

Space orientation and bonding properties of thiourea in *N*-salicylidene-glycinatocopper(II) complex

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Dedicated to Corresponding Member M. Zikmund, in honour of his 65th birthday

On the basis of structural data which are known for copper(I) and copper(II) complexes with thiourea the conditions for back donation between copper(II) and thiourea have been analyzed. The back donation is considered to occur in complexes where atoms of thiourea molecule and a copper(II) atom are coplanar.

Unusually short Cu—S bond length found in the [Cu(salalgly)(tu)] complex is probably caused by contribution of dative π -bond to the total bonding character.

На основе структурных данных, известных для комплексов меди(I) и меди(II) с тиомочевинной проанализированы условия для наличия обратной донорности между медью(II) и тиомочевинной. Сделан вывод, что дативная π -связь может иметь место в комплексах, в которых атомы молекулы тиомочевины и атом меди(II) лежат в одной плоскости.

Необычно малые длины связей Cu—S, найденные в комплексе [Cu(salalgly)(tu)], вероятно, являются следствием вклада дативной π -связи в общий характер связи.

The X-ray structure analysis of [Cu(salalgly)(tu)] complex (salalgly = *N*-salicylidene-glycinate anion, tu = thiourea) showed [1] a square-pyramidal coordination of Cu(II) atom with the sulfur atom of thiourea molecule and with two oxygen and one nitrogen atoms from tridentate Schiff's base in the positions of basal plane. The apex of the square pyramid is occupied by an oxygen atom being at the same time in the base of the adjacent structure unit. Thus the two structure units form the dimer [Cu(salalgly)(tu)]₂.

It is noteworthy that the structure of [Cu(salalgly)(tu)] exhibits an unusually

Table 1

Values of structure characteristics for copper(II) and copper(I) complexes with thiourea

No.	Complex	CN*	$d(\text{Cu}-\text{S})/\text{pm}$	$\text{DA}/^\circ$	Angle $\text{CuSC}/^\circ$	$d(\text{S}-\text{C})/\text{pm}$	Multiplicity**	Ref.
1	$[\text{Cu}(\text{pic})_2(\text{tu})_2]^a$	4 + 2	294.3(1)	87.0	100.2	169.2	2	[15]
2	$[\text{Cu}(\text{phen})_2(\text{tu})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}^b$	5	240.4	71.1	105.3	173.3	1	[16]
3	$[\text{Cu}(\text{bipy})_2(\text{tu})](\text{ClO}_4)_2^c$	5	236.9(4)	58.6	103.5	172(1)	1	[17]
4	$[\text{Cu}(\text{pib})(\text{tu})](\text{ClO}_4)_2^d$	5	234.4(3)	54.4	105.3	172(1)	1	[17]
5	$[\text{Cu}(\text{salalgly})(\text{tu})]$	5	227.3(3)	15.5	116.1(4)	171.2(11)	1	[1]
6	$[\text{Cu}_2(\text{tu})_6](\text{BF}_4)_2$	4	231.3(3)	20.1	110.1(4)	169(1)	2	[12]
		4	229.5(3)	0.2	113.4(5)	168(1)	2	
7	$\{[\text{Cu}(\text{tu})_3\text{Cl}]_n\}$	4	227.8(5)	18.3	105.0(4)	174(2)	1	[18]
		4	234.6(5)	17.1	108.0(4)	171(2)	1	
8	$[\text{Cu}_2(\text{tu})_6](\text{ClO}_4)_2$	4	232.6(5)	1.8	111.9(7)	174.5	2	[11]
		4	232.1(4)	18.7	109.5(7)	174.5	2	
9	$[\text{Cu}(\text{phen})(\text{tu})_2]\text{I} \cdot \text{phen}^b$	4	229.5	20.3	105.9	172.3	1	[20]
		4	228.0	11.7	108.0	170.0	1	

Table 1 (Continued)

