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# Photochemical synthesis and interconversions of organocopper(II) complexes in low-temperature matrices: an EPR study

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**The EPR spectra of new paramagnetic copper(II) complexes generated by the photolysis of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ were identified, and a quantitative study of the dynamics of photochemical product formation and interconversions at 77–110 K was carried out.**

The charge-transfer photochemistry of copper complexes in non-aqueous solvents is of considerable interest.[1] The main pathways of the phototransformations are photoreduction with formation of copper(I) complexes and free-valence species (atoms and radicals). Nevertheless, in some cases, copper(II) complexes can undergo transformations to new $Cu^{II}$ compounds, which are proposed to be organometallics.[2,3] As compared with profuse organometallic chemistry of copper(I),[4] stable copper(II) organic complexes are very rare.[5] Most of them have life-times of no more than $10^{-6}$ s.[6] Such compounds are obtained under photolysis of tetraalkylammonium tetrachlorocuprate $[(RH)_4N^+]_2$-$[Cu^{II}Cl_4]^{2-}$.[3] A recent EPR study has shown that at least two novel paramagnetic copper(II) complexes (**1**-Cu and **2**-Cu) and a small amount of alkyl radicals ($R^\bullet$) form under the photolysis of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ ($RH = C_6H_{13}$) at LMCT band ($\lambda_{max}$ = = 405–415 nm) in the matrices of non-complexing vitreous solvents at 77 K.[7] It was found that the photochemical transformations of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ were accompanied by dark reactions.[7] The dark reactions were responsible for a decrease in the quantum yield of photolysis products, its discrepancy with the quantum yield of $[Cu^{II}Cl_4]^{2-}$ consumption and a decrease of the total amount of paramagnetic particles.

On the basis of spectral data[3(*a*)] and quantum-chemical calculations,[8] it was supposed that complexes **1**-Cu and **2**-Cu were organocupric(II) compounds. During the heating of photolysis products from 77 to 100 K, the EPR spectra of $R^\bullet$ and **2**-Cu disappeared, and the intensity of **1**-Cu spectrum raised.[7] Temperature increase to 110 K resulted in the transformation of **1**-Cu to diamagnetic products.[3(*a*),7]

The EPR spectrum of **1**-Cu was simulated as a spectrum of an individual substance with three different principal values of *g*-tensor and tensor of hyperfine splitting on copper nucleus: $g_1 = 2.082\pm0.003$, $g_2 = 2.033\pm0.001$, $g_3 = 2.024\pm0.001$, $A(^{63}Cu)_1 =$ $= 4.1\pm0.2$ mT, $A(^{63}Cu)_2 = 3.8\pm0.1$ mT, $A(^{63}Cu)_3 = 11.0\pm0.2$ mT. These spin Hamiltonian parameters are typical of non-symmetrical copper(II) complexes with weak ligands.[9] However, it was unclear whether the increase in **1**-Cu amount during annealing was a result of the reaction of $R^\bullet$ with diamagnetic $Cu^I$ complex or **1**-Cu was a product of **2**-Cu transformation. Moreover, the question about the individuality of **2**-Cu remained open. The separation of spectra of the individual products of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ photolysis from the overall EPR spectrum has not been realized up to now. At the same time, the availability of these spectra might give an opportunity to carry out the quantitative study of the dynamics of formation and interconversions of the all paramagnetic products of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ photolysis. Here, we report the first results of separating the EPR spectra of the individual products of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ photolysis in frozen 2-chlorobutane,[†] their interpretation, and the dynamics of transients transformations.

The sample preparation and photolysis procedures were described earlier.[7] Helium-filled samples were also prepared; however, no influence of helium on the photolysis was found. The dependences of the amount of initial tetrachlorocuprate anion and photolysis products upon the irradiation dose and the corresponding quantum yields were determined according to known procedures.[11] The correction for light absorption at the wavelength of photolysis by forming products was introduced taking into account corresponding molar absorption coefficients of these products.[7] Annealing of irradiated samples from 77 to 130 K by the stream of nitrogen vapour was carried out with a device assembled specially.[7]

The separation of the EPR spectra[‡] of reaction systems at various conversions was performed with the assumption that paramagnetic products were only **1**-Cu, **2**-Cu complexes and alkyl radicals $R^\bullet$. Thus, the EPR spectrum of irradiated system was considered to be the superposition of four overlapping spectra relating to **1**-Cu, **2**-Cu, $R^\bullet$ and residual $[Cu^{II}Cl_4]^{2-}$. The individual EPR spectrum of $[Cu^{II}Cl_4]^{2-}$ is availiable.[3,7,12] The EPR spectrum of $R^\bullet$ was estimated as a difference between any two spectra of samples irradiated to ~85%, when the amount of **1**-Cu and **2**-Cu did not change noticeably during photolysis, but the accumulation of $R^\bullet$ took place still.[3] The contribution of individual spectra to the total EPR spectrum was estimated

