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# SYNTHESIS, SPECTROSCOPY, AND XRD OF COPPER (II) COMPLEXES BASED ON AROYL HYDRAZONES 2-TENOYLTRIFLUOROACETONE

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## ANNOTATION

Complexes Of Copper (II) With The Composition $CuL{\cdot}NH_3$ Were Synthesized And Investigated In The Interaction Of Alcohol Solutions Of Para-Substituted Aroylhydrazones Of 2-Tenoyltrifluoroacetylmethane ($H_2L^1$-$H_2L^4$)And An Aqueous Ammonia Solution Of Copper (II) Acetate In An Equimolar Ratio. The Composition And Structure Of Copper (II) Complexes Were Studied By Elemental Analysis, IR And EPR Spectroscopy, And The Grown $CuL^2{\cdot}NH_3$ Single Crystals Based On Para-Methylbenzoylhydrazone 1- (2-Tenoyl) -3,3,3-Trifluoroacetone Were Studied By X-Ray Diffraction Analysis.

**Key words:** complex, spectroscopy, substituent, organic ligands, solution

## INTRODUCTION

Hydrazones of fluorinated β-dicarbonyl compounds currently occupy a leading position among organic ligands used to obtain coordination compounds with metals. The introduction of a fluorine atom into ligand molecules leads to an increase in their complexing activity or a change in the spectrum of action. The complexation creates a competition between the electronic properties of the complexing ion with the implementation of the most favorable coordination environment on the one hand, the electronic nature and stereochemical properties of organic ligands on the other hand [1-3].

## EXPERIMENTAL PART

**Synthesis of the $CuL^1{\cdot}NH_3$ complex.** A hot solution of 0.34 g (0.001 mol) of benzoylhydrazone 1- (2-tenoyl) -3,3,3-trifluoroacetone ($H_2L^1$) in 30 ml of ethanol was poured into a round-bottom flask of 100 ml, and then an aqueous ammonia solution of 0.2 g was added with stirring (0.001 mol) copper (II) acetate. The reaction flask was heated under reflux for 30 minutes. After 2 days, the precipitated green precipitate was filtered off, washed with water, ethanol, and dried in air. The yield of the product $CuC_{15}H_{12}N_3O_2SF_3$ is 0.27 g (65%).

Other complexes $CuL^2{\cdot}NH_3$-$CuL^4{\cdot}NH_3$ were synthesized in a similar way. The results of elemental analysis, the yield and melting points of the complexes are given in Table 1.

Table 1. Results of elemental analysis, yields and melting points of Cu (II) complexes based on benzoylhydrazones 1- (2-tenoyl) -3,3,3-trifluoroacetone

| Compound | Gross-formula | $T_{mel.}$, °C | Output, % | Content (found / calculated), % | | |
|---|---|---|---|---|---|---|
| | | | | M | C | H |
| $CuL^1 \cdot NH_3$ | $CuC_{15}H_{12}N_3O_2SF_3$ | 235 | 65 | 15.02/15.17 | 42.85/43.01 | 2.60/2.89 |
| $CuL^2 \cdot NH_3$ | $CuC_{16}H_{14}N_3O_2SF_3$ | 261 | 78 | 14.50/14.68 | 44.33/44.39 | 2.15/3.26 |
| $CuL^3 \cdot NH_3$ | $CuC_{16}H_{14}N_3O_3SF_3$ | * | 75 | 14.00/14.16 | 42.60/42.81 | 3.10/3.14 |
| $CuL^4 \cdot NH_3$ | $CuC_{15}H_{11}N_3O_2SClF_3$ | 248 | 67 | 13.97/14.02 | 32.61/39.74 | 2.36/2.45 |

* Melts with decomposition.

The EPR spectra of polycrystalline samples and liquid solutions in toluene were recorded on an SE/X-2542 radio spectrometer (Radiopan) with an operating frequency of 9.4 GHz. The magnetic field was calibrated using an NMR magnetometer.

