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Interleaved and entangled divalent metal thiophenedicarboxylate coordination polymers with an extremely long-spanning and flexible dipyridylamide ligand

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ABSTRACT

Hydrothermal reaction of metal nitrates, 2,5-thiophenedicarboxylic acid (H_2tdc) and the conformationally flexible and very long spanning dipyridylamide ligand propane-1,3-diylbis(piperidine-4,1-diyl)bis(pyridin-4-ylmethanone) (4-ppbp) produced three new coordination polymers which were structurally characterized by single-crystal X-ray diffraction. $[Cu(tdc)(4\text{-ppbp})(H_2O)]\cdot 2H_2O\}_n$ (**1**) manifests a slab topology with pairs of interleaved (4,4) layer motifs. $[Co(tdc)(4\text{-ppbp})(H_2O)]_n$ (**2**) shows a 2,4-connected 1-D tubular structure that engages in very rare 1D + 1D → 2D parallel polycatenation. $[Ni(tdc)(4\text{-ppbp})_2(H_2O)]_n$ (**3**) possesses a unique system of 2D + 2D → 2D interpenetrated 2,6-connected layers, derived from the edge-crossed SP 2-periodic (4,4)IIb net, when O–H···N hydrogen bonding patterns are taken into account. The conformational flexibility of the 4-ppbp ligand affords the requisite loops for the unique polycatenation patterns in **2** and **3**. Thermal decomposition properties of these three new materials are discussed.

1. Introduction

Basic research efforts towards the synthesis and structural characterization of crystalline coordination polymers have continued unabated over the past decade. These materials can possess diverse applications in hydrogen storage [1], selective separations [2], ion exchange [3], heterogeneous catalysis [4], non-linear optics [5], and explosives residue detection [6]. The near limitless combination of divalent metal ions, anionic dicarboxylate ligands, and ancillary neutral dipyridyl ligands continues to spur exploratory synthetic investigations, not only due to their efficacious properties but also because of their often striking structural aesthetics. Interpenetrated networks are quite common in coordination polymer structures [7], but self-penetrated networks, in which the smallest circuits in the net penetrate through other smallest circuits in the same net, are much rarer [8–13]. In many cases, these intriguing networks are built from V-shaped or looped ligands. $\{[Ni(dpa)_2(succinate)_{0.5}]Cl\}_n$ (dpa = 4,4′-dipyridylamine) is the unique example to date of a regular 5-connected 6^{10} **rld-z** self-penetrated topology, built from the simple pillaring of four interpenetrated 6^6 diamondoid nets [10]. One of the most complicated uninodal self-penetrated topologies is observed in $[Co_3(oba)_3(bpmp)_2]$ (oba = oxy(bisbenzoate), bpmp = bis(4-pyridylmethyl)piperazine), which possesses a multiple helix-based 8-connected net with a $4^4 5^{17} 6^7$ topology [11]. Most self-penetrated networks have coordination bonds arrayed in three-dimensional networks, although a few self-penetrated layered motifs have been reported [12–14]. $\{[Co(oba)(dpa)]\cdot H_2O\}_n$ and its nickel congener both contain 2D 4-connected self-penetrated layers with 6^6 topology [12]. Cationic layers with 4-connected 6^6 self-penetrated topologies are seen in $\{[Ag(sebn)]SbF_6\}_n$ (sebn = sebaconitrile), but in this case these layer motifs engage in 2D + 2D → 3D parallel polycatenation, one of the vanishingly rare examples of co-existing self-penetration and polycatenation [13].

