Spectroscopic study of ternary copper(II) complexes on a silica surface*

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The formation of ternary surface complexes of copper(II) with one or two molecules of 2,2′-bipyridine (bpy) or α-picolinic acid (Hpic), which were obtained after adsorption on the silica surface in different ways, was studied by electronic and ESR spectroscopy. Coordination of the ligands, which were preliminarily adsorbed by copper ions, afforded only 1 : 1 ternary surface complexes. In both cases, coordinatively more saturated ternary surface complexes were formed only when $Cu(bpy)_2^{2+}$ and $Cu(pic)_2$ were adsorbed on the SiO_2 surface from solutions. The compositions and structures of the ternary surface complexes containing bipyridine ligands are temperature independent, whereas in the picolinate-containing ternary surface complexes, the coordination spheres of the adsorbed complexes are rearranged as the temperature changes.

Key words: copper, 2,2′-bipyridine, picolinic acid; complex formation, structure, surface; UV-Vis spectroscopy, ESR spectroscopy.

The formation of ternary complexes of transition metals adsorbed on the SiO_2 surface and containing various organic ligands has been extensively studied.[1–6] Ternary surface complexes play an important role in the migration of metal ions in natural waters, heterogeneous catalysis, and natural photocatalytic processes, and they are also of interest in problems of environmental protection.[7–9] Most works were devoted to studies of the thermodynamics of the sorption of metal ions on the SiO_2 surface and of the further coordination of ligand molecules to metal ions from aqueous solutions, whereas the structures of ternary surface complexes have received little attention.

In this work, the compositions and structures of the SiO_2—Cu^{II}—2,2′-bipyridine (bpy) and SiO_2—Cu^{II}—α-picolinic acid (Hpic) ternary surface complexes were studied by spectroscopic methods. Two cases were considered, namely, adsorption of the complexes, which were preliminarily formed in solution, on the surface and successive adsorption of all components of ternary surface complexes on SiO_2. The choice of the ligands was determined by the fact that the thermodynamics of the sorption of these ligands has been well studied and the corresponding stability constants have been measured.[2,3,6,9]

Experimental

We used a highly dispersed amorphous low-porous pyrogenic A-300 silica (Kalush Industries, Ukraine) with specific surface 300±20 m^2 g^{-1}, 2,2′-bipyridine (Fluka), α-picolinic acid (Reanal), and $NaClO_4 \cdot H_2O$ (Merck). A solution of copper perchlorate was prepared by neutralizing copper basic carbonate (Reakhim, chemical purity grade) with perchloric acid (Reakhim, chemical purity grade). The concentration of copper in the solution was determined by trilonometric titration with murexide. The pH of the solutions was adjusted by adding NaOH or $HClO_4$ solutions. The concentrations of 2,2′-bipyridine and α-picolinic acid were determined spectrophotometrically.

Adsorption of copper ions on SiO_2. A solution of $Cu(ClO_4)_2$ containing $NaClO_4$ (0.1 mol L^{-1}) was added to a slurry of SiO_2 (10 g L^{-1}) in a solution of $NaClO_4$ (0.1 mol L^{-1}) preliminary prepared and kept at pH ~5 for 2 weeks. The values of pH of the solutions were adjusted to 5.8—5.9 by adding a solution of NaOH (0.01 mol L^{-1}) dropwise with stirring. The slurry was stored for 2 h (pH control) and then centrifuged. The resulting samples were dried at room temperature for 2 days. The concentration of the adsorbed copper was determined from the difference in the concentrations of copper ions in the initial and equilibrium solutions and by removing copper ions from the silica surface in an acidic solution. In both cases, trilonometric titration was used. Both methods gave identical results.

Adsorption of bpy and Hpic on the surface of silica modified with copper ions. Solutions of bipyridine or picolinic acid were added to a slurry of silica, which contained Cu^{II} and a solution of $NaClO_4$ (0.1 mol L^{-1}), so that the ratio of the concentration of copper ions adsorbed on the silica surface and the

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concentration of organic ligands in the solution was 1 : 1 or 1 : 2. The pH was adjusted to 5.9—6.0. The slurry was stored for 2 h. The precipitate was separated by centrifugation and dried at room temperature.

Simultaneous adsorption of Cu^{2+} ions and ligands. A solution of copper perchlorate and bipyridine (or picolinic acid) taken in the ratio 1 : 1 or 1 : 2 in a solution of $NaClO_4$ (0.1 mol L^{-1}) at pH 6.0 (6.5 in the case of picolinic acid) was added to a slurry of silica. After storage of the slurry, the precipitate was separated by centrifugation and dried at room temperature.

The concentrations of the adsorbed components of the ternary surface complexes in samples of both types were determined from the difference in the concentrations of copper ions and organic ligands in the initial and equilibrium solutions.

