

基于醚氧桥联四羧酸配体构筑的铜(II)/钴(II)/镍(II)配位聚合物的合成、结构和在 Knoevenagel 缩合反应中的催化性质

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广东省特种建筑材料及其绿色制备工程技术研究中心,广州 510300)

摘要: 采用水热方法,选用醚氧桥联四羧酸配体 2,3',4,4'-二苯醚四羧酸(H₄deta)与 2,2'-联吡啶(2,2'-bipy)、4,4'-联吡啶(4,4'-bipy)分别与 CuCl₂·2H₂O、CoCl₂·6H₂O 和 NiCl₂·6H₂O 在 160 °C 下反应,得到了 3 个配位聚合物:二维层结构的 {[Cu₂(μ₅-deta)(2,2'-bipy)₂·2H₂O]}_n (**1**)、一维链结构的 [Co₂(μ₄-deta)(2,2'-bipy)₂(H₂O)₃]_n (**2**) 和三维网络结构的 {[Ni₂(μ₃-deta)(μ-4,4'-bipy)_{2,5}(H₂O)₅·3H₂O]}_n (**3**),并对其结构和催化性质进行了研究。研究表明,在室温下化合物 **1** 在 Knoevenagel 缩合反应中显示出很好的催化活性。

关键词: 配位聚合物; 四羧酸; 催化性质; Knoevenagel 缩合反应

中图分类号: O614.121; O614.81²; O614.81³

文献标识码: A

文章编号: 1001-4861(2021)10-1900-11

DOI: 10.11862/CJIC.2021.208

Synthesis, Structures and Catalytic Activity in Knoevenagel Condensation Reaction of Cu(II)/Co(II)/Ni(II) Coordination Polymers Based on Ether-Bridged Tetracarboxylic Acid

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Abstract: Three Cu(II)/Co(II)/Ni(II) coordination polymers, namely {[Cu₂(μ₅-deta)(2,2'-bipy)₂·2H₂O]}_n (**1**), [Co₂(μ₄-deta)(2,2'-bipy)₂(H₂O)₃]_n (**2**) and {[Ni₂(μ₃-deta)(μ-4,4'-bipy)_{2,5}(H₂O)₅·3H₂O]}_n (**3**), have been constructed hydrothermally using H₄deta (2,3',4,4'-diphenyl ether tetracarboxylic acid), 2,2'-bipy (2,2'-bipyridine)/4,4'-bipy (4,4'-bipyridine) and CuCl₂·2H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, respectively, at 160 °C. The products were isolated as stable crystalline solids and were characterized by IR spectra, elemental analyses, thermogravimetric analyses and single-crystal X-ray diffraction analyses. Single-crystal X-ray diffraction analyses reveal that the three compounds crystallize in the triclinic or monoclinic systems, space groups $P\bar{1}$ or $P2_1/n$. Compound **1** discloses a 2D sheet. Compound **2** features a 1D chain structure. Compound **3** shows a 3D framework. The catalytic activity in the Knoevenagel condensation reaction of these compounds were investigated. Compound **1** exhibited an excellent catalytic activity in the Knoevenagel condensation reaction at room temperature. CCDC: 2086961, **1**; 2086962, **2**; 2086963, **3**.

Keywords: coordination polymer; tetracarboxylic acid; catalytic properties; Knoevenagel condensation reaction

收稿日期: 2021-06-01。收修改稿日期: 2021-06-26。

福建工程学院重点科研创新平台开放基金(No.KF-C19004)、广东省普通高校特色创新类项目(No.2019GKTSCX014)、广州市科技计划项目(No.201904010381, 201804010499)和广东轻工职业技术学院拔尖人才项目(No.152241202)资助。

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Coordination polymers with ordered structures are built from metal ions as nodes with versatile coordination geometry and multidentate organic linkers. The functional coordination polymers has caught increasing attention in recent years and turn out to be one of the fastest growing areas in synthetic chemistry and material science^[1-12]. In the last five years, organic carboxylate ligands have been widely used in synthesizing coordination polymers due to strong coordination ability of the carboxyl group and rich coordination modes^[6-7,13-16]. Among them, ether-bridged carboxylic acids have been extensively applied as versatile building blocks toward the assembly of metal-organic architectures^[17-18]. 2,3',4,4' - diphenyl ether tetracarboxylic acid (H_4deta) is a good bridging ligand for constructing coordination polymers^[19], under considering structural semi-rigidity, which has multiple coordinate sites involving eight carboxylate oxygen atoms and one O-ether donor.

Knoevenagel condensation is one of the imperative and essential condensation processes in synthetic organic chemistry, in which α, β -unsaturated products formed via carbon-carbon double bond involve a nucleophilic addition reaction between active methylene and carbonyl compounds followed by a dehydration reaction^[20-24]. Products obtained are extensively used as specialty chemicals and intermediates in the synthesis of fine chemicals such as carbocyclic, substituted alkenes, biologically active compounds, therapeutic drugs, calcium antagonists, natural products, functional polymers, coumarin derivatives, flavors and perfumes. Transition metal - catalyzed Knoevenagel condensation reactions have recently received much attention^[25-27], mainly due to low price and moderate toxicity of the catalysts in combination with their high activity.

