研究简报

配合物$[Cu_2(phen)_2](SiW_{12}O_{40})(H_2O)_7$的合成、晶体结构及电化学分析

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Synthesis, Crystal Structure and Electrochemical Properties of Complex $[Cu_2(phen)_2](SiW_{12}O_{40})(H_2O)_7$

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Abstract: The title complex has been synthesized by the reaction of silicotungstic acid, 1,10-phenanthroline (phen) monohydrate and cupric acetate. The crystal structure belongs to triclinic system, space group $P\bar{1}$ with a=1.158 46(15) nm, b=1.658 8(2) nm, c=1.664 4(2) nm, α=82.090(2)°, β=76.001(2)°, γ=86.531(2)°, and V=3.072 6(7) nm^3, D_c=3.887 g·cm^{-3}, Z=2, F(000)=3 196. R_1=0.086 7, wR_2=0.185 8. The structure shows that the copper(Ⅱ) atom is coordinated with two nitrogen atoms from the one phen and three oxgygen atoms from three water, forming a distorted square-pyramid configuration The cyclic voltametric behavior of the complex is also reported. CCDC: 298807.

Key words: copper(Ⅱ) complex; silicotungstic acid; crystal structure; electrochemical property

0 Introduction

Since silicotungstic acid was synthesized and characterized, the polyacid compounds have been widely studied[1-4]. In recent years, the major use of the polyacid compounds have been paid extensive attention in the field of catalysis, biology, materials science, pharmaceutical chemistry and electronics, besides in analysis reagent in the past. It has become an important branch in the field of the inorganic chemistry[5-7]. The unsaturated heteropolyacid-radical ion possesses special coordination properties as a kind of huge inorganic ligand. It is widely used in organic synthesis reaction, because this kind of complex has

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curious structure, predominant physical chemistry properties and act as oxidation-type and double functional-type catalyst[8~10]. In the present, the study of the compound coordinated between heteropolyacid and metal is a hot topic in present[11~18]. It is rarely reported that compound is consist of heteropolyacid anion and other ligand[19,20]. In this paper, we report the synthesis, structure and spectroscopic properties of the copper(Ⅱ) complex [$Cu_2(phen)_2$]($SiW_{12}O_{40}$)(H_2O)$_7$. The cyclic voltametric behavior of the compound is also investigated.

1 Experimental

1.1 Reagent and apparatus

Phen (A.R.), silicotungstic acid was synthesized according to the literature[4], Cupric acetate and other are analysis pure. The IR spectra were recorded on Shimadzu FTIR-8700 spectrophotometer using KBr discs. The crystal structure was recorded on Bruker SMART 1000 CCD. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer. Melting point was recorded on an XT_4 binocular stereoscopic micro melting point instrument and uncorrected. The electron transfer behavior of the complex was examined using cyclic voltammogram on a LK98 electrochemical analysis system.

1.2 Synthesis of the complex

Cupric acetate (2 mmol) and silicotungstic acid (1 mmol) was added into a mixture of heating alcohol-water. The mixture was stirred and heated by dropping slowly (4 mmol) phen in 5 mL alcohol and then the reaction continued for 5.0~6.0 hours at 50~60 ℃. The product was collected by filtration and evaporated at room temperature. The deep-green crystal that fit to X-ray structure analysis was graining a week later. The complex elemental analyses calcd (%) for $C_{24}H_{42}Cu_2N_4O_{53}SiW_{12}$, C,8.01; H 1.18, N 15.57; Found (%): C 7.99, H 1.20, N 15.53. melting point: 266.5~268.0 ℃. IR (KBr): 3 412(s) cm^{-1}, 1 611(m) cm^{-1}, 1 427(m) cm^{-1}, 976(s) cm^{-1}, 922(vs) cm^{-1}, 795(vs) cm^{-1}, 719(m) cm^{-1}, 536(w) cm^{-1}, 469(w) cm^{-1}.

1.3 X-ray structure determination

A deep-green single crystal of the title complex with dimensions of 0.22 mm × 0.18 mm × 0.12 mm was selected and mounted on the Bruker SMART 1000 CCD for X-ray diffraction studies. The data collection was performed with Mo $K\alpha$ radiation (λ = 0.071 073 nm). A total of 12 306 reflections were collected in the range of $1.27° \leqslant \theta \leqslant 26.39°$ at 293(2) temperature, in which 8 796 with $I>2\sigma(I)$ were considered as observed and used in the structural solution and refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were either put in calculated position or located from difference electron density maps, and were treated as riding mode with isotropic displacement parameters. Crystallographic data are summarized in Table 1.