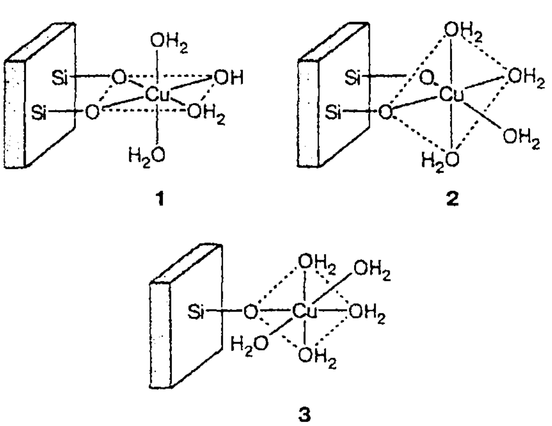
The absorption and reflection spectra in the UV and visible regions were recorded on a Specord M-40 spectrophotometer. The ESR spectra were measured on X-range Varian E-4 and Bruker ER-200D radiospectrometers at room temperature (298 K) and 77 K using 4 mm-diameter thin-walled quartz tubes. Precise calibration of the magnetic field was carried out with the use of diphenylpicrylhydrazyl (g = 2.0036) and Mn^{2+} ions in the MgO matrix as the standards. The principal values of the g tensor ($g_{\|}$ and $g_{\perp}$), the constants of the hyperfine interaction between the unpaired electron and the nuclei of copper atoms ($A_{\|}$), and the constants of the hyperfine interaction between the unpaired electron and the nuclei of ^{14}N atoms of the ligands ($a_{\perp}{}^{N}$) were determined from the ESR spectra according to a procedure reported previously.[10]

Results and Discussion

The adsorption of $Cu(H_2O)_6{}^{2+}$ aqua ions on the SiO_2 surface at 5.5 < pH ≤ 6.0 is highly efficient. Under the experimental conditions, up to ~50% of copper ions, which were present in the initial solution, were adsorbed.

The shape of the ESR spectrum of the adsorbed copper $\{(\equiv SiO)_2Cu\}$ (**1**) (Fig. 1) and the parameters of the spin-Hamiltonian (Table 1) are typical of the Cu^{II} complexes, which are characterized by the axial symmetry of the coordination sphere (a slightly distorted octahedron) in the ground state b_{1g} and by localization of the unpaired electron on the $3d_{x^2-y^2}$-orbital ($g_{\|} > g_{\perp} > 2$). In all the samples under study, unlike the samples studied previously,[3] Cu^{II} ions noncoordinated on the SiO_2 surface were absent. The possible types of the polyhedra that formed are shown in Scheme 1.

Scheme 1



Structure **1** is, apparently, most probable because this complex should possess a high stability constant,[1] and its ESR spectrum should be described by the axially symmetrical spin-Hamiltonian. Structures **2** and **3** do not meet this condition, and the manifestation of the triaxial symmetry should be expected in the ESR spectra of these structures. Moreover, complexes of type **3** should be substantially less stable and more mobile than **1**.

The integrated intensity of the ESR signal of $\{(\equiv SiO)_2Cu\}$ samples increases several times after adsorption of bipyridine. This is indicative of the possibility of formation of polynuclear hydroxo clusters of copper with the compensated total spin, *i.e.*, formally diamagnetic complexes, as has been observed previously in the case of many carboxyl-containing cation exchangers.[11] Previously, an analogous suggestion was made in Ref. 4. Our results agree well with the data on the copper aqua ions adsorbed on the TiO_2 and Al_2O_3 surfaces.[12,13]

The SiO_2+Cu^{II}+bpy system. The samples containing copper ions (from 10^{-5} to $1.6 \cdot 10^{-4}$ mol g^{-1} of SiO_2) in the presence of bipyridine at the initial ratios γ = [Cu^{II}] : [bpy] = 1 : 1 and 1 : 2 were studied by ESR and optical spectroscopy. The typical ESR spectra are

