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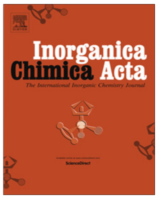

Research paper

Structurally diverse divalent metal pyromellitate coordination polymers with very long spanning dipyridylamide ligands

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ABSTRACT

Hydrothermal reaction of divalent metal nitrates, pyromellitic acid (pymH$_4$), and either 1,6-hexanediaminebis(nicotinamide) (hbn) or 1,6-hexanediaminebis(isonicotinamide) (hbin) afforded crystalline coordination polymers whose dimensionality depends synergistically on the dipyridylamide nitrogen donor disposition and metal coordination environment. These new phases were structurally characterized via single-crystal X-ray diffraction. $[Cd(pymH_2)(hbn)(H_2O)_2]_n$ (**1**) and $[Co(pymH_2)(hbn)(H_2O)_2]_n$ (**2**) display isostructural (4,4) grid topologies with $[M(pymH_2)(H_2O)_2]_n$ chains pillared by hbn ligands. $\{[Cu_2(pym)(hbn)(H_2O)_2]\cdot 2H_2O\}_n$ (**3**) manifests a 3D 3,4-connected network with a rare $(8^3)_2(8^6)$ topology built from the hbn pillaring of $[Cu_2(pym)(H_2O)]_n$ layer motifs. $\{[Zn_2(pym)(hbin)_2(H_2O)]\cdot H_2O\}_n$ (**4**) shows a 1D ribbon motif based on $[Zn_2(OCCCCO)_2]$ 14-membered circuits. $\{[Ni_2(pym)(hbin)(H_2O)_4]\cdot 3H_2O\}_n$ (**5**) exhibits 3,4-connected layer motifs with rare $\{4.6^2\}_2\{4^2 6^2 8^2\}$ topology. Luminescent behavior in **1** and **4** is ascribed to intra-ligand molecular orbital transitions. These phases were also surveyed for the ability to detect nitrobenzene in ethanol suspension. Thermal decomposition behavior of **1**–**5** is also discussed herein.

1. Introduction

The enticing utility of crystalline divalent metal coordination polymers in gas storage [1], selective absorption [2], ion exchange [3], industrially relevant catalysis [4], and explosives trace detection [5] has spurred an intense basic research focus on this class of materials over the past two decades. A key side benefit is their beautiful interlocked and interdigitated topologies, which provides an additional intangible impetus for continued investigation [6]. Aromatic dicarboxylates ligands provide both the crystal integrity and required charge balance for the construction of coordination polymers, and thus are clearly the most popular linking ligand choice [7–10]. Specific coordination geometric preferences at the divalent metal centers (*e.g.* square planar, square pyramidal, trigonal bipyramidal, octahedral, pentagonal bipyramidal) can induce significant structural alterations across a series of related coordination polymers [11–13], accommodated by the variety of energetically similar carboxylate binding modes. As a result of the enormous parameter space defined by all the possible metal and ligand choices, deliberate tuning of coordination polymer structure and topology has only been achieved in systems of a narrow structural scope [14,15].

The four carboxylate donor groups of the pyromellitate ligand (pym, 1,2,4,5-benzenetetracarboxylate, Scheme 1) can induce a tremendous diversity of possible dicarboxylate binding and bridging modes, and therefore *a priori* prediction of the final topology of an extended phase is problematic. Thus exploratory synthesis still presents the best means of expanding the scope of divalent metal pym-containing coordination polymers. Previous reports of this class of crystalline compound have illustrated that the pym ligand can connect from two to up to ten divalent metal ions [16]. Control of pH during coordination polymer self-assembly can afford completely deprotonated tetraanionic pym ligands [16], trianionic pymH ligands [17], dianionic pymH$_2$ ligands [18], or monoanionic pymH$_3$ ligands [19]. The tunable negative charges on the pym ligand backbone imparts different stoichiometric ratios with divalent metal ions, thereby imposing marked alterations in coordination polymer topology. At times, alkali metal cations [20] or non-ligating organoammonium cations [21] can be incorporated into voids and serve important templating roles in pym-containing coordination polymers.

