Structure and Composition of the Anionic Chloride Complexes of Copper(II) as the Precursors of Catalysts for C–Cl Bond Metathesis

E. N. Golubeva*, A. I. Kokorin**, D. I. Kochubei***, V. I. Pergushov*, and V. V. Kriventsov***

* Moscow State University, Moscow, 119899 Russia
** Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia
*** Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia
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Abstract—The chloride complexes of copper(II) (catalysts or catalyst precursors for various reactions of halogenated hydrocarbons) were characterized using electron, EPR, and EXAFS spectroscopy. It was found that chlorocuprates occur as mononuclear ($[CuCl_4]^{2-}$), binuclear ($[Cu_2Cl_6]^{2-}$), and, probably, polynuclear species in chlorobenzene solutions. The Cu–Cl bond length in $[CuCl_4]^{2-}$ is 2.25 ± 0.2 Å, which is close to the same values for crystalline tetrachlorocuprates. It was assumed that the chloride complexes of copper with counterions occur as globules in chlorobenzene.

INTRODUCTION

Chloride complexes of copper are successfully used as catalysts or catalyst precursors for the chlorination [1], oxychlorination [2], and hydrochlorination [3] of hydrocarbons. In a number of cases, the addition of chloride anions to copper complexes with organic ligands can considerably improve their catalytic activity [4]. The question of the relationship between the catalytic activity and the structure and composition of the chloride complexes of copper(II) is still an open question, because reliable structural data were obtained only for crystalline chlorocuprates, whereas complexes in solutions or on the surfaces of various supports are used in catalysis. The structural data for chlorocuprate single crystals are indicative of various compositions and geometries of the complexes. They can occur as mononuclear complexes with the coordination numbers 4 ($[CuCl_4]^{2-}$) and, rarely, 5 ($[CuCl_5]^{3-}$) and as dimers or polymer chains [5]. The nature of the counterion is the main factor affecting the geometry of the coordination environments of copper ions in chloride complexes [5]. Thus, mononuclear chlorocuprates can exhibit either a square-planar coordination (point symmetry group D_{4h}) or a near-tetrahedral coordination (D_{2d}). An the same geometry of ligand environments is also typical of binuclear complexes [5].

The composition and geometry of chlorocuprates in solutions can be considerably affected by the nature of the solvent. In polar media (DMF and DMSO), the mononuclear chloride complexes of copper(II) $[CuCl_4]^{2-}$ and $[CuCl_3]^-$ were mainly detected [6, 7]. These complexes resulted from the autoionization of neutral copper(II) chloride or from the addition of quaternary ammonium salts to copper(II) chloride. It is

likely that solvent molecules also enter the coordination sphere of the $[CuCl_3]^-$ complex. Structural data on chloride copper complexes in weakly polar solvents are almost absent from the literature; this is primarily due to their low solubility in these systems. The structure and composition of the chloride complexes of copper(II) in weakly polar noncomplexing solvents, such as chlorinated hydrocarbons, over a wide concentration range should be known in order to interpret the results of catalytic experiments. To solve this problem, we used a set of physicochemical techniques, namely, UV–VIS, EPR, and EXAFS spectroscopy, for studying metal complexes. Chlorobenzene was chosen as a chemically inert low-polar solvent. The bulky benzyltributylammonium (BTBA) cation, which enhances the solubility of copper complexes in chlorobenzene, was used as the counterion for anionic chlorocuprates.

EXPERIMENTAL

Anhydrous copper(II) chloride and benzyltributylammonium chloride (BTBAC) were prepared in accordance with published procedures [8, 9]. Reagent-grade chlorobenzene was purified by distillation in an inert atmosphere followed by drying with molecular sieves 4 Å. Solutions with various ratios between copper and chloride ions were prepared by adding the required weighed portions of copper(II) chloride and BTBAC to chlorobenzene in vessels shielded from sunlight at room temperature. The concentrations of copper(II) ions and BTBAC were varied within the limits 2×10^{-4}–1×10^{-2} and 5×10^{-4}–3×10^{-2} M, respectively.

