Isomerism of copper(II) coordination compounds with hydroxamic acids

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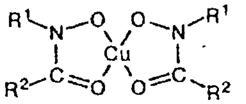
The structure of Cu^{II} complexes with hydroxamic acids $Cu[R^1N(O)—(O)CR^2]_2$, where R^1 = Ph, R^2 = Me; R^1 = Me, R^2 = Ph, was studied by ESR spectroscopy. In toluene solutions and low-temperature glasses, the complexes exist as two forms, which were identified as *cis*- and *trans*-isomers. The proportions of the isomers were determined.

Key words: copper(II) complexes, hydroxamic acids, ESR, HFS, isomerism.

Study of *cis—trans*-isomerism of coordination compounds has played an important role in the development of A. Werner's coordination theory.[1,2] However, the interest in the study of the properties of *cis*- and *trans*-isomers still has not attenuated.[3,4]

cis—trans-Isomerism is usually related to those complex compounds, whose coordination sphere contains atoms of two different sorts, for example, [O, N], [O, S], [N, S], *etc.*

This work deals with an ESR study of the structures of coordination compounds of copper(II) with hydroxamic acids; the coordination sphere in these complexes consists of atoms of only one sort (oxygen).



R^1 = Ph, R^2 = Me (**1**); R^1 = Me, R^2 = Ph (**2**)

The ESR spectra of compounds **1** and **2** recorded in toluene solutions at room temperature have been tentatively discussed previously.[5]

Experimental

The complexes were prepared by a known procedure.[6]

Compound 1. A solution of copper acetate monohydrate (1.32 g) in 60 mL of water was added dropwise with stirring to a solution of *C*-methyl-*N*-phenylhydroxamic acid (2 g) in 60 mL of dioxane. This gave a yellow-green solution, whose pH was brought to 7 by adding an aqueous solution of KOH. Then the solution was concentrated, the resulting crystalline precipitate was dissolved in chloroform, and the solution was filtered. The filtrate was concentrated on a rotary evaporator. The residue was recrystallized from toluene. The resulting compound was colored dark-green, m.p. 148 °C. Found (%): Cu, 17.8. $C_{16}H_{16}O_4N_2Cu$. Calculated (%): Cu, 17.46. Complex **2** was synthesized in a similar way. The complex was colored light-green, m.p. 174 °C. Found (%): Cu, 17.6. $C_{16}H_{16}O_4N_2Cu$. Calculated (%): Cu, 17.46.

ESR spectra were recorded on a Radiopan SE/X-2542 radiospectrometer operating at 9.45 GHz. The magnetic field was calibrated with a nuclear magnetometer using the DPPH radical as the standard. The spectra were processed on a PC using a previously described procedure.[7]

To narrow the lines in the ESR spectra, solutions of compounds **1** and **2** were freed from O_2 by bubbling Ar. To facilitate interpretation of the ESR spectra, the ^{63}Cu isotope was employed in the synthesis of compounds **1** and **2** (enrichment 99.8%).

The experimental spectra were subjected to computer processing by minimization of the error functional[7]:

$$R = \Sigma_i(I_i^{\exp} - I_i^{t})^2/N.$$

Here $I_i^{\exp}$ are the experimental intensities of ESR signals recorded as arrays of points with a constant step of the magnetic field H; I_i^{t} are theoretical intensities found for the same H values as the sum of the derivatives of the Lorentz and Gauss functions centered around the resonance H values; N is the number of points.

During minimization, the values of g-factors, HFS constants at the ^{63}Cu nucleus, and the widths of resonance lines were varied. The line width was specified by the expression

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

where m_I is the projection of the nuclear spin in the direction of the external magnetic field, α is the term taking into account all the broadening effects identical for all the HFS lines. The β coefficient is defined as the product of the g-tensor and the tensor of hyperfine coupling (HFC). The γ coefficient characterizes the anisotropy of HFC and depends on the correlation time of the rotational motion of a paramagnetic species in a liquid. The minimization was terminated when the attained R value ensured good agreement between the theoretical and experimental spectra and further iteration steps did not change the R value (the spectral amplitude was normalized to 1). Normally this was attained at $R < 0.003$.

