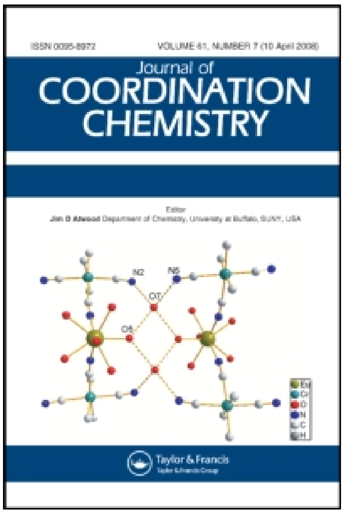

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Syntheses, crystal structures and luminescence of two isostructural coordination polymers constructed from 4,5-imidazoledicarboxylate

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Syntheses, crystal structures and luminescence of two isostructural coordination polymers constructed from 4,5-imidazoledicarboxylate

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The syntheses, IR, molecular structures, and luminescence of $[M(HIMDC)(4,4'\text{-bipyO})_{0.5}(H_2O)]_n$ [$H_3IMDC = 4,5$-imidazoledicarboxylate, $4,4'$-bipyO $= 4,4'$-bipyridine-*N*, *N′*-dioxide, M = Co (**1**) and Zn (**2**)] are reported. The most notable structure feature of **1** and **2** is that the left-handed and right-handed helical chains constructed from 4,5-imidazoledicarboxylate and metal are linked by 4,4′-bipyO to generate infinite 2-D herringbone architectures. **2** exhibits strong fluorescent emission in the solid state at room temperature.

Keywords: Crystal structure; 4,5-Imidazoledicarboxylate; Luminescence; Hydrogen bond

1. Introduction

Rational design, synthesis and characterization of coordination polymers have developed rapidly from their intriguing architectures and topologies [1], as well as their potential applications in electronic, magnetic, optical, absorbent and catalytic materials [2–4]. However, assembly of coordination polymers with desired structures and properties is still a great challenge. Multidentate organic aromatic polycarboxylate ligands such as 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, and 1,2,4, 5-benzenetetracarboxylate have been employed in construction of high-dimensional structures [5–7].

Ligand 4,5-imidazoledicarboxylate (H_3IMDC) possessing both imidazole and carboxylate functionalities potentially exhibits rich coordination chemistry. It can be partially or fully deprotonated to generate H_2IMDC^-, $HIMDC^{2-}$, and $IMDC^{3-}$ at different pH values, resulting in a variety of interesting coordination polymers [8, 9]. Herein, we report the hydrothermal syntheses and structures of two isostructural

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2-D coordination polymers of $[M(HIMDC)(4,4'\text{-bipyO})_{0.5}(H_2O)]_n$ (M = Co (**1**) and Zn (**2**), 4,4′-bipyO = 4,4′-bipyridine-*N*,*N*′-dioxide).

2. Experimental

2.1. *Physical measurements and materials*

The C, H, and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyzer. IR spectra were recorded with KBr discs on a Bruker Vector 22 spectrophotometer in the 4000–400 cm^{-1} region. Luminescence spectra for the solid samples were recorded with a Hitachi 850 fluorescence spectrophotometer. The reagents and solvents employed were commercially available and used as received. Ligand 4,4′-bipyO was prepared according to the previously reported procedure [10].

2.2. *Syntheses of $[M(HIMDC)(4,4'\text{-bipyO})_{0.5}(H_2O)]_n$ [M = Co (1) and Zn (2)]*

