Asian Journal of Chemistry Vol. 19, No. 3 (2007), 1956-1962

Synthesis, Characterization and Electrochemical Behaviour of One-dimensional Cu(II) Polymer $[Cu(C_{16}H_{14}N_2O_3)\cdot H_2O]_n$

XUE-MEI LI, WEI WANG, XIANG-TAO MENG and SHU-SHENG ZHANG*
College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P.R. China
E-mail: shushang@126.com

A new complex of catena-poly[µ-N-salicylidene-*p*-methyl-phenoxyacetylhydrazino-κ^4 O,N,O':N'-copper(II)] was synthesized and characterized by X-ray crystallography and thermal analysis methods. The compound crystallizes in the tetragonal system, space group P-42_1c, with cell dimensions of $a = b$ = 1.9866(3) nm, c = 0.9097(2) nm, V = 3.590(1) nm^3, and Z = 8. The title compound consists of [Cu(sal-mpah)] coordination units (sal-mpah = salicylidene-*p*-methyl-phenoxyacetylhydrazino) and free water molecules. The Cu(II) ion adopts a distorted square planar geometry. The sal-mpah ligand acts as a μ_4-bridge connecting Cu atoms into chains along the *c* direction. The electrochemical experimental results indicate that $[Cu(C_{16}H_{14}N_2O_3)\cdot H_2O]_n$ can bind to DNA by intercalative binding.

Key Words: Copper polymer, X-ray analysis, Electrochemical behaviour.

INTRODUCTION

In recent years, the crystal engineering of coordination polymers are of considerable interest due to their great potential applications in molecular magnetism[1], heterogeneous catalysis, molecular sieving and non-linear optics[2]. Schiff base polymers may exhibit a variety of interesting physical properties such as electronic[3], optoelectronic, nonlinear optical or liquid crystalline properties that make this kind of polymer particularly interesting in materials science[4]. Metal-complexes of Schiff base polymers have been described which exhibit a wide variety of properties such as luminescence or catalytic properties[5]. However, only a few studies have been reported concerning metal-containing LCPs[6]. Puértolas reported the copper(II) cross-linked polymeric materials with liquid crystalline properties[7]. It was reported that the metal coordination compound of Schiff base could inhibit tumour and bacteria growth by interacting with DNA[8-10]. In order to investigate the biological activities of Schiff base-metal complexes, the interaction between $[Cu(C_{16}H_{14}N_2O_3)\cdot H_2O]_n$ (Fig. 1) and DNA has been studied by cyclic voltammetry. The experimental results have proved that the complex could interact with DNA mainly by intercalative binding. This will bring further insight about the interaction mechanism between Cu(II)-polymer and DNA and is helpful for further research to design novel anti-tumor drugs and/or diagnosis disease.

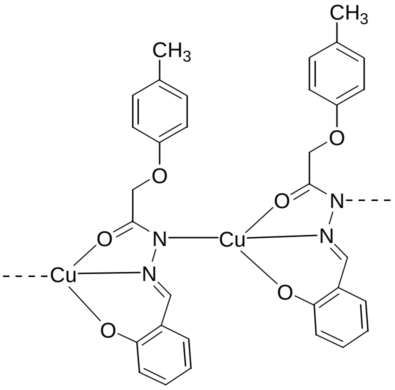

Fig. 1. Catena-poly[μ-N-salicylidene-*p*-methylphenoxyacetylhydrazino-κ^4 O,N,O':N'-copper(II)]

EXPERIMENTAL

CHI832 electrochemical analyzer was produced by Shanghai Chenhua Instrument Company of China; the three-electrode system was composed of a glassy carbon electrode (GCE) as working electrode, a Ag/AgCl as the reference electrode and a platinum electrode as auxiliary electrode.

Salmon sperm DNA was purchased from Shanghai Huashun Biologic Engineering Company. Its concentration was determined by the ultraviolet absorption at 260 nm ($\varepsilon = 6600$ L mol^{-1} cm^{-1}), used without further purification. $[Cu(C_{16}H_{14}N_2O_{.})\cdot H_2O]_n$ solution was prepared by dissolving Cu(II)-polymer in DMF. 0.2 mol L^{-1} BR, pH 2.3, was used as buffer solution. The other reagents were all analytical reagents prepared with doubly deionized water.