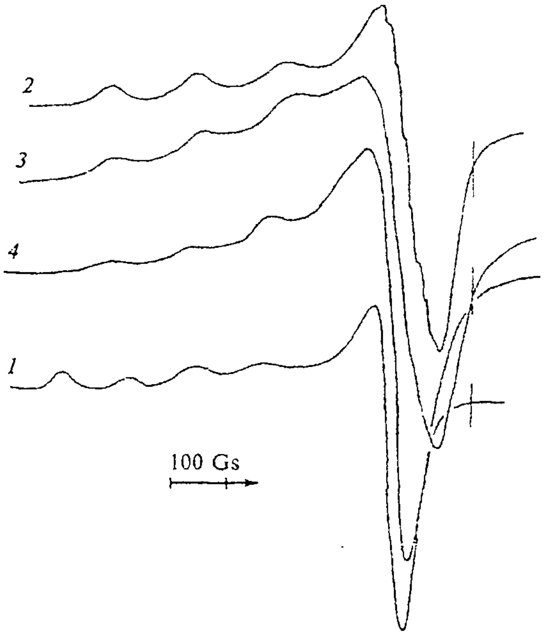


Fig. 1. ESR spectra of the adsorbed complexes: SiO_2—Cu^{II} (*1*); SiO_2—Cu(bpy)(*2*, *3*); SiO_2—$Cu(bpy)_2$ (*4*) at 77 K (*1*—*3*) and 298 K (*4*). [Cu^{II}] = $2 \cdot 10^{-5}$ (*1*, *2*); $1.2 \cdot 10^{-4}$ (*3*); $5.8 \cdot 10^{-5}$ mol g^{-1} of SiO_2 (*4*). The vertical corresponds to g = 1.981.

Table 1. Parameters of the ESR spectra of the Cu^{II} complexes adsorbed on the SiO_2 surface

Sample	$[Cu^{II}] \cdot 10^4$ /mol g^{-1} of SiO_2	298 K			77 K		
		$A_{\parallel}$[a]	$g_{\parallel}$[b]	$g_{\perp}$[b]	$A_{\parallel}$[a]	$g_{\parallel}$[b]	$g_{\perp}$[b]
$Cu(ClO_4)_2$	0.002[c]				11.7	2.424	2.092
SiO_2+$Cu(ClO_4)_2$	0.5	—	—	—	12.3	2.389	2.079
[SiO_2+Cu]+bpy (1 : 1)	0.1	15.9	2.279	2.065			
[SiO_2+Cu]+bpy (1 : 1)	0.2	16.1	2.280	2.067[d]	16.0	2.280	2.066[f]
[SiO_2+Cu]+bpy (1 : 1)	1.2	16.1	2.273	2.062	16.3	2.281	—
[SiO_2+Cu]+bpy (1 : 2)	0.2	16.1	2.273	2.064	16.2	2.280	2.067
[SiO_2+Cu]+bpy (1 : 2)	1.2	16.3	2.272	2.070	16.3	2.276	—
SiO_2+$Cu(bpy)^{2+}$	0.25	16.0	2.276	2.064[e]	16.2	2.282	2.065
SiO_2+$Cu(bpy)_2^{2+}$	0.2	14.6	2.255	2.080			

[a] $A_{\parallel}$±0.3/mT. [b] ($g_{\parallel}$, $g_{\perp}$)±0.005. [c] mol L^{-1} in a 1 : 1 MeOH—D_2O mixture. [d] $a_{\perp}^N$ = 1.31±0.02 mT. [e] $a_{\perp}^N$ = 1.29±0.02 mT. [f] $a_{\perp}^N$ = 1.45±0.03 mT.

shown in Fig. 1. The measured parameters are given in Table 1. The reflection spectra are shown in Fig 2.

Analysis of the ESR spectra at 298 and 77 K demonstrated that, regardless of the procedure for the preparation of {(≡SiO)$_2$Cu} + n·bpy or SiO_2 + $Cu(bpy)_n^{2+}$ samples (where n = 1 or 2), these samples do not contain (within the experimental error (≤5%)) copper ions, which have no organic ligands (bpy) in the coordination sphere. The number of paramagnetic [SiO_2—Cu^{II}—bpy] ternary surface complexes adsorbed on SiO_2 is more than an order of magnitude higher than the maximum number of paramagnetic {(≡SiO)$_2$Cu} ternary surface complexes, which agrees with the data obtained previously.[3]

When a solution containing copper ions and bipyridine in the ratio of 1 : 1 (in this solution in the absence of silica at pH > 3, the $Cu(bpy)^{2+}$, $Cu(bpy)_2^{2+}$, and $Cu(H_2O)_6^{2+}$ complexes occur in the equilibrium in the ratio of 90 : 5 : 5%, respectively[3]) was added to a slurry of silica, only $Cu(bpy)^{2+}$ complexes were adsorbed on the SiO_2 surface. Absorption from a solution containing Cu^{II} and bipyridine in the ratio of [Cu^{II}] : [bpy] = 1 : 2 (in the solution, ~100% of $Cu(bpy)_2^{2+}$ occur)[3] gave a sample whose ESR spectrum (see Fig. 1) is more typical of a mixture of complexes of several types rather than of an individual ternary surface complex. A decrease in the concentration of the ternary surface complex on the surface to $2 \cdot 10^{-5}$ mol g^{-1} made it possible to determine the parameters of the second complex {(≡SiO)$_2$Cu(bpy)$_2$} (see Table 1).

