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Ionothermal Syntheses of Two New 2D Metal-Organic Frameworks: $(EMIM)_2[M(Pydc)_2]$ (M = Co, Zn)[1]

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Abstract—Two new coordination polymers, $(EMIM)_2[M(Pydc)_2]$ (M is Co, Zn; EMIM is 1-ethyl-3-methylimidazolium; H_2Pydc is 2,5-pyridinedicarboxylic acid), have been synthesized through the reaction of cobalt or zinc nitrate with H_2Pydc in the ionic liquid medium. The structures exhibit a two-dimensional 4.4-network with the imidazolium cations, acting as charge compensating agent, located between the layers of the coordination anion polymeric frameworks.

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INTRODUCTION

The synthesis of metal-organic materials have attracted increasing attention owing to their intriguing structural chemistry and potential applications in ion-exchange, sorption, catalytic, and nonlinear optical materials [1–7]. Recently, the effort to find novel materials leads to a new type of solvothermal and ionothermal syntheses [8–10]. Ionothermal synthesis is novel materials synthesis method in which ionic liquid (**ILs**) function as reaction media, template, or charge-compensating agent. ILs have many interesting physicochemical properties, such as high thermal stability, high ionic conductivity, tunable solvation strength, and negligible vapor pressure, which eliminates safety concerns of high solvothermal pressures [11–16]. With these attributers, ionothermal synthesis is considered to be more environment-fridently and safer than the traditional hydrothermal reactions, which are usually used in the exploratory syntheses of inorganic-organic hybrid materials. Ionothermal solvent systems can provide different reaction conditions by which novel structure types, such as zeolite and zeolite-type frameworkes [9, 10, 17–20] and metal-organic frameworks (**MOF**) can be obtained [21–25].

There are several examples in which ILs have been successfully applied to the syntheses of novel MOFs. However, to the best of our knowledge, the ionothermal synthesis between the 2,5-pyridinedicarboxylic acid and transition metals has not reported. Here we report the syntheses of two new two-dimensional (2D) metal-organic frameworks: $(EMIM)_2[Co(Pydc)_2]$ (**I**) and $(EMIM)_2[Zn(Pydc)_2]$ (**II**), which have anionic frameworks and 1-ethyl-3-methylimidazolium $[EMIM]^+$ cations as the charge compensating species. The complexes were prepared from the reaction between $Co(NO_3)_2 \cdot 4H_2O$/$Zn(NO_3)_2 \cdot 6H_2O$, H_2Pydc, and triethylamine under the inothermal condations.

[1] The article is published in the original.

EXPERIMENTAL

Materials and methods. All reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyzer. The FT-IR spectrum were recorded from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer. X-ray powder diffraction patterns were recorded with a Bruker AXS D8 advanced automated diffractometer with CuK_α radiation.

Ionothermal synthesis. Complex **I** was prepared by the reaction between $Co(NO_3)_2 \cdot 4H_2O$ (1.5 mmol), H_2Pydc (1.0 mmol), and triethylamine (1.0 ml) dissolved completely in [EMIM]Br (5.0 mmol). The mixture was placed in a 23-ml Teflon-lined stainless-steel autoclave and then heated at 160°C for 4 days to give purple crystals for **I**.

For $C_{26}H_{28}CoN_6O_8$

anal. calcd, %:	C 51.07;	H 4.62;	N 13.74.
Found, %:	C 51.05;	H 4.64;	N 13.77.

IR spectrum (ν, cm^{-1}): 1612 $\nu_{as}(COO^-)$, 1458 $\nu_s(COO^-)$, 1400 $\nu_s(COO^-)$.

