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4-氯苯氧乙酸及 4,4′-bipy=4,4′-联吡啶构筑的层状锌配合物的合成、晶体结构

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摘要: 水热条件下,合成了一个新的锌(Ⅱ)配位聚合物[Zn(PCPA)$_2$(4,4′-bipy)(H$_2$O)]$_n$(PCPA=4-氯苯氧乙酸,4,4′-bipy=4,4′-联吡啶),并通过元素分析、红外光谱、紫外光谱、热重分析、X-射线粉末衍射和 X-射线单晶衍射对其进行了表征。锌(Ⅱ)分别与来自 2 个 4,4′-bipy 的 2 个氮原子、3 个 4-氯苯氧乙酸的 3 个氧原子和 1 个水分子中的 1 个氧原子配位, 形成变形的八面体的配位构型。由于 4-氯苯氧乙酸和 4,4′-bipy 的桥联作用,配合物在空间形成了二维层状结构,在此二维层状结构中存在的 O–H…O 氢键起到了稳定结构的作用。

关键词: 4-氯苯氧乙酸; 4,4′-联吡啶; 锌(Ⅱ)配合物; 晶体结构
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Hydrothermal Synthesis, Crystal Structure and Characterization of Two-Dimension Zinc(Ⅱ) Complex Based on *p*-Chlorophenoxyacetic Acid and 4,4′-Bipyridine

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Abstract: The title complex [Zn(PCPA)$_2$(4,4′-bipy)(H$_2$O)]$_n$ with *p*-chlorophenoxyacetic acid (PCPA), 4,4′-bipyridine (4,4′-bipy) has been hydrothermally synthesized and characterized by elemental analysis, IR spectra, UV spectra, thermal analyses, powder X-ray diffraction and single crystal X-ray diffraction. The zinc(Ⅱ) ion is six-coordinated with two nitrogen atoms from two 4,4′-bipy, three oxygen atoms from three PCPA and one water oxygen atom, forming a slightly distorted octahedral configuration. The complex molecules form a 2D layer structure through bridged PCPA and 4,4′-bipy which is consolidated by O–H…O hydrogen bonds. CCDC: 850113.

Key words: *p*-chlorophenoxyacetic acid; 4,4′-bipyridine; Zinc(Ⅱ) complex; crystal structure

There has been great interest in the field of design and synthesis of coordination polymeric complexes, in particular, the carboxyl complexes, owing to their fascinating molecular topologies along with potential applications as functional materials[1-12]. In the past few years, much emphasis was laid on using the rigid aromatic carboxylic acids as ligands[13-15] to synthesis the carboxyl complexes. But flexible aromatic carboxylic acids ligands have not been studied much maybe their varied geometries and conformations make it difficult to control the expected structures[15]. *P*-chlorophenoxyacetic acid as a flexible ligand owing to the presence of the -OCH$_2$- spacer has been extensively studied and well understood for mono-, dinuclear complexes[16]. In order to obtain further information about the complex construction

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with flexible aromatic carboxylic acid, we synthesized a complex $[Zn(PCPA)_2(4,4'\text{-bipy})(H_2O)]_n$. We report here the synthesis, crystal structure and thermal stability.

1 Experimental

1.1 Materials and physical measurements

All reagents and solvents were used as purchased without further purification. IR spectra were recorded on a Nicolet 6700 spectrometer in the 4 000~400 cm^{-1} region using the KBr pellet technique. The UV spectra was obtained on a Heliosa UV spectrometer in the 200~400 nm range at room temperature. Crystal structure determination was carried out on a Bruker Smart APEX Ⅱ CCD diffractometer. Elemental analyses of C, H and N were performed on a PE-2400(Ⅱ) apparatus. Thermogravimetric analysis (TG) data were collected on a METTLER TGA/DSC 1100 instrument under air atmosphere with a heating rate of 10 ℃·min^{-1}. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu $K\alpha$ radiation (0.154 18 nm), in which the X-ray tube was operated at 40 kV and 30 mA.

