第4期 2003年4月 无机化学学报 CHINESE JOURNAL OF INORGANIC CHEMISTRY Vol. 19, No. 4 Apr., 2003

研究简报

高氯酸二水邻菲咯啉合铜配合物的合成和晶体结构

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关键词: 铜(I)配合物 邻菲咯啉配体 平面正方形几何 氢键网络 分子空穴
分类号: O614.121

Synthesis and Crystal Structure of $Cu(phen)(H_2O)_2 \cdot ClO_4$(phen = phenanthroline)

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Crystal structure of the title compound, $Cu(phen)(H_2O)_2 \cdot ClO_4$(phen = 1, 10-phenanthroline), was determined by X-ray crystallography. It crystallizes in the monoclinic system, space group $C2/c$ with lattice parameters $a = 1.49071(4)$ nm, $b = 1.38594(4)$ nm, $c = 0.70292(1)$ nm, $\beta = 108.509(1)°$ and $Z = 4$; The Cu(I) ion is chelated by a phen ligand and two aqua ligands in cis arrangement and assumes a $C2$ symmetric square-planar geometry with the CuN_2O_2 core. Eight $Cu(phen)(H_2O)_2 \cdot ClO_4$ molecules are interconnected by strong hydrogen bonds between coordinated water molecules and uncoordinated perchlorate anions to form a molecular scale cavities along c axis. The bond distances of Cu-N and Cu-O are 0.2003(4) nm and 0.1973(3) nm, respectively. CCDC: 197600.

Keywords: copper (I) complexes phenanthroline-N^1, N^{10} ligands square-planar geometry hydrogen bond networks molecular scale cavity

0 Introduction

Molecular recognition between host and guest molecules, inclusion phenomena and non-covalent molecular interaction are fundamental problems in the frontiers of both organic and inorganic chemistry[1]. Inclusion compounds with the special cavities, windows and channels have received increasing attention in recent years due in part to them being useful as molecular sieves and in catalysts[2]. The inclusion ability of the cavity structures could be utilized in separation of guest molecules from their isomeric mixtures, and also in the heterogeneous catalysis field[3]. To the best of our knowledge, strong (O – H···O and N – H···O hydrogen bonds), weak (van der Waals, $\pi\cdots\pi$ stacking) and potentially weak (C – H···Y hydrogen bonds, Y = O, N) intermolecular interactions generally play an im-

收稿日期:2002-11-15。收修改稿日期:2002-12-29。
山东省自然科学基金资助项目(No. Y2002B06),山东省教育厅重点项目(No. J01C05)。
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portant role during the process of molecular recognition and self-assembly of molecules[4]. We now report a novel structure of the title compound with molecular scale cavity formed by strong hydrogen interactions.

1 Experimental

All chemicals were of analytical reagent grade and used directly without further purification.

To a warm solution of 1, 10-phenanthroline (2.70 g, 15mmol) in H_2O(50mL) was added with stirring $CuClO_4$(2.14g, 15mmol) and refluxed for 2h. The solution was filtered and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, the light blue crystalline solid appeared several weeks later and was separated by filtration. The C, H and N contents were determined by elemental analysis (Anal. calcd for $C_{12}H_8ClCuN_2O_6$, C 38.42, H 2.15, N 7.47%. Found: C 38.36, H 2.09, N 7.41%).

A summary of the key crystallographic information is given in Table 1. The selected crystal of Cu(phen)$(H_2O)_2 \cdot ClO_4$ was mounted on an SMART CCD diffractometer. Reflection data were measured at 293K, using graphite monochromated Mo $K\alpha$ ($\lambda = 0.071073$ nm) radiation ω-2θ scan mode. Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction using SADABS[5] ($T_{min} = 0.6914$, $T_{max} = 0.8120$) program.

The structure was solved by direct methods using SHELXS-97[6]. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. Hydrogen atoms were located from the difference Fourier map and added to the structure calculations, but their positions were not refined. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave $R = 0.0608$, $R_w = 0.1590$ for 1269 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.1043P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography[7]. The final position parameters of non-hydrogen atoms are given in Table 2.