Table 1. Crystallographic data and details of the experiment and refinement of structures **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	611.48	617.92
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
Unit cell dimensions:		
a, Å	14.667(4)	14.565(4)
b, Å	9.166(3)	9.280(2)
c, Å	20.939(8)	20.699(5)
β, deg	109.07(3)	108.01(2)
Volume, Å^3	2660.6(15)	2660.7(12)
Z	4	4
ρ_{calcd}, g/cm^3	1.527	1.543
μ, mm^{-1}	0.707	0.985
θ Range, deg	2.06–26.03	2.07–26.05
Reflections collected	3351	3339
Independent reflections (R_{int})	2633 (0.0469)	2624 (0.0367)
Max, min transmission	0.8634, 0.8027	0.8008, 0.7131
Goodness-of-fit on F^2	1.015	1.083
Parameters	187	187
Final *R* indices ($I > 2\theta\ (I)$)*	$R_1 = 0.0453$ $wR_2 = 0.1062$	$R_1 = 0.0511$ $wR_2 = 0.1207$
R indices (all data)	$R_1 = 0.0880$w $wR_2 = 0.1306$	$R_1 = 0.0901$ $wR_2 = 0.1306$
Largest diff. peak and hole, *e*/Å^3	0.400 and –0.542	0.583 and –0.615

Note: * $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$;

$$wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}.$$

Complex **II** was prepared similarly to that of **I** by using $Zn(NO_3)_2 \cdot 6H_2O$ instead of $Co(NO_3)_2 \cdot 4H_2O$.

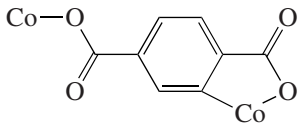
For $C_{26}H_{28}N_6O_8Zn$			
anal. calcd, %:	C 50.54;	H 4.57;	N 13.60.
Found, %:	C 50.55;	H 4.55;	N 13.58.

IR spectrum (ν, cm^{-1}): 1630 ν_{as}(COO$^-$), 1453 ν_s(COO$^-$), 1405 ν_s(COO$^-$).

X-ray crystallographic determination. Crystallographic data of **I** and **II** were collected at room temperature (293(2) K) with a Bruker SMART Apex CCD area-detector diffractometer with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator using the ω-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [26, 27]. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were added theoretically and riding on their parent atoms. Crystallographic data and experimental details for structural analysis are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 706691; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single-crystal X-ray analyses revealed that the two complexes crystallize in the monoclinic space group *C*2/*c*, and are isomorphous, so only the structure of complex **I** is described here. The asymmetrical unit of the unit cell contains one Co center, one Pydc ligand and one [EMIM]$^+$ cation. The Co center is six-coordinate with four oxygen atoms (O(1), O(1*A*), O(4*A*), O(4*B*)) and two nitrogen atoms (N(1) and N(1*A*)) from four individual Pydc ligands (Co(1)–O(4) 2.054(2), Co(1)–O(1) 2.119(2), Co(1)–N(1) 2.157(3) Å) forming a distorted octahedron geometry (Fig. 1). Each Pydc ligand adopts chelating and monodentate coordination modes as it is shown on the scheme below, to connect two individual Co(II) centers.



The pyridyl nitrogen atom and adjacent carboxylate oxygen atom chelate one cobalt atom, forming a five-membered chelate ring, while one oxygen atom of the second carboxylate group coordinates another Co center in *trans* position, and two such asymmetric units form a larger 24-membered ring. Thus, an extended two-dimensional layer structure is formed, which contains rhombic grids with four Co atoms at the centers