CCDC: 298807.

Table 1 Crystallographic data for the complex

Empirical formula	$C_{24}H_{42}Cu_2N_4O_{53}SiW_{12}$	γ / (°)	86.531(2)
Formula weight	3 595.99	V / nm^3	3.072 6(7)
Color / habit	Green / square	D_c / ($g \cdot cm^{-3}$)	3.887
Size / mm	0.22 × 0.18 × 0.12	Z	2
θ range for data collection / (°)	1.27 to 26.39	F(000)	3 196
Crystal system	Triclinic	μ(Mo $K\alpha$) / cm^{-1}	23.171
Space group	$P\bar{1}$	Reflections collections	12 306
a / nm	1.158 46(15)	Independent reflections	12 306 (R_{int}=0.024)
b / nm	1.658 8(2)	R_1, wR_2 [($I>2\sigma(I)$]	0.063 9, 0.167 0
c / nm	1.664 4(2)	R_1, wR_2 (all data)	0.086 7, 0.185 8
α / (°)	82.090(2)	Largest difference peak and hole / ($e \cdot nm^{-3}$)	3 937, −2 656
β / (°)	76.001(2)		

2 Results and discussion

2.1 Infrared absorption spectrum

The infrared spectrum of the complex shows one strong and wide band at 3 412 cm^{-1}, which is most likely ascribed to the hydroxide of the water molecule. Compared to the characteristic absorption bands of the free ligand of the silicotungstic acid at 1 611 cm^{-1}, 980 cm^{-1}, 926 cm^{-1}, 777 cm^{-1}, 540 cm^{-1}, the absorption bands at 1 611 cm^{-1}, 976 cm^{-1}, 922 cm^{-1}, 795 cm^{-1}, 536 cm^{-1} are not obviously moved. It shows that the complex anion of the silicotungstic acid ion acts as charge balance in the molecule. The bands at 1 427 cm^{-1} and 719 cm^{-1} can be attributed to the characteristic absorption bands of the coordinated phen.

2.2 Crystal structure

The crystal structure and packing diagram of the complex is shown in Fig.1 and Fig.2 respectively. Selected bond lengths, bond angles and hydrogen bond distances are presented in Tables 2 and 3 respectively.

The title compound consists of two center copper ions, two coordination phens, six coordination water molecules, one silicotungstic acid and seven free water molecules. Each copper(Ⅱ) ion displays a distorted square-pyramid coordination geometry with two nitrogen atoms of one phen and three oxygen atoms of three water molecules. The bond angles N(2)-Cu(1)-N(1), O(42)-Cu(1)-N(1), O(42)-Cu(1)-O(43), and O(43)-Cu(1)-N(2) around the center copper atom are 81.7(7)°, 90.3(6)°, 93.3(6)°, (93.9(7)°) respectively. The total angles is 359.2°, which shows that oxygen atom O(41) from water molecule occupies the axial position and the basal plane consists of N(1), N(2), O(42), O(43). In the molecular structure, The bond lengths Cu(1)-N(1), Cu(1)-N(2) between the nitrogen atoms from the phen and copper ion are 0.201 4(16) nm; 0.197 8(17) nm, which the average length is 0.199 6 nm. The bond lengths Cu(1)-O(41), Cu(1)-O(42) and Cu(1)-O(43) between the oxygen atoms from the water and copper ion are 0.225 3(17) nm, 0.200 2(15) nm and 0.198 6(14) nm respectively, which average length is 0.208 0 nm. The length of the former is shorter than the latter. It is noteworthy that the coordination molecular of the nitrogen of the phen is stronger than that of the oxygen

