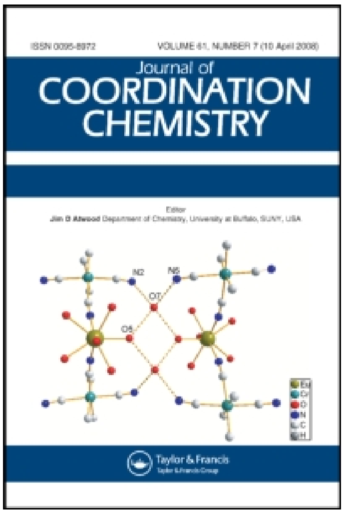

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A 3D interpenetrating supramolecular compound based on Cu ··· N weak coordination: synthesis, crystal structure and DFT investigation

Jian Li[a]; Dongsheng Li[a]; Long Tang[a]; Yapan Wu[a]; Wenliang Wang[b]; Yaoyu Wang[c]
[a] Department of Chemistry and Chemical Engineering, Yan'an University, Yan'an, P.R. China [b] Department of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, P.R. China
[c] Department of Chemistry and Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an 710069, P.R. China

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A 3D interpenetrating supramolecular compound based on Cu···N weak coordination: synthesis, crystal structure and DFT investigation

JIAN LI†, DONGSHENG LI*†, LONG TANG†, YAPAN WU†,
WENLIANG WANG‡ and YAOYU WANG§

†Department of Chemistry and Chemical Engineering, Yan'an University,
Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan'an, 716000, P.R. China
‡Department of Chemistry and Materials Science, Shaanxi Normal University,
Xi'an 710062, P.R. China
§Department of Chemistry and Shaanxi Key Laboratory of
Physico-Inorganic Chemistry, Northwest University, Xi'an 710069, P.R. China

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A metal-organic hybrid compound, $Cu[(pyc)_2(4,4'\text{-bipy})]\cdot H_2O$ (pyc = pyridine-2-carboxylate, 4,4′-bipy = 4,4′-bipyridine), has been hydrothermally synthesized and characterized by X-ray determination, IR and elemental analysis. The compound crystallizes in tetragonal, space group $I4_1/acd$ with $a = 24.797(2)$ Å, $b = 24.797(2)$ Å, $c = 14.811(2)$ Å, $\beta = 90°$, $V = 9106.7(18)$ Å^3, $C_{22}H_{18}N_4O_5Cu$, $Mr = 481.94$, $Dc = 1.406\ \mathrm{g\,cm^{-3}}$, $\mu(\text{Mo-K}\alpha) = 0.999\ \mathrm{mm^{-3}}$, $F(000) = 3952$, $Z = 16$, the final $R = 0.0712$ and $wR = 0.1886$ for 21727 observed reflections ($I > 2\sigma$). Compound **1** exhibits a three-dimensional interpenetrating network induced by weak Cu···N noncovalent interaction, C–H···π and π–π interactions. Based on crystal data, quantum chemistry calculation at the DFT/B3LPY level was used to reveal the electronic structure of **1**.

Keywords: Cu(II) compound; Weak coordination interaction; Interpenetration; DFT investigation

1. Introduction

Supramolecular chemistry and crystal engineering are active fields due to the novel structural topologies and potential applications in molecular recognition, catalysis, and electrical conductivity [1]. Development of supramolecular assemblies provides the possibility to rationally design and synthesize them through noncovalent interactions, which meet geometric and energetic considerations [2]. Noncovalent interactions stabilize important molecules like proteins, DNA, etc. and arrange structural units inside the crystal lattice [3]. Physical properties of solid-state materials depend on the structure of the building units but also on the arrangement of these structural units inside the crystal lattice [4]. The role of noncovalent interactions in determining the supramolecular structure of crystalline materials is a focus of crystal engineering.

