

SYNTHESIS, CHARACTERIZATION, AND CRYSTAL STRUCTURE OF A NEW COORDINATION POLYMER, $\{[\text{Ba}_2(\text{HPydc})_2(\text{Pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}(\text{H}_2\text{Pydc})\}_n$

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ABSTRACT. The reaction of barium chloride with 2,6-pyridinedicarboxylic acid, H₂pydc, in water led to the formation of a novel polymeric complex formulated as $\{[\text{Ba}_2(\text{Hpydc})_2(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}(\text{H}_2\text{pydc})\}_n$ (**I**). The crystal structure of (**I**) was characterized by X-ray diffraction methods. This polymeric complex was crystallized in the monoclinic system with space group P2/c, with four molecules per unit-cell. The unit-cell parameters are a = 15.320(3) Å, b = 6.902(1) Å, c = 19.930(4) Å; β = 97.39° (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 neutral 2,6-pyridinedicarboxylic acid, H₂pydc, anionic Hpydc⁻ and pydc²⁻.

KEY WORDS: Barium, Crystal structure, 2,6-Pyridinedicarboxylic acid

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 [1-5]. The creation of metal-organic coordination networks based on complexes of transition metals and multifunctional bridging ligands, such as polyamine and polyacid, has 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 (H₂pydc) is a natural compound involved in various metal chelation reactions related to the thermal resistance of certain bacteria spores [6] as well as in the activation [7] or inhibition [8] of some metallo-enzymes. This amino di-acid differs from most common zwitterionic amino acids in adopting a well known molecular structure [9] and in rather peculiar coordination chemistry, markedly influenced by its constrained planar conformation [10]. A large variety of structures have been reported for H₂pydc, Hpydc⁻ and/or pydc²⁻.

Recently, 2,6-pyridinedicarboxylic acid has been used as a ligand coordinated to some transition or rare earth metals, and a series of novel complexes having infinite or discrete structure have been obtained. 2,6-Pyridinedicarboxylic acid is a good chelating reagent with a limited steric hindrance and can provide further possibilities by forming polymeric complexes through bridging coordination of carboxylates under approximate conditions [11, 12]. Now, in a continuation of our previous work [13-17], we wish to report the synthesis and crystal structure of a polymeric compound formed by the 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 (4000-200 cm⁻¹) of the solid sample were taken

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as 1 % dispersion in KBr pellets using a Shimadzu-470 spectrometer. Solution spectra were recorded in a 1 cm quartz cell. Microanalyses were performed on a GNBH-West Ger. elemental analyzer. Melting points were obtained by using a Thermal 9100 Certain. NMR spectra were acquired on a Bruker AC-300 MHz spectrometer at ambient temperature in D₂O. All chemical shifts are quoted in parts per million (ppm) relative to tetramethylsilane.

Synthesis of $[[\text{Ba}_2(\text{Hpydc})_2(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}(\text{H}_2\text{pydc})]_n$

BaCl₂ (1 mmol, 0.21 g) in 50 mL water was added to 100 mL aqueous solution of 2,6-pyridinedicarboxylic acid (2 mmol, 330 mg) and 2,2'-bipyridine (2 mmol, 320 mg). Then, the reaction mixture was stirred at 60 °C for 20 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 HCl (0.1 M) liquors, resulting in suitable colorless crystals for X-ray purposes. Crystals of the desired product appeared over a period of 2 weeks (74 % yield). This product melted at 300 °C (decomposition) with anal. found (%): C 33.02 (calcd. 33.25), H 2.23 (2.37) and N 5.61 (5.54). Analytical data were consistent with the empirical formula of $[[\text{Ba}_2(\text{Hpydc})_2(\text{pydc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}(\text{H}_2\text{pydc})]_n$ (F.W. 1010.64). A ¹³C NMR signal at δ 42 revealed that all Carbon atoms were identical. Major IR bands (KBr; ν, cm⁻¹): 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_α radiation. The data were processed with SAINT [18] and corrected for absorption with SADABS [19]. 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) Å, b = 6.902(1) Å, c = 19.930(4) Å; β = 97.39(3), fw = 656.82, Z = 4, μ = 2.894 mm⁻¹, data/restraints/parameters 4789/6/328, D_{calc} = 2.087 Mgm⁻³. Crystallographic data files of (**I**) 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

