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Research Article

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Synthesis and structural characterization of homophthalic acid and 4,4-bipyridine

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ABSTRACT

A new network structure compound constructed by hydrogen bonds and π-π stacking has been synthesized by the reaction of homophthalic acid with 4,4-bipyridine in the CH_3OH/H_2O (v:v = 1:1). It was characterized by elemental analysis and X-ray single crystal diffraction analysis. The crystal of the title complex belongs to monoclinic, space group P_{21} with a = 0.50711(10) nm, b = 2.0581(4) nm, c = 0.81465(16) nm, β = 105.24(3) °, V = 0.8203(3) nm^3, Z = 2, Dc = 1.362 $\mu g \cdot m^{-3}$, μ = 0.097 mm^{-1}, F(000) = 352, and final R_1 = 0.0525, wR_2 = 0.1379. The molecules are connected by hydrogen bonds and π-π stacking to form one dimensional chain structure. The interaction of 1D chains form 2D layered and 3D network structure.

Key words: Homophthalic acid; 4,4-bipyridine; structural characterization; network

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INTRODUCTION

The design and synthesis of transition metal complexes with ligands containing nitrogen heterocyclic ring have been studied widely during the past decades [1-3], because they have potential applications as luminescent probe, catalyst, gas adsorption, and antitumor agents [4-6]. bipyridine and its derivates also could be form stable complexes with many metal ions, which have potential applications in biological probes, antitumor drugs and luminescent materials [7-11]. As an extension of our studies on complexes of transition metal with ligands containing nitrogen heterocyclic ring, we report here the synthesis and structural characterization of a new network structure compound constructed by hydrogen bonds and π-π stacking.

EXPERIMENTAL SECTION

Homophthalic acid, 4, 4'-bipyridine and all the other reagents were of analytical grade and used without further purification. The experiments were carried out in open air. Elemental analyses (C, H and N) were carried out on a Elementar Vario EL III elemental analyzer. The crystal data was collected on a Bruker smart CCD Area Detector.

Synthesis of the title compound

The compound was prepared by the following procedure: 1.0 mmol homophthalic acid (0.1801 g) and 1.0 mmol 4, 4'-bipyridine (0.1562 g) in 10 mL of CH_3OH / H_2O (v:v = 1:1). The mixture was continuously stirred for 3 h at refluxing temperature. The single crystal suitable for X-ray determination was obtained by evaporation from the above filtrate after two weeks. Yield: 58%. Elemental analysis calc. for $C_{19}H_{16}N_2O_4$: C, 67.79, H, 4.76, N, 8.32 (%); Found: C, 67.92, H, 4.51, N, 7.98 (%).

X-ray Crystallography

A colourless block single crystal with dimensions of 0.26 mm×0.20 mm×0.18 mm was selected for measurement. Diffraction data of the single crystal were collected by φ~ω scan mode using a graphite-monochromatic Mo *Kα*

radiation (λ = 0.71073 Å) at 293 (2) K on a Bruker Smart Apex CCD diffractometer. A total of 7526 reflections were collected in the range 3.26-27.48°, of which 3686 were unique (R_{int} = 0.0466) and 2930 were observed with $I>2\sigma(I)$. The data were corrected for *Lp* factors. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. The structure was solved by direct methods [12] using SHELXL-97 and expanded using Fourier techniques. All of the non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The final refinement by full-matrix least squares method was converged at R = 0.0525, and wR = 0.1379 ($w = 1/[\delta^2(Fo^2)+(0.1000P)^2+0.0000P]$, $P = (Fo^2+2Fc^2)/3$, S = 0.920, $(\Delta/\sigma)_{max}$ = 0.000). The largest peak in the final difference fourier map is 0.244 e / Å^3 and the minimum peak is - 0.165 e / Å^3. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package [13]. The most relevant crystal data for the title compound are quoted in Table 1, and the selected bond distances and angles are listed in Table 2.

Table 1: Crystallographic data for the title compound

Formula	$C_{19}H_{16}N_2O_4$
Formula weight	336.34
Crystal system	Monoclinic
Space group	P_{21}
a (Å)	5.0711(10)
b (Å)	20.581(4)
c (Å)	8.1465(16)
β (º)	105.24(3)
Z	2
F(000)	352
Temperature (K)	293(2)
V (Å^3)	820.3(3)
Calculated density (μg·m^{-3})	1.362
Crystal size (mm^3)	0.26×0.20×0.18
μ (mm^{-1})	0.097
S	0.920
Limiting indices	-6≤h≤5, -26≤k≤26, -10≤l≤10
Reflections collected / unique	7526/3686
Parameters	234
Restraints	1
R_{int}	0.0466
R_1, wR_2 [all data]	0.0599, 0.1462
R_1, wR_2 [$I>2\sigma(I)$]	0.0525, 0.1379
Largest diff.peak and hole (e·Å^{-3})	0.244, -0.165

