

利用水熱合成含吡啶雙羧酸之鈷金屬配位化合物及其結構分析

Hydrothermal Synthesis and Structure of the Cobalt(II) Complex based on Pyridinedicarboxylate

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摘要：將 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 、2,5-吡啶雙羧酸以及 4,4'-雙吡啶加水混合，利用水熱合成，得到單核的鈷(II)錯合物，其化學式為 $[\text{Co}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{H}_2\text{O})_2]$ 。利用元素分析儀、FTIR 光譜儀以及 X-Ray 晶體繞射儀，測定產物晶體結構及性質，結果顯示錯合物是以鈷(II)離子為反置中心，含兩個吡啶環上的 N 原子、兩個第二位置羧酸上的 O 原子以及兩個配位水分子，配位構成六配位扭曲八面體型的幾何結構，具有 C_2 的對稱性。由於吡啶雙羧酸以及配位水分子，因分子間的氫鍵作用，使得此晶體結構很穩定。

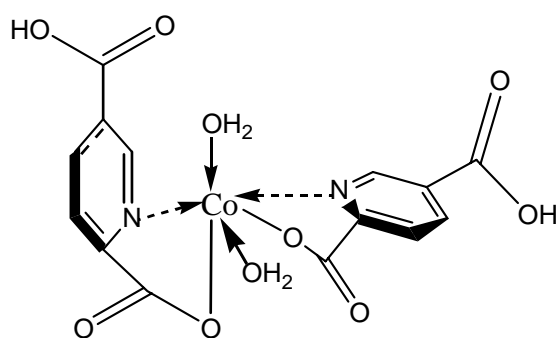
關鍵字：水熱合成、2,5-吡啶雙羧酸、4,4'-雙吡啶、氫鍵

Abstract: The hydrothermal reaction of cobalt(II) chloride hexahydrate with 2,5-pyridinedicarboxylic acid and 4,4'-dipyridyl gave a mononuclear Co(II) compound, the empirical formula of $[\text{Co}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{H}_2\text{O})_2]$. The crystalline product have been characterized by elemental analysis, FTIR spectroscopy, and X-ray diffraction. The title compound, the coordination sphere of the Co metal, is distorted octahedral coordination with an approximate C_2 symmetry. It is defined by two pyridine N atom, two carboxylato O atoms and two water O atoms in cis positions. The crystal structure is stabilized by intermolecular O-H...O hydrogen bonds between carboxy and water O atoms.

Key words : Hydrothermal synthesis, 2,5-pyridinedicarboxylic acid, 4,4'-dipyridine, Hydrogen bonding

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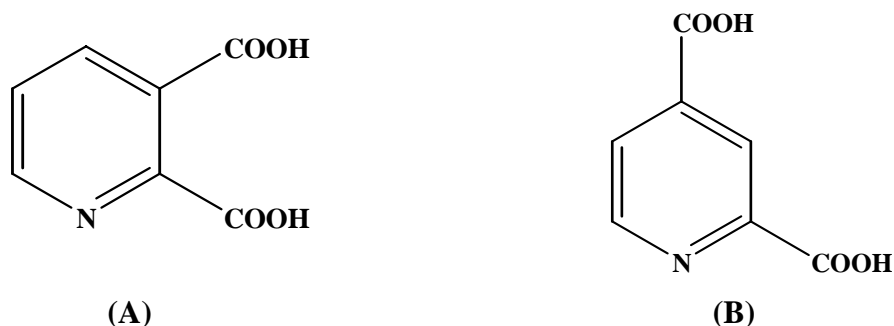


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I. Introduction

The design of crystalline materials of polymeric coordination networks stems from their potential applications as zeolite-like materials for molecular selection, catalysis and ion exchange, as well as in the variety of architectures and topologies¹⁻⁶. Recently, the extended structure of supra-molecular compounds by the self-assembly of metal-organic units via hydrogen bonds has attracted much interest⁷. Proper selection of metal ions and ligands is the key to designing⁸⁻⁹. In preparing coordination polymers, pyridine dicarboxylates have been frequently employed, including 2,3-pyridinedicarboxylic acid (**A**), 2,4-pyridinedicarboxylic acid (**B**), 2,5-pyridinedicarboxylic acid (**C**), 2,6-pyridinedicarboxylic acid (**D**), 3,4-pyridinedicarboxylic acid (**E**), 3,5-pyridinedicarboxylic acid¹⁰⁻¹² (**F**) (Chart 1).