No.	Complex	CN*	$d(\text{Cu}-\text{S})/\text{pm}$	$\text{DA}/^\circ$	Angle $\text{CuSC}/^\circ$	$d(\text{S}-\text{C})/\text{pm}$	Multiplicity**	Ref.
10	$[\text{Cu}(\text{tu})_4]_2(\text{SiF}_6)$	4	235.7(6)	9.7	109.4	174.0	1	[19]
		4	233.5(6)	19.6	106.7	176.4	1	
		4	236.2(6)	7.2	110.8	176.9	1	
		4	234.0(5)	32.8	106.6	174.1	1	
		4	232.3(5)	0.5	112.4	175.3	1	
		4	233.7(6)	15.7	110.2	170.8	1	
		4	235.9(6)	12.8	(119.3) ^f	170.4	1	
		4	234.0(5)	22.1	104.7	171.5	1	
11	$\{[\text{Cu}_2(\text{tu})_5]\text{SO}_4 \cdot 3\text{H}_2\text{O}\}_n$	4	231.3	34.0	104.7	172.4	1	[21]
		4	233.5	0.5	105.4	172.2	1	
		3	221.3	64.8	108.6	171.7	1	
12	$\{[\text{Cu}_2(\text{tu})_4](\text{Cl})_2\}_n$	3	224.4(5)	24.1(14)	106.2(7)	170.6(21)	1	[22]
		3	222.9(5)	1.2(15)	107.2(7)	(160.4(22)) ^f	1	
13	$[\text{Cu}(\text{tu})_3](\text{C}_8\text{H}_5\text{O}_4)^e$	3	224.7(4)	26.6	109.7(2)	171.7(5)	1	[23]
		3	223.8(3)	11.2	109.9(2)	170.8(7)	1	
		3	223.0(4)	8.1	110.4(2)	172.1(6)	1	

* CN = coordination number.

** Multiplicity of data found for complex of given formulae.

a) pic = picolinate anion; b) phen = 1,10-phenanthroline; c) bipy = 2,2'-bipyridine; d) pib = *N,N'*-tetramethylenebis(2-pyridinaldimine); e) $\text{C}_8\text{H}_5\text{O}_4$ = hydrogen-*o*-phthalate anion; f) probably erroneous values.

short bond length Cu—S = 227.3(3) pm, being the shortest [1] of Cu—S bond lengths found in the structure of copper(II) complexes with thiourea.

For the square-pyramidal coordination polyhedra of copper(II) complexes with ligands of reducing properties (I^- , CN^- , NCS^- , tu, triphenylphosphine) in the apex and with polydentate ligands in the basal plane of square pyramid the stabilization of Cu(II) against reduction to Cu(I) has been explained [2] by minimum overlap of reducing ligand orbitals with $d_{x^2-y^2}$ orbital which contains an unpaired electron of Cu(II) atom [3]. In this respect the square-pyramidal [Cu(salalgly)(tu)] complex serves as an exception, though it must be taken into consideration that the complex is dimeric and the thiourea molecule is bonded also with $NH\cdots O$ hydrogen bonds [1].

In addition to the structural aspects this complex is remarkable also by the high stability of the oxidation state of Cu(II) since the complex can also be prepared [4] by reaction of thiourea copper(I) complexes with (H_2 salalgly) ligand.

The reducing influence of thiourea but also of some other ligands may be explained by their ability to form dative π -bonds (back donation) with copper [5]. The existence of these bonds between copper and thiourea should appear in dependence of the bond length Cu—S on the oxidation state of copper.

The above-mentioned properties of [Cu(salalgly)(tu)] complex led us to investigate the bonding mode of thiourea in this complex compared with other copper(I) and copper(II) complexes with thiourea, the structure of which is known.

Experimental

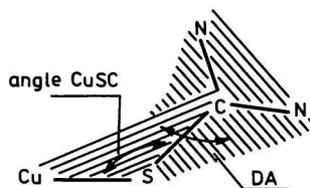
The data necessary for an analysis of the dependence of Cu—S bond length on the space orientation of thiourea in copper complexes were obtained either directly from published data or they were computed from atomic coordinates. The data obtained by us are listed in Table I without standard deviations. The atomic coordinates and the necessary structural data were partly obtained from Cambridge Crystallographic Database — CCD. More detailed data (atomic coordinates) of the structure of $[Cu_4(tu)_6](NO_3)_4 \cdot 4H_2O$ [6], $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$ [6], and $[Cu_4(tu)_{10}](SiF_6)_2 \cdot H_2O$ [7] were not available.