The UV–VIS spectra of solutions were measured on a Shimadzu C-160 spectrophotometer. The EPR spec-

tra were measured on a Varian E-3 radiospectrometer at 77 K. The following reference standards were used for the precise calibration of the g-factor scale: Mn^{2+} ions in a matrix of MgO (the apparent values of the g-factors of third and fourth components and the splitting between them were $g_3 = 2.0328 \pm 0.0001$, $g_4 = 1.9812 \pm 0.0001$, and $\Delta H_{3-4} = 86.76 \pm 0.05$ G, respectively) and a 10^{-3} M copper(II) nitrate solution in a 50% mixture of $CD_3OD + D_2O$ ($g_\parallel = 2.424 \pm 0.005$, $g_\perp = 2.092 \pm 0.005$, and $A_\parallel = 117 \pm 3$ G [10]). To determine the number of paramagnetic centers in the test sample, its spectrum was graphically integrated and compared to the corresponding data for a standard single crystal of $CuCl_2 \cdot 2H_2O$ with a known number of paramagnetic centers.

The values of $g_\parallel^{\mathrm{eff}}$ and $g_\perp^{\mathrm{eff}}$ were determined at the corresponding characteristic points of the EPR spectra. EXAFS spectra (transmission and fluorescence modes) of the CuK edge were measured at the EXAFS Station of the Siberian Synchrotron Radiation Center. The storage ring VEPP-3 with an average stored current of 70–90 mA was used as a source of radiation. The radial distribution function of atoms was calculated from the EXAFS spectra in k^3. $\chi(k)$ as the modulus of Fourier transform at the wavenumber interval 2.5–12.0 Å^{-1}. Curve fitting procedure with the EXCURV92 code was employed to exactly determine the distances and coordination numbers.

RESULTS AND DISCUSSION

According to EXAFS data, copper(II) ions occur as monomers in the chlorobenzene solutions of BTBA chlorocuprates at $\gamma > 4$ ($\gamma = [Cl^-]/[Cu^{2+}]$), because the radial atomic distribution curve ($\rho(R - \delta)$) exhibits only one pronounced maximum that corresponds to a Cu–Cl distance equal to 2.25 ± 0.20 Å. The coordination number is approximately equal to 4 (Fig. 1). These values are close to the same values for crystalline tetrachlorocuprates (2.23 Å $< R(CuCl) < 2.30$ Å) [5]. At $\gamma \leq 4$, the solubility of the chloride complexes of copper(II) in chlorobenzene is insufficient for the reliable measurement of EXAFS spectra.

The UV–VIS spectra exhibit a number of intense bands in the ultraviolet and visible regions; these bands were ascribed to Cl–Cu charge-transfer bands [5] (Fig. 2). A complex broad band in the near-IR region corresponds to the superposition of d–d transition bands. In the presence of a more than twofold excess of BTBAC over copper chloride ($\gamma > 4$), two bands due to n–d transitions with maximums at 415 and 290 nm were observed in the region 280–600 nm (Fig. 2a, curves 1, 2). Bands with similar transition maximums were observed for tetrachlorocuprate anions in polar solvents [6, 7]. The molar absorption coefficient $\varepsilon = D/([Cu^{2+}]l)$, where D is the absorbance, and l is the optical path length, at 415 nm is equal to 2270 ± 50 l mol^{-1} cm^{-1}. At $\gamma < 4$, a band at 480 nm appeared in the spectrum (Fig. 2a, curves 4–7). According
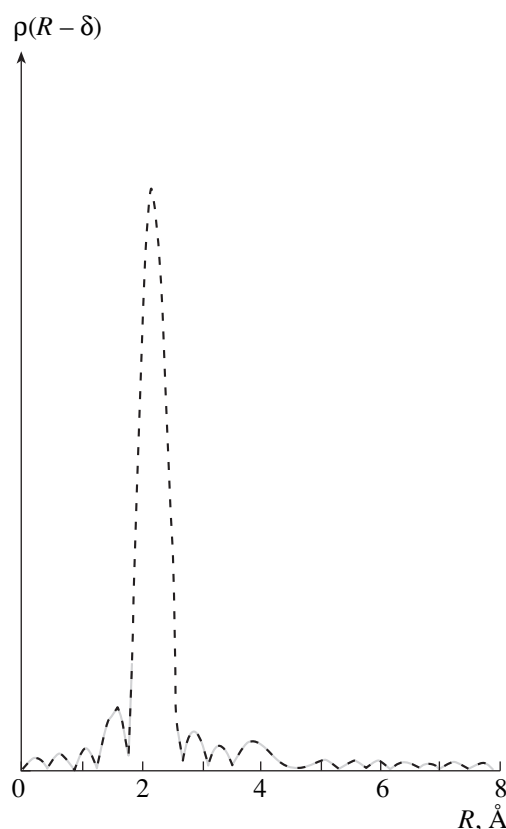