2,5-pyridinedicarboxylic acid, with divergent function groups, which could give more possibility to form bridging hydrogen bonds, is interesting and has potential for self-assembly. The complexation of metal ions using the deprotonated conjugate base of 2,5-pyridinedicarboxylic acid as a ligand has been reported in the literature^{13,14,15}. 2,5-pyridinedicarboxylate is a polydentate ligand having the coordination ability of both dicarboxylate and pyridyl ligands. Presumably as a result of the presence of one pyridine N atom and two carboxylate groups in this ligand, it was found that the ligand synthesized hydrothermally coordinates two or more metal ions in bridging and chelating mode. Owing to the unique ability of the ligand to form stable chelates with various coordination modes and its biological activity, many crystal structures have been determined. We report herein the preparation of crystal structure of the cobalt complex() $\text{cis-[Co(C}_7\text{H}_4\text{NO}_4)_2(\text{H}_2\text{O})_2]$.



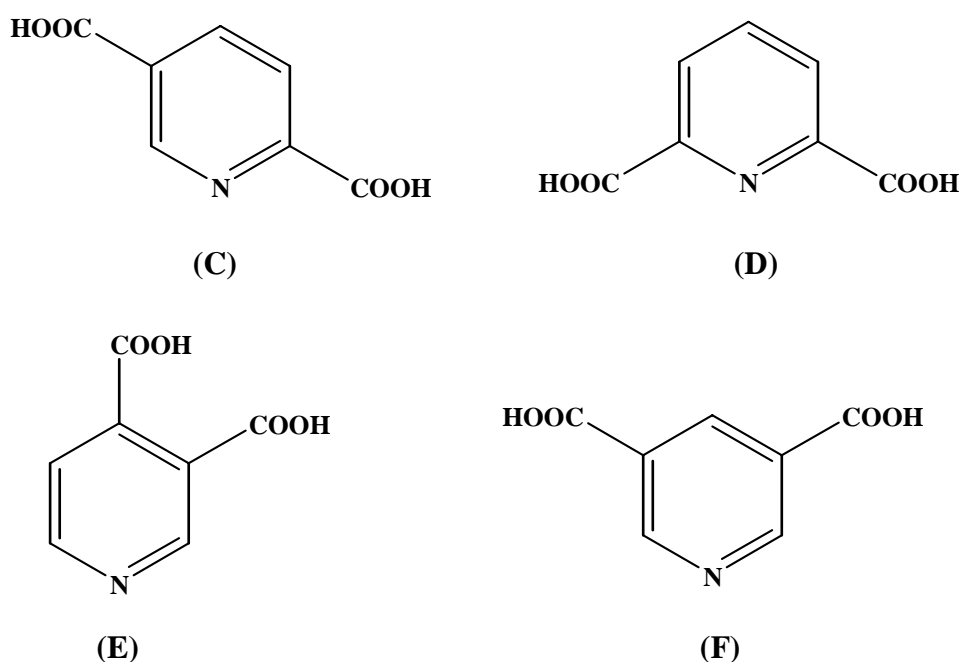


Chart 1

II. Results and discussion

Compound(I) has been prepared by hydrothermal reactions under nearly neutral conditions (the pH value adjusted to ~7.0). Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) reacts with 2,5-pyridinedicarboxylic acid and 4,4'-dipyridyl at 145°C to give 2,5-pyridinedicarboxylato cobalt(II). 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(I) was tried in the absence of 4,4'-dipyridyl, only very poor crystalline products were obtained, and therefore we gave up further characterizations.

Compound(I) has been obtained as orange yellow crystals in relatively high isolation yield (84.78%). The FTIR spectrum of compound(I) exhibits peaks at 1715 , 1625 , and 1494 cm^{-1} that can be assigned to the asymmetric and symmetric C=O stretches, respectively. The FTIR spectrum of ligand also shows strong peaks characteristic of the carboxylate groups at 1732 , 1636 , and 1597 cm^{-1} . (Fig 1).

