



Research on the Construction
and Application of
Metal-organic Supramolecular Polymers

系列金属有机超分子聚合物 的构筑及应用研究

主 编◎ 宋文东

副主编◎ 李世杰 纪丽丽 郭 健



暨南大学出版社
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中国·广州

2561639

图书在版编目 (CIP) 数据

系列金属有机超分子聚合物的构筑及应用研究 = Research on the Construction and Application of Metal-organic Supramolecular Polymers: 英文/宋文东主编; 李世杰, 纪丽丽, 郭健副主编. —广州: 暨南大学出版社, 2011. 12

ISBN 978 - 7 - 5668 - 0008 - 4

I. ①系… II. ①宋… ②李… ③纪… ④郭… III. ①有机金属化合物—超分子结构—聚合物—研究—英文 IV. ①O627

中国版本图书馆 CIP 数据核字 (2011) 第 208078 号

出版发行: 暨南大学出版社

地 址: 中国广州暨南大学

电 话: 总编室 (8620) 85221601

营销部 (8620) 85225284 85228291 85228292 (邮购)

传 真: (8620) 85221583 (办公室) 85223774 (营销部)

邮 编: 510630

网 址: <http://www.jnupress.com> <http://press.jnu.edu.cn>

排 版: 广州市友间文化传播有限公司

印 刷: 广州市怡升印刷有限公司

开 本: 787mm × 1092mm 1/16

印 张: 24

字 数: 675 千

版 次: 2011 年 12 月第 1 版

印 次: 2011 年 12 月第 1 次

定 价: 48.00 元

(暨大版图书如有印装质量问题, 请与出版社总编室联系调换)

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The author's research interests mainly include marine environment and resource utilization, and syntheses and exploration of environment-friendly materials.

Preface

The rational design and synthesis of metal-organic coordination polymers based on supramolecular chemistry and crystal engineering have attracted considerable attention not only due to their intriguing varieties of topologies and structures, but also their unique properties, such as photoluminescence, magnetism, conductivity, ion exchange, gas adsorption/separation and catalysis, etc.

Our research group have been engaged in designing and synthesizing metal-organic coordination polymers with certain properties in the past ten years. This book mainly covers our findings in designing and synthesizing coordination polymers, their biological activities and potential application in culturing special pearl.

As ever, I am very grateful for the assistance, suggestions and comments of my colleagues and most of all the undergraduate students of laboratory of marine applied chemistry, who have contributed a lot to this book.

The inspiration to write the book came from the importance and potential applications of the coordination polymers, which will help people understand the importance of the new coordination polymers.

Song Wendong

Guangdong Ocean University

August, 2011

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Chapter 1

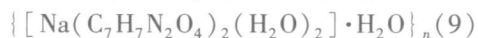
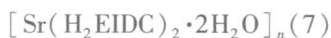
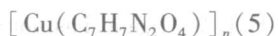
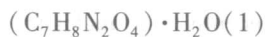
Syntheses, Crystal Structures, Characterization of New Coordination Polymers Built from Imidazole Derivatives

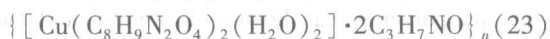
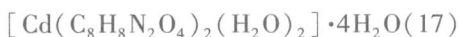
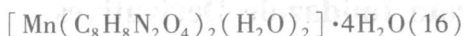
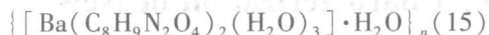
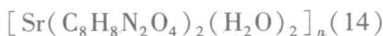
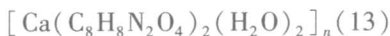
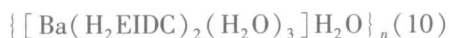
The design and construction of functional metal-organic coordination polymers has attracted great interest due to their potential applications in heterogeneous catalysis, ion exchange, magnetic and photochemical areas, as well as their intriguing variety of topologies. And the self-assemble process can be affected by the pH, temperature, the species of metal centers, the choice of ligands, etc. Weak intermolecular force in these coordination polymers has been well studied and can be used to design and synthesize complexes with interesting architectures and functions, thus choosing a proper multifunctional ligand to link metal ions to generate a fascinating configuration is of vital importance.

