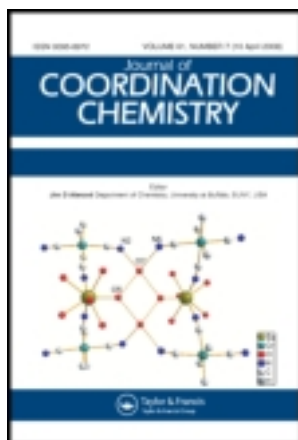


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Assembly of two coordination polymers [Cu(BIM)(suc)]_n and [Cd(BIM)(ox)(H₂O)]_n constructed from bis(imidazol-1-yl)methane

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Assembly of two coordination polymers [Cu(BIM)(suc)]_n and [Cd(BIM)(ox)(H₂O)]_n constructed from bis(imidazol-1-yl)methane

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Two coordination polymers [Cu(BIM)(suc)]_n (**1**) and [Cd(BIM)(ox)(H₂O)]_n (**2**) (where BIM = bis(imidazol-1-yl)methane, suc = succinic dianion, and ox = oxalic dianion) have been solvothermally synthesized and characterized by single-crystal X-ray diffraction. Complex **1** crystallizes in the monoclinic space group *C2/c* with *a* = 12.2302(8) Å, *b* = 11.4007(6) Å, *c* = 10.1791(6) Å, *β* = 118.4090(10)°, *V* = 1248.38(13) Å³, and *Z* = 4. Cu(II) is square planar with nitrogen from BIM ligand and oxygen from the suc in the *trans* arrangement. Each BIM is bidentate bridging two Cu(II)s to generate a 1-D zigzag chain; the suc bridges two Cu(II)s in a monodentate *gauche* conformation, which results in the formation of wavy 2-D (4, 4) grid arrays. Complex **2** crystallizes in the monoclinic space group *P2(1)/n* with *a* = 10.8042(3) Å, *b* = 9.1053(2) Å, *c* = 12.0134(6) Å, *β* = 96.394(1)°, *V* = 1174.47(7) Å³, and *Z* = 4. Cd(II) is coordinated in a distorted decahedral geometry. Each BIM is bidentate bridging two Cd(II)s to form a 1-D infinite zigzag chain; each ox bridges two neighboring Cd(II)s in a distinct zigzag chain in a chelating/chelating coordination mode, which extends the 1-D chain to a 2-D supramolecular network.

Keywords: Cadmium; Copper; Bis(imidazol-1-yl)methane; Crystal structure; Oxalate; Succinate

1. Introduction

Self-assembly of metal–organic coordination polymers and the field of crystal engineering have been rapidly developing areas in supramolecular chemistry [1–5]. Supramolecular self-assembly has led to the formation of a wide variety of 0-D, 1-D, 2-D, and 3-D frameworks possessing different structural features and functional properties that can be exploited in magnetism, catalysis, nonlinear optics, molecular separation, toxic material adsorption, and molecular sensors [6–10]. Some molecular architectures have been designed and synthesized by judicious combination of a metal “node” and an organic ligand “spacer.” In the self-assembly process, many factors influence the formation of the final architectures, such as solvent system, template,

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central metal, and anion [11–13]. Minor changes in the ligands may lead to the formation of different structures and complicate the fine-tuning of the framework [14, 15]. A large number of inorganic–organic hybrid compounds have been self-assembled using different nitrogen-containing organic ligands [16–19].

Multidentate N-donor spacer ligands play key roles in the fabrication of molecular materials as well as in crystal engineering involving supramolecular self-assembly, because of their molecular geometry and flexibility. As an example, ligands such as 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, and trans-bis-(4-pyridyl)ethene form various coordination polymers with distinct structural features [20, 21]. A flexible N-donor ligand, i.e. bis(imidazol-1-yl)methane (BIM), has attracted considerable attention in the field of crystal engineering. Several coordination compounds of BIM with metal Cu(II), Zn(II), Cd(II), or Ag(I) have been reported [22, 23]. In previous studies, we have shown that coordination polymers with interesting topological structures can be obtained *via* self-assembly of BIM with suitable metal ions [24]. As an extension of our previous study, we herein report the syntheses and structures of two coordination polymers, [Cu(BIM)(suc)]_n (**1**) and [Cd(BIM)(ox)(H₂O)]_n (**2**).