Recently we reported some copper aromatic dicarboxylate coordination polymers containing the very long and conformationally flexible dipyridylamide ligand propane-1,3-diylbis(piperidine-4,1-diyl))bis(pyridin-4-ylmethanone) (4-ppbp, Scheme 1) [15]. $\{[Cu(tere)(4\text{-ppbp})(H_2O)]\cdot 1.5H_2O\}_n$ (tere = terephthalate) and $\{[Cu(iph)(4\text{-ppbp})(H_2O)]\cdot 2H_2O\}_n$ (iph = isophthalate) manifested interdigitated, but not interpenetrated simple (4,4) grid layers. However the longer-arm congener $\{[Cu_2(phda)(phdaH)_2(4\text{-ppbp})_2]\cdot 6H_2O\}_n$ (phda = 1,4-phenylenediacetate) displayed a 4-connected $6^5 8$ **cds** topology. $\{[Cu_2(phtH)_2(4\text{-ppbp})_2(H_2O)_4](NO_3)_2\cdot H_2O\}_n$ (pht = phthalate) formed ring-like dinuclear coordination complex cations with anionic phtH ligands threading into supramolecular

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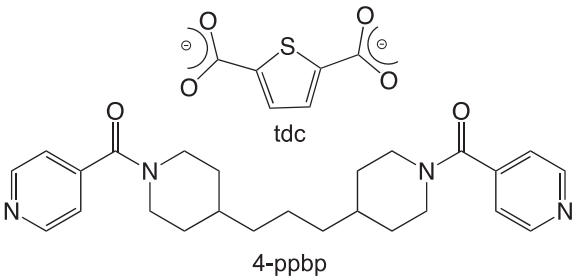

Scheme 1. Ligands used in this study.

loops. This proof of concept result indicated that 4-ppbp has an ability to adopt "*S*", "*L*", or "*U*" conformations depending on the specific N···N···N···N dihedral angle (defined as **Ψ**) locked into the solid-state structure in response to metal geometric requirements and dicarboxylate binding mode. A **Ψ** dihedral angle of 0° would instill an idealized looped *U*-conformation, and a **Ψ** dihedral angle of 180° would portend an *S*-conformation. The twisted *L*-conformation is generated from intermediate **Ψ** angles. We therefore aimed to produce divalent metal coordination polymers with self-penetrated or polycatenated features predicated on the locking of 4-ppbp in a looped *L*- or *U*-conformation, with the rigid dicarboxylate ligand 2,5-thiophenedicarboxylate (tdc, Scheme 1) serving as a potential threading component [16–18]. In this contribution we report the synthesis, single crystal structures, topological features, and thermal properties of the three new coordination polymer solids $[Cu(tdc)(4\text{-ppbp})(H_2O)]\cdot 2H_2O\}_n$ (**1**), $[Co(tdc)(4\text{-ppbp})(H_2O)]_n$ (**2**), and $[Ni(tdc)(4\text{-ppbp})_2(H_2O)]_n$ (**3**).

2. Experimental

2.1. General considerations

Metal nitrates and 2,5-thiophenedicarboxylic acid were purchased commercially. The 4-ppbp ligand was prepared via condensation of two molar equivalents of isonicotinoyl chloride hydrochloride and one molar equivalent of trimethylenepiperidine in dry pyridine solvent, in a manner similar to that used for the preparation of 4-pyridylisonicotinamide (Scheme S1) [15]. Water was deionized above 3 MΩ-cm in-house. 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 TGA Q50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Network topologies were calculated using TOPOS software [19]. Incipient solvent-accessible void volumes were calculated using PLATON [20].

2.2. Preparation of $[Cu(tdc)(4\text{-ppbp})(H_2O)]\cdot 2H_2O\}_n$ (*1*)

$Cu(NO_3)_2\cdot 2.5H_2O$ (86 mg, 0.47 mmol), 2,5-thiophenedicarboxylic acid (64 mg, 0.37 mmol) and 4-ppbp (156 mg, 0.37 mmol) and 0.5 mL of a 1.0 M NaOH solution were placed into 10 mL distilled H_2O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2d, and then cooled slowly to 25 °C. Blue crystals of **1** (165 mg, 50% yield based on Cu) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{31}H_{36}CuN_4O_9S$ **1**: C, 52.87; H, 5.15; N, 7.96. Found: C, 53.67; H, 6.07; N, 8.05%. IR (cm^{-1}): 2927 (w), 2850(w), 1663(m), 1631(m), 1565(w), 1527(w), 1475(w), 1415(w), 1379(w), 1349(w), 1264(m), 1230(w), 1114(w), 1097 (w), 1067(w), 1038(w), 1018(w), 925(w), 853(w), 810(w), 754(s), 707(w), 696(w).