It is well known that ligands containing N and O atoms are highly accessible to metal ions to form novel network structures 4,5-imidazoledicarboxylic acid (H_3IDC) ligand has been widely used to construct novel supramolecular architectures based on the following reasons: (i) It possesses the biologically important imidazole ring, which is known as a functional group of histidine and play a key role in life activities; (ii) It possesses flexible multi-functional coordination sites involving both two N atoms of the imidazole ring and four carboxyl O atoms; (iii) It can be partially or fully deprotonated to generate H_2IDC^- , $HIDC^{2-}$ and IDC^{3-} anions by controlling the pH carefully to produce a variety of fascinating structures; (iv) The arrangement of two N atoms with a N-X-N angle in IDC is close to 145° , which is coincident with the Si-O-Si angle commonly found in many zeolites, it is a favorite candidate for constructing ZIFs (zeolitic imidazolate frameworks).

H_3EIDC (2-ethyl-1H-imidazole-4,5-dicarboxylate) and H_3PIDC (2-propyl-1H-imidazole-4,5-dicarboxylate) as derivatives of H_3IDC with an ethyl or propyl substituent at the C2 atom of the imidazole group, which could be used to generate novel frameworks with biological activities. In addition, they have been rarely explored up to now.

Inspired by the above consideration, in this chapter, we choose H_3EIDC and H_3PIDC to react with metal salts to construct a series of supramolecular frameworks, namely:





In addition, two imidazole coordination polymers with barbital or 3-thienylacetic acid as the auxiliary ligand are also studied here, namely:



In the title compound, $(\text{C}_7\text{H}_8\text{N}_2\text{O}_4) \cdot \text{H}_2\text{O}$, the imidazole N atom is protonated and one of the carboxylate groups is deprotonated, forming formally a zwitterion. The two carboxyl groups are approximately coplanar with the imidazole ring. The solvent water molecules are linked to the organic ligands via hydrogen bonds. In the crystal packing, the three-dimensional supramolecular framework is stabilized by extensive $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds^[1].

Comment

4,5-imidazoledicarboxylic acid (H_3IDC) ligand possesses great potential for coordination interactions and hydrogen bonding, and it can be deprotonated to generate H_2IDC^- , HIDC^{2-} and IDC^{3-} anions at different pH values. Up until now, it has been widely studied. 2-propyl-1H-imidazole-4,5-carboxylate (H_3PIDC) ligand as one derivative of H_3IDC with efficient N, O-donors has been used to obtain new metal-organic complexes by our research group. Recently, an analogue of H_3IDC , 2-ethyl-1H-imidazole-4,5-dicarboxylate (H_3EIDC) ligand has also been used to construct intriguing coordination polymers^[2-4]. However, the crystal structure of H_3EIDC ligand has not been determined. Considering that in mind, we focus on obtaining the crystal and its crystal structure will be reported here.

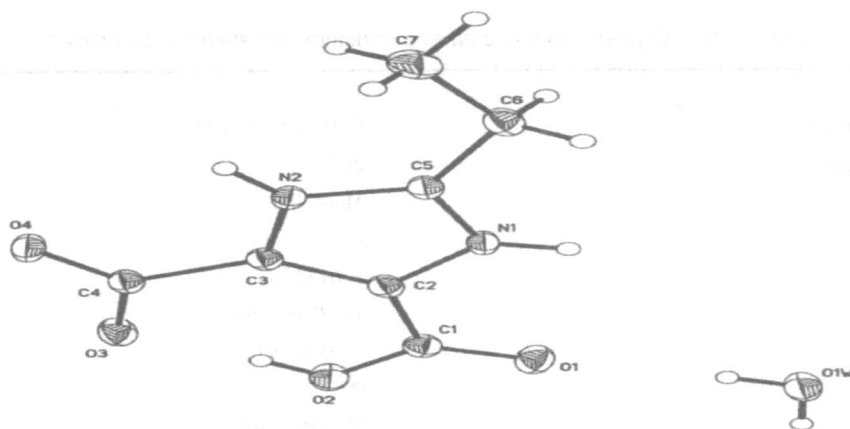


Fig. 1 – 1a The structure of the title compound 1, showing the atomic numbering scheme. Non-H atoms are shown with 30% probability displacement ellipsoids.

