

## КРАТКИЕ СООБЩЕНИЯ

UDC 548.737;541.572.7

NOVEL COPPER(II) COMPLEX WITH UNUSUAL  $\pi$ -STACKING STRUCTURE,  $[\text{Cu}(\text{SSC})\text{Cl}]_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$   
(SSC = SALICYLALDEHYDE SEMICARBAZONE ANION)© 2008 J.-L. Wang<sup>1</sup>, B. Liu<sup>1</sup>, B.-S. Yang<sup>1\*</sup>, S.-P. Huang<sup>2</sup><sup>1</sup>*Institute of Molecular Science, Chemical Biology and Molecular Engineering Laboratory of Education Ministry, Shanxi University, Taiyuan, 030006, China*<sup>2</sup>*Institute of Modern Chemistry, Shanxi University, Taiyuan, 030006, China*

Received 3 September, 2007

The crystal structure of  $[\text{Cu}^{\text{II}}(\text{SSC})\text{Cl}]_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  (SSC = salicylaldehyde semicarbazone anion) was determined by single crystal X-ray diffraction method at 293 K. Crystal data for  $\text{Cu}_2\text{C}_{17}\text{H}_{24}\text{Cl}_2\text{N}_6\text{O}_7$ :  $a = 10.272(2)$ ,  $b = 10.297(2)$ ,  $c = 11.462(2)$  Å,  $\alpha = 82.860(3)^\circ$ ,  $\beta = 78.384(3)^\circ$ ,  $\gamma = 81.330(2)^\circ$ , triclinic, space group  $P\bar{1}$ ,  $Z = 2$ ,  $d_{\text{calc}} = 1.769$  g/cm<sup>3</sup>,  $R_1 = 0.038$ . One N and two O atoms of  $\text{SSC}^-$  occupy three coordination sites around Cu(II). The fourth site is occupied by Cl<sup>-</sup> to yield distorted square-planar environment. Two molecules of the complex form a planar dimer through intermolecular N—H $\cdots$ O hydrogen bonds. The most striking feature of the crystal structure is the packing of the planar dimers within the crystal. The interplanar distances between adjacent two layers are 3.280 Å, indicative of strong  $\pi$ — $\pi$  non-covalent interactions. Molecules of solvent methanol and water are included in the crystal as additional components.

**Key words:** HSSC, copper(II), complex, crystal structure,  $\pi$ — $\pi$  interactions, weak interactions.

Aromatic—aromatic or  $\pi$ — $\pi$  interactions are important non-covalent intermolecular forces known for over half a century [ 1 ]. They contribute to the stabilization of the complex structures of nucleic acids and proteins [ 2 ], the construction of supramolecular architectures [ 3 ], and the packing of aromatic molecules in the crystal [ 4 ]. Hunter and Sanders [ 1 ] assumed that  $\pi$ — $\pi$  interactions are a result of that the attractive forces between  $\pi$  electrons and  $\sigma$ -framework ( $\pi$ — $\sigma$  attraction) outweigh  $\pi$  electron repulsion and suggested a set of rules to explain these interactions. One of the rules is that  $\pi$ — $\sigma$  attraction dominates in an offset  $\pi$ -stacked geometry. Janiak [ 5 ], based on a Cambridge Structural Database search and X-ray data examples from the literature on metal—ligand complexes, came to the following conclusions: (1) The face-to-face  $\pi$ — $\pi$  alignment with a near to perfect facial stacking is a rare phenomenon and the usual  $\pi$  interaction is an offset or slipped stacking. (2) The centroid—centroid distances between two ligand fragments start slightly below 3.4 Å and a relative maximum in a number of examples is found around 3.8 Å. (3) The distances of the  $\pi$ — $\pi$  planes are an important criterion to suggest  $\pi$ -stacking. Stronger interactions are around 3.3 Å and weaker interactions lie above 3.6 Å, with 3.8 Å being approximately the maximum contact distance for which  $\pi$ — $\pi$  interactions are still significant.

