COMPLEX COMPOUNDS OF 1-(2-THENOYL)-3,3,3-TRIFLUOROACETONE WITH METALS

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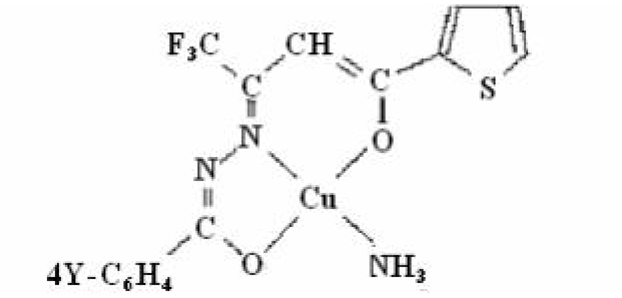
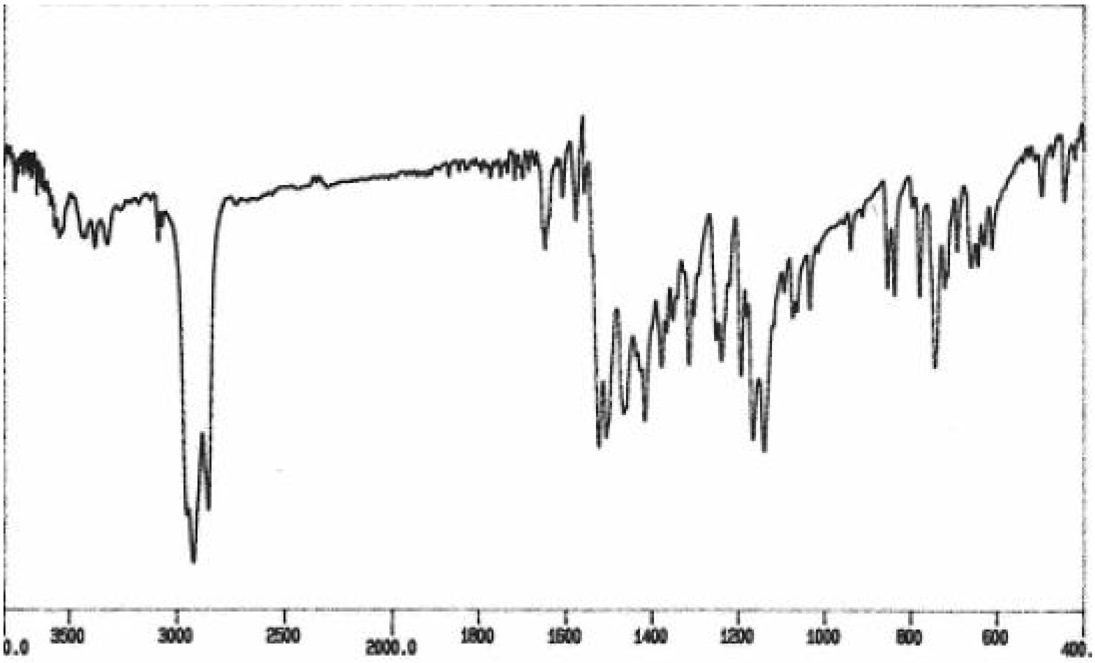
Abstract: Copper(II) complex compounds with aroylhydrazones of 1(2-thenoyl)-3,3,3-trifluoroacetone were synthesized by the interaction of equimolar amounts of alcoholic solutions of the ligands H2L12–H2L17 and an ammonia solution copper(II) acetate, similar to the corresponding nickel(II) complex compounds.

Key words : copper (II) with aroylhydrazones of 1(2-thenoyl)-3,3,3-trifluoroacetone , IR spectra , OCH3 (CuL14 NH3), Br (CuL16 NH3).

IR The spectra of nickel(II) complexes (XLVII) with the same ligands (XLVI) are consistent with the corresponding copper complexes in terms of characteristic absorption bands and fingerprint identity. Based on the IR spectra and elemental analysis results, the following square-planar structure XLIX can be ascribed to the obtained copper(II) complexes of the composition CuL · NH3:



Y = H (CuL12 NH3); CH3 (CuL13 NH3); OCH3 (CuL14 NH3); Cl (CuL15·NH3); Br (CuL16 NH3); NO2 (CuL17 NH3). Since the IR spectra of nickel(II), zinc(II), and copper(II) complexes with the same ligands are very similar, and therefore we will not discuss them in detail, but limit ourselves to presenting one of the IR spectra; Fig. 20 shows the spectrum of the copper(II) complex compound CuL13 NH3. The copper(II) complexes (XLIX) obtained according to the EPR spectra in chloroform and toluene solution have a planar square structure. The EPR spectra are similar to the spectra of the previously studied compounds XLV and represent a superposition of the spectra from the 63Cu and 65Cu nuclei (I Cu = 3⁄2) with four hyperfine structure lines (Fig. 21 a, b, Table 19). To reduce the line width and improve spectral resolution, the complex solutions were degassed by repeated freezing and thawing with liquid nitrogen before recording the EPR spectra. The narrowest high-field component exhibits lines from two copper isotopes, 63Cu and 65Cu.