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Results and Discussion

The ESR spectra of solutions of compounds **1** and **2** in toluene are quintets (Fig. 1) rather than quartets (the intensity ratio is 1 : 1 : 1 : 1); this is due to the HFC of the spin of the unpaired electron with nuclear spin (I) of the copper isotope ($I_{Cu} = 3/2$).[8]

Theoretical analysis of the spectra of compounds **1** and **2** showed that each of them is a superposition of two quartet spectra of two copper complexes. The spectra of copper(II) compounds are described by an isotropic spin Hamiltonian (SH) of the following form:

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

where β is the Bohr magneton; $S = 1/2$ is the electron spin; $I = 3/2$ is the nuclear spin of the copper isotope. The other SH parameters are listed in Table 1.

The ESR spectra of frozen solutions (glasses) at 77 K are also superpositions of spectra of two copper(II) compounds (Fig. 2). Each individual spectrum is a typical spectrum of a copper(II) complex occurring in a magnetically dilute solid matrix. It contains four well-resolved low-intensity HFS lines due to the copper nucleus in the parallel orientation and four resolved HFS lines due to the copper nucleus in the perpendicular orientation. In this particular case, in a weak magnetic field, only three HFS lines of the copper nucleus in the parallel orientation can be seen, because the fourth component is overlapped by intense HFS lines of the copper nucleus in the perpendicular orientation. The high-field region contains a well-resolved intense peak of extra absorption.[8,9] The existence of two copper compounds in the low-temperature glass is indicated by splitting of the HFS component for the copper nucleus in the parallel orientation in weak magnetic fields into two peaks and by the presence of eight HFS lines due to the copper nucleus in the case of the perpendicular orientation (see Fig. 2). The spectra of all copper compounds in glass are described by an axially symmetrical SH of the following form:

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

The SH parameters of the spectra of copper compounds in low-temperature glasses are presented in Table 2.

Thus, ESR spectra of both toluene solutions and low-temperature toluene glasses of each of the two complexes studied show the presence of two different copper(II) compounds. This may be due to several reasons.

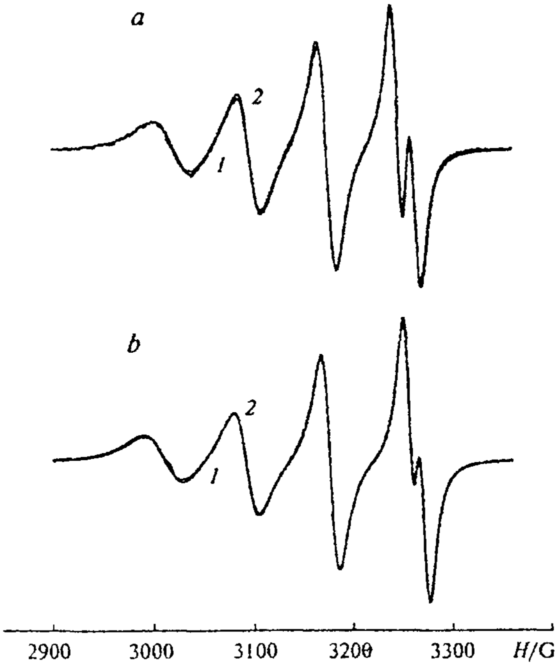


Fig. 1. Experimental (*1*) and theoretical (*2*) ESR spectra of solutions of compounds **1** (*a*) and **2** (*b*) in toluene.

