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Cobalt 5-bromoisophthalate coordination polymers containing bis(pyridyl)piperazine-type long spanning ligands and water molecule aggregations

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HIGHLIGHTS

- ▶ Cobalt coordination polymers with bis(pyridyl)piperazines and 5-bromoisophthalate (Brip).
- ▶ 1-D and 2-D inclined interpenetrated topologies.
- ▶ Different intriguing water molecule aggregations including novel water tapes or clusters.

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ABSTRACT

Divalent cobalt coordination polymers containing long-spanning bis(pyridyl)piperazine and 5-bromoisophthalate (Brip) ligands have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. $\{[Co(H_2O)_2(4\text{-bpmp})_2](HBrip)_2{\cdot}14H_2O\}_n$ (**1**, 4-bpmp = bis(4-pyridylmethyl)piperazine), and $\{[Co(Brip)(H_2O)_3(4\text{-bpfp})]{\cdot}6.5H_2O\}_n$ (**2**, 4-bpfp = bis(4-pyridylformyl)piperazine) both show 1-D coordination polymer connectivity, but with different intriguing water molecule aggregations. An unprecedented T4(4)6(6)6(6)10(8) classification water tape is seen in **1**, while a discrete 11-molecule water cluster is observed in **2**. $\{[Co_2(Brip)_2(H_2O)_4(3\text{-bpmp})]{\cdot}4H_2O\}_n$ (**3**, 3-bpmp = bis(3-pyridylmethyl)piperazine) manifests a 2D + 2D → 3D mutually inclined interpenetrated system of parallel sets of (4,4) rhomboid grids, with isolated water molecule pairs.

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1. Introduction

Because they manifest industrially important applications in gas storage [1], molecular separation [2], ion exchange [3], catalysis [4], luminescence [5], and non-linear optics [6], the crystal engineering and structural characterization of divalent metal coordination polymers remain under intensive investigation. Especially efficacious choices for charge balancing anionic ligands are the aromatic dicarboxylates terephthalate [7] or isophthalate [8]. These can instill the necessary structural scaffolding for the formation of a stable neutral crystalline framework. The geometric requirements of the specific metal environment, the carboxylate geometric disposition, the ability of the carboxylate ligands to adopt different binding and bridging modes, and the inclusion of any neutral coligands, synergistically promote extremely wide structural diversity [9]. Additionally, the supramolecular interactions provided by carboxylate group hydrogen bonding acceptors can promote unique container environments for trapping diverse water molecule clusters [10] and tapes [11] with a coordination polymer matrix.

A tested method of enhancing the structural scope of metal isophthalate (ip) coordination polymers is the inclusion of *meta*-disposed 5-position substituents. Recently, some intriguing new coordination polymer topologies have been uncovered through this approach [12]. For example, Batten et al. prepared $[Co_2(mip)_2(bpp)_2(H_2O)]_n$ (mip = 5-methylisophthalate, bpp = 1,3-bis(4-pyridyl)propane), which exhibits a rare pseudo-rotaxane 2-D 4-connected binodal $(4{\cdot}6^4{\cdot}8)_2(4^2{\cdot}6^4)$ topology [12a]. Yang et al. have structurally characterized a series of coordination polymers with different 5-position substituents, namely $[Zn_4(H_2O)(ip)_4(py)_6]_n$ (py = pyridine), $\{[Zn_2(OHip)_2(py)_4]_2(py)\}_n$ (OHip = 5-hydroxyisophthalate), and $[Zn(tBuip)(py)_2]_n$ (tBuip = 5-tert-butylisophthalate). Increasing the steric bulk of the substituent provoked a decrease in coordination polymer dimensionality, from a 2-D grid-like layer to 1-D single- and double-stranded chains [12e].