The structural data of $[\text{Co}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{H}_2\text{O})_2]$ are listed in Table 1. In title compound(I), the complex is located on a twofold axis of symmetry which passes through C3, N1, Co1, N1 and C4 (Fig 2) and contains two identical monoanionic ligands. The coordination environment of cobalt ion centers is shown in Fig 2. The cobalt ion center is in the distorted octahedron coordination environment and is coordinated with two 2,5-pyridinedicarboxylato ligands, and two aqua ligands. The formal oxidation state of the Co metal is +2 (d^7). The metal ion shows six-coordination with an approximate C_2 symmetry. The equatorial plane, defined by Co1, N1', O2', O1' and N1 atom. The Co^{II} ion bonded to the nitrogen [(Co(1)-N(1) 2.149(5) Å] and one negatively charged O atom [(Co(1)-O(2) 2.091(3) Å] of the monoanionic ligand and one aqua ligand [(Co(1)-O(1) 2.058(3) Å]. The axial positions by one negatively charged O atom [(Co(1)-O(2) 2.091(3) Å] and one aqua ligand [(Co(1)-O(1) 2.058(3) Å] (table 1). The carboxy group at position 5 is not ionized. Both of the carboxy groups are



nearly coplanar with the pyridine ring, as indicated by the torsion angles [O(2)-C(6)-C(1)-N(1) -0.99(59) and C(5)-C(4)-C(7)-O(5) 10.07(67)⁰].

The contradiction is apparently caused by five intermolecular hydrogen-bonding interactions between H atoms of the coordinated water molecules and O atoms of the 2,5-pyridinedicarboxylate ligand. In the intermolecular hydrogen bonds, C2 acts as a H-donor to O5: C2-H2A=0.892(4) Å, H2A...O5=2.396(6) Å, C2...O5=3.258(6) Å and C2-H2A-O5=162.7⁰; O4 acts as a H-donor to O2: O4-H4A=0.943(4) Å, H4A...O2=1.729(3) Å, O4-O2=2.614(5) Å and O4-H4A-O2=154.9⁰; O1 acts as a H-donor to O3: O1-H1B=0.987(4) Å, H1B...O3=1.722(5) Å, O1-O3=2.686(6) Å and O1-H1B-O3=164.5⁰; C5 acts as a H-donor to O3: C5-H5A=0.885(4) Å, H5A...O3=2.442(4) Å, C5-O3=3.307(5) Å and C5-H5A-O3=165.6⁰; O1 acts as a H-donor to O5: O1-H1A=0.805(4) Å, H1A...O5=1.993(4) Å, O1-O5=2.783(6) Å and O1-H1A-O5=166.8⁰. The hydrogen-bonding interactions are normal¹⁶, based on H...A distances of 1.72-2.44 Å, D...A distances of 2.614-3.307 Å, and bond angles of 155-167⁰(table 2).

Compound(1) as zero-dimensional(0-D) complex was assembled into 3-D networks via O-H...O hydrogen bond (Fig 3).

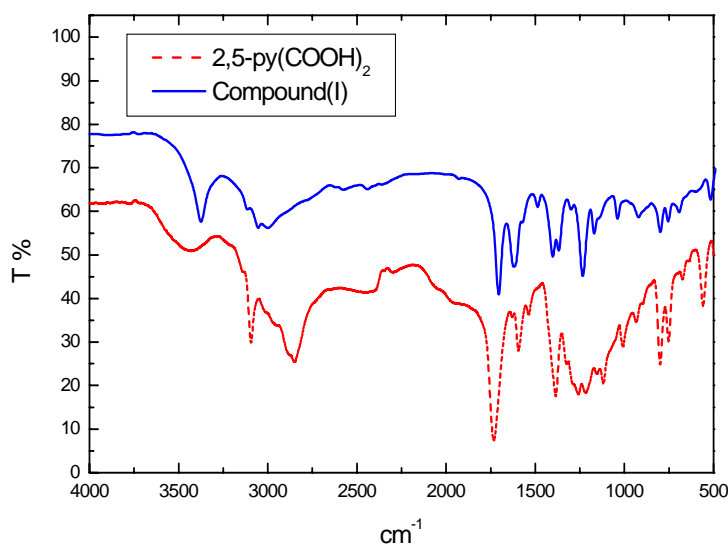


Figure 1 The FTIR spectroscopy of ligand and compound(1)

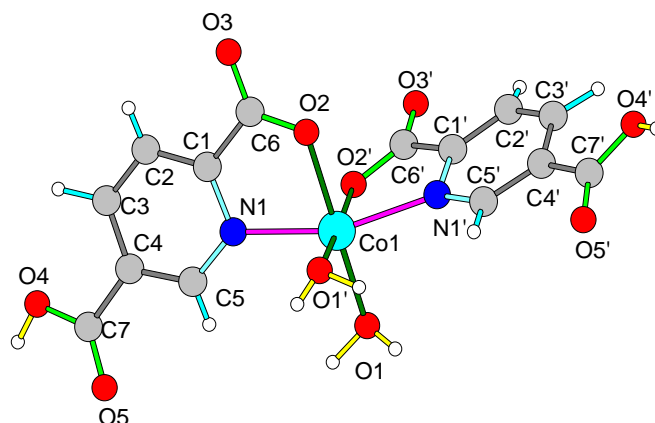


Figure 2 The molecular structure of (I). showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level