In this paper, the synthesis and crystal structure of a copper(II) complex  $[\text{Cu}^{\text{II}}(\text{SSC})\text{Cl}]_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  (SSC = salicylaldehyde semicarbazone anion) have been reported. The most striking feature of the crystal structure is the packing of the planar dimers within the crystal. The interplanar distances between the adjacent two layers are 3.280 Å, shorter than literature given examples of copper(II)

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Table 1

## Crystal Data for the Compound Studied

Compound	[Cu <sup>II</sup> (SSC)Cl] <sub>2</sub> ·CH <sub>3</sub> OH·2H <sub>2</sub> O	Compound	[Cu <sup>II</sup> (SSC)Cl] <sub>2</sub> ·CH <sub>3</sub> OH·2H <sub>2</sub> O
Gross formula	Cu <sub>2</sub> C <sub>17</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>7</sub>	Crystal size, mm	0.40×0.20×0.20
Formula weight	622.4	R <sub>int</sub>	0.017
Temperature, K	293(2)	Independent data	4040
Crystal system	Triclinic	Refined parameters	333
Space group	<i>P</i> -1	GOOF	1.057
<i>a</i> , <i>b</i> , <i>c</i> , Å	10.272(2), 10.297(2), 11.462(2)	<i>R</i> values ( <i>I</i> > 2σ <sub><i>I</i></sub> )	R <sub>1</sub> = 0.038, wR <sub>2</sub> = 0.100
α, β, γ, deg.	82.860(3), 78.384(3), 81.330(2)	<i>R</i> values (all data)	R <sub>1</sub> = 0.049, wR <sub>2</sub> = 0.107
<i>V</i> , Å <sup>3</sup>	1168.4(4)	Residual max/min, e/Å <sup>3</sup>	+0.56 / -0.39
<i>Z</i>	2	CCDC deposition number	648546
<i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.769		

complexes [ 5 ], even less than the average inner interlayer spacing of multi-wall carbon nanotubes (3.4 Å) [ 6 ], or ideal graphite crystal (3.354 Å) [ 7 ]. Therefore, the title compound probably exhibits stronger π—π or d—π interactions.

The ligand HSSC was prepared according to the published general procedure [ 8 ] by reacting the semicarbazide hydrochloride with the salicylaldehyde in methanol in a molar ratio of 1:1. The elemental analysis results are consistent well with the HSSC formula. HSSC (0.179 g, 1 mmol) dissolved in 20 ml methanol was slowly added to a solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.170 g, 1 mmol) in 20 ml methanol in a flask and was stirred for about 3 hours. A dark blue precipitate was obtained from the resulting reaction solution, separated by filtration, washed with methanol and dried. The dried powder was dissolved in THF and the crystals suitable for X-ray analysis were obtained by slow evaporation of the above solution at room temperature.

A single crystal of the title compound with dimensions of 0.4×0.2×0.2 mm was studied. Unit cell constants and diffraction intensity data were measured with a Smart CCD area detector system using graphite-monochromatized MoK<sub>α</sub> radiation (λ = 0.71073 Å) at 293 K in the range of 5.16 < 2θ < 53.84°. A total of 4841 reflections were collected of which 4040 were unique. The structure was solved by direct methods and refined on *F*<sup>2</sup> in the approximation of anisotropic thermal vibrations for all non-hydrogen atoms. All calculations were performed with SHELX-97 software.

Crystal data for the complex are listed in Table 1. Selected interatomic distances and bond angles for the complex can be seen in Table 2. Structural information on the reported structure was deposited with CCDC database (deposition no. 648546) and is freely available via www.ccdc.cam.ac.uk.

