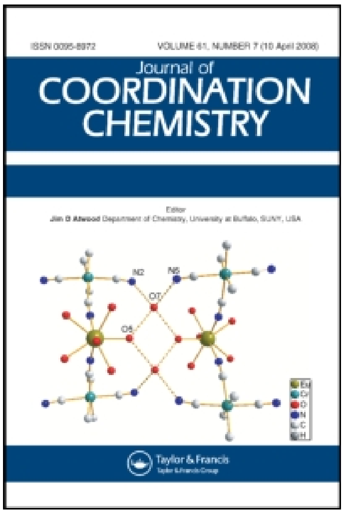

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Experimental and theoretical investigation of a coordination polymer [Cu(pda)(2,2'-bpy)(H₂O)]<i>_n · 2nH$_2$O

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Experimental and theoretical investigation of a coordination polymer $[Cu(pda)(2,2'\text{-}bpy)(H_2O)]_n \cdot 2nH_2O$

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A new coordination polymer $[Cu(pda)(bpy)(H_2O)]_n \cdot 2nH_2O$ ($H_2pda = 1,3$-phenylenediacetic acid, bpy = 2,2′-bipyridine) was synthesized and studied by experimental and theoretical methods. In the complex each pair of adjacent Cu(II) ions is bridged by a pda dianion to form a zigzag chain running along a crystallographic 2_1 axis in the *c* direction; these chains are further linked by O–H–O hydrogen bonds and aromatic π–π stacking interactions into a three-dimensional framework. On the basis of Density Functional Theory in GAUSSIAN 03 the experimental, structural, and spectroscopic data were reproduced.

Keywords: Copper complex; 1,3-phenylenediacetic acid; DFT calculation; Hydrogen bond; Aromatic π–π stacking interaction

1. Introduction

The design and assembly of supramolecular architectures based on crystal engineering are currently of great interest in material science because they can provide intriguing architectures and functional materials [1–8]. An efficient way to obtain coordination polymers is to use multifunctional ligands, especially multi-carboxylate ligands, to link metal ions to an infinite configuration. Polycarboxylate aromatic ligands such as 1,3-benzenedicarboxylate (H_2IPA), 1,4-benzenedicarboxylic acid (H_2BDC), trimesic acid (H_3BTC), and 1,2,4,5-benzenetetracarboxylic acid (H_4BTEC) are chosen to generate frameworks with various structural motifs, including channel, double-helix and helical chains [9, 10]. Many factors influence the final conformation of the complex, such as the length of ligand, synthesis method and so on. Chen's group published their work about $[Cu(ipa)(bpy)]_n \cdot 2nH_2O$ (ipa = isophthalate) [11]. Far less work has been done with the similar flexible 1,3-phenylenediacetate (pda), which possesses two longer terminal groups ($–CH_2COO^-$) [12, 13]. Herein, in order to investigate the influence of the length of carbon chain while preserving the framework topology, we report the synthesis, crystal structure and thermal properties of $[Cu(pda)(bpy)(H_2O)]_n \cdot 2nH_2O$.

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In addition, density functional theory (DFT) calculation was employed to parametrize the crystal structure of the title complex; the experimental crystal structure and vibrational infrared spectrum are reproduced reasonably well.

2. Experimental

2.1. *Materials and analytical methods*

Commercially available reagents were used as received without further purification. Elemental analyses (C, H and N) were performed on a Vario EL III analyzer. Infrared spectra were obtained from KBr pellets on a BEQ VZNDX 550 FTIR instrument within the 400–4000 cm^{-1} region. Thermogravimetric analysis was carried out on a TA Instruments NETZSCH STA 449C simultaneous TGA with a heating rate of 10°C min^{-1} under hydrostatic air.

2.2. *Synthesis of the complex*

A mixture of H_2pda (1 mmol), NaOH (2 mmol), bpy (1 mmol) and distilled water (10 mL) was stirred and heated to form a clear solution, to which 10 mL aqueous solution containing 1 mmol $CuCl_2 \cdot 2H_2O$ was added and stirred for two hours. After a few hours, some blue, rectangular single crystals of the complex were cultured in the mother liquid. Anal. (%) Calcd for the title complex: C, 51.55; H, 4.76; N, 6.01. Elemental analysis (%) Calcd for $CuC_{20}H_{22}N_2O_7$: C, 51.38; H, 4.353; N, 5.911.