Inclusion of neutral nitrogen base coligands has been efficacious in formation of functional coordination polymers containing the pym ligand and its partially protonated congeners; in nearly all

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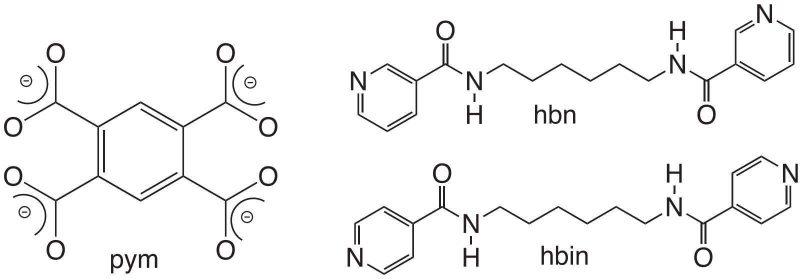

Scheme 1. Ligands used in this study.

cases wide diversity in topology is observed [22–25]. [Cu(pymH$_2$)(2,2′-bipyridine)]$_n$ is an excellent catalyst for cyclohexene oxidation [22a]; the 1D phase [Cu$_2$(pym)(triethanolamine)$_2$]$_n$ can catalytically C—H activate cyclohexane in the presence of aqueous hydrogen peroxide [22b]. The rigid tetracarboxylate and dipyridyl ligands in {[Ni$_2$(pym)(4,4′-bipyridine)$_3$]·3DMF}$_n$ allow it to maintain a 3-D microporous structure and nitrogen absorption capacity after co-crystallized solvent removal [22c]. {[H$_2$dpa][Cu$_3$(pyro)$_2$(H$_2$O)$_3$]·2.5H$_2$O}$_n$ (dpa = 4,4′-dipyridylamine) displays an acentric 3-D 4,4,6-connected anionic network with a complicated topology, built from conjoined antiferromagnetic {Cu$_2$(OCO)$_4$} paddlewheel dimers and isolated copper ions [23]. Its lower temperature analog, {[Cu$_3$(pyro)$_2$(dpa)$_2$(dpaH)$_2$]·3H$_2$O}$_n$ manifests a 3-D neutral network with $(4^2 6^4)_4(6^4 8^2)$ **frl** topology based on weakly ferromagnetically coupled {Cu$_3$(OCO)$_2$} linear trimers [23]. Alteration of nitrogen donor disposition within a isomeric dipyridyl ligands resulted in significant topological adjustment in a pair of 3D zinc/pym coordination polymers. {[Zn$_2$(pymH)$_2$(H$_2$O)$_2$(H$_2$-3-bpmp)]·H$_2$O}$_n$ (3-bpmp = bis(3-pyridylmethyl)piperazine) possesses a rarely encountered 4,5-connected $(4^4 6^2)(4^4 6^6)$ **tcs** topology. {[Zn$_2$(pymH)$_2$(H$_2$-4-bpmp)]·4H$_2$O}$_n$ (4-bpmp = bis(4-pyridylmethyl)piperazine) exhibited a novel yet elegant 3,4-connected binodal $(4.8^2)(4.8^2 10^3)$ self-penetrated topology [24]. Use of the longer-spanning dipyridylamide ligand bis(4-pyridylformyl)piperazine (bpfp) generated 1D or 3D coordination polymers with the pym ligand and its protonated variants [25]. {Cd(pymH$_2$)(bpfp)]·2H$_2$O}$_n$ possesses an uncommon 3-D **fsc** network, while {[Zn$_2$(pym)(bpfp)(H$_2$O)$_8$]·4H$_2$O}$_n$ shows a supramolecular aggregation of 1D chain motifs. Heretofore there have been no reports of pym-containing divalent metal coordination polymers containing the extremely long-spanning isomeric dipyridylamide ligands 1,6-hexanediaminebis(nicotinamide) (hbn, Scheme 1) or 1,6-hexanediaminebis(isonicotinamide) (hbin, Scheme 1). In this contribution we report the synthesis and single-crystal structures of a series of divalent metal pyromellitate coordination polymers with the hbn or hbin ligands: [Cd(pymH$_2$)(hbn)(H$_2$O)$_2$]$_n$ (**1**), [Co(pymH$_2$)(hbn)(H$_2$O)$_2$]$_n$ (**2**), {[Cu$_2$(pym)(hbn)(H$_2$O)$_2$]·2H$_2$O}$_n$ (**3**), {[Zn$_2$(pym)(hbin)$_2$(H$_2$O)]·H$_2$O}$_n$ (**4**), and {[Ni$_2$(pym)(hbin)(H$_2$O)$_4$]·3H$_2$O}$_n$ (**5**). Thermal properties are also discussed herein, as well as luminescent properties and nitrobenzene detection capability of the d^{10} derivatives.

