guest water molecules. They represent the first examples of metal-organic frameworks based on mixed bridging ligands that contain a low-carbon-number alkylphosphonate. Notably, the cationic framework of **2** manifests an unprecedented (4,5)-connected net topology with point symbol of $(4^2\cdot6\cdot8^3)\cdot(4^3\cdot6^5\cdot8^2)_2$.

Keywords Cadmium · Phosphonate-based MOF · Crystal structure · Topology

Introduction

The synthesis and characterization of metal-organic frameworks (MOFs) is one of the most rapidly developing areas of chemistry due to their structural diversity and vast range of potential application in fields such as adsorption, ion exchange, separation and catalysis [1–4].

Among the classes of MOFs, phosphonate-based MOFs are quite unique, considering that they usually have moderate stability in an acidic solution whereas their carboxylate-based counterparts are subject to hydrolysis in acid solution. However, phosphonate-based MOFs are considerably rarer in the literature than carboxylate-based MOFs [5], which is in part because metal phosphonates tend to form densely packed layered structures that are not porous [6, 7]. Bearing this in mind, we think that one practicable method for the design and syntheses of phosphonate-based MOFs is to introduce a competitive bridging coligand; thus, the synergistic coordination of the mixed ligands may increase the possibility of constructing three-dimensional MOFs.

In order to address the above issue, here we select vinylphosphonic acid (H_2L) as a simple low-carbon-number alkylphosphonate ligand, and the most common bidentate-bridging 4,4′-bipyridine (bipy) as a coligand. So far, metal phosphonates purely based on a vinylphosphonate ligand have been intensively investigated, but all of them feature classic densely packed layer structures, which are mainly ascribed to the multi-dentate coordination modes of the phosphonate ligand [8–11]. For instance, the L^{2-} ligand in $[Cu(L)(H_2O)]$ [8], $[Zn(L)(H_2O)]$ [9], $[Cu_2(L)(OH)]$ [10] and $[Pb(L)(H_2O)]$ [10] acts as a multi-dentate bridging ligand, as shown in Scheme 1a–d, respectively.

Up to now, although a few MOFs based on mixed bridging ligands that containing a bisfunctional or multifunctional phosphonate ligand (such as diphosphonate, aminophosphonate and phosphonocarboxylate) have been reported [12–15], those based on a simple alkylphosphonate, $C_xH_yPO_3H_2$ (i.e., $C_xH_y– = CH_3–, C_2H_5–, C_3H_7–, C_6H_6–$, etc.), have never been documented. Our current research efforts yielded two such MOFs, namely, $[Cd_4(L)_3(NO_3)(bipy)_4(H_2O)_3]\cdot(NO_3)\cdot3(H_2O)$ (**1**) and $[Cd_3(HL)_3(L)(bipy)_3(H_2O)_4]\cdot(NO_3)\cdot3.5(H_2O)$ (**2**). As far as we know, they represent the first examples of metal-organic frameworks based on mixed bridging ligands that containing a low-carbon-number alkylphosphonate. Herein, we

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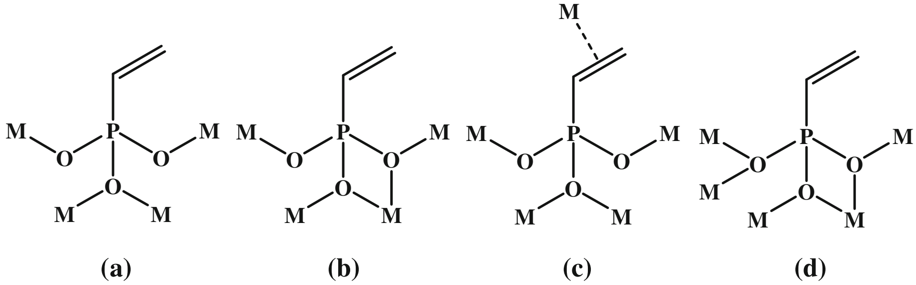


Scheme 1 The coordination modes of the L^{2-} ligand previously reported in references [8–11]

