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Anomalous line broadening in the ESR spectra of copper(II) dithizonate

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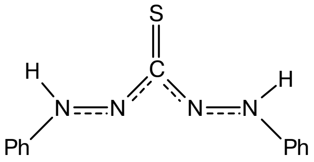
The structure of the copper(II) complex with dithizone (H_2Dz) was studied by ESR spectroscopy. The lines of the ESR spectra of the $Cu(HDz)_2$ complex in solutions are so broad that the superhyperfine structure (SHFS) from the ligand atoms is unobservable and even the hyperfine structure (HFS) from the copper nuclei is poorly resolved. In polycrystalline magnetically dilute powders with the ratio $Ni(HDz)_2 : Cu(HDz)_2 = 60 : 1$, the SHFS from the N atoms is well resolved in both perpendicular and parallel orientations. The copper(II) complex with dithizone has a square-planar structure in both liquid solutions and $Ni(HDz)_2$ matrix. Reasons for the unusual linewidths in the ESR spectra of $Cu(HDz)_2$ are discussed.

Key words: copper(II) complexes, dithizone, ESR spectroscopy, superhyperfine structure, distortions, relaxation.

Structures of coordination compounds in the solid phase are usually established by single crystal X-ray diffraction analysis. However, the structures of coordination compounds in the solid phase and in solutions are often different. Reliable information on their geometric structure in solutions is of doubtless interest. This is especially important for complexes with polyfunctional and polydentate ligands, such as diphenylthiocarbazone* (dithizone, H_2Dz).

Dithizone is widely used in analytical chemistry for detecting metal traces.[1] According to published data,[1] dithizone can act as both singly $(HDz)^-$ and doubly protonated $(Dz)^{2-}$ bidentate ligand.

X-ray diffraction analysis[2] of dithizone crystals shows that the H atoms are localized at the utmost N atoms bound to the phenyl rings.



According to the X-ray diffraction data,[3—5] dithizone forms bis-chelate complexes with Ni^{II}, Cu^{II}, and Zn^{II} with the general formula $M(HDz)_2$, in which dithizone manifests bidentate coordination through the S and N atoms to form five-membered metallocycles.

This work is devoted to the ESR study of solutions of the Cu^{II} complex with dithizone to determine its geometric structure and reveale the influence of low-symmetry distortions in solution on the linewidths in the ESR spectra.

Reliable information on the structure of coordination compounds can be obtained by the ESR study of magnetically dilute polycrystalline samples. Therefore, we prepared monosubstituted copper(II), nickel(II), and zinc(II) bis-dithizonates and magnetically dilute powders of nickel and zinc dithizonates containing ~2% copper(II) dithizonate.

Experimental

Solid metal dithizonates were synthesized by the extraction method. An aqueous solution of the metal salt with the corresponding pH was shaken with a solution of dithizone in chloroform, and the organic phase was evaporated. The pH regions of extraction of mono- and disubstituted dithizonates in the extraction method are presented in the monograph.[1] $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $ZnCl_2 \cdot 1.5H_2O$, and diphenylthiocarbazone (analytically pure grade) were used as starting compounds. The composition of the synthesized compounds was established from elemental analysis data.

Monosubstituted nickel dithizonate $Ni(HDz)_2$. Ammonia was added to a solution of $NiCl_2 \cdot 6H_2O$ (0.26 g) in water (20 mL) to pH 8.5—9. The reaction mixture was shaken with a solution of dithizone (0.5 g) in chloroform (250 mL) for ~30 min until the color of the organic layer changed completely from emerald-green to brown-violet. The aqueous layer was separated, and chloroform was distilled off on a rotary evaporator. The product was obtained in a 37% yield (0.23 g). Found (%): C, 54.75; H, 3.90; N, 19.35; S, 11.02. $NiC_{26}H_{22}N_8S_2$. Calculated (%): C, 54.83; H, 3.86; N, 19.68; S, 11.25.

Monosubstituted copper dithizonate $Cu(HDz)_2$. A solution of $CuCl_2 \cdot 2H_2O$ (0.18 g) in water (20 mL) was shaken with a solution of dithizone (0.6 g) in chloroform (250 mL) at pH 2—4 for ~1 h until the color of the organic layer changed completely from emerald-green to red-violet. The aqueous layer was separated, and chloroform was distilled off on a rotary evaporator. The product was obtained in 83% yield (0.50 g). Found (%): C, 55.30; H, 3.50; N, 19.01; S, 11.07. $CuC_{26}H_{22}N_8S_2$. Calculated (%): C, 54.35; H, 3.8; N, 19.51, S, 11.16.