$\rho(R - \delta)$

Fig. 1. Curve of the radial distribution function of atoms of the local copper arrangement of the sample studied.

to published data [11], this band may correspond to the absorption of the dimeric complex $[Cu_2Cl_6]^{2-}$; however, there is no reliable evidence for this assumption. At $\gamma < 3$, the bands at 415 and 290 nm almost completely disappeared, the band intensity at 480 nm remained almost unchanged, and an absorption band appeared at 315 nm (Fig. 2a, curve 7). On the dilution of solutions with chlorobenzene, the absorbance was a linear function of $[Cu^{2+}]$. On this basis, we obtained the effective molar absorption coefficients $\varepsilon_{\mathrm{eff}} = D/([Cu^{2+}]l)$ for systems with a given value of γ. The $\varepsilon_{\mathrm{eff}}$–$\lambda$ relationships can be separated into Gaussian components with a high accuracy, and $\varepsilon_{\mathrm{eff}}$ can be calculated for individual bands with the maximums at 415 and 480 nm. Figure 2b demonstrates the values of $\varepsilon_{\mathrm{eff}}$ at absorption maximums as functions of γ. In the case of the band at 415 nm, the function exhibits a clearly defined point of inflection at $\gamma = 4$. This fact supports the initial hypothesis that the band at 415 nm is due to the absorption of the tetrachlorocuprate anion. The function for the band at 480 nm exhibits an inflection point at $\gamma = 3$. The coordination number 3 is not typical of copper(II), and it is likely that the solvent cannot form complexes with copper ions. Therefore, it is most likely that the dimeric complexes $[Cu_2Cl_6]^{2-}$ are formed. At $\gamma = 2.6$ (close to the lower solubility limit of chlorocuprate complexes), the dimeric band intensity remained almost unchanged; however, a new absorption band appeared at 320 nm. It is likely that oligo-
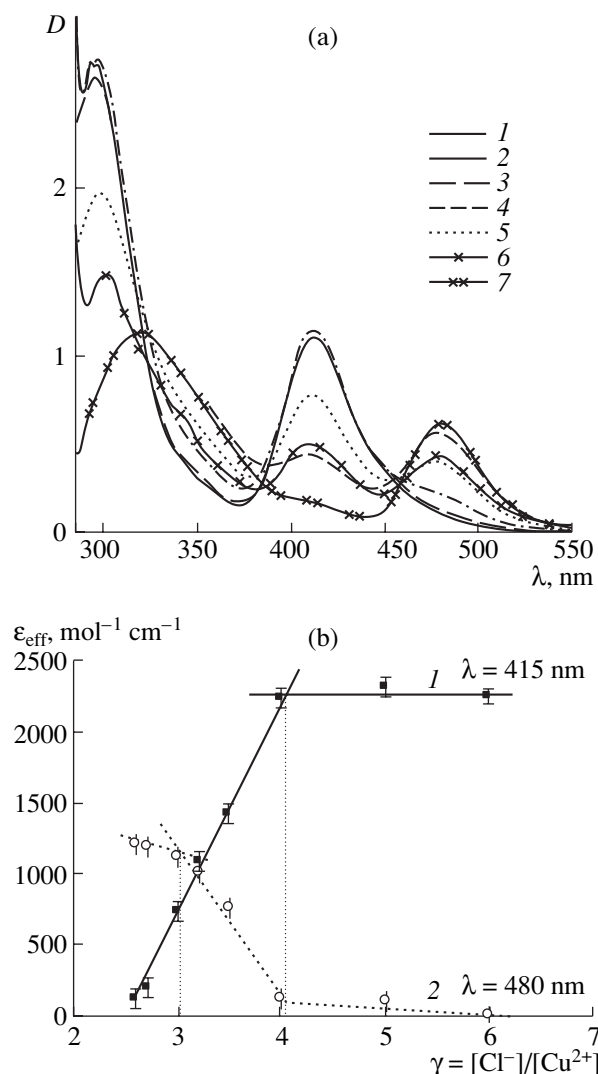
Fig. 2. (a) UV–VIS spectra of benzyltributylammonium chlorocuprate solutions in chlorobenzene at γ = (*1*) 6.0, (*2*) 5.0, (*3*) 4.0, (*4*) 3.5, (*5*) 3.0, (*6*) 3.2, and (*7*) 2.6; $[Cu^{2+}]$ = 0.005 M (curves *1* and *2* coincide). (b) Effective molar absorption coefficients of bands at (*1*) 415 and (*2*) 480 nm as functions of γ.