2.3. *X-ray crystallography*

All diffraction data for the complex were collected on a Bruker SMART CCD area-detector diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K using the program SMART and processed by SAINT-plus. Absorption corrections were applied by SADABS. The structures were solved by direct methods and refined with full-matrix least-squares using SHELXTL [14]. All nonhydrogen atoms were refined anisotropically. All H-atoms were located theoretically and refined. The structural plots were drawn using SHELXTL, OLEX and Diamond programs. The dimensions of the crystal used for X-ray diffraction data collection are given in table 1. Selected bond lengths and angles are listed in table 2. The geometries of the hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. *Description of the crystal structure*

Single-crystal X-ray diffraction analysis reveals that the title complex crystallizes in the monoclinic space group $P2_1$. The asymmetric unit is shown in figure 1, in which the Cu(II) is coordinated by two oxygen atoms from two bis(monodentate) pda^{2-} ligands

Table 1. Crystallographic data and structure refinement parameters for the title complex.

Empirical formula	$CuC_{20}H_{22}N_2O_7$
Formula weight	465.94
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	10.641(5)
b	17.603(7)
c	13.776(4)
β	129.64(2)
Volume (Å^3)	1987.1(14)
Z	4
Calculated density (mg m^{-3})	1.557
Absorption coefficient (mm^{-1})	1.145
$F(000)$	964
Crystal size (mm^3)	0.30 × 0.25 × 0.11
Range for data collection (°)	2.24 to 25.05
Limiting indices	$-12 \leq h \leq 12$, $-20 \leq k \leq 20$, $-16 \leq l \leq 15$
Reflections collected/unique	8805/3506 [$R_{(\mathrm{int})} = 0.1208$]
Completeness to $\theta = 26.99$ (%)	99.5
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3506/0/288
Goodness-of-fit on F^2	0.977
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0811$, $wR_2 = 0.1647$
R indices (all data)	$R_1 = 0.1626$, $wR_2 = 0.2020$
Largest diff. peak and hole (e Å^{-3})	0.641 and −0.490

Table 2. Selected bond lengths (Å) and angles (°) for the title complex.

Cu(1)–O(1)	1.925(5)	Cu(1)–N(2)	2.024(6)
Cu(1)–O(4)#1	1.963(5)	Cu(1)–O(1w)	2.288(8)
Cu(1)–N(1)	1.997(6)		
O(1)–Cu(1)–O(4)#1	90.9(2)	O(1)–Cu(1)–N(1)	172.0(2)
O(4)#1–Cu(1)–N(1)	94.7(2)	O(1)–Cu(1)–N(2)	92.6(2)
O(4)#1–Cu(1)–N(2)	163.0(2)	N(1)–Cu(1)–N(2)	80.4(3)
O(1)–Cu(1)–O(1W)	90.0(3)	O(4)#1–Cu(1)–O(1W)	98.9(3)
N(1)–Cu(1)–O(1W)	94.8(3)	N(2)–Cu(1)–O(1W)	97.7(3)

Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, $z-1/2$.

Table 3. Hydrogen bonding geometry (Å, °) of the title complex.

D–H···A (Å)	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
O2W–H2WA···O3W	0.85	2.05	2.782(11)	143.4
O2W–H2WB···O3	0.85	2.22	2.898(7)	143.4
O1W–H1WA···O2W	0.67(7)	2.30(7)	2.924(10)	156(9)
O3W–H3WA···O2	1.00(14)	1.79(14)	2.786(12)	173(13)
O1W–H1WB···O3	0.92(9)	1.92(9)	2.783(10)	155(8)
O3W–H3WB···O2	0.67(8)	2.56(9)	3.172(11)	154(11)

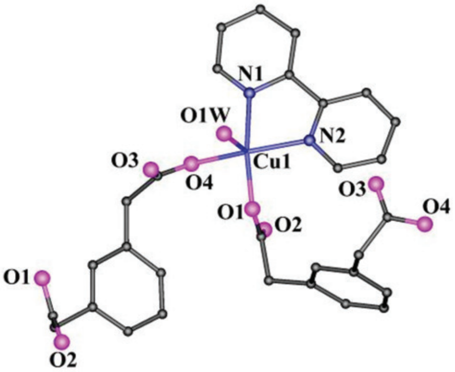

Figure 1. Coordination environment of Cu(II). The hydrogen atoms are omitted for clarity.