Herein, we report the synthesis, crystal structures and catalysis activity in Knoevenagel condensation of three Cu (II)/Co (II)/Ni (II) coordination polymers with H_4deta and 2,2'-bipy (2,2'-bipyridine)/4,4'-bipy (4,4'-bipyridine) ligands.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of AR grade and used without further purification. Carbon, hydrogen

and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectrum was recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku-Dmax 2400 diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154\text{ }06\text{ nm}$); the X-ray tube was operated at 40 kV and 40 mA; the data collection range (2θ) was between 5° and 45° . Solution ^1H NMR spectra were recorded on a JNM ECS 400M spectrometer.

1.2 Synthesis of $\{[\text{Cu}_2(\mu_5\text{-deta})(2,2'\text{-bipy})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**1**)

A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.034 g, 0.2 mmol), H_4deta (0.035 g, 0.1 mmol), 2,2' - bipy (0.031 g, 0.2 mmol), NaOH (0.016 g, 0.4 mmol) and H_2O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at $120\text{ }^{\circ}\text{C}$ for three days, followed by cooling to room temperature at a rate of $10\text{ }^{\circ}\text{C} \cdot \text{h}^{-1}$. Blue block-shaped crystals were isolated manually, and washed with distilled water. Yield: 45% (based on H_4deta). Anal. Calcd. for $\text{C}_{36}\text{H}_{26}\text{Cu}_2\text{N}_4\text{O}_{11}(\%)$: C 52.88, H 3.20, N 6.85; Found(%): C 52.63, H 3.18, N 6.88. IR (KBr, cm^{-1}): 3 507w, 3 070w, 1 602s, 1 495w, 1 473w, 1 447w, 1 424w, 1 370s, 1 313w, 1 290w, 1 254w, 1 232w, 1 175w, 1 139w, 1 082w, 1 032w, 957w, 903w, 836w, 778m, 735w, 690w, 663w.

1.3 Synthesis of $[\text{Co}_2(\mu_4\text{-deta})(2,2'\text{-bipy})_2(\text{H}_2\text{O})_3]_n$ (**2**)

Synthesis of **2** was similar to **1** except using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.048 g, 0.2 mmol) instead of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Orange block-shaped crystals of **2** were isolated manually, and washed with distilled water. Yield: 56% (based on H_4deta). Anal. Calcd. for $\text{C}_{36}\text{H}_{28}\text{Co}_2\text{N}_4\text{O}_{12}(\%)$: C 52.32, H 3.41, N 6.78; Found(%): C 52.55, H 3.39, N 6.81. IR (KBr, cm^{-1}): 3 422w, 3 062w, 1 602s, 1 543s, 1 489w, 1 473m, 1 440s, 1 374s, 1 307w, 1 262m, 1 233w, 1 150w, 1 121w, 1 063w, 1 022w, 952w, 902w, 840w, 803w, 770m, 736w, 687w, 637w.

1.4 Synthesis of $\{[\text{Ni}_2(\mu_3\text{-deta})(\mu\text{-4,4'}\text{-bipy})_{2.5}(\text{H}_2\text{O})_5] \cdot 3\text{H}_2\text{O}\}_n$ (**3**)

A mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.048 g, 0.2 mmol),

H₄deta (0.035 g, 0.1 mmol), 4,4'-bipy (0.031 g, 0.2 mmol), NaOH (0.016 g, 0.4 mmol) and H₂O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 120 °C for three days, followed by cooling to room temperature at a rate of 10 °C · h⁻¹. Green block-shaped crystals were isolated manually, and washed with distilled water. Yield: 50% (based on H₄deta). Anal. Calcd. for C₄₁H₄₂Ni₂N₅O₁₇(%): C 49.53, H 4.26, N 7.04; Found(%): C 49.77, H 4.28, N 7.02. IR (KBr, cm⁻¹): 3 436m, 1 607s, 1 553s, 1 495w, 1 418w, 1 383s, 1 263w, 1 232w, 1 161w, 1 122w, 1 072w, 1 046w, 1 010w, 952w, 814m, 770w, 699w, 637w.

The compounds are insoluble in water and common organic solvents, such as methanol, ethanol, acetone and DMF.

1.5 Structure determination

The single crystals with dimensions of 0.23 mm × 0.22 mm × 0.20 mm (**1**), 0.22 mm × 0.18 mm × 0.17 mm

(**2**) and 0.23 mm × 0.21 mm × 0.20 mm (**3**) were collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer with Mo K α (λ =0.071 073 nm). The structures were solved by direct methods and refined by full matrix least-square on F^2 using SHELXTL-2014 program^[28]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms (except for the ones bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of water molecules were located by different maps and constrained to ride on their parent O atoms. A summary of the crystallography data and structure refinements for **1**~**3** is given in Table 1. The selected bond lengths and angles for **1**~**3** are listed in Table 2. Hydrogen bond parameters of **1**~**3** are given in Table 3~5.

CCDC: 2086961, **1**; 2086962, **2**; 2086963, **3**.