X-ray diffraction analysis of the $CuL^2{\cdot}NH_3$ complex was carried out on a Bruker P4 automatic diffractometer (λ $MoK_\alpha$-radiation, graphite monochromator, ω--scanning, $2\theta_{max} = 50^o$. Scanning interval θ from 2.5 ° to 25 °, index ranges -8 =< h =<9, -14=<k=<

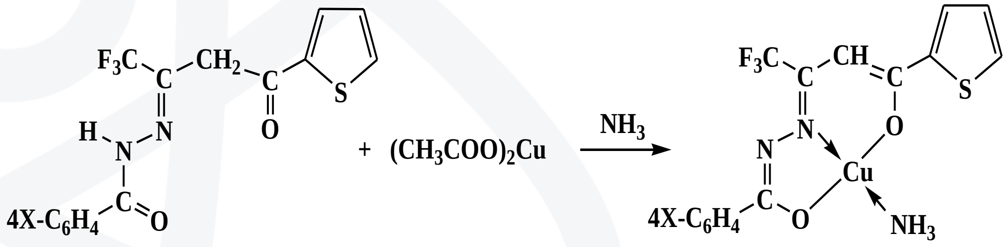
15, 0=< l=<11, crystal dimensions 0.1 x 0.2 x 0.4 mm. The structure was solved by the direct method with a total number of measured reflections of 3190 and refined by the full-matrix least squares method in the anisotropic approximation of non-hydrogen atoms for 2840 independent reflections $R_{int} = 0.0603$ with 266 refinement parameters with a GOOF factor = 1.092 using the SHELXL [4] and Olex2 [5] software package. Hydrogen atoms were localized from difference syntheses and refined isotropically. Convergence factors: $R_1 = 0.052$ and $wR_2 = 0.153$ for reflections with $I > 2\sigma(I)$ Residual electron density $\Delta\rho_{max}/\Delta\rho_{min} = 0.99/-0.63$ e/Å$^3$.

## RESULTS AND THEIR DISCUSSION

We have studied the condensation reaction and the tautomeric behavior of the condensation products of aromatic acid hydrazides with 1,3-diketone, which carries a trifluoromethyl group and an electron-donor thienyl group as a strong electron-withdrawing substituent [3, 6, 7]. The selected β-dicarbonyl compound is unsymmetrical, and its interaction with nucleophilic reagents can lead to the formation of positional isomers. The reaction of 1- (2-tenoyl) -3,3,3-trifluoroacetone with aromatic acid hydrazides, $NH_2NHCOC_6H_4X$-4, under mild conditions (ethyl alcohol as a reaction medium, room temperature, absence of catalysts) leads to, as indicated, to the condensation products of trifluoroacetyl carbonyl, which have a hydrazone structure in the crystalline state [3,6,8-10].

The interaction of equimolar amounts of an aqueous ammonia solution of copper (II) acetate and an alcoholic solution of aroylhydrazones 1- (2-tenoyl) -3,3,3-trifluoroacetone was used to synthesize copper (II) $CuL^n{\cdot}NH_3$ complexes, where $L^n$ - are doubly deprotonated residues of the ligands $H_2L^1$-$H_2L^4$. The composition and structure of the obtained complexes were established by the methods of elemental analysis, IR-, EPR spectroscopy and X-ray diffraction analysis. The obtained IQS of copper (II) according to the IR and EPR spectra in the solid state and in solution have the following structure:

X = H ($CuL^1{\cdot}NH_3$); $CH_3$ ($CuL^2{\cdot}NH_3$); $OCH_3$ ($CuL^3{\cdot}NH_3$); Cl ($CuL^4{\cdot}NH_3$).