Table 1. Parameters of the ESR spectra of *cis*- and *trans*-isomers of compounds **1** and **2** in solutions

Compound	g±0.002	$a_{Cu} \cdot 10^{-4}$ /cm^{-1}	Concentration (%)	α	β	γ
					Oe	
1A	2.116	8.31	40	19.2	7.8	1.9
1B	2.119	7.34	60	20.4	7.1	1.3
2A	2.117	8.86	53	20.99	7.6	1.1
2B	2.118	7.97	47	20.25	7.9	1.7

Table 2. Parameters of the ESR spectra of *cis*- and *trans*-isomers of compounds **1** and **2** in low-temperature glasses at 77 K

Compound	$g_{\parallel}$±0.002	$g_{\perp}$±0.002	A	B	Concentration (%)
			10^4 cm^{-1}		
1A	2.233	2.048	210.0	22.7	51
1B	2.234	2.055	194.7	22.0	49
2A	2.231	2.049	218.7	25.4	40
2B	2.233	2.052	213.2	25.6	60

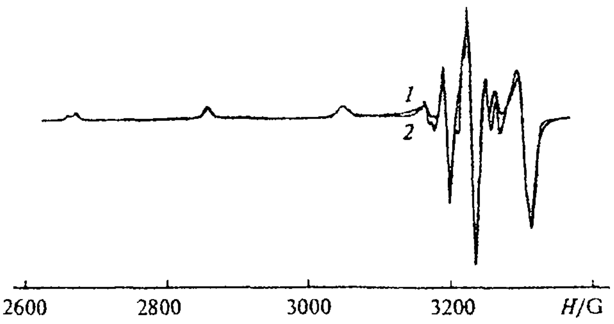
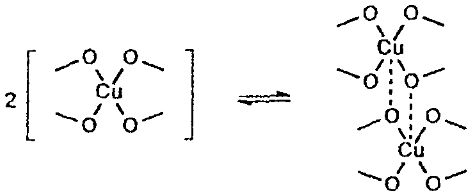


Fig. 2. Experimental (*1*) and theoretical (*2*) ESR spectra of solutions of compound **1** in a low-temperature toluene glass at 77 K.

First, an individual compound might decompose on dissolution to form several paramagnetic compounds. However, the composition and the ESR spectra remain unchanged after repeated recrystallization of complexes **1** and **2**.

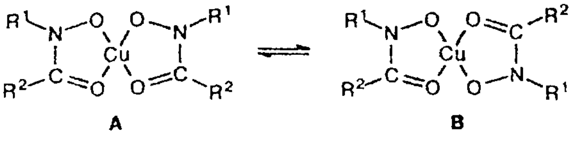
Second, molecules of polar solvents can form coordination bonds with square-planar copper complexes, which results[8,10] in the change of SH parameters. The occurrence of equilibrium between tetra- and pentacoordinated complexes accounts for the appearance of spectra for two types of complexes. Since neither the spectral patterns nor the SH parameters depend on the degree of purity of toluene and toluene itself is unable to be coordinated by the copper atom, one can conclude that in this particular case, an equilibrium of this type is not involved. Moreover, addition of polar solvents to toluene solutions of complexes **1** and **2** changes the spectral pattern and the SH parameters.

Third, copper(II) complexes might dimerize in solutions due to additional coordination of oxygen of one molecule to an axial position of the copper atom of a neighboring molecule.[11]



If the Cu...O distances are large enough (to rule out strong exchange interactions of the antiferromagnetic type), the formation of this type of dimers reduces to the second case. Since polar solvents always destroy these dimers,[11] and, as noted above, superposition of spectra of two complexes is still observed for both compounds in the presence of polar solvents, it can be concluded that dimers are not formed under these conditions. In addition, the position of a monomer—dimer equilibrium depends on the initial concentration of complexes. Study of the concentration dependence of the presence of two species over the $5 \cdot (10^{-4}—10^{-2})$ mol L^{-1} range demonstrated that the spectral pattern, the ratio of the concentrations of the two species (see Table 1), and the SH parameters remain constant.

Yet another possible reason for the appearance of two spectra on dissolution of compounds **1** and **2** is associated with *cis—trans*-isomerism. It has been shown previously that remote substituents in chelating ligands (copper(II) complexes with fluorinated derivatives of acetylacetone[12] and with sulfur-containing ligands[13]) have a noticeable effect on the SH parameters. Depending on the mutual arrangement of substituents not bound directly to the copper atom, compounds **1** and **2** can exist as *cis*- (**A**) and *trans*-forms (**B**).