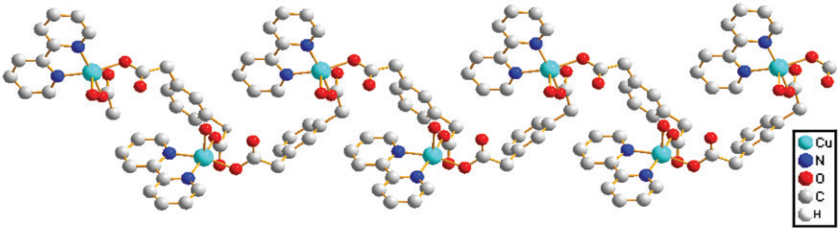

Figure 2. Single-stranded helical chains: adjacent Cu(II) ions are bridged by pda dianion, and bpy decorates both sides.

(Cu1–O1 1.925(5) Å, Cu1–O4 1.963(5) Å), one oxygen atom from one coordinated water (Cu1–O1w 2.288(8) Å) and two nitrogen atoms from a chelating bpy (Cu1–N1 1.997(6) Å, Cu1–N2 2.024(6) Å) in square-pyramidal geometry (figure 1).

In $[Cu(ipa)(bpy)]_n \cdot 2nH_2O$, in which Cu is a distorted square-planar geometry, all bond lengths are a little longer than those of the title complex. Because of the increasing ligand length from C–COOH to C–C–COOH, the coordination number changes from four to five [11].

As shown in figure 2, each pair of Cu(II) atoms is bridged by a V-shaped pda ligand in bis(monodentate) coordination to give an infinite single-stranded zigzag chain and bpy decorates both sides; viewing from the *c* axis the infinite zigzag chain resembles a saddle (figure 3a).

The one-dimensional infinite zigzag chain extended into two-dimensional networks by offset face-to-face π–π stacking interaction between parallel bpy rings with centroid-centroid distance of 3.4842 Å (figure 3b).

Various O–H–O hydrogen bonds are formed involving two lattice water molecules (O2w, O3w), coordinated water molecules (O1w) and two oxygen atoms (O2, O3) of the pda ligands. There are six types of O–H–O hydrogen bonds (figure 4, table 3) classified into three kinds: (i) from the *c* axis, three hydrogen bonds connect the two vertical one-dimensional zigzag chains, including O2W–H2WA···O3W, O3W–H3WA···O2, O1W–H1WA···O2W with O···O distance from 2.782(11) Å to 2.924(10) Å and O–H–O angles from 143.4° to 173(13)°; (ii) from the same direction, another kind of hydrogen bond connects horizontal ones, O3W–H3WB···O2 with the O···O distance

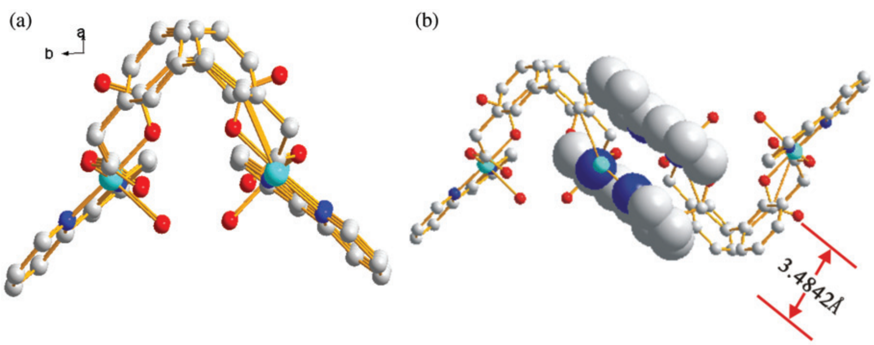

Figure 3. (a) The saddle like single-stranded helical chain, viewed from the *c* axis. (b) Viewed from the *c* axis, the π–π stacking interaction between horizontal adjacent chains.