2. Experimental

2.1. Materials and methods

All chemicals were obtained commercially and used as received. BIM was prepared by the literature method [25]. FT–IR spectra were recorded from 4500 to 400 cm⁻¹ as KBr pellets on a Bio-Rad FTS 3000 Excalibur series infrared spectrometer. Thermogravimetric analysis (TGA) measurements were made using a TA instrument TA50. Samples were heated at 10°C min⁻¹ from 40°C to 800°C in a dynamic nitrogen atmosphere. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

2.2. Synthesis of [Cu(BIM)(suc)]_n (**1**)

CuCl₂·2H₂O (85 mg, 0.5 mmol), succinic acid (59 mg, 0.5 mmol), NaOH (40 mg, 1.0 mmol) and BIM (75 mg, 0.5 mmol) were dissolved in H₂O (8 mL) and ethanol (2 mL), and the resulting mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure at 160°C for 2 days and then slowly cooled to room temperature at a rate of 10°C h⁻¹. Blue crystals of [Cu(BIM)(suc)] suitable for X-ray analysis were obtained in 46% yield based on Cu. Anal. Calcd for C₁₁H₁₂CuN₄O₄. C, 40.31; H, 3.69; N, 17.09; Found: C, 39.51; H, 3.27; N, 16.95; IR (KBr, cm⁻¹): $\nu = 3114s, 3022w, 2959w, 1581s, 1498m, 1444w, 1312s, 1226s, 1111m, 1083s, 1041w, 948s, 887s, 762s, 710w, 685w, 661s, 628s, 519m$.

2.3. Synthesis of [Cd(BIM)(ox)(H₂O)]_n (**2**)

CdCl₂·2.5H₂O (114 mg, 0.5 mmol), oxalic acid (40 mg, 0.5 mmol), NaOH (40 mg, 1.0 mmol) and BIM (75 mg, 0.5 mmol) were dissolved in H₂O (10 mL), and the resulting

mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure at 160°C for 2 days and then slowly cooled to room temperature at a rate of 10°C h⁻¹. Colorless crystals of [Cd(BIM)(ox)(H₂O)]_n suitable for X-ray analysis were obtained in 58% yield. Anal. Calcd for C₉H₁₀Cd N₄O₅. C, 29.49; H, 2.75; N, 15.28; Found: C, 29.60; H, 2.32; N, 15.23; IR (KBr, cm⁻¹): ν = 3426s, 3128m, 3112m, 1615s, 1524w, 1507m, 1442w, 1417w, 1302s, 1230m, 1113m, 1088s, 1038w, 840m, 793s, 745m.

2.4. Crystal structure determination

A single crystal of **1** or **2** with dimensions 0.3 mm × 0.2 mm × 0.2 mm or 0.4 mm × 0.04 mm × 0.02 mm was removed and covered with a layer of hydrocarbon oil, attached to a glass fiber and data were collected at 273(2) K for **1**, 298(2) K for **2** using a Bruker/Siemens SMART APEX instrument (Mo-K α radiation, λ = 0.71073 Å). Data were measured using a ω - φ scan mode in the range 2.3 < θ < 28.1 for **1**. A total of 4363 reflections were collected with 1371 unique ones (R_{int} = 0.058), of which 1200 reflections with $I > 2\sigma(I)$ were observed. For **2**, in the range 2.4 < θ < 27.0, a total of 12,787 reflections were collected with 2554 unique ones (R_{int} = 0.103), of which 2119 reflections with $I > 2\sigma(I)$ were observed. Cell parameters were retrieved using SMART software [26] and refined using SAINTplus [27] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINTplus software. Absorption corrections were applied using SADABS [28]. The structure was solved by direct methods and refined by least squares on F^2 using the SHELXTL program package [29] with R = 0.045, wR = 0.121 ($w = [\sigma^2(F_0^2) + (0.0538P)^2 + 4.7264P]^{-1}$, where $P = (F_0^2 + 2F_C^2)/3$), S = 1.11, $(\Delta/\delta)_{\text{max}}$ < 0.001, $(\Delta\rho)_{\text{max}}$ = 1.39 and $(\Delta\rho)_{\text{min}}$ = -0.81 e Å⁻³ for **1** and R = 0.036, wR = 0.074 ($w = [\sigma^2(F_0^2) + (0.0315P)^2 + 0.0000P]^{-1}$, where $P = (F_0^2 + 2F_C^2)/3$), S = 0.97, $(\Delta/\delta)_{\text{max}}$ = 0.001, $(\Delta\rho)_{\text{max}}$ = 0.80, and $(\Delta\rho)_{\text{min}}$ = -0.92 e Å⁻³ for **2**. All non-hydrogen atoms were refined anisotropically and hydrogens were placed in riding mode. No decomposition was observed during data collection. The crystallographic data and structure refinement are presented in table 1; selected bond distances and angles are given in tables 2 and 3.

