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Chain, ladder and self-penetrated cobalt and nickel coordination polymers containing sterically bulky isophthalate and long-spanning dipyridylamide ligands

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Hydrothermal reaction of cobalt or nickel nitrate with 5-*tert*-butylisophthalic acid (H_2tbip) and bis(4-pyridylformyl)piperazine (bpfp) under varying synthetic conditions afforded four coordination polymers that were subsequently structurally characterized via single-crystal X-ray diffraction. $\{[Co(Htbip)_2(H_2O)_2(bpfp)]\cdot H_2O\}_n$ (**1**), prepared with a lower concentration of added base, exhibits a 1D sawtooth chain structure. $\{[Co_2(tbip)_2(H_2O)_4(bpfp)]\cdot 2H_2O\}_n$ (**2**), prepared under higher base conditions, and its analog $\{[Ni_2(tbip)_2(H_2O)_4(bpfp)]\cdot 2H_2O\}_n$ (**3**), show isostructural 1D ladder topologies. $\{[Ni(tbip)(H_2O)_2(bpfp)]\cdot 2.25H_2O\}_n$ (**4**), prepared using a higher concentration of reactants than for **3**, manifests an extremely rare 6^58 4T10 4-connected self-penetrated topology and represents the first metal dicarboxylate coordination polymer to possess this network. Thermal decomposition behavior of these materials is also discussed.

1. Introduction

The development of new coordination polymers, involving exploratory synthesis, structural determination, and physical properties measurements, has remained a key focus of inorganic chemistry basic research over the past two decades. Their growing utility as gas storage substrates [1], molecular absorbents [2], optical materials [3], heterogeneous catalysts [4], and explosives residue sensors [5] all provide critical impetus for continued study. Additionally, the molecular frameworks of these materials provide a striking aesthetic appeal and spur efforts to carefully enumerate and catalog their underlying topologies [6]. The most common anionic ligand choices for the construction of multi-functional divalent metal coordination polymers are the aromatic dicarboxylates such as phthalate [7], terephthalate [8], or isophthalate [9], as they provide both a rigid scaffolding and necessary charge balance. The incorporation of dipyridyl-type neutral ligands, such as 4,4-bipyridine (bpy) [10], 1,2-di(4-pyridyl)ethane (dpe) [11], and 1,3-di(4-pyridyl)propane (dpp) [12], can permit extension of coordination polymer structures into higher dimensionality and more complicated topologies.

A useful strategy employed to enhance the topological scope of isophthalate-containing coordination polymer solids has been the inclusion of substituents at the 5-position of the aromatic ring [13–17]. Several dual-ligand coordination polymers containing 5-substituted isophthalates and a dipyridyl derivative display intriguing entangled structures. *Batten* has recently reported the synthesis and structure of $[Co_2(mip)_2(dpp)_2(H_2O)]_n$ (mip = 5-methylisophthalate), which displayed a unique *pseudo*-rotaxane $(4.6^4.8)_2(4^2.6^4)$ layered net [13]. The steric bulk at the isophthalate 5-position can be further increased by utilizing the *tert*-butyl substituent in 5-*tert*-butylisophthalate (tbip, Scheme 1). This large group can certainly alter the supramolecular environment during self-assembly of coordination polymers, resulting in substantially different topologies when compared with less sterically hindered congeners. For example, careful adjustment of synthetic conditions resulted in a series of polymorphous cobalt tbip coordination polymers containing either bpy [14] or dpp [15] coligands. $\{[Co(tbip)(bpy)(H_2O)_3]\cdot 0.5(bpy)\cdot H_2O\}_n$ showed a simple bpy-bridged 1D zig-zag chain structure, with pendant tbip ligands. Synthetic conditions using a higher pH than for the previous compound afforded $[Co(tbip)(bipy)]_n$, which adopted a dimer-based decorated (4,4) grid 2D topology [14]. In the dpp system, no less than four different tbip-containing 1D, 2D, or 3D polymorphs could be obtained through judicious variance of synthetic method [15].