Table 1 Summary of crystal data and structural refinements for **1** and **2**

Compound	1	2
Empirical formula	$C_{46}H_{53}N_{10}O_{21}P_3Cd_4$	$C_{38}H_{52}N_7O_{22.5}P_4Cd_3$
Formula weight	1,624.5	1,427.95
Space group	*P*3	*P*-1
a (Å)	11.9225(2)	13.2041(4)
b (Å)	11.9225(2)	13.7867(5)
c (Å)	11.6421(3)	15.3818(5)
α/deg	90	93.625(2)
β/deg	90	101.696(2)
γ/deg	120	95.857(2)
V/Å^3	1,433.17(5)	2,717.53(16)
Z	3	2
D_{calcd}/g cm^{-3}	1.882	1.745
μ/mm^{-1}	1.632	1.363
GOF on F^2	1.023	1.013
Flack	0.01(4)	–
R1, wR2 [$I > 2\sigma(I)$]	0.0457, 0.1017	0.0427, 0.1037
R1, wR2 (all data)	0.0519, 0.1059	0.0552, 0.1114

$R1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR2 = \{\sum w[(Fo)^2 - (Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$

Table 2 Selected bond lengths (Å) for **1** and **2**

1			
Cd(1)–O(1)	2.186(3)	Cd(1)–N(2)#1	2.315(3)
Cd(1)–N(1)	2.325(3)	Cd(1)–O(1 W)	2.328(3)
Cd(1)–O(2)#2	2.338(3)	Cd(1)–O(4)	2.712(2)
Cd(2)–N(4)	2.282(4)	Cd(2)–N(3)#3	2.287(4)
Cd(2)–O(2)	2.337(3)	P(1)–O(3)	1.498(5)
P(1)–O(1)	1.541(4)	P(1)–O(2)	1.556(3)
P(1′)–O(3′)	1.513(6)	P(1′)–O(1)	1.544(4)
P(1′)–O(2)	1.577(3)		
2			
Cd(1)–O(10)	2.285(3)	Cd(1)–O(1 W)	2.311(3)
Cd(1)–O(3)	2.315(3)	Cd(1)–N(6)#1	2.325(3)
Cd(1)–O(8)	2.323(4)	Cd(1)–N(1)	2.333(3)
Cd(2)–O(11)#2	2.221(3)	Cd(2)–O(1)	2.311(3)
Cd(2)–O(4)	2.324(3)	Cd(2)–N(2)	2.328(3)
Cd(2)–N(4)#3	2.360(3)	Cd(2)–O(2 W)	2.360(3)
Cd(3)–O(9)	2.263(3)	Cd(3)–N(3)	2.309(4)
Cd(3)–O(3 W)	2.383(3)	Cd(4)–O(6)	2.236(3)
Cd(4)–O(4 W)	2.326(3)	Cd(4)–N(5)	2.352(4)
P(1)–O(2)	1.512(3)	P(1)–O(1)	1.517(3)
P(1)–O(3)	1.524(3)	P(2)–O(6)	1.491(3)
P(2)–O(4)	1.503(3)	P(2)–O(5)	1.566(3)
P(3)–O(9)	1.498(3)	P(3)–O(8)	1.502(3)
P(3)–O(7)	1.566(3)	P(4)–O(11)	1.485(3)
P(4)–O(10)	1.501(3)	P(4)–O(12)	1.558(4)

Symmetry codes

For **1**: #1 x, y, z + 1; #2 –y + 2, x − y + 1, z; #3 x, y, z − 1

For **2**: #1 –x + 1, –y, –z + 1; #2 x − 1, y, z; #3 x, y + 1, z

report their syntheses, crystal structures and topology analysis.

Experimental Section

Synthesis of 1 and 2

All chemicals were obtained from commercial sources and used without further purification. A mixture of $Cd(NO_3)_2$ (0.30 mmol), H_2L (0.30 mmol), and bipy (0.30 mmol) in 8 mL distilled water was allowed to stand at room temperature. Colorless block-shaped crystals formed three days later and the pH value of the solution was ≈ 5. These crystals were collected in approximately 55 % yield based on Cd. The subsequent studies based on single-crystal X-ray diffraction reveal that there exist two kinds of crystals as a mixture, *i.e.*, **1** and **2**. Since the two crystals have similar shapes, it is hard to distinguish them by appearance. In addition, we have made many efforts in synthesizing single phase material of the two compounds, by changing the molar ratio of the reactants, or adjusting the pH of the solution, but all efforts proved to be unsuccessful. Hence, further characterizations of them have not been done.

