The structure of catalytically active complexes in copper chloride—dialkyl sulfide—chloroolefin systems

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The formation of mixed Cu^I and Cu^{II} polynuclear complexes with dialkyl sulfide, which are active in the catalytic isomerization of chloroolefins, has been investigated by UV-Vis and ESR spectroscopy. The role of these complexes in catalysis is discussed.

Key words: copper, dialkyl sulfide, polynuclear complexes, structure, UV-Vis spectra, ESR spectra, chlorolefins; catalysis; isomerization.

Copper sulfide complexes attract the attention of researchers due to similarity between their structures and those of metal-containing fragments of some proteins.[1—3] These complexes are catalytically active in the isomerization of 1,4-dichloro-2-butene to 3,4- dichloro-1-butene.[4] The studies of the isomerization in the presence of complexes of dialkyl sulfides with copper(I) chloride that were carried out previously allowed one to suggest that heterovalent polynuclear complexes containing Cu^I and Cu^{II} in a ~2 : 1 ratio and the molecules of sulfide and dichlorobutene (DCB)[5] were responsible for catalysis.

The possibility of the formation of these complexes both during oxidation of copper(I) complexes by oxygen and reduction of copper(II) complexes by excess sulfide represents one of the peculiarities of the systems under consideration. The Cu^{II} complexes are characterized, as a rule, by the bands in the visible and near UV regions of spectra as well as by typical ESR spectra. This makes it possible to obtain information on their structure and mutual transformations. In this work, the structure of catalytically active complexes forming in the $CuCl_2$—R_2S—DCB system as well as the process of their formation from the Cu^{II} complexes are studied by electron and ESR spectroscopy.

Experimental

Preparation and purification of the starting reagents are described in Ref. 4. The purity of the starting substances and the compositions of the products were determined with a Chrom-5 chromatograph (a flame-ionization detector, stationary phase SE-30 silicon on celite, temperature programmed from 373 to 453 K).

The optical spectra in the 250—1200 nm region were recorded with UV-3100 and Specord M40 spectrophotometers.

The ESR spectra in liquid and frozen solutions were registered on Varian E-3 and Varian E-4 radiospectrometers in thin-walled quartz ampules. Diphenylpicrylhydrazyl (DPPH, g = 2.0036) and Mn^{II} ions in a MgO matrix were used as the standards for calibration of magnetic field. The content of Cu^{II} was estimated by comparison of integral intensities of the spectra of the probes of a specified volume with those of the standard similarly to the procedure described previously.[6] The parameters of spin-Hamiltonian were determined according to the known procedure.[7] Modeling of the spectra was carried out with a PC-486 using programs developed by A. A. Shubin in the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, which were similar to those used in Ref. 8.

Results and Discussion

The $CuCl_2$—dialkyl sulfide systems. The pattern of the spectra of systems $CuCl_2$—R_2S is determined by the nature of the R group and is independent of the composition and polarity of the chlorocarbon solvent, because identical results are obtained for solutions in chloroform, chlorobenzene and other solvents of this type. Dialkyl sulfides in which the R group contain more than three carbon atoms form stable green solutions. A typical optical spectrum for the system with R = heptyl, with less that a 10-fold excess of the sulfide to copper (Fig. 1), is characterized by maxima at 308, 455, and 710 nm, a shoulder in the 360 nm region, and intense absorption at λ < 290 nm. The Lambert—Beer law is obeyed for the spectra obtained under these conditions for the bands at 455 and 710 nm in the region of $CuCl_2$ concentrations of 10^{-2}—10^{-4} mol L^{-1}; the extinction coefficients are equal to 2500 and 220 mol^{-1} L cm^{-1}, respectively. It is known[9] that the low-intensity bands in the spectra of copper(II) complexes with derivatives of

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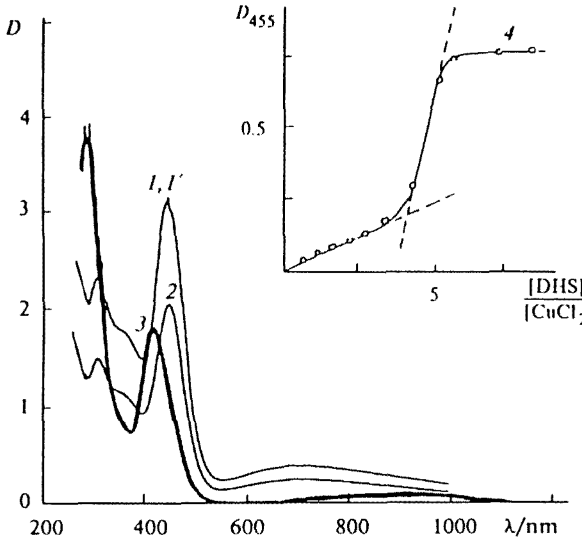