Synthesis: To a warm solution of 0.15 mol *p*-methyl phenoxyacetylhydrazine[11] and catalytic amount of acetic acid in EtOH, 0.15 mol salicylaldehyde was added dropwise and refluxed for 2 h with stirring. The precipitate collected was N'-[(2-hydroxyphenyl)methylidene]-2-(4-methyl)acetohydrazide. 0.10 mol schiff base and 0.10 mol $Cu(NO_3)_2$ were solved in ethanol, refluxed for 4 h. The darkbrown products were obtained by filtration and the filtrate was left to stand undisturbed. After 2 weeks, the single crystal suitable for X-ray analysis appeared.

Crystallographic study: A 0.30 × 0.26 × 0.22 mm crystal of the title compound was mounted on a CCD diffractometer. Reflection data were measured at 293 ± 2 K using MoKα radiation ($\lambda = 0.071073$ nm) with a graphite monochromator. The technique used was ω-scan with θ limits $4.93 < \theta < 24.97°$. Empirical absorption correction was carried out by using the

SADABS program[12]. 2503 reflections were measured, of which 1308 were unique [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by least squares on F^2 using the SHELXTL software package[13]. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The final conventional R = 0.0814, and *w*R = 0.1964 for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(Fo^2) + (0.1249P)^2 + 7.8359P]$ where $P = (Fo^2+2Fc^2)/3$. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography[14].

Electrochemical studies of the interaction between copper(II)-polymer and DNA: A certain volume of NCS solution was added to 5 mL of 0.2 mol L^{-1} BR buffer solution, whose pH was 2.3. Then 20 µL of 4.68 × 10^{-2} mol L^{-1} DNA were added to the solution followed by recording the figure. The potential scanning range is from -0.8 to 1.2 V. The scanning rate is 0.2 V s^{-1}; the sample interval is 0.001 V and the quiet time 2 s.

RESULTS AND DISCUSSION

X-ray crystal structure: The data on the single crystal structure of the coordination polymer, $[Cu(C_{16}H_{14}N_2O_3)\cdot H_2O]_n$, are as follows: molecular weight, 361.83; crystal system, tetragonal; space group, $P\text{-}42_{1c}$; *a* = *b* = 1.9866(3) nm, *c* = 0.9097(2) nm, V = 3.590(1) nm^3 and Z = 8.

Crystal data and structure refinement for the title compound are shown in Table-1. The selected data on the bond lengths and bond angles of the single crystal are listed in Table-2. A view of the title compound, showing the displacement ellipsoids and the atomic numbering, is given in Figs. 1 and 2 shows a perspective view of the crystal packing in the unit cell for the complex.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT PARAMETERS FOR THE TITLE COMPOUND

Formula	$C_{16}H_{14}CuN_2O_3.H_2O$	Crystal size (mm)	0.30 × 0.26 × 0.22
Formula weight	361.83	Temperature (K)	293(2)
Color/shape	Brown/block	θ ranges (°)	$4.93 < \theta < 24.97$
Crystal system	tetragonal	h/k/l	-22.0/-23.0/-10.0
Space group	$P\text{-}42_{1c}$	Reflections collected	2503
Cell parameters (nm)	a = b = 1.9866(3) c = 0.9097(2)	Independent reflections	1308
V (nm^3)	3.590(1)	Absorption correction	empirical
Z	8	R indices [$I > 2\sigma(I)$]	0.0814
$D_{calcd.}$ ($g\ cm^{-3}$)	1.339	wR	0.1964
μ (mm^{-1})	1.235		

TABLE-2
SELECTED BOND DISTANCES (nm) AND BOND ANGLES (°) OF THE TITLE COMPOUND

Cu1-O3	0.186(2)	O1-C8	0.143(3)
Cu1-N2	0.192(1)	O2-C9	0.132(2)
Cu1-O2	0.198(2)	O2-Cu1^i	0.198(2)
Cu1-N1	0.198(1)	O3-C16	0.134(3)
O1-C5	0.136(3)	O3-Cu1^i	0.186(2)
N1-N2	0.133(3)	N1-C9	0.141(3)
O3-Cu1-N2	92.4(8)	O3-Cu1-N1	93.9(7)
O3-Cu1-O2	174.1(5)	N2-Cu1-N1	166.1(11)
N2-Cu1-O2	81.7(8)	O2-Cu1-N1	91.8(6)