3. Results and discussion

3.1. Description of the crystal structure of **1**

The crystal structure reveals that **1** consists of one Cu(II), one BIM, and one dicarboxylate in the asymmetric unit. The Cu(II) is coordinated in a square-planar geometry with nitrogens from BIM and oxygens from carboxylate *trans* with N–Cu and O–Cu bond lengths of 1.996(3) and 1.944(2) Å, respectively (figure 1), similar to those of other Cu(II) complexes containing N-coordinated ligand [30]. Each BIM is bidentate, bridging two Cu(II)s to generate a 1-D zigzag chain along the *b*-axis. The dihedral angle between the two imidazole rings in the same BIM is 71.4°, consistent with literature results [22]. Succinate coordinates monodentate with Cu(II) bridging the two Cu(II)s in a distinct 1-D zigzag chain, resulting in wavy 2-D (4, 4) grid arrays, as shown in figure 2. Succinates adopt *gauche* conformation, as shown in scheme 1, different from other coordination polymers containing succinate, which have the more stable *anti*

Table 1. Crystal data and structure refinement summary for **1** and **2**.

Compound number	1	2
Empirical formula	C ₁₁ H ₁₂ CuN ₄ O ₄	C ₉ H ₁₀ Cd N ₄ O ₅
Formula weight	327.79	366.61
Temperature (K)	273(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/n
Unit cell dimensions (Å, °)		
<i>a</i>	12.2302(8)	10.8042(3)
<i>b</i>	11.4007(6)	9.1053(2)
<i>c</i>	10.1791(6)	12.0134(6)
α	90	90
β	118.4090(10)	96.394(1)
γ	90	90
Volume (Å ³), <i>Z</i>	1248.38(13), 4	1174.47(7), 4
Calculated density (Mg m ⁻³)	1.744	2.073
Absorption coefficient (mm ⁻¹)	1.77	1.88
<i>F</i> (000)	668	720
Crystal size (mm ³)	0.30 × 0.20 × 0.20	0.40 × 0.04 × 0.02
θ range for data collection (°)	2.3–28.1	2.4–27.0
Limiting indices	–15 ≤ <i>h</i> ≤ 8; –14 ≤ <i>k</i> ≤ 12; –12 ≤ <i>l</i> ≤ 12	–13 ≤ <i>h</i> ≤ 13; –11 ≤ <i>k</i> ≤ 11; –15 ≤ <i>l</i> ≤ 15
Reflections collected	4363	12787
Independent reflections	1371 [<i>R</i> (int) = 0.058]	2554 [<i>R</i> (int) = 0.103]
Absorption correction	SADABS	SADABS
Max. and min. transmission	0.7186 and 0.6189	0.963 and 0.914
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1371/0/93	2554/3/178
Goodness-of-fit on <i>F</i> ²	1.11	0.97
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0446, <i>wR</i> ₂ = 0.1086	<i>R</i> ₁ = 0.0360, <i>wR</i> ₂ = 0.0708
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0521, <i>wR</i> ₂ = 0.1213	<i>R</i> ₁ = 0.0460, <i>wR</i> ₂ = 0.0744
Largest difference peak and hole (e Å ⁻³)	1.39 and –0.81	0.80 and –0.92

Table 2. Selected bond lengths (Å) and angles (°) for [Cu(BIM)(suc)]_n.

