Journal of Molecular Structure 1120 (2016) 156–162

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Dipyridylamide ligand dependent dimensionality in luminescent zinc 2,4-pyridinedicarboxylate coordination complexes

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 29 March 2016
Received in revised form
28 April 2016
Accepted 28 April 2016
Available online 7 May 2016

Keywords:
Crystal structure
Coordination polymer
Luminescence
Zinc

ABSTRACT

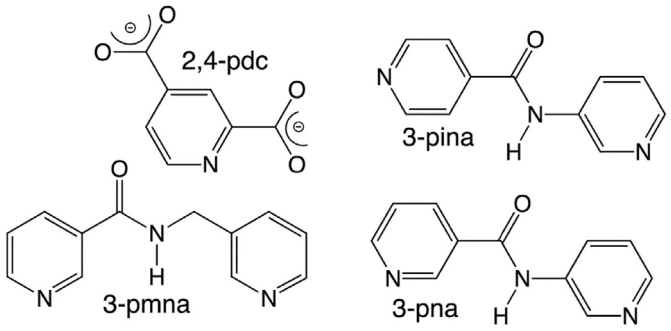
Zinc nitrate, 2,4-pyridinedicarboxylic acid (2,4-pdcH_2), and a hydrogen-bonding capable dipyridylamide ligand were combined in aqueous solution and subjected to hydrothermal reaction conditions. Three new crystalline coordination complexes were generated; their dimensionality depends crucially on the dipyridylamide length and geometric disposition of the pyridyl nitrogen donors. The three new phases were structurally characterized via single-crystal X-ray diffraction. {[$H_2$3-pina][Zn(2,4-pdc)$_2$(H_2O)$_2$]·H_2O} (**1**, 3-pina = 3-pyridylisonicotinamide) is a salt with protonated dipyridylamide cations and coordination complex anions. {[Zn_2(2,4-pdc)$_2$(H_2O)$_4$(3-pna)]·3H_2O}$_n$ (**2**, 3-pna = 3-pyridylnicotinamide) shows a system of two-fold interpenetrated ruffled (6,3) coordination polymer layers. {[Zn(2,4-pdc)(H_2O)$_2$(3-pmna)]$_n$ (**3**, 3-pmna = 3-pyridylmethylnicotinamide) manifests a simple 1D chain topology. Luminescence was observed for two of the zinc complexes; this behavior is attributed to π–π* or π–n molecular orbital transitions. Thermal decomposition properties of the new phases are also probed.