As illustrated in Fig. 1 – 1a, the title compound, $(C_7H_8N_2O_4) \cdot H_2O$, crystallizes as a zwitterion in which the imidazole N atom is protonated, one of the carboxylate groups is deprotonated. The two carboxyl groups are approximately coplanar with the imidazole ring, as indicated by the fact that the $O1 - C1 - C2 - C3$ and $O2 - C1 - C2 - C3$ torsion angles are $-176.8(2)^\circ$ and $2.9(4)^\circ$, respectively; the $O3 - C4 - C3 - C2$ and $O4 - C4 - C3 - C2$ torsion angles are $-4.6(3)^\circ$ and $176.4(2)^\circ$, respectively. The solvent water molecules are linked to the organic ligands via $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds (Tab. 1 – 1b), which stabilizes the three-dimensional network (Fig. 1 – 1b).

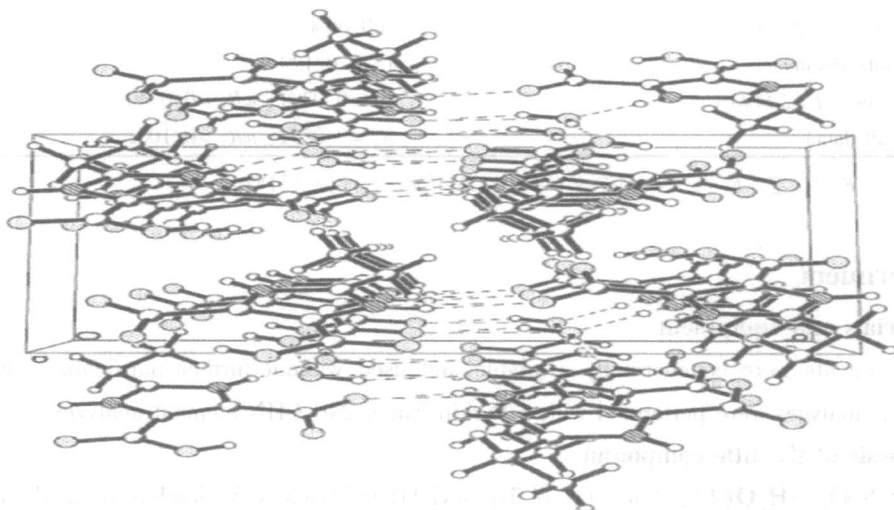


Fig. 1 – 1b A view of the three-dimensional network constructed by $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonding interactions along a axis

Tab. 1 – 1a Crystallographic data and structure refinement of complex 1

Compound	1
Empirical formula	C ₇ H ₈ N ₂ O ₄ · H ₂ O
Formula weight	202. 17
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7. 6132(6)
<i>b</i> (Å)	14. 3779(16)
<i>c</i> (Å)	7. 9396(8)
α (°)	90
β (°)	97. 7990(10)
γ (°)	90
<i>V</i> (Å ³)	861. 04(15)
<i>Z</i>	4
<i>F</i> (000)	424
<i>D</i> _{calc} (mg/cm ³)	1. 56
Absorption coefficient (mm ⁻¹)	0. 134
GOF	1. 046
Crystal size (mm)	0. 50 × 0. 41 × 0. 40
θ range for data collection (°)	2. 70 to 25. 00
Limiting indices	$-9 \leq h \leq 8$ $-17 \leq k \leq 13$ $-9 \leq l \leq 7$
Reflections collected/unique	4224/1510
Completeness to $\theta = 25. 00$	100. 00%
Data/restraints/parameters	1510/0/129
Final <i>R</i> indices [$I > 2\sigma(I)$]	<i>R</i> ₁ = 0. 0381, <i>wR</i> ₂ = 0. 0940
<i>R</i> indices (all data)	<i>R</i> ₁ = 0. 0531, <i>wR</i> ₂ = 0. 1061

$$R_1 = \sum (|F_o| - |F_c|) / \sum |F_o| , wR_2 = [\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w (F_o)^2]^{1/2} .$$

Experiment

Materials and equipment

All chemicals were commercially available and used without further purification. Elemental (C, H, N) analyses were performed with a Perkin-Elmer 240 CHN element analyzer.