The calculations of (a, b) parameters of linear correlation ($y = a + bx$), of the correlation coefficient (ρ), standard deviations (s, s_a, s_b), reliability interval for linear regression and the tests of hypothesis for regression straight line (linearity test and the independence test, respectively) were performed by relations usual in mathematical statistics [8] using programmable calculator TI 58 — Texas Instruments. The statistical evaluations (test of the hypotheses and the reliability interval) were performed applying Student's or Fischer's distribution, respectively, for the significance level 95 %.

Results and discussion

All atoms of thiourea molecule (including hydrogen atoms of NH_2 groups) are arranged in one plane [9]. From this arrangement follows that thiourea molecule may be coordinated only through the sulfur atom. An analysis of the space orientation of bridging thiourea molecules in cobalt complexes [10] led to the conclusion, that in addition to electrons from nonbonding sp^2 -orbitals of the sulfur atom, the donor-acceptor bonding thiourea (donor) \rightarrow central atom (acceptor) can be realized also by means of electrons from delocalized π -orbitals of thiourea molecule. An analogical bonding mode of bridging thiourea molecules is assumed [6, 7, 11–13] also in the case of some Cu(I) complexes. A dihedral angle (DA), defined (Fig. 1) as the angle between the plane containing the Cu—S—C atoms and the plane in which atoms of thiourea molecule occur is considered to be a criterion of the different bonding modes of thiourea to the central atom. The coplanarity of the planes, *i.e.* a small value of the dihedral angle, indicates the formation of σ -donor bonding $\text{tu} \rightarrow$ central atom by means of electrons from nonbonding sp^2 -orbitals of the sulfur atom. In the case of perpendicular orientation of the two planes ($\text{DA} = 90^\circ$), the spatial conditions for the participation of sp^2 -orbitals of the sulfur atom in the bond to the central atom are not fulfilled and therefore the use of electrons from π -orbitals of the thiourea is considered [10].

Fig. 1. Structure characteristics of the space orientation of nonbridging thiourea ligands.



In Cu(I) complexes thiourea often appears to be bridge-bonded. The bonding mode of bridging thiourea in Cu(I) complexes was already analyzed [14]. However, until present, in copper(II) complex no bridging thiourea was found.

Table 1 presents the data characterizing the nonbridging thiourea in copper(II) and copper(I) complexes, for which structure data were available [1, 11, 12, 15–23]. As evident from the comparison of bond lengths Cu—S for copper(II) and copper(I) complexes (Table 1), with the exception of complex $[\text{Cu}(\text{pic})_2(\text{tu})_2]$ (pic = picolinate anion) [15] these lengths are in a relatively narrow interval (221.3–240.4 pm). The intervals of Cu—S bond lengths for copper(II) complexes (227.3–240.4 pm) and for copper(I) complexes (221.3–236.2 pm) are mutually overlapped. This indicates that Cu(II)—S and Cu(I)—S bonds do not differ significantly in their character (multiplicity).

The data for copper(I) complexes show that the Cu(I)—S distance is expressively influenced by the type of the coordination polyhedron (the coordination number) of the Cu(I) atom. In the group of complexes with the coordination number four the Cu(I)—S distances were found in the interval of 227.8—236.2 pm [11, 12, 18—21], while Cu(I) complexes with the coordination number three exhibit these distances within the interval of 221.3—224.7 pm [21—23]. The two distinct intervals of Cu(I)—S distances have been found mainly for $[\text{Cu}_2(\text{tu})_3]\text{SO}_4 \cdot 3\text{H}_2\text{O}$ complex, in the structure of which the Cu(I) atoms are trigonally or tetrahedrally surrounded by thiourea ligands [21]. Similarly also in the group of copper(II) complexes the different Cu(II)—S distances may be expected for $[\text{Cu}(\text{pic})_2(\text{tu})_2]$ complex with the Cu(II) coordination number six (4 + 2), in difference to the other copper(II) complexes with the coordination number five [1, 16, 17]. In this respect it is interesting that the interval of Cu(II)—S distances for pentacoordinate Cu(II) complexes totally overlaps that of Cu(I)—S distances for copper(I) complexes with the coordination number four.

