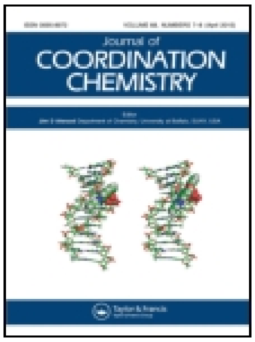

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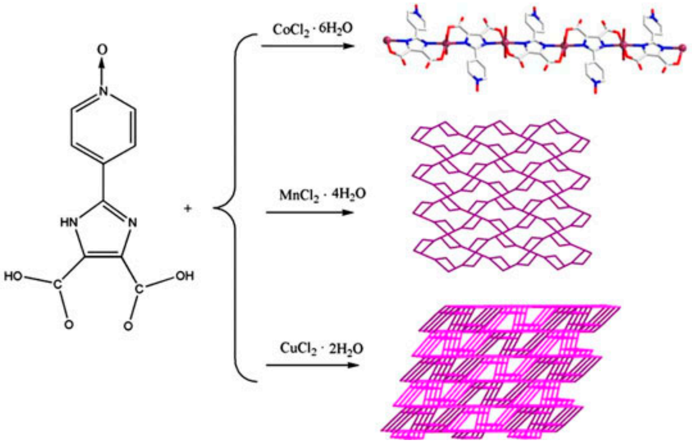

Three metal-organic coordination polymers, $\{[Co(C_{10}H_5N_3O_5)(H_2O)_2]\cdot H_2O\}_n$ (**1**), $\{[Mn_3(C_{10}H_5N_3O_5)_2Cl_2(H_2O)_6]\cdot 2H_2O\}_n$ (**2**), and $\{[Cu_3(C_{10}H_4N_3O_5)_2(H_2O)_3]\cdot 4H_2O\}_n$ (**3**), based on a T-shaped tripodal ligand 4-(4,5-dicarboxy-1H-imidazol-2-yl)pyridine 1-oxide (H_3DCImPyO), were synthesized by the hydrothermal method.

Three coordination polymers, $\{[Co(C_{10}H_5N_3O_5)(H_2O)_2]\cdot H_2O\}_n$ (**1**), $\{[Mn_3(C_{10}H_5N_3O_5)_2Cl_2(H_2O)_6]\cdot 2H_2O\}_n$ (**2**), and $\{[Cu_3(C_{10}H_4N_3O_5)_2(H_2O)_3]\cdot 4H_2O\}_n$ (**3**), based on a T-shaped tripodal ligand 4-(4,5-dicarboxy-1H-imidazol-2-yl)pyridine 1-oxide (H_3DCImPyO), were synthesized under hydrothermal conditions. The polymers showed diverse coordination modes, being characterized by elemental analysis, infrared spectroscopy, and single-crystal X-ray structure analysis. In **1**, the $HDCImPyO^{2-}$ generated a 1-D chain by adopting a μ_2-*k*N, O : *k*N′, O′ coordination mode to bridge two Co(II) ions in two bis-N,O-chelating modes. In **2**, the $HDCImPyO^{2-}$ adopted a μ_3-*k*N, O : *k*O′, O″ : O‴ coordination mode to bridge two crystallographically independent Mn(II) ions, forming a 2-D **hcb** network with $\{6^3\}$ topology. In **3**, by adopting μ_4-*k*N, O : *k*O′, O″ : *k*N″, O‴ : O⁗ coordination, $DCImPyO^{3-}$ bridged three crystallographically independent Cu(II) ions to form a 3-D framework having the **stb** topology.

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Keywords: Coordination polymers; Crystal structure; 4-(4,5-dicarboxy-1H-imidazol-2-yl)pyridine 1-oxide; Hydrothermal condition

1. Introduction

Metal-organic coordination polymers with selected metals and multifunctional ligands have been studied in crystal engineering and supramolecular chemistry because of structural diversities and potential applications as functional materials [1–7]. Most consist of metal ions as connecting centers and multidentate polyfunctional bridging ligands as linkers [8, 9]. New structural architectures with fascinating framework topologies with multifunctional ligands containing N- and O-donors have attracted attention because of diverse coordination modes and interesting properties [10, 11]. Particularly, heterocyclic carboxylic acids such as imidazole carboxylate, pyridine carboxylate, and pyrazole carboxylate have been used as building blocks to investigate the constructions of coordination polymers due to their coordination features under hydrothermal conditions [12–17]. As a bridging ligand, 4-(4,5-dicarboxy-1H-imidazol-2-yl)pyridine 1-oxide (H_3DCImPyO) has seven potential donors allowing formation of higher dimensional structures from which one to three hydrogens can be removed to give H_nDCImPyO ($n = 0, 1, 2$) species by controlling pH. Thus, deprotonated H_nDCImPyO ($n = 0, 1, 2$) exhibits flexible coordination. Frameworks based on H_3DCImPyO have rarely been studied. In our continuing efforts [18–20], we chose H_3DCImPyO as a building block to construct metal-organic frameworks. Herein, we report the syntheses and crystal structures of three metal-organic polymers, $\{[Co(C_{10}H_5N_3O_5)(H_2O)_2]\cdot H_2O\}_n$ (**1**), $\{[Mn_3(C_{10}H_5N_3O_5)_2Cl_2(H_2O)_6]\cdot 2H_2O\}_n$ (**2**), and $\{[Cu_3(C_{10}H_4N_3O_5)_2(H_2O)_3]\cdot 4H_2O\}_n$ (**3**).