A comparison of the parameters of the ternary surface complexes measured by us with the data reported in the literature (Table 2) demonstrated good agreement within the experimental error. The slightly lower values

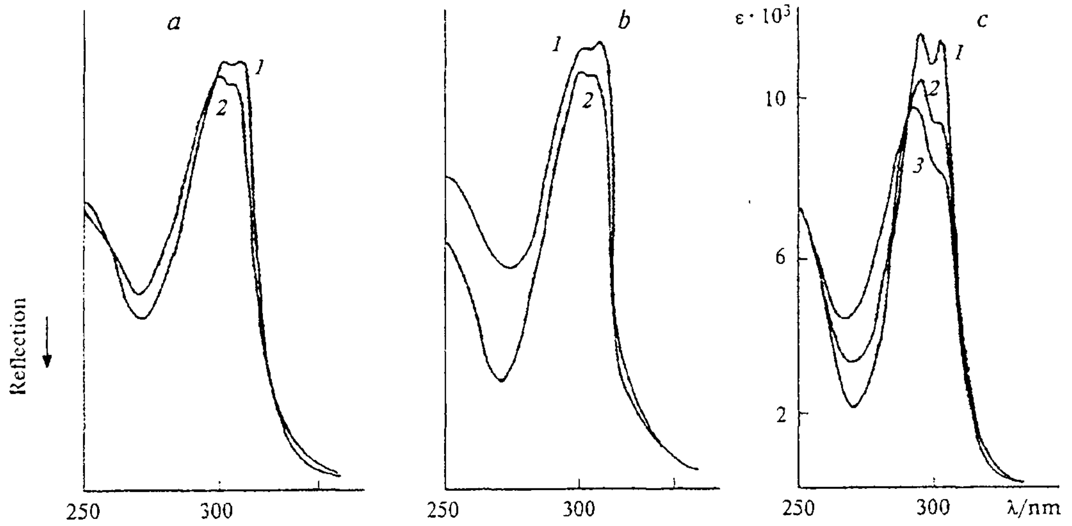


Fig. 2. Reflection spectra of the samples obtained after adsorption of the $Cu(bpy)^{2+}$ (*1*) and $Cu(bpy)_2^{2+}$ (*2*) complexes on the SiO_2 surface (*a*); bipyridine on the surface of copper-containing silica at the ratios of γ = 1 (*1*) and γ = 2 (*2*) (*b*); and the absorption spectra of solutions of the $Cu(bpy)^{2+}$ (*1*), $Cu(bpy)_2^{2+}$ (*2*), and $Cu(bpy)_3^{2+}$ (*3*) complexes in a solution of $NaClO_4$ (0.1 mol L^{-1}) (*c*).

Table 2. Parameters of the ESR spectra of the Cu^{II} complexes with bpy

Complex	$A_{\|}$[a]	$g_{\|}$[b]	$g_{\perp}$[b]
$\{(\equiv SiO)_2Cu\}$	136.0	2.389	2.079
$\{(\equiv SiO)_2Cu(bpy)\}$	170.0	2.281	2.066
$\{(\equiv SiO)_2Cu(bpy)_2\}$	152.5	2.255	2.080
$\{(\equiv SiO)_2Cu\}$ [4,14]	139.0	2.380	2.080
$\{(\equiv SiO)_2Cu\}$ [3]	128.0	2.380	2.085
$\{(\equiv SiO)_2Cu(bpy)\}$ [3]	165.0	2.290	2.067
$\{(\equiv SiO)_2Cu(bpy)_2\}$ [3]	150.0	2.259	2.073
$Cu(bpy)^{2+}$	164.0	2.316	2.071
$Cu(bpy)_2{}^{2+}$	156.0	2.275	2.074
$Cu(bpy)_3{}^{2+}$	160.4	2.268	2.069
$Cu(bpy)^{2+}$ [16]	165.0	2.315	2.072
$Cu(bpy)_2{}^{2+}$ [16]	165.0	2.285	2.082
$Cu(bpy)_3{}^{2+}$ [16]	161.0	2.271	2.073

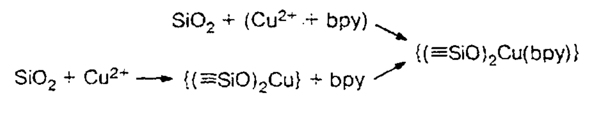
[a] $(A_{\|}\pm 3)\cdot 10^4/\mathrm{cm}^{-1}$. [b] $(g_{\|}, g_{\perp})\pm 0.005$.

of $A_{\|}$ and higher values of $g_{\|}$ (see Ref. 3) are most likely attributable to the inadequate accuracy of measurements of the frequency of the microwave field or accuracy of calibration of the magnetic field. The substantially lower value of $g_{\|}$ in the case of the ternary surface complex compared to that of the corresponding bipyridine complex in a solution is worthy of note. This is indicative of some differences in the structures of these complexes affecting the electron density distribution, which is reflected in the parameters of the spin-Hamiltonian.