The IR spectra of $CuL\cdot NH_3$ complexes lack absorption bands in the range of 1660-1670 and 3400 $cm^{-1}$, which are characteristic of free ligands. This indicates the deprotonation of the ligands during complexation. The spectra are characterized by absorption bands at 3344-3382 $см^{-1}$,which are apparently caused by symmetric and antisymmetric stretching vibrations of the coordinated $NH_3$ molecule. The spectrum contains a number of bands of medium and strong intensity in the range of 1068-1075, 1494-1507, 1523-1532 and 1570-1600 $см^{-1}$,corresponding to stretching, deformation, stretching-deformation vibrations of formally single and double bonds of five- and six-membered metal cycles, which is generally consistent with the proposed structure [1-3,6,7]. In many respects, the IR spectra of the complexes are identical with the IR spectra of the previously studied copper (II) complexes in [1,3,6,7].

The conclusions on the structure of copper (II) complexes based on the results of IR spectra were supplemented by the data of EPR spectra. According to these data, the obtained VCS of Cu (II) in a solution of chloroform and toluene have EPR spectra characteristic of mononuclear copper (II) complexes of flat-square structure. They are similar to the spectra of previously studied compounds and represent a superposition of spectra from $^{63}Cu$ and $^{65}Cu$ nuclei ($I_{Cu} = 3/2$).

Isotropic EPR spectra are described by symmetric SG of the form (1) with four HFS lines, equidistant components of different intensities and line widths:

$$\bar{H} = g\cdot\beta\cdot H_o\cdot S + \langle a_{Cu}\rangle I_{cu}\cdot S + a_{Nj}\cdot I_{Nj}\cdot S \qquad (1)$$

where $S = ½$, β- is the Bohr magneton for an electron, $I_{Cu} = 3/2$ is the spin of the nucleus of the copper atom, $I_N$- is the spin of the nucleus of the nitrogen atom. The narrowest high-field component exhibits lines from two isotopes $^{63}Cu$ and $^{65}Cu$ (Table 2, Fig. 1) [1,3,6,7,11].

It should be noted the small width of the lines in the EPR spectra of the complexes in comparison with the previously studied analogous complex compounds with the coordination sphere Cu [N2, O2]. This can be explained by the influence of the sulfur atom of the thienyl heterocyclic ring present in the terminal position of the β-dicarbonyl part of the ligand molecule. The presence of two joined five- and six-membered metallocycles in the copper (II) complex compounds, regardless of the nature of the coordinated atoms, leads to a planar configuration. Therefore, the observed changes in the parameters of the EPR spectrum (g-factor and constants of CTC and DSTC, Table 2, Fig. 1) should be explained by the different electronic nature of substituents in the 4 position of the phenyl substituent of the benzoyl part of the molecule. It is well known that substitution of long-range substituents with more electron-donating groups leads to an increase in the g-factor and a decrease in the CTC constant (Table 2.).

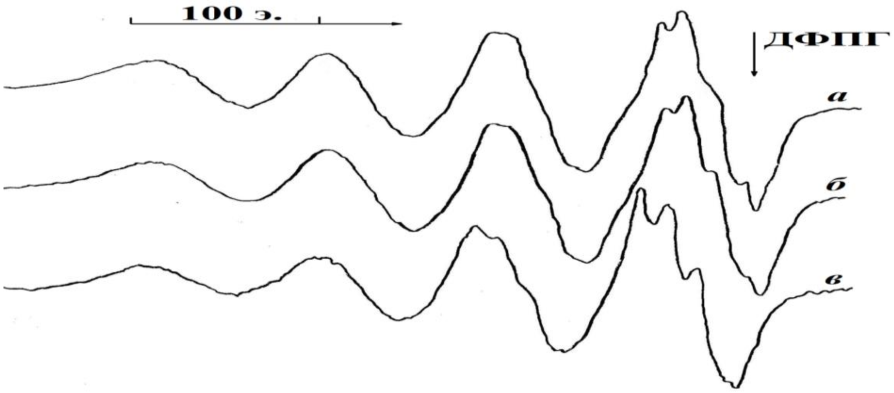


Fig. 1. EPR spectra of complexes $CuL^1 \cdot NH_3$ (a), $CuL^2 \cdot NH_3$ (b), $CuL^4 \cdot NH_3$ (c) in a toluene solution at 293 K.