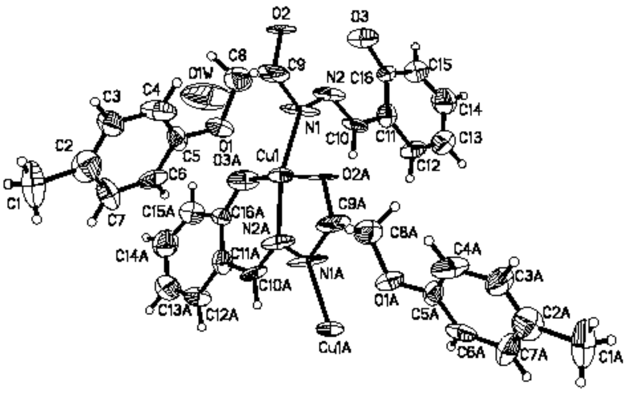

Fig. 1. Molecular structure of the title compound with the atomic numbering scheme

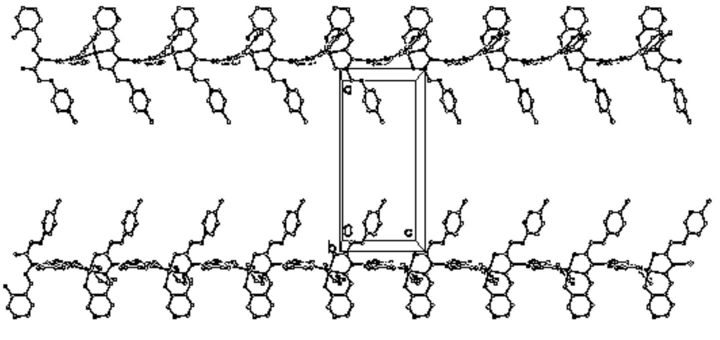

Fig. 2. Packing diagram of the unit cell of the title compound

The title compound consists of [Cu(sal-mpah)] coordination units (sal-mpah = salicylidene-*p*-methyl-phenoxyacetylhydrazino) and free water molecules. The Cu(II) ion adopts a distorted square planar geometry, defined by an O,N,O'-tridentate N-salicylidene-*p*-methyl-phenoxy- acetylhydrazine dianion and the N atom from the adjacent sal-mpah ligand in the basal plane. Thus, [Cu(sal-mpah)] form infinite one-dimensional polymeric molecules in the [001] direction. The Cu1-O3 and Cu1-N2 bond lengths are 0.186(2) and 0.192(1) nm, respectively, which are shorter than those corresponding values of 0.1921(2) and 0.1950(3) nm in a related salicylidene-β-alaninato Cu complex[15]. The Cu1-O2 bond length [0.198(2) nm] is longer than Cu-O1 bond [0.1965(2) nm] in salicylidene-β-alaninato Cu complex. The sum of the bond angles around the Cu atom is 359.8(8)°, indicating the four basal atoms are slightly out of planarity. For the five and six-membered chelate rings A and B, the Cremer-Pople puckering parameters[16] are $Q = 0.012(2)$ nm, $\phi_2 = 159(1)°$ and $Q = 0.013(1)$ nm, $\theta = 93.1(1)°$, $\phi = 182(1)°$, respectively. The dihedral angle between the mean planes of these two rings is 6.5(1)°. The two benzene rings make angle of 52.9(4)° each other.

The sal-mpah ligands act as a μ_4-bridge connecting Cu atoms into chains along the c direction. The ligands are parallel alternatively, and the two neighboring sal-mpah groups are crossed to each other. The packing is further stabilized by C-H···π intermolecular interactions.