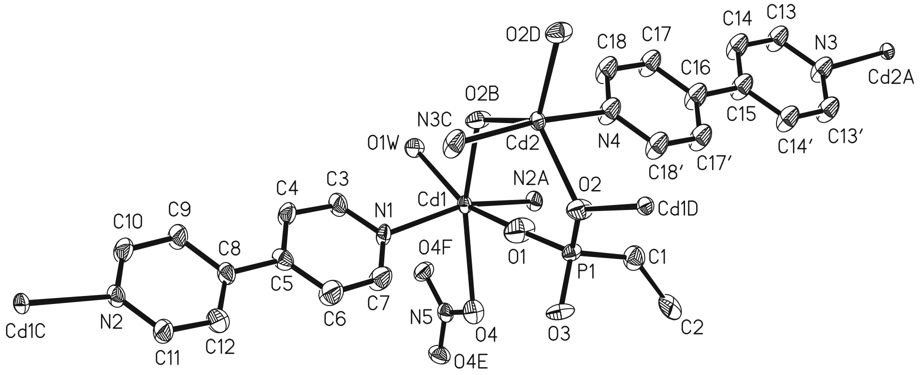
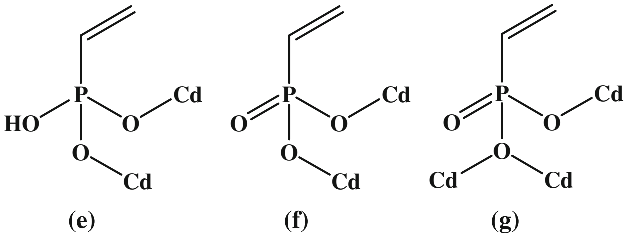


Fig. 1 ORTEP representation of the selected unit of **1**. The thermal ellipsoids are drawn at 30 % probability. Only one orientation was shown for a disordered bipy molecule for clarity. The non-coordinated nitrate anion, lattice water molecules and all hydrogen atoms have been omitted for clarity. Symmetry codes for the generated atoms: **a** x, y, z + 1. **b** –y + 2, x – y + 1, z. **c** x, y, z – 1. **d** –x + y + 1, –x + 2, z. **e** –y + 1, x – y, z. **f** –x + y + 1, –x + 1, z. **g** –y + 1, x – y + 1, z. **h** –x + y + 1, –x + 1, z

Crystal Structure Determination for 1 and 2

Data collections for **1** and **2** were performed on a Smart ApexII CCD diffractometer equipped with a graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at temperature of 296 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by SADABS program [16]. All structures were solved by the direct method using SHELXS-97 and refined by full-matrix least-squares fitting on F^2 by SHELXL-97 [17, 18]. All non-hydrogen atoms except one guest nitrate anion in **1** were refined with anisotropic thermal parameters. All hydrogen atoms except those of the water molecules were generated geometrically and refined isotropically. For **1**, the disordered L^{2-} ligand displays two orientations with 50 % occupancy for each site, and the disordered bipy ligand containing N3 and N4 atoms shows three orientations with 33.3 % occupancy for each position. For **2**, the carbon atoms (C3, C7 and C8) of two HL^- ligands are also disordered and each displays two orientations for each site, and the occupancy factors of the lattice water molecules O(7W), O(8W) and O(8W′) was reduced to 50 % because of their larger displacement parameters. Crystallographic data and structural refinements for **1** and **2** are summarized in Table 1. Important bond lengths are listed in Table 2.