Fig. 3. (a) EPR spectra of benzyltributylammonium chlorocuprate solutions in chlorobenzene at γ = (*1*) 5.0, (*2*) 3.5, and (*3*) 3.0; T = 77 K. (b) The fraction of EPR-detected copper ions in benzyltributylammonium chlorocuprate solutions in chlorobenzene as a function of γ; T = 77 K.

meric structures with Cl^-/Cu^{2+} < 3, for example, $[Cu_3Cl_8]^{2-}$, occur in solutions with low Cl^- concentrations.

The EPR spectra of the solutions of chloride copper(II) complexes in chlorobenzene at high BTBAC concentrations are characterized by an axial anisotropy of *g*-tensor values (Fig. 3a). At γ > 4, the calculated effective parallel and perpendicular *g*-tensor components are equal to 2.430 and 2.094, respectively (see the table). Although the average concentration of copper(II) ions in solution was ~0.005 mol/l, the lines of the EPR spectrum were significantly broadened (the width at half height ΔH in a parallel orientation was higher than 130–140 G), and the hyperfine structure was absent. The concentration of paramagnetic centers ($[Cu_{EPR}]$) at $\gamma \geq 4$ was equal to the total concentration of
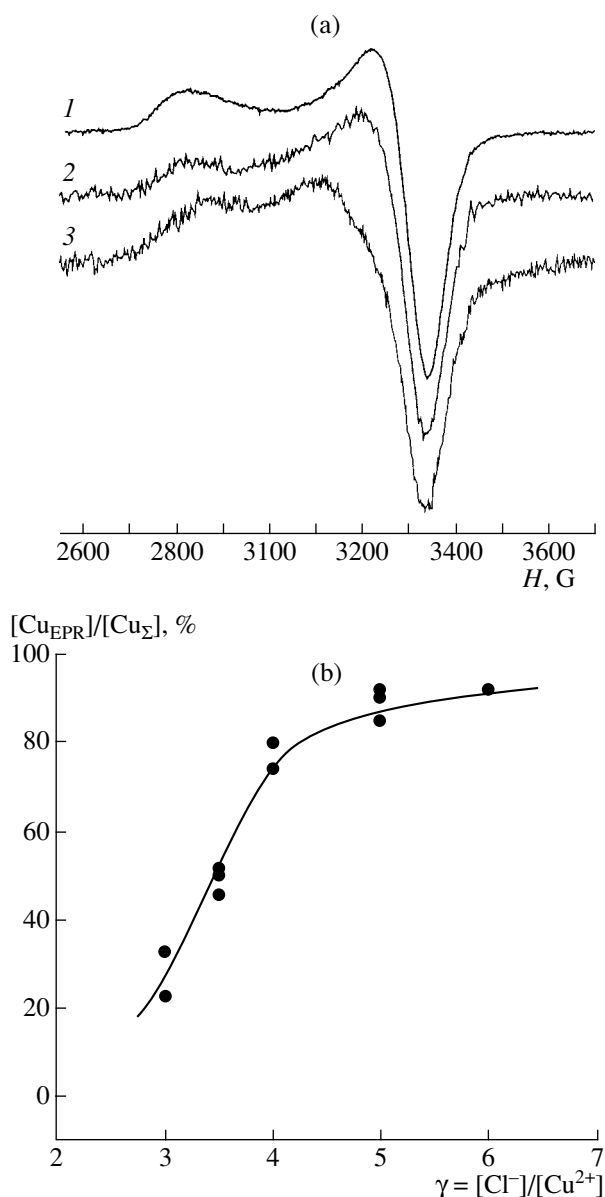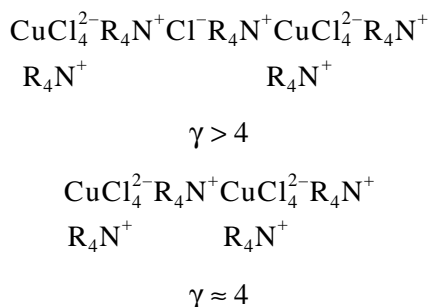
copper(II) ($[Cu_\Sigma]$) within the limits of experimental error (Fig. 3b); that is, the fraction of Cu(II) ions detected by EPR spectroscopy was close to 100%. At γ < 4, the values of $g_\parallel^{eff}$ and $g_\perp^{eff}$ decreased, and the spectrum components were further broadened; in this case, the fraction of Cu(II) ions detected by EPR spectroscopy decreased (Fig. 3b). The curve of the fraction of EPR-detected copper plotted as a function of γ exhibited an inflection point at γ = 4.

