REFINEMENT OF THE STRUCTURE AND PROPERTIES OF THE N-SALICYLIDENEGLYCINATO-THIOUREACOPPER(II) COMPLEX

František PAVELČÍK[a], Juraj KRÄTSMÁR-ŠMOGROVIČ[b], Oľga ŠVAJLENOVÁ[b] and Jaroslav MAJER[a]

[a] *Department of Analytical Chemistry and*
[b] *Department of Inorganic and Organic Chemistry,*
Pharmaceutical Faculty, Comenius University, 880 34 Bratislava

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Dedicated Prof. Dr J. Klikorka on the occasion of his 60th birthday.

The stable N-salicyldeneglycinato-thioureacopper(II) complex crystallizes in the monoclinic system with a space group of $C2/c$ (No 15); $a = 1{\cdot}8599$ (11), $b = 1{\cdot}4275$ (5), $c = 1{\cdot}3617$ (6) nm; $\beta = 138{\cdot}64$ (4)°, $Z = 8$. ($R = 0{\cdot}060$). The Cu(II) coordination in this complex is approximately square-pyramidal. The pyramid base is formed by the O(1), N(1) and O(3) donor atoms of the Schiff base (salalgly) and the S-atom of the thiourea (tu); Cu ↔ S = 0·2273 (3) nm. The apex of the pyramid is formed by the O(3^{iv}) atom, provided by two complex* molecules, thus joined to form a dimer $[Cu(salalgly)(tu)]_2$. The cryomagnetic properties of the complex in the interval 90—330 K obey the Curie-Weiss law. Its magnetic moment is practically temperature independent: $\mu_{ef} = 1{\cdot}82 \pm 0{\cdot}01$ B.M. The polycrystalline sample of complex (X band, room temperature) exhibits the axial type of EPR spectrum with $g_{\parallel} = 2{\cdot}210$, $g_{\perp} = 2{\cdot}044$, $\bar{g} = 2{\cdot}099$ (the Curie constant yields $g = 2{\cdot}101$).

In reaction systems containing excess thiourea, incorporation of this S-ligand into the inner sphere of Cu(II) usually results in an oxidation-reduction process within the complex, connected with the formation of the corresponding thioureacopper(I) complexes and $[(NH_2)_2CS\text{-}SC(NH_2)_2]^{2+}$ cations.

However, stable thioureacopper(II) complexes are also known which, in addition to the S-ligand, also contain either bi- or multidentate chelate ligands. In these complexes the coordination of Cu(II) atom is tetragonally bipyramidal[1] (axially bonded tu; Cu ↔ S = 0·2943 nm) or trigonally bipyramidal[2] (equatorially coordinated tu; Cu ↔ S = 2344 – 0·2369 nm.

The previous work in this series demonstrated that in the square-pyramidal N-salicylideneglycinato-aquacopper(II) complex hemihydrate[3] or tetrahydrate [4] the H_2O molecule in the base of the coordination polyhedron can be substituted[5] by

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* Part XXI in the series Copper(II) Complexes with Organic Ligands; Part XX: Chem. Zvesti *32* (1), 12 (1978).

various monodentate molecule ligands. An analogous reaction with thiourea led to isolation of the stable Cu(II)-complex[6,7] of composition [Cu(salalgly) (tu)]. X ray structural analysis, whose preliminary results have already been published[7], confirmed the square pyramidal structure of this thioureacopper(II) complex, with an equatorially coordinated S-donor molecule of thiourea in the base of the coordination polyhedron, where the remaining three sites are occupied by the tridentate Schiff base. The fifth coordination site (the apex of the pyramid) is filled in the N-salicylideneglycinato-thioureacopper(II) complex by formation of the [Cu(salalgly) (tu)]$_2$ dimer through axial coordination of the "phenolic" oxygen atoms.

This work was carried out in order to refine data on the molecular and crystal structure of the studied complex, which, compared with complexes studied so far, represents a new type of stable thioureacopper(II) complex. Considering the determined bridge system in the „dimer molecule", [Cu(salalgly) (tu)]$_2$, it was felt useful to carry out a more detailed study of its magnetic properties.

EXPERIMENTAL

The N-salicylideneglycinato-aquacopper(II) hemihydrate was prepared as described[8]. Thiourea was purified by recrystallization from ethanol.