Table 2: Selected bond lengths (Å) and angles (º) for the title compound

Bond	Distance	Bond	Distance
C13-O4	1.216(3)	C13-O3	1.316(3)
C6-N2	1.312(4)	C12-O1	1.315(3)
C10-N2	1.337(4)	C5-N1	1.325(4)
C1-N1	1.323(4)	C12-O2	1.201(3)
C1-C2	1.389(4)	C6-C7	1.377(4)
C9-C10	1.367(4)	C4-C5	1.386(4)
C2-C3	1.364(3)		
Angle	(º)	Angle	(º)
C6-N2-C10	117.1(2)	C1-N1-C5	116.7(2)
O1-C12-O2	122.8(2)	O3-C13-O4	122.6(2)
O4-C13-C14	124.3(2)	O3-C13-C14	113.1(2)
O2-C12-C11	125.5(2)	O1-C12-C11	111.71(18)
C1-C2-C3	120.1(2)	N2-C6-C7	122.9(3)
N2-C10-C9	123.5(2)	N1-C1-C2	123.5(2)
N1-C5-C4	123.2(3)	C6-C7-C8	120.7(2)

RESULTS AND DISCUSSION

The result of elemental analysis indicated that the title compound contains a homophthalic acid molecule and a 4,4-bipyridine molecule, and is accorded with the result of single crystal X-ray diffraction analysis.

Structure Description

A single-crystal X-ray diffraction study reveals that the title compound crystallizes in monoclinic system with P_{21} space group. The crystal structure of the title compound is revealed in Fig. 1. As shown in Fig. 1, we can see that the title compound consists a homophthalic acid molecule and a 4,4-bipyridine molecule. In the molecule, two double bonds C12-O2 (1.201(3) Å) and C13-O4 (1.216(3) Å) are as expected for this class of compound [14, 15]. And the

geometrical parameters are normal. The two planes of 4,4-bipyridine molecule are planar with a dihedral angle of 7.2 º between the planes formed by C1, C2, C3, C4, C5, N1 (plane 1) and C6, C7, C8, C9, C10, N2 (plane 2). The dihedral angle between the plane 1 and the benzene ring of homophthalic acid molecule (C14 to C19) is 19.1 º, and is significantly rotated out of the above two planes. From Fig. 2, it can be seen that the title molecules form zigzag structure by the intermolecular hydrogen bonds of O-H…N.

The molecules stack with each other by hydrogen bonds and π-π interaction in arrays to form a 1D chained structure (Fig. 2). The dimensionality is increased by π-π interaction to form 2D layered structure and 3D network structure (Fig. 3 and Fig. 4). It is doubt that these weak interactions of hydrogen bonds and π-π interactions are significantly to increase the stability of the crystal structure. The aromatic rings in the molecules do not show any unusual features, and the bond lengths and bond angles are within the range of normal values.

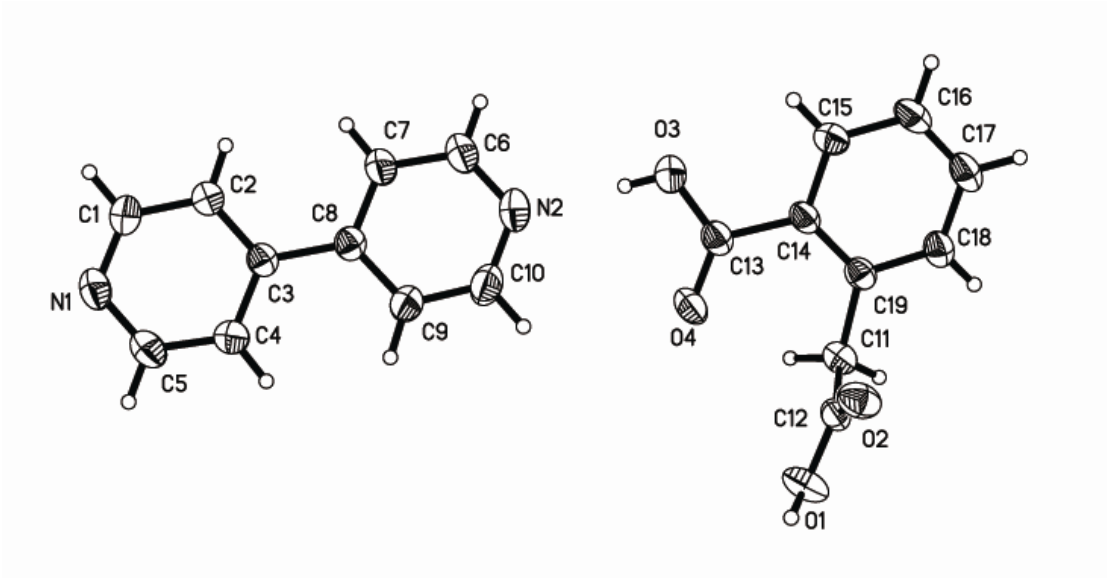

Fig 1: **Molecular structure of the title compound, where the thermal ellipsoids were drawn at 30% possibility**