Based on the data in Tables 1 and 2, three conclusions can be made. First, the parameters of the ESR spectra of the $\{(\equiv SiO)_2Cu(bpy)_n\}$ complexes measured at 298 and 77 K coincide within the experimental error. Second, the shape of the ESR spectrum of the $\{(\equiv SiO)_2Cu(bpy)\}$ ternary surface complex and, consequently, its structure are independent of the way of its formation on the surface. Third, the ESR spectrum of the sample obtained after adsorption of bipyridine on the silica surface from a solution containing a twofold excess of bipyridine with respect to copper ions demonstrated that in this case no noticeable amount of the $\{(\equiv SiO)_2Cu(bpy)_2\}$ ternary surface complex was observed.

Therefore, the two different methods of preparation of ternary surface complexes of copper ions with bipyridine formed on the SiO_2 surface (when γ = 1) gave samples with identical structures (Scheme 2).

Scheme 2

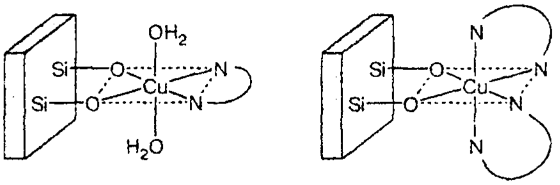


This is also confirmed by the fact that the UV reflection spectra of the ternary surface complexes prepared by the two procedures are identical (see Fig. 2).

Adsorption of the $Cu(bpy)_2{}^{2+}$ complex on the silica surface from a solution gave the ternary surface complexes of two types, $\{(\equiv SiO)_2Cu(bpy)\}$ (**4**) and $\{(\equiv SiO)_2Cu(bpy)_2\}$ (**5**). In this case, the amount of the second complex is substantially smaller, as was mentioned previously.[3] In the case of adsorption of bipyridine on the surface of SiO_2 modified with copper ions (at γ = 2), we failed to detect the ternary surface complex of type **5**. The formation of this ternary surface complex after adsorption of bipyridine on the copper-containing silica surface from a solution is hindered, which is confirmed by optical spectroscopy. Figure 2 shows the reflection spectra of the ternary surface complexes obtained after adsorption of the available $Cu(bpy)^{2+}$ and $Cu(bpy)_2{}^{2+}$ complexes from solutions (see Fig. 2, *a*), the reflection spectra of the ternary surface complexes obtained after adsorption of bipyridine on the surface of copper-containing SiO_2 at γ = 1 and 2 (see Fig. 2, *b*), and, for comparison, the absorption spectra of the $Cu(bpy)_n{}^{2+}$ complexes in a solution (see Fig. 2, *c*). As can be seen from Fig. 2, an increase in the number of the coordinated bipyridine molecules is accompanied by a decrease in the intensity of the long-wavelength band (λ = 310 nm). The analogous decrease in the intensity of this band is also observed in going from one sample to another, which were prepared by the adsorption of $Cu(bpy)^{2+}$ and $Cu(bpy)_2{}^{2+}$, respectively, on the SiO_2 surface. The change in the intensity of the long-wavelength band of the samples obtained after adsorption of bipyridine on the copper-containing silica surface is substantially smaller.

Apparently, adsorption of the $Cu(bpy)_2{}^{2+}$ complex, which was preliminarily synthesized, on the silica surface proceeds more readily than introduction of the second bipyridine molecule into the coordination sphere of the $\{(\equiv SiO)_2Cu(bpy)\}$ complex, which requires the substantial rearrangement of the structure of the ternary surface complex from **4** to **5** (Scheme 3). The most probable structures of the resulting ternary surface complexes can be represented as follows:

Scheme 3



4 **5**

Structure **4** for the $\{(\equiv SiO)_2Cu(bpy)\}$ ternary surface complex is additionally supported by the presence of the hyperfine splitting of the high-field components of the ESR spectra of this complex due to the interaction between the unpaired electron and the ^{14}N atoms of the bipyridine molecule (see Table 1) since it is known[17] that the hyperfine structure manifests itself only when N atoms are located in the equatorial plane of the coordination polyhedron about Cu^{II}, and it is absent when N-containing ligands occupy axial positions. Structure **5** was first suggested for the $\{(\equiv SiO)_2Cu(bpy)_2\}$ complex in Ref. 3.