Cu(1)–O(1)	1.944(2)	Cu(1)–N(1)	1.996(3)
O(1) ⁱⁱⁱ –Cu(1)–O(1)	180.0	O(1) ⁱⁱⁱ –Cu(1)–N(1)	90.57(10)
O(1)–Cu(1)–N(1)	89.43(10)	N(1) ⁱⁱⁱ –Cu(1)–N(1)	180.0

Symmetry transformations used to generate equivalent atoms: ⁱⁱⁱ –*x* + 1/2, –*y* + 1/2, –*z* + 1.

conformation [31]. The *gauche* conformation in succinate may favor the wavy 2-D (4, 4) grid arrays when combined with the V-shaped BIM. In **1**, because of the conformation and monodentate succinate, there exists hydrogen bonding between the coordinated oxygens in succinate and C–H in BIM (table 4). However, classical hydrogen bonding and π – π stacking interactions are not observed between neighboring layers.

3.2. Description of the crystal structure of **2**

Single-crystal X-ray diffraction revealed that **2** crystallized in a monoclinic space group *P*2(1)/*n*. The asymmetric unit of **2** contains one cadmium(II), one oxalate,

Table 3. Selected bond lengths (Å) and angles (°) for [Cd(BIM)(ox)(H₂O)]_n.

Cd(1)–N(4)	2.280(3)	Cd(1)–N(1)	2.284(3)
Cd(1)–O(1)	2.317(2)	Cd(1)–O(2)	2.389(2)
Cd(1)–O(6)	2.405(3)	Cd(1)–O(5) ⁱ	2.412(3)
Cd(1)–O(1) ⁱ	2.543(2)		
N(4)–Cd(1)–N(1)	171.13(11)	O(1)–Cd(1)–N(4)	98.07(10)
N(1)–Cd(1)–O(1)	86.84(10)	N(4)–Cd(1)–O(2)	86.09(10)
N(1)–Cd(1)–O(2)	88.64(10)	O(1)–Cd(1)–O(2)	70.36(8)
O(6)–Cd(1)–N(4)	91.96(10)	N(1)–Cd(1)–O(6)	96.24(10)
O(1)–Cd(1)–O(6)	78.99(8)	O(2)–Cd(1)–O(6)	148.65(9)
N(4)–Cd(1)–O(5) ⁱ	85.41(10)	N(1)–Cd(1)–O(5) ⁱ	92.75(10)
O(5) ⁱ –Cd(1)–O(1)	158.27(8)	O(2)–Cd(1)–O(5) ⁱ	131.36(8)
O(6)–Cd(1)–O(5) ⁱ	79.46(9)	N(4)–Cd(1)–O(1) ⁱ	90.42(9)
N(1)–Cd(1)–O(1) ⁱ	81.62(9)	O(1)–Cd(1)–O(1) ⁱ	148.31(3)
O(2)–Cd(1)–O(1) ⁱ	79.91(7)	O(6)–Cd(1)–O(1) ⁱ	131.42(8)
O(5) ⁱ –Cd(1)–O(1) ⁱ	52.40(7)		

Symmetry transformations used to generate equivalent atoms: ⁱ–x + 1/2, y – 1/2, –z + 3/2.

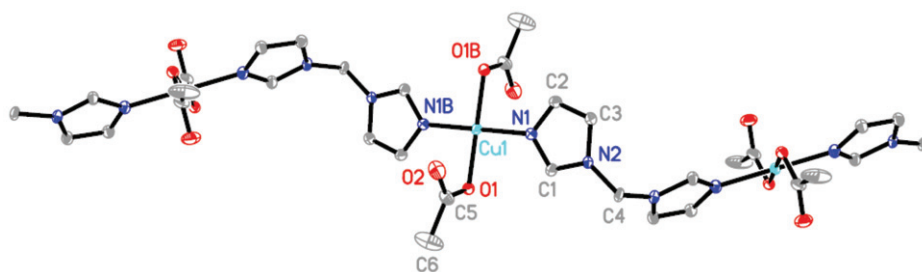


Figure 1. ORTEP of **1**, together with atom numbering scheme. The thermal ellipsoids are drawn at 30% probability. Hydrogens are omitted for clarity.

