



The pH-controlled synthesis of three zinc-based complexes modeled by 5-carboxyl-1-carboxymethyl-2-oxidopyridinium with luminescence studies



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ABSTRACT

Three new zinc compounds $\{[Zn_2(ccop)_2(4,4'-bpy)] \cdot H_2O\}_n$ (**1**), $\{[Zn(ccop)(bpp)] \cdot H_2O\}_n$ (**2**) and $[Zn(ccop)(H_2O)_5] \cdot H_2O$ (**3**) (H_2ccop = 5-carboxyl-1-carboxymethyl-2-oxidopyridinium, 4,4'-bpy = 4,4'-bipyridine, bpp = 1,3-bis(4-pyridyl) propane) have been prepared under hydrothermal conditions at different pH values, and characterized by elemental analysis, IR spectra, thermogravimetric analysis, powder X-ray diffraction, and single-crystal X-ray diffraction. Complex **1** features a 2D (4,4) net when the dinuclear $[Zn_2(COO)_2N_2O_2]$ unit is regarded as a quadruply-connected node. Complex **2** also displays a 2D (4,4) net constructed by Zn-carboxylate chains and bpp struts. While **3** is a mononuclear complex which is further assembled into a 3D supramolecular structure through hydrogen bonding interactions. All of **1–3** emit the intense indigotin photoluminescence at room temperature in solid state.

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1. Introduction

Metal–organic complexes involving multi-carboxylate ligands have received much attention in coordination chemistry due to their various topologies and potential applications, such as guest exchange, gas storage and separation, catalysis, drug delivery, luminescence, etc. [1–7]. Of those multi-carboxylate based MOFs, rigid aromatic multi-carboxylate ligands are found to be widely utilized and dominating the literature [4,8–10]. However, so far work on the construction of metal–organic complexes based on the flexible aromatic multi-carboxylate ligands is still scarce, especially when an aromatic multi-carboxylate ligands involving the mixed rigid and flexible carboxylate groups. It has been found that the rational design of organic building blocks plays the key role in adjusting the coordination frameworks, and the nature of the coordinating donors may lead to the formation of unique networks with desired properties and functions [11]. 5-Carboxyl-1-carboxymethyl-2-oxidopyridinium (H_2ccop) possesses one rigid carboxylate group and one flexible acetate group, which can act an excellent multidentate ligand with a range of versatile binding and coordination modes. Though as a good multidentate ligand, H_2ccop has not been well exploited in building coordination polymers, only few metal complexes of H_2ccop have been reported [12–15].

With these in mind, we obtained three new zinc-based complexes under hydrothermal conditions at different pH values. Luminescence data observed at room temperature show that all of the compounds emit bright blue fluorescence.

2. Experimental

2.1. Materials and physical measurements

All chemicals were commercially available and used as received without further purification. Elemental analyses for C, H, and N were carried out using a Vario EL III Elemental Analyzer. Infrared spectra were recorded ($4000\text{--}400\text{ cm}^{-1}$) as KBr disks on a Shimadzu IR-440 spectrometer. Thermogravimetric analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of N_2 at a heating rate of $10^\circ\text{C}/\text{min}$ between ambient temperature and 800°C . Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with $MoK\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. Luminescence spectra for crystalline samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz spectrometer. $^1\text{H-NMR}$ chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (C_2D_6OS , $\delta = 2.56$). Data are reported as follows: chemical shift (δ ppm), multiplicity (s: singlet, d: doublet, t: triplet, m: multiplet), coupling constants

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(Hz), integration, and assignment. ^{13}C -NMR spectra were collected on a 100 MHz spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane (TMS) with the solvent resonance as internal standard ($\text{C}_2\text{D}_6\text{OS}$, $\delta = 39.52$).

2.2. Preparation of H_2ccop

The preparation of H_2ccop was carried out according to the reported procedures [16]. Yield: 72%. ^1H NMR (400 MHz, $\text{C}_2\text{D}_6\text{OS}$) δ : 6.44–8.47 (3H, Ar–H), 4.69 (s, 2H, $-\text{CH}_2-$); ^{13}C NMR (100 MHz, $\text{C}_2\text{D}_6\text{OS}$) δ : 169.3, 165.5, 161.8, 145.1, 139.7, 118.7, 109.6, 50.7. Anal. Calcd for $\text{C}_8\text{H}_7\text{O}_5\text{N}$ (Mr = 197.21): C, 48.68; H, 3.55; N, 7.10. Found: C, 48.55; H, 3.61; N, 7.14. IR (KBr, cm^{-1}): 3472(s), 1704(vs), 1662(s), 1598(m), 1475(w), 1402(w), 1380(s), 1362(m), 1272(m), 1251(w), 1182(m), 1098(s), 1052(w), 935(s), 882(m), 765(m), 621(w), 589(w).