The N-salicylideneglycinate-thioureacopper(II) complex, [Cu(salalgly)(tu)], was prepared by the action of thiourea (in excess, [Cu^{2+}] : tu = 1 : 4) on [Cu(salalgly)(H_2O)] in hot ethanol solution (80%) ethanol). The dark to black-green crystals, precipitated from the reacting system were separated, washed with ethanol and ether and dried at laboratory temperature. For $C_{10}H_{11}$.N_3O_3SCu (316·8) was calculated: 37·91% C, 3·50% H, 20·06% Cu, 13·26% N; found: 38·10% C, 3·65% H, 19·95% Cu, 13·20% N.

TABLE I

Cryomagnetic properties of [Cu(salalgly) (tu)]

T K	$\chi_m \cdot 10^8$ $m^3\,kg^{-1}$	$\chi'_M \cdot 10^{11}$ $m^3\,mol^{-1}$	μ_{ef} B.M.
330	4·65	1 649	1·82
300	5·14	1 805	1·82
270	5·77	2 004	1·82
240	6·52	2 242	1·82
210	7·54	2 565	1·83
180	8·80	2 964	1·82
150	10·66	3 553	1·82
120	13·32	4 396	1·82
90	17·67	5 774	1·81

Single crystals of the [Cu(salalgly)(tu)] complex were obtained by slow evaporation of the solvent from a saturated solution in ethanol at laboratory temperature.

Cryomagnetic and Spectral Measurements

The magnetic susceptibility of the complex was found by the Gouy method on a commercial instrument (Newport, Instuments, Ltd)., in the temperature range 90—330 K. The measurement was carried out at four magnetic field intensities in the range 160—640 kA m^{-1}, $Hg[Co(SCN)_4]$ was used as a standard[9]. The molar susceptibility was corrected for the diamagnetism of the components using the appropriate Pascal constants[10] (($\sum\chi_{dia}$ = $-176 \cdot 10^{-11}$ m^3 mol^{-1}). The effective magnetic moment was calculated according to ref.[11], where the value[12] $N_\alpha =$ $= 75 \,.\, 10^{-11}$ m^3 mol^{-1} was substituted for the temperature-independent paramagnetism of the Cu^{2+} ion (Table I).

The EPR spectra of the complex were obtained by measuring the polycrystalline substance at laboratory temperature, X-band ($\nu = 9\,365$ MHz) on an ER-9 Spectrometer (Zeiss, Jena). DPPH was used as an internal standard. The spectrum was evaluated by the Kneubühl approximation[13]. The g-factor values found are $g_{\parallel} = 2{\cdot}210$, $g_{\perp} = 2{\cdot}044$, $\bar{g} = 2{\cdot}099$ and $G = 4{\cdot}80$.

Crystallographic data and measured intensities

$a = 1{\cdot}8599\,(11)$ nm $V = 2{\cdot}3889$ nm^3
$b = 1{\cdot}4275\,(5)$ $Z = 8$
$c = 1{\cdot}3617\,(6)$ $D_m = 1{\cdot}74$ Mg m^{-3}
$\beta = 138{\cdot}64\,(4)^\circ$ $D_c = 1{\cdot}76$ Mg m^{-3}
Monoclinic system $\mu(Mo) = 2{\cdot}07$ mm^{-1}
Mo K_α ($\lambda = 0{\cdot}071069$ nm)

The crystal used for the structural analysis had roughly pyramidal shape confined by the $\{110\}$ and $\{111\}$ planes with a rectangular base 0·2 × 0·3 mm and height of 0·35 mm. The density was measured by the flotation method in a dibromoethane–benzene mixture. The crystal symmetry and lattice parameters were found from photographic, oscillation and Weissenberg patterns. Systematic absence of diffractions of the hkl with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$ type indicated that space group $C2/c$ or Cc is involved. The lattice parameters were refined on the basis of the angle positions of 10 centred reflections on a Syntex $P2_1$, diffractometer, on which the intensity was also measured. The intensity was measured using the $\Theta - 2\Theta$ technique and graphite-monochromated Mo K_α radiation in the range $2{\cdot}9 < 2\Theta < 55^\circ$. The scan rate in the range 4·88—29·3° min^{-1} and was found on the basis of preliminary 2 second measurement of the intensity. To consider the effect of reflection splitting by the K_{α_1} and K_{α_2} radiation, the scan range was chosen so that it was 1° below the calculated value for the K_{α_1} radiation and 1° above the calculated value for the K_{α_2} radiation. The background was measured at each end of the scan for a period equal to half of the scanning time for the reflections. The intensity of two control reflections measured after recording 94 reflections indicated no significant fluctuations. After recording 320 reflections, the mutual orientation of the coordinate systems of the crystal and instrument (recentering) was refined. 2 243 reflections were measured, of which 1 182 reflections with $I > 1{\cdot}96\sigma(I)$ were considered observed and used for further calculations. The intensity was corrected for the Lorentz and polarization factors. Corrections for absorption and extinction were not carried out.