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*Corresponding author. Email: LLLn1832@sina.com.cn

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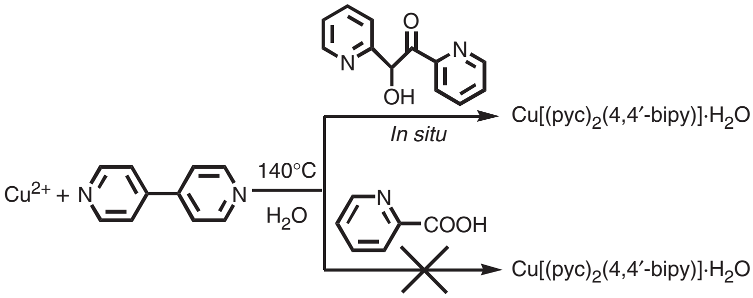

Scheme 1. The comparison synthesis process.

Intermolecular forces range from strong, e.g. classical hydrogen bond [5], to weaker, e.g. π–π stacking [6]. Classical hydrogen bonds and π–π stacking have been studied in detail, but other interactions, such as metal and ligand weak interaction (e.g. Ag···O [7], Zn···O [8], metal···halogen [9]), have received attention only recently. We have not found a report for a supramolecular compound based on weak Cu···N noncovalent interaction.

Herein, we report a new species Cu[(pyc)$_2$(4,4′-bipy)]·H_2O (pyc = pyridine-2-carboxylate, 4,4′-bipy=4,4′-bipyridine), containing supramolecular chains that are assembled via Cu···N weak coordination interactions into an intriguing 3D interpenetrating framework. Compound **1** cannot be obtained directly from picolinic acid, 4,4′-bipy and Cu(II). Through comparison (scheme 1), the possible mechanism was investigated [10] confirming that Cu(II) was important to the hydrolysis of hdpy. Based on these results, we studied the structural unit with density functional theory (DFT) examining the stabilization, molecular orbital composition and orbital energy, bonds and vibrational frequencies of the compound and contrasted them with experimental results.

2. Experimental

2.1. *Materials and methods*

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on an Elemental Vario EL III CHNOS system. IR spectra (KBr pellets) were recorded with a Bruker EQUINOX-55 FT-IR spectrophotometer.

2.2. *Syntheses*

Compound **1** was prepared from a mixture of Cu(OAC)$_2$·H_2O (0.5 mmol, 0.119 g), 2-hydroxy-1,2-di-2-pyridylethanone (0.5 mmol, 0.123 g), 4,4′-bipy (0.5 mmol, 0.096 g) and H_2O (8 mL) in a 25 mL Teflon-lined autoclave under autogenous pressure at 140°C for three days. After cooling to room temperature, blue block crystals were collected by filtration and washed with distilled water giving 64% yield based on Cu. Anal. Calcd

Table 1. Crystallographic data and experimental details for **1**.

Empirical formula	$C_{22}H_{18}N_4O_5Cu$
Formula weight	481.94
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	$I4_1/acd$
Unit cell dimensions (Å, °)	
a	24.797(2)
b	24.797(2)
c	14.811(2)
β	90
Volume, Z (Å^3)	9106.7(18), 16
D_{calcd} (g cm^{-3})	1.406
Absorption coefficient (mm^{-1})	0.999
Crystal size (mm^3)	$0.49 \times 0.47 \times 0.20$
Range hkl collected	$-29 \le h \le 29$, $-21 \le k \le 29$, $-17 \le l \le 16$
Reflections collected	21727
Independent reflection	1966 [$R_{int} = 0.0753$]
Final R indices [$I > 2\sigma$]	$R_1 = 0.0712$, $wR_2 = 0.1886$
R indices (all data)	$R_1 = 0.1347$, $wR_2 = 0.3014$
Largest difference peak and hole (e Å^{-3})	0.879 and −0.692

for $C_{22}H_{18}N_4O_5Cu$ (%): C, 54.75; H, 3.74; N, 11.60. Found: C, 54.88; H, 3.24; N, 11.66. IR (KBr): 3405(s), 1648(vs), 1608(s), 1475(w), 1352(vs), 773(s), 618(w), 338(vs), 256(m) cm^{-1}.