A **B**

The electronegativities of carbon (12.08 eV)* and nitrogen (13.98 eV)* and also the N—O and C—O distances are known to be somewhat different; hence, the corresponding Cu—O bonds are nonequivalent.

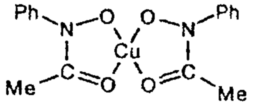
In fact, for chromium(III) complexes with hydroxamic acids, the existence of *trans*-isomers has been proved by X-ray diffraction analysis.[3] The difference between the M—O(N) and M—O(C) bond lengths is 0.024 Å; in analogous Th^{IV} complexes, it reaches[16] 0.14 Å. According to IR spectroscopy data, the Cu—O(C) and Cu—O(N) bond lengths in the copper(II) complexes with hydroxamic acids are also different and are equal[17] to 1.98 and 2.06 Å, respectively.

Thus, we attribute the presence of two species in the studied copper complexes in solutions and glasses to the *cis- and trans*-arrangement of the nitrogen (or carbon) atoms not bound directly to the copper atom and occurring in the second coordination sphere.

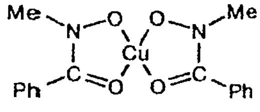
Based on published data[18] on *cis—trans*-isomerism in copper(II) chelates with the [2 O, 2 N] and [2 N, 2 S] coordination sphere, the species with larger HFS constants and smaller *g*-factors can be identified as *cis*-isomers (**1A** and **2A**).

It should be noted that in the same isomers, the arrangement of the R^1 and R^2 radicals (attached to either nitrogen or carbon) also has a noticeable effect on the SH parameters and the line widths, *i.e.*, in the copper(II) complexes with hydroxamic acids, structural position isomerism is manifested, associated with the different positions of the peripheral substituents R^1 and R^2 with identical arrangements of the bis-chelate core.

For example, the *cis*-isomer can exist as two structural forms, **C** (**1A**) and **D** (**2A**), in which either two phenyl or two methyl groups, respectively, are bound to the nitrogen atom.



C



D

In fact, the theoretical spectra for compounds **1A** and **2A**, constructed using the parameters determined from the experimental spectra (see Table 1), are substantially different (Fig. 3, *a*).

A similar situation with the position isomers is also observed for *trans*-isomers (Fig. 3, *b*).

Unlike *cis*- and *trans*-isomers, the position isomers are not genetically related to each other and are unable to undergo interconversion.[19]

Thus, the coordination compounds of copper(II) with hydroxamic acids in toluene solutions and low-temperature glasses exist in two forms, as *cis*- and *trans*-isomers.

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* The electronegativities of elements were determined according to Malliken. Published data[14,15] for the ionization potentials and electron affinities were used.

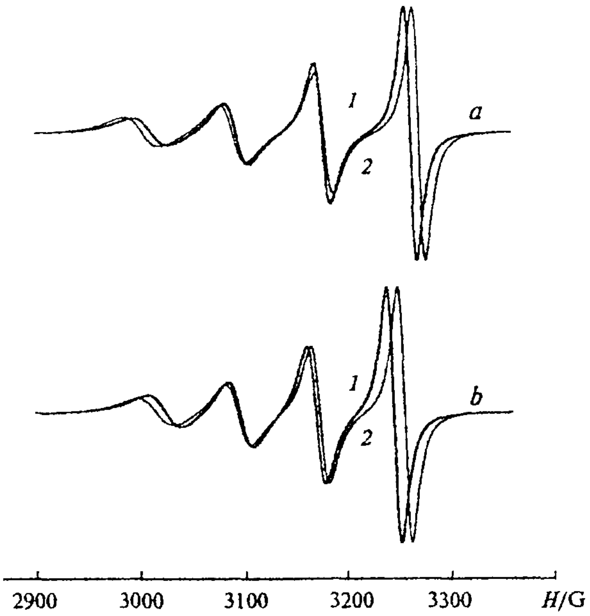

Fig. 3. Theoretical ESR spectra of compounds **1** (*1*) and **2** (*2*) constructed using the data of Table 1 for *cis-* (*a*) and *trans-* (*b*) position isomers.

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