Table 1 Crystal data for compounds **1**~**3**

Compound	1	2	3
Chemical formula	C ₃₆ H ₂₆ Cu ₂ N ₄ O ₁₁	C ₃₆ H ₂₈ Co ₂ N ₄ O ₁₂	C ₄₁ H ₄₂ Ni ₂ N ₅ O ₁₇
Molecular weight	817.69	826.48	994.21
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a / nm	0.940 73(8)	0.875 36(7)	1.402 65(19)
b / nm	0.989 43(13)	1.409 87(10)	2.398 95(15)
c / nm	1.867 3(2)	1.455 43(12)	1.440 0(2)
α / (°)	102.842(11)	75.435(7)	
β / (°)	100.142(9)	81.145(7)	118.577(19)
γ / (°)	97.289(9)	73.150(7)	
V / nm ³	1.643(3)	1.657 5(2)	4.255 2(11)
Z	2	2	4
$F(000)$	832	844	2 060
θ range for data collection / (°)	3.435~25.050	4.071~65.999	3.302~25.050
Limiting indices	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-22 \leq l \leq 22$	$-10 \leq h \leq 10$, $-12 \leq k \leq 16$, $-17 \leq l \leq 17$	$-16 \leq h \leq 15$, $-28 \leq k \leq 28$, $-17 \leq l \leq 17$
Reflection collected, unique (R_{int})	5 803, 3 322 (0.074 0)	5 737, 3 678 (0.059 8)	7 516, 3 680 (0.175 9)
D_c / (g · cm ⁻³)	1.653	1.656	1.552
μ / mm ⁻¹	1.367	8.494	0.967
Data, restraint, parameter	5 803, 0, 478	5 737, 0, 488	7 516, 0, 586
Goodness-of-fit on F^2	1.043	1.084	1.056
Final R indices [$I \geq 2\sigma(I)$] R_1 , wR_2	0.069 5, 0.113 5	0.063 2, 0.134 0	0.075 1, 0.103 0
R indices (all data) R_1 , wR_2	0.127 4, 0.147 7	0.107 5, 0.192 6	0.143 0, 0.168 3
Largest diff. peak and hole / (e · nm ⁻³)	697 and -561	559 and -1 127	832 and -585

Table 2 Selected bond distances (nm) and bond angles ($^{\circ}$) for compounds 1~3

1					
Cu1—O1	0.198 8(4)	Cu1—O1A	0.242 7(5)	Cu1—O6B	0.193 6(4)
Cu1—N1	0.199 2(5)	Cu1—N2	0.200 5(5)	Cu2—O3C	0.192 4(4)
Cu2—O9	0.197 4(4)	Cu2—N3	0.201 9(6)	Cu2—N4	0.201 2(6)
O6B—Cu1—O1	89.76(18)	O6B—Cu1—N1	95.97(19)	O1—Cu1—N1	169.7(2)
O6B—Cu1—N2	170.6(2)	O1—Cu1—N2	94.56(19)	N1—Cu1—N2	81.1(2)
O1A—Cu1—O6B	99.58(17)	O1A—Cu1—O1	74.76(19)	O1A—Cu1—N1	95.83(19)
O1A—Cu1—N2	89.60(19)	O9—Cu2—O3C	99.2(2)	N4—Cu2—O3C	167.1(2)
N4—Cu2—O9	91.3(2)	N3—Cu2—O3C	90.7(2)	N3—Cu2—O9	168.3(2)
N3—Cu2—N4	79.8(2)				
2					
Co1—O2	0.212 4(5)	Co1—O4A	0.207 7(5)	Co1—O10	0.214 0(4)
Co1—O11	0.210 4(5)	Co1—N1	0.212 9(6)	Co1—N2	0.213 5(6)
Co2—O1	0.204 3(5)	Co2—O6B	0.221 6(6)	Co2—O7B	0.223 2(5)
Co2—O12	0.212 2(5)	Co2—N3	0.210 6(6)	Co2—N4	0.208 8(6)
O11—Co1—O4A	87.4(2)	O4A—Co1—O2	90.5(2)	O2—Co1—O11	174.0(2)
N1—Co1—O4A	171.1(2)	O11—Co1—N1	90.0(2)	O2—Co1—N1	92.9(2)
O4A—Co1—N1	93.9(2)	O11—Co1—N2	90.2(2)	O2—Co1—N2	95.5(2)
N1—Co1—N2	77.6(2)	O4A—Co1—O10	95.05(18)	O10—Co1—O11	89.2(2)
O10—Co1—O2	85.37(17)	O10—Co1—N1	93.43(19)	O10—Co1—N2	171.00(19)
O1—Co2—N4	126.5(2)	O1—Co2—N3	89.0(2)	N3—Co2—N4	76.5(2)
O1—Co2—O12	89.01(19)	N4—Co2—O12	90.1(2)	N3—Co2—O12	161.6(2)
O1—Co2—O6B	87.1(2)	N4—Co2—O6B	142.4(2)	N3—Co2—O6B	89.5(2)
O12—Co2—O6B	108.7(2)	O1—Co2—O7B	145.5(2)	N4—Co2—O7B	87.9(2)
N3—Co2—O7B	97.4(2)	O12—Co2—O7B	94.60(19)	O6B—Co2—O7B	59.14(19)
3					
Ni1—O1	0.204 6(5)	Ni1—O3A	0.203 3(4)	Ni1—O10	0.210 0(4)
Ni1—O11	0.207 8(4)	Ni1—N1	0.213 2(6)	Ni1—N2	0.210 0(6)
Ni2—O9	0.201 3(4)	Ni1—O12	0.206 1(5)	Ni1—O13	0.205 3(5)
Ni1—O14	0.214 6(5)	Ni1—N3	0.209 1(7)	Ni1—N5	0.206 3(5)
O3A—Ni1—O1	88.46(19)	O3A—Ni1—O11	175.42(19)	O1—Ni1—O11	93.23(18)
O3A—Ni1—N2	88.8(2)	O1—Ni1—N2	91.2(2)	O11—Ni1—N2	86.9(2)
O3A—Ni1—O10	92.03(18)	O1—Ni1—O10	178.54(19)	O11—Ni1—O10	86.38(17)
N2—Ni1—O10	90.2(2)	O3A—Ni1—N1	92.9(2)	O1—Ni1—N1	87.0(2)
O11—Ni1—N1	91.48(19)	N2—Ni1—N1	177.5(3)	O10—Ni1—N1	91.6(2)
O9—Ni2—O13	84.26(18)	O9—Ni2—O12	92.44(18)	O13—Ni2—O12	175.6(2)
O9—Ni2—N5	171.9(2)	O13—Ni2—N5	90.3(2)	O12—Ni2—N5	93.3(2)
O9—Ni2—N3	92.0(2)	O13—Ni2—N3	88.9(2)	O12—Ni2—N3	88.4(2)
N5—Ni2—N3	93.8(2)	O9—Ni2—O14	87.25(19)	O13—Ni2—O14	90.6(2)
O12—Ni2—O14	92.1(2)	O14—Ni2—N5	86.8(2)	O14—Ni2—N3	179.1(2)