1.2 Synthesis of $[Zn(PCPA)_2(4,4'\text{-bipy})(H_2O)]_n$

A mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.110 g, 0.5 mmol), PCPA (0.187 g, 1.0 mmol), 4,4′-bipy (0.156 g, 1.0 mmol), Et_3N (1.0 mmol, 0.14 mL) were added into a mixed solvent of 10 mL anhydrous methanol and 5 mL water and stirred for 1 h. Then the mixture was transferred and sealed into a 23 mL Teflon-lined stainless steel autoclave, which was heated at 120 ℃ for 3 d and then cooled to room temperature. The colorless crystals were obtained in 36% yield (based on Zn). Anal. Calcd. for $C_{26}H_{22}ZnCl_2N_2O_7$(%): C, 51.12; H, 3.63; N, 4.59. Found(%): C, 51.07; H, 3.57; N, 4.65. IR (KBr, ν/cm^{-1}): 3 406, 1 630, 1 490, 1 474, 1 314, 1 236, 1 072, 826, 756, 508.

1.3 Crystal structure determination

The single crystals of the title complex with approximate dimensions of 0.30 mm×0.20 mm ×0.12 mm was placed on a Bruker Smart APEX Ⅱ CCD diffractometer. The diffraction data were collected at 295 K using a graphite-monochromatic Mo $K\alpha$ radiation (λ =0.071 073 nm) with the φ-ω scan mode in the range of $1.93° \leqslant \theta \leqslant 25.05°$. The correction for Lp factors was applied. The structure was solved by direct methods with SHELXS-97 program[17] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97[18]. All non-hydrogen atoms were treated anisotropically. The organic hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calcula-tions in the final stage of full-matrix least-squares refinement. The water hydrogen atoms were located in the difference Fourier map and refined isotropically. The final R=0.034 5, wR=0.091 4 (w=1/[$\sigma(F_o)$+(0.038 8P)^2 +0.983 5P], where P=(F_o^2+2F_c^2)/3), S=1.083, $(\Delta/\sigma)_{max}$= 0.000, $(\Delta\rho)_{max}$=629 and $(\Delta\rho)_{min}$=−533 e·nm^{-3}. The crystallographic data and structure refinements for the complex are summarized in Table 1. The selected bond lengths and bond angles of the title complex are listed in Table 2, and the hydrogen bond details in Table 3.

CCDC: 850113.

Table 1 Crystal data and structure refinements of the title complex

Empirical formula	$C_{26}H_{22}ZnCl_2N_2O_7$	Z	4
Formula weight	61 073	μ / mm^{-1}	1.208
Size / mm	0.30×0.20×0.12	D_c / (g·cm^{-3})	1.571
θ range for data collection / (°)	1.93 to 25.05	F(000)	1 248
Crystal system	Monoclinic	Reflections collected	12924
Space group	$P2_1/c$	Independent reflections (R_{int})	4 567 (0.068 7)
a / nm	1.135 1(3)	Goodness of fit on F^2	1.083
b / nm	0.849 2(2)	R_1, wR_2 (I>2σ(I))	0.034 5, 0.091 4
c / nm	2.875 2(6)	R_1, wR_2 (all data)	0.039 2, 0.094 2
V / nm^3	2.582 0(11)	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	629, −533