Scheme 2 The coordination modes of the HL^- or L^{2-} ligand in **1** and **2**

Results and Discussion

Structure Description for 1

Compound **1** crystallizes in the trigonal space group *P*3 and it features an cationic three-dimensional $[Cd_4(L)_3(NO_3)(bipy)_4(H_2O)_3]^+$ framework enclosing charge-balanced nitrate anions as well as guest water molecules. Such

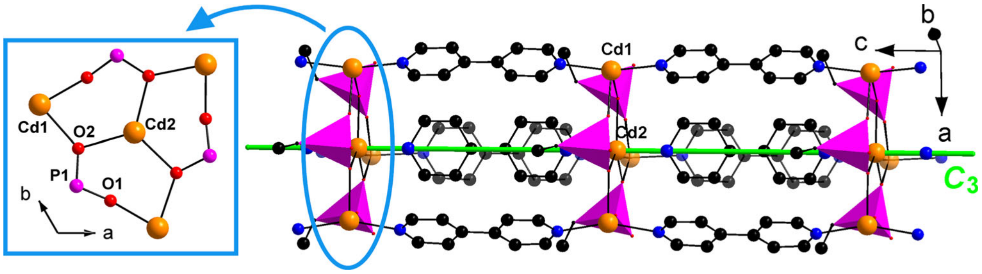


Fig. 2 One-dimensional $[Cd_4(L)_3(bipy)_4]^{2+}$ chain in **1**, which features a tetranuclear $[Cd_4(L)_3]^{2+}$ cluster. Only one orientation was shown for a disordered bipy molecule for clarity. Cd, P, O and C atoms are represented by *gold*, *purple*, *red* and *black circles*, respectively. CPO_3 tetrahedra are shaded in *purple* (Color figure online)