Fig. 1. Spectra of the solutions of 0.01 *M* $CuCl_2$ and 0.4 *M* diheptyl sulfide (DHS) in chlorobenzene (CB) (*1*) and DCB (*1′*) immediately after preparation and after heating for 1 h at 373 K in CB (*2*) and in DCB (*3*) (l = 1 mm) and the curve of the spectrophotometric titration of a solution of 0.003 *M* $CuCl_2$ in CB by DHS at the wave length of 455 nm (*4*).

divalent sulfur in the region of λ > 600 nm correspond to forbidden d—d transitions; the bands in the 300—600 nm region with extinction coefficients of some thousands in value correspond to the transitions with charge transfer from a ligand to a metal. According to the known work,[2] one can observe for the same complex two bands from the $R_2S(\sigma)\rightarrow d_{x^2-y^2}$ transitions due to the presence of two nonequivalent ligands in the complex. In this case, we observe three or even four (taking into account the absorption in the region <290 nm) bands of comparable intensity indicative of the presence, at a minimum, of two different complexes. Alternative explanations for the appearance of the additional bands are invalid, because their intensity is too high to assign them to the $R_2S(\pi)\rightarrow d_{x^2-y^2}$ transitions or to charge transfer from the apical chlorine atoms.

To determine the composition of the complexes, we used the procedure of spectrophotometric titration of a solution of copper chloride by dialkyl sulfide. The titration curve at the 455 nm (see Fig. 1) exhibits a distinct break at the 1 : 4 ratio that corresponds to $CuCl_2(R_2S)_4$. A less sharp break is observed in the concentration dependence of the bands at lower wave lengths, which does not allow one to determine clearly the composition of the complexes that absorb in this region. The ratio between copper chloride and sulfide in these complexes is less than 1 : 4, because the intensity of absorbance in the region <400 nm exceeds that in the maximum of the band at 455 nm when the initial components ratios are close to equimolar. As the excess sulfide increases, the relation between intensities changes, and the band at 455 nm, corresponding to the 1 : 4 complex, begins to substantially exceed in intensity the bands in the region of λ < 400 nm.

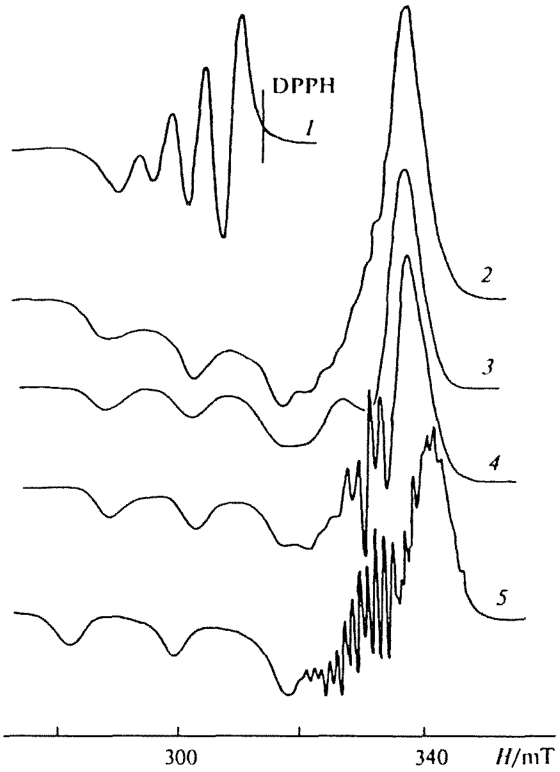


Fig. 2. ESR spectra of Cu^{II} complexes at 295 K (*1*) and 77 K (*2—5*): *1*, *2*, 0.01 *M* $CuCl_2$ and 0.4 *M* DHS in CB; *3*, the same in DCB; *4*, 0.01 *M* $CuCl_2$ and 0.4 *M* diisopropyl sulfide in DCB; *5*, theoretically calculated spectrum of the system (*c*) (parameters are shown in the text).

In the ESR spectrum of the diheptyl sulfide—$CuCl_2$ system (Fig. 2) at room temperature, four well-resolved bands with parameters g_0 = 2.095±0.003; a_0 = 5.7±0.2 mT are observed. The parameters of the spectrum at 77 K (Table 1) are typical of Cu^{II} complexes of an octahedral structure.[10] However, the shapes of the lines and the existence of inflection points in some regions of the spectrum (see Fig. 2, spectrum *2*) indicate the presence in the solution of at least two complexes differing in composition and structure.