Table 2. Parameters of the EPR spectra of copper (II) complexes in toluene solution at 293 K

| Compound | <g><br>± 0.001 | $a_{Cu}$,<br>$cm^{-1}$ | $a_N$<br>± 0.1 E. | $\alpha^2$ | $(\alpha')^2$ |
|---|---|---|---|---|---|
| $CuL^1 \cdot NH_3$ | 2.102 | 93 | 11.3 | 0.85 | 0.15 |
| $CuL^2 \cdot NH_3$ | 2.101 | 89.9 | 7.8 | 0.82 | 0.18 |
| $CuL^3 \cdot NH_3$ | 2.099 | 92.19 | 9.4 | 0.71 | 0.29 |
| $CuL^4 \cdot NH_3$ | 2.104 | 87.54 | 12.4 | 0.82 | 0.18 |

These conclusions are confirmed by the value of the degree of covalence of the copper-ligand bond ($\alpha^2$ = 0.71–0.85), calculated from the isotropic EPR parameters according to the well-known formula (2) [11]:

$$\alpha^2 = \frac{1}{0{,}43}\left(\frac{a_{Cu}}{0{,}036} + g - 2\right) + 0{,}02 \qquad (2)$$

Coefficients $\alpha$ and $\alpha'$- at the atomic orbitals of copper ($d_{x^2-y^2}$) and coordinated atoms of the ligands, characterize the degree of covalence of the copper-ligand bond. If $\alpha^2$ and $(\alpha')^2$are equal to 0.5, then the metal-ligand bond is purely covalent. In the case when $\alpha^2$ =1 and $(\alpha')^2$= 0, the nature of the bond will be ionic. The semantic expression of the coefficient a can be expressed through its square as the probability density of finding an unpaired electron in the $|x^2-y^2\rangle$. orbital. Then the quantity $(\alpha')^2$ naturally determines the degree of delocalization of the unpaired electron on the orbital of the ligand atoms.

In compounds $CuL^2{\cdot}NH_3$ and $CuL^3{\cdot}NH_3$, where substituents $CH_3$ and $OCH_3$ are introduced in the para-position of the phenyl nucleus, which weakly affects the parameters of the SG. At the same time, the appearance of a chlorine atom in the 4-position of the phenyl ring in the $CuL^4{\cdot}NH_3$ complex leads to an increase in the g factor and a decrease in the CTC constant. The values of the coefficients $\alpha^2$ and $(\alpha')^2$ indicate that in these compounds the degree of covalence of the Cu – N bond changes significantly depending on the nature of the substituents in the benzene ring. If it has a maximum value for the $CuL^1{\cdot}NH_3$ complex ($\alpha^2$= 0.85) compared to other complexes, the smallest value was recorded for the complex compound $CuL^3{\cdot}NH_3$ ($\alpha^2$= 0.71) with a methoxyl substituent. The degree of covalence for the complex compounds $CuL^2{\cdot}NH_3$ and $CuL^4{\cdot}NH_3$ has the same value (Table 2).

Concluding the discussion of the results of EPR spectroscopy of copper (II) complex compounds, we note that the resolution of the DSTC lines upon changing the H substituent to $CH_3$ or $OCH_3$ leads to a decrease in the constant, and upon the introduction of a chlorine atom, the DSTC constant increases.

The conclusions on the planar structure of copper (II) complexes with tridentate coordination of the ligand dianion, made from the results of IR and EPR spectra, were unambiguously proved by X-ray diffraction analysis for the grown $CuL^2{\cdot}NH_3$single crystal. $C_{16}H_{14}CuF_3N_3O_2S{\cdot}H_2O$ crystals are triclinic (M = 450.92): a = 7.7000(15), b = 12.977(3), c = 9.567(6) Å, $\alpha$ = 80.40(3)°, $\beta$ = 84.07(3)°, $\gamma$ =74.12(3)°, V = 904.9(6) Å$^3$, $\rho$(calc.) = 1.655 g / cm3, Z = 2, space gr. $P\overline{1}$.

