Research paper

Cadmium and cobalt oxybis(benzoate) coordination polymers with diverse topologies depending on dipyridylamide ligands including a new self-penetrated network

Torél A. Beard, Julie A. Wilson, Robert L. LaDuca *

Lyman Briggs College and Department of Chemistry, Michigan State University, East Lansing, MI 48825, USA

ABSTRACT

Hydrothermal reaction of cadmium or cobalt nitrate, oxybis(benzoic acid) (obaH$_2$), and a hydrogen-bonding capable dipyridylamide ligand afforded four crystalline coordination polymers whose dimensionality depends critically on the coordination environment or dipyridylamide length. The four new phases were structurally characterized via single-crystal X-ray diffraction. $\{[Cd(obaH)_2(3\text{-pina})_2]\cdot2(3\text{-pina})\cdot2H_2O\}_n$ (**1**, 3-pina = 3-pyridylisonicotinamide) shows 1D chain motifs, while $\{[Co(oba)(3\text{-pina})]\cdot H_2O\}_n$ (**2**) displays closely interdigitated 2D (4,4) grid layer motifs. The longer-spanning dipyridylamide ligand *N,N'*-(hexane-1,6-diyl)diisonicotinamide (hdin) afforded coordination polymers with more interesting self-penetrated or entangled 3D networks. $[Cd(oba)(hdin)]_n$ (**3**) manifests a unique 4,6-connected 3D self-penetrated network with $\{4^26^27^2\}(4^26^87^28^3\}$ topology. $[Co_2(oba)_2(hdin)]_n$ (**4**) exhibits a $\{Co_2(OCO)_4\}$ paddlewheel-dimer based 6-connected 3-fold interpenetrated **jsm** net with $5^{10}6^48$ topology. Luminescent behavior in **1** and **3** is attributed to intra-ligand molecular orbital transitions. The new d^{10} phases were also surveyed for the ability to detect nitrobenzene in ethanol suspension. Thermal decomposition behavior is also discussed herein.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Investigations into the "bottom-up" design of divalent metal coordination polymers have vigorously continued since just before the turn of the century. Coordination polymers have shown great utility as gas storage substrates [1], shape-selective adsorbents [2], molecular containers for active pharmaceuticals [3], industrially relevant heterogeneous catalysis [4], and more recently as potential detectors of nitroaromatics [5]. Many coordination polymers are built from aromatic dicarboxylate ligands in tandem with rigid or flexible dipyridyl-type ligands, thereby imparting a virtually limitless diversity of possible structural topologies during synthesis via self-assembly [6]. A common structural feature of 3D coordination polymers is interpenetration of multiple identical networks through incipient void space in a single network [7]. Less commonly encountered are self-penetrated networks, in which smallest circuits within a single network penetrate through other smallest circuits [8]. While deliberate design of self-penetrated coordination polymer frameworks remains an elusive goal, utilization of "V-shaped" ligands such as 4,4′-dipyridylamine (dpa) or oxy