Structure Solution and Results

The ($C/2c$) space group was refined and the position of the Cu atom was determined from the three-dimensional Patterson synthesis calculated from all the observed reflections. The subsequent three Fourier synthesis of the electron density indicated the positions of all the atoms except the hydrogen atoms. Block-diagonal refinement of the atom coordinates and the isotropic temperature factors yielded $R = 0{\cdot}1$. Further structural refinement was carried out anisotropically with the LALS full matrix program[14].

The functional $M = \sum w(|F_0| - |F_c|)^2$ was minimized. The atomic scattering curves from standard tables[15] were used to calculate the structural factors. The coordinates of the atoms, refined in two least squares cycles, were used to calculate the positions of the hydrogen atoms of the Schiff base (salalgly) (the length of the C—H bond was taken as 0·109 nm and the H—C—X angle as 120° or 109·5°, depending on the type of hybridization), using the HELPR program[16]. The coordinates of the non-hydrogen atoms were refined by a single least squares cycle at fixed positions and isotropic factors ($B = 0{\cdot}03\ \text{nm}^2$) for the hydrogen atoms. Differential synthesis calculated from reflections for which $\sin \Theta/\lambda < 0{\cdot}48$ indicated the positions of the remaining 4 hydrogen atoms of the thiourea. The positions of the hydrogen atoms were refined by a one least squares cycle at a fixed temperature factor for the hydrogen atoms ($B = 0{\cdot}03\ \text{nm}^2$) and fixed parameters for all the other atoms. In the refinement the $w = 1$ weighting scheme was used for all the reflections. The distribution of the minimized function $\sum w|\Delta F|^2$ over the intervals $|F_0|$ and $\sin \Theta/\lambda$ indicated that the weighing scheme used is satisfactory. The resultant factor R is 0·060. Zero synthesis of the electron density did not exhibit a maximum greater than 400 $\text{e}^- \text{nm}^{-3}$.

TABLE II

Crystallographic coordinates (. 10^4) of atoms in crystal structure [Cu(salalgly)(tu)] (with standard deviations in parentheses)

Atom	*x/a*	*y/b*	*z/c*
Cu	— 568(1)	765(1)	742(2)
S	— 878(2)	2 309(2)	129(3)
O(1)	—2 133(6)	647(5)	—1 104(8)
O(2)	—3 437(6)	— 357(6)	—2 773(8)
O(3)	927(5)	791(5)	2 617(8)
N(1)	— 587(7)	— 580(5)	559(9)
N(2)	120(8)	3 843(7)	664(11)
N(3)	1 232(7)	2 722(7)	2 504(10)
C(1)	—2 497(8)	— 169(8)	—1 638(11)
C(2)	—1 675(9)	— 969(7)	— 753(12)
C(3)	221(10)	—1 130(8)	1 433(14)
C(4)	1 316(8)	— 864(8)	2 750(12)
C(5)	1 633(9)	90(8)	3 257(12)
C(6)	2 117(11)	—1 557(9)	3 516(15)
C(7)	3 197(10)	—1 379(9)	4 777(15)
C(8)	3 488(9)	— 430(11)	5 263(14)
C(9)	2 746(9)	268(9)	4 543(12)
C(10)	253(8)	3 004(7)	1 193(12)

TABLE III

Anisotropic temperature coefficients (. 10^4) in the relation $T = \exp [-(B_{11}h^2 + \ldots + B_{12}hk + + \ldots)]$. The standard deviations are given in parentheses