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[†] Anhydrous copper(II) chloride was prepared by the azeotropic dehydration of $CuCl_2{\cdot}2H_2O$ with benzene[10] followed by degassing at $10^{-3}$ Torr. Tetrahexylammonium chloride $(C_6H_{13})_4N^+Cl^-$ from Sigma-Aldrich was used without additional purification. 2-Chlorobutane from Merck was purified by distillation from $P_4O_{10}$. The solutions of tetrahexylammonium tetrachlorocuprate in 2-chlorobutane were prepared as described earlier.[7] The concentrations of $[Cu^{II}Cl_4]^{2-}$ were $3.1\times10^{-3}$, $4.2\times10^{-3}$ and $5.2\times10^{-3}$ mol dm$^{-3}$. The ratio $[(C_6H_{13})_4N^+Cl^-]:[CuCl_2]^\bullet = 6:1$ was constant in all solutions. The purity of the solutions was monitored by spectrophotometry.[7] Electronic absorption spectra were recorded at 20 °C on a Shimadzu UV-2401PC spectrophotometer in quartz cells with an optical path length of 1 mm.

[‡] The EPR spectra were recorded on a Varian-E3 X-band radiospectrometer (100 kHz magnetic field modulation) at 77 K. The measurements were performed under conditions ruling out both saturation and modulation broadening of the signal. The *g*-tensor values were determined using $Mn^{2+}$-doped MgO as a standard. The values of spin Hamiltonian parameters were calculated by known recommendations.[11] Amounts of paramagnetic centres were determined with respect to the standard $CuCl_2{\cdot}2H_2O$ single crystal with a known amount of paramagnetic centres. The relative accuracy of the determination of paramagnetic particle concentrations was ±10%.

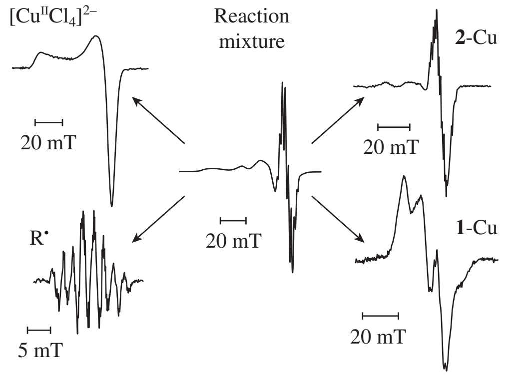


**Figure 1** EPR spectrum of the reaction mixture under $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ photolysis and the result of its separation into spectra of **1**-Cu, **2**-Cu, R$^\bullet$ and unreacted $[Cu^{II}Cl_4]^{2-}$.

considering values of their certain components intensity, *viz.* amplitudes of parallel component for $[Cu^{II}Cl_4]^{2-}$, intensities of low-field component for **1**-Cu, and intensities of one of hyperfine structure lines for R$^\bullet$. Thus, the EPR spectrum of **2**-Cu was found by the subtraction of spectra of $[Cu^{II}Cl_4]^{2-}$, **1**-Cu and R$^\bullet$ from the total EPR spectrum of the reaction system.

The decrease in the intensity of EPR spectrum components of tetrachlorocuprate anions and the appearance of components corresponding to the spectra of **1**-Cu, **2**-Cu and R$^\bullet$ were observed during the photolysis of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ in a vitreous 2-chlorobutane matrix at Cl–Cu charge transfer band ($\lambda_{max} = 414$ nm) at 77 K. Figure 1 shows a typical EPR spectrum of an irradiated sample and the EPR spectra of $[Cu^{II}Cl_4]^{2-}$, **1**-Cu, **2**-Cu and R$^\bullet$ separated from the total EPR spectrum. The EPR spectra of $[Cu^{II}Cl_4]^{2-}$, **1**-Cu and R$^\bullet$ were discussed earlier.[3] The EPR spectrum of **2**-Cu was obtained for the first time. The complicated structure of this spectrum (Figure 1) does not allow us to describe it definitely without thorough simulations. Nevertheless, the observed intense singlet with $g \approx g_e$ may arise due to the dipole-dipole or spin-exchange interaction of paramagnetic centres. Another reason of the appearance of this line may be the misalignment of *g*-tensor and hyperfine coupling tensor.[13] The shape of the **2**-Cu spectrum does not depend on the initial concentration of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ and the depth of photolysis. This fact justifies that the spectrum of species **2**-Cu corresponds to an individual complex, and, indeed, there are only two cupric complexes **1**-Cu, **2**-Cu, and R$^\bullet$, which appear to be paramagnetic products of photolysis at any photolysis time. The detailed identification of the EPR spectrum of **2**-Cu is beyond the scope of this work. Nevertheless, the separation of the **2**-Cu spectrum allows us to study the dynamics of formation and transformation of the paramagnetic products quantitatively.