In the $CuL^2{\cdot}NH_3$ molecule, the copper atom is located in the center of a square-planar polyhedron consisting of the tridentate residue of the ligand [Cu–O(1) 1.900(3), Cu–O(2) 1.940(3), Cu–N(1) 1.913(4) and $NH_3$ Cu–N(3) 1.980(4) molecules (Table 3). The difference (0.067 Å) between the lengths of Cu – N (1) and Cu – N (3) bonds is explained by the presence of a chelate effect for the tridentate residue of the ligand dianion and is consistent with the differences in chemical bonds of similar complexes [2,3,6,12-16]. The bond angles O (1) CuO (2) and N (1) CuN (3) are 175.83 (12) and 176.06 (18) °, respectively. The bond angles

O (1) CuN (1), O (1) CuN (3), O (2) CuN (1), and O (2) CuN (3) are within 94.85 (14), 88.58 (17) , 81.25 (13) and 95.37 (17) ° respectively. The deviation of these angles from the values of the right angle (90 °) is explained by the size of the five- and six-membered metal cycles, as well as by the presence of a conjugation system (Table 3). The bond angles O(1)CuO(2) and N(1)CuN(3) are 175.83 (12) and 176.06 (18) $^{o}$, respectively.

An analysis of the bond lengths in the ligand residue of the complex shows that the C (9) –C (10), N (1) –C (7) bonds are predominantly double (Table 3).

Table 3. Selected bond lengths and bond angles in the molecule $CuL^2 \cdot NH_3$