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	29(1)	21(1)	67(2)	0(1)	53(2)	2(2)
S	34(2)	23(1)	98(4)	0(3)	58(5)	11(4)
O(1)	43(5)	27(4)	87(11)	— 4(7)	77(13)	—17(11)
O(2)	30(5)	42(5)	63(10)	— 2(8)	23(13)	—27(11)
O(3)	29(5)	26(4)	85(10)	— 4(8)	40(12)	—20(12)
N(1)	36(6)	16(4)	54(11)	6(8)	5(14)	3(11)
N(2)	40(7)	36(5)	117(16)	—18(10)	68(18)	22(15)
N(3)	29(6)	36(5)	81(13)	5(10)	46(15)	4(14)
C(1)	35(7)	31(6)	48(13)	10(11)	52(17)	12(14)
C(2)	46(8)	17(5)	76(15)	10(9)	74(19)	3(13)
C(3)	56(9)	26(6)	95(17)	18(11)	102(22)	7(16)
C(4)	34(7)	28(5)	86(15)	—13(11)	71(18)	10(16)
C(5)	45(8)	37(6)	55(13)	8(12)	73(18)	28(15)
C(6)	61(10)	40(7)	14(21)	52(14)	142(27)	54(19)
C(7)	52(9)	45(7)	117(20)	52(13)	98(24)	56(10)
C(8)	32(7)	80(10)	95(17)	19(14)	78(20)	51(21)
C(9)	34(8)	40(7)	68(15)	16(11)	56(18)	11(16)
C(10)	30(7)	26(6)	82(15)	—16(10)	75(18)	— 4(14)

TABLE IV

Refined crystallographic coordinates (. 10^4) of hydrogen atoms in the crystal structure of [Cu(salalgly)(tu)]

Atom	x/a	y/b	x/c
NH2(1)	— 601	3 998	— 395
NH2(2)	617	4 238	1 117
NH3(1)	1 563	3 176	2 912
NH3(2)	1 388	2 193	2 827
HC2(1)	—1 634	—1 421	—1 414
HC2(2)	—1 830	—1 324	— 384
HC3(3)	82	—1 761	1 011
HC6(1)	2 001	—2 199	3 192
HC7(1)	3 826	—1 757	5 512
HC8(1)	4 205	— 220	6 129
HC9(1)	2 902	1 028	4 972

Except for hydrogen, the crystallographic coordinates of the atoms are given in Table II and the anisotropic thermal oscillation parameters in Table III. The refined coordinates of the hydrogen atoms are given in Table IV. Table V lists the significant bonding distances and angles A perspective projection of the complex molecule with the atoms numbered is depicted in Fig. 1. The calculations were carried out on a Syntex XTL module and in the Research Computer Center of Comenius University on a Siemens 4004/150 computer. The values of the observed and calculated structural factors are available from the authors on request.

DISCUSSION

Data on the structure[3] of the $[Cu(salalgly)(H_2O)].0{\cdot}5\,H_2O$ complex, used as the starting substance in the preparative reactions, permitted assumption of coordination of the S-donor ligand (tu) in the equatorial plane of the coordination polyhedron of the complex prepared, [Cu(salalgly) (tu)], together with the donor atoms of the Schiff base. Conditions valid during the preparation of this complex (excess thiourea in the reaction system, heating to the boiling point), also demonstrated its stability, with no apparent tendency to be reduced to the corresponding thiourea copper(I) complex.

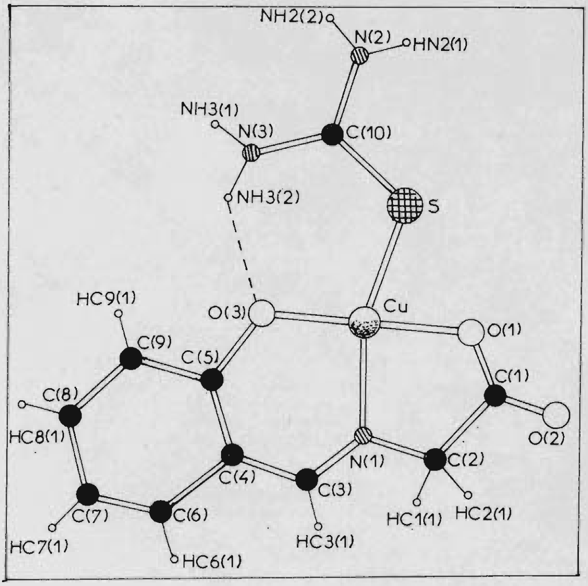

FIG. 1

Perspective projection and atom numbering in the crystal structure of the [Cu(salalgly)(tu)] complex