An increase in the concentration of complex **4** on the surface leads to a noticeable broadening of the components of its ESR spectrum (see Fig. 1) owing to magnetic dipole-dipole interactions between the paramagnetic centers. The average distance $<r>$ between the complexes can be determined from the value of this broadening δH measured at 77 K (when the complexes are immobile) using the known equations for the case of the equally probable (random) distribution of paramagnets:[15]

$$\delta H = \Delta H - \Delta H_0 = A \cdot c;\ <r> = c^{-1/3},$$

where ΔH is the width of the individual uniform ESR line, ΔH_0 is the width of the line in the absence of the dipole-dipole interaction, c is the local concentration of the paramagnet, and A is the coefficient, which depends on the character of the spatial distribution of the paramagnetic centers in the sample and on the shape of the individual line. The numerical values of A were reported in the literature for many cases[15] and are confirmed by the abundant experimental data. For the Lorentz shape of the lines (random distribution) for nonequivalent spins, $A = 5.4 \cdot 10^{-20}$ Gs cm^{-3} in the case of the line width between the points of the maximum slope.

The estimations made demonstrated that the average distance $<r>$ between the adsorbed complexes decreases from 3.5±0.4 to 1.4±0.1 nm as the concentration of Cu^{II} changes from $2 \cdot 10^{-5}$ to $1.2 \cdot 10^{-4}$ mol g^{-1} of SiO_2. The obtained values seem to be quite reasonable. Actually, the surface area of silica used is ~300 m$^2 \cdot$ g^{-1}, *i.e.*, at the above-mentioned concentration of copper, an average area of 25.0 and 4.17 nm^2, respectively, corresponds to each ion, and the average distance between ions should be no more than 5.0 and 2.0 nm, respectively.

The SiO_2+Cu^{II}+α-picolinic acid system. The study of this system was of great interest because the main difference between α-picolinic acid and electroneutral bidentate ligands (for example, bipyridine) is its negative charge at pH > 2.

In aqueous solutions (pH > 2) of $NaClO_4$ (0.1 *M*) containing Cu^{II} and picolinate ions in the ratio of γ = 1 : 1 in a wide concentration range in the absence of silica, the $Cu(pic)^+$ (65%, $\log K_1 = 7.95$), $Cu(pic)_2$ (17.5%, $\log\beta_2 = 14.95$), and $Cu(H_2O)_6^{2+}$ (17.5%) complexes (K_1 and β_2 are the corresponding stability constants of the complexes[3] and of the picolinate anion of α-picolinic acid) occur in equilibrium. In a solution containing $Cu(ClO_4)_2$ and picolinic acid in the ratio of 1 : 2, the concentration of $Cu(pic)_2$ is ~100% at pH > 4.

The UV reflection spectra of the samples obtained after adsorption from solutions with the ratios γ = 1 and γ = 2 are virtually identical (as well as in the case of individual complexes in solutions), whereas the visible regions of these spectra are different. The *d—d* transition band occurs at 720 and 690 nm for the $\{(\equiv SiO)_mCu(pic)\}$ and $\{(\equiv SiO)_mCu(pic)_2\}$ samples, respectively. This indicates that the coordination sphere about the copper ion in the second complex contains a larger number of N atoms than in the first complex.[18] The total amount of the copper complexes adsorbed from a solution with γ = 2 is several times smaller than that in the case of adsorption from a solution with the ratio of 1 : 1 at equal initial concentrations of copper perchlorate and picolinic acid. We failed to obtain samples of picolinate anions adsorbed on the surface of SiO_2 containing copper ions. When a solution of picolinic acid at pH 6.5 was added to a slurry of the copper-containing silica, the samples virtually did not contain picolinate anions on the SiO_2 surface. Analysis of equilibrium solutions demonstrated that Cu^{II} ions were virtually completely desorbed (>80%) from the silica surface to the solution with picolinate anions. Apparently, this is associated with the fact that the Cu^{II} complexes with a picolinate anion in solutions are thermodynamically more stable than the corresponding ternary surface complexes because the formation of the latter complexes is determined by competition for metal ions between the ligands in a solution and the surface groups of the oxide carrier.[9]

The major data on the structures of the ternary surface complexes of Cu^{II} ions with picolinate anions were obtained by ESR spectroscopy. Figure 3 shows the