Symmetry codes: A: $-x+2, -y, -z$; B: $x+1, y, z$; C: $x-1, y+1, z$ for **1**; A: $x+1, y, z$; B: $-x+1, -y, -z$ for **2**; A: $-x+2, -y+2, -z+1$ for **3**.

Table 3 Hydrogen bond parameters of compound 1

D—H...A	<i>d</i> (D—H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O10—H1W...O9	0.085 0	0.202 7	0.287 7	179.42
O10—H2W...O2A	0.085 0	0.194 5	0.279 5	179.36
O11—H3W...O10	0.085 0	0.196 5	0.281 5	179.48
O11—H4W...O4B	0.085 0	0.203 3	0.288 3	178.98

Symmetry code: A: $x-1, y, z$; B: $x-1, y+1, z$.**Table 4** Hydrogen bond parameters of compound 2

D—H...A	<i>d</i> (D—H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O10—H1W...O8A	0.088 8	0.179 4	0.264 6	160.05
O10—H2W...O3B	0.092 2	0.176 4	0.254 4	140.50
O11—H3W...O9A	0.088 1	0.189 5	0.267 5	146.78
O11—H4W...O9C	0.088 2	0.224 2	0.279 0	120.04
O12—H5W...O2	0.087 5	0.198 0	0.272 4	142.09
O12—H6W...O10D	0.087 5	0.196 5	0.273 1	145.38

Symmetry codes: A: $x, y, z+1$; B: $x+1, y, z$; C: $-x+1, -y+1, -z$; D: $-x+1, -y, -z+1$.**Table 5** Hydrogen bond parameters of compound 3

D—H...A	<i>d</i> (D—H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O10—H1W...O4A	0.086 5	0.172 2	0.257 3	167.21
O10—H2W...O7B	0.082 0	0.179 5	0.260 9	171.35
O11—H3W...O2	0.082 0	0.196 9	0.270 2	148.39
O11—H4W...O6B	0.085 0	0.185 4	0.270 4	179.28
O12—H5W...O8	0.095 1	0.204 7	0.297 6	165.23
O12—H6W...O17C	0.071 9	0.198 8	0.270 4	174.87
O13—H7W...O6	0.089 2	0.194 9	0.279 5	157.70
O13—H8W...O15D	0.061 7	0.208 5	0.264 8	152.40
O14—H9W...O2E	0.085 0	0.196 5	0.281 4	179.40
O15—H11W...O16	0.077 9	0.205 8	0.279 7	158.46
O15—H12W...O11A	0.089 4	0.217 2	0.302 5	159.05
O16—H13W...O10A	0.080 9	0.206 1	0.283 1	158.88
O16—H14W...O6	0.085 0	0.190 7	0.275 7	179.14
O17—H15W...O8F	0.085 0	0.191 0	0.276 0	179.33
O17—H16W...O2G	0.085 0	0.200 2	0.285 2	179.34

Symmetry codes: A: $-x+2, -y+2, -z+1$; B: $-x+3/2, y+1/2, -z+1/2$; C: $-x, -y+1, -z$; D: $x-1/2, -y+3/2, z-1/2$; E: $-x+1, -y+2, -z$; F: $x, y-1, z$; G: $x-1, y-1, z$.

1.6 Catalytic test for Knoevenagel condensation reaction of aldehydes

In a typical test, a suspension of an aromatic aldehyde (0.50 mmol, benzaldehyde as a model substrate), malononitrile (1.0 mmol) and the catalyst (Molar fraction: 2%) in methanol (1.0 mL) was stirred at room temperature. After a desired reaction time, the catalyst was removed by centrifugation, followed by an evaporation

of the solvent from the filtrate under reduced pressure to give a crude solid. This solid was dissolved in CDCl_3 and analyzed by ^1H NMR spectroscopy for quantification of products (Fig. S1, Supporting information). To perform the recycling experiment, the catalyst was isolated by centrifugation, washed with methanol, dried at room temperature and reused. The subsequent steps were performed as described above.