2. Experimental

2.1. *Materials and instruments*

Chemicals and solvents were commercially obtained and used without purification. H_3DCImPyO was prepared by the method reported previously [21]. Infrared spectra were recorded on a SHIMADZU IRprestige-21 FTIR-8400S spectrometer from 4000 to 500 cm^{-1}. Elemental analyses were taken on a Perkin-Elmer 240C elemental analyzer.

2.2. *Preparation of 1*

H_3DCImPyO (0.1 mmol, 0.025 g) and $CoCl_2\cdot 6H_2O$ (0.1 mmol, 0.023 g) were placed in a thick Pyrex tube (*ca.* 20 cm in length). After addition of water (2 mL), the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was heated at 160 °C for five days and then slowly cooled to room temperature; colorless block crystals were isolated by filtration, washed with distilled water, and dried in air. IR spectra of **1**: 3438(s), 3253(m), 1655(w), 1581(s), 1510(m), 1442(m), 1391(m), 1352(m), 1291(m), 1256(m), 1214(w), 1121(w), 1065(w), 1023(w), 849(m), 810(w), 795(w), 748(w), 733(w), 696(w), 577(w). Yield of 55% (based on Co). Anal. (%) calcd $C_{10}H_{10}CoN_3O_8$ for: C, 33.44; H, 2.81; N, 11.70. Found: C, 33.36; H, 2.75; N, 11.77.

2.3. *Preparation of 2*

A mixture of $MnCl_2{\cdot}4H_2O$ (0.1 mmol, 0.02 g) and $H_3DCImPyO$ (0.1 mmol, 0.025 g) was placed in a thick Pyrex tube (*ca.* 20 cm in length). After ethanol (0.2 mL) and water (1.7 mL) were added, the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was heated at 150 °C for three days. After being cooled slowly to room temperature, colorless crystals of **2** were isolated by filtration, washed with distilled water, and dried in air. IR spectra of **2**: 3384(s), 3168(m), 1585(s), 1526(m), 1460 (s), 1439(m), 1377(m), 1359(m), 1291(m), 1270(m), 1212(m), 1185(m), 1129(w), 1112(w), 978(w), 964(w), 858(m), 840(m), 817(m), 792(w), 737(w), 693(w), 658(w), 528(m). Yield of 53% (based on Mn). Anal. (%) calcd $C_{10}H_{12}ClMn_{1.50}N_3O_9$ for: C, 27.54; H, 2.77; N, 9.64. Found: C, 27.46; H, 2.71; N, 9.73.

2.4. *Preparation of 3*

A mixture of $CuCl_2{\cdot}2H_2O$ (0.1 mmol, 0.017 g) and $H_3DCImPyO$ (0.1 mmol, 0.025 g) was placed in a thick Pyrex tube (*ca.* 20 cm in length). After ethanol (0.5 mL) and water (1.7 mL) were added, the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was heated at 150 °C for three days. After being cooled slowly to room temperature, colorless crystals of **3** were isolated by filtration, washed with distilled water, and dried in air. IR spectra of **3**: 3421(s), 3091(m), 3052(m), 1685(s), 1635 (m), 1585(s), 1523(s), 1495(s), 1437(m), 1417(m), 1388(m), 1340(m), 1325(m), 1304(m), 1258(m), 1222(m), 1178(m), 1109(s), 1026(w), 825(m), 790(w), 743(w), 704(w), 679(w), 578(w), 550(w), 511(m). Yield of 51% (based on Cu). Anal. (%) calcd $C_{20}H_{22}Cu_3N_6O_{17}$ for: C, 29.69; H, 2.74; N, 10.39. Found: C, 29.62; H, 2.68; N, 10.33.

2.5. *Single-crystal X-ray diffraction*

Single crystals of **1**–**3** were selected for data collection on a Rigaku SCXmini diffractometer equipped with a graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) using an ω

Table 1. Data collection and processing parameters for **1**–**3**.

	1	**2**	**3**
Formula	$C_{10}H_{10}CoN_3O_8$	$C_{10}H_{12}ClMn_{1.50}N_3O_9$	$C_{20}H_{22}Cu_3N_6O_{17}$
M_r	359.14	436.09	809.06
Temperature/K	298(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	9.5100(2)	7.6400(13)	20.8420(5)
b (Å)	13.2000(3)	11.5794(16)	12.8290(3)
c (Å)	13.178(19)	16.947(3)	10.106(3)
α(°)	90	90	90
β(°)	127.500(3)	97.755(11)	96.261(16)
γ(°)	90	90	90
V (Å$^{3)}$	1312.0(4)	1485.5(4)	2686.0(11)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.818	1.950	2.001
μ (mm^{-1})	1.356	1.530	2.450
Total, unique	11,171, 2440	14,942, 3367	13,418, 3077
GOF on F^2	0.977	1.044	1.069
R_1, wR_2 [$I > 2\sigma(I)$]	0.0818, 0.2335	0.0483, 0.1051	0.0441, 0.1041
R_1, wR_2 (all data)	0.1221, 0.2715	0.0719, 0.1142	0.0512, 0.1084

scan mode at room temperature. The absorption correction was carried out by multi-scan method. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 with SHELXL-97 [22, 23]. Topology information for **2** and **3** was obtained using TOPOS 4.0 [24]. All non-H atoms were refined anisotropically. All hydrogens attached to C, N, and O were added theoretically and refined with a riding model and fixed isotropic thermal parameters. Detailed data collection and refinement of compounds **1**–**3** are summarized in table 1, and the selected bond distances and angles of **1**–**3** are listed in tables 2, 3, and 4, respectively. In addition, the hydrogen bonds of complexes **1**–**3** are listed in tables 5, 6, and 7, respectively.