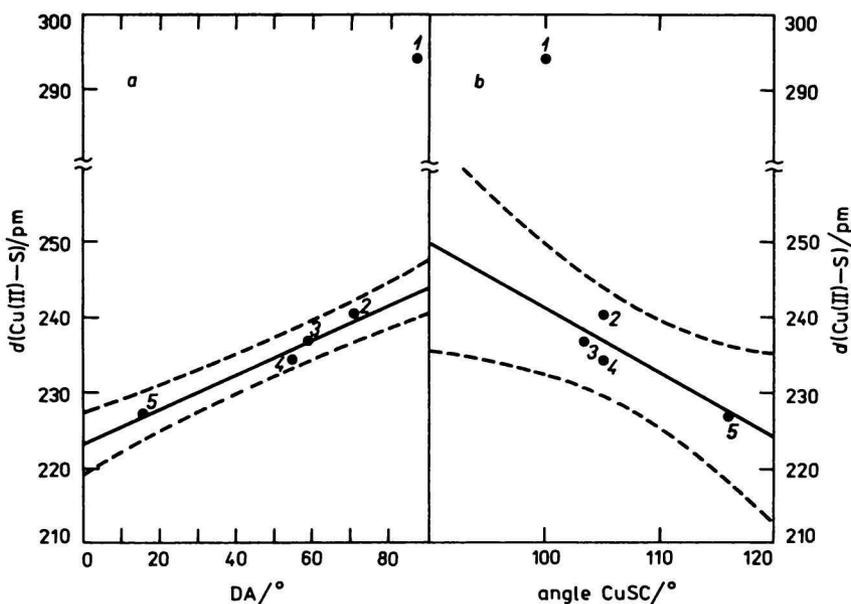


Fig. 2. Dependence of Cu—S distance in copper(II) complexes on dihedral angle DA (a) and CuSC angle (b).

Characteristics of lines:

$$a) \text{ Cu(II)—S/pm} = 223.4 + 0.2274 \text{ DA}/^\circ \quad (\rho = 0.98502)$$

$$b) \text{ Cu(II)—S/pm} = 325.8 - 0.8464 \text{ angle CuSC}/^\circ \quad (\rho = -0.88002)$$

The dashed line marks the reliability interval on the significance level 95 % (Student's distribution).

From the data of Fig. 2 it is evident that for copper(II) complexes (except $[\text{Cu}(\text{pic})_2(\text{tu})_2]$) there is a good correlation of Cu(II)—S distance with both parameters (DA and CuSC angle, respectively) which characterize orientation of the thiourea ligand. Also the almost identical values of Cu(II)—S distances obtained by extrapolation for $\text{DA} = 0^\circ$ and/or angle $\text{CuSC} = 120^\circ$, being 223.4 pm and 224.2 pm, respectively, are consistent with the assumption [10] that for planar arrangement of Cu(II) atom and the atoms of thiourea ligand the donor-acceptor bonding is realized by means of an electron pair from the nonbonding sp^2 -orbital of the sulfur atom. Besides it is interesting that the extrapolated values are within the reliability interval (Fig. 2) almost in accord with the sum of the covalent radius of sulfur (104 pm) and the value of 117.6 pm, often brought as the covalent radius of copper, though actually it is half of the distance copper—copper of the nearest copper atoms in the metallic copper [24].

However, the different slope of the two regression lines (Fig. 2) and the difference in Cu(II)—S distances extrapolated for $\text{DA} = 90^\circ$ (243.9 pm) and for angle $\text{CuSC} = 90^\circ$ (249.6 pm) indicates that these values do not correspond, *i.e.* they characterize different space orientation of Cu(II) and the thiourea ligand.