Synthesis of the title compound

(C₇H₈N₂O₄) · H₂O(**1**): A mixture of 2-propyl-1H-imidazole-4,5-dicarboxylic acid (H₃PIDC) (0. 1 g, 0. 5 mmol) and NaOH (0. 004 g, 0. 1 mmol) in 15 mL of distilled water was stirred for 10 mins in air, and then sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 110 °C for 72 h. The mixture was cooled to room temperature at a rate of 5 °C · h⁻¹ and colorless plate crystals were obtained in a yield of 43% based on Sr. C₇H₁₀N₂O₅: Calcd. (%): C 41. 15, H 4. 95, N 13. 84; Found (%): C 41. 34, H 4. 81, N 13. 53.

Structure determination

A single crystal with dimensions of 0.50 mm × 0.41 mm × 0.40 mm was mounted on a glass fiber for data collection which was performed on a Bruker SMART CCD 1000 diffractometer operating at 50 kV and 30 mA by using Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. Data collection and reduction were performed by using the SMART and SAINT software. Multi-scan absorption correction was applied with the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares techniques of the SHELXTL program package. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms belonging to C and N atoms were calculated theoretically.

Crystal data and details of the data collection and refinement for the title complex are listed in Tab. 1 – 1b:

Tab. 1 – 1b Hydrogen bonds for compound 1

D—H...A	d(D—H)	d(H...A)	d(D...A)	$\angle$ (DHA)
N(1)—H(1)...O(4) ⁱ	0.86	1.91	2.707(3)	154
N(2)—H(2)...O(1W) ⁱⁱ	0.86	1.84	2.631(3)	152
O(2)—H(2A)...O(3)	0.99(3)	1.62(3)	2.608(4)	176
O(1W)—H(1W)...O(2) ⁱⁱⁱ	0.93	2.59	3.486(4)	162
O(1W)—H(2W)...O(1)	0.93	2.66	3.486(3)	148

Symmetry codes: (i) $-x+1, 1/2+y, 1/2-z$; (ii) $1-x, -1/2+y, 1/2-z$; (iii) $2-x, 1-y, z$.



Complex 2 $[\text{Zn}(\text{C}_7\text{H}_7\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ is isostructural with complex 3 $[\text{Ni}(\text{C}_7\text{H}_7\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ and complex 4 $[\text{Co}(\text{C}_7\text{H}_7\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$. Complex 2 is representatively described here.

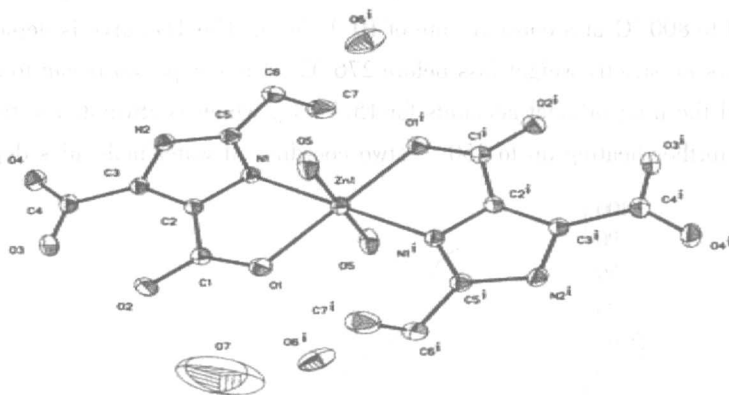


Fig. 1 – 2a The structure of the title compound 2, showing the atomic numbering scheme. Non-H atoms are shown with 30% probability displacement ellipsoids.

Single crystal X-ray diffraction reveals that complex 2 crystallizes in Triclinic space group $P\bar{1}$. The title compound is a discrete zero dimensional structure, as depicted in Fig. 1 – 2a, it has two

coordinated water molecules, three free water molecules and two 2-ethyl-4,5-imidazoledicarboxylate ligands. the Zn^{II} ion is in a slightly distorted octahedral coordination environment, formed by two water molecules, two nitrogen atoms and two oxygen atoms from two different 2-ethyl-4,5-imidazoledicarboxylate ligands. Each H_2EIDC chelates one Zn^{II} via its imidazole N atom and carboxyl O atom. It is noted that a wide range of hydrogen bonds contribute to the formation of three-dimensional supramolecular structure (Fig. 1-2b).

