

NOVEL COPPER(II) COMPLEX WITH UNUSUAL π -STACKING STRUCTURE, $[\text{Cu}^{II}(\text{SSC})\text{Cl}]_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (SSC = SALICYLALDEHYDE SEMICARBAZONE ANION)

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The crystal structure of $[\text{Cu}^{II}(\text{SSC})\text{Cl}]_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (SSC = salicylaldehyde semicarbazone anion) was determined by the single crystal X-ray diffraction method at 293 K. Crystal data for $\text{Cu}_2\text{C}_{17}\text{H}_{24}\text{Cl}_2\text{N}_6\text{O}_7$: $a = 10.272(2)$ Å, $b = 10.297(2)$ Å, $c = 11.462(2)$ Å, $\alpha = 82.860(3)$ °, $\beta = 78.384(3)$ °, $\gamma = 81.330(2)$ °, triclinic, space group $P\bar{1}$, $Z = 2$, $d_{\text{calc}} = 1.769$ g/cm³, $R_1 = 0.038$. One N and two O atoms of SSC^- occupy three coordination sites around Cu(II). The fourth site is occupied by Cl^- to yield distorted square-planar environment. Two molecules of the complex form a planar dimer through intermolecular N-H...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 π - π noncovalent interactions. The methanol solvent and water molecules are included as additional components in the crystal.

Keywords: HSSC, copper(II), complex, crystal structure, π - π interactions, weak interactions.

Aromatic–aromatic or π - π interactions are important noncovalent 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 π - π interactions were the result of the dominance of the attractive forces between the π electrons and the σ framework (π - σ attraction) over π electron repulsion and suggested a set of rules to explain these interactions. One of the rules is that π - σ attraction dominates in an offset π -stacked geometry. Based on a Cambridge Structural Database search and X-ray literature data on metal–ligand complexes, Janiak [5] came to the following conclusions: (1) The face-to-face π - π alignment with a nearly perfect facial stacking is a rare phenomenon and the usual π 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 is found around 3.8 Å in a number of examples. (3) The distances of the π - π planes are an important criterion to suggest π -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 π - π interactions are still significant.

In this paper, the synthesis and crystal structure of a copper(II) complex $[\text{Cu}^{II}(\text{SSC})\text{Cl}]_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (SSC = salicylaldehyde semicarbazone anion) are reported. 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, i.e., shorter than the

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TABLE 1. Crystal Data for the Compound Studied

Compound	$[\text{Cu}^{\text{II}}(\text{SSC})\text{Cl}]_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$
Gross formula	$\text{Cu}_2\text{C}_{17}\text{H}_{24}\text{Cl}_2\text{N}_6\text{O}_7$
Formula weight	622.4
Temperature, K	293(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	10.272(2), 10.297(2), 11.462(2)
α , β , γ , deg	82.860(3), 78.384(3), 81.330(2)
<i>V</i> , Å ³	1168.4(4)
<i>Z</i>	2
<i>d</i> _{calc} , g/cm ³	1.769
Crystal size, mm	0.40×0.20×0.20
<i>R</i> _{int}	0.017
Independent data	4040
Refined parameters	333
<i>GOOF</i>	1.057
<i>R</i> values (<i>I</i> > 2σ _{<i>I</i>})	<i>R</i> ₁ = 0.038, <i>wR</i> ₂ = 0.100
<i>R</i> values (all data)	<i>R</i> ₁ = 0.049, <i>wR</i> ₂ = 0.107
Residual max/min, e/Å ³	+0.56/-0.39
CCDC deposition number	648546

literature distances for copper(II) complexes [5] and even smaller than the average inner interlayer spacing of multiwall 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 HSSC ligand was prepared according to the published general procedure [8] by a reaction of semicarbazide hydrochloride with salicyl aldehyde in a molar ratio of 1:1 in methanol. The elemental analysis results are consistent with the formula of HSSC. HSSC (0.179 g, 1 mmol) dissolved in methanol (20 ml) was slowly added to a solution of CuCl₂·2H₂O (0.170 g, 1 mmol) in methanol (20 ml) in a flask and stirred for ~3 h. 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 crystals suitable for an 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_α radiation ($\lambda = 0.71073$ Å) at 293 K in the range $5.16 < 2\theta < 53.84^\circ$. A total of 4841 reflections were collected, of which 4040 were unique. The structure was solved by direct methods and refined on *F*² 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 are found 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.