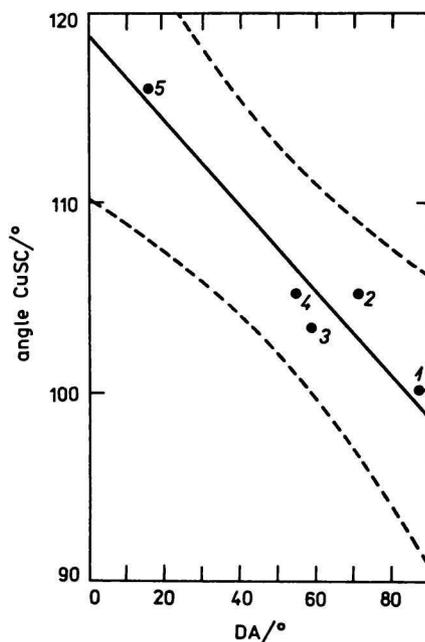


Fig. 3. Dependence of CuSC angle on the dihedral angle DA for copper(II) complexes. Characteristics of the line:

$$\text{angle CuSC}/^\circ = 118.7 - 0.2240 \text{ DA}/^\circ$$

$$(\rho = -0.93294)$$

The dashed line marks the reliability interval on the significance level 95 % (Student's distribution). The line characteristics were calculated from the data for complexes 2 to 5 (Table 1).

The dependence of the value of CuSC angle on that of DA for copper(II) complexes (Fig. 3) shows that between the parameters characterizing the space orientation of the thiourea molecule to Cu(II) there exists a good linear correlation.

tion. Also in this case the regression line shows that to $DA = 0^\circ$ corresponds angle $CuSC = (118.7 \pm 3.3)^\circ$ being in good agreement with foregoing results. Fig. 3 also demonstrates that to the maximum possible value of $DA = 90^\circ$ corresponds that of angle $CuSC = 98.6^\circ$; this means that the state, for which angle $CuSC = 90^\circ$ is probably unrealizable (*i.e.* hypothetical). The value of $Cu(II)$ —S distance 242.3 pm calculated for angle $CuSC = 98.6^\circ$ from linear regression (Fig. 2b) is in good agreement with that obtained by extrapolation of the dependence of $Cu(II)$ —S distance on DA value (Fig. 2a). Though it appears surprising that the values of angle $CuSC = 100.2^\circ$ and of $DA = 87.0^\circ$ found [15] for $[Cu(pic)_2(tu)_2]$ complex agree with the regression line in Fig. 3, yet at the same time this fact justifies to a certain extent the explanation of an expressively different $Cu(II)$ —S distance in this complex (influence of the coordination number, *i.e.* of the shape of the coordination polyhedron).

As it was already mentioned, the $Cu(I)$ —S distances are found in two comparatively narrow value intervals, in dependence on the coordination number of $Cu(I)$ atom. Similarly the interval of DA values (except one value for $[Cu_2(tu)_5]SO_4 \cdot 3H_2O$) and that of $CuSC$ angle values is relatively narrow. However, in contradiction to $Cu(I)$ —S distances, the DA and angle $CuSC$ values (Table 1) are not dependent on the $Cu(I)$ coordination number.

The calculated values of the linear regression parameters for the group of copper(I) complexes are in Table 2. In all the four cases the slope of the regression line is near zero, while the standard deviation of the slope is greater than the absolute value of the slope and also the values of correlation coefficients are small. The test of independence of $Cu(I)$ —S data on DA and $CuSC$ angle values evidenced (Table 2) that on the significance level 95% the $Cu(I)$ —S values may be considered to be independent of the space orientation of thiourea ligands and $Cu(I)$ —S distance is determined mainly by the type of coordination polyhedron.

Since the space orientation of thiourea ligands does not affect the $Cu(I)$ —S distances, it appeared interesting to estimate the relationship between DA and the $CuSC$ angle values also for the copper(I) complexes. From Table 2 it is clear that copper(I) complexes with the coordination number four exhibit a certain dependence of the two parameters characterizing the space orientation of thiourea ligands while for complexes with trigonal arrangement of thiourea ligands in coordination sphere of $Cu(I)$ the $CuSC$ angle does not depend on DA changes (Table 2). It is, however, interesting that for copper(I) complexes with the coordination number four the $CuSC$ angle value $(111.5 \pm 1.7)^\circ$ corresponds to $DA = 0^\circ$. That means that for an arrangement of copper atom and thiourea ligand in one plane ($DA = 0^\circ$), the $CuSC$ angle is significantly smaller than 120° .