The magnetic moment of the [Cu(salalgly)(tu)] complex is greater than the spin -only value for Cu^{2+} and is practically temperature independent in the cryomagnetic measurement range (90 – 330 K) (Table I). In the given temperature interval, the magnetic properties of Cu(salalgly)(tu) obey the Curie-Weiss law, used in the form[17-19]:

$$\chi'_M = C/(T + \theta) + N\alpha = N\beta^2 g^2/4k(T + \theta) + N\alpha\,,$$

TABLE V

Interatomic distances (nm) and bond angles (°) in Cu(salalgly)(tu) complex (standard deviations are in parentheses)

interatomic distances

Cu—N(1)	0·1933(7)	C(4)—C(5)	0·1438(16)
Cu—O(1)	0·1958(8)	C(4)—C(6)	0·1398(17)
Cu—O(3)	0·1896(7)	C(5)—C(9)	0·1405(15)
Cu—O(3^{iv})	0·2771(7)	C(5)—O(3)	0·1329(13)
Cu—S	0·2273(3)	C(6)—C(7)	0·1368(18)
C(1)—C(2)	0·1526(15)	C(7)—C(8)	0·1425(20)
C(1)—O(1)	0·1267(13)	C(8)—C(9)	0·1351(18)
C(1)—O(2)	0·1209(13)	C(10)—N(2)	0·1322(15)
C(2)—N(1)	0·1472(13)	C(10)—N(3)	0·1336(14)
C(3)—C(4)	0·1423(16)	C(10)—S	0·1712(11)
C(3)—N(1)	0·1268(14)		

bond angles

N(1)—Cu—O(1)	83·3(3)	O(1)—C(1)—O(2)	125·1(10)
N(1)—Cu—O(3)	93·4(4)	C(1)—C(2)—N(1)	109·0(8)
N(1)—Cu—O(3^{iv})	97·2(3)	C(4)—C(3)—N(1)	125·8(10)
N(1)—Cu—S	160·2(3)	C(3)—C(4)—C(5)	122·8(10)
O(1)—Cu—O(3)	174·1(3)	C(3)—C(4)—C(6)	117·8(11)
O(1)—Cu—O(3^{iv})	90·6(3)	C(5)—C(4)—C(6)	119·3(10)
O(1)—Cu—S	84·7(2)	C(4)—C(5)—C(9)	117·3(10)
O(3)—Cu—O(3^{iv})	84·9(3)	C(4)—C(5)—O(3)	123·5(10)
O(3)—Cu—S	100·8(3)	C(9)—C(5)—O(3)	119·1(10)
O(3^{iv})—Cu—S	97·8(2)	C(4)—C(6)—C(7)	122·9(12)
Cu—N(1)—C(2)	114·0(8)	C(6)—C(7)—C(8)	116·6(11)
Cu—N(1)—C(3)	126·9(8)	C(7)—C(8)—C(9)	122·6(11)
Cu—O(1)—C(1)	117·1(6)	C(5)—C(9)—C(8)	121·2(11)
Cu—O(3)—C(5)	126·6(7)	N(2)—C(10)—N(3)	120·7(10)
Cu—S—C(10)	116·1(4)	N(2)—C(10—S	117·1(8)
C(2)—C(1)—O(1)	116·6(9)	N(3)—C(10)—S	122·2(8)
C(2)—C(1)—O(2)	118·3(10)	C(2)—N(1)—C(3)	119·2(8)

where C is the Curie constant, θ is the Weiss constant and $N\alpha$ is the temperature independent paramagnetism of Cu^{2+}. (The other symbols have the usual significance.) Regression analysis (by the least squares method) indicated that the dependence of $(\chi'_M - N\alpha)^{-1}$ *vs* T is linear for the studied complex ($r^2 = 0{\cdot}9999$, where r is the correlation coefficient[17]), with values: $C = 5{\cdot}20 . 10^{-6}\ m^3\ Kmol^{-1}$ (0·414 cgsu K . mol^{-1}), $g = 2{\cdot}101$ and $\theta = 0{\cdot}3$ K. The magnetic moment, calculated from $\mu_{ef} = 798\ C^{1/2}$, was equal to 1·82 B.M., which is practically identical (±0·01 B.M.) with the value calculated from the determined susceptibility in the whole cryomagnetic measurement range (Table I).