The above data can be interpreted as described below. Copper complexes occur as different species,

either detectable or undetectable by EPR spectroscopy, in the test solutions. It is likely that the former species is the mononuclear anion $[CuCl_4]^{2-}$ and the latter species include binuclear or polynuclear chlorocuprates, which were detected by electron spectroscopy. Indeed, the g-tensor components are typical of copper(II) complexes with the coordination number 4 and the space configuration D_{2d} (distorted tetrahedron) [5].

Considerable line widths and no hyperfine structures in the EPR spectra can result from a high local concentration of copper(II) complexes when strong dipole–dipole and spin–exchange interactions occur between them [12, 13]. A similar situation was observed in polycrystalline inorganic copper salts. A high local concentration of chlorocuprates in chlorobenzene can occur in globules that include chlorocuprates and counterions, similarly to the structure of R_4NCl salt solutions in weakly polar organic solvents. For example, it is well known that tetraethylammonium chloride forms associates of 100 or more molecules in benzene at near-saturation concentrations [14].

It is likely that the broadening of spectrum components with decreasing γ is due to an increase in the local concentration of copper(II) ions; this can be illustrated by the following scheme:

$$CuCl_4^{2-}R_4N^+Cl^-R_4N^+CuCl_4^{2-}R_4N^+$$
$$R_4N^+ \qquad\qquad R_4N^+$$

$$\gamma > 4$$

$$CuCl_4^{2-}R_4N^+CuCl_4^{2-}R_4N^+$$
$$R_4N^+ \qquad\qquad R_4N^+$$

$$\gamma \approx 4$$

It is well known [15] that the g-tensor values for complexes with the spatial symmetry D_{2d} depend on the angle α (α is the ∠Cl–Cu–Cl angle). The values of $g_\parallel^{eff}$ and $g_\perp^{eff}$ measured at γ > 4 correspond to α ≈ 130° [5]. At γ ≤ 4, these values decreased; this fact is indicative of going to a more planar conformation of the polyhedron [5, 15].

The EPR spectrum can also exhibit broad unresolved lines when it is a superposition of several signals from similar copper(II) complex species that differ, for example, in angle α. In this case, the constants of the hyperfine interactions with Cu(II) ions should be lower than 40–50 G. Changes in the line widths and the values of $g_\parallel^{eff}$ and $g_\perp^{eff}$ can be explained in terms of this hypothesis by a difference in the equilibrium compositions of complexes at different γ.

Presently, we cannot give preference to one of these assumptions.

Thus, several types of complexes of copper(II) ions with the chloride anion can exist in weakly polar sol-

Effective g-tensor values for the chloride complexes of Cu(II) (a solution of $CuCl_2$ and BTBAC in chlorobenzene)

$\gamma = [Cl^-]/[Cu^{2+}]$	$g_\parallel^{eff} \pm 0.005$	$g_\perp^{eff} \pm 0.005$
5	2.430	2.094
3.5	2.420	2.082
3	2.390	2.058

vents; these are $[CuCl_4]^{2-}$, $[Cu_2Cl_6]^{2-}$, and polynuclear chlorocuprate complexes. It is likely that these complexes together with bulky quaternary ammonium cations form globules in solution. The geometry parameters of the tetrachlorocuprate anion in solution are close to those of crystalline complexes with structurally similar counterions. It is of importance to consider the complexes of various compositions in the interpretation of catalytic experiments with the participation of chloride copper complexes.

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