| Bonds | d, Å | Bonds | d, Å |
|---|---|---|---|
| Cu – O(1) | 1.900 (3) | C(2) – C(3) | 1.452 (6) |
| Cu – N(1) | 1.913 (4) | C(3) – C(4) | 1.469 (6) |
| Cu – O(2) | 1.940 (3) | C(4) – C(5) | 1.470 (6) |
| Cu – N(3) | 1.980 (4) | C(5) – C(6) | 1.386 (6) |
| S – C(1) | 1.672 (6) | C(6) – C(7) | 1.398 (6) |
| S – C(4) | 1.702 (4) | C(7) – C(8) | 1.523 (6) |
| O(1) – C(5) | 1.294 (5) | C(9) – O(2) | 1.307 (5) |
| O(2) – C(9) | 1.307 (5) | C(9) – C(10) | 1.487 (6) |
| N(1) – C(7) | 1.319 (5) | C(10) – C(15) | 1.393 (6) |
| N(1) – N(2) | 1.403 (5) | C(10) – C(11) | 1.395 (6) |
| N(2) – C(9) | 1.307 (5) | C(11) – C(12) | 1.376 (6) |
| F(1) – C(8) | 1.316 (6) | C(12) – C(13) | 1.395 (6) |
| F(2) – C(8) | 1.342 (6) | C(13) – C(14) | 1.390 (6) |
| F(3) – C(8) | 1.336 (7) | C(13) – C(16) | 1.506 (6) |
| C(1) – C(2) | 1.320 (8) | C(14) – C(15) | 1.368 (6) |
| Angle | ω, deg | Angle | ω, deg |
| O(1)–Cu–N(1) | 94.85 (14) | C(6)–C(5)–C(4) | 120.0 (4) |
| O(1)–Cu–O(2) | 175.83 (12) | C(5)–C(6)–C(7) | 125.7 (4) |
| N(1)–Cu–O(2) | 81.25 (13) | N(1)–C(7)–C(6) | 123.0 (4) |
| O(1)–Cu–O(2) | 175.83 (12) | N(1)–C(7)–C(8) | 118.8 (4) |
| N(1)–Cu–O(2) | 81.25 (13) | C(6)–C(7)–C(8) | 118.2 (4) |
| O(1)–Cu–N(3) | 88.58 (17) | F(1)–C(8)–F(3) | 107.1 (4) |
| N(1)–Cu–N(3) | 176.06 (18) | F(1)–C(8)–F(2) | 106.3 (4) |
| O(2)–Cu–N(3) | 95.37 (17) | F(3)–C(8)–F(2) | 105.8 (4) |
| O(2)–Cu–N(3) | 95.37 (17) | F(1)–C(8)–C(7) | 113.3 (4) |
| C(1)–S–C(4) | 92.6 (3) | F(3)–C(8)–C(7) | 112.2 (4) |
| C(5)–O(1)–Cu | 124.7 (3) | F(2)–C(8)–C(7) | 111.7 (4) |
| C(9)–O(2)–Cu | 110.5 (2) | N(2)–C(9)–O(2) | 123.9 (4) |
| C(7)–N(1)–N(2) | 119.2 (3) | N(2)–C(9)–C(10) | 117.4 (4) |
| Angle | ω, deg | Angle | ω, deg |
| C(7)–N(1)–Cu | 125.6 (3) | O(2)–C(9)–C(10) | 118.7 (3) |
| N(2)–N(1)–Cu | 115.1 (3) | C(15)–C(10)–C(11) | 118.2 (4) |
| C(9)–N(2)–N(1) | 109.2 (3) | C(15)–C(10)–C(9) | 120.3 (4) |
| C(2)–C(1)–S | 113.3 (4) | C(11)–C(10)–C(9) | 121.5 (4) |
| C(1)–C(2)–C(3) | 116.2 (5) | C(12)–C(11)–C(10) | 120.9 (4) |
| C(2)–C(3)–C(4) | 105.5 (4) | C(11)–C(12)–C(13) | 121.0 (4) |
| C(3)–C(4)–C(5) | 124.9 (4) | C(14)–C(13)–C(12) | 117.6 (4) |
| C(3)–C(4)–S | 112.2 (3) | C(14)–(13)–C(16) | 120.8 (4) |
| C(5)–C(4)–S | 122.9 (3) | C(12)–C(13)–C(16) | 121.6 (4) |
| O(1)–C(5)–C(6) | 125.6 (4) | C(15)–C(14)–C(13) | 121.9 (4) |
| O(1)–C(5)–C(4) | 114.4 (4) | C(14)–C(15)–C(10) | 120.5 (4) |

In the complex molecule, the distance metal – phenoxide oxygen atom [Cu–O(2)] is somewhat longer than the distance metal –α-oxyazine oxygen atom [Cu–O(1)] (Table

3, Fig. 2a), which correlates with the values of other similar complexes with chelating ligands [2,3].

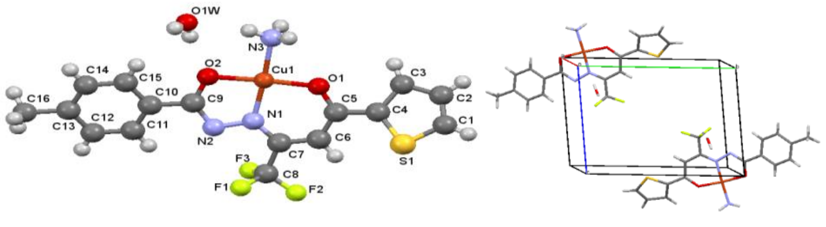


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Fig. 2. The crystal structure of the complex compound $CuL^2 \cdot NH_3$-(a) and the molecular packing of the cell - (b).