Table 2. Selected bond distances and angles for **I** and **II***

Bond	*d*, Å
I	
Co(1)–O(1)	2.119(2)
Co(1)–O(4)$^{\#2}$	2.054(2)
Co(1)–N(1)$^{\#3}$	2.157(3)
Angle	ω, deg
I	
O(1)$^{\#1}$Co(1)O(1)	87.27(15)
O(1)$^{\#1}$Co(1)O(4)$^{\#2}$	112.76(10)
O(1)$^{\#1}$Co(1)O(4)$^{\#3}$	84.33(10)
O(1)Co(1)O(4)$^{\#3}$	112.76(10)
O(4)$^{\#2}$Co(1)O(4)$^{\#3}$	157.04(14)
N(1)$^{\#3}$Co(1)N(1)$^{\#2}$	105.67(15)
Bond	*d*, Å
II	
Zn(1)–O(1)	2.046(3)
Zn(1)–N(1)$^{\#2}$	2.169(3)
Zn(1)–O(4)$^{\#2}$	2.183(3)
Angle	ω, deg
II	
O(1)$^{\#1}$Zn(1)O(1)	88.94(18)
O(1)$^{\#1}$Zn(1)N(1)$^{\#3}$	89.40(13)
O(4)$^{\#2}$Zn(1)O(4)$^{\#3}$	157.21(16)
O(1)Zn(1)N(1)$^{\#3}$	152.65(13)
N(1)$^{\#2}$Zn(1)N(1)$^{\#3}$	104.09(18)
O(1)Zn(1)O(4)$^{\#2}$	115.70(13)
N(1)$^{\#2}$Zn(1)O(4)$^{\#2}$	74.92(12)
O(1)Zn(1)O(4)$^{\#3}$	81.27(12)
N(1)$^{\#2}$Zn(1)O(4)$^{\#3}$	90.99(12)
O(4)$^{\#2}$Zn(1)O(4)$^{\#3}$	157.21(16)

Note: * Symmetry transformations used to generate equivalent atoms: $^{\#1}$ –*x*, *y*, –*z* + 1; $^{\#2}$ *x* – 1/2, *y* + 1/2, *z*; $^{\#3}$– *x* + 1/2, *y* + 1/2, –*z* + 1.

and four Pydc ligands linkers. The lateral Co–Co distances of the Co_4 rhombus are 8.648 Å, and the diagonal Co–Co distances are 14.667(3) and 9.166(2) Å.

The structure of **I** is different from that of complex $[NH_2(CH_3)_2]Fe(Pydc)_2$ (**III**), which was synthesized by using the DMF as reaction media [28]. In complex **III**, Pydc ligand links the adjacent Fe centers to form helical chain, and all the helices extend along the same direction forming a 2D layer structure. However, in complex **I**, the adjacent Co centers were linked by the Pydc ligand to form a linear –Co–Pydc– chain along the *x* direction. The neighboring Co(1) atoms are furthermore connected by O(1), N(1), and O(4*B*) from different Pydc ligands (Fig. 2a) to form a 2D layer structure (Fig. 2b). The layers are parallel to the plane *xy* with a C_2 symmetry for neighboring linear chains. All layers are stacked on the top of each other along the *y* axis (Fig. 3). The $[EMIM]^+$ cations lie between the layers to balance charges. In this context, the ILs as solvent and template play an important role in the assembly of the complex. Apart from affecting the coordination environment of metal ions, furthermore, the ILs possibly affect the structure of the complexes.

Thus, two new metal-organic frameworks $(EMIM)_2[M(Pydc)_2]$ (M is Co (**I**), and Zn (**II**)) are synthesized from the ionothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$/$Zn(NO_3)_2 \cdot 6H_2O$ and H_2Pydc in [EMIM]Br ionic liquid. These complexes are isomorphous, which are new examples of the application of ionic liquids in the synthesis of the metal-organic frameworks. In the reation, the ILs act as solvents, template, and charge compensating agent. In the structure of the title complexes, the compensating imidazolium cations, originated from ILs, are located between the layers of the coordination anion polymeric frameworks. This implies that the cations of the organic molten salts can be used as potential structure-directing templates for the crystal engineering of the porous coordination polymers. Certainly, a large number of experimental data is necessary in order to deeply understand the nature of the ionothermal systems.

The IR spectrum of complex **I** shows characteristic bands of carboxyl group at 1612 cm^{-1} for the antisymmetric stretching and at 1458 and 1400 cm^{-1} for the symmetric stretching. The separation (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ indicate that the presence of the monodentate coordination mode in compond **I** [29], which is consistent with the crystal structure of **I**. The absence of the characteristic bands at around 1700 cm^{-1} in the complex attributed to the protonated carboxylic group indicates that the complete deprotonation of Pydc ligand upon the reaction with Co ions [30].

