

經由 C-H $\cdots\pi$ 及 $\pi\cdots\pi$ 作用力自組裝形成 三維含銅(II)金屬配位化合物構造分析

Self-assembly of a Copper (II) Complex through C-H $\cdots\pi$ and $\pi\cdots\pi$ Interaction to a 3D Open-framework Structure

沈福銘 ^{*1}Fwu-Ming Shen

元培科技大學生物科技系

駱詩富 ²Shie-Fu Lush

元培科技大學通識教育中心

¹Department of Biotechnology, Yuanpei University

²General Education Center, Yuanpei University

(Received, January 14, 2011; Revised, February 23, 2011; Accepted, March 10, 2011)

摘要：將吡啶-3,4-雙羧酸與 NaOH 反應，再與 CuBr₂·4H₂O 與 1,10-菲囉啉加水混合，利用水熱反應合成，得到含銅(II)的配位錯合物，其化學式為 {[Cu(pda)(phen)]·H₂O}_n (pda = 吡啶-3,4-雙羧酸根, phen = 1,10-菲囉啉)。使用元素分析儀、FT-IR 光譜儀及 X-Ray 晶體繞射儀，測定產物晶體結構及其性質，X-Ray 測定結果顯示錯合物是以銅(II)離子為配位中心，含兩個 O 原子，以及三個 N 原子和一個未配位晶格水分子；分別來自兩個吡啶雙羧酸上的 O 原子，和吡啶雙羧酸上的氮原子及菲囉啉環上的兩個氮原子，配位構成些微扭曲平方角錐型幾何結構。晶體結構由於吡啶雙羧酸以及晶格水分子的分子內氫鍵 (C-H \cdots O) 作用、芳香環之間的 $\pi\cdots\pi$ 吸引力以及 C-H $\cdots\pi$ 作用力，自組裝成(3-D)三維空間無限延伸的網狀結構，使得此晶體結構很穩定。

關鍵詞：水熱合成、吡啶-3,4-雙羧酸、1,10-菲囉啉、氫鍵

*Corresponding author



Abstract: A metal-organic coordination polymer, $\{[\text{Cu}(\text{pda})(\text{phen})]\cdot\text{H}_2\text{O}\}_n$ (pda= pyridine-3,4-dicarboxylate, phen = 1,10-phenanthroline), has been hydrothermally synthesized from the reaction of $\text{CuBr}_2\cdot 4\text{H}_2\text{O}$, NaOH, 3,4-pdaH₂ and phen. The structure was characterized by elemental analysis, FT-IR and single-crystal X-ray diffraction. The asymmetric unit of the title compound contains a five-coordinate Cu(II) ion with a distorted square pyramidal geometry, defined by three N atoms and two carboxyl-O atoms from chelating 1,10-phenanthroline and pyridine-3,4-dicarboxylate ligands. The asymmetric unit also contains an uncoordinated water molecule. The structure exhibits a two-dimensional layer, which further forms a three-dimensional supramolecular network via weak C–H \cdots O hydrogen bonding, $\pi\cdots\pi$ stacking interaction and C–H $\cdots\pi$ interaction.

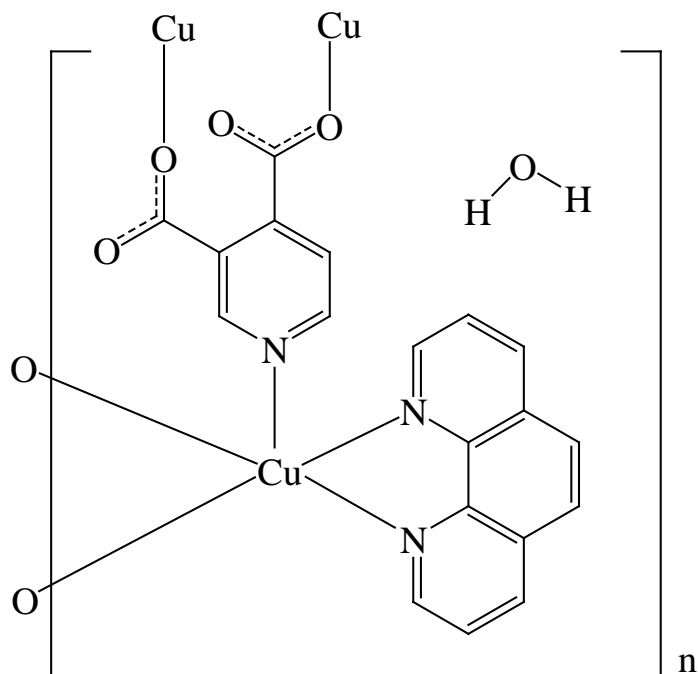
Key words: Hydrothermal Synthesis, Pyridine-3,4-dicarboxylic acid, 1,10-phenanthroline, Hydrogen bonding.