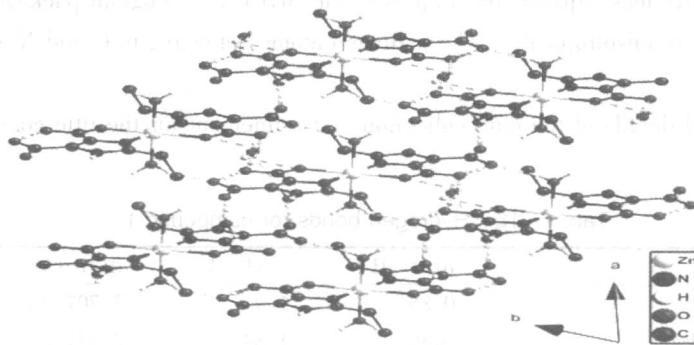


Fig. 1-2b A view of the three-dimensional network constructed by $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonding interactions along c axis

IR and TGA

The IR spectra of compound 2 show broad band at 3434 cm^{-1} , which may be assigned to the ν ($N-H$) stretching vibrations of imidazole rings. The features at 1544 cm^{-1} , 1468 cm^{-1} and 1420 cm^{-1} , 1358 cm^{-1} are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations.

Thermogravimetric analysis (TGA) of compound 2 was performed in a N_2 atmosphere when the sample was heated to $800\text{ }^\circ\text{C}$ at a constant rate of $10\text{ }^\circ\text{C}/\text{min}$. The TG curve is depicted in Fig. 1-2c, compound shows no strictly weight loss before $276\text{ }^\circ\text{C}$. The compound began to decompose upon further heating and the final product accounts for 15.74% , which is attributed to the MgO (Calcd. 15.22%). Upon further heating up to $250\text{ }^\circ\text{C}$, two coordinated water molecules departs.

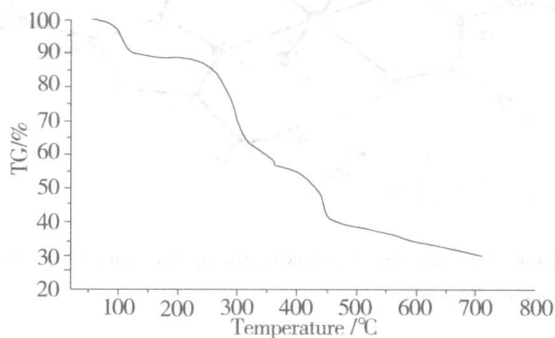


Fig. 1-2c The TGA trace of compound 2

Experiment

Materials and equipment

All chemicals were commercially available and used without further purification. Elemental (C, H, N) analyses were performed with a Perkin-Elmer 240 CHN element analyzer. Infrared (IR) spectra were recorded ($400 - 4000 \text{ cm}^{-1}$) as KBr disks with a Bruker 1600 FTIR spectrometer. Thermogravimetric analysis (TGA) experiments were carried out with a Perkin-Elmer TG/DTA 6300 system with a heating rate of $10 \text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ from room temperature to $600 \text{ }^{\circ}\text{C}$ in a nitrogen atmosphere.

Synthesis of the title compound

$[\text{M}(\text{C}_7\text{H}_7\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ [$\text{M} = \text{Zn}$ (2), Ni (3), Co (4)]: A mixture of $\text{Zn}(\text{NO}_3)_2$ (0.05 g, 0.5 mmol), 2-ethyl-1H-imidazole-4,5-dicarboxylic acid (H_3EIDC) (0.2 g, 1 mmol) and H_2O (10 mL) was stirred for 30 mins in air. Afterwards, it was sealed in a 20 mL Teflon reactor and kept under autogenous pressure at $180 \text{ }^{\circ}\text{C}$ for 72 h. The mixture was cooled to room temperature at a rate of $5 \text{ }^{\circ}\text{C} \cdot \text{h}^{-1}$ and colorless plate crystals were obtained in a yield of 41% based on Zinc. $\text{C}_{14}\text{H}_{24}\text{ZnN}_4\text{O}_{13}$: Calcd. (%): C 32.34, H 4.67, N 10.50. Found(%): C 32.20, H 4.6, N 10.73.

Structure determination

Diffraction data of the complexes 2, 3 and 4 were performed on a Bruker SMART CCD 1000 diffractometer operating at 50 kV and 30 mA by using Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. Data collection and reduction were performed by using the SMART and SAINT software. Multi-scan absorption correction was applied with the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares techniques of the SHELXTL program package. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms belonging to C and N atoms were calculated theoretically.