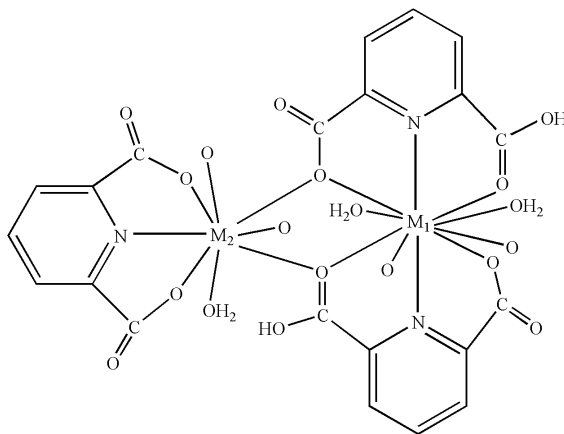
The rational design of novel metal-organic frameworks has attracted great interest from chemists in recent years [20-23] and considerable efforts have been focused on the design, synthesis and characterization of novel multidimensional materials not only because of their intriguing variety of architectures 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[24-26].

Complex **I** was prepared by the reaction of Ba(II) with H₂pydc and Hpydc⁻ ligands as described in the experimental section. The product was identified by physical techniques such as infrared and NMR spectroscopy, elemental analysis and X-ray diffraction techniques. The crystallographic studies revealed that compound (**I**) crystallized in a monoclinic system with space group P2/c. The monomer of this novel self-assembled pyridine containing ligand system involved two different kinds of eight and ten coordinate barium ions (Figure 1). Interestingly, Ba₁ was a ten-coordinate complex with a distorted square planar geometry surrounded by a trigonal anti-prism. Whereas, Ba₂ was an eight coordinate complex, with distorted bi-capped octahedron geometry.

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	0.71073 Å
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	$2090.1(7)\text{Å}^3$
Z	4
Calculated density	2.087 Mg/m^3
Absorption coefficient	2.894 mm^{-1}
F(000)	1264
Crystal size	$0.30 \times 0.09 \times 0.04\text{ mm}^3$
Theta range for data collection	1.34 to 27.60°
Limiting indices	$-19 \leq h \leq 19$, $-8 \leq k \leq 8$, $-25 \leq l \leq 25$
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^2
Data/restraints/parameters	4789/6/328
Goodness-of-fit on F^2	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^{-3}

It is noteworthy that compound **(I)** consists of three different kinds of neutral (H_2pydc) and anionic (Hpydc^- , pydc^{2-}) forms of pyridinedicarboxylic ligands in the crystal structure. The sp^2 oxygen atoms of Hpydc^- and pydc^{2-} acted as three centered nuclei and bridged the barium ions. Scheme 1 shows the coordination modes of pyridinedicarboxylic ligands in **(I)**.

Scheme 1. The coordination modes of pyridinedicarboxylic ligands in **(I)**.