2.3. *X-ray crystallography*

Single-crystal data were collected at 298(2)K on a Bruker Smart Apex II diffractometer equipped with graphite-monochromated Mo-Kα radiation. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97), and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [11]. The final agreement factor values are $R_1 = 0.0712$, $wR_2 = 0.1886$, $w = 1/[\sigma^2(F_o)^2 + 0.1512P)^2 + 0.7550P]$ where $P = \left(F_o^2 + 2F_c^2\right)/3$. Crystallographic data and other experimental details are given in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

Single-crystal X-ray diffraction reveals that **1** consists of neutral Cu[(pyc)$_2$(4,4′-bipy)] entities and a lattice water. The coordination geometry of Cu(II) is slightly distorted square pyramidal with two N atoms and two O atoms from two pyc and one N atom from 4,4′-bipy molecule. As shown in figure 1, the pyramid base is generally coplanar N(1), N(1A), O(1) and O(1A), and N(2) from the 4,4′-bipy molecule occupies the apical position. The Cu is shifted by 0.143 Å from the basal plane toward the apical

Table 2. Selected bond lengths (Å) and angles (°) and selected optimized geometric parameters for **1**.

Bond	Exp	Cal	Angle	Exp	Cal
Cu(1)–O(1)	1.961(5)	1.9536	O(1)–Cu(1)–O(1A)	170.1(3)	174.8957
Cu(1)–O(1A)	1.961(5)	1.9536	O(1A)1–Cu(1)–N(1A)	83.6(3)	83.0012
Cu(1)–N(1)	1.979(6)	2.038	O(1)–Cu(1)–N(1A)	95.8(3)	95.722
Cu(1)–N(1A)	1.979(6)	2.038	O(1A)–Cu(1)–N(1)	95.8(3)	95.7222
Cu(1)–N(2)	2.427(8)	2.3071	O(1)–Cu(1)–N(1)	83.6(3)	83.0013
C(1)–C(2)	1.487(12)	1.5252	N(1A)–Cu(1)–N(1)	173.3(3)	171.2042
C(2)–C(3)	1.386(12)	1.3926	O(1A)–Cu(1)–N(2)	94.93(17)	92.5523
C(3)–C(4)	1.381(15)	1.3941	O(1)–Cu(1)–N(2)	94.93(17)	92.552
C(4)–C(5)	1.361(14)	1.3976	N(1A)–Cu(1)–N(2)	93.36(17)	94.3979
C(5)–C(6)	1.377(12)	1.3933	N(1)–Cu(1)–N(2)	93.36(17)	94.3979
C(6)–N(1)	1.317(10)	1.3401	Cu(1)–N(1)–C(2)	111.0(5)	110.7811
C(7)–N(2)	1.336(9)	1.3426	Cu(1)–N(1)–C(6)	129.5(6)	128.7807
C(7)–C(8)	1.382(11)	1.3915	Cu(1)–N(2)–C(7)	122.7(5)	120.9157
C(9)–C(12)	1.516(14)	1.4835	Cu(1)–O(1)–C(1)	113.3(5)	116.1566
C(1)–O(1)	1.285(10)	1.3027	C(2)–N(1)–C(6)	119.5(5)	120.4357
C(1)–O(2)	1.233(9)	1.2245	O(1)–C(1)–O(2)	125.2(8)	126.7727

Symmetry transformations used to generate equivalent atom: A–$x + 3/2$, y, $-z$.