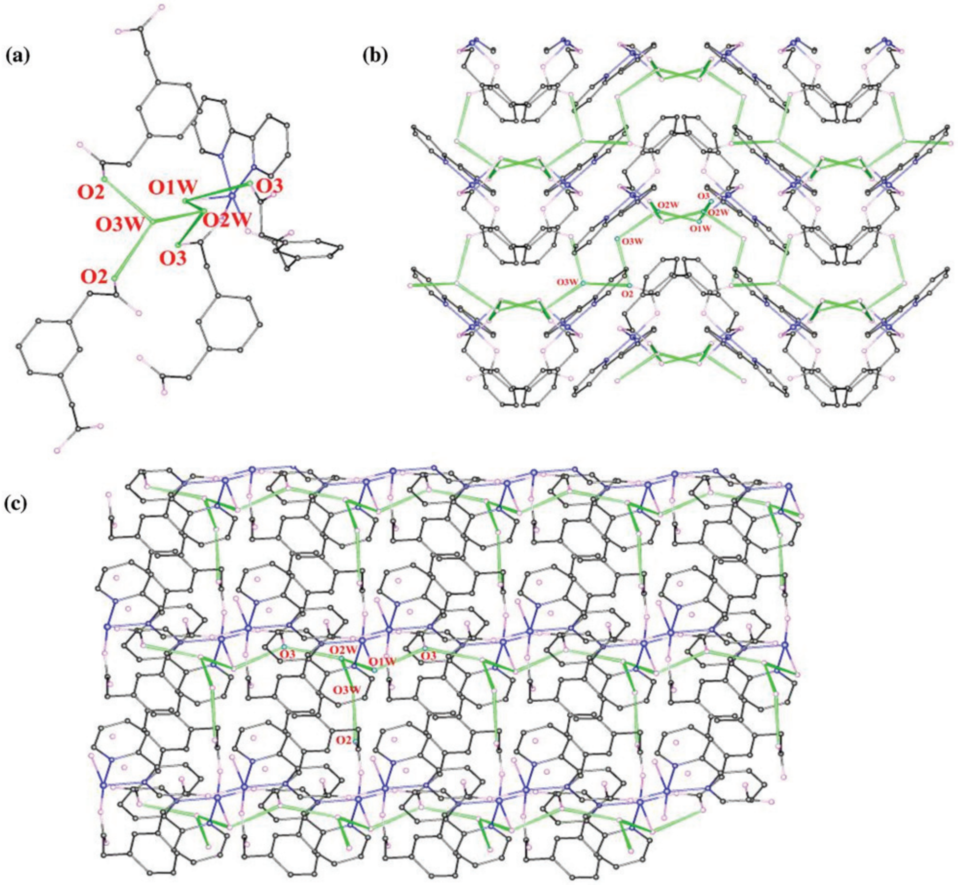

Figure 4. (a) The hydrogen bonds around Cu(II) ion in the title complex. Hydrogen bonds are shown as thick green lines. (b) View of the hydrogen bonds along the *c* axis. Some redundant atoms are omitted for clarity. (c) View of three-dimensional layer structure along *b*.

3.172(11) Å and O–H ··· O angle 154(11); (iii) the residual ones are O1W–H1WB ··· O3, O2W–H2WB ··· O3 with O ··· O distances from 2.783(10) Å to 2.898(7) Å and O–H–O angles from 143.4° to 155(8)° connecting two hydrogen bond chains together along the zigzag chain (figure 4c). All hydrogen bonds are checked by PLATON [15].

3.2. *IR spectroscopy*

The IR spectrum of the complex shows characteristic bands of dicarboxylate groups at 1610 and 1490 cm^{-1} for asymmetric stretching and 1380 cm^{-1} for symmetric stretching. Broad bands at 3240–3410 cm^{-1} are attributed to the water ligand. The numerous bands located around 1500 cm^{-1} are attributed to C=C bonds of the skeleton vibrations of aromatic rings. No absorption of protonated H_2pda (1715–1680 cm^{-1}) confirms that H_2pda is completely deprotonated by NaOH. The separations (Δ) between $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ are 230–110 cm^{-1}, attributed to monodentate binding of the carboxylate groups in agreement with the crystal structure.

3.3. *Thermal gravimetric analysis*

Thermal gravimetric analyses (TGA) for the crystal sample were performed from 30 to 800°C. The weight loss of 11.71% at the first stage corresponds to loss of three H_2O molecules from 95.50°C to 157.90°C (ca 11.60% for three H_2O). The further weight decrease from 229.48°C to 304.25°C suggests stepwise decomposition of the compound, namely the loss of 2′2-bpy and the benzyl of pda, with the residua 32.75% (ca 32.53% for $Cu(CO_2)_2$. Finally, the compound is completely converted to CuO of 16.50% (ca 17.07%) at 800°C. All the residues are characterized by IR spectroscopy.

3.4. *Quantum chemical calculation*

In order to understand the structural characteristics of the complex, Density Functional Theory (DFT) calculation on the nonperiodic model system with the aim to treat the full periodic metal–organic framework was employed. The boundary was saturated by H atoms (figure 6). The structure optimization of the selected monomer was performed by DFT (B3LYP) [16] with basis sets Lanl2dz [17] and 6-31G. The following calculation and discussion are based on the optimized monomer. The full geometry optimization was performed without constraints on symmetry, and the stationary point was characterized by frequency calculation. All computations were carried out with Gaussian 03 quantum chemistry program-package [18] on a Legend PC.