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Co(1)−O(6)	2.079(7)	Co(1)−N(2)	2.162(7)
Co(1)−O(5)	2.090(7)	Co(1)−O(2)$^{\#1}$	2.163(7)
Co(1)−O(4)	2.141(7)	Co(1)−N(1)$^{\#1}$	2.169(7)
O(6)−Co(1)−O(5)	173.7(2)	O(6)−Co(1)−O(4)	92.9(3)
O(5)−Co(1)−O(4)	91.9(2)	O(6)−Co(1)−N(2)	89.7(3)
O(5)−Co(1)−N(2)	87.2(3)	O(4)−Co(1)−N(2)	78.0(2)
O(6)−Co(1)−O(2)$^{\#1}$	84.0(3)	O(5)−Co(1)−O(2)$^{\#1}$	91.6(2)
O(4)−Co(1)−O(2)$^{\#1}$	174.3(2)	N(2)−Co(1)−O(2)$^{\#1}$	106.7(2)
O(6)−Co(1)−N(1)$^{\#1}$	93.6(3)	O(5)−Co(1)−N(1)$^{\#1}$	89.8(3)
O(4)−Co(1)−N(1)$^{\#1}$	97.7(2)	N(2)−Co(1)−N(1)$^{\#1}$	174.7(2)
O(2)$^{\#1}$−Co(1)−N(1)$^{\#1}$	77.8(2)		

Note: Symmetry transformation: #1: *x*, −*y* + 1/2, *z* + 1/2.

Table 3. Selected bond lengths (Å) and angles (°) of **2**.

Mn(1)−O(2)	2.136(3)	Mn(1)−O(6)	2.188(3)	Mn(2)−O(3)	2.148(2)
Mn(1)−O(7)	2.225(2)	Mn(1)−Cl(1)	2.4628(12)	Mn(2)−O(4)	2.083(2)
Mn(1)−O(5)$^{\#1}$	2.200(2)	Mn(1)−N(2)	2.426(3)	Mn(2)−O(8)	2.189(3)
O(2)−Mn(1)−O(6)	92.03(12)	O(2)−Mn(1)−O(5)$^{\#1}$	87.74(10)	O(6)−Mn(1)−O(5)$^{\#1}$	105.10(11)
O(2)−Mn(1)−O(7)	174.03(11)	O(6)−Mn(1)−O(7)	82.44(11)	O(5)$^{\#1}$−Mn(1)−O(7)	91.53(9)
O(2)−Mn(1)−N(2)	71.59(9)	O(6)−Mn(1)−N(2)	82.75(10)	O(5)$^{\#1}$−Mn(1)−N(2)	158.30(9)
O(7)−Mn(1)−N(2)	109.71(9)	O(2)−Mn(1)−Cl(1)	99.37(9)	O(6)−Mn(1)−Cl(1)	162.18(9)
O(5)$^{\#1}$−Mn(1)−Cl(1)	89.09(7)	O(7)−Mn(1)−Cl(1)	86.54(8)	N(2)−Mn(1)−Cl(1)	87.88(7)
O(3)$^{\#2}$−Mn(2)−O(3)	180.00(13)	O(4)−Mn(2)−O(3)	86.58(9)	O(4) −Mn(2)−O(8)	92.30(10)
O(3)$^{\#2}$−Mn(2)−O(8)	91.12(10)	O(4)$^{\#2}$−Mn(2)−O(8)	87.70(10)	O(4)$^{\#2}$−Mn(2)−O(4)	180.00(13)
O(3)−Mn(2)−O(8)	88.88(10)	O(4)$^{\#2}$−Mn(2)−O(3)	93.42(9)	O(8)$^{\#2}$−Mn(2)−O(8)	180.0

Notes: Symmetry transformation: #1: *x*, −*y* + 3/2, *z* + 1/2; #2: −*x* + 1, −*y* + 1, −*z*; #3: *x*, −*y* + 3/2, *z* − 1/2.

Table 4. Selected bond lengths (Å) and angles (°) of **3**.

Cu(1)−O(3)	2.075(3)	Cu(2)−N(2)	1.975(2)	Cu(3)−O(4)	1.959(3)
Cu(1)−O(1)	1.957(3)	Cu(2)−O(5)$^{\#3}$	2.183(3)	Cu(3)−N(1)	1.961(3)
Cu(1)−O(6W)	2.209(4)	Cu(2)−O(2)	2.203(3)		
O(1)$^{\#1}$−Cu(1)−O(1)	170.45(14)	O(3)−Cu(1)−O(3)$^{\#1}$	93.4(2)	O(5)$^{\#4}$−Cu(2)−O(2)	91.13(10)
O(1)$^{\#1}$−Cu(1)−O(3)	92.23(11)	O(6W)$^{\#1}$−Cu(1)−O(6W)	82.8(2)	O(5)$^{\#3}$−Cu(2)−O(2)	88.87(10)
O(3)−Cu(1) −O(6W)	91.88(15)	N(2)$^{\#2}$−Cu(2)−N(2)	180.00(13)	O(5)$^{\#3}$−Cu(2)−O(5)$^{\#4}$	180.0
O(1)$^{\#1}$−Cu(1)−O(6W)	85.34(12)	N(2) −Cu(2)−O(5)$^{\#4}$	96.38(10)	O(2)$^{\#2}$−Cu(2)−O(2)	180.0
O(1)−Cu(1)−O(3)	94.32(11)	N(2) −Cu(2)−O(2)$^{\#2}$	101.42(9)	O(4) −Cu(3)−N(1)	82.74(11)
O(1)−Cu(1)−O(6W)	87.51(13)	N(2)−Cu(2)−O(5)$^{\#3}$	83.62(10)	O(4)−Cu(3)−O(4)$^{\#5}$	180.0
O(3)$^{\#1}$−Cu(1)−O(6W)	174.73(16)	N(2)−Cu(2)−O(2)	78.58(9)	O(4)−Cu(3)−N(1)$^{\#5}$	97.26(11)
				N(1)−Cu(3)−N(1)$^{\#5}$	180.0

