第 26 卷第 4 期 无 机 化 学 学 报 Vol.26 No.4
2010 年 4 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 708-712

研究简报

四(4–乙烯基吡啶)硝酸铜(I)配合物的结构、电化学和热稳定性能研究

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关键词:铜(I)配合物;晶体结构;热性质;循环伏安法
中图分类号:O614.121 **文献标识码**:A **文章编号**:1001-4861(2010)04-0708-05

Crystal Structure, Electrochemical and Thermal Stability Studies of Tetrakis(4-vinylpyridine-κN^3) nitratocopper(I)

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Abstract: The title complex Cu(Vpy)NO_3 (Vpy=4-vinylpyridine) has been synthesized and structurally characterized by X-ray single crystal diffractometry. The complex crystallizes in triclinic system, $P\bar{1}$ space group with the cell parameters of a=1.004 2(2) nm, b=1.631 7(3) nm, c=1.887 7(4) nm, α=81.54(2)°, β=77.44(2)°, γ=79.39(2)°, V=2.948 9(11) nm^3, Z=4, and D_c=1.230 g·cm^{-3}, the final R_1=0.075 2, wR_2=0.139 1. The complex crystallizes with two molecules in the asymmetric unit. Each Cu(I) ion is coordinated by four N atom from the Vpy ligands and one O atoms from the nitrate anion, resulted in a square pyramidal geometry. The electrochemical studies reveal that redox of Cu^{2+}/Cu^+ in the complex is a quasi-reversible process. CCDC: 736638.

Key words: Copper(I) complex; crystal structure; thermal property; cyclic voltammetry

0 Introduction

Copp er (I) complexes for mimicking the Cu-containing enzymes have attracted much attention[1-4]. These models will lead to a better understanding of the active site structure and the reaction mechanisms of the enzymes. The copper(I) complexes have always novel structures[5-7], as well as the many chemical and physical properties due to irregular metal coordination environment, such as catalysis[8-9], oxygen transporting[2], photoelectric conversion[10-11], electroluminescence~and photoluminescence[12-14]. The copper(I) center has a labile metal-ligand bond arising from its d^{10} configuration. The tetrahedral coordination geometry is common structure in copper(I) complexes[15]. In this paper, we report the crystal structure, electrochemical and thermal stability of a square pyramidal copper(I) complex based on 4-vinylpyridine.

1 Experimental

1.1 Materials and instruments

All the chemical reagents for synthesizing the title compound were purchased commercially and used without further purification. Elemental analyses (C, H

收稿日期:2009-09-21。收修改稿日期:2009-12-31。
国家自然科学基金(No.20871072),山东省博士启动基金(No.2007BS04023),山东省自然科学基金(No.2009ZRA2071)和青岛科技大学博士启动基金资助项目。
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and N) were carried out on a Perkin-Elmer 1400C analyzer. Voltammetry was performed by using a CHI 832B electrochemical analysis system (China) with a three-electrode system consisting of a glass carbon (GC) electrode (U=3 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. All the electrochemical measurements were carried out in a 10 mL electrolyte cell with 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solution as electrolyte. TG curve was recorded on a NETZSCH-TG209 GmbH thermoanalyser in flow of N_2, in the temperature range from 20~500 ℃, with a heating rate of 5 ℃·min^{-1}.

1.2 Preparation

A mixture of 4-vinylpylidine (0.211 g, 2 mmol), $CuNO_3$ (0.63 g, 0.5 mmol), and H_2O (15 mL) was heated in a 20 mL Teflon autoclave at 160 ℃ for 2 days and then cooled to room temperature at the rate of 5 ℃·h^{-1}. The colorless block crystals were obtained. Yield: 73%. Anal. Calcd. for $C_{28}H_{28}CuN_5O_3$: C 61.54, H 5.13, N 12.82; found: C 61.86, H 5.02, N 13.12.

1.3 Crystal structure determination

A block shaped crystal with dimensions of 0.40 mm ×0.30 mm ×0.30 mm was mounted on a Bruker SMART 1000 CCD area detector X-ray single crystal diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) and a φ/ω scanning mode at 293(2) K. Intensities was corrected for Lorentz and polarization effects and empirical absorption.