The selected bond lengths and bond angles are shown in Tab. 1 – 2b. Crystal data and details of the data collection and refinement for the title complex are listed in Tab. 1 – 2a.

Tab. 1 – 2a Crystallographic data and structure refinement of complexes 2, 3, 4

Compounds	2	3	4
$F(000)$	260	268	244
Formula weight	521.74	515.08	492.12
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.1190(11)	7.1972(6)	7.1615(14)
b (Å)	8.7931(12)	8.8436(7)	8.8729(18)
c (Å)	9.2651(12)	9.3187(7)	9.3815(19)
α (°)	64.7332(9)	66.2410(10)	66.06(3)
β (°)	88.6171(7)	89.0610(10)	88.66(3)
γ (°)	70.0720(10)	70.5500(10)	70.97(3)
V (Å ³)	513.14(10)	507.09(7)	510.96(18)
Empirical formula	$[\text{Zn}(\text{C}_7\text{H}_7\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$	$[\text{Ni}(\text{C}_7\text{H}_7\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$	$[\text{Co}(\text{C}_7\text{H}_7\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$

(to be continued)

Compounds	2	3	4
<i>Z</i>	1	1	1
<i>D</i> _{calc} (mg/cm ³)	1.788	1.687	1.599
Absorption coefficient (mm ⁻¹)	1.179	1.035	0.914
GOF	1.084	1.651	1.125
Crystal size (mm)	0.21 × 0.20 × 0.19	0.40 × 0.30 × 0.25	0.29 × 0.22 × 0.19
θ range for data collection (°)	2.41 to 24.99	2.41 to 27.50	3.03 to 25.20
	-8 ≤ h ≤ 8	-9 ≤ h ≤ 9	-8 ≤ h ≤ 8
Limiting indices	-8 ≤ k ≤ 10	-11 ≤ k ≤ 11	-10 ≤ k ≤ 10
	-11 ≤ l ≤ 11	-12 ≤ l ≤ 12	-11 ≤ l ≤ 11
Reflections collected/unique	2676 / 1774	4907 / 2330	4151 / 1841
Completeness to θ = 25.00	98.10%	99.70%	99.80%
Data/restraints/parameters	1774 / 0 / 149	2330 / 16 / 159	1841 / 9 / 150
Final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0396, <i>wR</i> ₂ = 0.1023	<i>R</i> ₁ = 0.0490, <i>wR</i> ₂ = 0.1472	<i>R</i> ₁ = 0.0328, <i>wR</i> ₂ = 0.0861
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0490, <i>wR</i> ₂ = 0.1099	<i>R</i> ₁ = 0.0501, <i>wR</i> ₂ = 0.1480	<i>R</i> ₁ = 0.0587, <i>wR</i> ₂ = 0.1342

$$R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|, wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o)^2]^{1/2}.$$

Tab. 1 – 2b Selected bond lengths (Å) and angles (°) of complex 2

Bond distances(Å)		Bond distances(Å)	
Zn(1)—N(1)	2.003(1)	Zn(1)—O(5) ⁱ	2.115(3)
Zn(1)—N(1) ⁱ	2.103(1)	Zn(1)—O(1)	2.163(2)
Zn(1)—O(5)	2.205(1)	Zn(1)—O(1) ⁱ	2.163(2)
Bond angles(°)		Bond angles(°)	
N(1)—Zn(1)—N(1) ⁱ	180	O(5)—Zn(1)—O(1)	91.99(10)
N(1)—Zn(1)—O(5)	88.76(10)	O(5) ⁱ —Zn(1)—O(1)	88.01(10)
N(1) ⁱ —Zn(1)—O(5)	91.74(1)	N(1)—Zn(1)—O(1) ⁱ	101.02(10)
N(1)—Zn(1)—O(5) ⁱ	91.00(1)	N(1) ⁱ —Zn(1)—O(1) ⁱ	78.98(10)
N(1) ⁱ —Zn(1)—O(5) ⁱ	88.96(10)	O(5)—Zn(1)—O(1) ⁱ	88.01(10)
O(5)—Zn(1)—O(5) ⁱ	180.000(1)	O(5) ⁱ —Zn(1)—O(1) ⁱ	91.98(10)
N(1)—Zn(1)—O(1)	78.98(10)	O(1)—Zn(1)—O(1) ⁱ	180
N(1) ⁱ —Zn(1)—O(1)	102.00(10)		

Symmetry transformations used to generate equivalent atoms: (i) -x+1, -y+1, -z+1.