Photoluminescent properties of **II** are shown in Fig. 4. In the solid state, strong photoluminescent emission bands at 441 nm (λ_{exc} = 365 nm) are observed. There is no obvious emission observed for free H_2Pydc under the same experimental conditions. Therefore, the

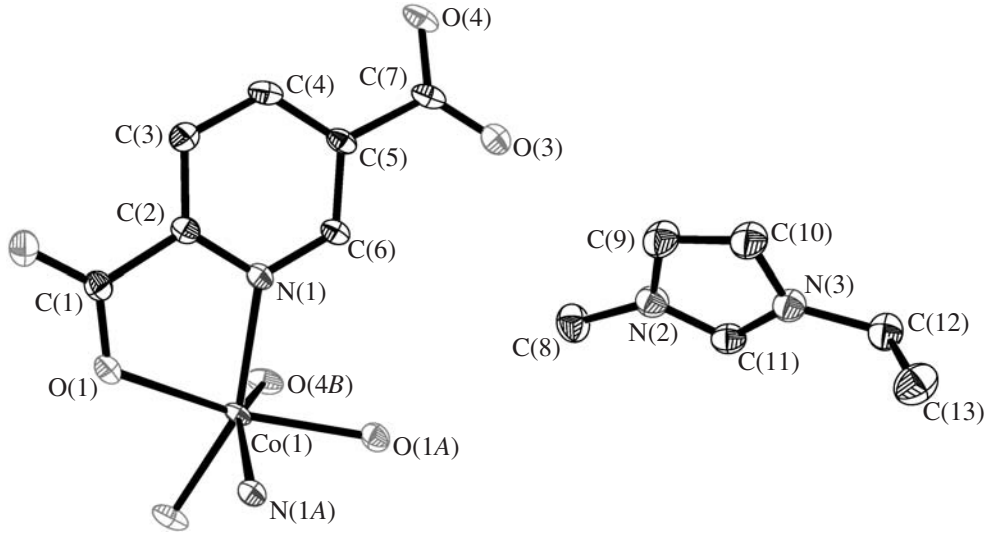


Fig. 1. Coordination environment of the Co ion in complex **I**.