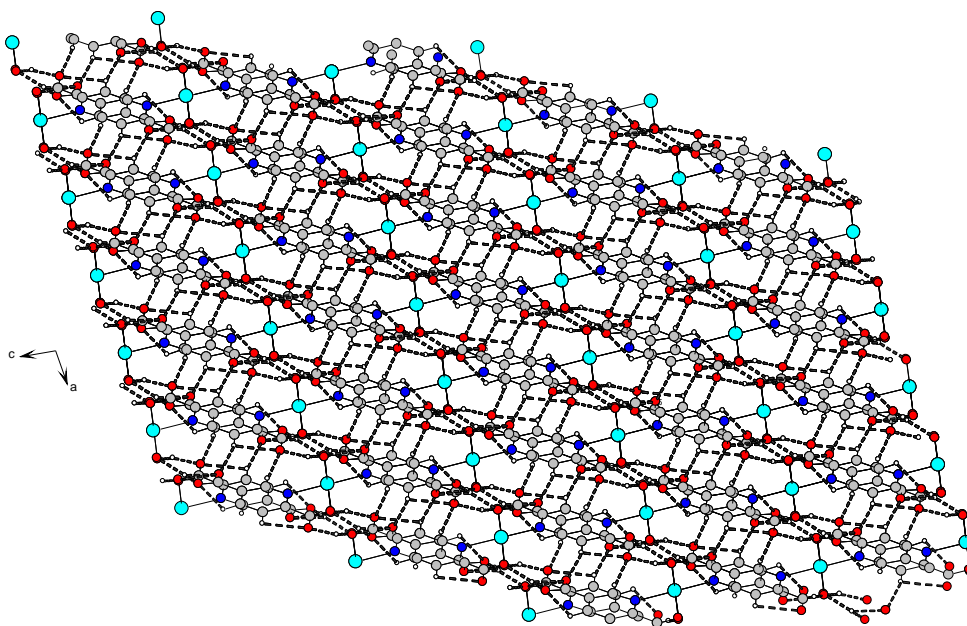


Figure 3 The crystal packing diagram of (I), with hydrogen bonds shown as dashed line, viewed along the b-axis

. Experimental

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0476g, 0.20mmole), pyridine-2,5-dicarboxylic acid (0.0334g, 0.20mmole), 4,4'-dipyridyl (0.0312g, 0.20mmole) and distilled water (7mL) was sealed in a 23 mL Teflon-lined stainless autoclave was heated to 145°C under autogenous pressure for 48h, then allowed to cool slowly to room temperature. Small orange yellow crystals were obtained (yield 84.78%). Anal. Calc. for $\text{CoC}_{14}\text{H}_{12}\text{N}_2\text{O}_{10}$ (Mr=427.19) : C, 39.33; H, 2.81; N, 6.55 (%). Found : C, 39.29; H, 2.78; N, 6.58(%). IR (KBr, cm^{-1}) : 3377, 3055, 1715(C=O), 1625(C=O), 1494(C=O), 1407, 1364, 1234, 1171, 1042, 792.



Table 1 Crystal data

[Co(C ₇ H ₄ NO ₄) ₂ (H ₂ O) ₂]	Z = 4
Mr = 427.19	Dx = 1.794 Mg m ⁻³
Monoclinic C2/c	Mo K α radiation
a = 8.6231(10) Å	Cell parameters from 1707 reflections
b = 12.0929(13) Å	θ = 2.5–25 ^o
c = 15.4323(17) Å	μ = 1.66 mm ⁻¹
α = 90.00 ^o	T = 294 (2) K
β = 100.567 (2) ^o	Organe
γ = 90.00 ^o	0.05x 0.10x 0.10 mm ³
V = 1582.0 (3) Å ³	
Data collection	
Bruker SMART CCD area-detector	1627 independent reflections
Diffractionmeter	1134 reflections with I > 2 σ (I)
ψ and ω scans	Rint = 0.0802
Absorption correction: multi-scan (SADABS; Sheldrick, 1995)	θ max = 26.41 ^o
Tmin = 0.872, Tmax = 0.968	h = -9→10
4488 measured reflections	k = -11→15
	l = -19 →19
Refinement	
Refinement on F ²	H-atom parameters not refined
R[F ² > 2 σ (F ²)] = 0.0512	w = 1/[σ^2 (Fo ²) + 5.5131P]
wR(F ²) = 0.0883	where P = (Fo ² + 2Fc ²)/3
S = 1.161	(Δ/σ)max = 0.000
1627 reflections	$\Delta\rho$ max = 0.625e Å ⁻³
123 parameters	$\Delta\rho$ min = -1.069 e Å ⁻³