The structure was solved by direct methods via SHELXS 97 program[16] and refined by full-matrix least squares on F^2 via SHELXL 97 program[17]. All the non-hydrogen atoms were located from the difference Fourier map and refined anisotropically. H atoms were positioned geometrically (C-H=0.093 nm,) and allowed to ride on their parent atoms with U_{iso}(H)=1.2 times U_{eq} (C). Crystalographic data for the title complex are listed in Table 1.

CCDC: 736638.

Table 1　Crystal and structure refinement data for the title complex

Empirical formula	$C_{28}H_{28}CuN_5O_3$	μ / mm^{-1}	0.775
Formula weight	546.10	F(000)	1136
Temperature / K	293(2)	Crystal size / mm	0.40×0.30×0.30
Crystal system	Triclinic	θ range for data collection / (°)	1.11~25.98
Space group	$P\bar{1}$	Limiting indices	$-11\leqslant h\leqslant 12$, $-19\leqslant k\leqslant 20$, $0\leqslant l\leqslant 23$
a / nm	1.004 2(2)	Reflections collected	13 532
b / nm	1.631 7(3)	Independent reflections (R_{int})	11 580 (0.028 8)
c / nm	1.887 7(4)	Reflection observed	6 090
α / (°)	81.54(2)	Refinement method	Full-matrix least-squares on F^2
β / (°)	77.44(2)	Data / restraints / parameters	11580 / 37 / 613
γ / (°)	79.39(2)	Goodness-of-fit on F^2	1.007
V / nm^3	2.948 9(11)	Final R indices [$I>2\sigma(I)$]	R_1=0.045 1, wR_2=0.079 3
Z	4	R indices (all data)	R_1=0.075 2, wR_2=0.139 1
D_c / (Mg·m^{-3})	1.230	Largest diff. peak and hole / (e·nm^{-3})	749 and −633

2 Result and discussion

2.1 Explanations to the crystal structure

Fig.1 shows the structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme, and Fig.2 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths and bond angles are presented in Table 2. Hydrogen-bonds are presented in Table 3.

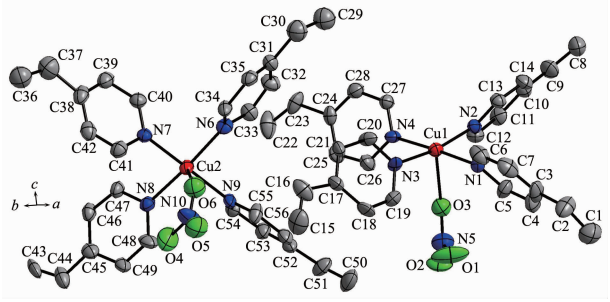
The crystal structure of the title compound crystallizes with two complexes in an asymmetric unit. The Cu atoms in both complexes adopt close coordination geometries, exhibiting a N4O square pyramidal coordination mode with four N atoms from four Vpy molecules and an O atom from a nitrate anion. The average Cu-N distances of the equatorial plane in

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

Cu(1)-N(2)	0.202 0(11)	Cu(1)-O(3)	0.238 0(12)	Cu(2)-N(8)	0.204 5(11)
Cu(1)-N(3)	0.205 0(10)	Cu(2)-N(7)	0.201 6(10)	Cu(2)-O(6)	0.240 9(11)
Cu(1)-N(4)	0.205 2(10)	Cu(2)-N(6)	0.202 7(11)	Cu(1)-N(1)	0.205 8(11)
Cu(2)-N(9)	0.203 2(10)				
N(2)-Cu(1)-N(3)	170.1(4)	N(4)-Cu(1)-O(3)	85.7(4)	N(7)-Cu(2)-O(6)	83.9(4)
N(2)-Cu(1)-N(4)	91.2(4)	N(1)-Cu(1)-O(3)	92.6(4)	N(6)-Cu(2)-O(6)	85.9(5)
N(3)-Cu(1)-N(4)	87.8(4)	N(7)-Cu(2)-N(6)	90.4(4)	N(9)-Cu(2)-O(6)	92.4(5)
N(2)-Cu(1)-N(1)	90.8(4)	N(7)-Cu(2)-N(9)	176.3(5)	N(8)-Cu(2)-O(6)	104.3(5)
N(3)-Cu(1)-N(1)	90.6(4)	N(6)-Cu(2)-N(9)	89.2(4)	N(4)-Cu(1)-N(1)	177.4(4)
N(7)-Cu(2)-N(8)	89.8(4)	N(2)-Cu(1)-O(3)	88.7(4)	N(6)-Cu(2)-N(8)	169.7(5)
N(3)-Cu(1)-O(3)	101.0(4)	N(9)-Cu(2)-N(8)	91.3(4)		