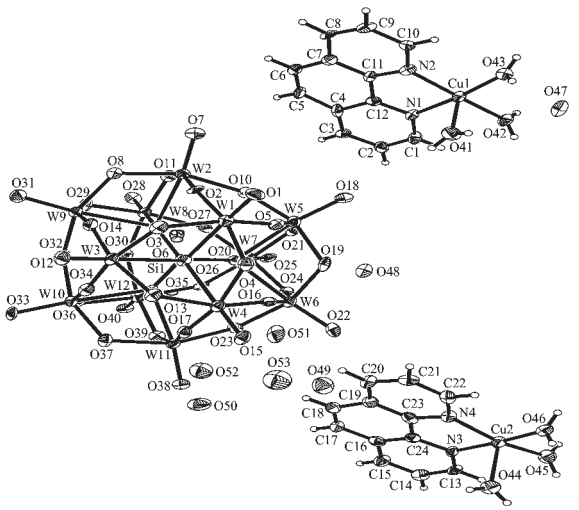

Fig.1 Crystal structure of the title complex

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

Si(1)-O(9)	0.160 5(12)	Si(1)-O(6)	0.161 5(12)	Si(1)-O(35)	0.162 3(14)
Si(1)-O(20)	0.162 5(12)	Cu(1)-N(2)	0.197 8(17)	Cu(1)-O(43)	0.198 6(14)
Cu(1)-O(42)	0.200 2(15)	Cu(1)-N(1)	0.201 4(16)	Cu(1)-O(41)	0.225 3(17)
Cu(2)-N(4)	0.196 7(17)	Cu(2)-O(46)	0.198 1(16)	Cu(2)-N(3)	0.198 3(17)
Cu(2)-O(45)	0.199 3(18)	Cu(2)-O(44)	0.220 9(16)		
N(2)-Cu(1)-O(43)	93.9(7)	N(2)-Cu(1)-O(42)	166.4(6)	O(43)-Cu(1)-O(42)	93.3(6)
N(2)-Cu(1)-N(1)	81.7(7)	O(43)-Cu(1)-N(1)	174.6(7)	O(42)-Cu(1)-N(1)	90.3(6)
N(2)-Cu(1)-O(41)	99.7(7)	O(43)-Cu(1)-O(41)	89.9(6)	O(42)-Cu(1)-O(41)	91.9(7)
N(1)-Cu(1)-O(41)	94.1(7)	N(4)-Cu(2)-O(46)	94.4(7)	N(4)-Cu(2)-N(3)	82.3(7)
O(46)-Cu(2)-N(3)	176.6(7)	N(4)-Cu(2)-O(45)	161.1(7)	O(46)-Cu(2)-O(45)	91.1(7)
N(3)-Cu(2)-O(45)	92.0(7)	N(4)-Cu(2)-O(44)	103.3(7)	O(46)-Cu(2)-O(44)	89.9(7)
N(3)-Cu(2)-O(44)	91.2(6)	O(45)-Cu(2)-O(44)	94.8(7)	N(4)-Cu(2)-H(44B)	103.8

Table 3　Hydrogen bonds

D–H···A	D-H	*d*(H-A) / nm	*d*(D···A) / nm	∠DHA / (°)
O(41)–H(41A)···O(52)	0.0849 9	0.228 43	0.274 46	114.21
O(41)–H(41B)···O(50)	0.085 00	0.213 85	0.292 97	154.72
O(42)–H(42A)···O(33)	0.085 00	0.214 71	0.282 25	136.20
O(42)–H(42B)···O(49)	0.085 02	0.186 51	0.270 99	172.25
O(43)–H(43A)···O(47)	0.085 00	0.202 37	0.276 17	144.73
O(43)–H(43B)···O(31)	0.085 01	0.218 91	0.286 68	136.58
O(44)–H(44A)···O(50)	0.085 00	0.211 43	0.278 66	135.69
O(45)–H(44B)···O(53)	0.085 00	0.191 36	0.271 50	156.65
O(45)–H(45B)···O(48)	0.085 00	0.189 79	0.269 74	156.20
O(46)–H(46A)···O(51)	0.084 99	0.217 76	0.298 80	159.37
O(46)–H(46B)···O(25)	0.085 00	0.244 16	0.290 82	115.30
O(46)–H(46B)···O(28)	0.085 00	0.222 99	0.285 97	130.92

Symmetry codes, a: 1–*x*, 2–*y*, 1–z; b: 1–*x*, 1–*y*, 1–*z*; c: –1+*x*, *y*, *z*; d: 2–*x*, 2–*y*, 1–*z*; e: 2–*x*, 1–*y*, 1–*z*; f: –1+*x*, 1–*y*, 1–*z*; g: –1+*x*, *y*, 1+*z*; h: *x*, y, 1+*z*; i: –*x*, 1–*y*, 1–*z*; j: –1+*x*, –1+*y*, *z*; k: *x*, –1+*y*, *z*.