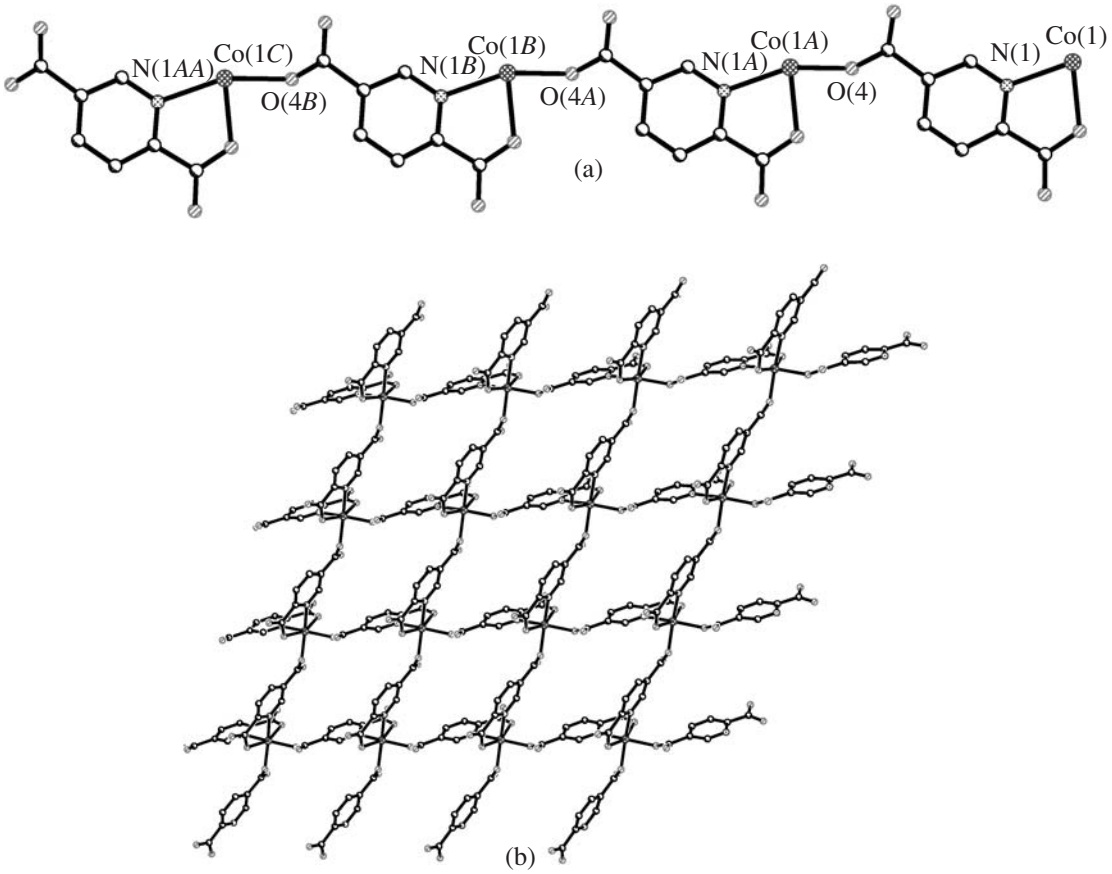


Fig. 2. Section of the linear polymer chain in **I** (a); 2D layer structure along the *xy* plane in **I** (b).

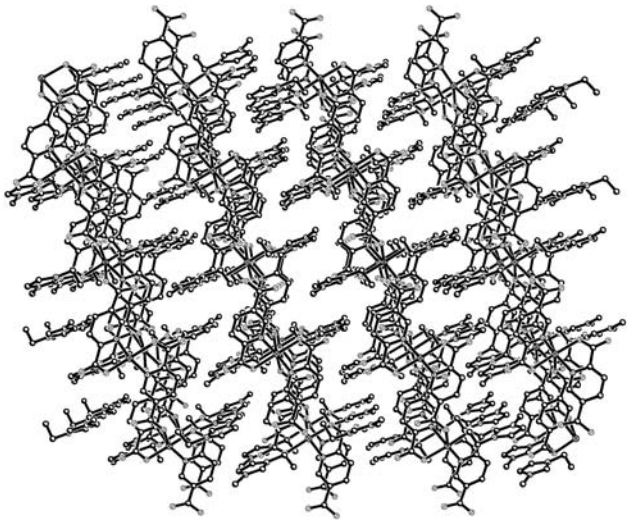


Fig. 3. View of **I** along the crystallographic *y*-axis showing parallel-stacked $[Co(Pydc)_2]^{2-}$ layers and $[EMIM]^+$ cations located between these layers.

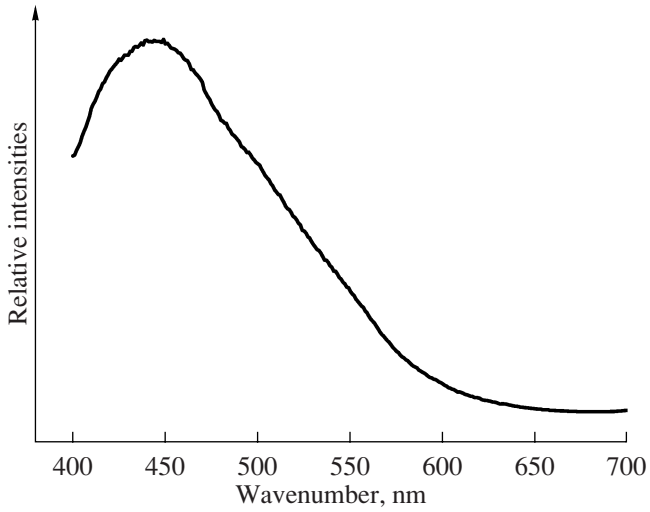


Fig. 4. Photoluminescent spectrum of **I** in the solid state at room temperature.

fluorescent emissions of **II** may be attributed to the charge transition of $Pydc^{2-}$ to zinc atom [31–33].

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