2 Results and discussion

2.1 Description of the structure

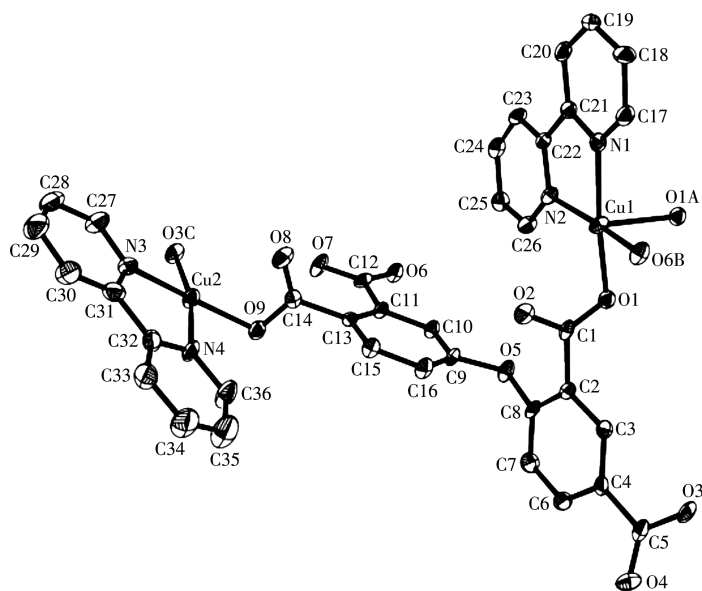
2.1.1 Crystal structure of **1**

X-ray crystallography analysis reveals that compound **1** crystallizes in the triclinic system space group $P\bar{1}$. As shown in Fig. 1, the asymmetric unit of **1** bears two crystallographically unique Cu(II) ions (Cu1 and Cu2), one μ_5 -deta⁴⁻ block, two 2,2'-bipy moieties and two lattice water molecules. The penta-coordinate Cu1 atom exhibits a distorted square pyramidal {CuN₂O₃} environment, which is occupied by three carboxylate O donors from three different μ_5 -deta⁴⁻ blocks and two N atoms from 2,2'-bipy moiety. The Cu2 center is tetra-coordinated and forms a distorted tetrahedral {CuN₂O₂} geometry. It is completed by two carboxylate O atoms from two individual μ_5 -deta⁴⁻ blocks and two N atoms from 2,2'-bipy moiety. The Cu—O and Cu—N bond distances are 0.192 4(4)~0.242 7(5) nm and 0.199 2(5)~0.201 2(6) nm, respectively; these are within the nor-

mal ranges observed in related Cu(II) compounds^[6,29]. In **1**, deta⁴⁻ ligand adopts the coordination mode I (Scheme 1) with four COO⁻ groups being monodentate or bidentate. In deta⁴⁻ ligand, a dihedral angle (between two aromatic rings) and a C—O_{ether}—C angle are 85.22° and 121.02°, respectively, and μ_5 -deta⁴⁻ blocks connect Cu atoms to give a 2D sheet (Fig. 2).

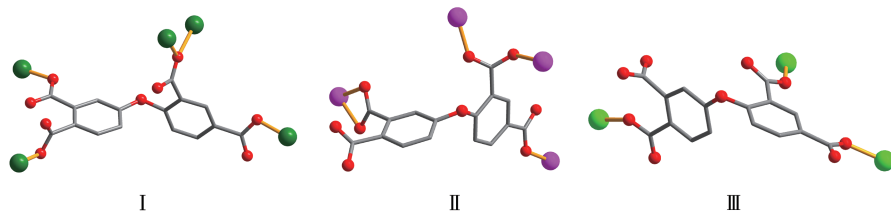
2.1.2 Crystal structure of **2**

The asymmetric unit of compound **2** contains two crystallographically unique Co(II) ions (Co1 and Co2), one μ_4 -deta⁴⁻ block, two 2,2'-bipy moieties and three H₂O ligands. As depicted in Fig. 3, the Co1 center is six-coordinated and possesses a distorted octahedral {CoN₂O₄} environment, which is populated by two carboxylate oxygen atoms from two μ_4 -deta⁴⁻ blocks, two O donors from two H₂O ligands and two N donors from 2,2'-bipy moiety. The six-coordinated Co2 center is surrounded by three oxygen donors from two μ_4 -deta⁴⁻ blocks, one H₂O ligands, and two N donors from 2,2'-

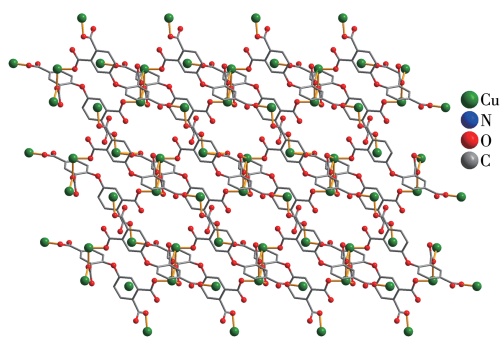


H atoms are omitted for clarity; Symmetry codes: A: $-x+2, -y, -z$; B: $x+1, y, z$; C: $x-1, y+1, z$

Fig.1 Drawing of asymmetric unit of compound **1** with 30% probability thermal ellipsoids