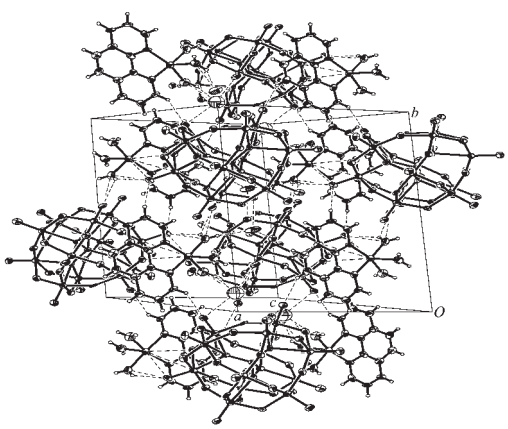

Fig.2　Packing diagram of the title complex

of the water. The bond lengths Cu(1)-O(41), Cu(1)-O(42) and Cu(1)-O(43) that coordinated oxygen atoms of the water are 0.225 3(17) nm, 0.200 2(15) nm and 0.198 6(14) nm respectively. The length of the former is longer than the latter. It indicates that O(41) is located at the top of the square pyramid. The bond angles O(42)-Cu(1)-O(41), O(43)-Cu(1)-O(41), N(1)-Cu(1)-O(41) and N(2)-Cu(1)-O(41) between the top atom and the plant atoms are 91.9(7)°, 89.9(6)°, 94.1(7)° and 99.7(7)° respectively. The initial three angles are close to 90°, and the remaining angle is deviated from 90°. The bond angles N(1)-Cu(1)-O(43), and N(2)-Cu(1)-O(42) are 174.6(7)° and 166.4(6)°, which the former close 180° and the latter depart from it. It is clearly that the complex of the copper is distorted square-pyramid configuration[21~23].

The copper ion is located in the center of the molecular structure, and O(41) is situated at the top. N(1), N(2), O(42) and O(43) are almost coplanar at the bottom. The complex anion $[SiW_{12}O_{40}]^{4-}$ is a kind of heteropoly complex. It consists of four sets of three-metal subgroups (W_3O_{13}), which around heteroatom (Si) forming tetrahedral cage structure[24,25].

As depicted in Fig.2 the neighboring chains are linked by hydrogen bonds between the coordinated oxygen[O(41), O(44)] of copper and oxygen [O(50), O(52)] of free water. The lengths and angles of them are 0.228 43 nm, 0.216 89 nm and 0.211 43 nm, 114.21°, 154.72° and 135.69°. The rare crossing hydrogen bonds has been formed among the coordinated oxygen O(46), the terminal group oxygen of the silicotungstic acid and the oxygen from free water molecule. The lengths and angles of them are 0.218 71 nm, 0.244 23 nm, 0.233 5 nm, 158.86°, 115.41°, 131.07°。In the packing of the cell, the center-to-center distance between two adjacent phen rings is 0.342 3 nm. It is obvious that they form the stronger π-π stacking interaction[26]. The crystal packing is stabilized by extensive hydrogen bonding. All those hydrogen bonds in this structure connect phen and $[SiW_{12}O_{40}]^{4-}$ anion formed a three-dimension framework with channels in which the lattice water molecules are located.

2.3 Cyclic voltammogram

The cyclic voltammogram of the title complex was obtained in methanol (2.5×10^{-6} mol·L^{-1}) using a conventional three-electrode system at 25 ℃. The glass-carbon working electrode was in the form of a disc and used in a stationary mode, the auxiliary electrode was a platinum plate, and the reference electrode was a saturated calomel electrode (SEC). The cyclic voltammogram were reported with 100 V·s^{-1} scan rate, at range from −0.400~1.000 V, and HAc-NaAc (pH= 4.74) as buffer solution. From the voltammogram curves, it shows only one pair of oxidation-reduction peaks corresponding to the oxidation-reduction couple of copper(Ⅱ)/copper(Ⅰ). E_{pa}=0.190 V, E_{pc}=0.559 V. The average formal potential [$E_{1/2}$=(E_{pa} + E_{pc})/2] is 0.374 5 V. The peak potential difference is 0.369 V and the proportional of the peak current is i_{pc}/i_{pa}=1.73, which exhibiting a quasi-reversible electrode process.

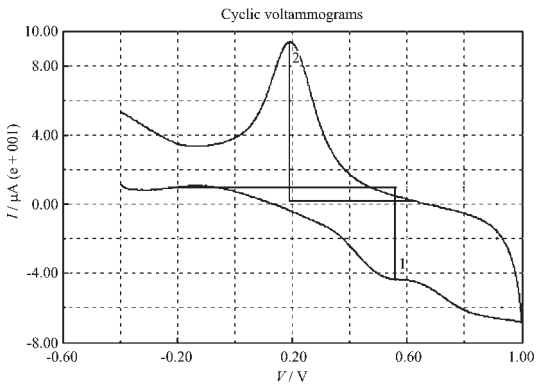

Fig.3 Cyclic voltammograms of the title complex

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