1. Introduction

Basic research into the preparation and structural determination of divalent metal coordination polymers has continued for over twenty years. These materials can serve in gas storage [1], or act as molecular adsorbents [2], agents for drug-delivery [3], and industrially important heterogeneous catalysts [4]. It has been recently shown that coordination polymers with optically transparent spectral windows, especially zinc- and cadmium-based materials constructed from aromatic dicarboxylate ligands, can act as sensors for the detection of nitroaromatics [5]. Pyridyldicarboxylate ligands such as 2,6-pyridinedicarboxylate (2,6-pdc) or 2,4-pyridinedicarboxylate (2,4-pdc, Scheme 1) possess an additional nitrogen donor atom and can therefore adopt binding modes not possible with simple dicarboxylate ligands. Coordination polymers containing 2,4-pdc can show non-linear optical properties and ferroelectric behavior, for example in the 3D acentric 10^3 **ths** topology anionic net in {[Me_2NH_2][Cd_2Na_3(2,4-pdc)$_4$]·2H_2O}$_n$ [6]. There are few reports of zinc-based 2,4-pdc coordination polymers with tethering bipyridyl-type ancillary ligands. {[Zn_2(2,4-pdc)$_2$(azpy)(H_2O)$_6$]·2H_2O} (azpy = 4,4′- azobipyridine) is a simple dinuclear coordination complex, with two neutral [Zn(2,4-pdc)(H_2O)]$_3$ fragments bridged by a single azpy tether [7]. The very long spanning dipyridylamide ligand *N*,*N*′-di(3-pyridyl) dodecanediamide (dpd) was utilized to prepare [Zn(2,4-pdc)(dpd)(H_2O)]$_n$, an intriguing nanotubular 1D coordination polymer built from a pillared system of quintuple helical motifs [8]. According to a CCDC database search, there are no other reported zinc 2,4-pdc coordination polymers that contain dipyridylamide ligands. We therefore sought to prepare a series of zinc 2,4-pdc coordination polymers containing the shorter dipyridylamide ligands 3-pyridylisonicotinamide (3-pina, Scheme 1) or 3-pyridylnicotinamide (3-pna, Scheme 1), or the slightly longer derivative 3-pyridylmethylnicotinamide (3-pmna, Scheme 1) [9–14]. In this study we have sought to probe the specific structural effects of pyridyl nitrogen donor disposition and tether length within the dipyridylamide component. The amide functional groups of these potential tethering ligands provide hydrogen bonding donating and accepting points of contact, inducing supramolecular interactions that are impossible if a rigid-rod tether such as 4,4′-bipyridine is used. In this article, we describe the synthesis, structural characterization, topological analysis, and thermal and luminescent properties of three new zinc 2,4-pdc dipyridylamide dual-ligand complexes: {[$H_2$3-pina][Zn(2,4-pdc)$_2$(H_2O)$_2$]·H_2O} (**1**), {[Zn_2(2,4-pdc)$_2$(H_2O)$_4$(3-pna)]·3H_2O}$_n$ (**2**), and {[Zn(2,4-pdc)(H_2O)2(3-pmna)]$_n$ (**3**).

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

http://dx.doi.org/10.1016/j.molstruc.2016.04.100
0022-2860/



Scheme 1. Ligands used in this study.

2. Experimental section

2.1. General considerations

Zinc nitrate hexahydrate and 2,4-pyridinedicarboxylic acid were commercially obtained from Fisher and Sigma-Aldrich, respectively. Reaction of 3-picolylamine and nicotinoyl chloride hydrochloride in water-free distilled pyridine afforded 3-pyridylmethylnicotinamide (3-pmna), which was isolated via CH_2Cl_2 extraction and subsequent solvent removal *in vacuo* [15]. Similar reactions between 3-pyridylamine and nicotinoyl chloride hydrochloride or isonicotinoyl chloride hydrochloride in dry pyridine afforded 3-pyridylnicotinamide (3-pna) and 3-pyridylisonicotinamide (3-pina), respectively. Water was deionized above 3MΩ–cm in-house. Infrared spectra were obtained using a Perkin Elmer Spectrum One DRIFT instrument, with a range from 650 to 4000 cm^{-1}. The excitation and emission spectra were acquired with a Hitachi F-4500 Fluorescence Spectrophotometer, on crystalline samples adhered to quartz microscope slides with an epoxy adhesive that is transparent to ultraviolet light. Thermal analysis was performed on a TA Instruments Q-50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C under flowing nitrogen gas. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

Table 2
Selected bond distance (Å) and angle (°) data for **1**.

