ARTICLE IN PRESS

Polyhedron xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Metal-dependent ribbon and self-penetrated topologies in nitroaromatic-sensing zinc and cadmium coordination polymers with terephthalate and dipyridylamide ligands

Megan J. Wudkewych, Robert L. LaDuca *

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

ARTICLE INFO

Article history:
Received 20 July 2015
Accepted 8 October 2015
Available online xxxx

Keywords:
Cadmium
Zinc
Coordination polymer
Crystal structure
Nitroaromatic detection

ABSTRACT

Hydrothermal reaction of the requisite metal nitrate, potassium terephthalate (K_2tere) and the dipyridylamide 3-pyridylisonicotinamide (3-pina) afforded a pair of crystalline coordination polymers whose dimensionality and topology depends critically on the metal coordination environment. The two new crystalline phases were structurally characterized via single-crystal X-ray diffraction. $\{[Zn(tere)(3\text{-}pina)_2]\cdot 2H_2O\}_n$ (**1**) manifests a 1-D zig-zag ribbon motif with monodentate 3-pina ligands. $[Cd(tere)(3\text{-}pina)_2]_n$ (**2**) displays a self-penetrated 3-D network with $4^4 6^{10} 8$ **mab** topology. Thermal and luminescent properties of these two new materials are also presented. Both **1** and **2** show capability as sensors for nitroaromatic compounds via luminescence quenching, with better absorption for nitrobenzene than the more sterically bulky analyte *m*-nitrophenol.

1. Introduction

Over the past fifteen years, there has been an intense research spotlight on the exploratory synthesis and structure of crystalline coordination polymer solids. Interest remains strong due to potential of this genre of solid state materials in gas storage [1], molecular separations [2], ion exchange [3], heterogeneous catalysis [4], and as luminescent explosives trace detectors [5]. The undeniable esthetic appeal of their underlying 1-D, 2-D, or 3-D topologies also provides an impetus for continued research efforts [6]. Divalent zinc or cadmium ions have proven efficacious choices as the requisite cationic component, predicated on their closed shell d^{10} electronic configurations. Full *d* shell population results in forbidden visible light *d*–*d* transitions, imparting the transparent visible light spectral window required for fluorescent sensing [7] or second harmonic generation applications [8]. Due to the lack of crystal field stabilization for divalent zinc and cadmium ions, coordination polymer structure direction is ascribed to the combined effects of ligand donor disposition, carboxylate binding mode and steric requirements, as opposed to a specific preferred metal coordination geometry.

A myriad number of different topologies have been reported for divalent zinc and cadmium coordination polymers with aromatic dicarboxylate and neutral dipyridyl linkers [9–14]. Some of these display intriguing and rare self-penetrated networks, in which the shortest rings within the topology pass through other shortest rings. For example, $[Cd(Hpht)_2(bpy)]_n$ (pht = phthalate, bpy = 4,4′-bipyridine) manifests a self-penetrated 6-connected 3-D network with $5^{10}6^4 7$ topology [9]. Using the kinked and hydrogen bonding capable dipyridyl ligand 4,4′-dipyridylamine (dpa) afforded $\{[Cd(pht)(dpa)(H_2O)]\cdot 4H_2O\}_n$, which displays a unique chiral self-penetrated 4-connected $7^4 8^2$ **yyz** topology based on interlocked helical subunits [10]. In other cases, this combination of ligand types has allowed self-assembly of coordination polymers with enticing adsorptive properties. For example, the desolvated apohost of $\{[Zn_2(tere)_2(bpy)]\cdot H_2O\cdot DMF\}_n$ can separate challenging mixtures of low molecular weight alkanes [11].