Table 1 Crystal Data and Structure Refinement for the Title Compound

empirical formula	$C_{12}H_8ClCuN_2O_6$
formula weight	375.2
temperature/K	293(2)
wavelength/nm	0.071073
crystal system, space group	monoclinic, $C2/c$
a/nm	1.49071(4)
b/nm	1.38594(4)
c/nm	0.70292(1)
β/(°)	108.509(1)
volume/nm^3	1.37714(6)
Z	4
calculated density/(Mg · m^{-3})	1.810
absorption coefficient/mm^{-1}	1.811
F(000)	752
crystal size/mm^3	0.22 × 0.18 × 0.12
theta range for data collection/(°)	2.06 to 28.28
limiting indices	$-16 \leqslant h \leqslant 19$, $-15 \leqslant k \leqslant 18$, $-9 \leqslant l \leqslant 8$
reflections collected/unique	4815/1697 [R(int) = 0.1223]
completeness to θ = 28.28	98.4%
absorption correction	empirical
max. and min. transmission	0.8120 and 0.6914
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1697/0/101
goodness-of-fit on F^2	1.032
final R indices [$I > 2\theta(I)$]	$R_1 = 0.0608$, w$R_2 = 0.1590$
R indices (all data)	$R_1 = 0.0935$, w$R_2 = 0.1905$
largest diff. peak and hole/(e · Å^{-3})	0.920 and −1.951

CCDC: 197600.

2 Results and Discussion

The structure of the title compound consists of [Cu(phen)$(H_2O)_2$] cations and ClO_4^- anions. An ORTEP drawing of the structure around the copper (I) with the atom numbering scheme is shown in Fig. 1. Selected bond lengths, angles and hydrogen bond distances are presented in Tables 3 and 4.

In the title compound, each copper (I) atom is coordinated by two nitrogen atoms of phenanthroline ligand, and two oxygen atoms of water molecules. The coordination geometry of the copper (I) atom is slightly distorted square-planar. Because of the phenanthroline chelate, N-Cu-N bond angle is 81.5(2)°, which is significantly less than 90°. The O-Cu-O is 93.2(2)°.

Table 2　Atomic Coordinates(× 10⁴) and Equivalent Isotropic Displacement Parameters (nm² × 10⁵)

	x	y	z	Ueq		x	y	z	Ueq
Cu(1)	5000	2994(1)	2500	20(1)	Cl(1)	5000	3608(1)	-2500	22(1)
O(1)	4030(2)	3972(2)	2444(5)	24(1)	O(2)	4619(3)	3017(2)	-1194(5)	30(1)
O(3)	4234(2)	4242(2)	-3765(5)	25(1)	N(1)	4106(3)	1899(3)	2372(6)	21(1)
C(1)	4503(3)	1019(3)	2421(6)	18(1)	C(2)	3190(3)	1926(4)	2270(8)	30(1)
C(3)	2667(4)	1088(5)	2217(9)	42(1)	C(4)	3073(4)	207(4)	2264(8)	35(1)
C(5)	4039(4)	146(4)	2377(7)	28(1)	C(6)	4531(4)	-738(4)	2437(8)	36(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3　Bond Lengths(nm) and Angles(°) for the Title Compound

Cu(1)-O(1)	0.1973(3)	Cu(1)-N(1)	0.2003(4)	Cl(1)-O(2)	0.1472(3)
Cl(1)-O(3)	0.1491(3)	N(1)-C(2)	0.1345(6)	N(1)-C(1)	0.1351(6)
C(1)-C(5)	0.1389(6)	C(2)-C(3)	0.1393(8)		
O(1)-Cu(1)-O(1)ᵃ	93.2(2)	O(1)-Cu(1)-N(1)	92.7(1)	O(1)a-Cu(1)-N(1)	173.9(1)
N(1)-Cu(1)-N(1)ᵃ	181.5(2)	O(2)b-Cl(1)-O(2)	112.4(3)	O(3)-Cl(1)-O(3)ᵇ	107.8(3)
O(2)b-Cl(1)-O(3)	109.3(2)	O(2)-Cl(1)-O(3)	109.0(2)		