Zn1–O5	2.133 (2)	Zn2–O9	2.090 (2)
Zn1–O1W	2.173 (2)	Zn2–O13	2.089 (2)
Zn1–O1	2.117 (2)	Zn2–N4	2.070 (3)
Zn1–O2W	2.092 (2)	Zn2–N3	2.076 (3)
Zn1–N1	2.071 (3)	Zn2–O3W	2.181 (2)
Zn1–N2	2.094 (3)	Zn2–O4W	2.158 (2)
O5–Zn1–O1W	84.36 (9)	O9–Zn2–O3W	91.12 (9)
O1–Zn1–O5	173.66 (9)	O9–Zn2–O4W	94.61 (9)
O1–Zn1–O1W	89.49 (9)	O13–Zn2–O9	179.02 (8)
O2W–Zn1–O5	94.80 (9)	O13–Zn2–O3W	89.11 (9)
O2W–Zn1–O1W	174.25 (9)	O13–Zn2–O4W	85.20 (9)
O2W–Zn1–O1	91.48 (9)	N4–Zn2–O9	98.68 (10)
O2W–Zn1–N2	91.51 (10)	N4–Zn2–O13	80.36 (10)
N1–Zn1–O5	101.77 (9)	N4–Zn2–N3	176.15 (11)
N1–Zn1–O1W	85.30 (9)	N4–Zn2–O3W	90.54 (10)
N1–Zn1–O1	79.19 (9)	N4–Zn2–O4W	90.62 (10)
N1–Zn1–O2W	89.31 (10)	N3–Zn2–O9	80.52 (10)
N1–Zn1–N2	179.18 (11)	N3–Zn2–O13	100.45 (9)
N2–Zn1–O5	78.13 (9)	N3–Zn2–O3W	85.72 (9)
N2–Zn1–O1W	93.88 (10)	N3–Zn2–O4W	93.19 (10)
N2–Zn1–O1	100.82 (9)	O4W–Zn2–O3W	173.91 (9)

2.2. Preparation of {[$H_2$3-pina][Zn(2,4-pdc)$_2$(H_2O)$_2$]·H_2O} (**1**)

$Zn(NO_3)_2·6H_2O$ (115 mg, 0.39 mmol), 3-pina (81 mg, 0.41 mmol), and 2,4-pyridinedicarboxylic acid (64 mg, 0.39 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 4 d, and then was cooled slowly to 25 °C. Colorless crystals of **1** (171 mg, 67% yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{50}H_{46}N_{10}O_{24}Zn_2$ **1**: C, 46.13; H, 3.56; N, 10.76% Found: C, 46.01; H, 3.45; N, 10.42%. IR (cm^{-1}): 3247 (w), 1683 (w), 1668 (w), 1631 (w), 1589 (m), 1547 (m), 1488 (w), 1420 (w), 1361 (m), 1332 (m), 1305 (m), 1257 (w), 1096 (w), 1067

Table 1
Crystal and structure refinement data for **1**–**3**.

Data	1	2	3
Empirical formula	$C_{50}H_{46}N_{10}O_{24}Zn_2$	$C_{25}H_{29}N_5O_{16}Zn_2$	$C_{19}H_{18}N_4O_7Zn$
Formula weight	1301.71	786.27	479.74
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	Cc	$P\bar{1}$
a (Å)	18.086 (3)	27.512 (3)	8.839 (2)
b (Å)	13.620 (2)	7.4573 (7)	9.887 (2)
c (Å)	22.138 (4)	18.3552 (18)	11.396 (3)
α (°)	90	90	83.320 (3)
β (°)	108.887 (2)	122.9484 (12)	71.163 (3)
γ (°)	90	90	81.765 (3)
V (Å^3)	5159.6 (14)	3160.2 (5)	930.2 (4)
Z	4	4	2
D (g cm^{-3})	1.676	1.653	1.713
μ (mm^{-1})	1.031	1.600	1.375
Min./max. transmission	0.8991	0.8626	0.9055
hkl ranges	$-21 \le h \le 21$, $-16 \le k \le 16$, $-25 \le l \le 26$	$-32 \le h \le 32$, $-8 \le k \le 8$, $-22 \le l \le 22$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-13 \le l \le 13$
Total reflections	42132	12679	11325
Unique reflections	9452	5713	3404
R(int)	0.0518	0.0309	0.0726
Parameters	782	434	292
R_1 (all data)	0.0677	0.0532	0.0785
R_1 ($I > 2\sigma(I)$)	0.0434	0.0425	0.0482
wR_2 (all data)	0.1228	0.1114	0.1069
wR_2 ($I > 2\sigma(I)$)	0.1068	0.1034	0.0943
Max/min residual (e^-/Å^3)	0.735/−0.673	1.129/−0.404	0.538/−0.387
G.O.F.	1.028	1.045	1.020