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* Diphenylthiocarbazone is shortly named dithizone (molecular formula $C_{13}H_{12}N_4S$; molecular weight 256.3).

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Monosubstituted zinc dithizonate $Zn(HDz)_2$. Ammonia was added to a solution of $ZnCl_2 \cdot 1.5H_2O$ (0.1 g) in water (20 mL) to pH 6.5—7.5. The reaction mixture was shaken with a solution of dithizone (0.24 g) in chloroform (250 mL) for ~15 min until the color of the organic layer changed completely from emerald-green to purple-red. The aqueous layer was separated, and chloroform was distilled off on a rotary evaporator. The product was obtained in 60% yield (0.21 g). Found (%): C, 55.10; H, 3.40; N, 19.05; S, 11.01. $ZnC_{26}H_{22}N_8S_2$. Calculated (%): C, 54.19; H, 3.89; N, 19.50, S, 11.14. The magnetically dilute samples of Cu and Ni, Cu and Zn compounds were prepared as follows. A mixture of Cu dithizonate (1 mg) and Ni dithizonate (60 mg) was dissolved in chloroform (20 mL). Then both complexes were precipitated in combination with a slow evaporation of the solvent and maintaining of a constant temperature. Magnetically dilute samples of the Cu and Zn compound were obtained similarly.

ESR spectra were recorded on a Radiopan SE/X-2542 radiospectrometer with a working frequency of 9.45 GHz. The magnetic field was calibrated by a nuclear magnetometer. The diphenylpicrylhydrazine (DPPH) radical was used as a standard. Experimental spectra were processed on a computer using the procedure[6] that provides the best correspondence between experimental and theoretical spectra by minimization of the error functional R. Dioxane and chloroform were used as solvents. The spectra were obtained at a concentration (in solutions) of 10^{-3} mol L^{-1}. Dilution to 10^{-5} mol L^{-1} showed that, within these boundaries, the linewidth is independent of the concentration of the copper(II) compound.

The values of g factor, hyperfine structure (HFS) constants from the copper nuclei, superhyperfine structure (SHFS) from the ligand atoms, and resonance linewidths were varied during minimization. The linewidth was specified by the expression

$$\Delta H = \alpha + \beta m_I + \gamma m_I^2,$$

where m_I is the projection of a nuclear spin on the direction of the external magnetic field, and α is the term taking into account all broadening effects similar for all HFS lines. The β coefficient is determined by the product of the g tensor and hyperfine coupling (HFC) tensor. The γ coefficient corresponds to HFC anisotropy and depends on the correlation time of the rotation motion of a paramagnetic species in the liquid. The α, β, and γ coefficients determine the contributions of the ESR spectra of coordination compounds to the linewidths due to the relaxation times of the spin of an unpaired electron and the spin of the central metal nucleus and are measured in units of magnetic field strength. Minimization was stopped at R for which a good agreement of the theoretical and experimental spectra was achieved and further iterations did not change R (the amplitude of the spectrum was normed by 1). This usually occurs at $R < 0.003$. The obtained degree of correspondence is illustrated, in particular, in Fig. 1.

Results and Discussion

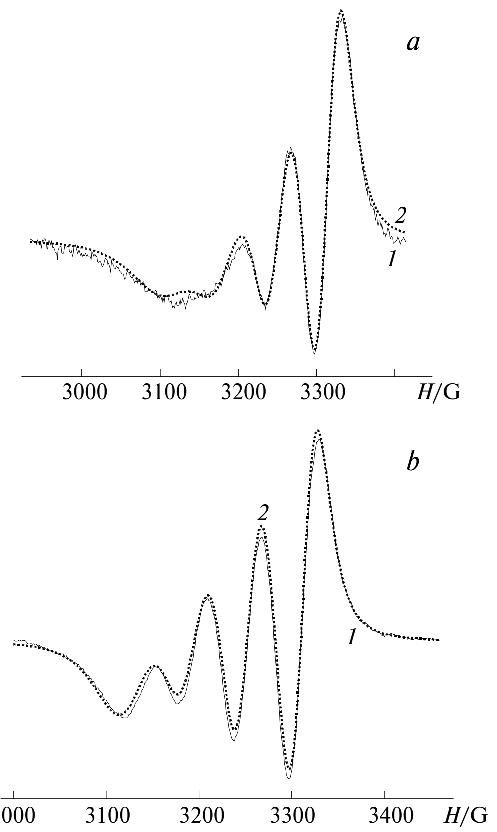


Fig. 1. Experimental (*1*) and theoretical (*2*) ESR spectra of solutions of $Cu(HDz)_2$ in dioxane (*a*) and in chloroform (*b*).