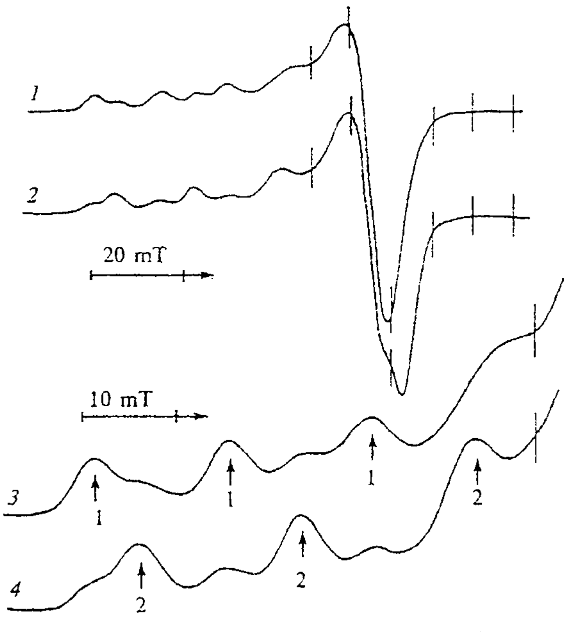


Fig. 3. ESR spectra of the adsorbed SiO_2—$Cu(pic)^+$ (*1*, *3*) and SiO_2—$Cu(pic)_2$ (*2*, *4*) complexes at 298 K. $[Cu^{II}] = 10^{-4}$ (*1*, *3*) and 10^{-5} mol g^{-1} of SiO_2 (*2*, *4*); (*3*, *4*) are the low-field components of spectra *1* and *2* at the large amplification. The verticals belong to the Mn^{2+} in MgO used as the standard.

Table 3. Parameters of the ESR spectra of the Cu^{II} complexes with Hpic at 298 K

Complex	$A_{\|}$[a]	$g_{\|}$[b]	$g_{\perp}$[b]
$\{(\equiv SiO)_nCu(pic)\}$	159.0	2.304	—
	180.0	2.245	—
$\{(\equiv SiO)_nCu(pic)\}$[c]	155.0	2.304	2.065
$\{(\equiv SiO)_nCu(pic)\}$[d]	165.0	2.308	2.065
$\{(\equiv SiO)_nCu(pic)_2\}$	179.4	2.243	2.066
$\{(\equiv SiO)_nCu(pic)_2\}$[c]	179.0	2.240	2.061
$\{(\equiv SiO)_nCu(pic)\}$ [3]	155.0	2.318	—
$\{(\equiv SiO)_nCu(pic)_2\}$ [3]	180.0	2.255	—
$Cu(pic)^+$ [19]	160.5	2.332	2.070
$Cu(pic)_2$ [19]	178.0	2.259	2.059
$Cu(pic)_3^-$ [19]	165.0	2.284	2.059
$Cu(pic)^+$ [20]	162.0	2.332	—
$Cu(pic)_2$ [20]	175.0	2.261	—

[a] $(A_{\|} \pm 3) \cdot 10^4/cm^{-1}$. [b] $(g_{\|}, g_{\perp}) \pm 0.005$. [c] Another silica series. [d] At 77 K.

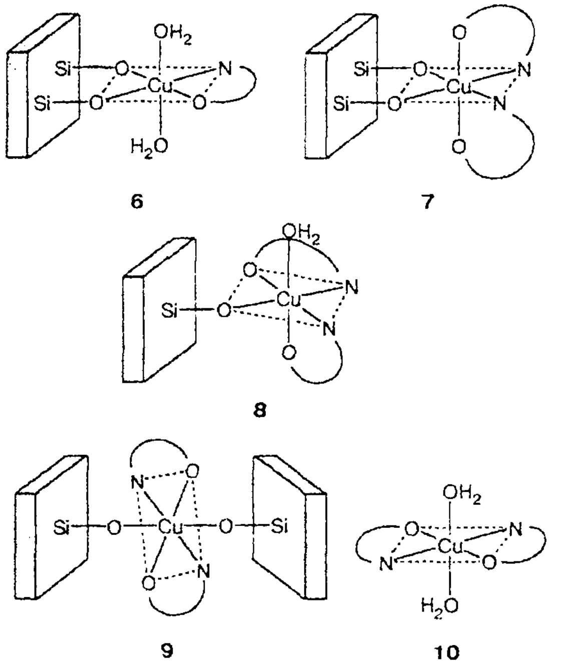
ESR spectra of the samples obtained after adsorption of the complexes on SiO_2 from solutions containing Cu^{II} and picolinic acid in the ratios of 1 : 1 and 1 : 2. It can be seen that, in both cases, ternary surface complexes of two types occur on the surface, whereas the $\{(\equiv SiO)_2Cu^{II}\}$ complexes, which do not contain picolinate anions, are absent. It is interesting that the distribution of the ternary surface complexes containing one and two picolinate anions remained unchanged as the concentration of the adsorbed Cu^{II} ions changed by an order of magnitude (from 0.2 to $2.0 \cdot 10^{-4}$ mol g^{-1}). The data in Table 3 demonstrated that the ternary surface complexes observed are actually adsorbed complexes of the above-mentioned composition. As in the case of the copper complexes with bipyridine, the adsorption of the $Cu(pic)_n$ complexes on SiO_2 leads to a substantial decrease in the value of $g_{\|}$ with a fixed value of $A_{\|}$ compared to the corresponding complexes in solutions (Table 3).