I. Introduction

In the last few years, several studies have used rigid, multifunctional ligands to bridge metal ions into two- or three-dimensional structures. Multi-carboxylate ligands have been proved to be good candidates because they can be regarded not only as hydrogen-bonding acceptors but also as hydrogen-bonding donors, depending upon the number of deprotonated carboxylic groups¹. These ligands usually possess high symmetry, for instance, pyridine-2,6-dicarboxylic acid and pyridine-3,5-dicarboxylic acid has been used successfully to synthesize such materials²⁻¹⁹.

Recently, several metal complexes containing anionic forms of pyridine-3,4-dicarboxylic acid, have been synthesized²⁰⁻²³. In this study, we report the synthesis, crystal structure and characterization of a copper(II) polymer, $\{[\text{Cu}(\text{pda})(\text{phen})]\cdot\text{H}_2\text{O}\}_n$, where pda represents pyridine-3,4-dicarboxylate and phen represents 1,10-phenanthroline (Scheme 1). The title compound is a 2-D supramolecular material based on mixed ligands of pyridine-3,4-dicarboxylate and 1,10-phenanthroline.





Scheme 1

II. Experimental Section

Materials and methods

All chemicals purchased were reagent grade and used without further purification. Elemental analysis (C, H and N) was performed on a Heraeus CHN-O-Rapid elemental analyzer. FT-IR spectra were recorded in the range 400-4000 cm^{-1} on a Bruker Vector 22 FT-IR spectrophotometer using a KBr pellet. All measurements were performed at room temperature.

X-ray Crystallographic Analysis

Diffraction data of the title compound were collected on a Bruker SMART CCD area detector diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in ψ and ω scan modes. All the structures were solved by direct methods using the program SHELXS 97²⁴ and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths for the title compound are listed in Table 2.



Synthesis

A mixture of pyridine-3,4-dicarboxylic acid (0.0336 g, 0.20 mmol), NaOH (0.10 M, 4 mL) and 5 mL deionized water was stirred for 30 min in air. A mixture of $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$ (0.0455 g, 0.20 mmol), 1,10-phenanthroline (0.0365 g, 0.20 mmole) and 5 mL deionized water was stirred for 30 min in air. The two solutions were transferred to a 23-mL Teflon-lined stainless steel autoclave, and the autoclave was sealed, heated to 418 K under autogenously pressure for 2 day, and then cooled to RT at a rate of 0.5 K/ hr. Blue crystals were obtained (yield 66.83 % based on copper). Elemental analysis calcd. for $\text{CuC}_{19}\text{H}_{13}\text{N}_3\text{O}_5$ (Mw = 426.86) : C, 53.41; H, 3.06; N, 9.84 %. Found : C, 54.03; H, 3.05 ; N, 9.75 %. IR(KBr)(cm^{-1}): 3537(m) 、3461(m) 、1640(s) 、1614(s) 、1516(w) 、1433(m) 、1386(s) 、1154(w) 、854(s) 、683(w).

III. Results and Discussion

The title compound has been prepared by hydrothermal reactions under nearly neutral conditions (the pH value adjusted to ~ 7.0). Copper (II) bromide ($\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$) reacts with pyridine-3,4-dicarboxylic acid, NaOH and 1,10-phenanthroline at 418 K to give pyridinedicarboxylate-copper(II) compound. The product is stable in air and insoluble in water and common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, 1,2-dichloroethane, acetone and DMF.

When the preparation of compound was tried in the absence of NaOH, the reaction only gave very poor crystalline products, and therefore we gave up further characterizations.