The Cu^{II} complexes with dithizone have been studied[7,8] by the ESR method. The ESR spectrum of the $Cu(HDz)_2$ complex at 293 K in dioxane consists of four HFC lines from the interaction of the spin of an unpaired electron with the spin of the Cu nucleus (see Fig. 1, *a*) and is described by the following isotropic spin Hamiltonian (SH):

$$H = \langle g \rangle \beta SH + \langle a_{Cu} \rangle SI,$$

where β is the Bohr magneton, $S = 1/2$ is the spin of an electron, $I = 3/2$ is the nuclear spin of two copper ^{63}Cu and ^{65}Cu isotopes (natural content 69.1 and 30.9%, respectively), and H is the external magnetic field strength. Other SH parameters are presented in Table 1.

According to the X-ray diffraction data,[4] the $Cu(HDz)_2$ molecule has a square-planar structure. The Cu atom is linked to two S atoms and two N atoms with *trans*-arrangement. However, the Cambridge Structural Database does not cite this work because the X-ray structural study[4] was incorrect.

In the square-planar copper(II) complexes with the d^9 electronic configuration, an unpaired electron is on the $\langle d_{x^2-y^2} \rangle$ orbital.[9] The appearance of S atoms in the coordination sphere of complex compounds of transition elements usually results in a strong line narrowing in the ESR spectra and favors a good resolution of SHFS from the ligand atoms.[10] For example, the lines in the ESR spectra of the copper complexes with bis(α-thiopicoline anilide) {$Cu(\alpha\text{-tpa})_2$} and bis(8-thioquinoline) {$Cu(tox)_2$}, in which the coordination sphere consists of

Table 1. Parameters of SH for the copper compounds in solutions

Compound	Solvent	$\langle g\rangle^a$	$\langle a_{Cu}\rangle \cdot 10^4/\mathrm{cm}^{-1}$	$\langle a_N\rangle$/G	Ref.
$Cu(HDz)_2$	Dioxane	2.075	57	—	7,8
	Dioxane	2.068	55.5, 59.5 ^{b}	—	This work
$Cu(\alpha\text{-tpa})_2$	Benzene	2.073	58	15.0	11
$Cu(tox)_2$	Benzene	2.076	61	14.0	12
$Cu(tag)_2$	Toluene	2.068	74.9, 80.2 ^{b}	16.0	15
$Cu(HDz)_2$	Chloroform	2.068	54.3, 58.2 ^{b}	—	This work
Cu(HDz,ddc)	Chloroform	2.056	74.2, 79.4 ^{b}	12.1	This work

[a] Some difference between the SH parameters is most likely related to different methods of their determination.
[b] HFS constants for the ^{65}Cu isotope.

two N atoms and two S atoms ([*trans*-N_2S_2]), are so narrow that the SHFS from two N atoms is resolved to HFS several components from the Cu atoms.[11,12] Based on this, we could expect that the ESR spectrum of $Cu(HDz)_2$ should contain, along with four HFS lines from the Cu nuclei, the SHFS from two N atoms, but it is not observed. In the ESR spectrum of $Cu(HDz)_2$, even the HFS from the Cu nucleus is poorly resolved (see Fig. 1, *a*), although it is known[9] that the lines in the ESR spectra are narrowed with an increase in the number of the S atoms in the coordination sphere.

This raises the question: why are the lines in the ESR spectrum of $Cu(HDz)_2$ with the [*trans*-N_2S_2] coordination sphere so broadened that the SHFS from two N atoms is not resolved? Several reasons can be found for this broadening of the lines in the spectra. One of them is a low-symmetry distortion of the square-planar coordination sphere (for example, the tetrahedral distortion associated with the turn of two metallocycles about the central metal atom, as well as the deviation of the coordinated chelate cycles to the same or different sides).[13,14] Another possible reason is a change in the shape and sizes of the copper(II) dithizonate molecule, which affects the time of spin-lattice relaxation. These possibilities cannot be examined without additional studies of the $Cu(HDz)_2$ structure.