A mixture of $CoCl_2 \cdot 6H_2O$ (47.8 mg, 0.20 mmol), H_3IMDC (31.2 mg, 0.20 mmol), 4,4′-bipyO (37.5 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol) and deionized water (3 mL) was placed in a Parr Teflon-lined stainless steel vessel (25 cm^3), and then the vessel was sealed and heated at 160°C for 3 days. After the mixture was slowly cooled to room temperature, red crystals of **1** were obtained (yield: 56% based on Co). Anal. Calcd for $C_{10}H_8CoN_3O_6$ (%): C, 36.94; H, 2.48; N, 12.92. Found (%): C, 36.90; H, 2.52; N, 12.94. IR spectrum (cm^{-1}): 3340(s), 3112(w), 1630(s), 1572(s), 1553(s), 1492(s), 1471(s), 1444(m), 1406(s), 1388(s), 1324(w), 1226(s), 1177(s), 1074(m), 1030(m), 970(w), 892(w), 854(m), 839(s), 814(m), 785(m), 700(w), 656(s), 555(m), 528(w), 459(w). The synthesis of **2** was similar to that described for **1** except using $Zn(NO_3)_2 \cdot 6H_2O$ (0.20 mmol) instead of $CoCl_2 \cdot 6H_2O$, and colorless crystals of **2** were obtained (yield: 54% based on Zn). Anal. Calcd for $C_{10}H_8N_3O_6Zn$: C, 36.22; H, 2.43; N, 12.67. Found: C, 36.26; H, 2.41; N, 12.68%. IR spectrum (cm^{-1}): 3423(m), 3113(m), 1627(m), 1561(s), 1493(s), 1469(m), 1446(m), 1408(s), 1354(m), 1230(s), 1177(m), 1075(m), 1030(m), 904(m), 865(m), 842(m), 813(m), 787(m), 700(m), 655(m), 555(m), 521(w), 463(w).

2.3. *X-ray crystallography*

Intensities of **1** and **2** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the SMART and SAINT programs [11]. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods with SHELXTL version 5.1 [12]. Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogens attached to carbon and nitrogen were positioned geometrically (C–H = 0.93 Å, N–H = 0.86 Å) and included in the refinement in a riding model approximation with isotropic thermal displacement parameters fixed at 1.2 times U_{eq} of the atom to which they are attached. Crystallographic data and other pertinent information for **1** and **2** are summarized in table 1. Selected bond lengths and angles with their estimated standard deviations are listed in table 2.

Table 1. Crystal data and structure refinement parameters.

Compound	**1**	**2**
Empirical formula	$C_{10}H_8CoN_3O_6$	$C_{10}H_8N_3O_6Zn$
Formula weight	325.12	331.58
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Units of dimensions (Å, °)		
a	7.0867(16)	7.0814(9)
b	8.398(2)	8.4329(11)
c	19.073(5)	19.147(2)
β	99.872(4)	99.495(2)
V (Å^3)	1118.3(5)	1127.7(2)
Z	4	4
D_{Calcd} (g cm^{-3})	1.931	1.953
μ(Mo–Kα) (mm^{-1})	1.568	2.211
$F(000)$	656	668
θ range for data collection (°)	2.2–26.0	2.2–27.0
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 9$, $-10 \le l \le 23$	$-8 \le h \le 9$, $-10 \le k \le 10$, $-24 \le l \le 24$
Reflections collected	5812	10138
Independent reflections	2208	2445
Observed data	2067	2136
R(int)	0.067	0.085
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0383$, $wR_2 = 0.1080$	$R_1 = 0.0348$, $wR_2 = 0.0961$
Goodness-of-fit on F^2	0.99	1.05

Table 2. Selected bond length (Å) and angles (°) for **1** and **2**.

		Complex **1**^{a}			
Co1–O1	2.034(2)	Co1–O2	2.079(3)	Co1–O3	2.122(2)
Co1–N1	2.102(2)	Co1–O4^{i}	2.1408(19)	Co1–O6^{i}	2.034(2)
O2–Co1–O4^{i}	172.71(9)	O6^{i}–Co1–N1	170.25(8)	O1–Co1–O3	171.42(10)
		Complex **2**^{b}			
Zn1–O1	2.1687(17)	Zn1–O5	2.0998(19)	Zn1–O6	2.035(2)
Zn1–N1	2.083(2)	Zn1–O2^{i}	2.1822(18)	Zn1–O3^{i}	2.017(2)
O2^{i}–Zn1–O5	172.20(8)	O1–Zn1–O6	170.94(8)	O3^{i}–Zn1–N1	168.79(8)

^{a}Symmetry codes: (i) $2-x$, $1/2+y$, $1/2-z$. ^{b}Symmetry codes: (i) $1-x$, $-1/2+y$, $1/2-z$.

