

---

**Journal of Physical & Theoretical Chemistry**  
**Islamic Azad University of Iran 3 (3)**  
**(2006)**

*Science and Research Campus*  
ISSN: 1735-2126

---

**Synthesis, Characterization, and Crystal Structure of a New  
Coordination Polymer,  $\{[\text{Ba}_2(\text{Hpydc})_2(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\cdot(\text{H}_2\text{pydc})\}_n$**

Massoud Rafizadeh

Department of Textile, Shahre-Ray Branch, Islamic Azad University, Tehran Iran

**ABSTRACT**

The reaction of barium chloride with 2, 6-pyridinedicarboxylic acid in water led to the formation of a novel polymeric complex formulated as  $\{[\text{Ba}_2(\text{Hpydc})_2(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\cdot(\text{H}_2\text{pydc})\}_n$  (**I**). The crystal structure of (**I**) was characterized by single crystal X-ray diffraction method. The complex was crystallized in the monoclinic system with space group P2/c, with four molecule in unit-cell, e.g Z=4. The unit-cell parameters were a= 15.320(3) Å, b= 6.902(1) Å, c= 19.930(4) Å;  $\beta = 97.39^\circ$  (3). The unit-cell of this novel self assembled pyridine containing ligand system was constructed from eight and ten coordinate barium ions. Noteworthy, compound (**I**) consisted of three different kinds of neutral  $\text{H}_2\text{pyd}$  and anionic  $\text{Hpydc}^-$ ,  $\text{pydc}^{2-}$  forms of 2,6-pyridinedicarboxylic acid ligands.

## INTRODUCTION

In recent years, the crystal engineering of supramolecular architectures based on metal and organic building blocks has rapidly emerged as an exciting area of supramolecular chemistry because of their novel and diverse topologies and potential applications in host-guest chemistry, catalysis, electrical conductivity, and magnetism [1, 2]. The creation of metal-organic coordination networks based on complexes of transition metals and multifunctional bridging ligands, such as polyamine, polyacid, and so on, have proven to be a fertile field due to the intriguing network topologies and potential functions as new classes of materials.

Dipicolinic or 2,6-pyridinedicarboxylic acid (H<sub>2</sub>pydc) is a natural compound involved in various metal chelation reactions related to the thermal resistance of certain bacteria spores [3] as well as in the activation [4] or inhibition [5] of some metallo-enzymes. This amino diacid differs from most common zwitterionic amino acids in adopting a well known molecular structure [6] and in a rather peculiar coordination chemistry, markedly influenced by its constrained planar conformation [7]. A large variety of structures have been reported to H<sub>2</sub>pydc, Hpydc<sup>-</sup> and/or pydc<sup>2-</sup> ligand forms.

Recently, 2, 6- pyridinedicarboxyl acid has been used as a ligand coordinated to some transition metal or rare earth, and a series of complexes having infinite or discrete structure have been obtained [8,9]. 2,6-Pyridinedicarboxylic acid is a good chelating reagent with limited steric hindrance and can provide further possibility to form polymeric complexes through bridging coordination of carboxylates under approximate conditions [8, 9]. Now, in continuation to our previous works [10], we wish to report the synthesis and crystal structure of a polymeric compound formed by reaction of 2,6-Pyridinedicarboxylic acid with Ba(II).

## Experimental

All of the starting materials and reagents were obtained commercially and used after further purification. Fourier transform

(FT)-IR spectra (KBr pellets) were taken on a Perkin-Elmer 8343 Spectrophotometer. UV-vis spectra carried out on a Shimadzu- 3100 Spectrophotometer. Solution spectra recorded in a 1cm quartz cell. Microanalyses performed on a GNBH-West Ger. elemental analyzer. Melting points obtained by using a Thermal 9100 Certain .

Infrared spectra (4000-200 cm<sup>-1</sup>) of solid samples were taken as 1% dispersion in KBr pellets using a Shimadzu-470 spectrometer. <sup>1</sup>H-NMR spectra were acquired on a Bruker AC-300 MHz spectrometer at ambient temperature in D<sub>2</sub>O. All chemical shifts are quoted in parts per million (ppm) relative to tetramethylsilane .