Previously,[11] on the basis of the analysis of the ESR spectrum of similar complexes in a toluene solution, an equilibrium between octahedral and square-pyramidal complexes was assumed to exist.

$$CuCl_2(R_2S)_3 + R_2S \rightleftharpoons CuCl_2(R_2S)_4 \qquad (1)$$

The data obtained is in complete agreement with this scheme under suggestion that the complexes of the octahedral structure prevail when diheptyl sulfide is taken in excess. This complex is characterized by the absorption band at 455 nm and one of the bands in the region <400 nm; a small amount of five-coordinated copper complex is present in the solution and is charac-

Table 1. Parameters of the ESR spectra of Cu^{II} complexes at 77 K

Complex	$g_\parallel \pm 0.005$	$g_\perp \pm 0.005$	$a_\parallel \pm 0.3$/mT	$a_\perp \pm 0.3$/mT	Note
$CuCl_2$ + $(iso\text{-}C_3H_7)_2S$ + 3,4-DCB	2.195	2.06±0.01	17.8	—	a_0 = 1.31 mT
$CuCl_2$ + $(n\text{-}C_7H_{15})_2S$	2.193	~2.053	13.4	—	
$CuCl_2$ + $(n\text{-}C_7H_{15})_2S$ + 3,4-DCB	2.175	2.057	14.4	—	g_R = 2.032; a_0 = 1.8 mT
$CuCl_2$ + $(n\text{-}C_7H_{15})_2S$ + TCP*	2.175	~2.05	14.7	—	g_R = 2.033; a_0 = 1.8 mT
$CuCl_2$+$(n\text{-}C_7H_{15})_2S$ + DCB**	2.004	2.160	5.8	9.2	g_2 = 2.060
$[Cu(bpy)_2Cl]ClO_4$	2.01	2.19	—	—	[14]
$Cu(bpy)_2Cl_2$	2.02	2.19	—	—	[14]
$[Cu(bpy)_2SC(NH_2)_2](ClO_4)_2$	2.020	2.168	—	—	g_2 = 2.141 [15]
$[CuN(CH_2CH_2NH_2)_3OH]^+$	2.006	2.210	7.2	10.7	[16]
$[CuN(CH_2CH_2N(CH_3)_2]_3Br_2$	1.956	2.182	8.7	9.8	[17]
$[CuN(CH_2CH_2SC_2H_5)_3Cl]ClO_4$	2.005	2.128	—	—	[18]

* TCP — 1,2,3-trichloropropene. ** The spectrum was recorded after heating the sample for 1 h at 373 K.

terized by the absorption bands at ~330 and <300 nm. Assignment of the bands to the suggested complex of five-coordinated copper is in line with the data obtained previously,[2] where similar spectra have been found for sulfide complexes of known structure in which the coordination number of copper was equal to 5. It was shown in that work that square, trigonal-bipyramidal, and square-pyramidal copper complexes with sulfides exhibit no absorbtion bands at λ < 400 nm. The combined results of the ESR spectra and the compositions of the complexes allow one to assign a shape of a distorted octahedral to the complex with λ_{max} = 455 nm with a reasonable degree of probability.

Oxidation of organic sulfides *via* interaction with $CuCl_2$. When solutions of $CuCl_2$ are heated to 373 K with excess diheptyl sulfide (DHS), the intensity of the bands in the electronic spectrum (see Fig. 1) and of the Cu^{II} signals in the ESR spectrum decrease without any substantial change in a shape of the lines and become close to zero as the duration of heating increases (more than 5 h). This provides evidence for the reduction of copper to Cu^I. According to the GLC analysis, 1-chloro- and 2-chloro-heptanes (5 : 1) and likely the complex of diheptyl sulfide with CuCl are the products of the reaction. These complexes are known to be significantly stronger than the Cu^I complexes with dialkyl sulfides.[12]

Figure 3 presents the kinetic curves for a decrease in the copper(II) concentration obtained from the integral intensities of the ESR signals recorded in liquid and frozen solutions of chlorobenzene together with their linearization in the coordinates of kinetic equations of different orders. The values obtained by different methods are seen to be practically identical, and curve *1* is well linearized in the coordinates of a second-order kinetic equation. The rate constant of the pseudo-second order is equal to $(3\pm0.3) \cdot 10^{-2}$ mol^{-1} L s^{-1}. The second order with respect to the copper concentration is confirmed when the series of kinetic curves are treated by the method of initial rates.