Table 2

## Selected Interatomic Distances and Bond Angles

Bond	<i>d</i> , Å	Angle	ω, deg.
Cu(1)—O(1)	1.888(2)	O(1)—Cu(1)—N(1)	92.51(9)
Cu(1)—N(1)	1.942(2)	O(1)—Cu(1)—O(2)	172.61(8)
Cu(1)—O(2)	1.963(2)	N(1)—Cu(1)—O(2)	80.68(9)
Cu(1)—Cl(1)	2.2101(9)	O(1)—Cu(1)—Cl(1)	93.17(7)
N(1)—C(7)	1.279(4)	N(1)—Cu(1)—Cl(1)	173.41(7)
N(1)—N(2)	1.372(3)	O(2)—Cu(1)—Cl(1)	93.80(6)
O(2)—C(8)	1.258(3)	C(7)—N(1)—N(2)	119.7(2)
C(6)—C(1)	1.414(4)	C(7)—N(1)—Cu(1)	128.2(2)
C(6)—C(7)	1.432(4)	N(2)—N(1)—Cu(1)	112.13(18)
C(1)—O(1)	1.327(4)	C(8)—O(2)—Cu(1)	113.87(19)
N(2)—C(8)	1.350(4)	O(2)—C(8)—N(3)	122.4(3)
N(3)—C(8)	1.311(4)	O(2)—C(8)—N(2)	118.7(3)

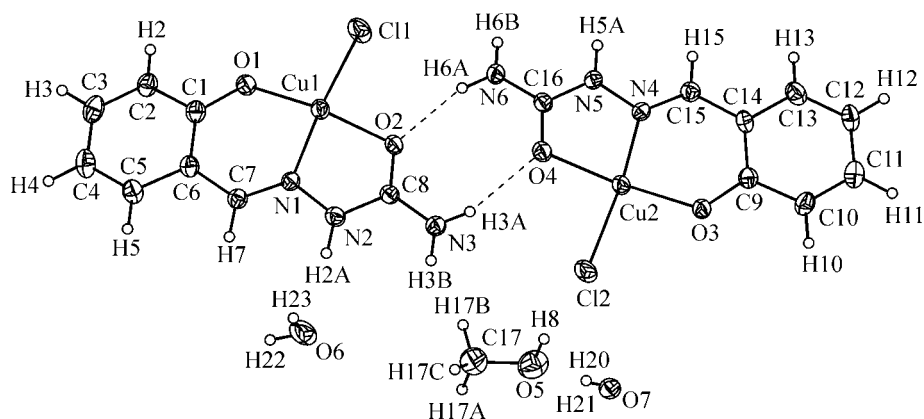


Fig. 1. Molecular structure of the complex

Molecular structure of title compound is illustrated in Fig. 1. The compound is composed of a dimeric complex unit  $[\text{Cu}^{\text{II}}(\text{SSC})\text{Cl}]_2$ , methanol and water molecules. The Cu(II) ion occupies the center of a distorted square-planar polyhedron and forms four coordination bonds. Three of the four coordination sites are occupied by the O, N and O atoms of  $\text{SSC}^-$ , while the fourth site is occupied by  $\text{Cl}^-$ . The corresponding bond lengths and angles are listed in Table 2.

Two independent but essentially identical molecules  $[\text{Cu}^{\text{II}}(\text{SSC})\text{Cl}]$  are bridged by intermolecular hydrogen bonds (Fig. 1). The dimers are further assembled through intermolecular  $\text{N}-\text{H}\cdots\text{Cl}$  interactions to form a planar band (Fig. 2, *a*), and the molecular bands are ABAB... stacking in an offset or slipped alignment (Fig. 2, *b*). The average interlayer distance of 3.280 Å indicates strong non-covalent interactions. The hydrogen-bond geometry is given in Table 3. The packing diagram for the title compound is shown in Fig. 3.