The specific changes of parameters for copper(I) complexes can be understood, if we accept the conception of dative π -bond $Cu \overset{\curvearrowright}{\leftarrow} S$ (back donation) for

Table 2

Calculated values of linear regression parameters $y = a + bx$ and of independence tests for the group of copper(I) complexes

Correlated quantities		Regression parameters		Correlation coefficient	Independence test*	
y	x	$a \pm s_a$	$b \pm s_b$		$ t_{\text{calc}} $	t_{crit}
Cu(I)—S/pm ^a	DA/°	232.3 ± 0.9	0.004 ± 0.053	0.01792	0.08	2.0860
Cu(I)—S/pm ^b	DA/°	224.0 ± 0.7	− 0.027 ± 0.024	− 0.49616	1.14	2.7764
Cu(I)—S/pm ^a	angle CuSC/°	232.8 ± 20.3	− 0.006 ± 0.186	− 0.00711	0.03	2.0930
Cu(I)—S/pm ^b	angle CuSC/°	226.9 ± 40.4	− 0.033 ± 0.372	− 0.04373	0.09	2.7764
Angle CuSC/° ^a	DA/°	111.5 ± 1.7	− 0.186 ± 0.098	− 0.67431	3.98	2.0930
Angle CuSC/° ^b	DA/°	108.8 ± 1.1	− 0.004 ± 0.036	− 0.05374	0.11	2.7764

* $|t_{\text{calc}}|$ = the calculated value of testing characteristic, t_{crit} = critical value of testing characteristic for the significance level 95 % (Student's distribution).

a) Data for copper(I) complexes with the coordination number four; b) data for copper(I) complexes with the coordination number three.

these complexes. Then *e.g.* the change of Cu(I)—S distances dependent on the number of thiourea ligand in the coordination of Cu(I) sphere is logical. The value of CuSC angle $< 120^\circ$ can be understood as a consequence of such a space orientation of thiourea ligands allowing an optimum overlap of occupied *d*-orbitals of Cu(I) with suitable orbitals of thiourea. The sum of covalent radii of copper (135 pm) for tetrahedral surroundings [24] and of sulfur (104 pm), being higher (239 pm) than the mean value of Cu(I)—S distance for copper(I) complexes (Table 2) corresponds with the conception of dative π -bonds. The lower value of Cu(I)—S distance for trigonal coordination is probably significantly evoked as by the increased contribution of dative π -bond for a smaller number of thiourea ligands, as also by the hybrid state (sp^2) of the copper atom.

In the pentacoordinate copper(II) complexes (as a consequence of the hybrid state dsp^3 , and because of the decreased ability of Cu(II) to form dative π -bonds) the Cu(II)—S distance should be greater than for copper(I) complexes. However, the Cu(II)—S distance in [Cu(salalgly)(tu)] complex (227.3 pm) is significantly shorter than in the other copper(II) complexes and also in tetracoordinate copper(I) complexes with thiourea. This unexpected short bond length can be caused by significant contribution of dative π -bond to the total bonding character. Complex [Cu(salalgly)(tu)] exhibits favourable conditions for dative π -bond formation since the presence of the Schiff's base dianion ligand causes the complex to be electroneutral and the position of the thiourea sulfur atom in the equatorial plane allows an effective overlap with the occupied *d*-orbitals of the copper atom. The stabilization of Cu(II) relative to Cu(I) in spite of dative π -bond between copper(II) atom and thiourea may be evoked by square planar coordination of copper(II) which is moreover fixed by dimeric structure of [Cu(salalgly)(tu)] complex and by effective hydrogen bonds.

The shortening of Cu(II)—S bond length by the increased contribution of dative π -bond does not cause an elongation of C—S bond (Table 1) in thiourea since dative π -bond is probably realized rather by means of *d*-orbitals of the sulfur atom than the antibonding π^* -orbital of the thiourea ligand. The preferential use of *d*-orbitals of the thiourea sulfur atom for the formation of dative π -bond is suggested [25] in explaining the comparatively high value of stability constants of the complex cations [Cu(tu)₃]⁺ and [Cu(tu)₄]⁺ and of Cu(I) complexes with other sulfur-containing ligands (*e.g.* 2-mercaptoethanol).

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