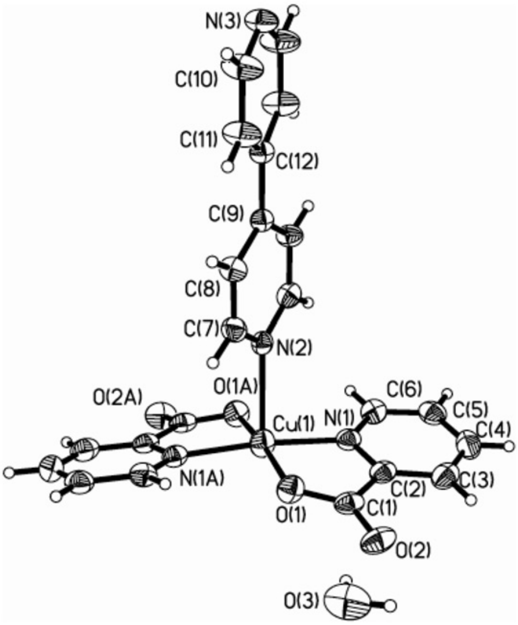

Figure 1. Molecular structure of Cu[$(pyc)_2$(4,4′-bipy)] · H_2O.

nitrogen atom. The Cu–N distances range from 1.979(6) Å to 2.427(8) Å, shorter than those of $[Cu(baa)_2(4,4'\text{-bipy})]_n$ (2.453 Å) [12]; Cu–N distance in the axial direction (2.427(8) Å) is longer than that in the bottom face due to the Jahn-Teller effect. The Cu–O distances are 1.961(5) Å; Cu–N distances are longer than Cu–O [13]. In contrast to the recent report of Cu/pyridine-2-carboxylate and Cu/4,4′-bipyridine complexes [14], all Cu–N bonds of **1** are through actual bonds; however, in **1**, weak Cu · · · N noncovalent interaction exists between Cu(1) and adjacent N(3).

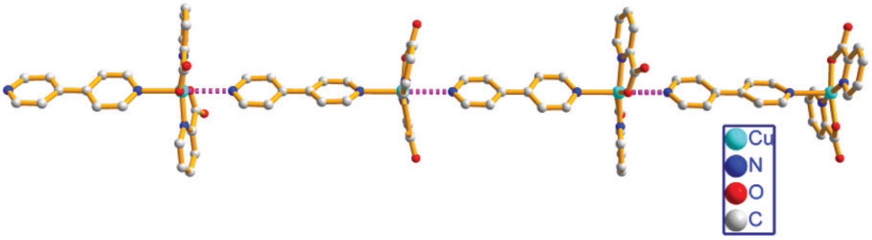

Figure 2. One-dimensional (1D) supramolecular chain based on Cu · · · N weak interaction between molecules.

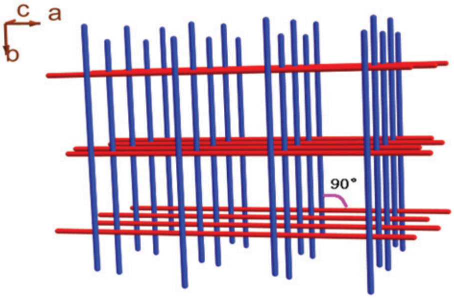

Figure 3. Rod-packing of the 1D chains spanning two different directions in **1**.

Adjacent mononuclear units are linked into one-dimensional (1D) supramolecular chains spanning two different directions based on Cu · · · N weak interaction (figure 2); the nearest Cu · · · N distance is 2.837 Å, significantly shorter than the van der Waals contact distance of 3.87 Å [15], illustrating weak interaction between Cu(II) and N, which leads to supramolecular organization. As shown by the rod-packing of figure 3, these supramolecular chains are arranged on parallel levels in different propagating directions, rotated by 90° on passing from one level to the next. Packing of 1D supramolecular structures usually occurs with a parallel orientation of all chains; less commonly they span two different directions on alternate layers [16]. The pyc pyridyl rings are almost perpendicular to the 4,4′-bipy groups of the nearest neighbor chains lying in identical layers [figure 4(a)], exhibiting strong edge-to-face C–H · · · π interactions between H · · · π 2.84 Å and C–H · · · π 151°. Also, face-to-face π–π stacking interaction from pyc pyridyl ring and a 4,4′-bipy ring at 3.396 Å exist (figure 4a). These supramolecular interactions give two identical sets of 2D grid layers from supramolecular chains of same levels that span two different stacking directions. Considering the Cu atoms as nodes, the layers are comprised of quadrangular meshes with a (4,4) net [figure 4(b)]; the dimensions of the distorted quadrangular windows, estimated from the maximum distances between opposite vertices, are 16.437 × 12.542 Å. Moreover, these layers interpenetrate in such a way that intercalation occurs on the quadrangular windows through C–H · · · π interactions (H · · · π 3.06 Å and C–H · · · π 140°), thus giving overall unique 3D networks with interpenetrating four-membered rings, as illustrated in figure 5. In addition, the intermolecular O–H · · · O bond (2.769 Å) between crystallization water and oxygen atoms of carboxylate groups further strengthen the stability of the compound.