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

Table 4　Hydrogen Bond Distances(nm) of the Title Compound

D	H	A	symm	D···A
O(1w)	H(1wa)	O(3)	$x, 1-y, 1+z$	0.26652
O(1w)	H(1wa)	O(3)	$x, y, 1/2+z$	0.26117
C(2)	H(2A)	O(1)		0.30865
C(3)	H(3A)	O(3)	$1/2-x, 1/2-y, -z$	0.33732
C(6)	H(6A)	O(2)	$x, -y, 1/2+z$	0.32919

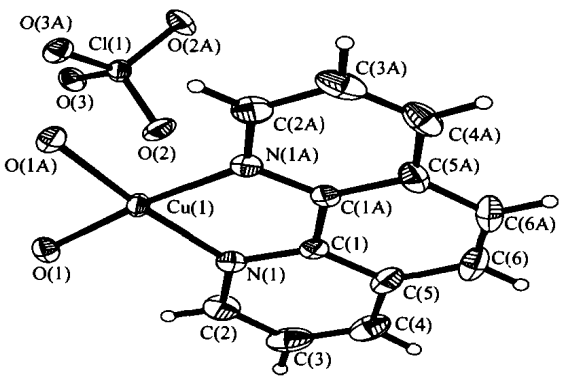

Fig. 1　Molecular structure for $Cu(phen)(H_2O)_2 \cdot ClO_4$ with the atomic numbering scheme

The two diagonal N-Cu-O angles of 173.9(2)° are less than 180°. The bond distance of Cu-N is 0.2003(4)nm which is slightly different with those observed in the tetrahedral structures with an average of 0.2082(6) nm[8] and a range of 0.1991(2) ~ 0.2105(2) nm[9]. The bond distance of Cu-O [0.1973(3) nm] is shorter than the values [0.2173(5) nm] found in $[Cu_2(dppm)_2(Py)_2(NO_3)](NO_3)\,CH_3OH$ (dppm = $Ph_2PCH_2PPh_2$, Py = pyridine)[10].

The three aromatic ring systems in each phen are coplanar under the experimental error. Because all two water molecules coordinated to copper(I) atom are hydrogen bonded to uncoordinated perchlorate anions acting as a bridges to connect adjacent molecules, they form a molecular scale cavities along *c* axis. Fig. 2 illustrates a prism cavity in the structure. The average (O···O) distance is 0.264nm, which is shorter than that of ice (0.276nm) and pure water (0.283nm)[11]. The cationic $[Cu(phen)(H_2O)_2]^{2+}$ square network is parallel to the ab plane and each network is made up of layers stacked upon each other. The layers interaction

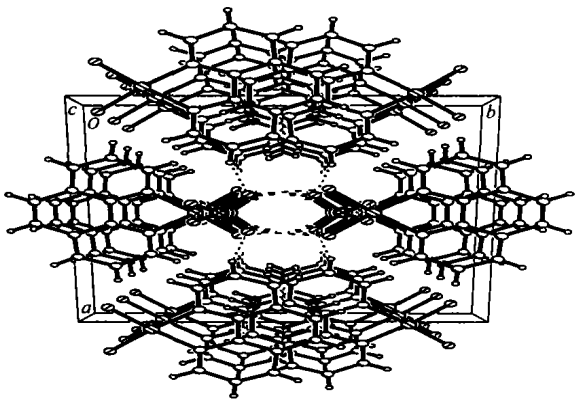

Fig. 2　Packing diagram of the unit cell of $Cu(phen)(H_2O)_2 \cdot ClO_4$ showing the hydrogen bond network

is due to π-π stacking interactions between the molecules in the crystal lattice. The center-to-center distance between two adjacent phen rings is 3.537Å. It is obvious that they form the stronger π-π stacking interaction[12]. The crystal packing is stabilized by extensive hydrogen bonding. The phen molecule is connected with ClO_4^- anions by intermolecular hydrogen bonding, the donor and acceptor distances are C(3)···O(3) 0.33732(1) nm [symmetry code: $1/2-x$, $1/2-y$, $-z$] and C(6)···O(2) 0.32919(1)nm [symmetry code: x, $-y$, $1/2+z$], respectively. All above hydrogen bonds in this structure connect $[Cu(phen)(H_2O)_2]^{2+}$ and perchlorate anion formed three dimensional hydrogen bonds network which stabilized the crystal structure.

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