We therefore aimed to expand the scope of cobalt 5-*tert*-butylisophthalate coordination polymers by incorporating the

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long-spanning and hydrogen bonding capable bis(4-pyridylformyl)piperazine ligand (bpfp, Scheme 1). Conformational flexibility of bpfp can afford either syn, anti, or intermediate skewed conformations, as determined by four-atom O···N···N···O torsion angles (defined as Ψ) within the central piperazinyldiamide moiety. Previous results from our group showed the efficacy of bpfp as a linker for the generation of divalent metal dicarboxylate coordination polymers with unique entangled or self-penetrated topologies [18–21]. For instance, $[Zn_2Cl_2(terephthalate)(bpfp)_2]_n$ represented the first example of a 1D + 1D → 1D polyrotaxane coordination polymer, while $\{[Cd_4(terephthalate)_4(bpfp)_3(H_2O)_2]\cdot 8H_2O\}_n$ exhibited a complicated and unique 3,4,8-connected trinodal self-penetrated network [18].

Herein we describe the hydrothermal synthesis, structural characterization, and thermal properties of two new cobalt tbip coordination polymers, $\{[Co(Htbip)_2(H_2O)_2(bpfp)]\cdot H_2O\}_n$ (**1**) and $\{[Co_2(tbip)_2(H_2O)_4(bpfp)]\cdot 2H_2O\}_n$ (**2**), with different 1D topologies that could be accessed by variance in synthetic method. We were also able to extend this chemistry to a related divalent nickel coordination polymer system. As is the case for the cobalt derivatives **1** and **2**, adjustment of synthetic conditions resulted in discrimination between the two nickel phases $\{[Ni_2(tbip)_2(H_2O)_4(bpfp)]\cdot 2H_2O\}_n$ (**3**) and $\{[Ni(tbip)(H_2O)_2(bpfp)]\cdot 2.25H_2O\}_n$ (**4**). While **3** is isostructural with its cobalt analog **2**, compound **4** manifests an exceptionally rare self-penetrated 3D topology.

2. Experimental

2.1. General considerations

Metal nitrates, 5-*tert*-butylisophthalic acid, and organic precursors were commercially obtained. The dipyridylamide ligand bis(4-pyridylformyl)piperazine was prepared by a literature procedure [22]. Water was deionized above 3 MΩ-cm in-house. Elemental analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One instrument. Thermogravimetric analysis was performed under flowing N_2 on a TA Instruments Q50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C.

2.2. Preparation of $\{[Co(Htbip)_2(H_2O)_2(bpfp)]\cdot H_2O\}_n$ (**1**)

$Co(NO_3)_2\cdot 6H_2O$ (109 mg, 0.37 mmol), bpfp (111 mg, 0.37 mmol), and 5-*tert*-butylisophthalic acid (83 mg, 0.37 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. Orange–pink blocks of **1** (48 mg, 30% yield based on tbip) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{40}H_{48}CoN_4O_{13}$: C, 56.40; H, 5.68; N, 6.58. Found: C, 56.05; H, 5.38; N, 6.11%. **IR** ($\tilde{\nu}$) = 3450 (w, br), 2959 (w), 1730 (s), 1709 (w), 1644 (w), 1592 (s), 1546 (m) 1457 (s), 1433 (w), 1403 (w), 1368 (w), 1328 (w), 1278 (s), 1262 (w), 1219 (w), 1155 (w), 1128 (w), 1104 (w), 1069 (w), 1048 (w), 1009 (s), 987 (w), 971 (w), 924 (w), 900 (w), 893 (w), 842 (s), 790 (w), 761 (w), 729 (s), 695 (s), 685 (w), 673 (w), 666 (w), 657 (w) cm^{-1}.