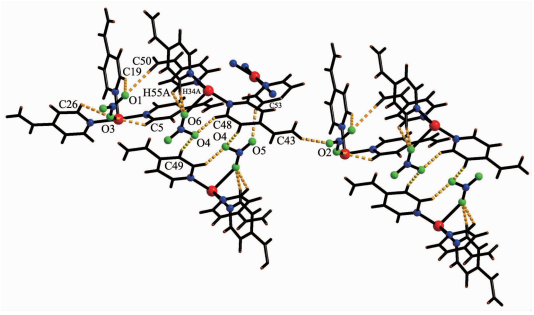
Table 3 Hydrogen bonds of the complex

D–H···A	Symmetry codes	*d*(H···A) / nm	*d*(D···A) / nm	∠(DHA) / (°)
C(5)–H(5A)···O(3)		0.256	0.317 2(16)	124
C(18)–H(18A)···O(2)	1–*x*, 1–*y*, –*z*	0.243	0.336 4(17)	176
C(19)–H(19A)···O(1)		0.258	0.342 4(14)	151
C(26)–H(26A)···O(3)		0.257	0.307 1(19)	114
C(34)–H(34A)···O(6)		0.255	0.306(2)	115
C(43)–H(43B)···O(2)	1–*x*, 2–*y*, –*z*	0.260	0.345 6(13)	154
C(48)–H(48A)···O(4)		0.230	0.286 4(17)	119
C(49)–H(49A)···O(4)	–*x*, 2–*y*, –*z*	0.245	0.336 8(19)	168
C(50)–H(50A)···O(1)	1–*x*, 1–*y*, –*z*	0.246	0.330 2(9)	150
C(53)–H(53A)···O(5)	1+*x*, *y*, *z*	0.243	0.323 0(17)	145
C(55)–H(55A)···O(6)		0.251	0.314 6(17)	126



Hydrogen atoms have been omitted for clarity

Fig.1 Structure of the title complex at 30% probability displacement ellipsoids with atomic numbering scheme



Some ligands have been omitted for clarity

Fig.2 3D network structure formed by C–H···O hydrogen bonds

two complexes are 0.204 5(10) and 0.203 0(10) nm, respectively, agreeing with those of the structurally analogous complex [Cu(stpy)(ONO_2)(ONO_2)′] (stpy = *trans*-4-styryl-pyridine, Cu-N=0.202 3(3) nm)[18]. The bond lengths of Cu-O in the axial plane are 0.238 0(12) nm and 0.240 9(11) nm, respectively, which are shorter than those in the complex [Cu(stpy)(ONO_2)(ONO_2)′][18] (Cu-O=0.243 4(3) nm and 0.260 9(3) nm). In the two complexes each Cu atom and four N atoms are almost coplanar since the mean plane deviations are within 0.013 nm. The Cu atoms are displaced by 0.007 01nm and 0.005 93 nm from the mean N1-N4 and N6-N9 planes toward the apical O atoms [O3, O6] (i.e., ρ = 0.007 01 nm and 0.005 09 nm), respectively. The low

value of ρ for the title compound agrees well with the relative lengthening of the Cu-O bond distances (0.238 0 (12) nm and 0.240 9 (11) nm) in the square pyramidal geometry. The trans N-Cu-N angles, 170.1(4)°, 177.4(4)°, 176.3(5)° and 169.7(5)° are less than the expected 180° for the idea square pyramidal geometry, indicating some distortion toward trigonal bipyramidal geometry. The bonds of N(4)-Cu(1)-N(1) and N(7)-Cu(2)-N(9) are almost linear (177.4(4)° and 176.3(5)° for N(4)-Cu(1)-N(1) and N(7)-Cu(2)-N(9), respectively). The coordinated nitrate anions are always planar [∑ΔO-N-O=360°] and there is no significant difference in the N-O distances, indicating almost no polarization effect exists and the coordination with metal atom does not affect the geometry of the nitrate group.