In the optimized structure, shown in table 4, the results from different basis sets are in conformity with those observed from X-ray analysis; Lanl2dz, 6-31G basis set gives better structural data. For example, in the title complex, the distances of copper with O4 are 1.963 Å (by exp.), 1.999 Å (by Lanl2dz) and 1.954 Å (by 6-31G); in $[Cu(ipa)(bpy)]_n \cdot 2nH_2O$ the distances of copper with O1 are 1.991 Å (by exp.), 1.974 Å (by Lanl2dz) and 1.983 Å (by 6-31G). The following calculation and discussion are based on 6-31G.

The computational IR spectral frequencies for the characteristic bands of dicarboxylate groups in the title complex are at 1680 and 1572 cm^{-1} for asymmetric stretching. The bands at 3532 and 3625 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of the coordinated water. The broad bands at 1491–1602 cm^{-1} are attributed to vibrations of benzene. Compared to the experimental values, the calculated dicarboxylate and water ligand frequencies were higher, which may be due to their participation in hydrogen bonding. All theoretical frequencies reported here are scaled by 0.9614 for the B3LYP functional with the 6-31G basis set and the intensity is the relative value [19].

To examine the HOMO and the LUMO for the complex, the calculation indicates that the complex has 111 occupied molecular orbitals (MOs). In general, as plotted in figure 5 (LUMO, HOMO), the two complexes $[Cu(pda)(bpy)(H_2O)]_n{\cdot}2nH_2O$ and $[Cu(ipa)(bpy)]_n{\cdot}2nH_2O$ have similar characteristic frontier molecular orbitals. As shown

Table 4. Selected bond lengths (Å) and angles (°) by calculation and experiment.

$[Cu(pda)(bpy)(H_2O)]_n \cdot 2nH_2O$				$[Cu(ipa)(bpy)]_n \cdot 2nH_2O$			
	Calcd				Calcd		
Basis	Lan2DZ	6-31G	Exp.	Basis	Lan2DZ	6-31G	Exp.
Cu(1)–O(1)	1.912	1.907	1.926	Cu(1)–O(1)	1.974	1.983	1.991
Cu(1)–O(1w)	2.342	2.343	2.288	Cu(1)–O(2)	2.843	2.618	2.502
Cu(1)–O(4)	1.999	1.954	1.963	Cu(1)–O(3)	1.875	1.838	1.979
Cu(1)–N(1)	2.045	2.006	1.997	Cu(1)–N(1)	2.044	2.007	2.014
Cu(1)–N(2)	2.077	2.018	2.024	Cu(1)–N(2)	2.072	2.024	2.014
O(4)–Cu(1)–O(1)	97.96	95.87	90.88	O(2)–Cu(1)–O(1)	53.06	57.08	58.08
O(4)–Cu(1)–N(1)	92.22	95.89	94.70	O(1)–Cu(1)–O(3)	97.45	100.20	92.30
N(1)–Cu(1)–N(2)	78.66	80.12	80.43	O(3)–Cu(1)–N(1)	89.09	89.62	96.84
N(2)–Cu(1)–O(1)	91.08	91.31	92.59	N(1)–Cu(1)–N(2)	78.87	79.70	81.37
O(1w)–Cu(1)–O(4)	103.61	97.14	98.90	N(2)–Cu(1)–O(1)	95.05	93.20	93.07
O(1w)–Cu(1)–N(2)	86.79	99.46	97.67				

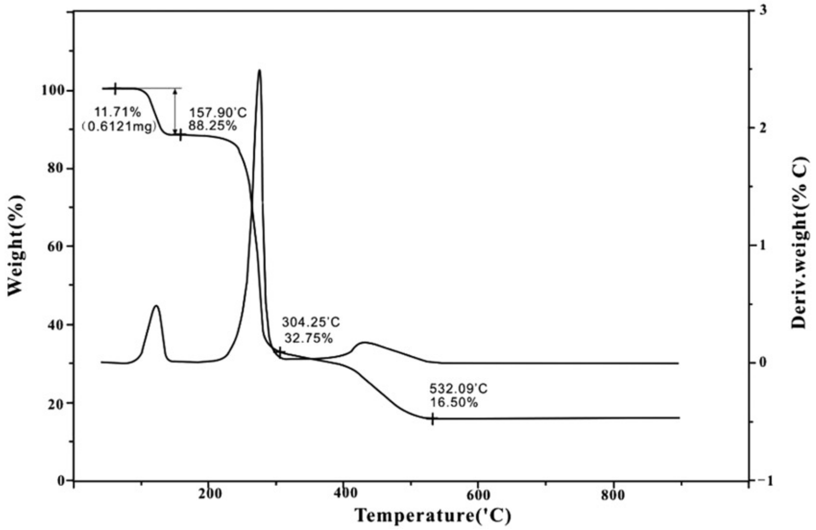

Figure 5. The TG-DTG curves of the title complex.