Notes: Symmetry transformation: #1: −*x* + 1, *y*, −*z* + 1/2; #2: −*x* + 1/2, −*y* + 3/2, −*z*; #3: −*x* + 1/2, *y* + 1/2, −*z* − 1/2; #4: *x*, −*y* + 1, *z* + 1/2; #5: −*x* + 1, −*y* + 1, −*z*; #6: −*x* + 1/2, *y* − 1/2, −*z* − 1/2.

Table 5. Hydrogen bond lengths (Å) and angles (°) of **1**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	(DHA)
O1 W−H1 WA···O1$^{\#2}$	0.85	2.16	2.799(11)	132
O1 W−H1 WB···O7	0.85	1.90	2.586(14)	137
O1 W−H1WB···N3	0.85	2.48	3.317(13)	169
O5−H5A···O7$^{\#3}$	0.82	1.86	2.660(16)	166
O5−H5B···O1W$^{\#4}$	0.85	1.95	2.756(11)	157
O6−H6A···O3$^{\#5}$	0.82	2.10	2.849(11)	152
O6−H6B···O1W$^{\#6}$	0.83	2.05	2.717(13)	137
C8−H8···O2$^{\#7}$	0.93	2.53	3.095(15)	120

Notes: Symmetry transformation: #1: x, −y + 1/2, z + 1/2; #2: x, 1 + y, z; #3: 1 − x, 1 − y, 1 − z; #4: 1 − x, −1/2 + y, 1/2 − z; #5: 2 − x, 1/2 + y, 3/2 − z; #6: 2 − x, 1 − y, 1 − z; #7: x, 1/2 − y, 1/2 + z.

Table 6. Hydrogen bond lengths (Å) and angles (°) of **2**.

D−H···A	d(D−H)	d(HvA)	d(D···A)	(DHA)
O6−H6A···O4$^{\#4}$	0.90	2.27	2.960(4)	133
O6−H6B···O9$^{\#5}$	0.82	2.09	2.801(4)	146
O7−H7A···O1$^{\#6}$	0.82	1.98	2.783(4)	166
O7−H7B···O3$^{\#7}$	0.99	1.89	2.857(3)	163
O8−H8A···O1$^{\#8}$	0.82	2.05	2.735(4)	141
O8−H8B···O1$^{\#9}$	0.93	1.82	2.720(4)	162
O9−H9A···Cl1$^{\#10}$	0.82	2.72	3.463(4)	153
O9−H9A···O7$^{\#10}$	0.82	2.52	3.120(4)	131
O9−H9B···Cl1$^{\#11}$	0.89	2.58	3.449(4)	167
O9−H9B···O5$^{\#2}$	0.89	2.49	2.939(4)	112
C8−H8···Cl1$^{\#12}$	0.93	2.78	3.437(4)	128
C9−H9···O9$^{\#2}$	0.93	2.56	3.467(5)	166
C10−H10···Cl1$^{\#9}$	0.93	2.69	3.428(4)	137

Notes: Symmetry transformation: #1: x, −y + 3/2, z + 1/2; #2: −x + 1, −y + 1, −z; #3: x, −y + 3/2, z − 1/2; #4: x, 3/2 − y, 1/2 + z; #5: x, 1 + y, z; #6: −x, −1/2 + y, 1/2 − z; #7: 1 − x, 1/2 + y, 1/2 − z; #8: x, −1 + y, z; #9: −x, 2 − y, −z; #10: 1 + x, −1 + y, z; #11: 1 − x, −1/2 + y, 1/2 − z; #12: −x, 1/2 + y, 1/2 − z.

Table 7. Hydrogen bond lengths (Å) and angles (°) of **3**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	(DHA)
O6W−H6B···O9W$^{\#7}$	0.85	2.06	2.877(5)	163
O8W−H8A···O1$^{\#8}$	0.80	2.30	3.069(5)	163
O8W−H8A···O2$^{\#8}$	0.80	2.48	3.144(5)	142
O8W−H8B···O3$^{\#5}$	0.90	2.21	3.027(5)	151
O9W−H9A···O8W	0.73	2.13	2.817(6)	157
O9W−H9B···O5$^{\#9}$	0.94	1.91	2.833(5)	166
O7W−H9D···O9W$^{\#10}$	0.90	2.15	3.007(5)	159
C7−H7···O5$^{\#11}$	0.93	2.30	3.178(4)	157
C8−H8···O2$^{\#12}$	0.93	2.51	3.276(4)	140
C9−H9···O8W	0.93	2.35	3.197(6)	151

Notes: Symmetry transformation: #1: −x + 1, y, −z + 1/2; #2: −x + 1/2, −y + 3/2, −z; #3: −x + 1/2, y + 1/2, −z − 1/2; #4: x, −y + 1, z + 1/2; #5: −x + 1, −y + 1, −z; #6: −x + 1/2, y − 1/2, −z − 1/2; #7: 1−x, 1 + y, 1/2 − z; #8: x, −1 + y, z; #9: 1/2 − x, 1/2 − y, −z; #10: 1 − x, y, 1/2 − z; #11: 1/2 − x, 1/2 + y, −1/2 − z; #12: 1/2 − x, −1/2 + y, −1/2 − z.