The title compound was obtained as blue crystals in relatively high isolation yield (66.83 %). The FT-IR spectrum of compound exhibits peaks at 1640, 1614, and 1433 cm^{-1} that can be assigned to the asymmetric and symmetric C=O stretches, respectively (Fig 1). The absence of the characteristic bands at around 1724 cm^{-1} in compound attributed to the protonated carboxylic group indicates the full deprotonation of pda ligand upon reaction with Cu ions. The two absorption peaks at 3537 and 3561 cm^{-1} are assigned to $\nu_{\text{O-H}}$ of uncoordinated lattice water molecule²⁵.

The valence sum calculations give the average value of 1.89 for Cu atom²⁶, suggesting that all Cu centers are in the +2 oxidation state ($3d^9$). The subunit structure of title compound as shown in Fig. 2. The Cu(II) ion has a slightly distorted square pyramidal coordination geometry with an CuN_3O_2 core, involving two N atoms from one phen ligand and one N atom from pda ligand, two O atoms from two different pda dianions. The title compound has the same Cu–O bond distances of 1.976(3) Å, while the Cu–N bond distances range from 2.009(3) to 2.263(3) Å (Table 2). The Cu–N distance 2.263(3) Å is significantly longer than the normal bond length, which reflects the weak axial interactions as expected for Jahn-Teller distorted copper (II) complexes. The value of structural parameter τ is 0.13, showing a distorted square pyramidal structure, where τ is defined as



$\tau = (\alpha - \beta) / 60^\circ$, where α and β are the largest angles ($\alpha > \beta$) around a penta-coordinated metal center²⁷ (τ is equal to 0 for an ideal square pyramidal geometry).

The pda ligands act as tridentate ligand (Chart 1) and connect the Cu centers, forming a two-dimensional layer (Fig 3), Base plane vectors: (0 1 0). The pyridine ring plane of pda and the phen plane are nearly perpendicular to each other, the dihedral angle²⁸ being $99.4(5)^\circ$. The title compound is has no classic hydrogen bonding interactions, but weak C–H \cdots O hydrogen-bonding is observed in the crystal structure (Table 3)²⁹.

In addition, C–H \cdots π interaction C5–H5 \cdots Cg4 (N3/C13–C16) are present in the crystal structure (full details and symmetry codes given in Table 3). $\pi\cdots\pi$ stacking interactions are also observed, the centroid-centroid distances between Cg1 (Cu1/N1–N2/C11–C12) \cdots Cg5⁽ⁱⁱⁱ⁾ (C4–C7/C9/C11–C12), Cg2 (N1/C1–C4/C12) \cdots Cg5^(iv) and Cg3 (N2/C7–C11) \cdots Cg5⁽ⁱⁱⁱ⁾ are 3.975(2), 3.814(2) and 3.677(2) Å [symmetry code : (iii) -x, -y, 1-z, (iv) -x, -y, 1-z], respectively (Fig 4). The structure exhibits a two-dimensional layer, which further forms a three-dimensional supramolecular network via weak C–H \cdots O hydrogen bonding, $\pi\cdots\pi$ stacking interaction and C–H \cdots π interaction³⁰.

IV. Conclusions

In this study, a Cu(II) polymer has been synthesized and structurally characterized. The synthesis of the title compound not only proves that the hydrothermal reaction in preparing new metal-organic hybrid materials is successful but also shows that weak intermolecular interactions (C–H \cdots O hydrogen-bonding, $\pi\cdots\pi$ stacking interactions and C–H \cdots π interactions) contribute to the formation of higher-dimensional network.

Table 1 Crystal data

Cu (C ₁₂ H ₈ N ₂) (C ₇ H ₃ NO ₄)(H ₂ O)	Z = 4
Mr = 426.86	Dx = 1.691 Mg m ⁻³
Monoclinic P2(1)/n	Mo K α radiation
a = 7.6396(4) Å	Cell parameters from 3871
b = 19.6502(10) Å	Reflections
c = 11.3050(6) Å	$\theta = 2.5\text{--}25^\circ$
$\beta = 98.920(1)^\circ$	$\mu = 1.343\text{ mm}^{-1}$
V = 1676.58(15) Å ³	T = 295(2) K
Data collection	Blue
	0.15x 0.10x 0.05 mm ³