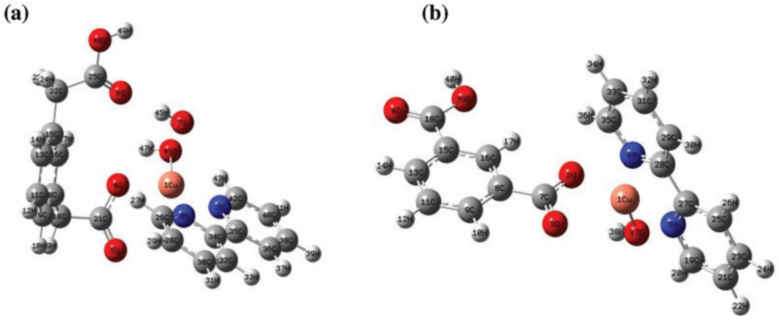

Figure 6. The optimized mode of (a): $[Cu(pda)(bpy)(H_2O)]_n \cdot 2nH_2O$ and (b): $Cu(ipa)(bpy)]_n \cdot 2nH_2O$.

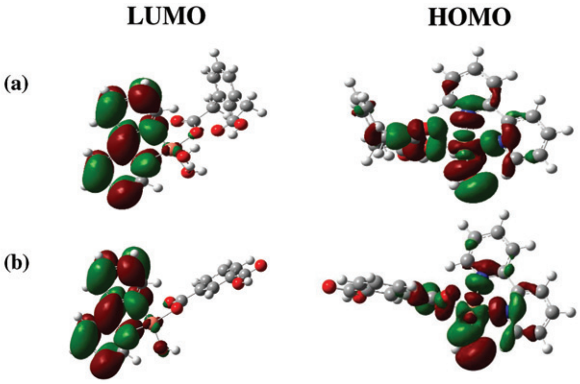

Figure 7. The contour plots of HOMO and LUMO orbitals of (a): $Cu(pda)(bpy)(H_2O)]_n \cdot 2nH_2O$ and (b): $Cu(ipa)(bpy)]_n \cdot 2nH_2O$.

Table 5. Main atomic orbital population (%) of the frontier molecular orbitals in the title complex.

	Cu			N1		N2		O1		O4		O1w	
Atomic orbital	*s*	*p*	*d*	*s*	*p*	*s*	*p*	*s*	*p*	*s*	*p*	*s*	*p*
HOMO	0.18	0.92	24.87	1.08	2.69	2.07	2.99	0.17	9.32	0.02	22.40	0.02	2.03

in table 5, the HOMO is mainly composed of d-orbitals of Cu1, p-orbitals of O1, O4, whereas the LUMO is associated with the bpy ligand. The energy separation between the HOMO and the LUMO was also calculated. The total energy of the title compound is −2975.06718766 a.u., when the energy of HOMO is −0.18879 a.u. and the energy of LUMO is −0.08266 a.u. The gap between the frontier molecular orbital energies is 0.10613 a.u. The total energy of [Cu(ipa)(bpy)] · compound is −2820.05387731 a.u., the energy of HOMO is −0.19715 a.u. and the energy of LUMO is −0.09562 a.u. The gap between the frontier molecular orbital energies is 0.10153 a.u. The larger absolute value of the gap energy means better stability, suggesting the title compound is a littler more stable. However, solid-state packing effects are not included in the DFT calculations, which tends to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculation. Even if these calculated energy levels are not accurate, one can get information by comparing the gap energies.

4. Conclusions

This study provides a complex based on H_2dpa. The coordination complex from the experimental and theoretical aspect are compared with $[Cu(ipa)(bpy)]_n \cdot 2nH_2O$, for the influence of the length of carbon chain, the title complex is more stable both because of the effect of bending of the acetoxy ($–CH_2COO^-$) and formation of hydrogen bonds.

Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as the supplementary data, CCDC No. 649404 for the title complex, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223336033 or E-mail: deposit@ccdc.cam.ac.uk).

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