(bisbenzoate) (oba, Scheme 1) has proven effective given their ability to provide the needed loops in the structure [9–13]. Self-penetrated structures can be relatively simple and elegant, such as that seen in the regular 6^{10} 5-connected topology constructed from connected fourfold interpenetrated diamondoid nets in $\{[Ni(dpa)_2(succinate)_{0.5}]Cl\}_n$ [9]. They can also be incredibly complex, yet still aesthetically remarkable, for instance as seen in the trimer-based 8-connected $4^45^{17}6^7$ topology of $[Co_3(oba)_3(bpmp)]_2$ (bpmp = bis(4-pyridylmethyl)piperazine), built from the interlocking of three distinct helical motifs of increasing girth [10]. Wang and co-workers have reported a self-penetrated 3,5-connected binodal (4.8^2) (4.6^48^410) topology net in $\{[Ni(oba)(4,4′-bipyridine)]\cdot H_2O\}_n$ [11]. $\{[Co_2(oba)_2(tpom)(H_2O)_2]\cdot8H_2O\}_n$ (tpom = tetrakis(4-pyridyloxymethylene)methane) has a unique 4,4,4-connected trinodal network with a 3D self-penetrated $(4^26^27^58)(4^26^37)(4^26^47^38)$ topology built from connected 1D looped motifs [12]. A cobalt coordination polymer with both oba and dpa ligands, $\{[Co(oba)(dpa)]\cdot H_2O\}_n$, is one of the very few examples of a self-penetrated 2D layer topology [13]. The kinked dipyridylamide ligand 3-pyridylisonicotinamide (3-pina, Scheme 1) has also been successfully employed in the synthesis of a self-penetrated copper-containing coordination polymer. $\{[Cu_2(t\text{-}14cdc)_2(3\text{-pina})_2(H_2O)]\cdot 5H_2O\}_n$ (t-14cdc = $trans$-1,4-cyclohexanedicarboxylate) shows two
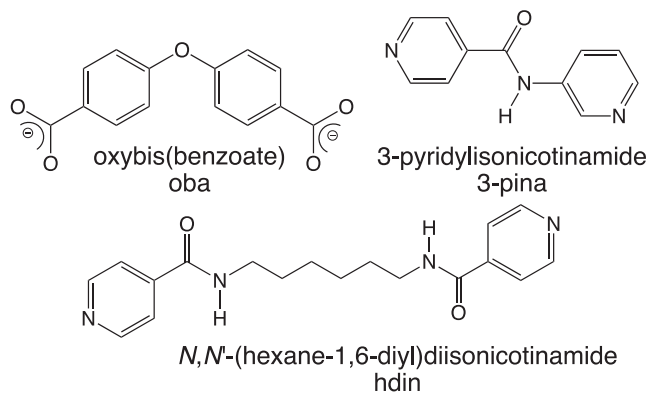
Scheme 1. Ligands used in this study.

different copper-dicarboxylate chain motifs, one with isolated copper ions and the other within embedded $\{Cu_2O_2\}$ dimeric units. The disparate chain motifs are linked together by 3-pina tethers to generate a self-penetrated 4,6-connected net with $(4.6^4.8)_2(4^26^{12}8)$ topology [14]. The more flexible dipyridylamide ligand N,N'-(hexane-1,6-diyl)diisonicotinamide (hdin) has not yet been employed in coordination polymer chemistry, as of a search of the CCDC database as of this writing [15]. We therefore endeavored to explore the structural chemistry of divalent metal oxy(bisbenzoate) and either 3-pina or hdin ligands in the hopes of uncovering additional novel self-penetrated topologies. In the course of our exploratory synthetic efforts we prepared and structurally characterized four new oba-containing coordination polymers: $\{[Cd(obaH)_2(3\text{-pina})_2]\cdot 2(3\text{-pina})\cdot 2H_2O\}_n$ (**1**), $\{[Co(oba)(3\text{-pina})]\cdot H_2O\}_n$ (**2**), $[Cd(oba)(hdin)]_n$ (**3**), $[Co_2(oba)_2(hdin)]_n$ (**4**). Thermal properties are also described herein, along with luminescence studies on the d^{10} configuration cadmium derivatives.

2. Experimental section

2.1. General considerations

Metal nitrates and oxybis(benzoic) acid were commercially obtained. Condensation of 3-pyridylamine and one molar equivalent of isonicotinoyl chloride hydrochloride in dry pyridine was used to prepare 3-pyridylisonicotinamide (3-pina), which was isolated via CH_2Cl_2 extraction and rotary evaporation [16]. A similar reaction between 1,6-hexanediamine and two molar equivalents of isonicotinoyl chloride hydrochloride in dry pyridine afforded N,N'-(hexane-1,6-diyl)diisonicotinamide (hdin) 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 $\{[Cd(obaH)_2(3\text{-pina})_2]\cdot 2(3\text{-pina})\cdot 2H_2O\}_n$ (**1**)