Single-crystal X-ray diffraction analysis reveals that compound 5 crystallizes in Monoclinic space group $P2_1/n$, and the asymmetric unit of 5 consists of one Cu(II) cation and one H₂EIDC anion ligand, the complex 5 is a 2D infinite layer structure, the Cu(II) center is surrounded by two N atoms and two carboxylate O atoms [N1, O1, N1ⁱ, O1ⁱ] from two individual H₂L⁻ ligands in the

equatorial plane and two O atoms [O2ⁱⁱ, O2ⁱⁱⁱ] from another two H₂L⁻ ligands in a slightly distorted octahedral environment (Fig. 1-3b). The Cu—N bond lengths are equal with the value of 1.9606(13) Å, the Cu—O bond lengths and O—Cu—O angles vary from 1.9999(11) Å to 2.5720(11) Å and 91.69° to 180.0°. And the CuO₄N₂ octahedron units are interconnected with each other by H₂EIDC ligands to generate a sheet composed of quasi-squares involving four H₂EIDC ligands and four Cu(II) centers, each H₂EIDC ligand chelates the Cu(II) centers via N1, O1 and connects the adjacent Cu(II) center via O2 atom, which is different from complex 5 with a similar layer structure.

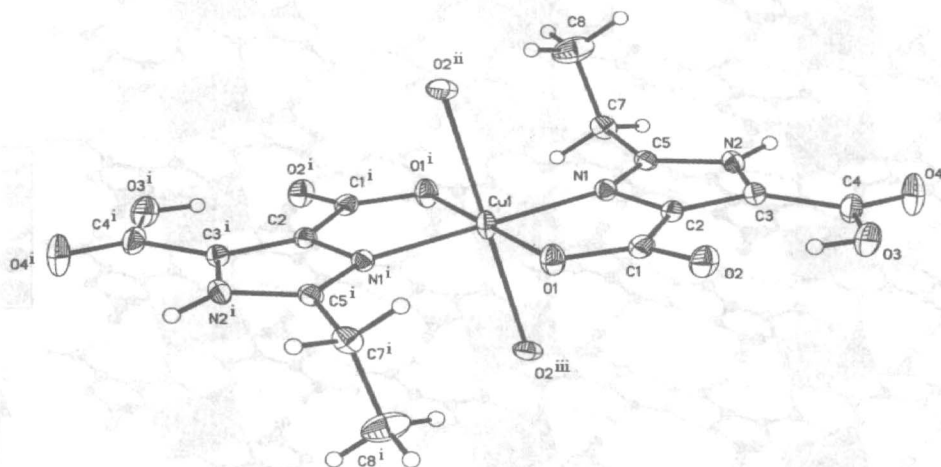


Fig. 1-3a The structure of the title compound 5, showing the atomic numbering scheme. Non-H atoms are shown with 30% probability displacement ellipsoids.