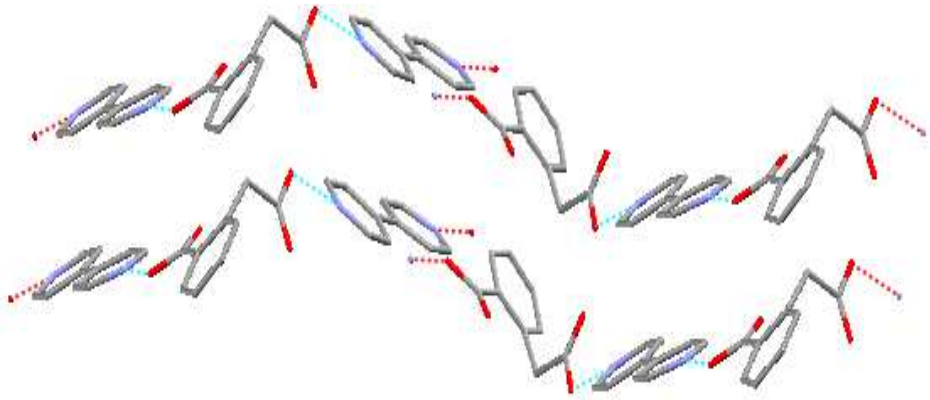

Fig 2: **One-dimensional Structure of the title compound**

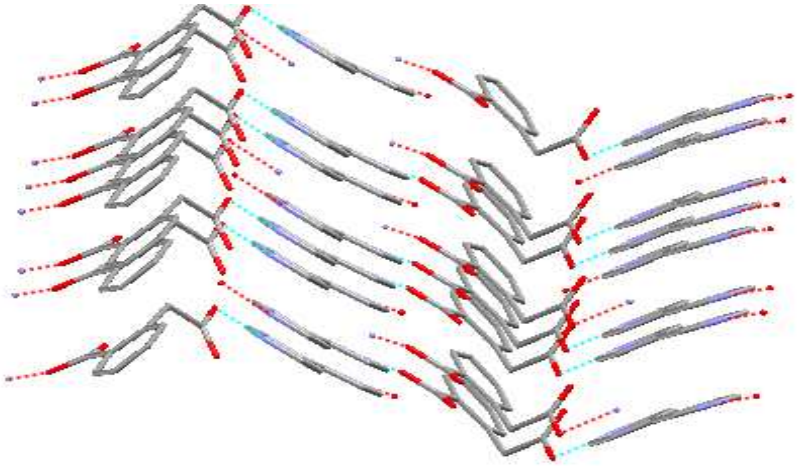

Fig 3: Two-dimensional layered structure of the title compound

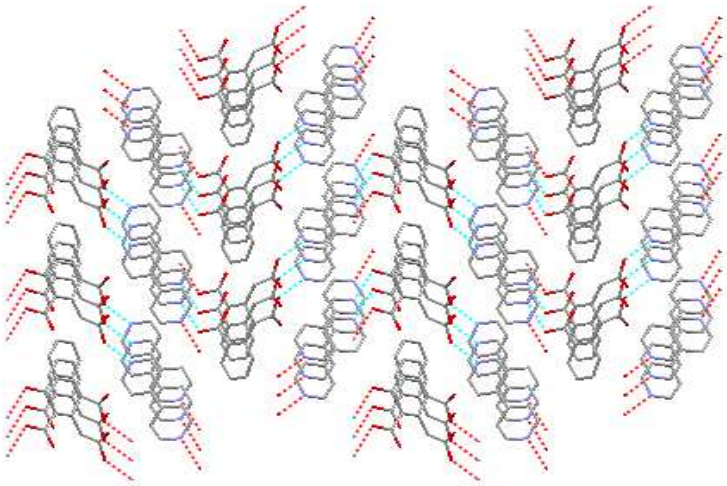

Fig 4: Three-dimensional network structure of the title compound

Table 3: Hydrogen-bond geometry (Å) for the title compound

D-H…A	D-H	H…A	D-A	∠DHA
O1-H1C…N1	1.03	1.69	2.67	157
O3-H3B…N2	0.79	1.93	2.67	156
C2-H2B…O2	0.93	2.47	3.29	147
C11-H11A…O4	0.97	2.37	2.81	107
O15-H15A…O3	0.93	2.39	2.72	100
O18-H18A…O2	0.93	2.56	3.44	160

CONCLUSION

In summary, a new compound made up by a homophthalic acid molecule and a 4,4-bipyridine molecule has been synthesized and structurally characterized. The results show that the molecules stack with each other by hydrogen bonds and π-π interaction in arrays to form a 1D chained structure. The chains are expanded to form 2D layered structure and 3D network structure by π-π interaction.

Supplementary Material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.CCDC 993487. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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