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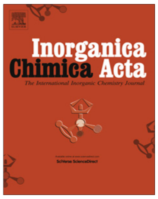

Cadmium carboxycinnamate coordination polymers with dimensionality differences depending on dipyridyl ligand

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ABSTRACT

Hydrothermal reaction of cadmium nitrate, carboxycinnamic acid (H_2cca), and a tethering hydrogen-bonding capable dipyridyl ligand afforded three new crystalline coordination polymers, which were characterized by single-crystal X-ray diffraction. $\{[Cd(cca)(dpa)_2]\cdot 2H_2O\}_n$ (**1**, dpa = 4,4′-dipyridylamine) shows a (4,4) coordination polymer layer, but with pendant dpa ligands curling in through the grid apertures. $\{[Cd(cca)(4\text{-bpmp})(H_2O)]\cdot 2H_2O\}_n$ (**2**, 4-bpmp = bis(4-pyridylmethyl)piperazine) also has a 2-D coordination polymer layer structure, but with closely interdigitated (6,3) herringbone motifs. $[Cd(cca)(4\text{-bpfp})]_n$ (**3**, 4-bpfp = bis(4-pyridylformyl)piperazine) manifests a $\{Cd_2(OCO)_2\}$ dimer-based 6-connected **pcu** 3-D network. All three materials undergo modest to strong blue-violet fluorescence under ultraviolet radiation. Thermal decomposition behavior is also probed.

1. Introduction

Exploratory synthesis and structural characterization of coordination polymer solid phases remains a very active research focus because of these materials' potential utility in gas storage [1], molecular separations [2], ion-exchange [3], catalysis [4], and optical applications [5]. Additionally, their molecular topologies can often be quite aesthetic, providing further appeal and motivation for research [6]. Because of their d^{10} closed-shell configuration, divalent zinc and cadmium ions are frequently used as the metal nodes in coordination polymer chemistry for two reasons. Due to the zero ligand field stabilization energy and flexible coordination geometry, donor disposition, steric requirements and conformational changes act together to impact the final crystal structure. Also, the absence of *d*–*d* electron transitions results in the necessary spectral window for useful light-emitting properties such as fluorescence or second harmonic generation [7].

Among cadmium coordination polymers, dual-ligand phases containing both aromatic *ortho*-dicarboxylate and neutral dipyridyl ligands can exhibit a wide variety of structural topologies, including a few very rare self-penetrated networks [8–14]. $[Cd(Hpht)_2(bpy)]_n$ (pht = phthalate, bpy = 4,4′-bipyridine) possesses a 6-connected 3-D self-penetrated $5^{10}6^47$ topological network with [8a], built from the tethering of an adamantoid $[Cd(Hpht)_2]_n$ network within itself by 4,4′-bpy ligands. $\{[Cd(pht)(dpa)(H_2O)]\cdot 4H_2O\}_n$ (dpa = 4,4′-dipyridylamine) has an aesthetic self-penetrated 3-D network 7^48^2 **yyz** topology constructed from the tethering of three chiral (12,3) regular subnets, themselves self-penetrated [9a].

Extension of one of the *ortho*-dicarboxylate arm lengths can institute significant differences in coordination polymer topology in some cases, but a negligible change in others. In contrast to the pht ligand that has two single-C short arm dicarboxylate groups, the homophthalate (hmp) ligand has one single-C shorter arm and one two-C longer arm for its two carboxylate moieties. $\{[Cd(hmp)(dpa)]\cdot H_2O\}_n$ (hmp = homophthalate) exhibits interdigitated herringbone grid (6,3) layers [15], different from the self-penetrated 3-D net of its pht analog. However, both $\{[Cd_2(pht)_2(\text{bpfp})(H_2O)_2]_n$ [11] and $\{[Cd_2(hmp)_2(\text{bpfp})]_n$ (bpfp = bis(4-pyridylformyl)piperazine) [12] display the same $(4^46^2)(4^46^6)$ **tcs** topology 4,5-connected 3-D network structure. The related phase $\{[Cd_2(mph)_2(H_2O)_2(\text{bpmp})(\text{Hbpmp})]ClO_4\cdot 4H_2O\}_n$ (mph = 4-methylphthalate, bpmp = bis(4-pyridylmethyl)piperazine) has $[Cd_2(mph)_2]$ dinuclear units linked into simple (4,4) grids [16], considering the dinuclear units as the connecting nodes. If the pairs of mph ligands are considered to be a single linker and individual Cd atoms are treated as the nodes, the layers can be viewed as (6,3) graphitic nets.