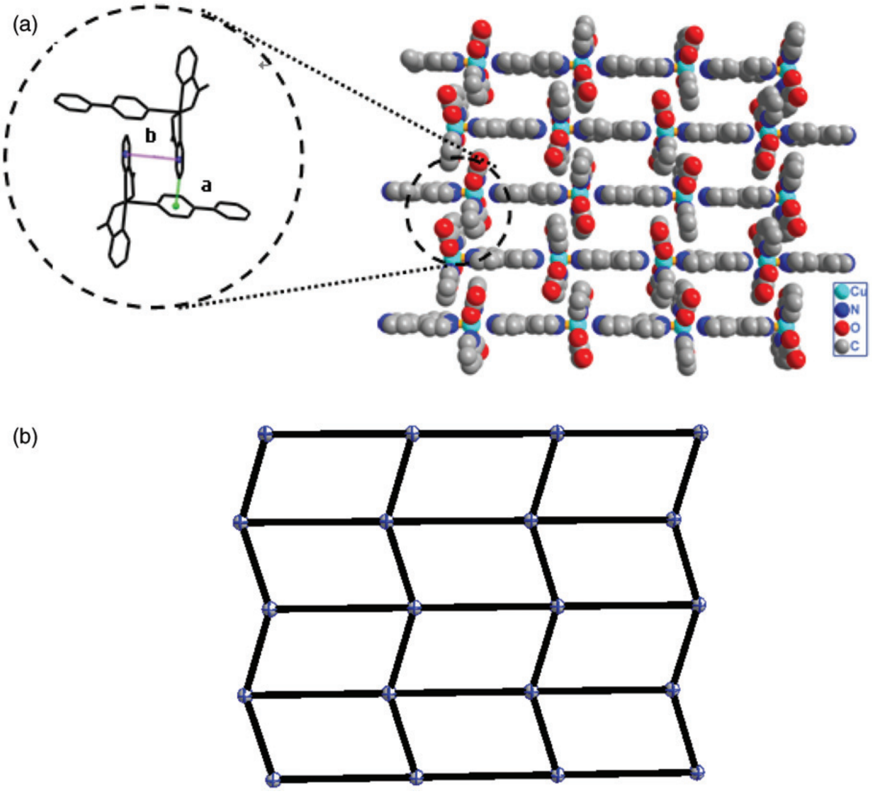

Figure 4. (a) A space-filling model of the 2D sheet, showing the C–H $\cdots\pi$ and π–π interactions between chains; (b) A schematic view of the 2D sheet of (4,4) topology.