Scheme 1 Coordination modes of deta⁴⁻ ligand in compounds **1**~**3**



2,2'-bipy ligands are omitted for clarity

Fig.2 Perspective of 2D metal-organic sheet viewed along c axis

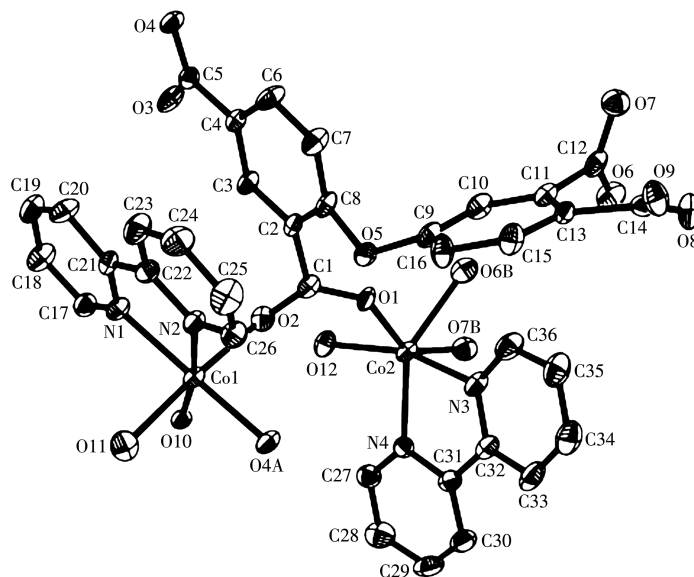
bipy moiety, generating the distorted octahedral $\{\text{CoN}_2\text{O}_4\}$ environments. The bond lengths of Co—O are in a range of 0.204 3(5)~0.223 2(5) nm, while the Co—N bonds are 0.208 8(6)~0.213 5(6) nm, being comparable to those found in some reported Co(II) compounds^[7,29-32]. In **2**, deta^{4-} block acts as a μ_4 -linker

(mode II, Scheme 1), in which four carboxylate groups adopt uncoordinated, monodentate, bidentate or μ -bridging bidentate modes. Besides, μ_4 - deta^{4-} ligand is considerably bent showing a dihedral angle of 89.87° (between two aromatic rings) and the $\text{C—O}_{\text{ether}}\text{—C}$ angle of 118.29° . So, μ_4 - deta^{4-} linkers interconnect the Co(II) ions to form a 1D coordination polymer chain (Fig.4).

Compounds **1** and **2** were assembled under similar conditions except for the type of metal chloride used ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for **1** and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ for **2**). The difference in their structures, 2D sheet in **1** vs 1D chain in **2**, indicates that the assembly process is dependent on the type of metal ion.

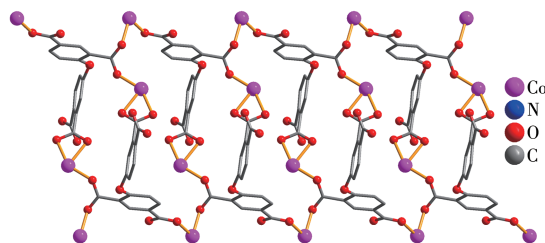
2.1.3 Crystal structure of **3**

This compound discloses a 3D metal-organic framework (MOF) structure. The asymmetric unit of compound **3** has two crystallographically unique Ni(II)



H atoms are omitted for clarity; Symmetry codes: A: $x+1, y, z$; B: $-x+1, -y, -z$

Fig.3 Drawing of asymmetric unit of compound **2** with 30% probability thermal ellipsoids

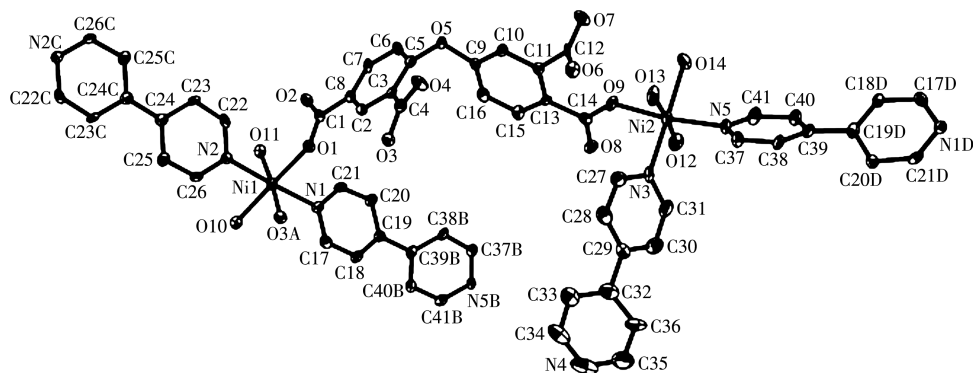


2,2'-bipy ligands are omitted for clarity

Fig.4 View of 1D metal-organic chain along a and b axes

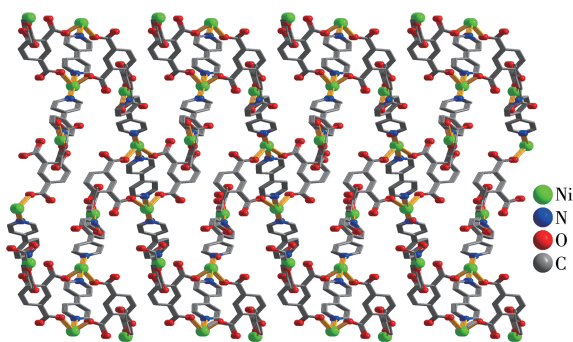
ions (Ni1 and Ni2), a μ_3 -deta⁴⁻ spacer, two and a half of μ -4,4'-bipy moieties, five H₂O ligands and three lattice water molecules (Fig. 5). The Ni1 center is six-coordinated and displays a distorted octahedral {NiN₂O₄} environment that is constructed from two carboxylate oxygen atoms from two μ_3 -deta⁴⁻ spacers, two O donors from two H₂O ligands, and two N atoms from two different 4,4'-bipy moieties. The Ni2 center is also six-coordinated and features a distorted octahedral {NiN₂O₄} geometry that is taken by one carboxylate oxygen donor from one μ_3 -deta⁴⁻ block, three O atoms from three H₂O ligands, and two N atoms from two individual 4,4'-bipy moieties. The Ni—O (0.201 3(4)~0.214 6(5) nm) and Ni—N (0.206 3(5)~0.213 2(6) nm) bonds are within typical values for these type of nickel deriva-