The molecular structure of the title compound is shown in Fig. 1. The compound is composed of a dimeric complex unit $[\text{Cu}^{\text{II}}(\text{SSC})\text{Cl}]_2$ and 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 SSC[−], while the fourth site is occupied by Cl[−]. The corresponding bond lengths and angles are listed in Table 2.

Two independent but very identical $[\text{Cu}^{\text{II}}(\text{SSC})\text{Cl}]$ molecules are bridged by intermolecular hydrogen bonds (Fig. 1). The dimers are further assembled through intermolecular N–H...Cl interactions to form a planar band (Fig. 2a), and the molecular bands are ABAB... stacked in an offset or slipped alignment (Fig. 2b). The average interlayer distance, 3.280 Å,

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)

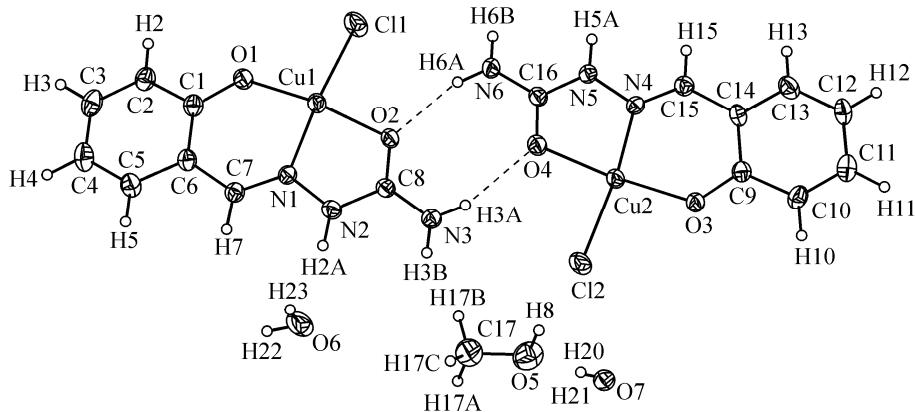


Fig. 1. Molecular structure of the complex.

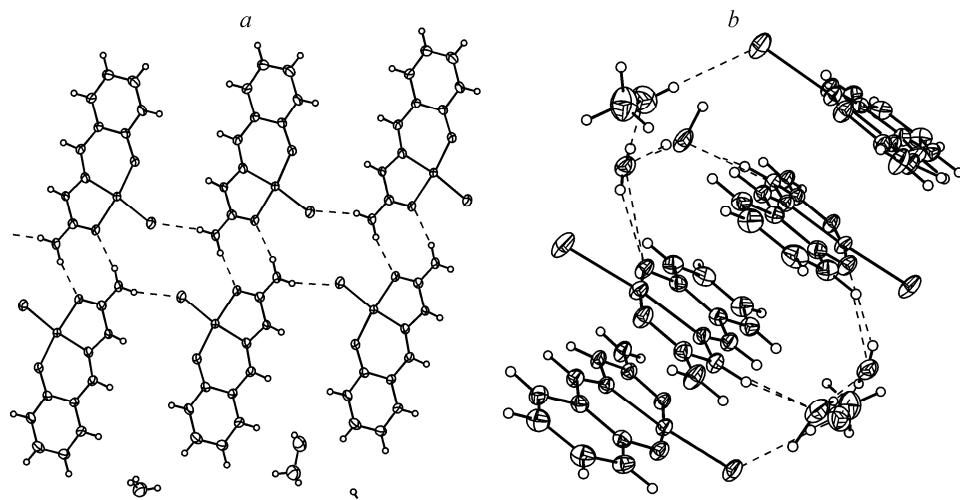


Fig. 2. H-bonding assembly and packing of the molecules in the crystal.

indicates strong noncovalent interactions. The hydrogen bond geometry is given in Table 3. The packing diagram for the title compound is shown in Fig. 3.

TABLE 3. Hydrogen Bond Geometry (Å, deg)

D–H...A	d(D–H)	d(H...A)	d(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) $-x + 1, -y + 1, -z + 2$.

