



Molecular tectonics of mixed-ligand metal-organic frameworks: Positional isomeric effect, and structural diversification



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ABSTRACT

To explore the influence of three structurally different polycarboxylate ligands H₂L¹ to H₄L³ in the system Cd(II)/PPAN, three coordination polymers, formulated as {Cd₂(PPAA)₂(L¹)₂}_n (**1**), {[Cd₂(PPAA)₂(HL²)(H₂O)]₂·2H₂O}_n (**2**), {Cd₂(PPAN)₂(L³)(H₂O)₂}_n (**3**) have been obtained under similar conditions (PPAA⁻ = 2-(3-(pyridin-2-yl)-1H-pyrazol-1-yl)acetate, PPAN = 2-(3-(pyridin-2-yl)-1H-pyrazol-1-yl)acetonitrile, H₂L¹ = 1,3-benzenedicarboxylic acid, H₃L² = 1,3,5-benzenetricarboxylic acid, H₄L³ = 1,2,4,5-benzenetetracarboxylic acid). In **1–2**, PPAN are hydrolyzed into a novel PPAA⁻ ligand. The structure determination reveals that complex **1** contains 1D double chains of {[Cd(PPAA)]⁺}_n cation structural units, which are further extended by these μ₃-(L¹)²⁻ ligands forming a novel 2D three-layered framework with (4.8²)₂(4³.6².8)₂(4³8³)₂(4⁸.6⁶.8) topology. Complex **2** is one-dimensional (1D) ribbon-like chains having two kinds of dimeric [Cd(PPAA)]₂ and [Cd(COO)]₂ subunits and dimeric Cd(II) units bridged by μ₃-(HL²)²⁻ ligands. Complex **3** shows an undulating 2D (4, 4)-network by μ₄-(L³)⁴⁻. In addition, photoluminescent properties of three coordination polymers were also investigated in this paper.

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1. Introduction

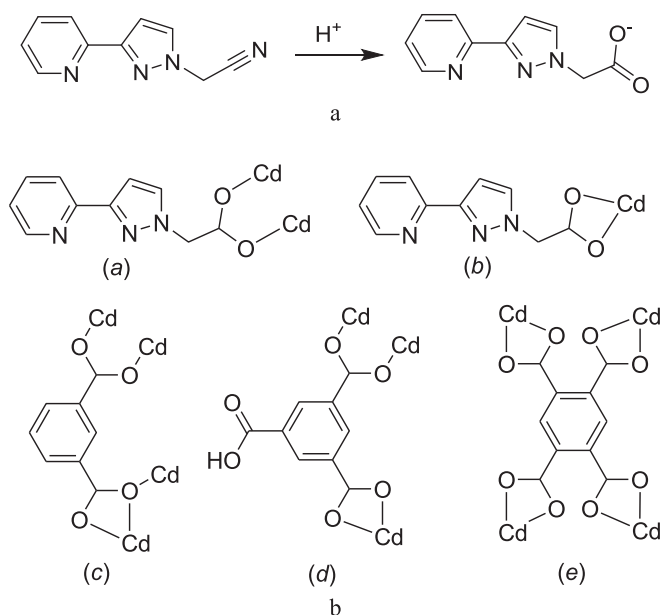
The current interest in the crystal engineering of coordination polymer frameworks is increasing not only because of their intriguing variety of architectures and topologies but also their fascinating potential applications in functional solid materials, ions exchange, catalysis, and the development of optical, electronic, and magnetic devices [1–5]. A successful strategy in building such networks is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve more new materials with interesting architectures and excellent physical properties [6–10]. Organic aromatic polycarboxylate ligands containing multidentate O donors, such as 1,3-benzenedicarboxylic acid [11–13], 1,3,5-benzenetricarboxylic acid [14–16], and 1,2,4,5-benzenetetracarboxylic acid [17–19], have been extensively employed in the construction of a rich variety of high dimensional structures.