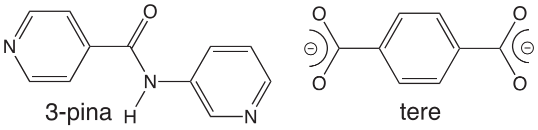
In comparison to coordination polymers containing bpy or dpa ligands, there are fewer reports of related materials containing the hydrogen-bonding capable dipyridylamide ligand 3-pyridylnicotinamide (3-pina, Scheme 1) or its isomeric dipyridylamide congeners [15–19]. A 3-pina ligand can engage in both supramolecular hydrogen bonding donating and accepting pathways due to its central amide moiety, unlike the kinked dpa or rigid-rod bpy linkers. Different locked conformations are possible for 3-pina ligands when entrained in a coordination polymer network, including *syn* (with the 3-pyridyl ring nitrogen atom positioned on the same side of the molecule as the carbonyl oxygen atom) or *anti* (with the 3-pyridyl ring nitrogen atom positioned on the opposite side of the molecule as the carbonyl oxygen atom, as depicted in Scheme 1). The isostructural phases $[M(tere)(3\text{-}pina)_2]_n$ (M = Mn, Co) display identical (4,4) grid layer

---

* Corresponding author.
E-mail address: laduca@msu.edu (R.L. LaDuca).

http://dx.doi.org/10.1016/j.poly.2015.10.011
0277-5387/© 2015 Elsevier Ltd. All rights reserved.

Please cite this article in press as: M.J. Wudkewych, R.L. LaDuca, Polyhedron (2015), http://dx.doi.org/10.1016/j.poly.2015.10.011



Scheme 1. Ligands used in this study.

topologies, with the 3-pina ligands adopting a slightly twisted *syn* conformation in which their 3-pyridyl rings do not ligate [15]. {[Cu(ip)(3-pina)]·H_2O}$_n$ (ip = isophthalate) exhibits dimeric units pillared into a non-interpenetrated 3-D 6^58 **cds** network by tethering *syn* conformation 3-pina ligands, while ({[Cu(tbip)(3-pina)$_2$(H_2O)]·H_2O}$_n$ (tbip = 5-*tert*-butylisophthalate) is a 1-D chain coordination polymer with a “butterfly” morphology brought about by syn conformation 3-pina ligands whose isonicotinamide 4-pyridyl rings do not ligate [16]. It is thus clear that 3-pina can afford access to a wide variety of coordination polymer topologies in the presence of different aromatic dicarboxylate ligands.

We have therefore attempted to extend this underdeveloped 3-pina coordination chemistry into closed-shell configuration divalent metal systems. In this contribution we report the synthesis, single-crystal structural characterization, luminescent and nitroaromatics sensing properties, and thermal degradation behavior of two new dual-ligand coordination polymers, {[Zn(tere)(3-pina)$_2$]·2H_2O}$_n$ (**1**) and [Cd(tere)(3-pina)$_2$]$_n$ (**2**). These phases show a very significant change in coordination polymer dimensionality and topology depending on the coordination environment present at the closed shell divalent metal ion.

2. Experimental

2.1. General considerations

Metal nitrates, terephthalic acid, and nitroaromatics were commercially obtained. Potassium terephthalate was obtained via the reaction of terephthalic acid with excess potassium hydroxide in ethanolic solution. The dipyridylamide ligand 3-pyridylisonicotinamide (3-pina) was prepared by a literature procedure [20]. Water was deionized above 3 M Ω-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. The luminescence spectra of **1** and **2** 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. The same Hitachi F-4500 Fluorescence Spectrometer instrument was used for nitroaromatic absorption studies. Thermogravimetric analysis was performed on a TA Instruments Q50 thermal analyzer under flowing N_2. Topological analysis of coordination polymer networks was carried out using TOPOS software [21].

2.2. Preparation of {[Zn(tere)(3-pina)$_2$]·2H_2O}$_n$ (**1**)

$Zn(NO_3)_2·6H_2O$ (113 mg, 0.38 mmol), 3-pina (74 mg, 0.37 mmol), and potassium terephthalate (89 mg, 0.37 mmol) were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 50 h, and then was cooled slowly to 25 °C. Colorless crystals of **1** (95 mg, 77% yield based on 3-pina) were isolated after washing with distilled water, ethanol, and acetone and drying in air. $C_{30}H_{26}N_6O_8Zn$ **1** calc. C, 54.27; H, 3.95; N, 12.66; found C, 54.13; H, 3.91; N, 12.43%. **IR** ($\tilde{\nu}$) = 3064 (w), 1687 (m), 1595 (s), 1556 (s), 1487 (m), 1422 (m), 1393 (m), 1359 (s), 1333 (s), 1303 (s), 1250 (m), 1200 (m), 1131 (w), 1067 (m), 1023 (w), 896 (w), 843 (m), 826 (m), 754 (s), 689 (s), 655 (m) cm^{-1}.