Difference UV spectra were recorded with a Hewlett Packard 8453 spectrophotometer. A methanol solution of 2000  $\mu\text{L}$  HSSC ( $5.0 \times 10^{-5}$  M) was added to a 1 cm sample cuvette, and then each time a 20  $\mu\text{L}$  portion of  $\text{CuCl}_2$  ( $5.0 \times 10^{-4}$  M) methanol solution was added to the HSSC solution gradually to determine a value of the molar absorptivity of the Cu—SSC complex at room temperature. Typical difference UV spectra of HSSC in the absence and presence of Cu(II) are shown in Fig. 4. Two major positive peaks were observed at 248 nm and 374 nm and a major negative absorbance appeared at 317 nm upon addition of Cu(II). The absorbance at 248 nm at each point of the titration was divided by the analytical concentration of HSSC to give a value of  $\Delta\epsilon$ . Titration curves were prepared by plotting  $\Delta\epsilon$  versus  $[\text{Cu}]/[\text{HSSC}]$ , as shown in Fig. 5. It can be seen that a sharp inflexion appeared at

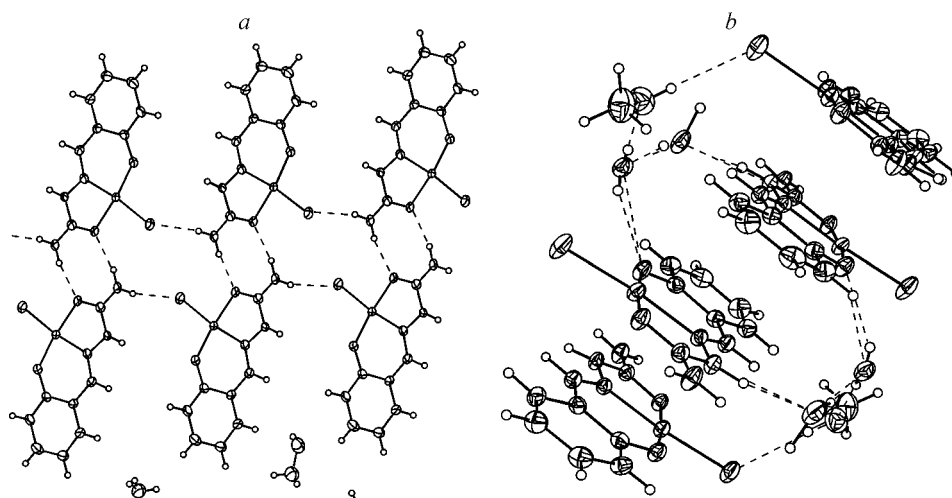


Fig. 2. H-bonding assembly and packing of the molecules in the crystal

Table 3

Hydrogen Bond Geometry (Å, deg.)				
D—H...A	<i>d</i> (D—H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O(7)—H(21)...O(5)	0.82(4)	1.94(5)	2.766(5)	176(4)
O(6)—H(22)...O(7)(i)	0.81(5)	2.08(6)	2.890(4)	172(4)
O(7)—H(20)...O(1)(ii)	0.63(4)	2.19(4)	2.751(4)	151(6)
O(5)—H(8)...Cl(2)	0.82	2.41	3.226(3)	173.5
N(6)—H(6B)...Cl(1)(iii)	0.86	2.60	3.400(3)	156.0
N(6)—H(6A)...O(2)	0.86	2.08	2.917(3)	162.8
N(3)—H(3B)...Cl(2)(iv)	0.86	2.60	3.411(3)	157.2
N(3)—H(3A)...O(4)	0.86	2.17	2.999(3)	161.7

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $-x, -y+1, -z+1$ ; (iv)  $-x+1, -y+1, -z+2$ .