Bruker SMART CCD area-detector	4064 independent reflections
Diffractionmeter	3142 reflections with $I > 2\sigma(I)$
ψ and ω scans	$R_{int} = 0.0556$
Absorption correction: multi-scan (SADABS; Sheldrick, 1995)	$\theta_{max} = 28.33^{\circ}$
$T_{min} = 0.88370$, $T_{max} = 0.96803$	$h = -9 \rightarrow 8$
11171 measured reflections	$k = -18 \rightarrow 26$
Refinement	$l = -15 \rightarrow 15$
Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.0563$	$w = 1/[\sigma^2(F_o^2) + 0.0487P^2 + 1.5843P]$
$wR(F^2) = 0.1121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.079$	$(\Delta/\sigma)_{max} = 0.001$
4064 reflections	$\Delta\rho_{max} = 0.627 e \text{ \AA}^{-3}$
253 parameters	$\Delta\rho_{min} = -0.386 e \text{ \AA}^{-3}$

Table 2 selected geometric parameters (\AA , $^{\circ}$)

N2–Cu1	2.037(2)	N1–Cu1	2.009(3)
O3–Cu1	1.976(2)	O1–Cu1	1.976(3)
N3–Cu1	2.263(3)	O1–Cu1–N1	174.58(11)
N2–Cu1–O3	166.71(19)		

Table 3 Hydrogen-bonding geometry (\AA , $^{\circ}$)

Cg4 is the centroid of the N3/C13–C16 ring

D–H \cdots A	D–H	H \cdots A	D \cdots A	\angle D–H \cdots A
Intra C1–H1A \cdots O2 ⁽ⁱ⁾	0.929	2.326	3.249(3)	172
C2–H2A \cdots O2 ⁽ⁱⁱ⁾	0.930	2.522	3.217(5)	132
Intra C10–H10A \cdots O3	0.930	2.586	3.392(4)	145
Intra C14–H14A \cdots O4 ⁽ⁱ⁾	0.930	2.414	3.188(4)	141
C5–H5C \cdots Cg4 ⁽ⁱⁱⁱ⁾	0.931	2.733	3.609(2)	159

Symmetry code: (i) 0.5+x, 0.5-y, 0.5+z (ii) -0.5+x, 0.5-y, 0.5+z (iii) -x, -y, 1-z



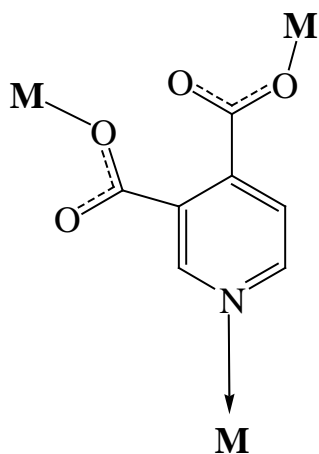


Chart 1 The 3-connected mode of the pda ligand.

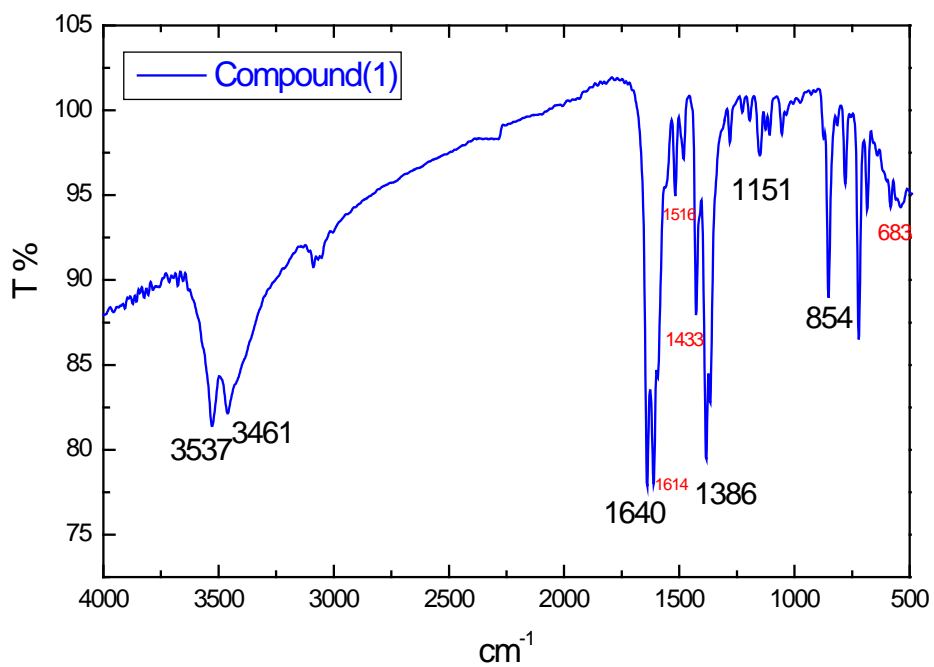


Figure 1 The FT-IR spectrum of the title compound.