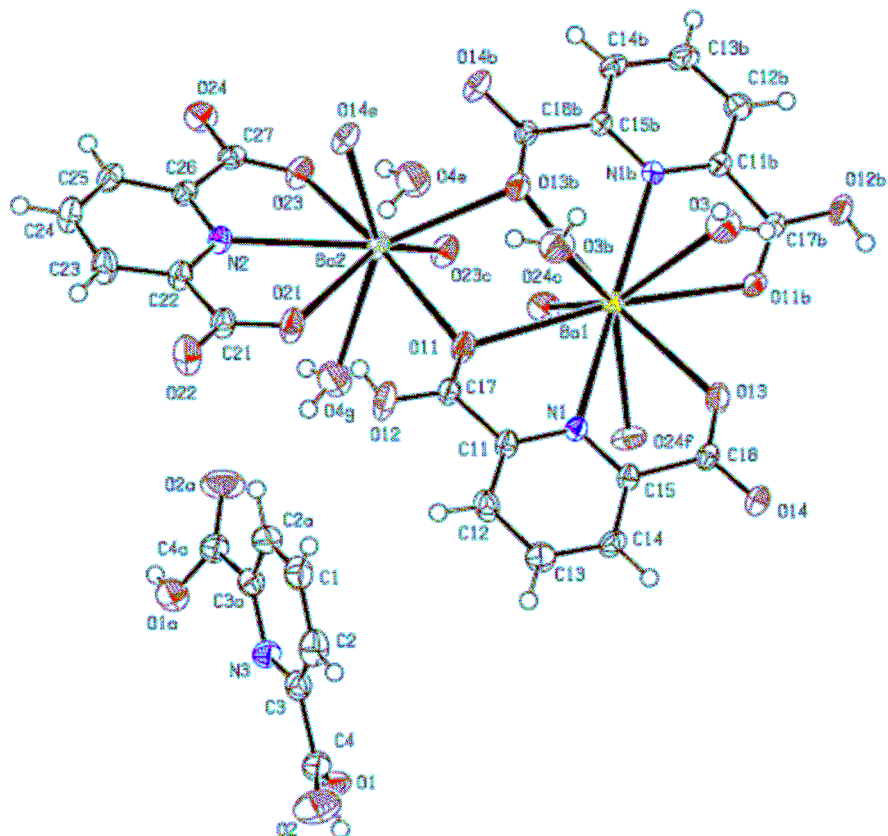


Figure 1. ORTEP diagram and numbering scheme of (I) with the atom labelling.

One set of barium ions (Ba_2) was involved with one $pydc^{2-}$ that acted as a tridentate ligand, a water molecule, and four bridging oxygen atoms. These bridging groups originated from the deprotonated O-carboxylate groups of the pyridine fragment of $Hpydc^-$ and $pydc^{2-}$ ligands. Therefore, the coordination number around Ba_2 was 8. The bond length of Ba_2-N is 2.878(3) Å and that of Ba_2-O are 2.722(2), 2.754(3), 2.881(2), 2.782(2), 2.783(2), 2.722(2), and 2.895(3) Å, respectively. The bond angles of O- Ba_2 -N range from 56.88(7)° to 153.43(7)°, while the O- Ba_2 -O range from 67.52(8)° to 148.07(9)°. Selected bond length and bond angles are given in Table 2.

The six coordination sites around Ba_1 were occupied by the two bridging O-carboxylates and N-pyridine donor atoms of two trans $Hpydc^-$. The four remaining positions were occupied by two water molecules and two bridging O-carboxylate oxygen atoms of neighboring $pydc^{2-}$ ions. The bond lengths of Ba_1-N_1 is 2.934(3) Å and that of Ba_1-O range from 2.773(2) to 2.912(3) Å, respectively. The bond angles of O- Ba_1 -N range from 55.91(7)° to 104.44(8)°, while the O- Ba_1 -O range from 65.28(10)° to 164.22(11)°. The distance of Ba_1 - Ba_2 is 4.4830(10) Å.

This coordination polymer is part of a 3D network of hydrogen bonds according to Figure 2. The linkers were the hydrogen bonds formed between free H_2pydc and trapped water molecules

with the coordinated ligands. This interaction determines the formation of a network formed by $\text{Ba1-O(11)-O(13b)-Ba}_2$ links that run along the c-axis and free H_2Pydc along the a-axis.

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

O(4)-H(4B)	0.810(2)	C(17)-O(11)	1.219(4)
O(4)-H(4A)	0.794(2)	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)	0.790(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)	4.483(1)	O(3)-Ba(1)	2.844(3)
Ba(2)-Ba(2)#5	4.521(1)	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)	134.9(5)		
O(23)-Ba(2)-O(23)	67.87(9)	O(13)-Ba(1)-O(13)	164.2(1)
O(23)-Ba(2)-O(21)	113.4(8)	O(13)-Ba(1)-O(24)	65.89(8)
O(23)-Ba(2)-O(13)	114.2(8)	O(24)-Ba(1)-O(24)	65.28(1)
O(21)-Ba(2)-O(13)	127.7(8)	O(13)-Ba(1)-O(3)	68.56(8)
O(23)-Ba(2)-O(14)	91.22(7)	O(24)-Ba(1)-O(3)	127.9(9)
O(21)-Ba(2)-O(14)	79.32(8)	O(3)-Ba(1)-O(3)	68.41(1)
O(23)-Ba(2)-N(2)	56.88(7)	O(13)-Ba(1)-O(11)	70.19(7)
O(21)-Ba(2)-N(2)	56.80(8)	O(24)-Ba(1)-O(11)	77.44(7)
O(13)-Ba(2)-N(2)	153.4(7)	O(3)-Ba(1)-O(11)	65.28(9)
O(14)-Ba(2)-N(2)	76.24(8)	O(11)-Ba(1)-(11)	163.4(1)
O(23)-Ba(2)-O(11)	103.8(7)	O(13)-Ba(1)-N(1)	64.40(7)
O(21)-Ba(2)-O(11)	67.52(8)	O(13)-Ba(1)-O(13)	164.2(1)
N(2)-Ba(2)-O(11)	123.9(7)	O(3)-Ba(1)-N(1)	104.4(8)
O(23)-Ba(2)-O(4)	70.45(8)	O(11)-Ba(1)-N(1)	55.91(7)
O(21)-Ba(2)-O(4)	72.76(9)	O(13)-Ba(1)-N(1)	56.40(7)
O(13)-Ba(2)-O(4)	130.62(8)	O(24)-Ba(1)-N(1)	69.33(7)
O(14)-Ba(2)-O(4)	148.1(9)	O(3)-Ba(1)-N(1)	72.38(8)
N(2)-Ba(2)-O(4)	75.66(8)	O(11)-Ba(1)-N(1)	55.91(7)
O(11)-Ba(2)-O(4)	82.87(8)	N(1)-Ba(1)-N(1)	176.3(1)