Table 2 selected geometric parameters(Å, °)

N1-Co1	2.149(5)	O1-Co-O2	176.31(11)
O1-Co1	2.058(3)	N1-Co1-N2	160.19(17)
O2-Co1	2.091(3)		

Table 3 Hydrogen-bonding geometry(Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
C2-H2A...O5 ⁽ⁱ⁾	0.892(4)	2.396(4)	3.258(6)	162.7
O4-H4A...O2 ⁽ⁱⁱ⁾	0.943(4)	1.729(3)	2.614(5)	154.9
O1-H1B...O3 ⁽ⁱⁱⁱ⁾	0.987(4)	1.722(5)	2.686(6)	164.5
C5-H5A...O3 ^(iv)	0.885(4)	2.442(4)	3.307(5)	165.6
O1-H1A...O5 ^(v)	0.805(4)	1.993(4)	2.783(6)	166.8

Symmetry code: (i)0.5+x,0.5+y,z (ii)-0.5+x,1.5+y,0.5+z (iii)-1.5-x,-0.5+y,0 (iv)-0.5+x,-0.5+y,z (v)-2-x,1-y,1-z

The H atoms were located in a difference Fourier synthesis but were not refined; their U_{iso} values were set to 0.05 Å².

Data collection SMART¹⁷; cell refinement: SMART; data reduction: SAINT¹⁸ program(s) used to solve structure: SHELXS97¹⁹; program(s) used to refine structure: SHELXL97²⁰; molecular graphics: SHELXTL¹⁷; software used to prepare material for publication SHELXTL.

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References

1. Zaworotko, M. J., *Chem. Soc. Rev.*, 1994, p. 283.
2. Abrahams, B. F., Michall, B. F., Hoskins, D. M. and Robson, R., *Nature* 374, 1995, p. 727.
3. Gardner, G. B., Venkataraman, D., Moore, J. S. and Lee, S., *Nature* 374, 1995, p. 792.
4. Yaghi, O. M., Davis, H. L., Richardson, C. D. and Groy, T. L., *Acc.Chem. Res.* 31, 1998, p. 474.
5. Braga, D. F., Grepioni, Desiraju, G. R., *Chem. Rev.* 98, 1998, p. 1375.
6. Hagrman, P. J., Hagrman, D. and Zubieta, J., *Angew. Chem., Int. Ed.Engl.* 38, 1999, p. 2638.
7. Feng, P., Bu, X. and Stucky, G. D., *Nature* 388, 1997, p. 735.
8. Baten, S. R., Hoskin, B. F. and Robson, R. *J. Am. Chem. Soc.* 117, 1995, p. 5385.
9. Gardner, G. B., Venkataraman, D., Moore, J. S. and Lee, S., *Science.* 374, 1995, p. 792.
10. Yaghi, O. M., Davis, C. E., Li, G. and Li, H. *J. Am. Chem. Soc.* 119, 1997, p. 2861.
11. Reineke, T. M., Eddaoudi, M., O'Keeffe, M., Yaghi, O. M. *Angew, Chem., Int. Ed. Engl.* 38, 1999, p. 2590.
12. Lin, W., Evans, O. R., Xiong, R. G. and Wang, Z. *J. Am. Chem. Soc.* 120, 1998, p. 13272.
13. Liang, Y., Hong, M., Su, W., Cao, R. and Zhang, W., *Inorg. Chem.* 40, 2001, pp. 4574-4582.
14. Liang, Y., Hong, M. and Cao, R., *Acta Cryst.* E57, 2001, pp. m145-m147.
15. Plater, M. J., Foreman, M. R. St J., Howie, R. A. and Lachowski, E. E. *J. Chem. Res. (S)*, 1998, pp. 754-755.
16. Steed, J. W. and Atwood, J. L., *In Supramolecular Chemistry*, New York: Wiley, 2000.
17. Bruker, *SMART and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
18. Bruker, *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA, 1998.
19. Sheldrick, G. M., *Acta Cryst.* A46, 1990, p. 467
20. Sheldrick, G. M., *HELXL97*, University of Gottingen, Germany, 1997.