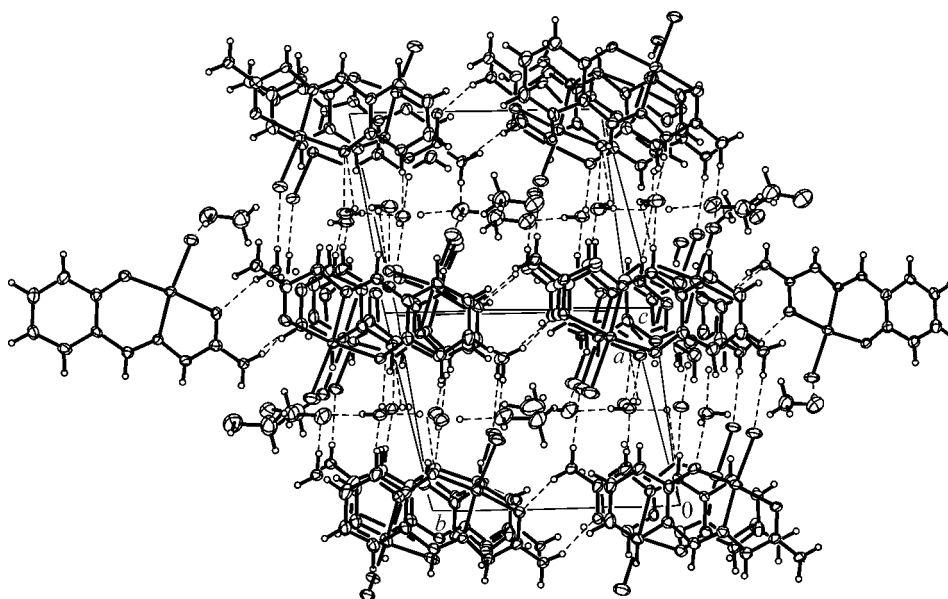


Fig. 3. Unit cell contents for the compound studied

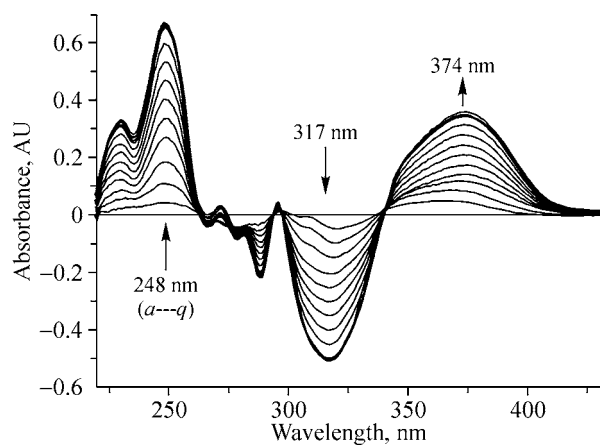


Fig. 4. Difference UV spectra produced by the addition of Cu(II) ( $5.0 \times 10^{-4}$  M) to 2.0 ml of HSSC ( $5.0 \times 10^{-5}$  M). The volume of Cu(II) (a) 0  $\mu$ L; (b) 20  $\mu$ L; (c) 40  $\mu$ L; (d) 60  $\mu$ L; ... (q) 320  $\mu$ L

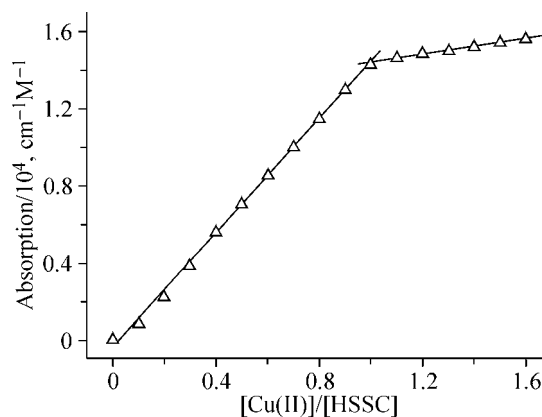


Fig. 5. UV titration curve derived by the addition of Cu(II) titrant to HSSC in methanol (see Fig. 4)

about  $[Cu]/[HSSC] = 1.0$ , which confirmed 1:1 stoichiometric ratio of a complex between Cu(II) and HSSC. At  $[Cu]/[HSSC] \leq 1$ , the molar absorptivity of Cu—HSSC was calculated to be  $(1.53 \pm 0.01) \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ .

#### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of P.R. China (No. 20771068) and the Natural Science Foundation of Shanxi Province (N 2007011024).

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