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

Zn(1)-O(1)	0.212 34(15)	Zn(1)-N(1)	0.214 55(19)	C(1)-O(1)	0.125 2(3)
Zn(1)-O(4)	0.208 62(16)	Zn(1)-N(2)^{D}	0.214 6(2)	C(1)-O(2)	0.124 0(3)
Zn(1)-O(2)^{C}	0.212 16(16)	Zn(1)^{B}-O(2)	0.212 16(16)	C(9)-O(4)	0.125 3(3)
Zn(1)-O(1W)	0.209 36(17)	Zn(1)^{A}-O(2)	0.214 6(2)	C(9)-O(5)	0.122 9(4)
O(1)-Zn(1)-O(2)^{C}	83.48(6)	O(1)-Zn(1)-N(1)	85.15(7)	O(4)-Zn(1)-N(2)^{D}	92.86(7)
O(1)-Zn(1)-O(4)	173.44(6)	O(2)C-Zn(1)-N(1)	90.61(7)	N(1)-Zn(1)-N(2)^{D}	176.78(7)
O(1)-Zn(1)-O(1W)	96.69(6)	O(4)-Zn(1)-N(1)	90.28(7)	N(1)-Zn(1)-O(1W)	89.58(7)
O(4)-Zn(1)-O(2)^{C}	91.89(6)	O(1)-Zn(1)-N(2)^{D}	91.67(7)		
O(1W)-Zn(1)-O(2)^{C}	179.76(6)	O(2)C-Zn(1)-N(2)^{D}	88.56(6)		

Symmetry transformations used to generate equivalent atoms: ^{A} $x+1, y, z$; ^{B} $-x, y-1/2, -z+1/2$; ^{C} $-x, y+1/2, -z+1/2$; ^{D} $x-1, y, z$.

Table 3　Hydrogen bond length and angles for the title complex

D–H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠DHA / (°)
O(1W)–H(1W)···O(5)	0.085	0.179	0.258 5(2)	155.4
O(1W)–H(2W)···O(1)^{B}	0.085	0.200	0.279 1(2)	155.0

Symmetry transformations used to generate equivalent atoms: ^{B} $-x, y-1/2, -z+1/2$.

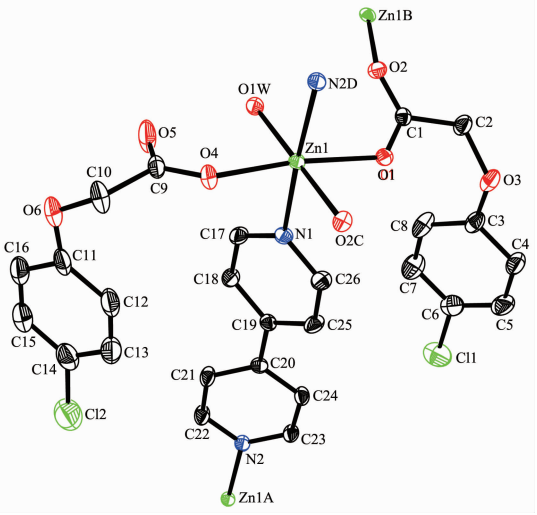
2　Results and discussion

2.1　IR spectra

The IR spectra of the title complex $[Zn(PCPA)_2(4,4'\text{-bipy})(H_2O)]_n$ clearly shows both the presence of the PCPA and coordinated 4,4′-bipy. The strong peaks at 1 630 and 1 474 cm^{-1} are attributed to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ respectively. The value of $\Delta(\nu_{as}(COO^-)-\nu_s(COO^-))$ is 156 cm^{-1}, which is larger than 100 cm^{-1} but smaller than 200 cm^{-1}, indicating that part PCPA adopting chelating coordination mode[19] of the carboxyl group to the metal atom, which are finally confirmed by X-ray diffraction analysis. The adsorption at 1 490, 826 and 615 cm^{-1} are the characteristic adsorption peak of 4,4′-bipy. In addition to the above, the wide adsorption peak at about 3 406 cm^{-1} is characteristic of ν(O-H) group in H_2O.