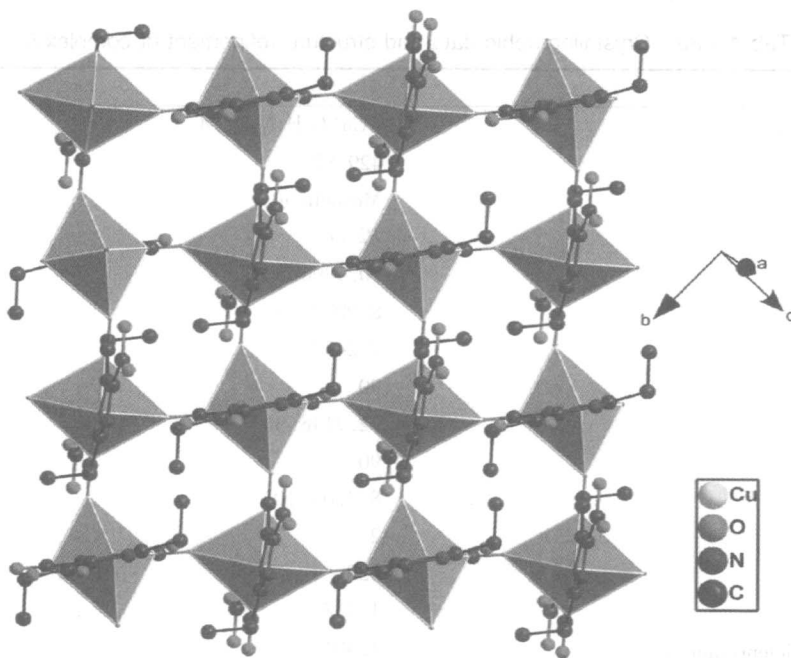


Fig. 1-3b The infinite 2D layer structure of complex 5

And the adjacent layers are interconnected via (N—H···O and O—H···O) hydrogen bonding interactions into a 3D supramolecular framework (Fig. 1-3c).

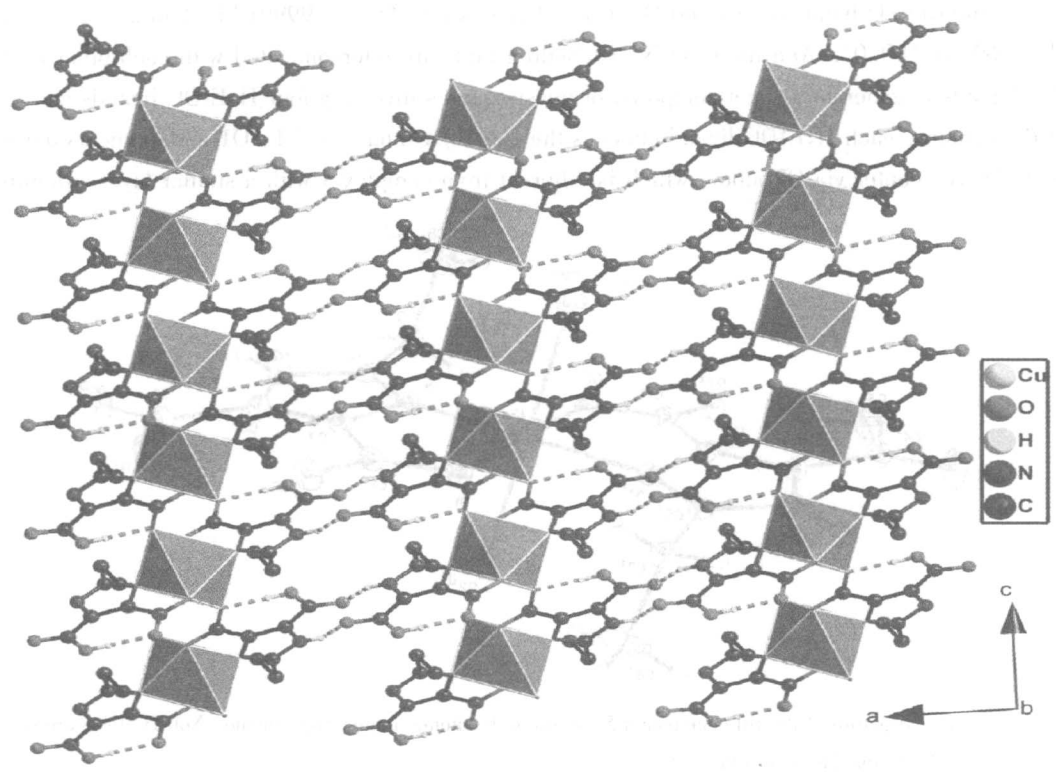


Fig. 1-3c The 3D supramolecular structure of complex 5

Tab.1-3a Crystallographic data and structure refinement of complex 5

Compound	5
Empirical formula	$[Cu(C_7H_7N_2O_4)]_n$
Formula weight	429.83
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.9896(8)
b (Å)	8.0027(6)
c (Å)	9.2439(7)
α (°)	90
β (°)	92.7146(9)
γ (°)	90
V (Å ³)	812.06(10)
Z	2
$F(000)$	438
D_{calc} (mg/cm ³)	1.758
Absorption coefficient (mm ⁻¹)	1.401
GOF	1.058
Crystal size (mm)	0.30 × 0.20 × 0.10