2.3. Preparation of $[Co(tdc)(4\text{-ppbp})(H_2O)]_n$ (*2*)

$Co(NO_3)_2\cdot 6H_2O$ (108 mg, 0.37 mmol), 2,5-thiophenedicarboxylic acid (64 mg, 0.37 mmol) and 4-ppbp (156 mg, 0.37 mmol) and 1.5 mL of a 1.0 M NaOH solution were placed into 10 mL distilled H_2O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2d, and then cooled slowly to 25 °C. Purple crystals of **2** (50 mg, 20% yield based on Co) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{62}H_{70}Co_2N_8O_{14}S_2$ **2**: C, 55.85; H, 5.29; N, 8.40. Found: C, 57.19; H, 6.21; N, 8.51%. IR (cm^{-1}): 3383 (w), 3001(w), 2918(w), 2857(w), 1698(w), 1626(s), 1613(s), 1602 (m), 1551(w), 1527(m), 1499(w), 1462(w), 1439(m), 1413(m), 1403(m), 1354(s), 1315(m), 1282(m), 1255(w), 1221(w), 1142 (w), 1119(w), 1092(w), 1046(w), 1065(w), 1019(w), 999(w), 965 (w), 941(w), 881(w), 842(m), 821(w), 765(s), 732(w), 707(w), 684(w).

2.4. Preparation of $[Ni(tdc)(4\text{-ppbp})_2(H_2O)]_n$ (*3*)

$Ni(NO_3)_2\cdot 6H_2O$ (108 mg, 0.37 mmol), 2,5-thiophenedicarboxylic acid (64 mg, 0.37 mmol) and 4-ppbp (156 mg, 0.37 mmol) and 1.0 mL of a 1.0 M NaOH solution were placed into 10 mL distilled H_2O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120° C for 2d, and then cooled slowly to 25 °C. Green–blue crystals of **3** (135 mg, 34% yield based on 4-ppbp) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{56}H_{68}N_8NiO_9S$ **3**: C, 61.82; H, 6.30; N, 10.30. Found: C, 59.44; H, 6.02; N, 9.64%. IR (cm^{-1}): 3409 (w), 2927(w), 2854(w), 1635(m), 1612(m), 1553(w), 1523(w), 1501(w), 1440(m), 1413(w), 1357(s), 1282(m), 1246(w), 1224 (w), 1162(w), 1146(w), 1119(w), 1063(w), 1017(w), 968(w), 943 (w), 899(w), 843(s), 807(w), 774(s), 739(w), 704(m), 675(w).

3. X-ray crystallography

Single crystal X-ray diffraction on crystals of **1**–**3** was performed using a Bruker-AXS ApexII CCD instrument at 173 K. Reflection data were acquired using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data was integrated via SAINT [21]. Lorentz and polarization effect and empirical absorption corrections were applied with SADABS [22]. The structures were solved using direct methods and refined on F^2 using SHELXTL [23] within the OLEX2 crystallographic software suite [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. The crystal of **1** was non-merohedrally twinned; its twin law was found using CELLNOW [25]. Relevant crystallographic data for **1**–**3** are listed in Table 1.

4. Results and discussion

4.1. Synthesis and spectral characterization

Compounds **1**–**3** were prepared by hydrothermal reaction of the requisite metal nitrate, 2,5-thiophenedicarboxylic acid, and 4-ppbp. Their infrared spectra were consistent with structural components determined by single-crystal X-ray diffraction. Intense, slightly broadened asymmetric and symmetric carboxylate C–O stretching bands for the dicarboxylate ligands were observed at 1600 and 1350 cm^{-1} for **1**, 1604 and 1364 cm^{-1} for **2**, and 1612 and 1356 cm^{-1} for **3**. Sharp and medium intensity bands in the range of ~1600–1300 cm^{-1} were attributed to stretching mode of the pyridyl rings of the dipyridylamide ligands and the thiophene rings in **1**–**3**. Broad weak spectral bands in the