Syntheses of  $\{[Ba_2(Hpydc)_2(pydc)(H_2O)_3].H_2O.(H_2pydc)]_n BaCl_2 (1 \text{ mmol}, 0.21 \text{ g}) \text{ in } 50 \text{ ml} \text{ was added to } 100 \text{ ml} \text{ aqueous solution of } 2, 6\text{-pyridinedicarboxylic acid (2 mmol}, 0.33 \text{ g}) \text{ and } 2,2'\text{-bipyridine (2 mmol}, 0.32 \text{ g}). \text{ Then, the reaction mixture was stirred at } 60^\circ \text{C for } 20 \text{ min. The clear purple solution was concentrated slowly under air at ambient temperature to produce fine white prismatic crystals (86\% Yield). The product was re-crystallised from the mother HCl (0.1 M) liquors, resulting in suitable white crystals for X-ray purposes. Crystals of the desired product appeared over a period of 2 week (74 \% yield). This product melted at } \{mp: 300^\circ \text{C (decomposition)}\} \text{ with anal. Found Found C } 33.02 \text{ (calcd. } 33.25), \text{ H } 2.23 \text{ (2.37)\% and N } 5.61(5.54)(\%), \text{ for (I)(\%), Analytical data were consistent with the empirical formula of } \{[Ba_2(Hpydc)_2(pydc)(H_2O)_3].H_2O.(H_2pydc)]_n \text{ (F.W., } 1010.64). \text{ }^{13}\text{C-NMR signal at } 42 \delta, \text{ ppm revealed that all carbon atoms were identical. Major IR bands (KBr; } \nu, \text{ Cm}^{-1}\text{):$

3511 s, 3360 m, 3285 w, 3085 w, 1693 m, 1660 m, 1611 s, 1563 s, 1440 m, 1370 s, 1326 m, 1263 m, 1170 m, 1079 m, 1003 m, 902 m, 823 m, 765 s, 731 s, 706 s, 655 s, 585 m, 524 m, 449 m, 433 m, 375 m.

### X-ray crystallographic data collection and structural determination

The crystal was studied at 297(2) K on a Bruker SMART CCD 1000 diffractometer using Mo  $K_{\alpha}$  radiation. The data were processed with SAINT [11] and corrected for absorption with SADABS [12]. The structure was solved by direct methods and refined to a good final agreement factor  $R1 = 0.025$ . Other relevant crystal data were  $a = 15.320(3)$ ,  $b = 6.902(1)$ ,  $c = 19.930(4)$  Å;  $\beta = 97.39(3)$ ,  $fw = 656.82$ ,  $Z = 4$ ,  $\mu = 2.894 \text{ mm}^{-1}$ , data / restraints / parameters 4789 / 6 / 328,  $D_{\text{calc}} = 2.087 \text{ Mg m}^{-3}$ . Crystallographic data files of  $\{[\text{Ba}_2(\text{Hpydc})_2(\text{pydc})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O} \cdot (\text{H}_2\text{pydc})\}_n$  have been deposited with the Cambridge Crystallographic Data Centre, number CCDC 273364. The crystal data and experimental parameters are given in Table 1.

### Results and Discussion

The rational design of novel metal-organic frameworks has attracted great interest from chemists in recent years [13, 14] and considerable efforts have been focused on the design, synthesis and characterization of novel multidimensional complex not only because of their intriguing variety of architectures and topologies but also because of their fascinating potential applications in functional solid materials, ion exchange, catalysis, and the development of optical, electronic, and magnetic devices [15].

Complex **I** was prepared by the reaction of Ba(II) with  $\text{H}_2\text{pydc}$  and  $\text{Hpydc}^-$

ligands as described in the experimental. The product was identified by physical techniques such as infrared NMR spectroscopy, elemental analysis and X-ray diffraction techniques. The crystallographic studies resulted in compound (**I**) is crystallized in a monoclinic system with space group  $P2_1/c$ . The monomer of this novel self assembled pyridine containing ligand system was involved two different kinds of eight and ten coordinate barium ions (Fig. 1). The ten-coordinate  $\text{Ba}_1$  geometry was distorted square planar surrounded by a trigonal anti-prism. Whereas the  $\text{Ba}_2$  was also an eight coordinate barium, with was in a distorted bi-capped octahedron geometry.

It is noteworthy, compound (**I**) consisted in three different kinds of neutral ( $\text{H}_2\text{pydc}$ ) and anionic ( $\text{Hpydc}^-$ ,  $\text{pydc}^{2-}$ ) forms of pyridine dicarboxylic ligands in the crystal structure. The  $\text{sp}^2$  oxygen atoms of  $\text{Hpydc}^-$  and  $\text{pydc}^{2-}$  acted as the three centered nuclei and bridged barium ions together.