In contrast to the *ortho*-dicarboxylate ligands pht and hmp, the carboxycinnamate ligand (cca, Scheme 1) has been employed far less frequently in the construction of crystalline coordination

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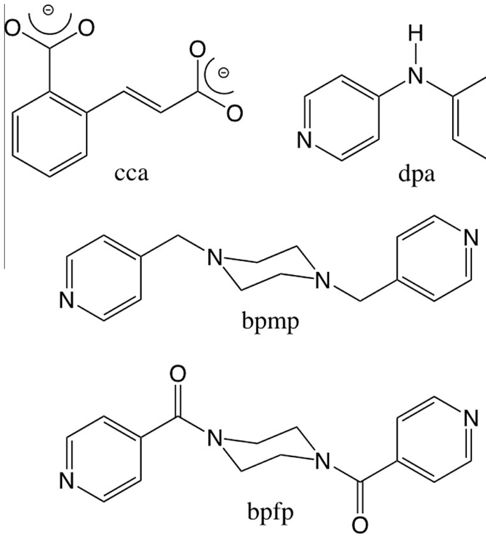

Scheme 1. Ligands used in this study.

polymer phases. The cca ligand possesses a single-C shorter arm and a three-C longer arm, with restricted conformational degrees of freedom within the longer arm due to the presence of the C–C π bond. To the best of our knowledge there are only two known cadmium cca coordination polymers with dipyridyl-type ligands [17]. $[Cd(cca)(dpp)(H_2O)]_n$ (dpp = 1,3-bis(4-pyridyl)propane) shows a simple 1-D double-stranded chain containing *gauche*-conformation dpp ligands, while $[Cd(cca)(bpy)]_n$ possesses a (4,4) grid 2-D layer built from $[Cd_2(cca)_2]$ double chains pillared by bpy ligands. We thus sought to expand the scope of known cadmium cca coordination polymers by using the hydrogen-bonding capable dipyridyl coligands dpa, bpmp, and bpfp (Scheme 1). We herein report the synthesis, structural characterization, and preliminary physical property determinations of the three new cadmium coordination polymers $\{[Cd(cca)(dpa)_2]\cdot 2H_2O\}_n$ (**1**), $\{[Cd(cca)(4\text{-}bpmp)(H_2O)]\cdot 2H_2O\}_n$ (**2**), and $[Cd(cca)(4\text{-}bpfp)]_n$ (**3**).

2. Experimental

2.1. General considerations

Cadmium nitrate and carboxycinnamic acid were commercially obtained. The dipyridyl ligands dpa [18], 4-bpmp [19], and 4-bpfp [20] were prepared via published procedures. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One instrument. The luminescence spectra were obtained with a Hitachi F-4500 Fluorescence Spectrometer on solid crystalline samples anchored to quartz microscope slides with Rexon Corporation RX-22P ultraviolet-transparent epoxy adhesive. Thermogravimetric analysis was performed on a TA Instruments TGA 2050 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 650 °C under flowing N_2. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