Complexes of diethyl and especially dimethyl sulfide are already unstable at room temperature, and the reduction of copper is completed in a few minutes. This difference in the stability of the Cu^{II} complexes depending on the bulk of the substituent has been noted previously for complexes of mercaptans and was explained by steric hindrances for the radical stages of the process in the coorditnation sphere of the metal.[3]

The $CuCl_2$—dialkyl sulfide—chloroolefin systems. The behavior of the dialkyl sulfide—$CuCl_2$ complexes in the presence of chloroolefins containing a chlorine atom in an allylic position changes significantly. Although at the first moment the electronic spectra of the complexes in a medium of chloroolefin are nearly the same as those observed in any other chlorocarbon solvents, keeping these solutions for 1 day at room temperature results in a change in color of the complexes from green to orange-red and respective changes in the spectra. Changes in the spectra proceed faster with a rise in temperature and appear immediately at 373 K. The spectrum of the complex in a medium of 3,4-DCB-1 in excess dialkyl sulfide (see Fig. 1) shows that in this case, the maxima of the bands are observed at 290 and 418 nm; in addition, a broad weak band in the 900 nm region appears whose position and intensity allow one to assign it uniquely to forbidden d—d transitions.

In the system in which the ratio of dialkyl sulfide to copper chloride that is close to equimolar, there are absorption bands at 480 and 826 nm.[5] When the component ratios take intermediate values, the absorption spectrum represents a superposition of all the absorption bands observed. The relation of the intensities of the bands in the electronic spectrum depends on the temperature and the concentration of sulfide. A decrease in $[R_2S]$ and a rise in temperature result in an increase in the ratio of optical densities d_{480}/d_{418}. The absorption in the near IR region of the spectrum exhibits similar behavior: with a 10-fold excess of sulfide at room temperature, a nearly symmetric band with a maximum at 910 nm is observed. In dilute solutions and especially upon heating, the maximum is shifted to 826 nm. Taking into account the fact that the bond between Cu^{II} and the sulfide ligands is indoubtedly stronger than that with chloroolefin, the changes observed can be explained by reversible replacement of one sulfide molecule in the coordination sphere of the metal with a chloroolefin molecule. The use of the method of isomolar series for the bands at 480 and 826 nm resulted in the brutto-formula $Cu^{I}_{2}Cu^{II}D_{2}L_{2}Cl_{n}$, where D and L are dichlorobutene and sulfide, respectively, and *n* is close to 4. It is not improbable that the second complex that absorbs at 418 and 910 nm has the brutto-formula $Cu_3Cl_nL_3D$.

The ESR spectrum of the complex in the liquid phase recorded immediately after adding chloroolefin is similar to that described previously (see Fig. 2, spectrum *1*). At 77 K, the pattern of the spectrum is typical of the Cu^{II} complexes with axial symmetry of the coordination sphere in the form of a slightly distorted octahedron in the main state b_{1g}, and localization of an unpaired electron on the $3d_{x^2-y^2}$ orbital ($g_{\parallel} > g_{\perp} > 2$). This is confirmed by the theoretical calculation of the ESR spectrum (see Fig. 2) carried out for the values: $g_x = g_y = 2.0277$; $g_z = 2.165$; $a_x = a_y = 3.2$ mT; $a_z = 15.0$ mT, the width of the components of the Gaussian line was $D_x = D_y = 2.86$ mT; $D_z = 2.56$ mT. Due to the proximity of the experimental values of g_0 and $g_0' = (g_{\parallel} + 2g_{\perp})/3$, one can assume the identity of the composition and structure of the Cu^{II} complexes both at 295 K in solution and at 77 K in the solid phase. In addition, in a frozen solution, the spectrum of an organic radical or radical-cation,[13] whose HFS is determined by the nature of the R radical in the starting sulfide, is superimposed on the spectrum of copper. It was shown by a comparison of the spectra of the complexes of diheptyl sulfide and diisopropyl sulfide (see Fig. 2, spectra *4*, *5*). Typical parameters of the spectrum are presented in Table 1. Double integration of the spectra revealed that the concentration of radicals did not exceed 0.01—0.1 % of the copper concentration.