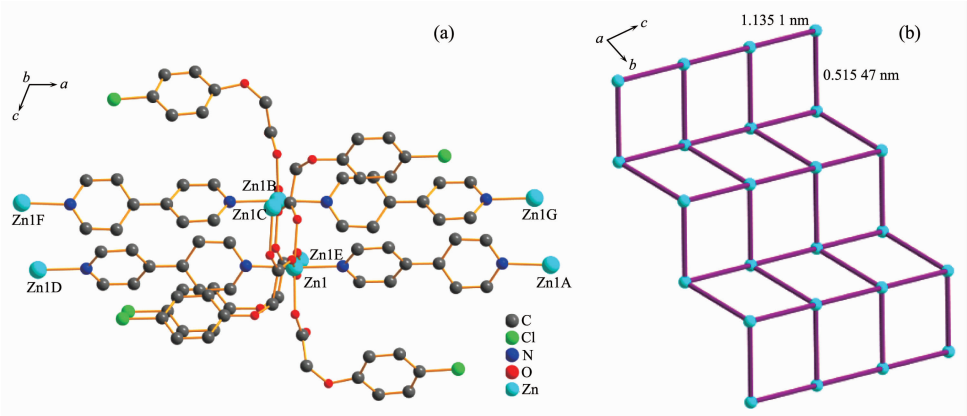
2.2　Crystal structural

X-ray diffraction study demonstrates that the complex crystallizes in the monoclinic system with space group $P2_1/c$. The coordination environment around the Zn centers is shown in Fig.1. The Zn(Ⅱ) centers lie in a slightly disordered octahedral environment with the axial positions occupied by one water hydrogen atom and one carboxylate oxygen atom from one PCPA ligand, and the equatorial positions occupied by two carboxylate oxygen atoms of two different PBCA ligands and two nitrogen atoms from two 4,4′-bipy ligands. Here, the sum of the angles subtended at the Zn(Ⅱ) atom in the equatorial plane is 359.96° (close to 360°), so that the atoms N(1), N(2)^{D}, O(1), O(4) and Zn(1) are almost in the same plane. The equatorial equation is $0.074\ 4x+8.431\ 2y-3.262\ 2z=1.559\ 0$. The deviation of the atoms N(1), N(2)^{D}, O(1), O(4) and Zn(1) from equatorial trigonal plane is 0.003 31, 0.001 52, 0.003 35, 0.000 29 and −0.005 44



Symmetry codes: A: $x+1, y, z$; B: $-x, y-1/2, -z+1/2$; C: $-x, y+1/2, -z+1/2$; D: $x-1, y, z$; Hydrogen atoms are omitted for clarity

Fig.1　ORTEP view of the coordination environment of Zn(Ⅱ) of the title complex showing 30% thermal probability ellipsoids

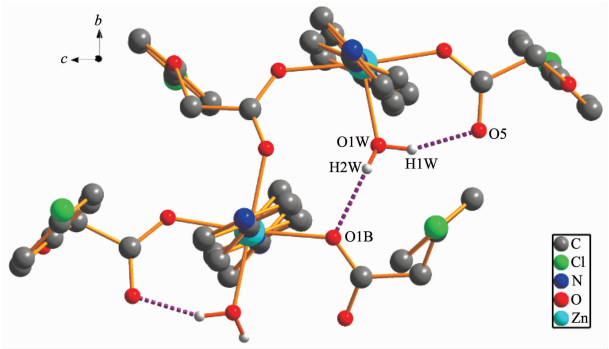


Symmetry codes: A: x+1, y, z; B: −x, y−1/2, −z+1/2; C: −x, y+1/2, −z+1/2; D: x−1, y, z; E: x, −1+y, z; F: −1−x, −1/2+y, 1/2−z G: 1−x, −1/2+y, 1/2−z; Hydrogen atoms are omitted for clarity

Fig.2 (a) 2D layer structure of the title complex; (b) Ladder-like motif constructed by adjacent Zn atoms

nm, respectively. The average deviation is −0.000 001 nm. Futhermore, the angles O(1W)-Zn(1)-O(2)^{C} in the axial place is 179.76(6)° which is almost close to the idea value of 180°. So conclusion could be drawn that the central Zn(Ⅱ) atom adopts a slightly distorted octahedral environment. The Zn-O bond lengths are ranging from 0.208 62(16) to 0.212 34(15) nm, which are slightly longer than the reported related Zn complex[20]. The C-O bond length of carboxyl group in the two PCPA ligands are obvious different, (C(1)-O(1) 0.125 2(3) nm and C(1)-O(2) 0.124 0(3) nm) nearly identical while (C(9)-O(4) (0.125 3(3) nm) and C(9)-O(5) (0.122 9(4) nm) obvious different with the value of Δ=0.0024 nm indicating that the PCPA liagands adopting monodentate and bidentate two coordination modes[18-19].