IR spectrum of the copper(II) complex compound CuL13·NH3 structure

XLIX based on 1-para-toluyl-3-trifluoromethyl-5-hydroxy-5-thienyl-2-pyrazoline (H2L13). All this clearly indicates a square-planar structure of the coordination sphere of the central copper(II) atom with trans-located [N2,O2] atoms. It is worth noting the small line width in the EPR spectra of complexes (LIX) compared to LIV or with previously studied similar complex compounds [76, 78, 90, 119, 154, 159] with the coordination sphere of 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. When passing from the frequency sweep to the field sweep, even lines with equal values broaden unequally. The mechanism of non-uniform line broadening in liquid solutions leads to the conservation of information on the anisotropic tensors of magnetic interactions and they are described as follows-

following equation [167–169]: $H = \alpha i + \beta im + \gamma im2$ (3) where m is the projection of the nuclear spin of the copper atom in the direction of the external magnetic field; α−, β−, γ are coefficients due to different contributions to the relaxation mechanisms; i = x, y, z.

Table 1.

Parameters of the EPR spectra of copper(II) complexes of structure XLIX

in a toluene solution at room temperature

Соединение	<g> ± 0,001	a_{Cu}, $см^{-1}$	a_N * ± 0,1 Э.	α^2	$(\alpha')^2$
$CuL^{12}{\cdot}NH_3$	2,102	93	11,3	0,85	0,15
$CuL^{13}{\cdot}NH_3$	2,101	89,9	7,8	0,82	0,18
$CuL^{14}{\cdot}NH_3$	2,099	92,19	9,4	0,71	0,29
$CuL^{15}{\cdot}NH_3$	2,104	87,54	12,4	0,82	0,18

Note * − In the EPR spectrum, due to line broadening under the influence of

electronegative fluorine atoms DSTS from two nonequivalent atoms
nitrogen is poorly resolved. The presence of two fused five- and six-membered metallocycles in copper(II) complexes, regardless of the nature of the coordinated atoms, leads to a planar configuration. Therefore, the observed changes in the EPR spectrum parameters (g-factor and the HTS and DSTS constants, Table 19) should be explained by the different electronic nature of the substituents at position 4 of the phenyl substituent of the benzoyl part of the molecule. It is well known that the substitution of distant substituents with more electron-donating groups leads to an increase in the g-factor and a decrease in the STS constant (Table 19). At the same time, it is known that the data on the influence of the composition of substituents on the STS and DSTS constants are somewhat contradictory [90,119,154]. In the studied copper (II) compounds, unpaired electrons are located in the B1g molecular orbital, the wave function of which is described by the following expression [157, 158]:
Where α And α1 - coefficients for the atomic orbitals of copper (dx2–y2) and

coordinated atoms of ligands (δi), respectively. Semantic expression

the expression of the coefficient α in equations (4) can be expressed through its square

as the probability density of finding an unpaired electron in an orbital

| x2 – y2 〉. Then the value of (α1)2, naturally, determines the degree of delocalization of the unpaired electron in the orbital of the ligand atoms. From equation (4) it follows that the coefficients α and α1 characterize the degree of covalency of the copper-ligand bond, the values of which can be calculated using formula (1). If α2 and (α1)2 are equal to 0.5, then the metal-ligand bond is purely covalent. In the case when α2 = 1 and (α1)2 = 0, the nature of the bond will

$$\varphi_{B1g} = \alpha dx^2 - y^2 - \frac{\alpha'(\delta_1 - \delta_2 + \delta_3 - \delta_4)}{2} \qquad (4)$$

be purely ionic. In the compounds CuL13 · NH3 and CuL14 · NH3, in which the hydrogen atom in the para-position of the phenyl ring is replaced by a substituent Y = methyl or methoxyl group, it has little effect on the parameters of the covalent bond. At the same time, the appearance of a chlorine atom in the phenyl substituent in the CuL15 · NH3 complex compound leads to an increase in the g-factor and a decrease in the HTS constant. The semantic values of the coefficients α2 and (α1)2 indicate that in these compounds the degree of covalence of the Cu – N bond varies significantly depending on the nature of the substituents in the benzene ring. While it has the maximum value for the CuL12 · NH3 complex (α2 = 0.85) compared to other complexes, the lowest value is recorded for the CuL13 · NH3 complex (α2 = 0.71) with a methoxyl substituent. The degree of covalence for the CuL13 · NH3 and CuL15 · NH3 complex compounds has the same value (α2 = 0.82). In conclusion of the discussion of the results of EPR spectroscopy of copper(II) complex compounds of structure LIX, we note that the resolution of the DSTS lines when the substituent H is changed to CH3 or OCH3, the constant decreases, and when a chlorine atom is introduced, the DSTS constant increases.

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