One set of barium ions ( $\text{Ba}_2$ ) was involved with  $\text{pydc}^{2-}$ , acted as a tridentate ligand, a water molecule, and four bridging oxygen atoms. These bridging groups were originated from the deprotonated O-carboxylate groups of pyridine fragment of  $\text{Hpydc}^-$  and  $\text{pydc}^{2-}$  ligands. Therefore, the coordination number around  $\text{Ba}_2$  was 8.

Whereas the six coordination sites around  $\text{Ba}_1$  were occupied by the two bridging O-carboxylates and N-pyridine donor atoms of two trans  $\text{Hpydc}^-$ . The four remaining positions around each  $\text{Ba}_1$  were occupied by two water molecules and two bridging O-carboxylate oxygen atoms of neighboring  $\text{pydc}^{2-}$  ions.

This coordination polymer is part of a 3D network of hydrogen bonds according to Figure 2. The linker were the hydrogen bonds included between free

H<sub>2</sub>pydc and trapped water molecules, in the crystal structure, with the coordinated ligands.

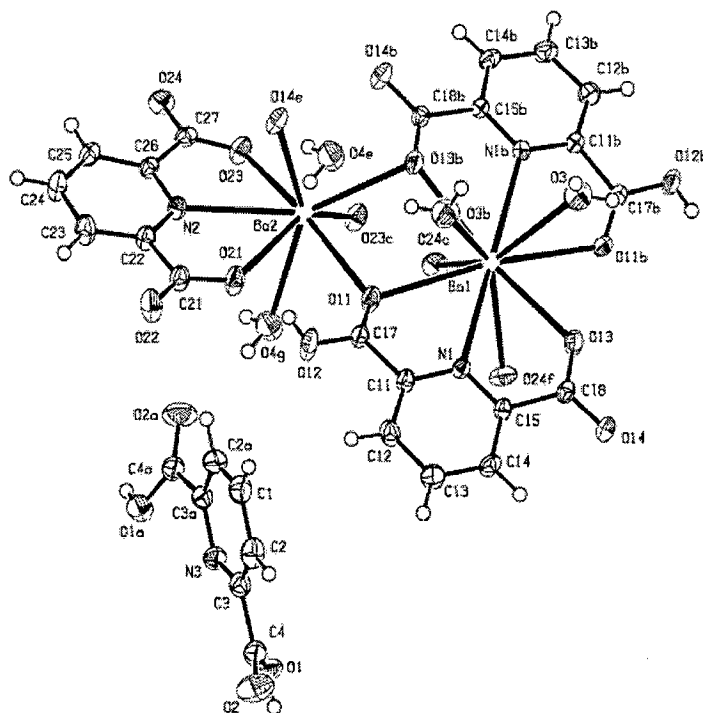


Fig. 1. ORTEP diagram and numbering scheme of (I) with the atom labeling.

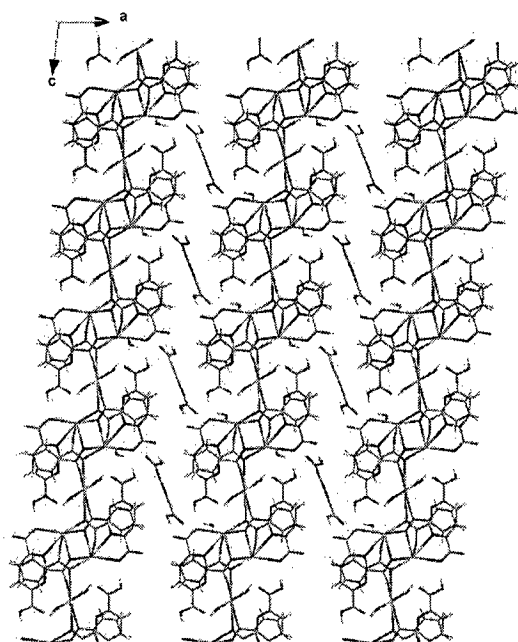


Fig. 2. Unit-cell packing diagram of (I).