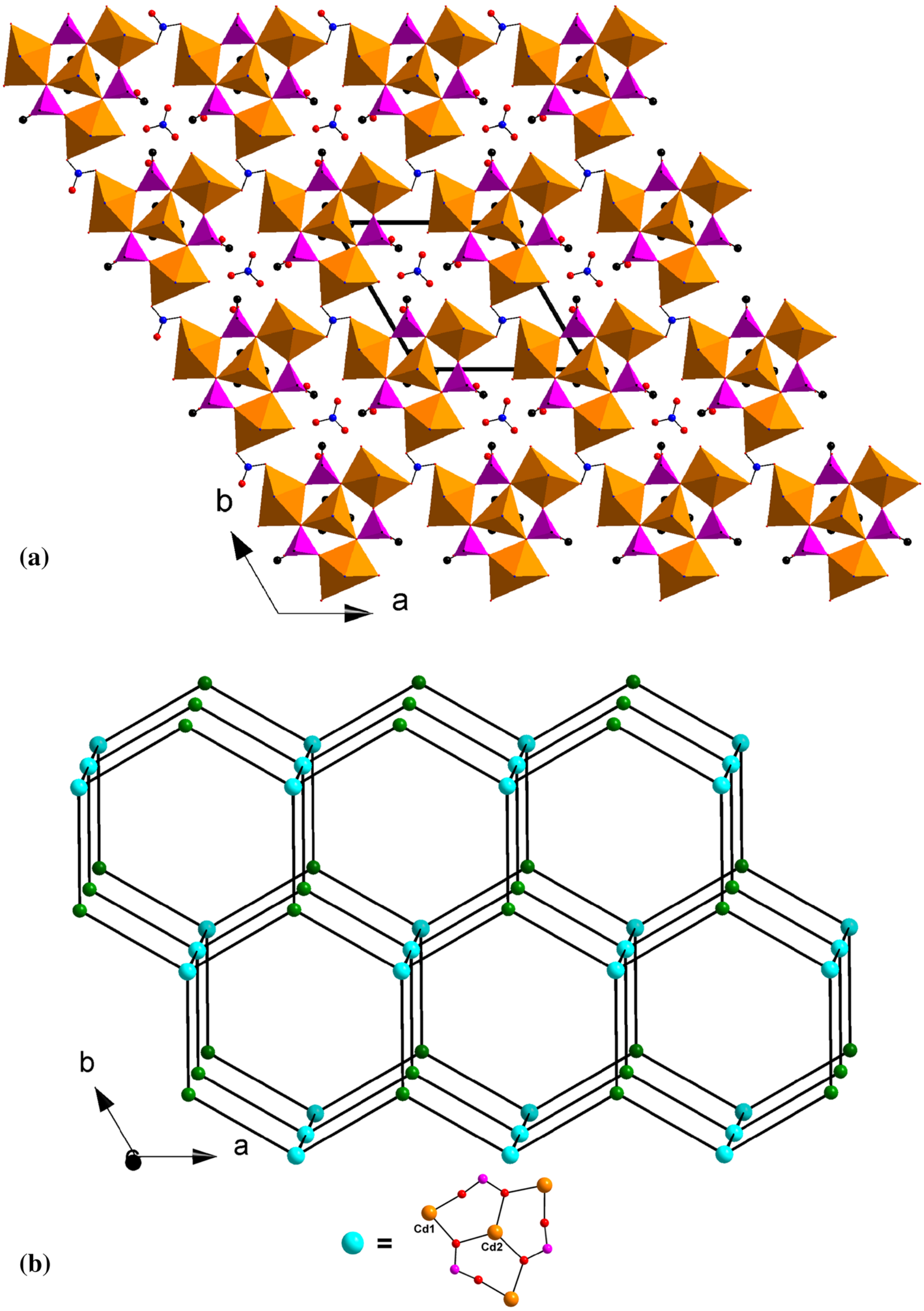


Fig. 3 **a** View of the structure of **1** down the *c*-axis. The CdO_3N_2/CdO_4N_2 polyhedra and CPO_3 tetrahedra are shaded in *gold* and *purple*, respectively. N, O and C atoms are represented by *blue*, *red* and *black circles*, respectively. **b** Topological structure of the cationic framework of **1**. The $\{Cd_4(L)_3\}^{2+}$ and NO_3^- nodes are represented by *cyan* and *green*, respectively (Color figure online)

cationic framework contains multiple components as follows: two crystallographically independent Cd^{2+} ions, one unique L^{2-} ligand, two crystallographically independent bipy ligands, one unique NO_3^- ligand, and an aqua ligand (Fig. 1). The Cd(1) ion residing on a general position has a distorted tetragonal bipyramid geometry, with two phosphonate O atoms of two L^{2-} ligands, one nitrate O atom and an aqua ligand as the equatorial atoms, and two N donors of two bipy ligands as the axial atoms. The Cd(2) ion lying on a threefold axis has a trigonal bipyramid geometry, with three equivalent phosphonate O atoms of three L^{2-} ligands as the equatorial atoms, and two non-equivalent N donors of two bipy ligands as the axial atoms. The Cd–O [2.186(3)–2.338(2) Å] and Cd–N [2.282(4)–2.325(3) Å] distances are normal [10, 19], with the exception of a slightly longer Cd(1)–O(4) distance [2.712(2) Å].

There are three kinds of bridging ligands in the $[Cd_4(L)_3(NO_3)(bipy)_4(H_2O)_3]^+$ framework. The unique L^{2-} ligand in **1** bridges three Cd^{2+} ions via its O(1) and O(2) atoms, of which O(2) acts as a μ_2-O (Fig. 1; Scheme 2g). The two crystallographically independent bipy ligands both function as a conventional bidentate-bridging ligand. It is noted that one bipy ligand containing N3 and N4 atoms runs across a threefold axis and thus exhibits a crystallographic disorder. The cooperative assembly of the L^{2-} and bipy ligands with the Cd^{2+} ions leads to a one-dimensional cylindrical-like $[Cd_4(L)_3(bipy)_4]^{2+}$ chain along the *c*-axis, which is related by a threefold axis symmetry, and such chain features a tetranuclear $[Cd_4(L)_3]^{2+}$ cluster (Fig. 2). Furthermore, a unique tridentate NO_3^- ligand, with its N atom lying on a threefold axis, links three $[Cd_4(L)_3(bipy)_4]^{2+}$ chains to form a three-dimensional cationic framework containing one-dimensional trigonal channels along the *c*-axis, and the free spaces in the cationic framework are occupied by additional charge-balanced NO_3^- anions as well as guest water molecules apart from the aqua ligands (Fig. 3a). Such framework can also be viewed as a pillar-layered structure, in which two-dimensional $[Cd_4(L)_3(NO_3)(H_2O)_3]^+$ layers are linked together by pillar-like bipy ligands at each Cd^{2+} site above and below. From the topological perspective, the $[Cd_4(L)_3]^{2+}$ cluster and NO_3^- ligand can be viewed as 5- and 3-connected nodes, respectively, whereas all the bipy ligands are defined as linkers, and the whole framework topology can be simplified as a (3,5)-connected topological net with the point symbol of $(6^3)\cdot(6^9\cdot8)$ (Fig. 3b).