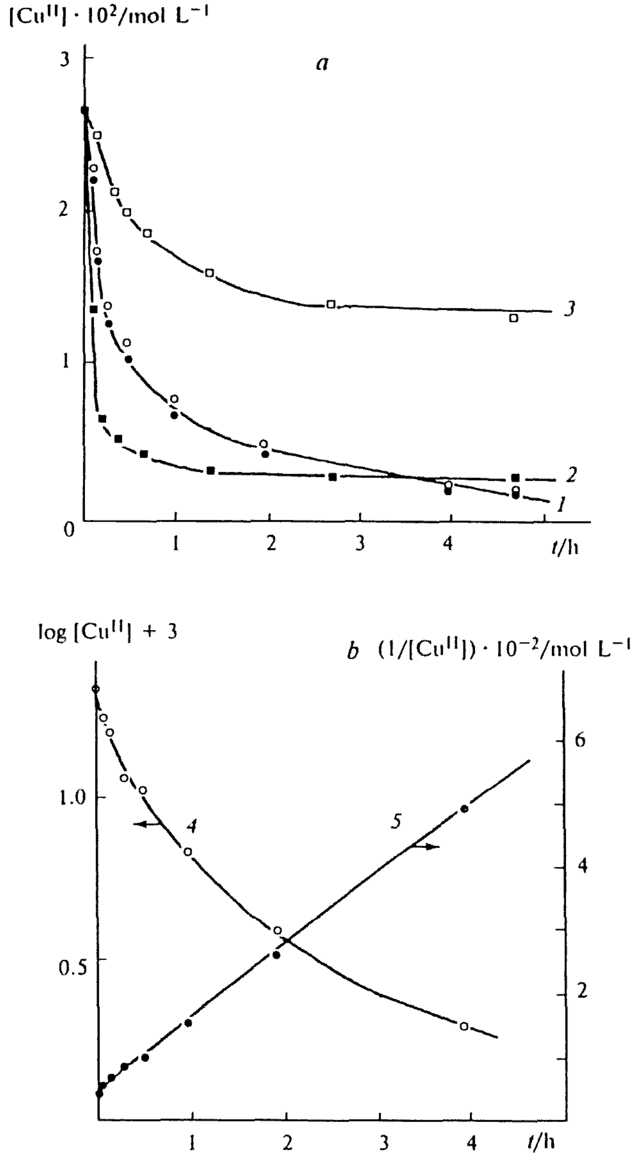


Fig. 3. Kinetic curves (*a*) of consumption of Cu^{II} in the reaction with 0.4 *M* DHS at 373 K on the basis of the integral intensities of the ESR signals in CB in a liquid phase and in a frozen solution (*1*), in DCB in a liquid phase (*2*), in a frozen solution (*3*) and the anamorphoses (*b*) of the curve (*1*) in the coordinates of kinetic equations of the first (*4*) and second (*5*) orders.

Heating the solutions of the Cu^{II} complexes with dialkyl sulfides in the presence of 3,4-DCB results in a substantial change in the pattern of the spectrum and a decrease in the intensity of the ESR signal, *i.e.*, a decrease in the concentration of paramagnetic centers. The character of the ESR spectra of the samples at 77 K after heating gives evidence for a deep restucturing of the coordination sphere of the metal. Such spectra (Fig. 4) are typical of complexes of five-coordinated copper in the D_{3h} state with an unpaired electron on the $3d_{z^2}$ orbital and a value of $g_{\parallel} < g_{\perp}$[14—17]. It has been known from the data of the X-ray structural analysis that these complexes have the structure of a slightly distorted trigonal bipyramid,[15,19—21] although the authors of a work[14] published previously suppose that the configuration of a strongly distorted tetragonal pyramid is also possible. One should expect tri-axial anisotropy of the ESR spectra for these complexes. Actually, the theoretical calculation gives strong evidence for this suggestion. In this case, a description with the aid of only $g_{\parallel}$, $a_{\parallel}$, $g_{\perp}$, and $a_{\perp}$ does not give a complete characteristic of the system. The spectrum *2* presented in Fig. 4 is calculated for the following values: $g_x = 2.007$, $g_y = 2.094$, $g_z = 2.163$; $a_x = 5.53$, $a_y = 3.0$, $a_z = 9.0$ mT and a line width $D_x = 1.69$, $D_y = 1.52$, $D_z = 2.16$ mT. It can be seen from Fig. 4 that in the region of 300—340 mT at 77 K, a good coincidence between the calculated and observed spectra is achieved.