Analysis of the components of the ESR spectrum, which correspond to the parallel orientation of the z axis of the complexes in the magnetic field (see Fig. 3), made it possible to determine the portion of ternary surface complexes of each type with an accuracy of ±10%. At 298 K, the sample obtained at the initial ratio of 1 : 1 contained 59% of the $\{(\equiv SiO)_nCu(pic)\}$ complex and 41% of the $\{(\equiv SiO)_mCu(pic)_2\}$ complex (74% and 26%, respectively, for another analogous series). The samples obtained at the ratio of 1 : 2 contained 38% and 62% of these complexes, respectively (27% and 73% for another series).

When the temperature at which the spectra were recorded was decreased from 298 to 77 K, the ESR spectrum changed substantially. These changes are associated with a decrease in the amount of the ternary surface complex containing $Cu(pic)_2$ and an increase in the amount of the $\{(\equiv SiO)_nCu(pic)\}$ ternary surface complex. This is is indicative of deep structural rearrangements in the system. Studies of the mechanism and thermodynamics of this process are in progress.

The probable structures of the ternary surface complexes containing picolinate anions is shown in Scheme 4.

Scheme 4



Structure **10** of the $Cu(pic)_2$ complex determined by X-ray structural analysis[21] is shown in Scheme 4 for comparison. This structure is characterized by the *trans* arrangement of the O and N atoms of two ligands in the equatorial plane of the complex.

Structure **6**, which corresponds to the electroneutral complex, seems to be the most probable for the $\{(\equiv SiO)_nCu(pic)\}$ complex because this ternary surface complex is most stable although its stability should be substantially lower than that of the $\{(\equiv SiO)_2Cu(bpy)\}$ complex (**4**) due to the smaller contribution of the Coulomb interaction between the $Cu(pic)^+$ cation and dissociated silanol $\equiv SiO^-$ groups of the surface compared to that of $Cu(bpy)^{2+}$.

In the ESR spectrum of structure **7**, the triaxial anisotropy of the parameters of the spin-Hamiltonian should be observed, and the values of $g_{\|}$ and $A_{\|}$ should differ noticeably from those of the vitrified solutions of $Cu(pic)_2$ due to the substantial deviation from the structure of a slightly elongated octahedron **10**. This is not the case with the $\{(\equiv SiO)_nCu(pic)_2\}$ complex (see Table 3). Therefore, the formation of the structure of type **7** is unlikely for the last-mentioned complex. Structure **8** seems to be most probable for this ternary surface complex. In principle, structure **9** is also possible for silica with the developed surface used in this work. The possibility of the formation of ternary surface complexes in which $Cu(pic)_2$ are bonded to the surface only through H bonds between donor atoms of the ligands and undissociated ≡SiOH groups of the surface must not be ruled out. This structure has been proposed previously for the $Cu(pic)_2$ complex[3] and for the amino acid (Aa) complexes of copper, $Cu(Aa)_2$, on the Al_2O_3 surface.[22] This suggestion accounts also for the close values of the parameters of the $\{(\equiv SiO)_nCu(pic)_2\}$ ternary surface complex and the $Cu(pic)_2$ complex in a vitrified solution (see Table 3).

Therefore, the systems with α-picolinic acid are substantially less stable than the ternary surface complexes with bipyridine. Actually, in the SiO_2—Cu^{II}—bpy system, 90—95% of complex copper ions $Cu(bpy)_n{}^{2+}$ were adsorbed at pH $\geq$ 6, whereas in the case of the SiO_2—Cu^{II}—Hpic system, the adsorption of the copper complexes under these conditions was no more than 30%. Apparently, the Coulomb factor plays a role due to the difference in the charges of the $Cu(bpy)_n{}^{2+}$, $Cu(pic)^+$, and $Cu(pic)_2$ complexes.

When ligands were coordinated by copper ions $\{(\equiv SiO)_2Cu\}$ that have been preliminarily adsorbed, only the 1 : 1 ternary surface complexes formed. In both cases (with both ligands), the coordinatively more saturated ternary surface complexes are formed only in the case of adsorption of the $Cu(bpy)_2{}^{2-}$ and $Cu(pic)_2$ complexes from solutions on the SiO_2 surface. The compositions and the structures of the $\{(\equiv SiO)_2Cu(bpy)_n\}$ complexes are temperature independent, whereas in the $\{(\equiv SiO)_mCu(pic)_n\}$ complexes, the coordination spheres of the adsorbed complexes undergo rearrangement as the temperature decreases.

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