2. Experimental

2.1. General considerations

Metal nitrates and pyromellitic acid were commercially obtained. Condensation of 1,6-hexanediamine and two molar equivalents of nicotinoyl chloride hydrochloride in dry pyridine resulted in the preparation of the hbn ligand, which was isolated via CH$_2$Cl$_2$ extraction and rotary evaporation [26]. A similar reaction between 1,6-hexanediamine and two molar equivalents of isonicotinoyl chloride hydrochloride in dry pyridine afforded hbin after similar workup. Water was deionized above 3 MΩ–cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT 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 Q-50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

2.2. Preparation of [Cd(pymH2)(hbn)(H2O)2]$_n$ (**1**)

Cd(NO$_3$)$_2$·4H$_2$O (114 mg, 0.37 mmol), pyromellitic acid (94 mg, 0.37 mmol), and hbn (120 mg, 0.37 mmol) were mixed with 10 mL of distilled H$_2$O and 1.5 mL of 1 M NaOH in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 48 h, and then was cooled slowly to 25 °C. Colorless crystals of **1** (114 mg, 42% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C$_{28}$H$_{30}$CdN$_4$O$_{12}$ **1**: C, 46.26%; H, 4.16%; N, 7.71% Found: C, 46.24; H, 3.74; N, 7.36%. IR (cm^{-1}): 3745 (w), 3350 (w), 2020 (w), 1701 (m), 1649 (m), 1574 (m), 1550 (m), 1499 (w), 1407 (w), 1370 (m), 1316 (m), 1223 (m), 1119 (m), 1047 (s), 934 (m), 834 (m), 811 (m), 759 (s), 693 (s), 665 (s).

2.3. Preparation of [Co(pymH2)(hbn)(H2O)2]$_n$ (**2**)

Co(NO$_3$)$_2$·6H$_2$O (108 mg, 0.37 mmol), pyromellitic acid (94 mg, 0.37 mmol), and hbn (120 mg, 0.37 mmol) were mixed with 10 mL of distilled H$_2$O and 1.5 mL of 1 M NaOH in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 48 h, and then was cooled slowly to 25 °C. Orange crystals of **2** (59 mg, 24% yield based on Co) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C$_{28}$H$_{30}$CoN$_4$O$_{12}$ **2**: C, 49.93%; H, 4.49%; N, 8.32% Found: C, 49.81; H, 4.51; N, 8.36%. IR (cm^{-1}): 3355 (w), 2945 (w), 1699 (m), 1650 (m), 1602 (m), 1573 (m), 1552 (s), 1506 (m), 1478 (m), 1413 (m), 1378 (m), 1317 (m), 1231 (m), 1173 (m), 1124 (m), 1034 (w), 938 (w), 895 (m), 831 (m), 812 (m), 764 (m),, 748 (m), 692 (s), 666 (s).

2.4. Preparation of {[Cu$_2$(pym)(hbn)(H$_2$O)$_2$]·2H$_2$O}$_n$ (**3**)

Cu(NO$_3$)$_2$·2.5H$_2$O (86 mg, 0.37 mmol), pyromellitic acid (94 mg, 0.37 mmol), and hbn (120 mg, 0.37 mmol) were mixed with 10 mL of distilled H$_2$O and 1.5 mL of 1 M NaOH in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 24 h, and then was cooled slowly to 25 °C. Blue