A few years ago our group prepared a series of divalent metal isophthalate coordination polymers containing the long-spanning

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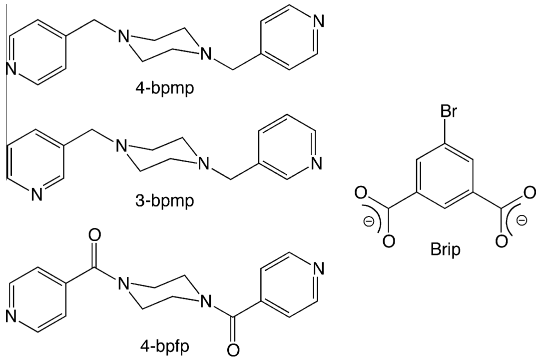

Scheme 1. Ligands used in this study.

and hydrogen-bonding capable, protonatable tethering bis(4-pyridylmethyl)piperazine (4-bpmp) ligand. Among the metal-dependent diverse 2-D and 3-D topologies, the cobalt derivative $\{[Co(ip)(4\text{-}bpmp)]\cdot H_2O\}_n$ manifests an uncommon (3,6) triangular grid network based on antiferromagnetically coupled *syn–syn* bridged $Co_2(OCO)_2$ dinuclear kernels [13]. Inclusion of a tert-butyl substituent afforded $\{[Co_3(tBuip)_2(HtBuip)_2(4\text{-}bpmp)]\cdot 4\text{-}bpmp\}_n$, which shows a (4,4) grid topology with embedded ferromagnetically coupled $\{Co_3(\mu\text{-}O)_4(\mu\text{-}OCO)_2\}$ trimeric units [14]. In order to further probe substituent effects in this genre of materials, we have investigated the preparation of cobalt 5-bromoisophthalate (Brip) coordination polymers with 4-bpmp, its isomeric analog 3-bpmp (bis(3-pyridylmethyl)piperazine, and its formyl analog 4-bpfp (bis(4-pyridylformyl)piperazine) (Scheme 1). Through the use of 3-bpmp and 4-bpmp we can explore the topological and structural effect of pyridyl nitrogen donor disposition, while 4-bpfp provides an additional hydrogen-bonding point of contact and the possibility for formyl oxygen ligation. Our efforts have resulted in the synthesis of $\{[Co(H_2O)_2(H4\text{-}bpmp)_2](HBrip)_2\cdot 14H_2O\}_n$ (**1**), $\{[Co(Brip)(H_2O)_3(4\text{-}bpfp)]\cdot 6.5H_2O\}_n$ (**2**), and$\{[Co_2(Brip)_2(H_2O)_4(3\text{-}bpmp)]\cdot 4H_2O\}_n$ (**3**). Herein we discuss the preparation, single crystal structures, and water molecule aggregations for these three new coordination polymer solids.

2. Experimental section

2.1. General considerations

Metal salts and 5-bromoisophthalic acid were commercially obtained. The pyridyl ligands 4-bpmp [15], 3-bpmp [15,16], and 4-bpfp [17] were prepared using 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.

2.2. Preparation of $\{[Co(H_2O)_2(H4\text{-}bpmp)_2](HBrip)_2\cdot 14H_2O\}_n$ (*1*)

$Co(NO_3)_2\cdot 6H_2O$ (51 mg, 0.18 mmol), 4-bpmp (148 mg, 0.55 mmol) and 5-bromoisophthalic acid (134 mg, 0.55 mmol) were placed into 10 mL distilled H_2O in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 24 h, whereupon it was cooled slowly to 25 °C. Pink blocks of **1** (68 mg, 28% yield based on Co) were isolated after washing with distilled water and acetone, and drying in air. Crystals of **1** soon effloresced in the absence of the mother liquor. Anal. Calc. for $C_{48}H_{80}Br_2CoN_8O_{24}$ **1**: C, 42.02; H, 5.88; N, 8.17% Found: C, 44.24; H, 5.72; N, 8.91% (consistent with ejection of four molar equivalents of water). IR (cm^{-1}): 3230 (w, br), 3073 (w), 1702 (w), 1602 (m), 1548 (m), 1505 (w), 1429 (m), 1371 (s), 1290 (w), 1257 (m), 1226 (m), 1158 (w), 1097 (w), 1060 (w), 1019 (w), 1003 (m), 969 (w), 893 (w), 840 (m), 802 (m), 770 (s), 706 (s), 662 (s).