3. Results and discussion

3.1. *Description of the crystal structure*

X-ray analysis reveals that the asymmetric unit of **1** contains one Co^{2+}, one HIMDC^{2-}, half 4,4′-bipyO and one coordinated water. As displayed in figure 1(a), Co1 has a distorted octahedral coordination, defined by one oxygen and one nitrogen from HIMDC^{2-}, one oxygen from another HIMDC^{2-} moiety and one coordinated water in equatorial positions while the axial positions are furnished by two oxygens from a HIMDC^{2-} and a 4,4′-bipyO. The Co–O distances vary from 2.034(2) to 2.1408(19) Å and the Co–N bond length is 2.102(2) Å. These distances are comparable to reported values [13, 14].

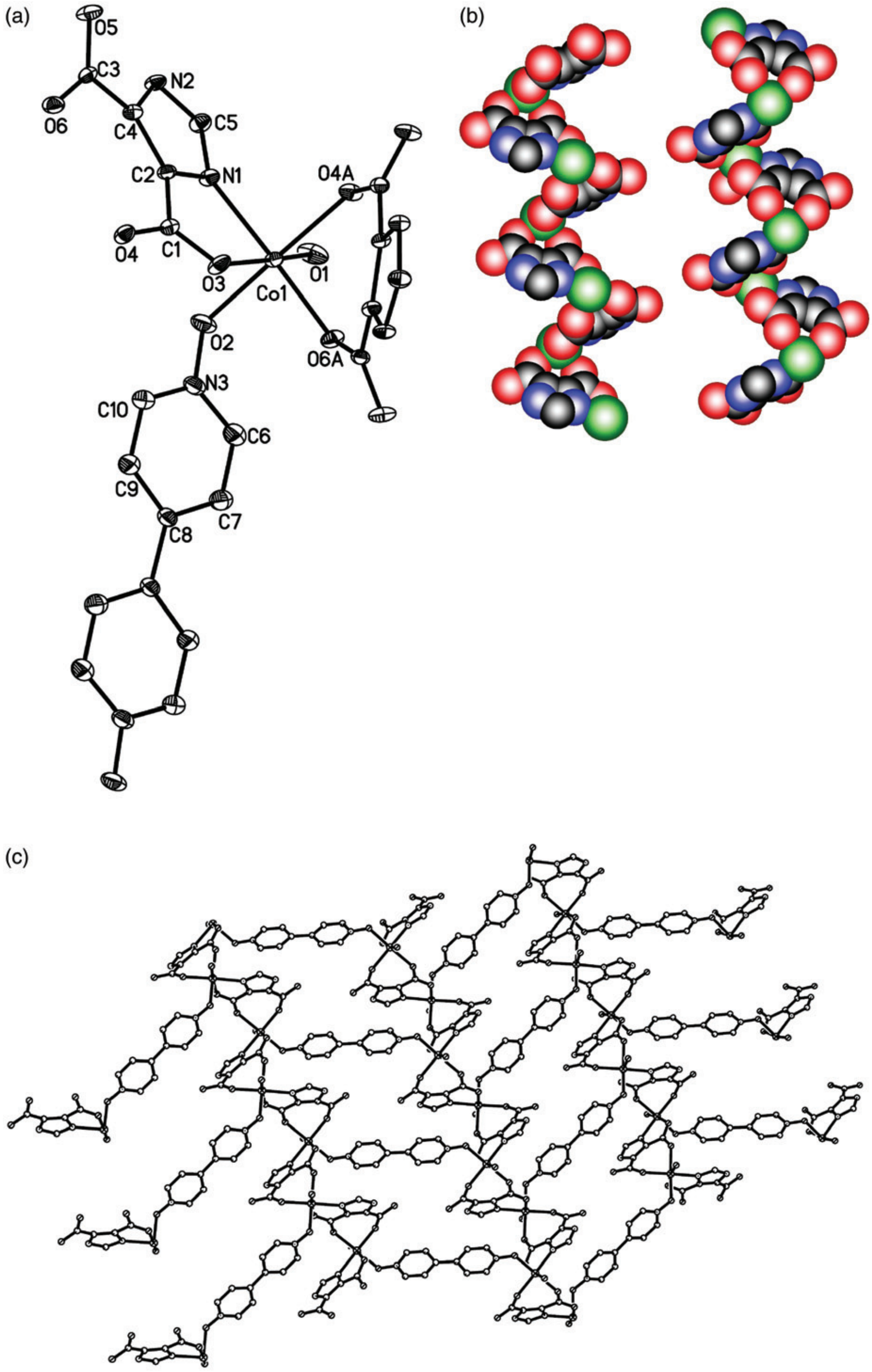

Figure 1. (a) Perspective view of the coordination environment of the Co ion; (b) the 1-D helical structure; (c) the 2-D herringbone architecture in **1**.

For $HIMDC^{2-}$, the two carboxylate groups are out of the plane of correspondingly linking imidazole rings, with dihedral angles between them being 16 and 25°, respectively. As depicted in figure 1(b), these distortions are reflected upon a 1-D helical chainlike structure with 2_1 helices along the *b*-axis with a pitch of 8.398 Å, constructed from μ^2-$HIMDC^{2-}$ and Co. The left-handed and right-handed helical chains are linked by 4,4′-bipyO spacer resulting in an infinite 2-D herringbone architecture extended in the *bc* plane [figure 1(c)]. Similar helical structures have been observed [15]. The coordinated water O1 forms a strong hydrogen bond with the uncoordinated carboxylate oxygen atom $O5^{i}$ [symmetry code: (i) $1-x, 1/2+y, 1/2-z$] with separation of 2.649 Å; the non-deprotonated imidazole nitrogen N2 forms a strong hydrogen bond with coordinated carboxylate oxygen $O4^{ii}$ [symmetry code: (ii) $-1+x, y, z$] with separations of 2.960 Å. In addition, there also exist weaker non-classical hydrogen bonds between C–H and carboxylate oxygens: $C6–H6\cdots O6^{iii}$ [symmetry code: (iii) $x, 1/2-y, -1/2+z$] distance of 3.456(4) Å and $C9–H9\cdots O5^{iv}$ [symmetry code: (iv) $2-x, -1/2+y, 1/2-z$] distance of 3.140(4) Å, respectively. All the interactions contribute to the formation of the final 3-D architecture.

Compound **2** is isostructural to **1**; each Zn^{2+} has a similar distorted octahedral coordination geometry of {ZnNO5} [figure 2(a)]. The Zn–O bond distances are in the range 2.017(2) to 2.1822(18) Å while Zn–N bond length is 2.083(2) Å, consistent with reported distances [16]. The two carboxylate groups form dihedral angles of 25 and 165° with the correspondingly imidazole also leading to a 1-D helical chainlike structure with 2_1 helices constructed from μ^2-$HIMDC^{2-}$ and Zn atoms with a pitch of 8.433 Å. The 2_1 helices are further connected by 4,4′-bipyO to form the same topology as in **1**.

As anticipated, the coordinated aqua molecule O6 forms a strong hydrogen bond with the uncoordinated carboxylate oxygen $O4^{i,ii}$ [symmetry code: (i) $x, 3/2-y, -1/2+z$; (ii) $-x, -1/2+y, 1/2-z$] with separation of 2.786(3) and 2.653(3) Å, respectively; the undeprotonated imidazole nitrogen N2 forms a strong hydrogen bond with coordinated carboxylate oxygen $O2^{iii}$ [symmetry code: (iii) $-1+x, y, z$] with distance of 2.940(3) Å. Furthermore, the O3 also has weak interaction with C10 *via* a nonclassical hydrogen bond, $C10–H10\cdots O3^{i}$ distance of 3.451(4) Å [figure 2(a)]. As a consequence, the hydrogen-bonding interactions further extend the 2-D arrangement to generate a 3-D supramolecular architecture.