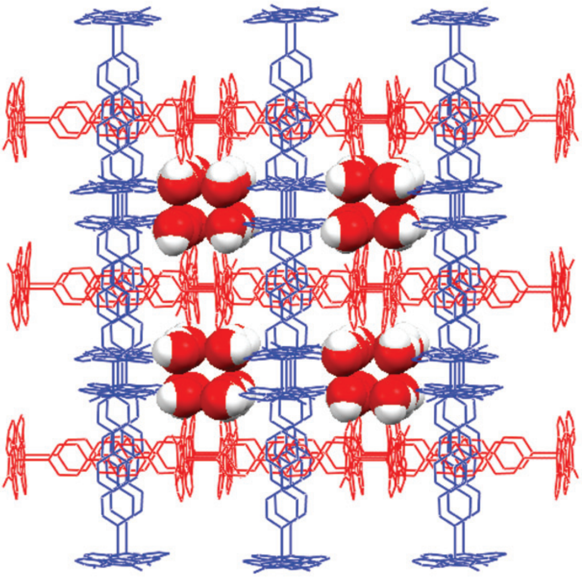

Figure 5. A perspective view of the packing down the *c*-axis in **1**, showing the free water molecules lying in the interlayer regions.

Table 3. Mulliken atomic charges (a.u.) and natural electron configuration.

Atoms	Net charge	Electron configuration
Cu(1)	0.50	[core]4s(0.34)3d(9.29)4p(0.02)5s(0.01)4d(0.01)5p(0.01)
N(1)	−0.45	[core]2S(1.33)2p(4.20)3p(0.02)
N(1A)	−0.45	[core]2S(1.33)2p(4.20)3p(0.02)
N(2)	−0.39	[core]2S(1.36)2p(4.16)3p(0.02)3d(0.01)
O(1)	−0.55	[core]2s(1.72)2p(5.09)3p(0.01)
O(1A)	−0.47	[core]2s(1.71)2p(4.91)3d(0.01)

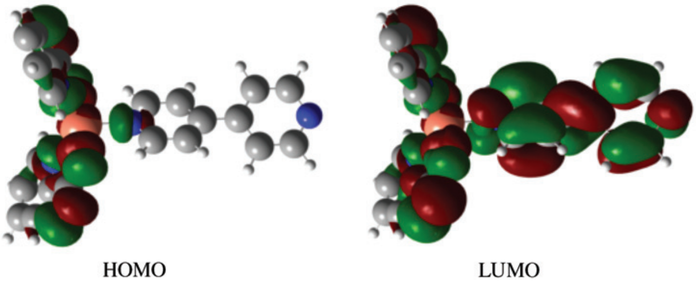

Figure 6. FMOs of **1**.

3.2. *Density functional study*

We used the Gaussian03 program and B3LYP method [17] of Becke to investigate the electronic structure of Cu[(pyc)$_2$(4,4′-bipy)]. GenECP basis sets are used for Cu, and C, N and O; NBO method is used for orbital analysis with 483 basis functions, 972 primitive gaussians, 114 alpha electrons and 113 beta electrons involved in the calculation. The Mulliken atomic charges and natural electron configuration of the title compound are shown in table 3. FMOs of **1** are revealed in figure 6.

3.2.1. Equilibrium geometry structure. Some optimized structural parameters of **1** are listed in table 2. The C(9)–C(12) bond (1.4835 Å), shorter than normal C–C bonds (1.54 Å), should be the result of delocalization, resulting in the coplanarity of two pyridine rings. Similarly, all carbon-carbon bond lengths in every pyridine ring tend to average and fall in the ranges of C–C and C=C bonds, possibly due to delocalization, too. All C–O bonds are shorter than the normal C–O bond (1.43 Å), with all C=O bonds longer than the normal C=O bond (1.22 Å), indicating the oxygens are conjugated with the pyridyl ring to form a big π conjugate system and every atom within the equatorial plane tends to be in plane to form a stable structure. The Cu–O and Cu–N(1) bond lengths calculate slightly shorter and longer in comparison to the X-ray determined value, respectively, and the Cu–N(2) bond length (2.3071 Å) is significantly shorter than experimental values (2.427(8) Å). The other bond lengths, however, are very close. The DFT calculated values for the bond angles are in agreement. The highest deviation is about 4.8° for the O(1)–Cu(1)–O(1A) bond angle.

3.2.2. Vibrational spectroscopy. Vibrational frequency calculation was performed at the B3LYP/GenECP level after optimization. The computational results show no imaginary frequency, suggesting the structure is stable with positive eigenvalues of second derivative matrix of energy.