2.2. Preparation of $\{[Cd(cca)(dpa)_2]\cdot 2H_2O\}_n$ (**1**)

$Cd(NO_3)_2\cdot 4H_2O$ (86 mg, 0.28 mmol), carboxycinnamic acid (54 mg, 0.28 mmol), and dpa (48 mg, 0.28 mmol) were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined Parr acid digestion bomb. The suspension was basicified with 1.0 mL of 1.0 M NaOH. The bomb was sealed and heated at 120 °C for 48 h, and then was cooled slowly to 25 °C. Colorless blocks of **1** (38 mg, 40% yield based on dpa) were isolated after washing with distilled water, ethanol, and acetone and drying in air. Anal. Calc. for $C_{30}H_{28}CdN_6O_6$ **1**: C, 52.91; H, 4.14; N, 12.34. Found: C, 51.92; H, 4.01; N, 12.03%. IR (cm^{-1}): 3414 (w, br), 3023 (w, br), 1625 (w), 1590 (s), 1554 (m), 1521 (s), 1439 (m), 1425 (w), 1387 (s), 1361 (m), 1348 (s), 1275 (w), 1212 (s), 1062 (w), 1010 (s), 1000 (m), 966 (w), 906 (w), 867 (w), 847 (w), 808 (s), 761 (w), 736 (m), 727 (m), 706 (m), 670 (m).

2.3. Preparation of $\{[Cd(cca)(4\text{-}bpmp)(H_2O)]\cdot 2H_2O\}_n$ (**2**)

$Cd(NO_3)_2\cdot 4H_2O$ (86 mg, 0.28 mmol), carboxycinnamic acid (54 mg, 0.28 mmol), and 4-bpmp (73 mg, 0.27 mmol) were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined Parr acid digestion bomb. The suspension was basicified with 1.0 mL of 1.0 M NaOH. The bomb was sealed and heated at 120 °C for 48 h, and then was cooled slowly to 25 °C. Colorless blocks of **2** (128 mg, 76% yield based on 4-bpmp) were isolated after washing with distilled water, ethanol, and acetone and drying in air. Anal. Calc. for $C_{26}H_{32}CdN_4O_7$ **2**: C, 49.97; H, 5.16; N, 8.96. Found: C, 49.81; H, 5.03; N, 8.92%. IR (cm^{-1}): 3400 (w, br), 1613 (m), 1572 (m), 1531 (m), 1391 (s), 1065 (w), 1011 (m), 978 (m), 845 (m), 806 (m), 770 (m), 731 (m), 670 (m).

2.4. Preparation of $[Cd(cca)(4\text{-}bpfp)]_n$ (**3**)

$Cd(NO_3)_2\cdot 4H_2O$ (86 mg, 0.28 mmol), carboxycinnamic acid (54 mg, 0.28 mmol), and 4-bpfp (84 mg, 0.28 mmol) were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined Parr acid digestion bomb. The suspension was basicified with 1.0 mL of 1.0 M NaOH. The bomb was sealed and heated at 120 °C for 48 h, and then was cooled slowly to 25 °C. Colorless blocks of **3** (101 mg, 60% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. Anal. Calc. for $C_{26}H_{22}CdN_4O_6$ **3**: C, 52.14; H, 3.70; N, 9.36. Found: C, 51.40; H, 3.73; N, 8.88%. IR (cm^{-1}): 1625 (s), 1570 (m), 1539 (s), 1462 (m), 1440 (m), 1384 (s), 1287 (m), 1263(s), 1166 (m), 1063 (w), 1045 (w), 1000 (s), 976 (m), 905 (w), 863 (m), 839 (s), 813 (m), 766 (m), 747 (m), 726 (m), 708 (m).

3. X-ray crystallography

Reflection data for **1**–**3** were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were processed via SAINT [21], and subjected for Lorentz and polarization effect and absorption corrections using SADABS [22]. The structures were solved using direct methods with SHELXTL [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon were placed in calculated positions and refined isotropically with a riding model. Hydrogen atoms within the water molecules and dpa ligand were found by Fourier difference map and then restrained. Crystallographic details for **1**–**3** are given in Table 1.

4. Results and discussion

4.1. Synthesis and spectra

Crystalline samples of **1–3** were produced by the hydrothermal reaction of cadmium nitrate, carboxycinnamic acid, and the requisite dipyridyl ligand. Their infrared spectra were consistent with their structural features as ascertained by single-crystal X-ray diffraction. Intense, slightly broadened asymmetric and symmetric C–O stretching bands within the carboxycinnamate ligands were observed at 1521 and 1360 cm^{-1} in **1**, at 1531 and 1397 cm^{-1} in **2**, at 1539 and 1384 cm^{-1} in **3**. The C=O stretching band for the