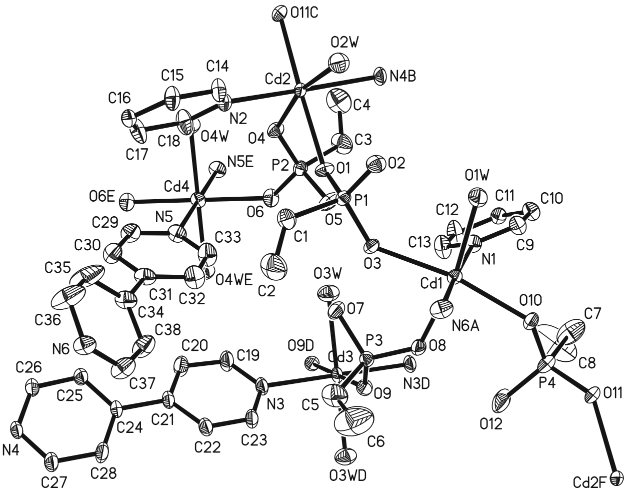


Fig. 4 ORTEP representation of the selected unit of **2**. The thermal ellipsoids are drawn at 30 % probability. The nitrate anion, lattice water molecules and all hydrogen atoms have been omitted for clarity. Symmetry codes for the generated atoms: **a** –x + 1, –y, –z + 1. **b** x, y + 1, z. **c** x – 1, y, z. **d** –x + 1, –y, –z. **e** –x, –y, –z. **f** x + 1, y, z

Structure Description for 2

Compound **2** crystallizes in the triclinic space group *P*-1 and it has another type of electropositive three-dimensional framework, $[Cd_3(HL)_3(L)(bipy)_3(H_2O)_4]^+$, which also encloses charge-balanced nitrate anions as well as guest water molecules. There are four crystallographically independent Cd^{2+} ions in **2**. The Cd(1) and Cd(2) ions residing on general positions both are octahedrally coordinated by three O atoms from three non-equivalent HL^-/L^{2-} ligands and two N donors of two non-equivalent bipy ligands as well as an aqua ligand, while Cd(3) and Cd(4) ions locating at inversion centers both are octahedrally coordinated by three pairs of equivalent donors: two O atoms from two HL^- ligands, two N atoms of two bipy ligands, and two aqua ligands (Fig. 4). It is noted that the geometry of these Cd^{2+} ions can also be viewed as a distorted tetragonal bipyramid, with four O atoms and two N atoms as the equatorial and axial atoms, respectively. The Cd–O [2.221(3)–2.383(3) Å] and Cd–N [2.309(4)–2.360(3) Å] distances are comparable to those of **1** and other reported cadmium(II) phosphonates [10, 19].