Some potentially weak (C–H···O) intramolecular and intermolecular interactions exist in the lattice[19-20], which link the complex units into a 3D network structure and further stabilize the packing structure in the crystal (Fig.2 and Table 3). The C(5), C(18), C(19), C(26), C(34), C(48), C(49), C(53),C(55) atoms with O(1), O(2), O(3), O(4), O(5), O(6) atoms form weak C–H···O intramolercular interactions (the donor and the acceptor distances are 0.317 2(16), 0.336 4(17), 0.342 4(14), 0.307 1(19), 0.306(2), 0.286 4(17), 0.336 8(19), 0.323 0(17), 0.314 6(17) nm, respectively). The C(43) with O(2) atoms and C(50) with O(1) atoms form C–H···O intermolecular interactions (the donor and the acceptor distances are 0.345 6(13) nm and 0.330 2(9) nm).

The short distances of 0.395 25(8) nm and 0.405 77(9) nm for $Cg(1)^{i}\cdots Cg(2)^{i}$ and $Cg(1)^{ii}\cdots Cg(3)^{i}$ (Cg(1) is the alkene double bond centroids of C22/C23; Cg(2) is the centroids of C32/C33 in pyridine rings, Cg(3) is the centroids of C34/C35 in pyridine rings, symmetry code: (i): –*x*, 1–*y*, 1–*z*; (ii): –*x*, 1–*y*, 1–*z*) show the presence of weak π···π stacking interactions, which link indepen dent complexes into an infinite 1D chain along a axis (Fig.3).

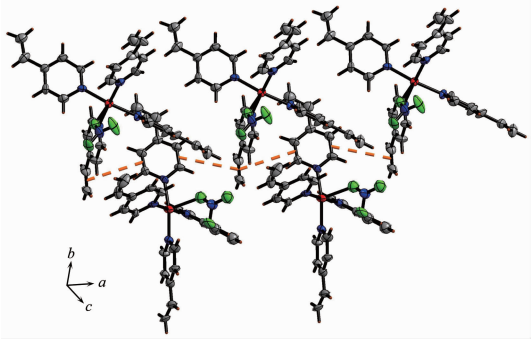


Fig.3　1D chains linked by weak π···π stacking interactions along a axis

2.2　Thermal properties

Thermal analyses reveal that the title complex retain stability below 84.5 ℃. On further heating the compound underwent four weight loss processes in a temperature range of 84.5~500 ℃. The first weight loss of 76.02% around 84.5~323 ℃ via three unidentified steps corresponds to the loss of four 4-vinylpyridine molecules (calculated 76.91%). In the temperature range of 323~472 ℃ weight loss of 10.94% was ascribed to the release of a nitrate anion (calculated 11.35%), to give expected Cu(observed 11.46%, calculated 11.72%).

2.3　Electrochemistry

Cyclic voltammetry curve for the title complex in 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solutions at scan rate 0.1 V·s^{-1} is shown in Fig.4.

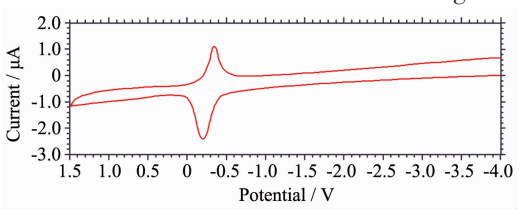


Fig.4　Cyclic voltammetry of 0.3 mmol·L^{-1} cobalt (Ⅱ) complex in 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solution, at a scan rate: 0.1 V·s^{-1}

The complex at 0. 1 V·s^{-1} has a anodic peak at –0.210 V and an cathodic peak at –0.351 V, corresponding to the electrochemical process of Cu^{2+}/Cu^{+}[10]. The separation of the cathodic and anodic peak potential, ΔE =0.141 V, indicates that the electrochemical behavior of the title complex on the glass carbon electrode is an quasi-reversible process.

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