2.3. Preparation of $\{[\text{Zn}_2(\text{ccop})_2(4,4'\text{-bpy})]\cdot\text{H}_2\text{O}\}_n$ (**1**)

Complex **1** was prepared by addition of stoichiometric amounts of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.15 g, 0.5 mmol) and 4,4'-bpy (0.039 g, 0.25 mmol) to a hot aqueous solution (10 mL) of H_2ccop (0.098, 0.5 mmol). The pH was then adjusted to 9 with NaOH (0.01 g, 0.25 mmol). The resulting mixture were sealed in a 23 mL teflon reactor and kept under autogenous pressure at 130 °C for 3 days. Colorless single crystals were obtained (yield: 62%, based on H_2ccop) upon cooling the solution to room temperature at 5 °C/h. Anal. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_6\text{Zn}$ (%): Calcd. C 43.75, H 3.08, N 7.85; found C 43.71, H 3.05, N 7.89. FTIR (KBr, cm^{-1}): 3445(s), 1654(s), 1609(m), 1572(m), 1534(m), 1453(w), 1333(w), 1221(w), 1138(m), 998(w), 901(w), 821(w), 781(w), 654(w), 525(w), 423(w).

2.4. Preparation of $\{[\text{Zn}(\text{ccop})(\text{bpp})]\cdot\text{H}_2\text{O}\}_n$ (**2**)

Complex **2** was prepared by the same procedure as **1**, except that the 4,4'-bpy was replaced by bpp. Colorless crystals were obtained in 70% yield based on H_2ccop . Anal. for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_6\text{Zn}$ (%): Calcd. C 52.74, H 4.40, N 8.79; found C 52.68, H 4.38, N 8.86. FTIR

(KBr, cm^{-1}): 3460(s), 1661(s), 1438(w), 1400(s), 1321(w), 1184(w), 1139(w), 1043(w), 925(w), 804(w), 661(m), 523(w).

2.5. Preparation of $[\text{Zn}(\text{ccop})(\text{H}_2\text{O})_5]\cdot\text{H}_2$ (**3**)

Complex **3** was prepared by the same procedure as **1** or **2**, except that the pH value was adjusted to about 4 through HCl. Colorless crystals were obtained in 56% yield based on H_2ccop . Anal. for $\text{C}_8\text{H}_{16}\text{NO}_{10}\text{Zn}$ (%): Calcd. C 26.70, H 4.45, N 3.89; found C 26.65, H 4.38, N 3.96. FTIR (KBr, cm^{-1}): 3475(vs), 1650(s), 1434(w), 1438(m), 1385(s), 1192(w), 1132(m), 915(w), 855(w), 797(w), 722(w), 665(m), 552(w).

2.6. X-ray crystal structural determination

Single crystal X-ray diffraction analyses of complexes **1–3** were performed on a Agilent Xcalibur (Eos Gemini) diffractometer operating at 50 kV and 30 mA using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and reduction were performed using the CrysAlis PRO software [17]. Multi-scan absorption corrections were applied for all the data sets using the CrysAlis PRO [17]. The structures were solved by direct methods and refined by least squares on F^2 using the SHELXTL program package [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Water hydrogen atoms were tentatively located in difference Fourier maps and refined with distance restraints of O–H = 0.84 Å and H...H = 1.39 Å, with an assigned standard deviation of 0.01 Å. Crystallographic data are listed in Table 1. Selected bond lengths and angles are given in Table 2. H-bonding parameters for **1–3** are given in Table 3.

3. Results and discussion

3.1. Crystal structure of complex **1**

Complex **1** crystallizes in the triclinic space group *P*-1 with one Zn atom, half a 4,4'-bpy ligand, one ccop ligand and one free water

Table 1
Crystal data and structure refinement details of **1–3**.

Compounds	1	2	3
Formula	$\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_6\text{Zn}$	$\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_6\text{Zn}$	$\text{C}_8\text{H}_{16}\text{NO}_{10.5}\text{Zn}$
Fw	356.61	476.78	359.59
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	$P2_1/n$	<i>P</i> -1
<i>a</i> (Å)	7.7802(10)	14.0125(9)	7.7313(8)
<i>b</i> (Å)	8.4955(9)	9.1278(5)	7.9951(15)
<i>c</i> (Å)	11.1403(16)	17.3834(9)	11.3788(11)
α (°)	106.505(11)	90.00	104.236(12)
β (°)	93.882(11)	111.550(6)	92.971(8)
γ (°)	101.494(10)	90.00	102.692(12)
<i>V</i> (Å ³)	685.76(15)	2068.0(2)	660.91(16)
<i>Z</i>	2	4	2
<i>D</i> _c (g/cm ³)	1.727	1.531	1.807
μ (mm ⁻¹)	1.823	1.232	1.913
<i>F</i> (000)	362	984	370
Reflections collected	4309	7839	4016
Independent reflections	2479	3709	2387
<i>R</i> _{int}	0.0673	0.0639	0.0519
Parameters	205	286	226
GOF	0.959	0.956	1.018
<i>R</i> ₁ [$I > 2\sigma(I)$] ^a	0.0593	0.0544	0.0500
<i>wR</i> ₂ (all data) ^b	0.0878	0.0813	0.0986
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ (e/Å ³)	0.433 and -0.505	0.534 and -0.352	0.417 and -0.525

$$^a R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$$

$$^b wR = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

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