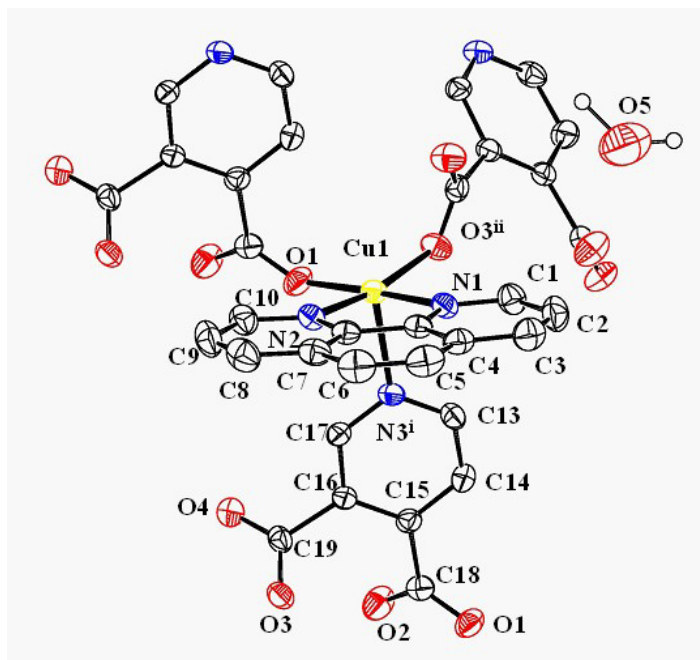


Figure 2 Molecule structure of the title compound (Symmetry code: (i) $0.5+x, 0.5-y, 0.5+z$
(ii) $-0.5+x, 0.5-y, 0.5+z$), the H atoms are omitted for clarity.

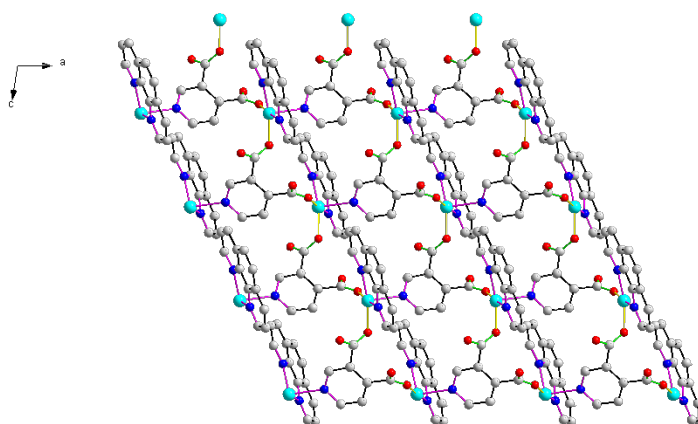


Figure 3 View of two-dimensional layer connected by the pda ligands in title compound from the *b* direction, the H atoms are omitted for clarity.



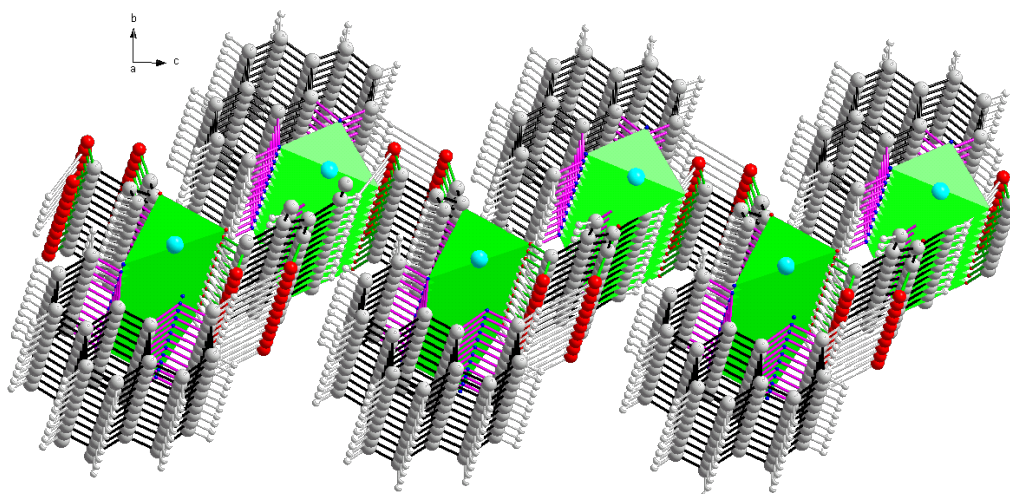


Figure 4 View of the stacking arrangement of the title compound along bc-planar, showing weak hydrogen-bonding and π - π stacking interactions