As shown in Fig.2a, the bidentate carboxylate groups of PCPA anions and 4,4′-bipy ligands bridge the Zn(Ⅱ) atoms to generate a two-dimensional (2D) layer structure. It is worth noting that a square grid coordination polymer is constructed by adjacent Zn atoms with dimensions of 1.135 13(5) nm×0.515 47(10) nm and the adjacent square grids are represented and formed ladder-like motif (Fig.2b). In the 2D layer structure, the intermolecular hydrogen bonds O(1W)−H(2W)···O(1)^{B} (0.279 1(2) nm, 155.0°, symmetry code: −x, y−1/2, −z+1/2) and intramolecular hydrogen bonds O(1W)−H(1W)···O(5)(0.258 2(2) nm, 155.4° further stabilize the crystal structure (Fig.3).



Symmetry code: B: −x, y−1/2, −z+1/2; Hydrogen atoms not included in hydrogen bonding are omitted for clarity

Fig.3 O−H···O hydrogen bonds in the 2D layer structure of the title complex

2.3 Thermal analysis and powder X-ray diffraction

The thermal analysis curve for the title complex is shown in Fig.4. The first weight loss of 3.08% (calcd. 2.95%) between 86 and 112 ℃ corresponds to the release of coordinated water molecules in the

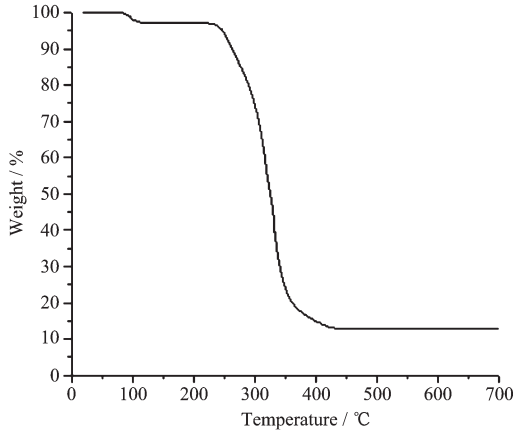


Fig.4 Thermal analysis curve of the title complex

complex. The further decomposition occurred in the range of 223~431 ℃, which may be attributed to the elimination of 4,4′-bipy and PCPA. The remaining products may be ZnO (Obsd. 13.02%, Calcd. 13.33%).

In order to check the phase purity of the title complex, the powder X-ray diffraction (XRPD) pattern was recorded at room temperature. As shown in Fig.5, the peak positions of simulated and experimental pattern is in good agreement with each other, demonstrating the phase purity of the product.

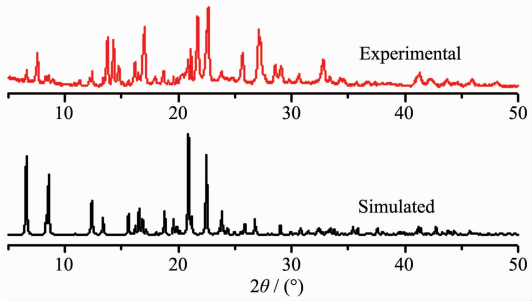


Fig.5　Experimental and Simulated powder X-ray diffraction patterns of the title complex

2.4　UV spectra

The UV spectra of the title complex and the free ligands PCPA and 4,4′-bipy have been studied in CH_3CN solvent at room temperature. As illustrated in Fig.6, the strong absorption peaks at approximate 214, 239 nm for ligand PCPA, 214, 227 nm for ligand 4,4′-bipy and 236 nm for the title complex, respectively. Comparing the complex and the free ligands, we can see that the absorption spectra peak shape of the title complex is essentially the same as the PCPA, but the location of the peak exhibits a certain blueshift about 3 nm. So the absorption is mainly due to the n-π^* transition of the ligand PCPA.