Electrochemical studies of the interaction between Cu(II)-polymer and DNA: The cyclic voltammograms of $[Cu(C_{16}H_{14}N_2O_{.})\cdot H_2O]_n$ before and after adding DNA were recorded at the glassy carbon electrode in 0.2 mol L^{-1} BR buffer solution as shown in Fig. 3. The scan rate is 0.2 V s^{-1}. The curve 1 is the cyclic voltammogram of (I) solution in the absence of DNA, in which two anodic peaks were observed, the anodic peak potentials (E_{pa}) are 0.900 V and -0.006 V, respectively. The curve 2 is the cyclic voltammogram of (I) in the presence of DNA, the peak current of (I) decreased with the addition of DNA. No new oxidation-reduction peaks appear in the presence of DNA. So (I) interacting with DNA forms electrochemically non-active complex, which results in a decrease of the equilibrium concentration of (I) as well as the peak current. According to Fig. 3 and the molecular structure of (I), the initial conclusion can be drawn that $[Cu(C_{16}H_{14}N_2O_3)H_2O]_n$ can bind to DNA by intercalative binding.

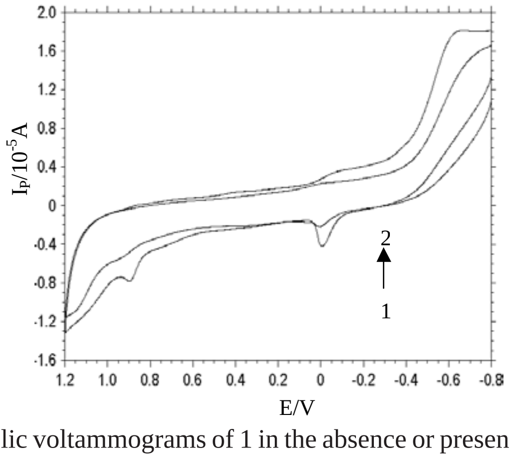

Fig. 3. Cyclic voltammograms of 1 in the absence or presence of dsDNA C_{NCS} : 5.68 ×10^{-4} mol L^{-1}; C_{DNA}: (1) 0; (2) 1.87 × 10^{-4} mol L^{-1}

Thermal analysis: Thermal analysis curves of the title compound are shown in Fig. 4. Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis show that the thermal decomposition of the title compound includes two transitions. There are two peaks corresponding to exothermal processes- that is, a weak peak at 197.0 correcponding to removal of Cu atom and a strong peak at 288.1 due to loss of the two aromatic moieties.

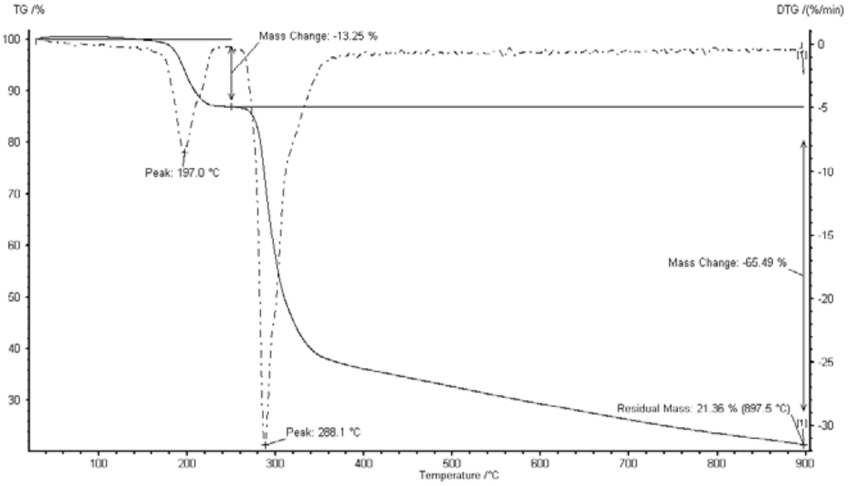

Fig. 4. Thermal analysis curves of the title compound

ACKNOWLEDGEMENTS

This work is supported by the Program for New Century Excellent Talents in University (No. NCET-04-0649) and the National Natural Science Foundation of China (No 20475030).

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(*Received*: 5 April 2006; *Accepted*: 17 October 2006) AJC-5206