3.2. *Spectroscopic properties*

The strong and broad absorption bands in the range 3400–3500 cm^{-1} in **1** and **2** indicate the presence of hydrogen-bonded water. The strong bands of the N–H stretching frequencies in **1** and **2** are covered by the broad absorption band of hydrogen bonded water. For **1**, the bands at 1630(1572), 1406(1388) cm^{-1} correspond to ν_{as}(OCO), ν_s(OCO), respectively. For **2**, the absorption bands at 1627(1561) cm^{-1} can be assigned to ν_{as}(OCO) and the band at 1408(1354) cm^{-1} can be attributed to ν_s(OCO). The differences between ν_{as}(OCO) and ν_s(OCO) for **1** are 224(184) cm^{-1} and for **2** are 219(207) cm^{-1}, indicative of carboxylate in unidentate coordination [17], consistent with the crystal structures. In addition, for free 4,4′-bipyO, ν(N–O) is 1241 cm^{-1}, whereas when coordinated to Co(II) or Zn(II), it shifts to 1177 cm^{-1} [18]. For the two compounds, the difference in the extent of the ligand conformational rigidity due to coordination to different metal ions exerts little influence on their stretching modes.

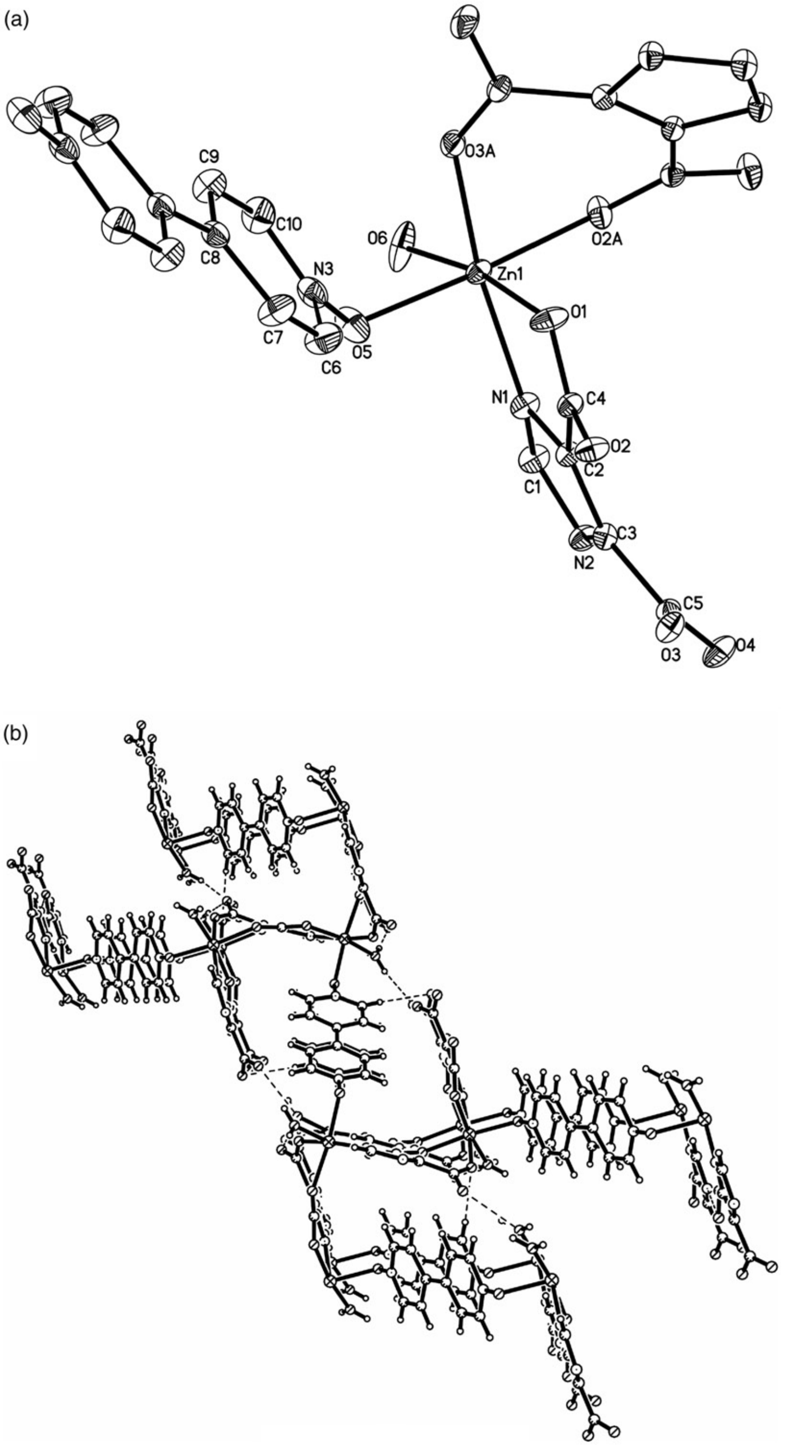

Figure 2. (a) Perspective view of the coordination environment of the Zn ion; (b) the packing diagram of a unit cell of **2** showing the hydrogen bonding interactions as dashed lines.

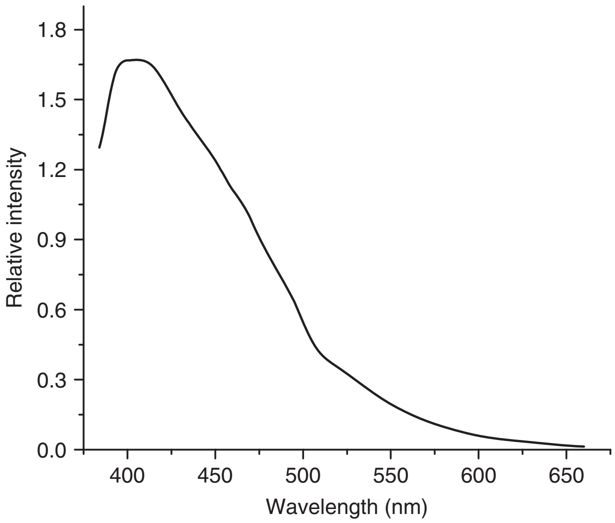

Figure 3. Fluorescence emission spectrum of **2** in the solid state at room temperature.

3.3. *Photoluminescence properties*

The emission spectrum of **2** in the solid state at room temperature was investigated (figure 3). Excitation at 342 nm leads to a strong emission band at 403 nm. Free H_3IMDC shows very weak luminescence in the solid state at ambient temperature upon photo excitation at 342 nm. Therefore, the nature of the organic ligand may play a critical role in the photoluminescence mechanism for **2**, indicating a ligand-centered π–π^* excitation is responsible for emission in **2**. The enhancement of emission for **2** compared with that of the free ligand may be ascribed to increase in ligand conformational rigidity due to coordination to zinc resulting in a decrease in the non-radiative decay of intraligand excited states [19, 20]. Compound **2** appears to be a good candidate of hybrid inorganic–organic photoactive materials.

4. Concluding remarks

We have isolated two new coordination polymers resulting from 4,5-imidazoledicarboxylate and divalent transition metals in the presence of 4,4′-bipyO spacers. Both complexes have been characterized by elemental analysis, FT-IR spectra and single-crystal X-ray diffraction. Compounds **1** and **2** are isostructural, both exhibiting infinite 2-D herringbone architectures. Hydrogen bonding interactions play important roles in formation of the complexes. Complex **2** displays strong emissions at room temperature.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 686156 and 686155 for **1** and **2**.

Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +/44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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