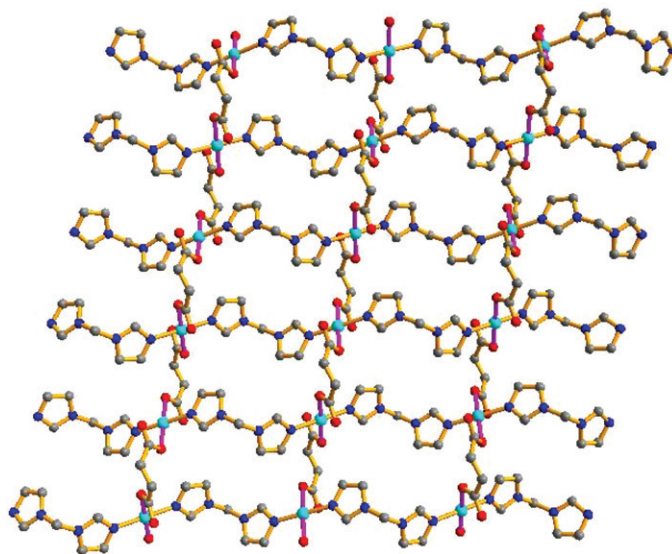
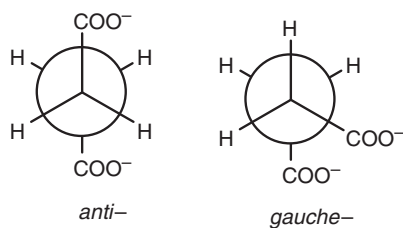


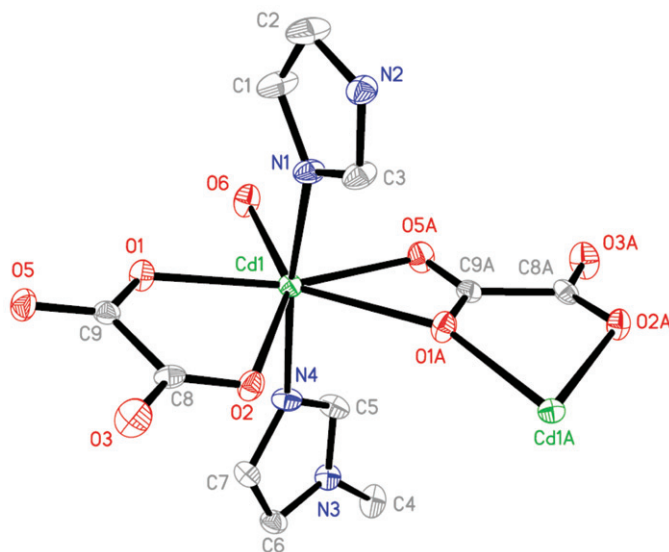
Figure 2. View of the 2-D square grid network showing *gauche* conformation of succinate in **1**.



Scheme 1. Two conformations of succinate in coordination polymers.

Table 4. Hydrogen-bond geometry for **1** (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
C1-H1...O1	0.93	2.49	2.902(4)	107
C4-H4A...O2 ⁱ	0.97	2.41	3.244(3)	144
C4-H4B...O2 ⁱⁱ	0.97	2.41	3.244(3)	144
C1-H1...O2 ⁱⁱ	0.93	2.44	3.212(4)	141
C2-H2...O1 ⁱⁱⁱ	0.93	2.31	3.241(4)	176

Symmetry codes: ⁱ $-x, -y, -z + 1$; ⁱⁱ $x, -y, z + 1/2$; ⁱⁱⁱ $x - 1/2, -y + 1/2, z - 1/2$.Figure 3. ORTEP of the local coordination environment around Cd(II) at 30% probability ellipsoids in **2**.

one coordinated water molecule, and one BIM. As illustrated in figure 3, each cadmium(II) is coordinated by two nitrogens of imidazole from two individual BIM ligands [Cd1-N4 = 2.280(3) Å and Cd1-N1 = 2.284(3) Å], four oxygens of two μ_2 -ox²⁻, and one independent water (O6) molecule in a distorted decahedral geometry [Cd1-O1 = 2.317(2) Å, Cd1-O6 = 2.405(3) Å, Cd1-O1A = 2.543(2) Å, Cd1-O2 = 2.389(2) Å,