The example of dependence of $[Cu^{II}Cl_4]^{2-}$, **1**-Cu, **2**-Cu and R$^\bullet$ concentrations on photolysis time is presented in Figure 2. As indicated, complex **2**-Cu is the main product of photolysis, while **1**-Cu and R$^\bullet$ form to a lesser extent (no more than 10–15%). The decrease of the total amount of paramagnetic particles ($N_\Sigma$) is supposed to take place due to dark reactions (*e.g.*, radical recombination).[3(*b*),7]

The composition of the product mixture changes during annealing from 77 to 100 K. The disappearance of complex **2**-Cu and alkyl radicals R$^\bullet$ and an increase in the amount of **1**-Cu are observed (Figure 2). The amount of residual $[Cu^{II}Cl_4]^{2-}$ does not change under heating. The subsequent raise in temperature to 110 K leads to the disappearance of complex **1**-Cu, the amount of $[Cu^{II}Cl_4]^{2-}$ does not change in the range of 100–110 K. The processes occurring under $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ photolysis and annealing of products are given in Scheme 1 (DP refers to diamagnetic products).

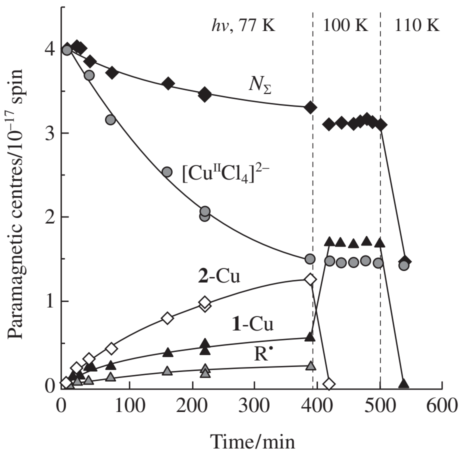
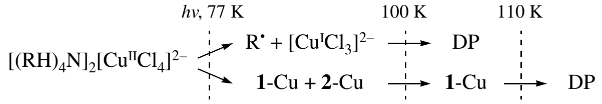


**Figure 2** Dependence of the amounts of $[Cu^{II}Cl_4]^{2-}$, **1**-Cu, **2**-Cu, R$^\bullet$, and total amounts of paramagnetic centres upon photolysis time at 77 K and following annealing to 100 and 110 K.



**Scheme 1**

The photochemical transformations of $[Cu^{II}Cl_4]^{2-}$ and posterior dark reactions of photolysis products depend on the initial concentrations of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$. The dependences of $[Cu^{II}Cl_4]^{2-}$ conversion in frozen solutions with different copper(II) concentrations upon the absorbed light dose are presented in Figure 3. Apparently, the efficiency of tetrachlorocuprate photoreduction decreases with concentration. The quantum yields of $[Cu^{II}Cl_4]^{2-}$ conversion corresponding to different initial concentrations of tetrachlorocuprate anions are given in Table 1.

The dependences of generation of R$^\bullet$, **1**-Cu and **2**-Cu upon the absorbed light dose are non-linear (Figure 4). The initial parts of the curves were used for the estimation of quantum yields of generation processes ($\varphi$) (Table 1). The dependences of $N_\Sigma$ upon the absorbed light dose are non-linear (Figure 3). The kinetic nonequivalences showing nonlinearity of dose

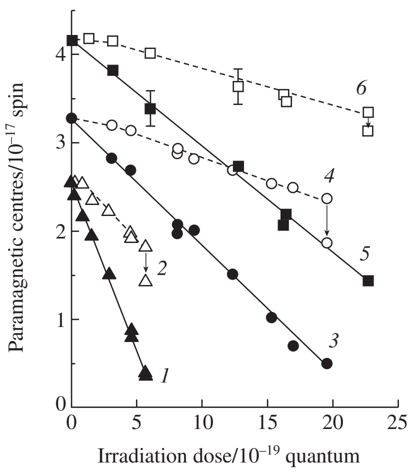


**Figure 3** Dependence of (*1*), (*3*), (*5*) the amounts of $[CuCl_4]^{2-}$ and (*2*), (*4*), (*6*) total amounts of paramagnetic centres upon the absorbed light dose in 2-chlorobutane at 77 K. The initial concentrations of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ were (*1*), (*2*) $3.1\times10^{-3}$, (*3*), (*4*) $4.2\times10^{-3}$ and (*5*), (*6*) $5.2\times10^{-3}$ mol dm$^{-3}$. Arrows show the decrease of the total amount of paramagnetic centres under annealing to 100 K.