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] 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.

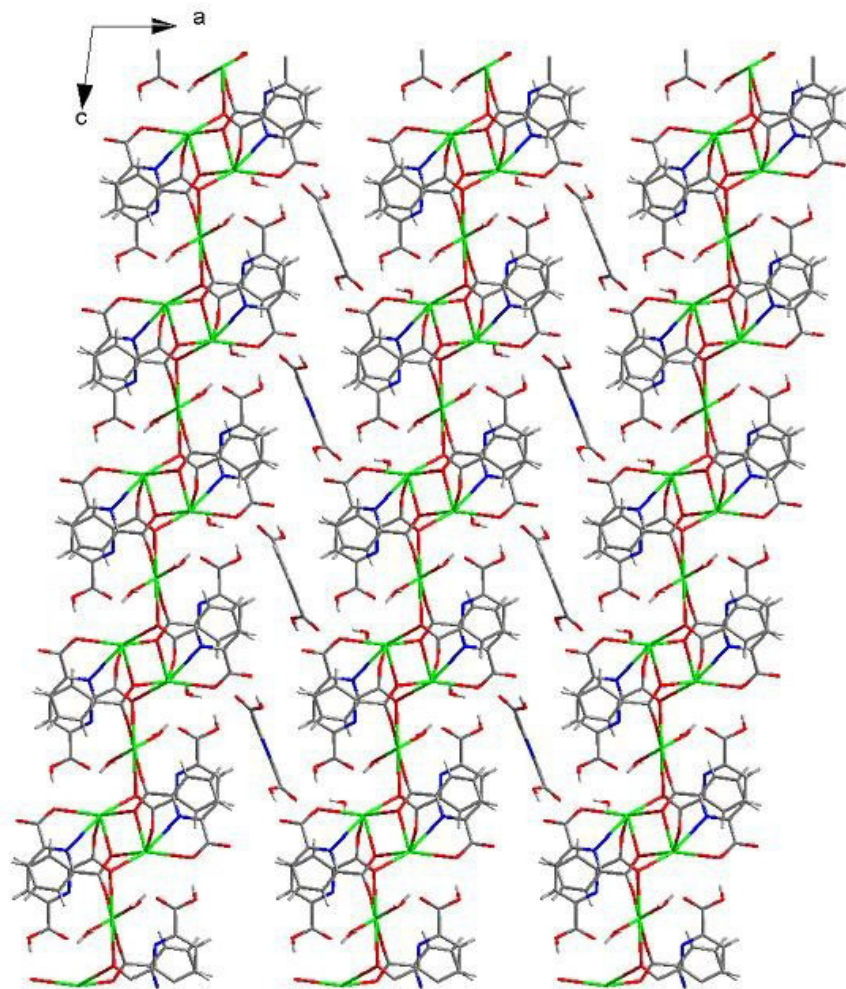


Figure 2. Unit-cell packing diagram of (I).

CONCLUSIONS

A simple route is described for the synthesis and characterization of a new coordination polymer involving neutral H_2pydc , anionic $Hpydc^-$ and $pydc^{2-}$. The unit-cell of this compound is constructed from two barium ions with different coordination numbers. One metal ion was a ten-coordinate complex with a distorted square planar geometry; whereas, the other was an eight coordinate complex with distorted bi-capped octahedron geometry. Some applications of this complex in electronic and optical sciences are under investigation.

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