2.3. Preparation of $\{[Co(Brip)(H_2O)_3(4\text{-}bpfp)]\cdot 6.5H_2O\}_n$ (*2*)

$Co(NO_3)_2\cdot 6H_2O$ (81 mg, 0.28 mmol), 4-bpfp (65 mg, 0.22 mmol) and 5-bromoisophthalic acid (68 mg, 0.28 mmol) were placed into 10 mL distilled H_2O in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 48 h, whereupon it was cooled slowly to 25 °C. Pink blocks of **2** (65 mg, 38% yield based on 4-bpfp) were isolated after washing with distilled water and acetone, and drying in air. Crystals of **2** soon effloresced in the absence of the mother liquor. Anal. Calc. for $C_{24}H_{38}BrCoN_4O_{15.5}$ **2**: C, 37.47; H, 4.98; N, 7.28% Found: C, 40.44; H, 4.12; N, 7.99% (consistent with ejection of 3.5 molar equivalents of water). IR (cm^{-1}): 3230 (w, br), 2597 (w), 1736 (m), 1706 (m), 1661 (m), 1631 (m), 1600 (s), 1553 (m), 1504 (m), 1467 (m), 1437 (m), 1409 (m), 1378 (m), 1291 (m), 1257 (s), 1223 (s), 1158 (s), 1097 (w), 1060 (w), 1044 (w), 1004 (s), 895 (m), 840 (s), 797 (m), 761 (s), 739 (s), 724 (s), 681 (s), 665 (s).

2.4. Preparation of $\{[Co_2(Brip)_2(H_2O)_4(3\text{-}bpmp)]\cdot 4H_2O\}_n$ (*3*)

$Co(NO_3)_2\cdot 6H_2O$ (50 mg, 0.17 mmol), 3-bpmp (73 mg, 0.27 mmol) and 5-bromoisophthalic acid (68 mg, 0.28 mmol) were placed into 10 mL distilled H_2O in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 24 h, whereupon it was cooled slowly to 25 °C. Pink blocks of **3** (76 mg, 84% yield based on Co) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for $C_{32}H_{42}Br_2Co_2N_4O_{16}$ **3**: C, 37.82; H, 4.17; N, 5.51% Found: C, 38.19; H, 4.00; N, 5.96%. IR (cm^{-1}): 3392 (w, br), 3068 (w), 1593 (m), 1536 (s), 1484 (w), 1459 (w), 1426 (m), 1363 (s), 1292 (w), 1254 (w), 1191 (w), 1103 (w), 1057 (w), 1039 (w), 989 (w), 946 (w), 926 (w), 840 (w), 799 (w), 779 (s), 710 (s), 675 (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 ($\lambda = 0.71073$ Å). The crystal for **3** was nonmerohedrally twinned. The twin law was ascertained using CELLNOW [18]; only the data from the major twin component was used for the structure solution and refinement. The data were processed via SAINT [19], and corrected for Lorentz and polarization effects and absorption corrections using SADABS [20] (for **1**–**2**) or TWINABS (for **3**) [21]. The structures were solved using direct methods with SHELXTL [22]. 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 were found where possible by Fourier difference map and then restrained. The carbon atoms within the piperazinyl rings in **2** are disordered equally over two sets of positions and were modeled successfully as such. 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 cobalt salts and 5-bromoisophthalic acid with the requisite dipyridine. Their infrared spectra were consistent with structural components determined by single-crystal X-ray diffraction. Intense, slightly broadened asymmetric and symmetric C—O

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