tives^[33-34]. In compound **3**, deta⁴⁻ spacer acts in a μ_3 -coordination fashion (mode III, Scheme 1), with its COO⁻ groups showing uncoordinated or monodentate modes, and 4,4'-bipy moiety adopts a bridging coordination mode. In μ_3 -deta⁴⁻ spacer, relevant angles are 79.84° (dihedral angle between aromatic rings) and 117.26° (C—O_{ether}—C functionality). Finally, μ_3 -deta⁴⁻ blocks and μ -4,4'-bipy moieties connect Ni centers to furnish a 3D MOF (Fig. 6). The structure of another Ni(II) coordination polymer with H₄deta and 4,4'-bipy ligands was reported^[35], in which deta⁴⁻ and 4,4'-bipy moieties adopt μ_4 - or μ -coordination fashions. Although these two Ni(II) coordination polymers possess different space groups and the number of the lattice water molecules, they have the same skeletons.



H atoms are omitted for clarity; Symmetry codes: A: $-x+2, -y+2, -z+1$; B: $-x+1/2, y+1/2, -z+1/2$; C: $-x+3, -y+2, -z+1$; D: $-x+1/2, y-1/2, -z+1/2$

Fig.5 Drawing of asymmetric unit of compound **3** with 30% probability thermal ellipsoids



Water molecules are omitted for clarity

Fig.6 View of 3D MOF (**3**) along *b* and *c* axes

2.2 TGA for compounds 1~3

To determine the thermal stability of **1~3**, their thermal behaviors were investigated under nitrogen atmosphere by TGA. As shown in Fig. 7, compound **1** lost its two lattice water molecules in a range of 137~

238 °C (Obsd. 4.6%, Calcd. 4.4%), followed by the decomposition at 316 °C. For **2**, one weight loss (Obsd. 6.3%, Calcd. 6.5%) in the 155~212 °C range corresponds to a removal of three coordinated water molecules; decomposition of the sample occurred only at

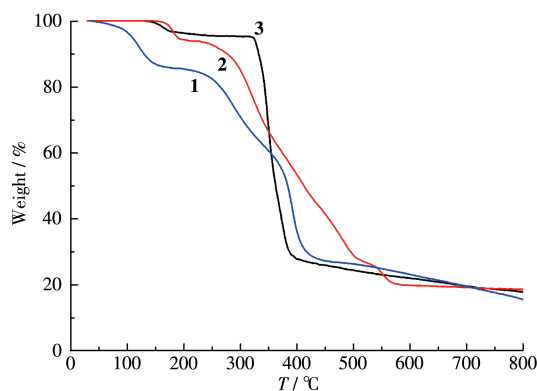


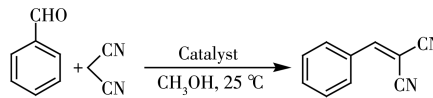
Fig.7 TGA curves of compounds 1~3

230 °C. For 3D MOF **3**, the TGA plot displayed a loss of three lattice and five coordinated water molecules between 41 and 178 °C (Obsd. 14.4%, Calcd. 14.5%), whereas a dehydrated solid was then stable up to 195 °C.

2.3 Catalytic activity in Knoevenagel condensation reaction

Given the potential of transition metal(II) coordination compounds to catalyze the organic reactions^[6-7,14,29,34], we explored the application of **1~3** as heterogeneous catalysts in the Knoevenagel condensation reaction of benzaldehyde as a model substrate to give 2-(phenylmethylene)-propanedinitrile. Typical tests were carried out by reacting a mixture of benzaldehyde,

malononitrile, and a catalyst in methanol at room temperature (Scheme 2, Table 6). Such effects as reaction time, catalyst loading, solvent composition, catalyst recycling and finally substrate scope were investigated.



Scheme 2 Knoevenagel condensation reaction of benzaldehyde (model substrate) catalyzed by CuCl_2 , H_4deta and **1~3**

Compound **1** revealed the highest activity among the obtained compounds **1~3**, resulting in a quantitative conversion of benzaldehyde to 2-benzylidenemalononitrile (Table 6). The latter was accumulated with a yield increasing from 42% to 100% on prolonging the reaction from 10 to 60 min (Table 6, Entry 1~6). The influence of catalyst amount was also investigated, revealing a yield growth from 91% to 100% on increasing the loading of catalyst (molar fraction) from 1% to 2% (Entry 6 and 11). In addition to methanol, other solvents were tested, in particular, water and ethanol showed a comparable efficiency (Yield: 99% and 98%, respectively). Acetonitrile and chloroform are less suitable (Yield: 85% and 67%, respectively).