As is seen in Fig. 3, changes in the areas of the integral ESR spectra of liquid and frozen solutions after a time of storage at 373 K show that these values differ significantly in the presence of 3,4-DCB, unlike a chlo-

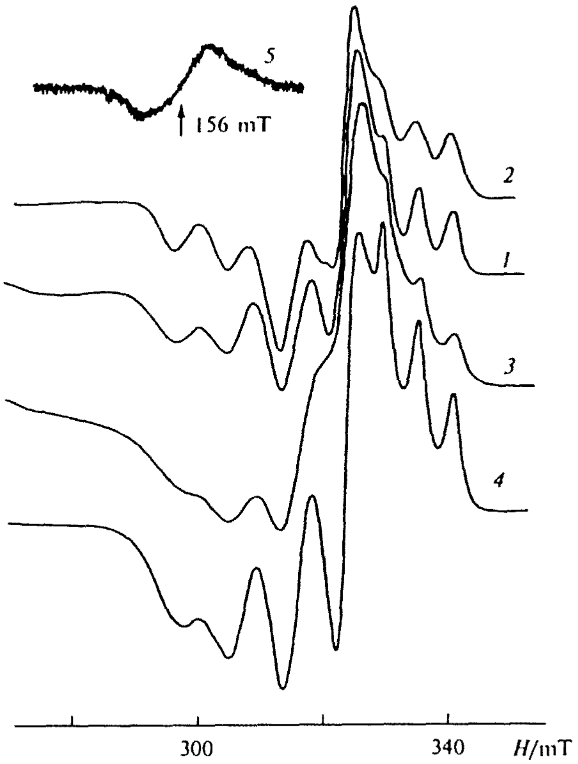


Fig. 4. ESR spectra at 77 K of Cu^{II} complexes with 0.4 *M* DHS in DCB after heating for 1 h at 373 K: *1*, 0.01 *M* $CuCl_2$; *2*, theoretically calculated spectrum of the system (*1*) (parameters are shown in the text); *3*, 0.05 *M* $CuCl_2$, solutions (*1*) and (*2*) are frozen starting at 298 K; *4*, the system (*3*) is frozen starting at 373 K; *5*, forbidden signal in a half field.

rocarbon solvent. The concentration of Cu^{II} calculated from the spectra for the liquid phase is close to zero; at the same time, this value estimated from the spectra of the frozen solutions is close to half of the initial Cu^{II} concentration. One can conclude that the ESR spectrum of the "heated" complex is not observed at room temperature for two reasons: either a sharp change in the relaxation properties (a decrease in the time of spin-lattice relaxation t_1 to 10^{-10} s and below at 295 K instead of $t_1 \sim 10^{-8}$ s at 77 K), or thermodynamic instability of this complex at 295 K. The latter seems to be more probable.

The reduction of copper(II) in the presence of chloroolefin is not completed and stops after $Cu^{I} : Cu^{II} \approx 1$. This allows one to assign the electronic and ESR spectra considered to polynuclear heterovalent complexes of copper. This assignment is uniquely confirmed by the parallel synthesis of the complex by mixing the copper(I) and copper(II) chlorides in a solution of diheptyl sulfide in 3,4-DCB in the ratio mentioned above. The above-described electronic and ESR spectra appear immediately at room temperature. The simultaneous addition of CuCl and $CuCl_2$ to a solution of DHS in DCB without preheating leads to a typical spectrum (Fig. 5, spectrum *1*). The heterovalent polynuclear copper complexes with sulfur-containing ligands have been described in the literature. Their stability is so high that the reaction of the formation of these complexes has been suggested for use in medicine for the purposes of binding the copper ions.[22] The electronic spectra of these complexes are close to those observed in this work. Thus, the complex of mercaptopropionic acid containing 2 atoms of mono- and 2 atoms of di-valent copper exhibits the most intense band at 485 nm,[22] *i.e.*, practically at the same wave length as in our case.

The existence of polynuclear complexes of several types is also confirmed by the ESR data. Other signals such as a broad line in the region of 280 mT (see Fig. 4, spectrum *3*) and a singlet signal of low intensity in a half field (forbidden transition) with $g = 4.21 \pm 0.02$ and a width of 12 ± 1.5 mT (see Fig. 4, spectrum *5*) are observed in the spectra of samples frozen in liquid nitrogen. A clear correlation between the intensities of the signals is absent, the amplitude of the signal in a half field increases with increasing copper concentration.