2.3. Preparation of $\{[Co_2(tbip)_2(H_2O)_4(bpfp)]\cdot 2H_2O\}_n$ (**2**)

$Co(NO_3)_2\cdot 6H_2O$ (81 mg, 0.28 mmol), 4-bpfp (83 mg, 0.28 mmol), and 5-*tert*-butylisophthalic acid (62 mg, 0.28 mmol) were mixed with 10 mL of distilled H_2O and 1.0 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. Dark magenta blocks of **2** (66 mg, 50% yield based on Co) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{40}H_{52}Co_2N_4O_{16}$: C, 49.90; H, 5.44; N, 5.82. Found: C, 50.00; H, 5.48; N, 5.78%. **IR** ($\tilde{\nu}$) = 3300 (w, br), 2948 (w), 1700 (w), 1680 (w), 1641 (s), 1612 (w), 1579 (w), 1554 (w), 1524 (m), 1503 (w), 1456 (m), 1433 (m), 1368 (s), 1348 (w), 1311 (w), 1284 (m), 1262 (w), 1227 (w), 1179 (w), 1167 (w), 1149 (w), 1135 (w), 1115 (w), 1067 (w), 1047 (w), 1025 (w), 1000 (s), 924 (w), 834 (s), 824 (w), 776 (s), 755 (w), 730 (m), 699 (w), 671 (w), 660 (w) cm^{-1}.

2.4. Preparation of $\{[Ni_2(tbip)_2(H_2O)_4(bpfp)]\cdot 2.25H_2O\}_n$ (**3**)

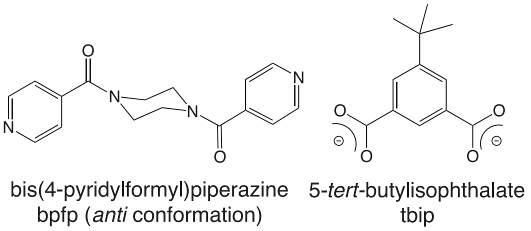
$Ni(NO_3)_2\cdot 6H_2O$ (81 mg, 0.28 mmol), 4-bpfp (83 mg, 0.28 mmol), and 5-*tert*-butylisophthalic acid (62 mg, 0.28 mmol) were mixed with 10 mL of distilled H_2O and 1.0 mL of 1 M NaOH in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 48 h, and then was cooled slowly to 25 °C. Green blocks of **3** (85 mg, 63% yield based on Ni) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{40}H_{52}N_4Ni_2O_{16}$: C, 49.92; H, 5.45; N, 5.82. Found: C, 50.19; H, 5.12; N, 5.86%. **IR** ($\tilde{\nu}$) = 3299 (w, br), 2945 (w), 1643 (s), 1617 (w), 1583 (w), 1522 (m), 1456 (m), 1431 (s), 1368 (s), 1351 (m), 1311 (w), 1285 (m), 1259 (w), 1148 (w), 1069 (w), 999 (s), 923 (w), 836 (s), 827 (w), 776 (s), 757 (w), 729 (s), 699 (w), 660 (w) cm^{-1}.

2.5. Preparation of $\{[Ni(tbip)(H_2O)_2(bpfp)]\cdot 2.25H_2O\}_n$ (**4**)

$Ni(NO_3)_2\cdot 6H_2O$ (108 mg, 0.37 mmol), bpfp (111 mg, 0.37 mmol), and 5-*tert*-butylisophthalic acid (83 mg, 0.37 mmol) were mixed with 10 mL of distilled H_2O and 1.0 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. Blue–green blocks of **4** (108 mg, 45% yield based on Ni) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{28}H_{36.50}N_4NiO_{10.25}$: C, 51.32; H, 5.54; N, 8.55. Found: C, 51.78; H, 5.21; N, 8.28%. **IR** ($\tilde{\nu}$) = 3525 (w, br), 2960 (w), 1732 (s), 1710 (m), 1647 (s), 1593 (s), 1547 (m), 1458 (w), 1433 (s), 1406 (m), 1370 (w), 1279 (s), 1263 (w), 1222 (s), 1155 (m), 1104 (w), 1069 (w), 1011 (s), 926 (w), 901 (w), 844 (s), 782 (m), 770 (m), 764 (w), 735 (s), 695 (m), 675 (w), 666 (w) cm^{-1}.

3. X-ray crystallography

Diffraction data for single crystals of **1**–**4** was collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. The data were processed via SAINT [23], and subjected to Lorentz and polarization effect and absorption corrections using SADABS [24] or TWINABS [25]. The structures were solved using direct methods with SHELXTL [26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon were placed in calculated



Scheme 1. Ligands used in this study.