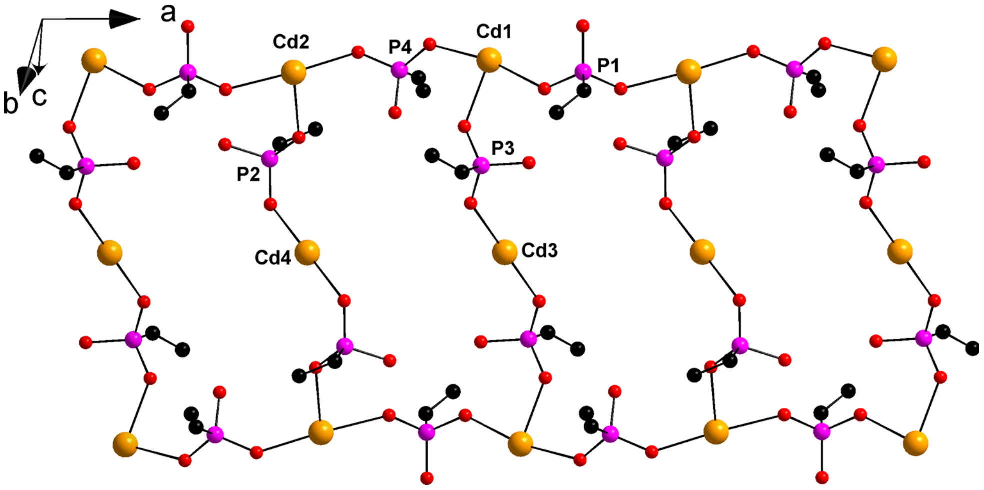


Fig. 5 One-dimensional $[Cd_3(HL)_3(L)]$ chain in **2**. Cd, P, O and C atoms are represented by *gold*, *purple*, *red* and *black circles*, respectively (Color figure online)