In comparison with **1**, compounds **2** and **3** were

Table 6 Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by CuCl_2 , H_4deta and **1~3**

Entry	Catalyst	<i>t</i> / min	Catalyst loading ^a / %	Solvent	Yield ^b / %
1	1	10	2.0	CH_3OH	42
2	1	20	2.0	CH_3OH	57
3	1	30	2.0	CH_3OH	69
4	1	40	2.0	CH_3OH	81
5	1	50	2.0	CH_3OH	93
6	1	60	2.0	CH_3OH	100
7	1	60	2.0	H_2O	99
8	1	60	2.0	$\text{C}_2\text{H}_5\text{OH}$	98
9	1	60	2.0	CH_3CN	85
10	1	60	2.0	CHCl_3	67
11	1	60	1.0	CH_3OH	91
12	2	60	2.0	CH_3OH	92
13	3	60	2.0	CH_3OH	87
14	Blank	60	—	CH_3OH	23
15	CuCl_2	60	2.0	CH_3OH	34
16	H_4deta	60	2.0	CH_3OH	30

^a Molar fraction; ^b Calculated by ^1H NMR spectroscopy: $\text{Yield} = n_{\text{product}} / n_{\text{aldehyde}} \times 100\%$.

only slightly less active, resulting in the maximum yields in the 87%~92% range (Entry 12 and 13, Table 6). It should be highlighted that under similar reaction conditions, the Knoevenagel condensation of benzaldehyde was significantly less efficient in the absence of catalyst (only 23% yield) or when using H_4deta (30% yield) or CuCl_2 (34% yield) as catalysts (Entry 14~16, Table 6). Although the relationship between the structural characteristics and the catalytic activity cannot be clearly established in the present study, the highest conversion shown by compound **1** may eventually be related to the presence of unsaturated open sites in the Cu(II) centers^[36-37].

Different substituted benzaldehyde substrates were used to study the substrate scope in the Knoevenagel condensation with malononitrile. These tests were run under optimized conditions (catalyst **1**: 2.0%, CH_3OH , 1 h). The corresponding products were obtained in the yields varying from 56% to 100% (Table 7). Benzaldehydes containing a strong electron-withdrawing group (*e.g.*, nitro and chloro substituent in the ring) revealed the best efficiency (Entry 2~5, Table 7), which can be explained by an increased electrophilicity of substrates. The benzaldehydes containing an electron-donating functionality (*e.g.*, methyl or methoxy group) led to lower yields (Entry 6~8, Table 7).

To examine the stability of **1** in the Knoevenagel condensation, we tested the recyclability of this hetero-

geneous catalyst. For this purpose, upon completion of a reaction cycle, we separated the catalyst by centrifugation, washed it with CH_3OH , and dried it at room temperature before its further use. For catalyst **1**, the catalytic system maintained the higher activity over at least five consecutive cycles (Yield: 100%, 100%, 99% and 98% for second to fifth run, respectively). According to the PXRD patterns (Fig. 8), the structure of **1** was essentially preserved after five catalytic cycles.

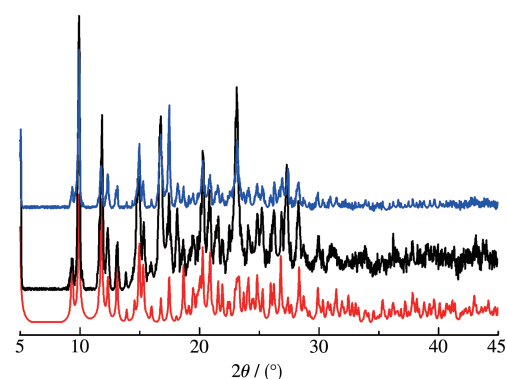


Fig.8 PXRD patterns of **1**: simulated (red), before (black) and after (blue) five catalytic cycles

The catalytic process is assumed to follow a mechanism, by which the copper Lewis acid center interacts with the carbonyl group of benzaldehyde, increasing the electrophilic character of the carbonyl carbon atom. The interaction of a cyano group of malononitrile with the Lewis acid metal site increase the acidity of its methylene moiety. The basic sites (carboxylate O atoms) can abstract a proton from the methylene group to generate the corresponding nucleophilic species, which attacks the carbonyl group of coordinated benzaldehyde with C—C bond formation and dehydration^[38-39].

3 Conclusions

In summary, we have synthesized three Cu(II) / Co(II) / Ni(II) coordination, polymers $\{[\text{Cu}_2(\mu_5\text{-deta})(2,2'\text{-bipy})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $[\text{Co}_2(\mu_4\text{-deta})(2,2'\text{-bipy})_2(\text{H}_2\text{O})_3]_n$ (**2**) and $\{[\text{Ni}_2(\mu_3\text{-deta})(\mu\text{-4,4'}\text{-bipy})_{2.5}(\text{H}_2\text{O})_5] \cdot 3\text{H}_2\text{O}\}_n$ (**3**), based on a tetracarboxylate ligand. Compounds **1**~**3** disclose a 2D sheet, 1D chain and 3D framework, respectively. The catalytic properties of these compounds were investigated. Compound **1** revealed an excellent catalytic activity in the Knoevenagel conden-

Table 7 Knoevenagel condensation reaction of various aldehydes with malononitrile catalyzed by compound **1**^a

Entry	Substituted benzaldehyde substrate ($\text{R}-\text{C}_6\text{H}_4\text{CHO}$)	Yield ^b /%
1	$\text{R}=\text{H}$	100
2	$\text{R}=2\text{-NO}_2$	100
3	$\text{R}=3\text{-NO}_2$	100
4	$\text{R}=4\text{-NO}_2$	100
5	$\text{R}=4\text{-Cl}$	100
6	$\text{R}=4\text{-OH}$	54
7	$\text{R}=4\text{-CH}_3$	98
8	$\text{R}=4\text{-OCH}_3$	76

^a Reaction conditions: 0.5 mmol aldehyde, 1.0 mmol malononitrile, catalyst **1** (Molar fraction: 2.0%), CH_3OH (1.0 mL), 25 °C;

^b Calculated by ^1H NMR spectroscopy.

sation reaction at room temperature.

Supporting information is available at <http://www.wjhxsb.cn>

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