The ESR study of $Cu(HDz)_2$ was performed in solutions and magnetically dilute polycrystalline powders at room temperature. The ESR spectra of $Cu(HDz)_2$ solutions in dioxane and chloroform are presented in Fig. 1. The SH parameters obtained by the computer simulation of the experimental spectra are summarized in Table 1.

Table 2. Coefficients in the equation for determination of lines in the ESR spectra of the copper(II) compounds

Compound	Coordination sphere	Solvent	α	β	γ
			G		
$Cu(HDz)_2$	[*trans*-N_2S_2]	Dioxane	45.2	13.7	3.4
		Chloroform	35.0	7.4	1.8
$Cu(tag)_2$	[*trans*-N_2S_2]	Toluene	12.6	6.4	1.1
Cu(HDz,ddc)	[NS_3]	Chloroform	9.7	5.0	1.7
$Cu(ddc)_2$	[S_4]	Toluene	7.5	1.7	0.46

It is seen from comparison of the spectra of $Cu(HDz)_2$ (see Fig. 1) that the HFS from the Cu atoms in a chloroform solution is better resolved than in dioxane, but the linewidth in the ESR spectra is still so large (Table 2) that the SHFS from the N atoms is not observed either in this case.

The isotropic SH parameters for several copper(II) compounds in solutions (see Table 1) with the same coordination atoms [*trans*-N_2S_2] coincide. It is known[11,12,15] that $Cu(\alpha\text{-tpa})_2$, $Cu(tox)_2$, and $Cu(tag)_2$ (tag are thioacylhydrazones of monocarbonyl compounds) have a square-planar structure in both the solid phase and solutions. Since the SH parameters in solutions for all compounds are the same, $Cu(HDz)_2$ in a solution also has a square-planar structure. However, the ESR spectra of $Cu(HDz)_2$ in solutions contain an anomalously broad line (see Table 2).

To decrease the linewidth in the ESR spectra, we increased the number of S atoms in the coordination sphere of Cu^{II}. With this purpose, we added copper diethyl dithiocarbamate {$Cu(ddc)_2$} to a solution of $Cu(HDz)_2$ in chloroform. The ESR spectrum shows (Fig. 2) that ddc^- substitutes one HDz^- anion in the internal coordination sphere to form a heteroligand Cu^{II} complex. A new spectrum appears against the background of unreacted $Cu(HDz)_2$, in which four HFS lines

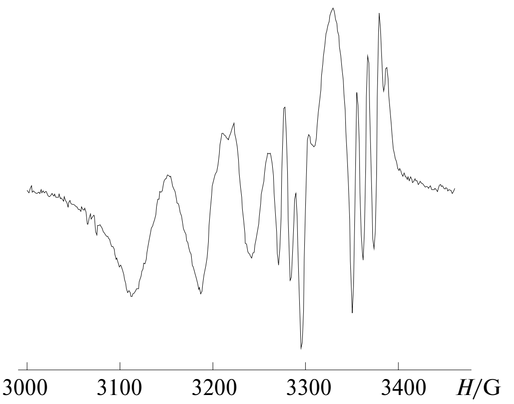


Fig. 2. ESR spectrum of the Cu(HDz,ddc) heteroligand complex formed by the addition of $Cu(ddc)_2$ to a solution of $Cu(HDz)_2$ in chloroform and $Cu(HDz)_2$.

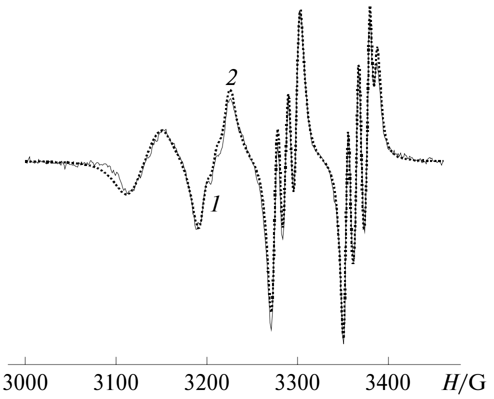


Fig. 3. Experimental (*1*) and theoretical (*2*) ESR spectra of a solution of the Cu(HDz,ddc) heteroligand complex in chloroform.

from the Cu atom are additionally split into three components. The ESR spectrum of the pure heteroligand complex prepared by mixing of $Cu(HDz)_2$ and $Cu(ddc)_2$ in a ratio of 1 : 1 has the SHFS from one N atom (Fig. 3). As we assumed, the appearance of the third S atom in the coordination sphere of the Cu^{II} atom narrows, indeed, the lines in the ESR spectrum (see Table 2).