The pattern of the ESR spectra depends on the conditions of sample freezing. If the samples are kept at 373 K for 1—3 min prior to introducing them to liquid nitrogen, then the individual lines of the main spectrum are significantly narrower than those observed after freezing, starting at 295 K; the signal at 280 mT disappears completely (see Fig. 4, spectrum *4*). The intensity of the singlet signal in a half field does not change within the limits of the experimental accuracy. Changes in the ESR spectrum in the 280—340 mT region are reversible and reproducible when the samples are refrozen upon refreezing. There are two reasons for this. First, several conformations of the copper complex occur in solution at room temperature and are retained during freezing, but only one structure is present after heating to 373 K, which is revealed after fast cooling of the sample. In this case, the scattering in the spin-Hamiltonian parameters around a middle value develops as line broadening in the ESR spectrum. Second, due to the presence in the sample of molecules differing strongly in physicochemical properties and because the matrix does not become glassy, the distribution of copper complexes in solution at 295 K is not equally probable (contrary to the situation at 373 K), and the enhanced local concentration of complexes causes broadening of the ESR lines due to the dipole-dipole interaction of the paramagnetics.[8,23] It is impossible to choose uniquely between the two reasons, because both are connected with dynamic restructuring either of the Cu^{II} complexes or in the matrix of the solvent. The character of the changes in the ESR spectra of the complexes upon variation in their content in solution also points to the role of structural inhomogeneities in the system. A rise in concentration results in the preferential formation of structures of one type. The spectrum of the type presented in Fig. 5 becomes predominant after heating solutions containing both CuCl and $CuCl_2$; it is seen that the broad line at 280 mT refers

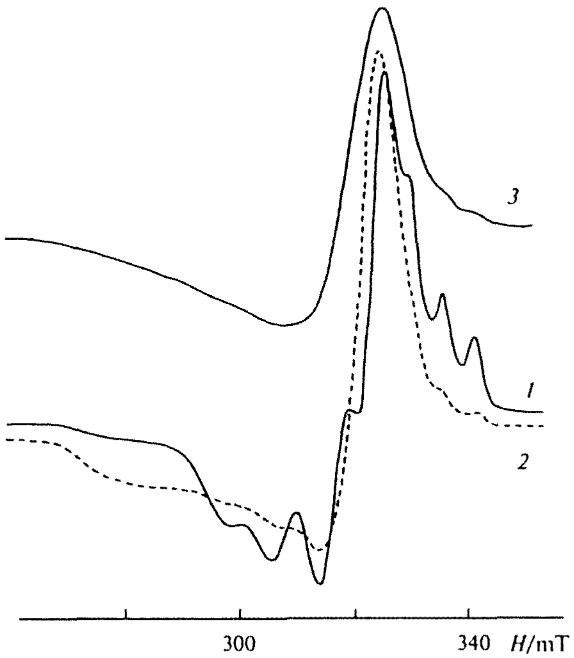


Fig. 5. ESR spectra at 77 K of the mixture of 0.01 mol L^{-1} $CuCl_2$ and CuCl with DHS in the ratio 1 : 1 : 2 in DCB immediately after preparation (*1*), heated for 1 h at 373 K (*2*) and 0.03 mol L^{-1} $CuCl_2$ and CuCl in a 10-fold excess of DHS (*3*).

to the compounds with parallel orientation of the complexes. It is impossible to estimate their parameters due to a poor resolution of the ESR spectrum, but it is obvious that they characterize mononuclear complexes of Cu^{II} having the structure of a tetragonal bipyramid with a typical relation $g_{\parallel} > g_{\perp}$.

At the same time, the existence of the signal in a half field gives evidence for the presence of polynuclear complexes containing two Cu^{II} atoms. The superposition of the signals in the spectra does not allow one to calculate correctly the concentration of the binuclear Cu^{II} complex; one can only conclude that this complex is not the only one and its fraction in the total content of Cu^{II} in a solution is not high. All these facts allow one to assume the existence of the following equilibrium at elevated temperature:

$$Cu^{I}_{2}Cu^{II} + M \rightleftharpoons Cu^{I}Cu^{II}_{2} + M^{\cdot -},$$

where M is chloroolefin or the product of its transformation.

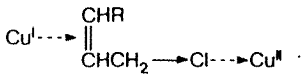
It is noteworthy that the picture considered is observed only in the case of olefins with a chlorine atom in the allylic position: replacement of 3,4-DCB-1 with 1,4-DCB-2 or allyl chloride brings virtually no changes; however, olefins containing no chlorine atoms (hexene-1), olefins with a chlorine atom in a vinyl position (1,1-dichloroethylene), and, as was mentioned above, chlorobenzene and chloroalkanes exhibit the properties of inert solvents. The data obtained points to the probable insertion of the chloroolefin molecules into the coordination sphere of the metal, facilitating the reduction of copper(II) by dialkyl sulfide.