3. Results and discussion

3.1. *Descriptions of crystal structures*

Single crystal X-ray analysis reveals that **1** crystallizes in the monoclinic system, space group $P2_1/c$. It consists of one Co(II), one partly deprotonated $HDCImPyO^{2-}$, two coordinated waters, and one lattice water in the asymmetric unit. As shown in figure 1(a), Co(II) is in a slightly distorted octahedral environment, six-coordinate by two deprotonated $HDCImPyO^{2-}$ ligands via two imidazole N, two O of carboxylate, and two waters. The N

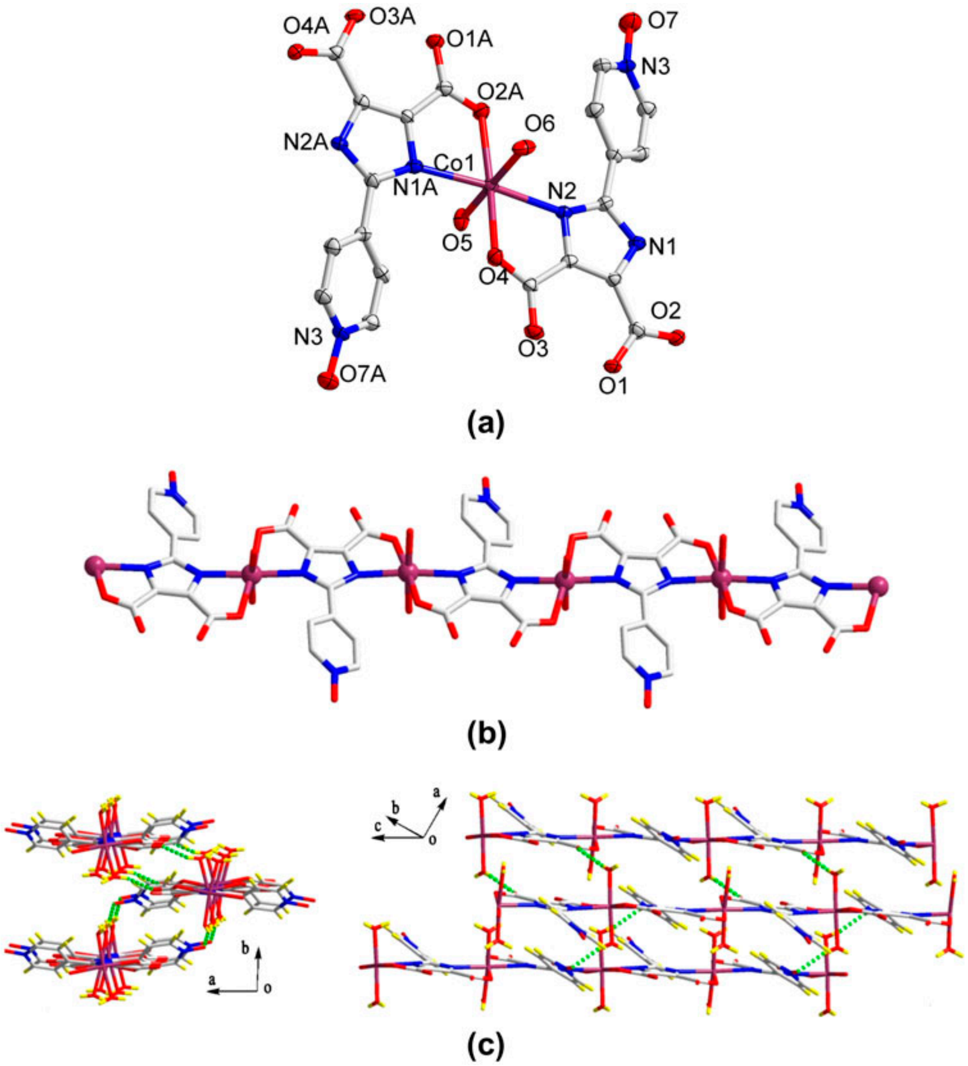
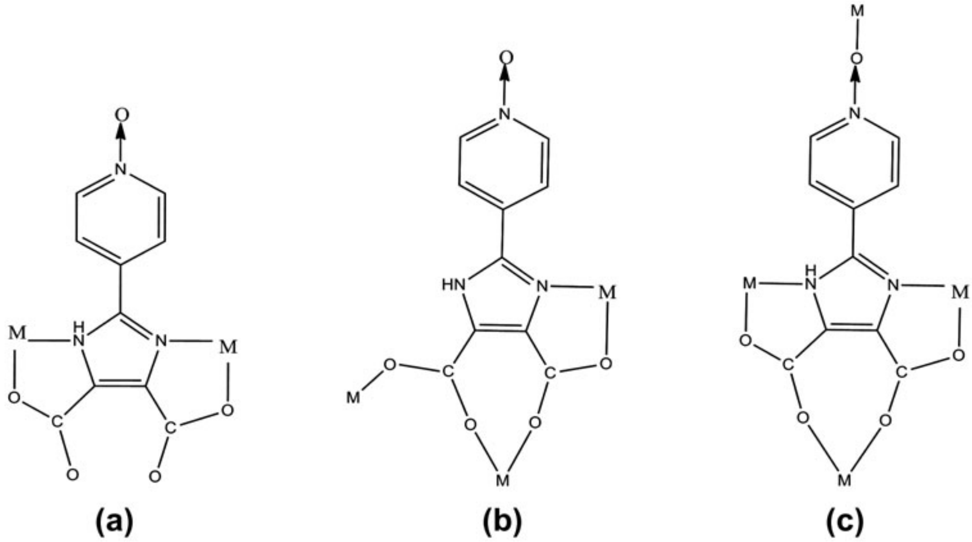