The formation of the Cu(HDz,ddc) heteroligand complex at the 1 : 1 ratio of reactants suggests the following: first, the starting copper (II) dithizonate has the $Cu(HDz)_2$ composition; second, when the coordination sphere of Cu^{II} contains only one dithizonate ligand, the lines in the ESR spectra are not broadened, which is indicated by the well-resolved SHFS from one N atoms (see Fig. 3) and the linewidths in the ESR spectra of the heteroligand complex (see Table 2).

Table 3. Anisotropic SH parameters for the copper compounds

Compound	$g_{\parallel}$	$g_{\perp}$	A	B	$\langle a_N \rangle_{\parallel}$	$\langle a_N \rangle_{\perp}$	Refs.
			10^4 cm^{-1}		G		
Cu(α-tpa)$_2$	2.131	2.037	154	12.0	15.0	15.0	11
Cu(tox)$_2$	2.147	2.036	172	25.0	—	15.2	12
Cu(HDz)$_2$	2.145	2.033	176	26.0	17.2	16.5	*

* This work.

The spectrum of the magnetically dilute polycrystalline powder of Ni^{II} and Cu^{II} dithizonate is typical of the copper(II) compounds with biaxial anisotropy of the parameters (Fig. 4) and described by the axial-symmetry SH in the form

$$H = [g_{\parallel}S_zH_z + g_{\perp}(S_xH_x + S_yH_y)] + AS_zI_z + B(S_xI_x + S_yI_y),$$

where $S = 1/2$ is the spin of an electron, $I = 3/2$ is the spin of the Cu nucleus, A is the HFS constant from the Cu nucleus in parallel orientation, and B is the HFS constant from the Cu nucleus in perpendicular orientation.

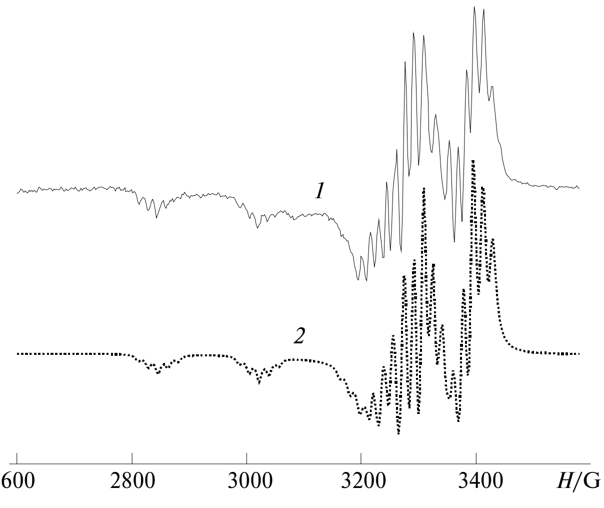


Fig. 4. Experimental (*1*) and theoretical (*2*) ESR spectra of the magnetically dilute powder of a $Ni(HDz)_2$ and $Cu(HDz)_2$ (60 : 1) mixture.

A comparison of the anisotropic SH parameters for $Cu(HDz)_2$, Cu(α-tpa)$_2$, and $Cu(tox)_2$ (Table 3) shows that they are close and can be attributed to the square-planar copper(II) complexes with the [*trans*-N_2S_2] coordination sphere.

In the ESR spectrum of the magnetically dilute polycrystalline powder of Ni and Cu dithizonate, the SHFS of five lines is well resolved in both perpendicular and parallel orientations (see Fig. 4). The computer simulation of the experimental spectrum showed that five SHFS lines have an intensity ratio of 1 : 2 : 3 : 2 : 1. Therefore, their appearance is due to the hyperfine splitting from two equivalent N atoms.

The ESR study of the Zn and Cu dithizonate powders showed that copper dithizonate does not enter the slightly distorted tetrahedral lattice of Zn^{II} dithizonate. Therefore, Cu^{II} dithizonate is such a structurally rigid coordination compound[14] that it retains its square-planar structure and does not undergo even insignificant distortions, which is indicated by the absence of traces of Cu^{II} dithizonate in the lattice of Zn^{II} dithizonate.