The nature of the processes leading to the formation of heterovalent copper complexes. The processes in the dialkyl sulfide—copper(II) chloride systems result, as we see, in equilibria between different species of the complexes with coordination numbers 5 and 6 as well as in the reduction of copper(II) by sulfide. The reduction rate depends on the nature of the R group and decreases in the sequence: methyl > ethyl > heptyl > isopropyl. This dependence indicates the important role of steric factors in the course of the reduction. For diphenyl sulfide, equilibrium (1) is apparently shifted to the right, and for dialkyl sulfides with a short chain (methyl, ethyl) it is shifted to the left. It is an interesting peculiarity of the reduction process that it is second order with respect to the copper complex. It is obvious that the simplest oxidation mechanism, assuming one-electron transfer from the sulfur atom to the metal followed by the decay of the sulfide radical-cation, is insufficient to describe the process. One can suggest that participation of two copper atoms is necessary for this process, likely *via* the intermediate formation of a bridged dimer. Coordinatively unsaturated copper complexes with coordination number 5, which are potentially capable of dimerization, can play an important role.

$$\begin{aligned}2\cdot Cu^{II}(R_2S)_3Cl_2 &= [Cu^{II}_2(R_2S)_6Cl_4] = \\ &= [Cu^{I}Cu^{II}Cl_4(R_2S)_5(R_2S)^{+\cdot}] = \\ &= CuCl(R_2S)_2 + RCl + CuCl_2(R_2S)_3 + RS^{\cdot}\end{aligned}$$

Recombination of the $RS^{\cdot}$ radicals leads to the formation of disulfide. The proposed scheme seems to be oversimplified and needs refinement, particularly the composition and nuclearity of the intermediate complexes. It is also unclear which processes occur in the coordination sphere of copper and whichat processes proceed after cropping out the species into solution. The fact that the coordinated radical in the complex and the radical-cation were found in the more active system containing dichlorobutene allows one to suggest the possibility of the relatively prolonged occurrence of these species in the coordination sphere. Similarly, only a relatively low degree of isomerization of R in the alkyl halide formed is not consistent with the suggestion about cropping out of the R^{+} ion into solution. Regardless of these possible refinements, the proposed scheme as a whole is consistent with the main body of the experimental data.

The role of chloroolefin is of the most interest, in particular, its effect on redox processes in the system. In addition, chloroolefin is a necessary component for the formation of a stable polynuclear complex. The specific features of its participation in this process are connected, in our opinion, with the existence of two coordination centers: the marked negative charge of the allylic chlorine atom that is capable of coordination with Cu^{II}, and the the double bond that is electron deficient due to the negative inductive effect of a substituent; Cu^I formed can coordinate with this bond. The latter effect likely decreases the enthalpy of the process as a whole and allows the chloroolefin to act as a bridging ligand and stabilize the complex due to the averaging of the charge:



$$\begin{array}{l} \qquad\quad \mathrm{CHR} \\ \mathrm{Cu^I}\dashrightarrow \| \\ \qquad\quad \mathrm{CHCH_2}\longrightarrow\mathrm{Cl}\dashrightarrow\mathrm{Cu^{II}} \end{array}$$

The stabilizing role of DCB develops obviously in the dimethyl sulfide—$CuCl_2$ system. When 0.01 *M* $CuCl_2$ and 0.1 *M* Me_2S are diluted in $CHCl_3$,, the optical density of the solution at the maximum of the absorption wave of the complex (440 nm) does not exceed 0.1 after 5 min at room temperature; under the same conditions, the optical density in DCB is equal to ~1.5. The ESR spectrum of a solution is similar to that presented in Fig. 4, spectrum *4*, *i.e.*, the complex includes the five-coordinated fragments of the Cu^{II} surrounding. Complexes of this type prevail in solution at 373 K under the conditions that are optimum for isomerization. The role of coordinatively unsaturated copper complexes in catalysis has also been shown in a series of processes,[1,11,24] which may be connected with the easy formation of labile polynuclear compounds including substrate molecules and forming favorable conditions for stabilization of charge at the stage of the electron transfer that is apparently of great importance in the mechanism of isomerization.[25] The formation of such polyassociated structures in the simultaneous presence of copper atoms with different degrees of oxidation follows from the analysis of the pattern of the ESR spectra (see Fig. 5).

The results presented in this work make it possible to conclude that the reaction system under consideration contains a series of copper complexes that equilibrate with each other. Their relation is determined by their concentrations and temperature. Heterovalent polynuclear complexes with different ligands seem to play a key role in both the transformations of the complexes and catalytic processes with their participation. The complexes mentioned are formed *via* coordinatively unsaturated (five-coordinated) species or contain these fragments in their composition.

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