Figure 1. (a) Coordination environment of Co(II) in **1** with the ellipsoids drawn at the 30% probability level. The hydrogens are omitted for clarity. Symmetry code: (A) *x*, 0.5 − *y*, 0.5 + *z*. (b) 1-D chain of **1**. (c) 2-D supramolecular structure of **1** linked by hydrogen bonds indicated by dashed line (green) in different directions (see http://dx.doi.org/10.1080/00958972.2015.1028926 for color version).



Scheme 1. Coordination modes of $H_3DCImPyO$ in **1**–**3**.

of imidazole and O of carboxylate form a five-membered metallocycle. The bond lengths of Co1−N2 and Co1−N1 are 2.162(7) and 2.169(7) Å, respectively, which are similar to the bond length of Co−N in $[Co(C_{10}H_6N_3O_4)_2(H_2O)_2]$ ($C_{10}H_6N_3O_4$ = 2-(pyridine-4-yl)-1H-4,5-imidazoledicarboxylic acid) [2.168(3) Å] [25]. The Co−O bond lengths ranged from 2.079(7) to 2.163(7) Å, comparable to Co−O bond lengths in $[Co_4(HL)_4(bpy)(py)(H_2O)_5]_2\cdot 0.5H_2O$ (H_3L = 2-(pyridin-2-yl)-1H-imidazole-4,5-dicarboxylate acid) [2.042(4)−2.114(3) Å] [26]. The dihedral angles between imidazole ring plane and pyridyl ring plane in $HDCImPyO^{2-}$ ligands are all 29.282°. The $HDCImPyO^{2-}$ in **1** adopts a μ_2-kN, O : kN′, O′ coordination mode [scheme 1(a)] to bridge two Co(II) ions in two bis-N,O-chelating modes. As shown in figure 1(b), the overall structure of **1** is a 1-D chain. Moreover, O–H···O and O–H···N hydrogen bonds give a 2-D supramolecular structure [figure 1(c)].

Single crystal X-ray diffraction reveals that **2** crystallizes in the monoclinic system, space group $P2_1/c$, and displays a 2-D coordination network. The asymmetric unit of **2** contains one and a half crystallographically independent Mn^{2+} ions, one deprotonated HDCImPyO^{2-}, three coordinated waters, one coordinated Cl^-, and one lattice water [figure 2(a)]. The two crystallographically independent Mn(II) ions, i.e. $[MnO_4NCl]$ and $[MnO_6]$, are in distorted octahedral coordination environments. The six-coordinate Mn1 is surrounded by two oxygens from two carboxylate groups of different $H_3DCImPyO$ ligands with Mn–O distances from 2.136(3) to 2.200(2) Å, one nitrogen from $H_3DCImPyO$ with Mn–N distance of 2.426(3) Å, and two coordinated waters. The bond lengths of Mn–O in **2** are comparable with those found in $[Mn_{1.5}(\mu_3\text{-PhIDC})(H_2O)_3]_n$ (μ_3-PhIDC = 2-phenyl-1H-imidazole-4,5-dicarboxylic acid) [2.1560(15)−2.1691(15) Å] [27], but the Mn–N bond lengths in **2** are longer than those found in $[Mn_{1.5}(\mu_3\text{-PhIDC})(H_2O)_3]_n$ [2.2223(19)−2.2249(18) Å]. The bond lengths between Mn1 and two oxygens from two lattice waters range from 2.188(3) to 2.225(2) Å, which are similar to those in $[Mn_3(IMDC)_2(H_2O)_4]$ (IMDC = 4,5-imidazoledicarboxylate) [28]. The bond length between Mn1 and chloride (Cl^-) [2.4628(12) Å]