References

1. Zhang, X. M., Tong, M. L., Gong, M. L. and Chen, X. M., "Supramolecular Organization of Polymeric Coordination Chains into a Three-Dimensional Network with Nanosized Channels that Clathrate Large Organic Molecule," *European Journal of Inorganic Chemistry*, 2003, pp. 138-142.
2. Okabe, N. and Oya, N., "Copper(II) and Zinc(II) Complexes of Pyridine-2,6-dicarboxylic Acid," *Acta Crystallographica Section C: Structural Science*, Vol. 56, 2000, pp. 305-307.
3. Aghabozorg, H., Ghadermazi, M., Sheshmani, S. and Nakhjavan, B., "Tris(piperazinedium) Bis[tris(pyridine-2,6-dicarboxylato)- κ^6 O,N,O' ; κ^2 O,N-indate(III)] dodecahydrate," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 2371-2373.
4. Devereux, M., Mccann, M., Leon, V., McKee, V., Richard, J. and Ball, R. J., "Synthesis and Catalytic Activity of Manganese (II) Complexes of Heterocyclic Carboxylic Acids: X-ray Crystal Structures of $[\text{Mn}(\text{pyr})_2]_n$, $[\text{Mn}(\text{dipic})(\text{bipy})_2] \cdot 4.5\text{H}_2\text{O}$ and $[\text{Mn}(\text{chedam})(\text{bipy})] \cdot \text{H}_2\text{O}$ (pyr = 2- pyrazine carboxylic acid; dipic = pyridine-2,6-dicarboxylic acid; chedam = chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid); bipy = 2,2-bipyridine)," *Polyhedron*, 21, 2002, pp. 1063-1071.
5. Aghabozorg, H., Ghasemikhah, P., Soleimannejad, J., Ghadermazi, M. and Gharamaleki, J.



- A., "Piperazinediium Bis(pyridine-2,6-dicarboxylato)manganate(II) Hexahydrate," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 2266-2268.
6. Aghabozorg, H., Nakhjavan, B., Ghadermazi, M. and Ramezanipour, F., "Bis(propane-1,3-diaminum)tris(pyridine-2,6-dicarboxylato- κ^3 O,N,O')cerate(III)nitrate 3.5-hydrate," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 1527-1529.
 7. Aghabozorg, H., Ghasemikhah, P., Ghadermazi, M., Gharamaleki, J. A. and Sheshmani, S., "Piperazinediium Bis(pyridine-2,6-dicarboxylato)mercurate(II) Hexahydrate," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 2269-2271.
 8. Shen, F. M., "Synthesis, Characterizations, and Crystal Structure of Copper(II) Complex Containing, 2, 6-Pyridinedicarboxylate and, 1, 2-Bis(4-pyridyl)ethane," *Journal of Yuanpei University*, Vol. 13, 2006, pp. 1-10.
 9. Shen, F. M., "Hydrothermal Synthesis and Structure of the Copper(II) Coordination Polymer based on Pyridinedicarboxylate and Bipyridine," *Journal of National University of Tainan*, Vol. 42, No. 2, 2008, pp. 29-40.
 10. Liu, Y., Dou, J. M., Wang, D., Zhang, X. X. and Zhou, L., "Diaqua(pyridine-2,6-dicarboxylato) nickel(II)," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 2208-2209.
 11. Rafizadeh, M., Mehrabi, B. and Amani, V., "Aqua chloro(dimethyl sulfoxide- κ O)(pyridine-2,6-dicarboxylato- κ^3 O,N,O')iron(III)," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 1332-1334.
 12. Jia, B., Meng, X. G., Shi, S. M., Hu, Z. Q. and Luo, F. H., "Tris(dimethylammonium) tris(pyridine-2,6-dicarboxylato- κ^3 O,N,O')europate(III) Dihydrate," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 1799-1801.
 13. Xiang, J., Yin, Y. G. and Huang, X. C., "Diammine(pyridine-2,6-dicarboxylato)copper(II)," *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 4-6.
 14. Wang, X., Qin, C., Wang, E., Hu, C. and Xu. L., "A Novel Three-dimensional Supramolecular Network Containing One-dimensional Trapezoid Channels based on Nickel and Mixed Organic Ligands Assembly," *Journal of Molecular Structure*, Vol. 692, 2004, pp. 187-193.
 15. Min, D., Yoo, S. S., Lee, J. H., Suh, M. and Lee, S. W., "A Three-dimensional Cobalt (II)Coordination Polymer based on 3,5-pyridinedicarboxylate," *Inorganic Chemistry Communications*, Vol. 4, 2001, pp. 297-300.
 16. Whitfield, T., Zheng, L. M., Wang, X. and Jacobson, A. J., "Syntheses and Characterization of Co(pydc)(H₂O)₂ and Ni(pydc)(H₂O) (pydc=3,5-pyridine-dicarboxylate)," *Solid State Science*, Vol. 3, 2001, pp. 829-835.
 17. Zheng, N., Xu, H., Wu, Y., Yang, R., Ye, E. and Jin, X., "Mn(II) Ion Center in Novel Coordination Environment: A New Two-dimensional Coordination Polymer [Mn(3,5-pdc)