Thus, the larger linewidth in the ESR spectra of the $Cu(HDz)_2$ complex in solutions is related to the low-symmetry distortions of the coordination sphere[14] because $Cu(HDz)_2$ has a square-planar structure in the solution and solid state.

Consider the influence of the shape and sizes of the $Cu(HDz)_2$ molecule on the time of spin-lattice relaxation. The time of spin-lattice relaxation in coordination copper(II) compounds is usually rather long, so that the ESR spectra have narrow lines. However, the spectra of the hexacoordinated copper(II) complexes with the $\{[CuX_6]^{n-}\}$ monodentate ligands in solutions exhibit[16] broad lines with the poorly resolved HFS from the Cu atoms. This is due to the dynamic Jahn—Teller effect. When at least one Cu—ligand bond is strengthened, the lines in the ESR spectra are sharply narrowed, which

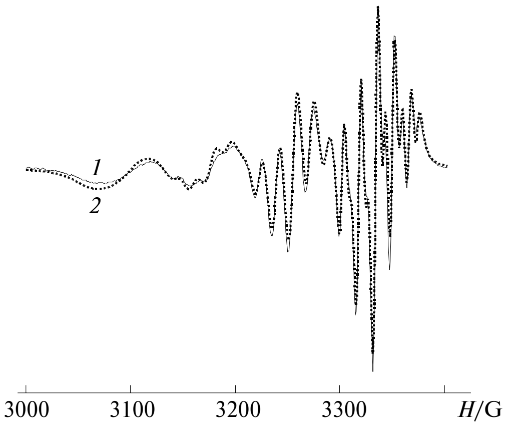


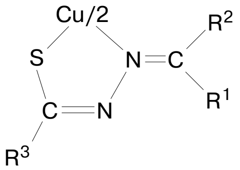
Fig. 5. Experimental (*1*) and theoretical (*2*) ESR spectra of a solution of Cu(tag)$_2$ in toluene.

occurs during the coordination of only one bidentate ligand by the Cu atom.

At the same time, the lines in the ESR spectra of viscous solutions or standard solutions for very high molecular weight of the polymacrocyclic ligand also have a large width and poorly resolved HFS from the Cu^{II} nuclei due to the influence of unresolved anisotropy of the HS parameters.**16** In all other cases, the lines in the ESR spectra of the copper(II) coordination compounds, especially with the coordination sphere containing S atoms, are narrow, due to which the HFS from the Cu^{II} atoms and SHFS from the ligand atoms are well resolved.

Evidently, both factors of line broadening in the ESR spectra of solutions are absent in the case of the Cu^{II} complexes with dithizone.

We have previously**15** studied the following copper(II) coordination compounds with tag ligands:



The R^1, R^2, and R^3 substituents were represented by various groups from H to 4-C$_6$H$_4$OMe, and the molecular weight of the Cu^{II} coordination compounds consisted of 500—700 units; the linewidth of the ESR spectra remained almost unchanged. The molecular weight of Cu(tag)$_2$ with R^1 = H, R^2 = 4-C$_6$H$_4$OMe, and R^3 = CH$_2$Ph is 597.8, whereas for Cu(HDz)$_2$ it is 573.8. Thus, the shape, size, and molecular weight of both compounds are almost the same, but the linewidth in the ESR spectra differ by nearly an order of magnitude (see Table 2). The lines in the ESR spectra of the Cu(tag)$_2$ compound with the [*trans*-N$_2$S$_2$] coordination sphere are so narrow that the HFS from the Cu atoms and the SHFS from two equivalent N atoms are well resolved along with the HFS at the most narrow upfield line from the ^{63}Cu, ^{65}Cu isotopes (Fig. 5).

The coordination compounds of copper with tag ligands are close in structure to copper dithizonate in which some dithizone molecules are replaced by the R^3 group. It is found**15** that, regardless of the nature, shape, and sizes of the R^3 substituents, the linewidths in the ESR spectra of the copper complexes with tag remain almost unchanged.

Based on the aforesaid, we may assert that the time of spin-lattice relaxation does not define the linewidths in the ESR spectra of the copper complexes with dithizone, and thus, the question about reasons for the line broadening in the spectra of Cu(HDz)$_2$ in solutions remains open.

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