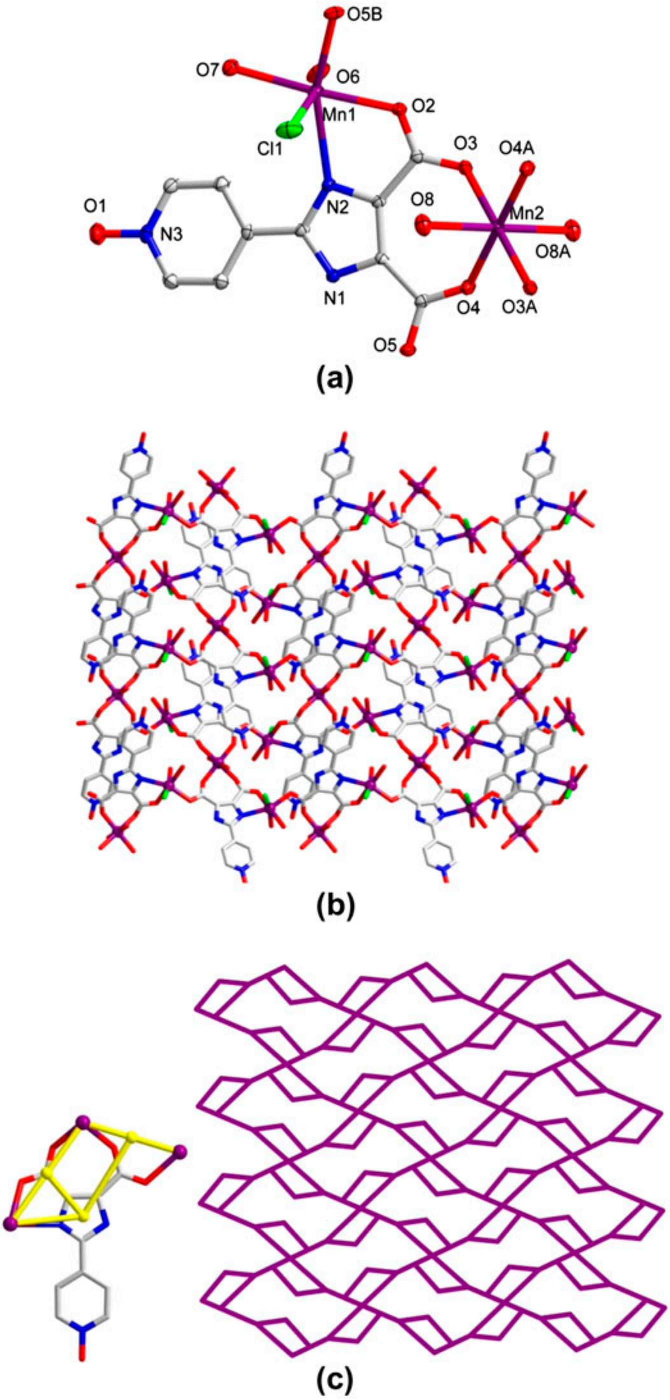


Figure 2. (a) Coordination environment of Mn^{2+} in **2**. Free water and most hydrogens are omitted for clarity (30% ellipsoid probability). Symmetry codes: (A) $1-x$, $1-y$, $-z$; (B) x, $1.5-y$, $0.5+z$. (b) 2-D network in **2**. (c) Single **hcb** network of **2**. (d) 3-D framework created by repeating 2-D network and multiple hydrogen bonding.

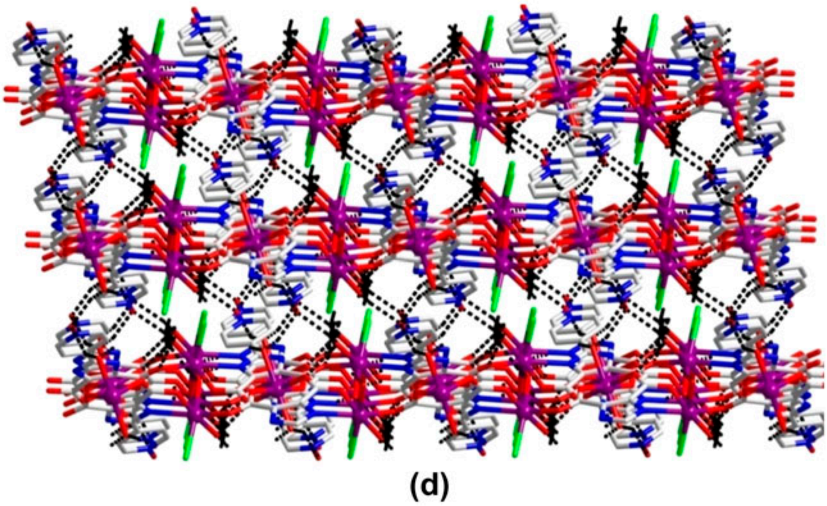


Figure 2. (*Continued*).

is consistent with that in [MnCl($C_{16}H_{14}N_2O_2$)(H_2O)] (aquachloro[N,N′-ethylenebis(salicylideneiminato)]) [2.4680(16) Å] [29]. Generally, the Mn–O bond lengths are 2.083(2)–2.189 (3) Å, comparable to those in similar coordination polymers based on heterocyclic dicarboxylate ligands and manganese [30]. The coordination modes of the two carboxylate groups from H_3DCImPyO in **2** are the same, monodentate (O2, O3, O4, and O5). Each HDCImPyO^{2-} adopts a μ_3-*k*N, O : *k*O′, O″ : O‴ coordination mode [scheme 1(b)] linking two Mn(II) ions and acting as a linker to form a 2-D network [figure 2(b)]. Mn1 and Mn2, as two-connected node and four-connected node, respectively, give a simple **hcb** network [figure 2(c)] with the Schlăfli symbol $\{6^3\}$ calculated by TOPOS software. Indeed, in **2**, each layer is entangled directly by multiple hydrogen bonding interactions between carboxylate oxygens from H_3DCImPyO and free waters. The 2-D layer structure became a 3-D framework via hydrogen bond interactions, as shown in figure 2(d).