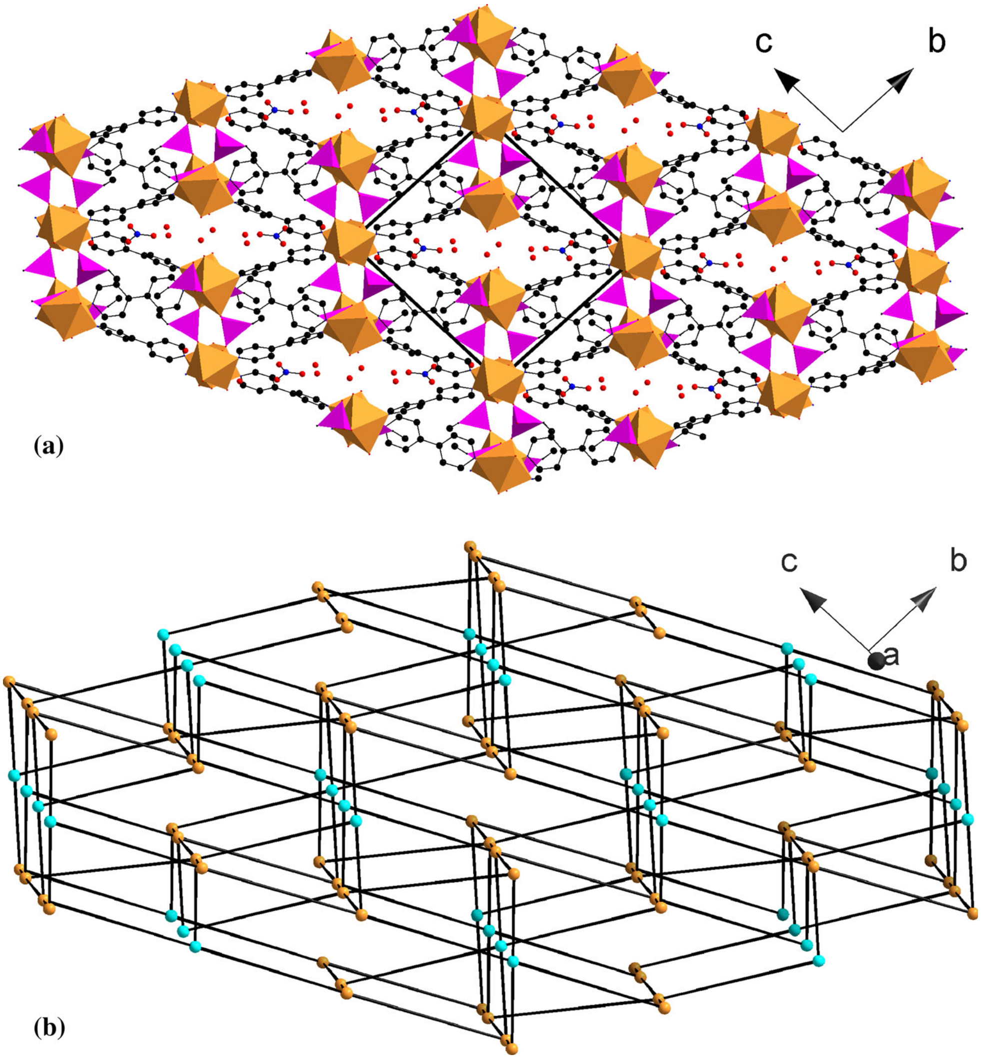


Fig. 6 **a** View of the structure of **2** down the *a*-axis. The CdO_4N_2 octahedra and CPO_3 tetrahedra are shaded in *gold* and *purple*, respectively. N, O and C atoms are represented by *blue*, *red* and *black circles*, respectively. **b** Topological structure of the cationic framework of **2**. The 5-connected Cd(1)/(2) and 4-connected Cd(3)/(4) nodes are represented by *gold* and *cyan circles*, respectively (Color figure online)

There are four unique HL^-/L^{2-} ligands in **2**, among which three of them are not completely deprotonated as the requirement for charge balance and also as indicated by three much longer non-coordinated P–O bonds (Table 2). Note: A long P–O bond distance (>1.55 Å) often is a credible evidence for the presence of a protonated P–O bond [6, 20]. All of the four HL^-/L^{2-} ligands feature a similar coordination mode and each bridges two Cd^{2+} ions via two O atoms (Scheme 2e, f), resulting a unique one-dimensional $[Cd_3(HL)_3(L)]^-$ chain (Fig. 5). In contrast, the four unique bipy ligands all function as bidentate-bridging ligands. The interconnection of the $[Cd_3(HL)_3(L)]^-$ chains by the above-mentioned four bipy ligands leads to the formation of a complicated three-dimensional cationic framework with large one-dimensional rhombic channels along the *a*-axis (Fig. 6a). These channels are filled with nitrate anions and lattice water molecules. From a topological point of view, the Cd(1)/Cd(2) and Cd(3)/Cd(4) centers can be simplified as 5- and 4-connected nodes, respectively, while the bidentate-bridging HL^-/L^{2-} and bipy ligands both are defined as linkers; and the complicated 3D framework of **2** can be described as a (4,5)-connected net topology with point symbol of $(4^2{\cdot}6{\cdot}8^3){\cdot}(4^3{\cdot}6^5{\cdot}8^2)_2$ (Fig. 6b), which is a new topological net by TOPOS analysis [21–23].

Conclusions

In summary, we present here two novel cadmium(II) vinylphosphonates with 4,4′-bipyridine as coligand, namely, $[Cd_4(L)_3(NO_3)(bipy)_4(H_2O)_3]{\cdot}(NO_3){\cdot}3(H_2O)$ (**1**) and $[Cd_3(HL)_3(L)(bipy)_3(H_2O)_4]{\cdot}(NO_3){\cdot}3.5(H_2O)$ (**2**). Both compounds feature a cationic framework which encloses charge-balanced nitrate anions as well as guest water molecules. The introduction of a competitive bipy coligand reduces the coordination sites available for the vinylphosphonate ligand; thus, different to the previously reported layer structures based on pure vinylphosphonate ligand [8–11], the combinations of the Cd^{2+} ions and the vinylphosphonates here lead to a tetranuclear cluster in **1** and a ribbon-like chain in **2**, both of which can be viewed as secondary building blocks for the construction of novel MOFs with the coexistence of other bridging ligand. The two compounds represent the first examples of metal-organic frameworks based on a simple low-carbon-number alkylphosphonate ligand and a mixed-bridging coligand. Notably, the cationic framework of **2** manifests an unprecedented (4,5)-connected net topology with point symbol of $(4^2{\cdot}6{\cdot}8^3){\cdot}(4^3{\cdot}6^5{\cdot}8^2)_2$. Further research will be extended to use such a method for the syntheses of other novel phosphonate-based MOFs.

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Conflict of interests The authors declare no conflict of interests.

Appendix: Supplementary Material

CCDC 951627 and 951628 contain the supplementary crystallographic data for this article. These 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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