- 2H₂O] .,” *Journal of Molecular Structure*, Vol. 610, 2002, pp. 47-52.
18. Zhang, X. P., Yang, G. and Ng, S. W., “Pentaaqua(pyridine-3,5-dicarboxylato- κ N)nickel(II) dihydrate,” *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 791-792.
 19. Tong, M. L., Wang, J., Hu, S. and Batten, S. R., “A New (3,4)-connected three-dimensional Anionic Porous Coordination Net Templated by Me₄N⁺ Cations,” *Inorganic Chemistry Communications*, Vol. 8, 2005, pp. 48-51.
 20. Wang, H. S., Shi, W., Zhai, B., Ma, J. G., Jun Xia, J. and Cheng, P., “Two 2D Cadmium Coordination Polymers with 3,4-pyridinedicarboxylic Acid,” *Journal of Molecular Structure*, Vol. 833, 2007, pp. 102-107.
 21. Xia, S. Q., Hu, S. M., Dai, J. C., Wu, X. T., Zhang, J. J., Fu, Z. Y. and Du, W. X., “Two 2D, 3D Cadmium-pyridinedicarboxylate Polymers: Structures and Photoluminescent Properties,” *Inorganic Chemistry Communication*, Vol. 7, 2004, pp. 51-53.
 22. Han, Z. B. and He, Y. K., “Catena-Poly[bis[di aquaisonicotinogadolinium(III)]-bis(μ ₃-pyridine-3,4-dicarboxylato)],” *Acta Crystallographica Section E: Structural Science*, E62, 2006, pp. 2374-2376.
 23. Wang, X. L., Qin, C. and Wang, E. B., “Poly[[(1,10-phenanthroline- κ ²N,N')cadmium(II)] - μ ₃-pyridine-3,4-dicarboxylato- κ ⁵N:O,O':O",O"'],” *Acta Crystallographica Section E: Structural Science*, E61, 2005, pp. 1234-1236.
 24. Sheldrick, G. M., HELXL97, University of Gottingen, Germany, 1997.
 25. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compound*, Wiley, New York, 1986.
 26. Brown, I. D. and Altermatt, D., “Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database,” *Acta Crystallographica Section B: Structural Science*, B41, 1985, p. 244.
 27. Ikram, B. and Fatma, Z., “ [4-(2-Aminoethyl)piperazin-1-ium]trichloridocopper (II) monohydrate,” *Acta Crystallographica Section E: Structural Science*, E65, 2009, p. 1539.
 28. Bruker, SMART and SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
 29. Spek, A. L., “Structure Validation in Chemical Crystallography,” *Acta Crystallographica Section D: Structural*, D65, 2009, pp. 148-155.
 30. Steiner, T., “The Hydrogen Bond in the Solid State,” *Angewandte Chemie International Edition*, Vol. 41, 2002, pp. 48-76.