Single crystal analysis reveals that **3** crystallizes in the monoclinic system, space group *C*2/*c*. The asymmetric unit of **3** contains one DCImPyO^{3-}, four waters, and three crystallographically independent Cu ions, two of which are located in a special position with the site occupancy factor of 0.5 (that of Cu2: 0.25). In addition, the carboxyl groups of H_3DCImPyO are completely deprotonated, and the completely deprotonated DCImPyO^{3-} participates in monodentate coordination. The imidazole groups of H_3DCImPyO take part in coordination with Cu ions. There are two types of coordination environments around the Cu ions. As shown in figure 3(a), metal centers Cu1 and Cu2 are both located in distorted octahedral coordination environments, thus only Cu2 is represented in detail. Cu2 is six-coordinate by two O from monodentate carboxylate groups of two different DCImPyO^{3-} ligands, two O from the O–N bond of DCImPyO^{3-} and two N from two different DCImPyO^{3-} ligands. The Cu2−N2 bond length [1.975(2) Å] is comparable with those in Cu_2(ppt)·1.5H_2O (H_2ppt = 5-(4-pyridyl)-1H-1,2,4-triazole-3-thiol) [31]. The bond lengths of Cu2−O2 and Cu2−O5 are 2.203(3) and 2.183(3) Å, respectively, which are similar to Cu−O bond lengths in coordination polymers based on pyridine-4,5-imidazoledicarboxylic acid ligands [32]. In addition, the bond angles of N2−Cu2−O2 and N2−Cu2−O5 are 78.58

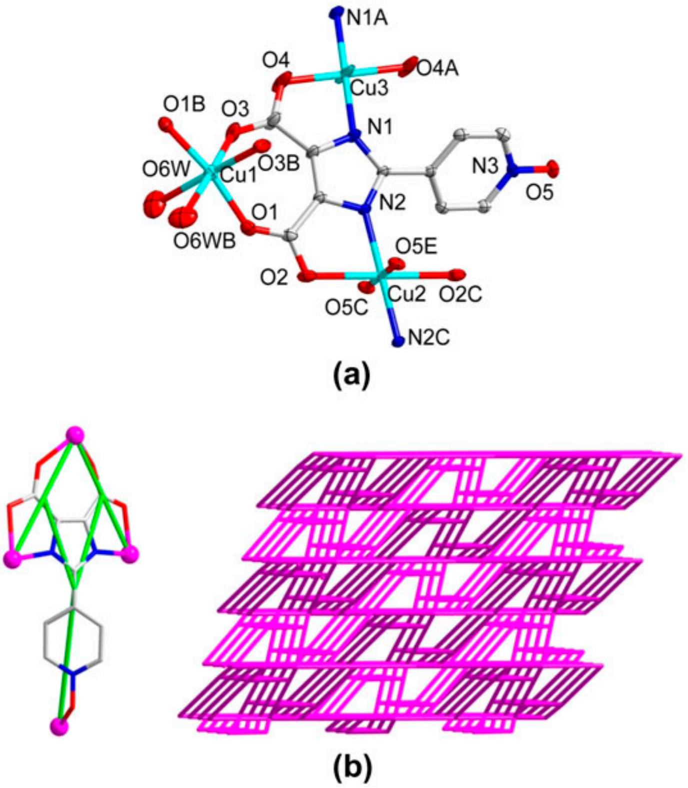


Figure 3. (a) Coordination environment of Cu^{2+} in **3**. Free water and most hydrogens are omitted for clarity (30% ellipsoid probability). Symmetry codes: (A) $1-x$, $1-y$, $-z$; (B) $1-x$, y, $0.5-z$; (C) $0.5-x$, $0.5+y$, $-0.5-z$; (D) $0.5-x$, $1.5-y$, $-z$; (E) x, $1-y$, $0.5+z$. (b) Schematic representation of the $\{4^2.8^2.10^2\}\{4^3.6^2.8\}_2$ topology.

(9)° and 96.38(10)°, respectively. Cu3 has a square planar coordination environment, with the equatorial sites occupied by two oxygens of a monodentate carboxylate group and two nitrogens from two $DCImPyO^{3-}$ ligands. The bond angle of N1−Cu3−O4 is 82.74(11)°. As a three-connected node, each $DCImPyO^{3-}$ adopting a μ_4-*k*N, O : *k*O′, O″ : *k*N″, O‴ : O⁗ coordination mode [scheme 1(c)] in **3** bridges three Cu(II) ions with Cu−Cu separations of 5.862(12) Å (Cu1−Cu2), 10.4091(13) Å (Cu1−Cu3), and 6.118(4) Å (Cu2−Cu3) Å. When viewed along the *c* axis, the 1-D rectangular channels are ~6.2 × 10.3 Å. To better understand the framework topology, **3** was simplified as four-connected rectangular planar nodes (organic linker), and the assembly of these nodes generates a 3-D framework with **stb** topology [figure 3(b)].

4. Conclusion

Three metal-organic coordination polymers based on the T-shaped tripodal ligand H_3DCImPyO were synthesized under hydrothermal conditions and structurally characterized. Complex **1** was a 1-D chain with a μ_2-*k*N, O:*k*N′, O′ coordination. Complex **2** displayed a 2-D

hcb network with the {6^3} topology. By being simplified as three-connected rectangular planar nodes, **3** generated a 3-D framework having the **stb** topology. The three complexes with various coordination modes containing the H_3DCImPyO ligand provide a good comparison with the reported coordination polymers based on other tripodal ligands [33]. It is assumed that such 1-D, 2-D, and 3-D stacking in complexes have an impact on photophysical properties in solid state as a result of effective intermolecular π–π interactions. H_3DCImPyO exhibits diverse coordination modes, and is thus a good candidate for constructing novel frameworks.

Supplementary material

CCDC Nos. 984428, 982268, and 982267 contain the supplementary crystallographic data of **1**, **2**, and **3** for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Disclosure statement

No potential conflict of interest was reported by the authors.

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