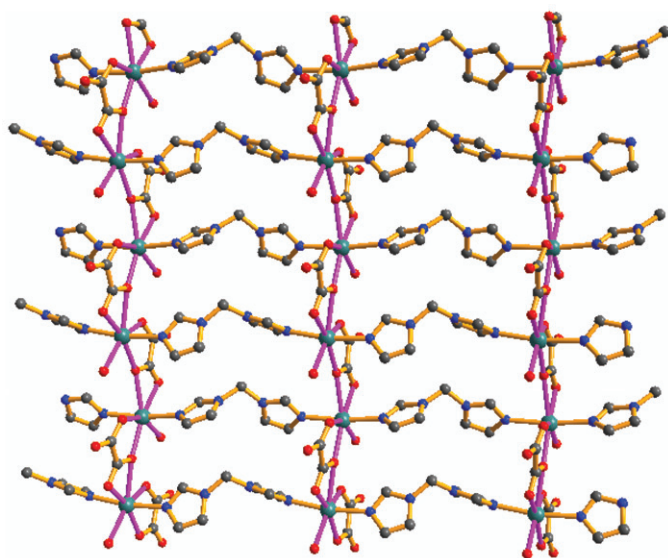


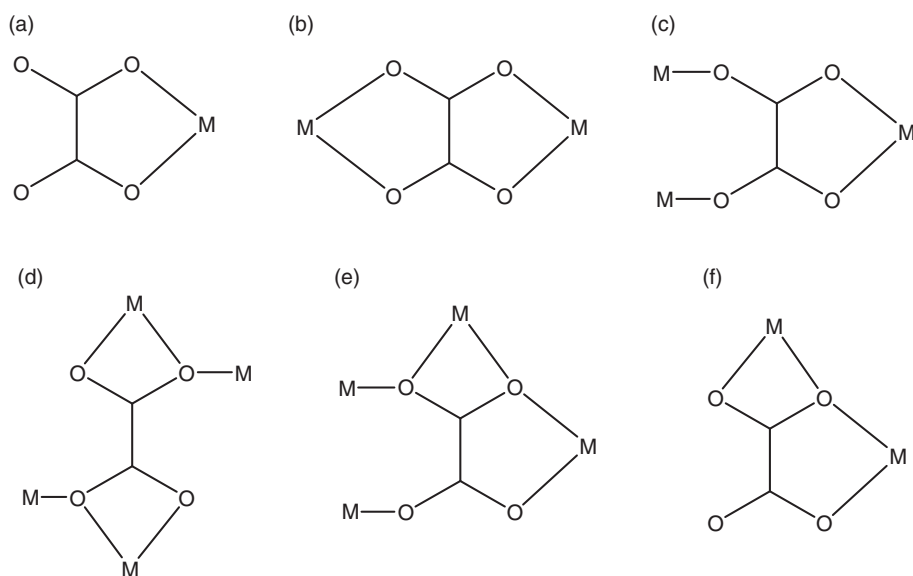
Figure 4. View of the 2-D layer from 1-D zigzag chains in **2**.

and $\text{Cd1-O5A} = 2.412(3) \text{ \AA}$]. The O1, O2, O1A, O5A, and O6 comprise the equatorial plane, and N1 and N4 are located at the axial positions [$\text{N1-Cd1-N4} = 171.13(11)^\circ$].

Each BIM is bidentate, bridging two Cd(II)s to form a 1-D infinite zigzag chain along the *a*-axis (figure 4), with a pitch of 10.804 \AA . The dihedral angle between the two imidazole rings in the same BIM is 78.2° . As shown in scheme 2 (mode f), each oxalate bridges two neighboring Cd(II)s in the zigzag chain in a chelating/chelating coordination mode, which extends the 1-D chain to a 2-D supramolecular network (figure 4). The oxalates in **2** adopt $\eta^2:\eta^2:\mu_2$ coordination. Oxalate as a polycarboxylate has versatile binding modes (scheme 2) [32]; however, the $\eta^2:\eta^2:\mu_2$ coordination mode has not been described before for metal-organic frameworks. Significant hydrogen-bonding interaction ($\text{O6-H6A} \cdots \text{O3}^i$, $2.896(4)$, $153(3)$, symmetry codeⁱ: $x + 1/2, -y + 1/2, z + 1/2$, $\text{O6-H6B} \cdots \text{O2}^{ii}$, $2.790(4)$, $169(5)$, symmetry codeⁱⁱ: $-x + 1/2, y + 1/2, -z + 3/2$) between the carboxylate oxygen and coordinated water is also observed in **2** (table 5); this interaction causes the two neighboring layers to further pack into a 3-D structure (figure 5). By comparison, in our earlier reported cadmium coordination polymer based on BIM [33], the cadmium was coordinated in distorted octahedral geometry and an overall 3-D supramolecular network was formed through bridging, uncoordinated water.