Thus the cryomagnetic properties in the interval 90–330 K did not reveal a perceptible magnetic coupling between the Cu^{2+} ions in Cu(salalgly) (tu), representing the cupric complex with the dimer structure[7], with oxygen bridge atoms. The N,N'-ethylenebis(salicylideneiminato)copper(II) complex, which has a binuclear structure and bridge system[20] similar to the ^{2}Cu(salalgly) (tu)] complex, also did not exhibit any marked spin–spin interaction between the Cu^{2+} ions in its magnetic properties above 81 K (ref.[21–23]).

The EPR spectrum of Cu(salalgly) (tu) is of the axial type with $g_{\parallel} > g_{\perp}$ ($g_{\parallel} = 2{\cdot}21$, $g_{\perp} = 2{\cdot}044$). The value $\bar{g}$ is equal to 2·099 and is very close to the Landé splitting factor resulting from equiv. (1): $g = 2{\cdot}101$. This is also reflected in the same values of the magnetic moment calculated from $\mu_{ef} = \bar{g}[S(S + 1)]^{1/2} = 1{\cdot}82$ B.M., ($S = 1/2$) or from the Curie constant (or the χ'_M values found for the individual temperatures). The line shape is well developed and the value $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4{\cdot}8$ indicates that the exchange interaction between the Cu^{2+} ions which can be expected on the basis of the determined dimeric structure of the complex is so small that it does not lead to any marked difference between the found and local g-values, which satisfactorily reflect the microsymmetry of the complex species itself[24,25]. Consequently, the value $g = 2{\cdot}044$, found as the smallest g-value, permits the assumption that $d_{x^2-y^2}$ is the ground state in the series of single-electron levels of this complex[25].

The coordination polyhedron in the [Cu(salalgly) (tu)] complex is approximately a square pyramid, with a penta-coordinated Cu atom. The base of the pyramid is formed by the O(1), N(1) and O(3) atoms from the anion of the Schiff base (salalgly) and the S-atom from the thiourea. The apex of the pyramid contains the phenolic $O(3^{iv})$ atom from the neighbouring molecule. The molecules are connected in the $[Cu(salalgly)(tu)]_2$ dimer through two axial Cu—$O(3^{iv})$ bonds, 0·278 nm long. In the crystal two complex molecules are symmetrical with respect to the two-fold axis. The angles contained by the S—Cu—X bonds (X = O(1). O(3), N(1), $O(3^{iv})$) exhibit the greatest deviations from the angles in an ideal square pyramid (90 and 180°). This is a result of the arrangement of the molecule in the crystal and of the intramolecular N(3)—H···O(3) bond. The HN3(2)···O(3) distance is 0·211 nm and N(3)···O(3), 0·284 nm.

In the square base of the coordination polyhedron of Cu(salalgly) (tu) the O(1) and O(3) atoms are bent above the central plane towards the O(3^{iv}) atom and S and N(1) atoms below the plane, as is apparent from the data in Table VI and the apex of the pyramid contains the phenolic O(3^{iv}) atom coordinated in the neighbouring molecule. Thus the coordination polyhedra of the studied complex differ from the square pyramids in the [Cu(salalgly) (H$_2$O)].0·5 H$_2$O and [Cu(salalgly) (H$_2$O)].4 H$_2$O complex[3,4], where the apex of the pyramid contains a free oxygen atom from the carboxyl group of the neighbouring molecule or, for the tetrahydrate, an oxygen atom from a water molecule in which the axial Cu–O bond is shorter (0·233 or 0·235 nm).

TABLE VI

Deviations (nm) of atoms from the least-square planes

Atoms included in calculations	Deviations from the plane					
All Cu(salalgly) atoms:						
Vu, C(1), C(2), C(3),	Cu	0·0051,	C(1)	0·0026,	C(2)	—0·0049,
C(4), C(5), C(6), C(7),	C(3)	—0·0055,	C(4)	—0·0053,	C(5)	—0·0029,
C(8), C(9), N(1), O(1),	C(6)	0·0019,	C(7)	0·0054,	C(8)	0·0064,
O(2), O(3)	C(9)	0·0022,	N(1)	—0·0026,	O(1)	0·0057,
	O(2)	0·0039,	O(3)	—0·0121,	S	0·0721,
	C(10)	0·1208,	N(2)	0·1888,	N(3)	0·0920
Benzene ring:						
C(4), C(5), C(6), C(7),	C(4)	—0·0012,	C(5)	0·0005,	C(6)	0·0012,
C(8), C(9)	C(7)	—0·0006,	C(8)	—0·0001,	C(9)	0·0001,
	Cu	0·0206				
Salicylaldiminato copper(II) ring:						
Cu, O(3), C(5), C(4),	Cu	0·0051,	O(3)	—0·0074,	C(5)	0·0043,
C(3), N(1)	C(4)	0·0016,	C(3)	—0·0018,	N(1)	—0·0018
Glycinato copper(II) ring:						
Cu, O(1), C(1), C(2),	Cu	0·0000,	O(1)	—0·0005,	C(1)	0·0009,
N(1)	C(2)	—0·0008,	N(1)	0·0004,	O(2)	0·0023
Donor atoms:						
O(1), N(1), O(3), S	O(1)	—0·0181,	N(1)	0·0183,	O(3)	—0·0149,
	S	0·0147,	Cu	—0·0091		
Thiourea:						
S, C(10), N(2), N(3)	S	—0·00002,	C(10)	0·00007,	N(2)	—0·00002,
	N(3)	—0·00003				