$Cd(NO_3)_2\cdot 4H_2O$ (86 mg, 0.28 mmol), 3-pina (116 mg, 0.56 mmol), and oxybis(benzoic) acid (72 mg, 0.28 mmol) were mixed with 10 mL of distilled H_2O and 0.5 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** (112 mg, 55% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{72}H_{56}CdN_{12}O_{16}$ **1**: C, 59.32; H, 3.87; N, 11.53% Found: C, 59.11; H, 3.71; N, 11.37%. IR (cm^{-1}): 3295 (w), 1655 (m), 1595 (m), 1525 (m), 1485 (m), 1397 (s), 1300 (m), 1229 (m), 1159 (m), 880 (m), 849 (m), 804 (w), 780 (s), 687 (s), 663 (s).

2.3. Preparation of $\{[Co(oba)(3\text{-pina})]\cdot H_2O\}_n$ (**2**)

$Co(NO_3)_2\cdot 6H_2O$ (81 mg, 0.28 mmol), 3-pina (53 mg, 0.28 mmol), and oxybis(benzoic) acid (72 mg, 0.28 mmol) were mixed with 10 mL of distilled H_2O and 0.5 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. Magenta crystals of **2** (50 mg, 34% yield based on Co) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{25}H_{19}CoN_3O_7$ **2**: C, 56.40; H, 3.60; N, 7.89% Found: C, 56.10; H, 3.45; N, 7.64%. IR (cm^{-1}): 1680 (m), 1586 (m), 1556 (m), 1424 (s), 1333 (m), 1292 (m), 1233 (s), 1161 (m), 876 (s), 814 (m), 785 (s), 756 (m), 690 (s), 659 (s).

2.4. Preparation of $[Cd(oba)(hdin)]_n$ (**3**)

$Cd(NO_3)_2\cdot 4H_2O$ (114 mg, 0.37 mmol), hdin (120 mg, 0.37 mmol), and oxybis(benzoic) acid (96 mg, 0.37 mmol) were mixed with 10 mL of distilled H_2O and 0.75 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 72 h, and then was cooled slowly to 25 °C. Colorless crystals of **3** (115 mg, 45% yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{32}H_{28}CdN_4O_7$ **3**: C, 55.46; H, 4.07; N, 8.08% Found: C, 55.32; H, 4.00; N, 7.97%. IR (cm^{-1}): 3277 (m), 1640 (m), 1597 (m), 1543 (s), 1496 (m), 1381 (s), 1319 (m), 1229 (s), 1157 (m), 1014 (m), 869 (m), 847 (m), 782 (m), 763 (m), 692 (s).

2.5. Preparation of $[Co_2(oba)_2(hdin)]_n$ (**4**)

$Co(NO_3)_2\cdot 6H_2O$ (108 mg, 0.37 mmol), hdin (120 mg, 0.37 mmol), and oxybis(benzoic) acid (96 mg, 0.37 mmol) were mixed with 10 mL of distilled H_2O and 0.75 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 72 h, and then was cooled slowly to 25 °C. Magenta crystals of **4** (95 mg, 54% yield based on Co) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{46}H_{38}Co_2N_4O_{12}$ **4**: C, 57.75; H, 4.00; N, 5.86% Found: C, 57.51; H, 4.01; N, 5.56%. IR (cm^{-1}): 3305 (w), 2366 (w), 2023 (w), 1705 (w), 1640 (m), 1596 (m), 1540 (m), 1391 (m), 1284 (m), 1246 (s), 1160 (s), 1063 (w), 1010 (m), 881 (m), 850 (m), 776 (m), 682 (m), 660 (m).

3. X-ray crystallography

Diffraction data for **1–4** were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173 K. The data were processed via SAINT [17], and subjected for Lorentz and polarization effect and absorption corrections using SADABS [18]. The structures were solved using direct methods with SHELXTL [19] within the OLEX2 crystallographic software suite [20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. The crystal structure of **3** was best refined as an inversion twin in space group *Ccc*2. The amide carbonyl oxygen atoms in **3** were disordered in a