3.3. Thermal properties of **1** and **2**

The thermal analysis (TGA) under nitrogen showed the first weight loss for **1** of 37.8% from 266 to 279°C corresponds to loss of succinate (Calcd: 36.0%). Upon further heating, weight loss occurs in the temperature range 480°C to 542°C , corresponding to release of BIM and complete decomposition of **1** with 25.8% residual weight

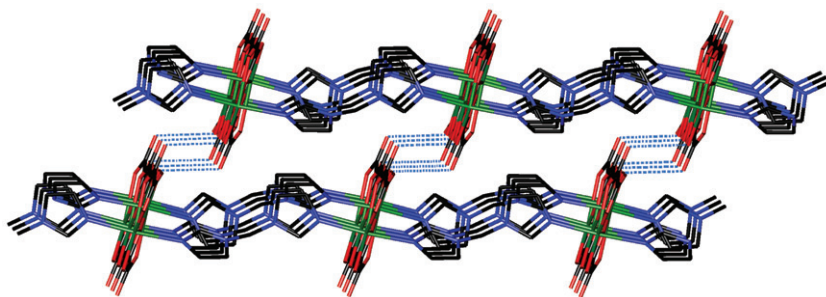


Scheme 2. Coordination modes of oxalate.

Table 5. Hydrogen-bond geometry for **2** (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
C5-H5...O5 ⁱ	0.93	2.59	3.128 (5)	117
C5-H5...O5 ^v	0.93	2.34	3.060 (4)	134
O6-H6B...O2 ^{iv}	0.82(1)	1.98(1)	2.790(4)	169(5)
O6-H6A...O3 ^v	0.82(1)	2.14(2)	2.896(4)	153(3)

Symmetry codes: ⁱ $-x+1/2, y-1/2, -z+3/2$; ^{iv} $-x+1/2, y+1/2, -z+3/2$; ^v $x+1/2, -y+1/2, z+1/2$.

Figure 5. View of the 3-D supramolecular network formed *via* weak hydrogen-bond interactions in **2**.

corresponding to CuO (Calcd: 24.3%). A three-step weight loss can be identified in **2**. The first step from 210°C to 232°C with a weight loss of 5.7% is attributed to loss of coordinated water (Calcd: 4.9%), while the second step with a weight loss of 39.6% occurred from 340°C to 366°C, corresponding to loss of BIM (Calcd: 40.4%).

The third step, which was observed in a temperature range from 402°C to 580°C with a residual weight 36.2%, probably corresponds to the complete decomposition of **2** at 580°C.

4. Conclusions

In summary, two coordination polymers, $[\text{Cu}(\text{BIM})(\text{suc})]_n$ (**1**) and $[\text{Cd}(\text{BIM})(\text{ox})(\text{H}_2\text{O})]_n$ (**2**), were synthesized using MCl_2 ($\text{M} = \text{Cu}$ or Cd) and BIM in the presence of succinic acid or oxalic acid. Compound **1** has wavy 2-D (4, 4) grid arrays, in which the Cu(II) is coordinated in a square-planar geometry with nitrogens from BIM and oxygens from succinate in the *trans* arrangement. Each BIM is bidentate bridging to generate a 1-D zigzag chain; the monodentate succinates bridge two Cu(II)s with *gauche* conformation. Compound **2** has a 3-D supramolecular network that results from hydrogen bonding; Cd(II) is coordinated in a distorted decahedral geometry. Each BIM is bidentate bridging two Cd(II)s to form a 1-D infinite zigzag chain; each oxalate bridges two neighboring Cd(II)s in the zigzag chain in chelating/chelating coordination. Both **1** and **2** exhibit some novel structural features, such as succinate and oxalate adopting *gauche* conformation and $\eta^2 : \eta^2 : \mu_2$ coordination, respectively, and also show good stabilities.

Supplementary material

Additional crystallographic details and complete bond lengths and angles, coordinates, and displacement parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publication no: CCDC 688403 for **1** and CCDC 789811 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

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