On the other hand, N-donor building blocks, such as traditionally employed 2-(1H-pyrazol-3-yl)pyridine, have been extensively studied in coordination chemistry [20–24]. However, 2-(3-

pyridin-2-yl)-1Hpyrazol-1-yl)acetonitrile (PPAN) used in this work has not been explored in the coordination chemistry. Such ligand presents cyanide functional group which is easy hydrolyzed into the corresponding carboxylate groups (PPAA⁻) under solvothermal conditions in the presence of acid or base synthetic conditions (Scheme 1a). PPAA⁻ has been the subject of limited study with metal ions, and thus coordination frameworks have been reported [25]. However, studies on such ligand behavior containing aromatic polycarboxylate and PPAA⁻ toward coordination polymers are limited. In our recent research, we have concentrated on the construction of these novel mixed-ligand coordination polymers based on PPAN and various polycarboxylate species. For example, metal-directed assemblies of Cd(II) coordination polymer {[Cd₂(PPAA)₂(pa)(H₂O)]₂·2H₂O}_n, {[Cd₄(PPAA)₄(ip)₂·2H₂O]_n and {[Cd₂(PPAA)₂(tp)]₂·2H₂O}_n with PPAA⁻ and rigid dicarboxylate (pa = phthalate, ip = isophthalate, tp = terephthalate), displaying diverse 2D layered networks [26]. In this context, we describe three novel Cd(II) complexes with PPAA⁻ and polycarboxylate (1,3-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid), namely, {Cd₂(PPAA)₂(L¹)₂}_n (**1**), {[Cd₂(PPAA)₂(L²)(H₂O)]₂·2H₂O}_n (**2**), {Cd₂(PPAN)₂(L³)(H₂O)₂}_n (**3**). Interestingly, complex **1** has a different 2D structure, although the reagents and reaction conditions are the same with the {[Cd₄(PPAA)₄(ip)₂·2H₂O]_n.

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Scheme 1. a) *In Situ* hydrothermal syntheses of PPAA⁻; b) Different coordination modes for the new PPAA⁻ and polycarboxylate.

2. Experimental

2.1. Materials and general procedures

With the exception of the ligand **PPAN**, which was prepared according to the reported method [27], all reagents and solvents for synthesis and analysis were commercially available and used as received. Fourier transform (FT) IR spectra (KBr pellets) were taken on an AVATAR-330 (Nicolet) spectrometer. Microanalyses of C, H, and N were carried out on a CE-440 (Leeman labs) analyzer. Thermogravimetric analysis (TGA) was carried out on a Dupont thermal analyzer from room temperature to 600 °C N₂ atmosphere at a heating rate of 10 °C/min. Solid-state UV–Vis diffuse reflectance spectra was performed at room temperature using Shimadzu UV-3600 double monochromator spectrophotometer, BaSO₄ was used as a 100% reflectance standard for all material. Fluorescence spectra of the polycrystalline powder samples were performed on a HITACHI spectrofluorimeter (F7000) equipped with a xenon lamp and quartz carrier at room temperature.

2.2. Synthesis of complexes 1–3

2.2.1. {Cd₃(PPAA)₂(μ₄-L¹)₂}_n (**1**)

A mixture containing Cd(OAc)₂·2H₂O (26.6 mg, 0.10 mmol), PPAN (18.4 mg, 0.10 mmol), H₂L¹ (16.6 mg, 0.10 mmol) and (10 mL) was sealed in a Teflon-lined stainless steel vessel (20 mL), which was heated at 140 °C for 3 days and then cooled to room temperature at a rate of 5 °C h⁻¹. Colorless block crystals of **1** were obtained with 43% yield. Anal. Calc. for C₃₆H₂₄Cd₃N₆O₁₂: C, 40.42; H, 2.26; N, 7.86. Found: C, 40.53; H, 2.19; N, 7.93. IR (KBr, cm⁻¹): 3420 b, 1604 vs, 1504 m, 1434 s, 1328 s, 1248 m, 1154 m, 1095 w, 1077 m, 1053 w, 1016 m, 960 m, 932 w, 904 w, 778 s, 744 m, 690 m, 640 m.