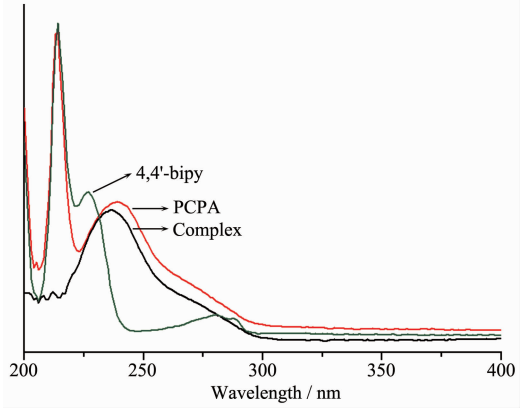


Fig.6　UV spectra of the title complex and ligands PCPA and 4,4′-bipy

Reference:

[1] Maspoch D, Ruiz-Molina D, Veciana J. *Chem. Soc. Rev.*, **2007**,36:770-818

[2] Nouar F, Eubank J F, Bousquet T, et al. *J. Am. Chem. Soc.*, **2008**,**130**:1833-1835

[3] Chun H P, Jung H J. *Inorg. Chem.*, **2009**,**48**:417-419

[4] Ono K, Yoshizawa M, Akita M, et al. *J. Am. Chem. Soc.*, **2009**,**131**:2782-2783

[5] XU Gui-Ji(徐贵基), PAN Zhao-Rui(潘兆瑞), ZHENG He-Gen(郑和根), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2009**,**25**(9):1551-1556

[6] SHI Zhi-Qiang(石智强), JI Ning-Ning(季宁宁), ZHAO Xue(赵雪), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2010**,**26**(2):251-256

[7] JI Ning-Ning(季宁宁), SHI Zhi-Qiang(石智强), ZHAO Ren-Gao(赵仁高). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2010**,**26**(6):1025-1030

[8] LIU Tong-Fei(刘同飞), ZNI Guang-Hua(崔广华), JIAO Zni-Huan(焦翠欢), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2011**,**27**(7):1417-1422

[9] SHI Zhi-Qiang(石智强), JI Ning-Ning(季宁宁), HE Guo-Fang(何国芳), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2011**,**27**(8):1507-1512

[11]LIU Jia-Lu(刘家禄), ZHAO Guo-Liang(赵国良). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2011**,**27**(8):2021-2026

[12]Shi Z Q, Ji N Ning, Zhao R G, et al. *Struct. Chem.*, **2011**, **22**:225-233

[13]Zhang S S, Niu S Y, Wang L, et al. *Asian J. Chem.*, **2006**, **18**:1885-1887

[14]Miyazawa M, Irie Y, Kashimoto K, et al. *Inorg. Chem. Commun.*, **2009**,**12**:336-339

[15]YANG Ying-Qun(杨颖群), LI Chang-Hong(李昶红), LI Wei(李薇), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2010**,**26**(10):1890-1894

[16]Sun Y X, Wang Z, Zhang H H, et al. *Inorg. Chim. Acta*, **2007**,**360**:2565-2572

[17]Sheldrick G M. *SHELXL* 97, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.

[18]Sheldrick G M. *SHELXL* 97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.

[19]Nakamota K, Translated by HUANG De-Ru(黄德如), WANG Ren-Qing(汪仁庆). *Infrand and Raman Spectra of Inorganic and Coordination Compounds*, 3*rd Ed.*(无机和配位化合物的红外和拉曼光谱.3 版). Beijing: Chemical Industry Press, **1986**.

[20]Wang Z, Zhang H H, Chen Y P, et al. *J. Solid. State. Chem*, **2006**,**179**:1536-1544