Table 1
Crystal and structure refinement data for **1** and **2**.

Data	1	2
Empirical formula	$C_{30}H_{26}N_6O_8Zn$	$C_{30}H_{22}CdN_6O_6$
Formula weight	663.94	674.94
Crystal system	monoclinic	monoclinic
Space group	*C*/2*c*	*P*2$_1$/*n*
a (Å)	21.6696(15)	8.9838(15)
b (Å)	9.2376(5)	7.3016(12)
c (Å)	15.9194(9)	20.264(3)
α (°)	90	90
β (°)	115.921(1)	101.657(3)
γ (°)	90	90
V (Å^3)	2866.1(3)	1301.8(4)
Z	4	2
D (g cm^{-3})	1.539	1.722
μ (mm^{-1})	0.921	0.899
Crystal size (mm)	0.21 × 0.18 × 0.16	0.24 × 0.17 × 0.04
Minimum/maximum trans.	0.9528	0.8447
hkl ranges	$-25 \leqslant h \leqslant 25$, $-11 \leqslant k \leqslant 11$, $-19 \leqslant l \leqslant 19$	$-10 \leqslant h \leqslant 10$, $-8 \leqslant k \leqslant 8$, $-24 \leqslant l \leqslant 24$
Total reflections	22651	10364
Unique reflections	2575	2379
R_{int}	0.0303	0.0421
Parameters	212	196
R_1[a] (all data)	0.0251	0.0342
R_1[a] ($I > 2\sigma(I)$)	0.0231	0.0260
wR_2[b] (all data)	0.0585	0.0668
wR_2[b] ($I > 2\sigma(I)$)	0.0573	0.0621
Maximum/minimum residual (e Å^{-3})	0.333/−0.273	0.393/−0.507
Goodness-of-fit	1.065	1.064

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$.

2.3. Preparation of [Cd(tere)(3-pina)$_2$]$_n$ (**2**)

$Cd(NO_3)_2·4H_2O$ (114 mg, 0.37 mmol), 3-pina (74 mg, 0.37 mmol), and potassium terephthalate (89 mg, 0.37 mmol) were mixed with 10 mL of distilled H_2O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 144 h, and then was cooled slowly to 25 °C. Colorless crystals of **2** (112 mg, 89% yield based on 3-pina) were isolated after washing with distilled water, ethanol, and acetone and drying in air. $C_{30}H_{22}CdN_6O_6$ calc. C, 53.39; H, 3.29; N, 12.45; found C, 52.87; H, 3.11; N, 11.98%. **IR** ($\tilde{\nu}$) = 3591 (w), 3056 (w), 2911 (w), 1677 (m), 1560 (s), 1537 (s), 1486 (w), 1424 (m), 1366 (s), 1330 (m), 1303 (s), 1008 (m), 895 (m), 840 (w), 812 (s), 746 (s), 693 (s) cm^{-1}.

2.4. Nitroaromatic detection studies

A 5 mg sample of coordination polymer **1** or **2** was suspended in 5 mL ethanol in a volumetric flask, with immersion in an ultrasonic bath for 60 s to ensure an even dispersion. The fluorescence spectrum was recorded with an excitation wavelength of 300 nm. Stock solutions of nitrobenzene, *m*-nitrophenol, and benzene (1×10^{-4} M) in dimethyl sulfoxide were prepared. Aliquots of these stock solutions (10 μL) were added sequentially to coordination polymer ethanol suspensions with sonication for 30 s after each addition. The emission spectra were measured before any analyte addition and after each aliquot of analyte solution.

3. X-ray crystallography

Diffraction data for **1** and **2** were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were processed via SAINT

Please cite this article in press as: M.J. Wudkewych, R.L. LaDuca, Polyhedron (2015), http://dx.doi.org/10.1016/j.poly.2015.10.011