The polyhedron of the CuO(1)O(2)N(1)N(3) metallocycle is almost flat, the maximum yield of atoms from the “middle” plane of the polyhedron does not exceed 0.0296 Å. In the complex, the five- and six-membered metallocycles are practically coplanar, the deviation of atoms from the “middle” planes is 0.0130 and 0.0272 Å, respectively, for the first and second planes, and the angle between these metal chelates is 1.373° (Table 4).

Table 4. Deviation of atoms from the “middle” planes in the structure of $CuL^2 \cdot NH_3$

| The atom and its deflection, Å | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cu<br>0.0045 | O(1)<br>0.0279 | O(2)<br>0.0291 | N(1)<br>-0.0323 | N(3)<br>-0.0291 | N(2)*<br>-0.0662 | C(5)*<br>-0.0926 | C(7)*<br>-0,0418 | C(9)*<br>-0,0436 |
| Cu<br>-0.0215 | O(1)<br>0.0443 | N(1)<br>-0.0078 | C(5)<br>-0.0296 | C(6)<br>-0.0147 | C(7)<br>0.0293 | O(2)*<br>-0,0365 | N(2)*<br>-0,0575 | C(4)*<br>-0,1259 |
| Cu<br>-0.0136 | O(2)<br>0.0175 | N(1)<br>0.0129 | N(2)<br>-0.0035 | C(9)<br>-0.0134 | N(3)*<br>-0,1127 | C(7)*<br>0,0305 | C(10)*<br>-0,0869 | |
| C(10)<br>-0.0067 | C(11)<br>-0.0008 | C(12)<br>0.0060 | C(13)<br>-0.0035 | C(14)<br>-0.0041 | C(15)<br>0.0093 | C(9)*<br>-0,0550 | C(16)*<br>-0,0126 | |
| S<br>-0.0110 | C(1)<br>-0.0021 | C(2)<br>0.0158 | C(3)<br>-0.0236 | C(4)<br>0.0209 | C(5)*<br>0,0466 | | | |
| * – Atoms not included in the calculation of this plane | | | | | | | | |

## CONCLUSION

This correlates well with the values of the torsion angle O(1)CuN(1)N(2), which is -1.9°. The benzene ring and the five-membered metal cycle CuO(2)C(9)N(2)N(1) rotate somewhat (13.943°) relative to each other in space, as evidenced by the values of the torsion angles O(2)C(9)C(10)C(11) equal to 167.7 (4)° and O(2)C(9)C(10)C(15) -13.5 (6)°. The planes of the six-membered metal cycle and the thienyl ring are also rotated relative to each other, as indicated by the values of the torsion angles S(1)C(4)C(5)O(1) and S(1)C(4)C(5)C(6), which are equal to 156.7 (3) and 23.8 (6)°, respectively [2,3,14-16].

The molecular packing of the cell in the $CuL^2 \cdot NH_3$ crystal is shown in Fig.2b. Crystallization water takes part in the formation of the intermolecular hydrogen bond O1W–H2W···O(2) (+x,+y,+z) и O1W–H1W···N(2) (-x,-y1,-z), the bond lengths are: O1–H2 0.820(1) Å,H···O2 2.055(21) Å, O1···O2 2.857(5) Å, угол O1–H2···O2 angle is 166 (8)$^o$ ; the O1–H1 0,820(1) Å, H1···N2 2.444(26) Å, O1···N2 3.211(6) Å, and the O1–H1···N2angle is 156 (6)$^o$, respectively. Molecules in a cell are located along a centered motif along the x-axis.

Thus, as a result of studies by IR, EPR spectroscopy and X-ray diffraction analysis, it was found that in the process of complexation, regardless of the geometric structure of the initial ligands, the 5-hydroxypyrazoline ring opens.

The doubly deprotonated residue of 1-aroyl-3-aryl-5-hydroxy-2-pyrazolines in the linear enhydrazine-α-hydroxyazine form is coordinated to the central ion by three donor atoms $(N,O_2)$, forming conjugated five- and six-membered metallocycles $[CuN_2O_2]$, the fourth place is occupied by the ammonia molecule.

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