The C=N stretch is red-shifted from 1604 (Exp. 1646 $\mathrm{cm^{-1}}$) of pyc ligand (a) to 1573 $\mathrm{cm^{-1}}$ (Exp. 1608 $\mathrm{cm^{-1}}$) of **1**, indicating C=N is weakened by coordination with Cu (II), in agreement with changes of bond order and length. The stretching frequency at 264 $\mathrm{cm^{-1}}$ (Exp. 256 $\mathrm{cm^{-1}}$) and 349 $\mathrm{cm^{-1}}$ (Exp. 338 $\mathrm{cm^{-1}}$) proves formation of Cu–N bond and Cu–O bonds, respectively. For carboxylate ($\mathrm{COO^-}$), the calculated asymmetric and symmetric stretching frequencies shift from 1621 $\mathrm{cm^{-1}}$ (Exp. 1645 $\mathrm{cm^{-1}}$) and 1230 $\mathrm{cm^{-1}}$ (Exp. 1353 $\mathrm{cm^{-1}}$) of pyc ligand to 1657 $\mathrm{cm^{-1}}$ (Exp. 1648 $\mathrm{cm^{-1}}$) and 1368 (Exp. 1352 $\mathrm{cm^{-1}}$) of **1**. The value of Δv, 289 $\mathrm{cm^{-1}}$, indicates carboxylate coordinates with metal in a monodentate chelating mode. The information obtained from the IR about the coordination configurations of the copper(II) atoms is in good agreement with those found from the structural data [18].

3.2.3. Energies and components of molecular orbitals. The energy of the title compound is −3007.578579 a.u. after 12 cycles of calculation with HOMO energy of −0.22663 a.u. (alpha electrons), LUMO energy −0.07196 a.u. (alpha electrons), and the band gap 0.15467 a.u. (4.21 eV), indicating that this configuration is stable.

The quantum chemical calculations show that the net charge of Cu is 0.50, deviating significantly from +2. The net charges of coordinated N and O atoms range from −0.45 to −0.39 and −0.55 to −0.47, respectively, showing electron transfer from N and O, to Cu. The axial uncoordinated N(3) atom has a negative charge of −0.33, indicating that N(2)'s donor electron ability is slightly stronger than that of each N(3). As shown in table 3, the electron number of the Cu 3d orbital is 9.29 and 4s orbital is 0.34 (the electron numbers of 4d, 4p, 5s and 5p are small and can be omitted). We conclude that the Cu forms coordinate bonds with N and O with 3d ($3d_{x^2-y^2}$ and $3d_{z^2}$ as revealed by NBO orbital analysis) and 4s orbitals. The electron numbers of N 2s orbitals range from 1.33 to 1.36 and 2p orbitals from 4.16 to 4.20, indicating that N atoms form coordinate bonds with Cu atom using 2s and 2p (mainly $2P_x$ as indicated by NBO analysis). Similarly, O(1) and O(1A) supply 2s and 2p electrons to Cu and form coordination bonds. The orbital contribution and atomic net charge results provide agreement with the crystal structure, helping to understand the compound and assist material design.

4. Conclusions

A mononuclear Cu(II) compound with hdpy and 4,4′-bipy ligand has been synthesized under hydrothermal conditions and characterized by X-ray determination, IR and elemental analysis. The mononuclear units of the compound have weak $\mathrm{Cu\cdots N}$ interactions cooperating with $\mathrm{C{-}H\cdots\pi}$ and π–π interactions to form a 3D interpenetrating network. Such $\mathrm{Cu\cdots N}$ weak coordination interaction is rare in assembly of supramolecular compounds. In addition, we used density functional theory (DFT) B3LYP to fully optimize **1** and discuss the vibrational frequencies, molecular orbital composition and orbital energy. The results from DFT calculations were in good agreement with the X-ray crystallography structures for the compound.

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC-654672. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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