**Table 1.** Crystallographic data and data-collection parameters for the complex (I)

Chemical formula	$\{[\text{Ba}_2(\text{Hpydc})_2(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\cdot(\text{H}_2\text{pydc})\}_n$
Empirical formula	$\text{C}_{28}\text{H}_{24}\text{Ba}_2\text{N}_4\text{O}_{20}$
Formula weight	1010.64
Temperature	297(2)K
Wavelength	0.71073Å
Crystal system	Monoclinic
Space group	P2/c
Unit cell dimensions	$a = 15.320(3)\text{Å}$ , $\alpha = 90^\circ$ $b = 6.902(1)\text{Å}$ , $\beta = 97.39(3)^\circ$ $c = 19.930(4)\text{Å}$ , $\gamma = 90^\circ$
V	2090.1(7) Å <sup>3</sup>
Z	4
Calculated density	2.087 Mg/m <sup>3</sup>
Absorption coefficient	2.894 mm <sup>-1</sup>
F(000)	1264
Crystal size	0.30 × 0.09 × 0.04 mm <sup>3</sup>
Theta range for data collection	1.34 to 27.60°
Limiting indices	-19 ≤ h ≤ 19, -8 ≤ k ≤ 8, -25 ≤ l ≤ 25
Reflections collected	39817
Independent reflections	4789 [R(int) = 0.079]
Completeness to theta = 27.60°	99.1 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4789 / 6 / 328
Goodness-of-fit on F <sup>2</sup>	1.189
Final R indices [I > 2σ(I)]	R1 = 0.025, wR2 = 0.071
R indices (all data)	R1 = 0.034, wR2 = 0.087
Largest diff. peak and hole	0.659 and -1.367 e. Å <sup>3</sup>

**Table 2.** Selected bond lengths [ $\text{\AA}$ ] and angles [deg] for (I)

O(4)-H(4B)	0.810(19)	C(17)-O(11)	1.219(4)
O(4)-H(4A)	0.794(19)	C(17)-O(12)	1.294(4)
O(11)-Ba(2)	2.881(2)	C(18)-O(13)	1.244(4)
O(11)-Ba(1)	2.912(3)	C(18)-O(14)	1.261(4)
O(12)-H(12O)	0.79(2)	C(21)-O(22)	1.248(4)
O(13)-Ba(1)	2.773(2)	C(21)-O(21)	1.263(4)
O(13)-Ba(2)#2	2.782(2)	C(27)-O(24)	1.245(4)
O(14)-Ba(2)#4	2.783(2)	C(27)-O(23)	1.264(4)
O(21)-Ba(2)	2.754(3)	N(1)-Ba(1)	2.934(3)
O(23)-Ba(2)	2.722(2)	N(2)-Ba(2)	2.878(3)
O(24)-Ba(1)#5	2.832(2)	O(1)-H(1O)	0.830(19)
Ba(1)-Ba(2)	4.4830(10)	O(3)-Ba(1)	2.844(3)
Ba(2)-Ba(2)#5	4.5210(10)	O(3)-H(3B)	0.80(2)
		O(3)-H(3A)	0.80(2)
		O(4)-Ba(2)#3	2.895(3)
O(11)-Ba(1)-Ba(2)	134.93(5)	O(13)-Ba(1)-O(13)	164.22(11)
O(23)-Ba(2)-O(23)	67.87(9)	O(13)-Ba(1)-O(24)	65.89(8)
O(23)-Ba(2)-O(21)	113.38(8)	O(24)-Ba(1)-O(24)	65.28(10)
O(23)-Ba(2)-O(13)	114.19(8)	O(13)-Ba(1)-O(3)	68.56(8)
O(21)-Ba(2)-O(13)	127.69(8)	O(24)-Ba(1)-O(3)	127.89(9)
O(23)-Ba(2)-O(14)	91.22(7)	O(3)-Ba(1)-O(3)	68.41(14)
O(21)-Ba(2)-O(14)	79.32(8)	O(13)-Ba(1)-O(11)	70.19(7)
O(23)-Ba(2)-N(2)	56.88(7)	O(24)-Ba(1)-O(11)	77.44(7)
O(21)-Ba(2)-N(2)	56.80(8)	O(3)-Ba(1)-O(11)	64.28(9)
O(13)-Ba(2)-N(2)	153.43(7)	O(11)-Ba(1)-(11)	163.35(10)
O(14)-Ba(2)-N(2)	76.24(8)	O(13)-Ba(1)-N(1)	6.40(7)
O(23)-Ba(2)-O(11)	103.84(7)	O(13)-Ba(1)-O(13)	164.22(11)
O(21)-Ba(2)-O(11)	67.52(8)	O(3)-Ba(1)-N(1)	104.44(8)
N(2)-Ba(2)-O(11)	123.94(7)	O(11)-Ba(1)-N(1)	55.91(7)
O(23)-Ba(2)-O(4)	70.45(8)	O(13)-Ba(1)-N(1)	56.40(7)
O(21)-Ba(2)-O(4)	72.76(9)	O(24)-Ba(1)-N(1)	69.33(7)
O(13)-Ba(2)-O(4)	130.62(8)	O(3)-Ba(1)-N(1)	72.38(8)
O(14)-Ba(2)-O(4)	148.07(9)	O(11)-Ba(1)-N(1)	55.91(7)
N(2)-Ba(2)-O(4)	75.66(8)	N(1)-Ba(1)-N(1)	176.31(10)
O(11)-Ba(2)-O(4)	82.87(8)		

Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336033; E-mail: [deparite@ccdc.cam.ac.uk](mailto:deparite@ccdc.cam.ac.uk)] quoting the depository no. CCDC 273364. Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+3/2. #2 -x+2, y, -z+3/2. #3 x, -y+1, z-1/2. #4 x, -y, z-1/2. #5 -x+2, -y+1, -z+2. #6 x, -y, z+1/2. #7 x, -y+1, z+1/2.

## REFERENCES

1. (a) Atwood, J. L.; *Supramolecular Chemistry*; Wiley and Sons: New York, 2000. (b) Bond, A. D.; Jones, W. *Supramolecular Organization and Materials Design*; Jones, W., Rao, C. N. R., Eds.; Cambridge University Press: Cambridge, U.K., 2002. (c) Desiraju, G. R. *Crystal Design: Structure and Function; Perspectives in Supramolecular Chemistry Vol. 6*; Wiley: Chichester, U.K., 2003
2. (a) Janiak, C. J.; *Chem. Soc., Dalton Trans.* **2003**, 2781. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; *Coord. Chem. Rev.* **2003**, 246, 247.
3. Okabe, N.; Oya, N.; *Acta Cryst. C.* **2000**, 56, 1416.
4. Martin, B. L.; *Arch. Biochem. Biophys.* **1997**, 345, 332.
5. Scapin, G.; Reddy, S.G.; Zheng, R.; Blanchard, J.S.; *Biochemistry* **1997**, 36, 15081.
6. Carranza-Tellez, V.; Sa'nchez-Gayta'n, B.; Berne's, S.; Gonza'lez-Vergara, E.; *Acta Cryst. C.* **2002**, 58, 228.
7. Nathan, L.C.; *Trends Inorg. Chem.* **1993**, 3, 415.
8. Zhao, B.; Cheng, P.; Dai, Y.; Cheng, C.; Liao, D.-Z.; Yan, S.-P.; Jiang, Z.-H.; Wang, G.-L.; *Angew. Chem., Int. Ed.* **2003**, 42, 934.
9. Takusawa, F.; Hisotsu, K.; Shimada, A.; *Bull. Chem. Soc. Jpn.* **1973**, 46, 2020.
10. (a) Rafizadeh, M.; Ranjbar, M.; Amani, V.; *Acta Cryst.* **2004**, E60, m479-m481.
11. (b) Rafizadeh, M.; Amania, V.; Neumüllerb, B.; *Z. Anorg. Allg. Chem.* **2005**, 631, 1753-1755. (c) Rafizadeh, M.; Amania, V.; Iravanib, E.; Neumüllerb, B.; *Z. Anorg. Allg. Chem.* **2005**, 631, 952-955. (d) Rafizadeh, M.; Amania, V.; Neumüllerb, B.; *Z. Anorg. Allg. Chem.* **2006**, 632, 2383-2384. (e) Rafizadeh, M.; Amania, V.; Neumüllerb, B.; *Z. Anorg. Allg. Chem.* **2006**, 632, 2190-2192.
12. *Area Detector Control and Integration Software*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1997.
13. Sheldrick, G.M.; *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Goettingen, Germany, 1997.
14. (a) Batten, S. R.; Robson, R.; *Angew. Chem., Int. Ed.* **1998**, 37, 1461. (b) Moulton, B.; Zaworotko, M. J.; *Chem. Rev.* **2001**, 101, 1629.
15. (a) Janiak, C.; *J. Chem. Soc., Dalton Trans.* **2003**, 2781. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; *Coord. Chem.ReV.* **2003**, 246, 247.
16. (a) N. V.; Schroder, M.; *Coord. Chem. Rev.* **2001**, 222, 155. (b) Moulton, B.; Zaworotko, M. J.; *Chem. Rev.* **2001**, 101, 1629. (c) Inoue, K.; Imai, H.; Ghalsasi, P. S.; Kikuchi, K.; Ohba, M.; Okawa, H.; Yakhmi, J. V.; *Angew. Chem., Int. Ed.* **2001**, 40, 4242.