**Table 1** The quantum yields ($\varphi \times 10^3$) of consumption of total number of paramagnetic centres and $[Cu^{II}Cl_4]^{2-}$ and formation of paramagnetic products of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ photolysis.

| Compound | Concentration of $[(RH)_4N^+][Cu^{II}Cl_4]^{2-}$/mol dm$^{-3}$ | | |
|---|---|---|---|
| | $3.1\times10^{-3}$ | $4.2\times10^{-3}$ | $5.2\times10^{-3}$ |
| $N_\Sigma$ | 0.1 | 0.1 | 0.1 |
| $[Cu^{II}Cl_4]^{2-}$ | 3.9 | 1.4 | 1.2 |
| **1**-Cu | 1.1 | 0.4 | 0.4 |
| **2**-Cu | 2.5 | 0.9 | 0.8 |
| R$^\bullet$ | 0.5 | 0.2 | 0.2 |

dependences are often observed under photolysis of metal complexes in solid matrices.[14] Breaks of dose dependences of product formation and $N_\Sigma$ decrease correspond to nearly equal $[Cu^{II}Cl_4]^{2-}$ conversion degrees. The largest value of $N_\Sigma$ is recorded in the case of the lowest $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ concentration. As it was early supposed, this fact may be explained by various degrees of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ self-association.[3] As is well known, the photochemical properties of light-absorbing metal complexes can change because of their local concentration and permolecular organization.[15] For instance, the self-quenching of photoexcited complexes can take place.

As mentioned above, the total disappearance of **2**-Cu and an increase in **1**-Cu content occur under annealing to 100 K (Figures 2 and 4). The total conversion of **2**-Cu to **1**-Cu takes place only at $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ concentration of $5.2\times10^{-3}$ mol dm$^{-3}$. In solutions with lower concentrations, the conversion of **2**-Cu to **1**-Cu is not quantitative and obviously is accompanied by different reactions of diamagnetic product formation considered elsewhere.[7] In addition, $N_\Sigma$ reduces on heating to 100 K for the samples with initial concentrations of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ equal to $3.1\times10^{-3}$ and $4.2\times10^{-3}$ mol dm$^{-3}$. Most likely this peculiarity as well as unusual concentration dependences of photochemical transformations of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ relate to the effect of self-association of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ in 2-chlorobutane. The EPR data do not allow us to assign complexes **1**-Cu and **2**-Cu to certain molecular structures, but **1**-Cu and **2**-Cu could differ by the amounts of chloride anions in the first coordination sphere of copper(II).[8] Note that the formation of **1**-Cu with the participation of R$^\bullet$ and Cu$^I$ complexes, as observed earlier,[2] cannot be mapped out; however, the possibility of this process is unclear due to a small amount of alkyl radicals (< 10%) in the products mixture.

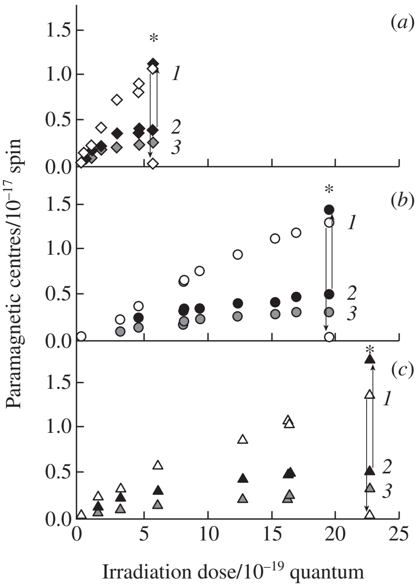


**Figure 4** Dependences of the amounts of (*1*) **2**-Cu, (*2*) **1**-Cu, and (*3*) R$^\bullet$ upon the absorbed light dose in the low-temperature matrices of 2-chlorobutane. The initial concentrations of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ were (*a*) $3.1\times10^{-3}$, (*b*) $4.2\times10^{-3}$ and (*c*) $5.2\times10^{-3}$ mol dm$^{-3}$. Arrows show transformations of **1**-Cu and **2**-Cu under annealing to 100 K. Asterisks designate the amount of **1**-Cu which could be observed if **2**-Cu transforms into **1**-Cu quantitatively.

In summary, the photolysis of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ (concentration $\leq 5\times10^{-3}$ mol dm$^{-3}$) at LMCT band in frozen weakly polar solvents allows one to generate two types of copper(II) complexes, probably, with alkyl fragments formed from quaternary ammonium residues. The total amount of these complexes is about 70% in the product mixture. The annealing from 77 to 100 K gives rise to a transformation of a complex to another, in some cases, qualitatively. As a general conclusion, for the first time, the EPR spectrum of the least stable organocopper compound was obtained as an addition to spectra of other photolysis paramagnetic products known earlier.

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