The geometry of the Cu(salalgly) parts of the three complexes is very similar. The bond distances and angles are not significantly different. This part of the complex exhibits only very small deviations from planarity. Data on the individual rings are given in Table VI; the maximum deviations from the central plane in the benzene ring are 0·001 nm, and in the glycine ring 0·0009 nm. Larger deviations from linearity in the six-membered ring (maximally 0·007 nm) probably result from attempts to decrease the large strain resulting from deformation of the bond angles, as all the angles are larger than 120° for ideal sp^2 hybridization or 90° in the coordination sphere of Cu(II). The plane of the benzene ring encloses an angle of 3·9° with the plane of the six-membered chelate ring and 4·1° with the plane of the five-membered ring. The five-membered and six-membered rings enclose an angle of 2·9°.

The coordination polyhedra of [Cu(salalgly) (tu)] are basically different from those of the stable thioureacopper(II) complex found in the crystal structures[2] of [Cu(pib) . . (tu)] $(ClO_4)_2$ and [Cu(bipy)$_2$ (tu)] $(ClO_4)_2$ (pib = N,N'-tetramethylenebis(2-pyridinaldimine) bipy = bis(2,2'-bipyridyl), which have the shape of trigonal bipyramids. The Cu—S bond in these complexes is longer (0·2344 and 0·2369 nm, respectively) than in the [Cu(salalgly) (tu)] complex, where it has a value of 0·227 nm; this length is less than the sum of the covalent radii (0·239 nm). In the bis(picolinato-thiourea) copper(II) complex, where the coordination polyhedron has the shape of a tetragonal bipyramid[1] with the S-atoms at the apices, the Cu—S distance is 0·2943 nm, *i.e.* much longer.

It is interesting that the lengths of the other bonds in the thiourea molecule coordinated in [Cu(salalgly) (tu)] are practically the same as in free (uncoordinated) thiourea[26] or in the bis(picolinato-thiourea)copper(II) complex[1]. There are

TABLE VII

Hydrogen bonds N—H···O in the crystal structure Cu(salalgly)(tu)

Hydrogen bond	Distance, nm N···O	Distance, nm H···O	Angle, ° N—H···O
N(2)—HN2(1)...O(2^{iii})	0·2846(13)	0·189	156·3
N(2)—HN2(2)...O(2^{ii})	0·2797(12)	0·199	164·4
N(3)—HN3(1)...O(1^{ii})	0·3100(12)	0·237	158·1
N(3)—HN3(2)...O(3^{i})	0·2842(12)	0·211	150·1

Symmetry codes used: ^{i}: x, y, z, ^{ii}: $x - 1/2, 1/2 - y, z - 1/2$, ^{iii}: $-x, 1 - y, -z$, ^{iv}: $-x, y, 1/2 - z$.

differences only in the bond angles. In free thiourea, the N—C—N angle is 115·6° and in the studied complex the N(2)—C(10)—N(3) angle is 120·7°. The C(10), S, N(2) and N(3) atoms all lie exactly in a single plane. The hydrogen atoms deviate from the plane by a maximum of 0·026 nm.

A system of intermolecular hydrogen bonds is formed in the crystal structure of [Cu(salalgly)(tu)], composed of hydrogen atoms from thiourea coordinated in a single molecule of the complex and both carboxyl oxygen atoms from a neighbouring molecule (see the data in Table VII). The HN(2)···O(2) and HN(3)···O(1) hydrogen bonds, which thus form eight-membered rings, are of key importance for the structure of the whole crystal.

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