2.2.2. {[Cd₂(PPAA)₂(L²)(H₂O)]₂(H₂O)_n (**2**)

The same synthetic method as that for **1** was used except that H₂L¹ was replaced by H₃L² (21 mg, 0.1 mmol). Colorless block crystals of **2** were obtained with 36% yield. Anal. Calc. for

C₃₆H₂₄Cd₃N₆O₁₂: C, 41.47; H, 2.84; N, 7.64. Found: C, 41.53; H, 2.79; N, 7.65. IR (KBr, cm⁻¹): 3414 b, 1583 vs, 1483 m, 1442 s, 1394 vs, 1369 m, 1324 m, 1252 m, 1194 w, 1171 m, 1110 m, 1079 m, 1053 w, 1023 w, 863 w, 830 w, 805 w, 772 s, 714 m, 654 w, 586 w, 541 w.

2.2.3. {Cd₂(PPAN)₂(L³)(H₂O)₂}_n (**3**)

The same synthetic method as that for **1** was used except that H₂L¹ was replaced by H₄L³ (25.4 mg, 0.1 mmol). Colorless block crystals of **3** were obtained with 51% yield. Anal. Calc. for C₂₉H₂₅Cd₂N₆O₁₃: C, 41.47; H, 2.84; N, 7.64. Found: C, 41.53; H, 2.79; N, 7.65. IR (KBr, cm⁻¹): 3415 b, 1642 s, 1570 vs, 1506 m, 1393 vs, 1315 s, 1246 m, 1190 m, 1157 m, 1135 m, 1097 m, 1070 m, 1014 w, 960 w, 936 w, 880 w, 836 w, 801 w, 779 s, 745 m, 687 w, 623 m, 568 m, 524 m.

2.3. X-ray single-crystal diffraction

Single-crystal X-ray diffraction data for complexes **1–3** were collected on a Bruker Apex II CCD diffractometer at 293(2) K with Mo Kα radiation (k = 0.71073 Å). There was no evidence of crystal decay during data collection. In general, a semi-empirical absorption correction (SADABS) was applied and the program SAINT was used for integration of the diffraction profiles [28]. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [29]. The final refinement was performed by full-matrix least-squares methods on F₂ with anisotropic thermal parameters for all non-H atoms. Hydrogen atoms attached to carbon were generated geometrically and those of methanol or water were first located in difference Fourier syntheses and then treated as riding. Isotropic displacement parameters of H were derived from their parent atoms. A summary of the crystallographic data are shown in Table 1 and selected bond parameters are listed in Table S1 (in Supplementary material).

3. Results and discussion

3.1. Structural analysis of 1–3

3.1.1. {Cd₃(PPAA)₂(μ₄-L¹)₂}_n (**1**)

As depicted in Fig. 1a, the fundamental building unit of complex **1** contains two independent Cd(II) ions. With respect to Cd1, the distorted octahedral sphere is provided by one axial pyrazolyl nitrogen and one oxygen atom from two different PPAA⁻ molecules (O1–Cd1–N2 = 164.04(8) °) as well as three oxygen atoms from carboxylate, water and pyridyl nitrogen that define the equatorial plane. The Cd2 ion also shows a distorted octahedral geometry, which is completed by four oxygen atoms of two (L¹)²⁻ dianions in the basal plane and two oxygen atoms of two PPAA⁻ ligands at the apical sites with O2–Cd2–O2A angle of 180.00(12) °. In this structure, the carboxylate groups of H₂L¹ behave in monodentate bridging, bidentate chelating *syn-skew* bridging mode and the carboxylate groups of PPAA⁻ is *syn-syn* bridging mode. As a consequence, PPAA⁻ ligands bridge Cd(II) centers to form 1D double chains structure. As illustrated in Fig. 1b, this 1D array is further interlinked through μ₃-(L¹)²⁻ to generate a 2D coordination framework along the *bc* plane. In this 2D network, with each PPAA⁻ serving as a 3-connected node, (L¹)²⁻ and Cd1 as equivalent 4-connected nodes, and Cd2 as a 6-connected node, this 2D pattern displays an unreported (3,4,4,6)-connected (4.8²)₂(4³.6².8)₂(4³.8³)₂(4⁸.6⁶.8) topology (see Fig. 1c).

3.1.2. {[Cd₂(PPAA)₂(μ₃-HL²)(H₂O)]₂(H₂O)_n (**2**)

The fundamental structural unit of **2** (see Fig. 2a) contains two crystallographic independent Cd(II) centers, two PPAA⁻, one water ligands, and (HL²)²⁻ spacer. The distorted pentagonal bipyramidal

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