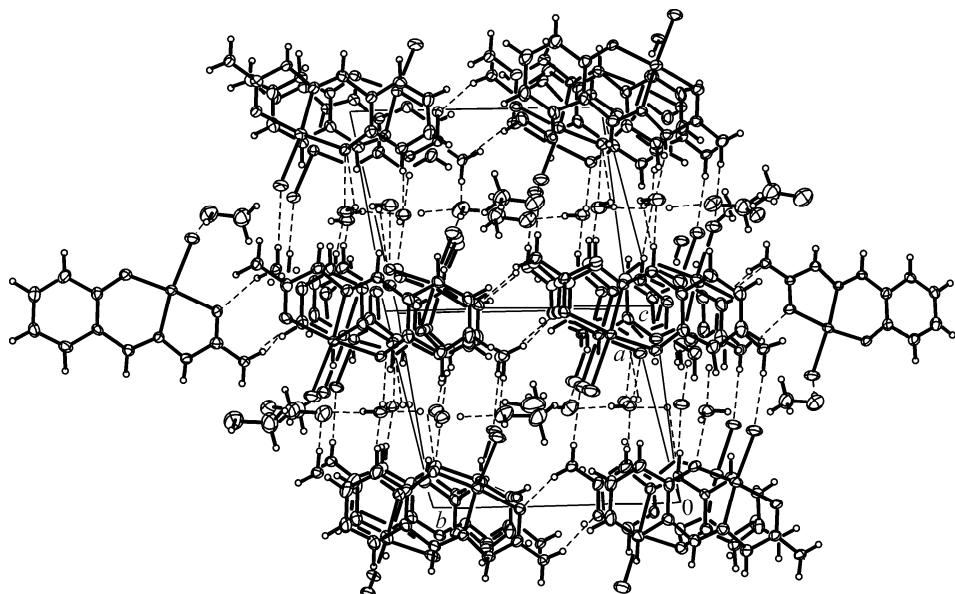


Fig. 3. Unit cell contents for the compound studied.

Difference UV spectra were recorded with a Hewlett Packard 8453 spectrophotometer. A methanol solution of HSSC ($2000 \mu\text{l}$, $5.0 \times 10^{-5} \text{ M}$) was added to a 1 cm sample cuvette, and then each time a $20 \mu\text{l}$ portion of a methanol solution of CuCl_2 ($5.0 \times 10^{-4} \text{ M}$) was added to the HSSC solution gradually to determine the molar absorptivity of the Cu–SSC complex at room temperature. The 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 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 the 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 inflection appeared at about $[\text{Cu}]/[\text{HSSC}] = 1.0$, which confirmed the 1:1 stoichiometric ratio of Cu(II) and HSSC in the complex. At $[\text{Cu}]/[\text{HSSC}] \leq 1$, the molar absorptivity of Cu–HSSC was calculated to be $(1.53 \pm 0.01) \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$.

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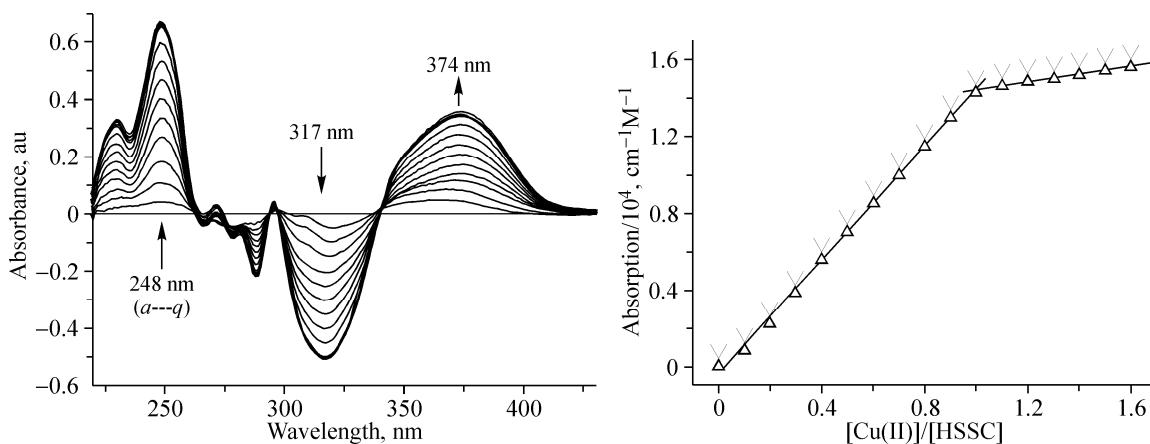


Fig. 4. Difference UV spectra produced by the addition of Cu(II) (5.0×10^{-4} M) to 2.0 ml of HSSC (5.0×10^{-5} M). The volume of Cu(II) is (a) 0 μ l; (b) 20 μ l; (c) 40 μ l; (d) 60 μ l; ... (q) 320 μ l.

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

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