

Provided for non-commercial research and educational use only.  
Not for reproduction or distribution or commercial use.



This article was originally published in a journal published by Elsevier in cooperation with Mendeleev Communications, and the attached copy is provided for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

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

Anton V. Lobanov,\* Elena N. Golubeva and Mikhail Ya. Mel'nikov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.  
Fax: +7 495 939 1814; e-mail: avlobanov@mail.ru

DOI: 10.1016/j.mencom.2010.11.014

The EPR spectra of new paramagnetic copper(II) complexes generated by the photolysis of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  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.<sup>1</sup> 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  $\text{Cu}^{\text{II}}$  compounds, which are proposed to be organometallics.<sup>2,3</sup> As compared with profuse organometallic chemistry of copper(I),<sup>4</sup> stable copper(II) organic complexes are very rare.<sup>5</sup> Most of them have life-times of no more than  $10^{-6}$  s.<sup>6</sup> Such compounds are obtained under photolysis of tetraalkylammonium tetrachlorocuprate  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ .<sup>3</sup> 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 ( $\text{R}^\cdot$ ) form under the photolysis of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  ( $\text{RH} = \text{C}_6\text{H}_{13}$ ) at LMCT band ( $\lambda_{\text{max}} = 405\text{--}415$  nm) in the matrices of non-complexing vitreous solvents at 77 K.<sup>7</sup> It was found that the photochemical transformations of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  were accompanied by dark reactions.<sup>7</sup> The dark reactions were responsible for a decrease in the quantum yield of photolysis products, its discrepancy with the quantum yield of  $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  consumption and a decrease of the total amount of paramagnetic particles.

On the basis of spectral data<sup>3(a)</sup> and quantum-chemical calculations,<sup>8</sup> 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  $\text{R}^\cdot$  and **2-Cu** disappeared, and the intensity of **1-Cu** spectrum raised.<sup>7</sup> Temperature increase to 110 K resulted in the transformation of **1-Cu** to diamagnetic products.<sup>3(a),7</sup>

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:  $g_1 = 2.082 \pm 0.003$ ,  $g_2 = 2.033 \pm 0.001$ ,  $g_3 = 2.024 \pm 0.001$ ,  $A(^{63}\text{Cu})_1 = 4.1 \pm 0.2$  mT,  $A(^{63}\text{Cu})_2 = 3.8 \pm 0.1$  mT,  $A(^{63}\text{Cu})_3 = 11.0 \pm 0.2$  mT. These spin Hamiltonian parameters are typical of non-symmetrical copper(II) complexes with weak ligands.<sup>9</sup> However, it was unclear whether the increase in **1-Cu** amount during annealing was a result of the reaction of  $\text{R}^\cdot$  with diamagnetic  $\text{Cu}^{\text{I}}$  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  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  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  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  photolysis. Here, we report the first results of separating the

EPR spectra of the individual products of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  photolysis in frozen 2-chlorobutane,<sup>†</sup> their interpretation, and the dynamics of transients transformations.

The sample preparation and photolysis procedures were described earlier.<sup>7</sup> 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.<sup>11</sup> 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.<sup>7</sup> Annealing of irradiated samples from 77 to 130 K by the stream of nitrogen vapour was carried out with a device assembled specially.<sup>7</sup>

The separation of the EPR spectra<sup>‡</sup> of reaction systems at various conversions was performed with the assumption that paramagnetic products were only **1-Cu**, **2-Cu** complexes and alkyl radicals  $\text{R}^\cdot$ . Thus, the EPR spectrum of irradiated system was considered to be the superposition of four overlapping spectra relating to **1-Cu**, **2-Cu**,  $\text{R}^\cdot$  and residual  $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ . The individual EPR spectrum of  $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  is available.<sup>3,7,12</sup> The EPR spectrum of  $\text{R}^\cdot$  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  $\text{R}^\cdot$  took place still.<sup>3</sup> The contribution of individual spectra to the total EPR spectrum was estimated

<sup>†</sup> Anhydrous copper(II) chloride was prepared by the azeotropic dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with benzene<sup>10</sup> followed by degassing at  $10^{-3}$  Torr. Tetrahexylammonium chloride ( $\text{C}_6\text{H}_{13}$ )<sub>4</sub> $\text{N}^+\text{Cl}^-$  from Sigma-Aldrich was used without additional purification. 2-Chlorobutane from Merck was purified by distillation from  $\text{P}_4\text{O}_{10}$ . The solutions of tetrahexylammonium tetrachlorocuprate in 2-chlorobutane were prepared as described earlier.<sup>7</sup> The concentrations of  $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  were  $3.1 \times 10^{-3}$ ,  $4.2 \times 10^{-3}$  and  $5.2 \times 10^{-3}$  mol  $\text{dm}^{-3}$ . The ratio  $[(\text{C}_6\text{H}_{13})_4\text{N}^+\text{Cl}^-]:[\text{CuCl}_2]^\cdot = 6:1$  was constant in all solutions. The purity of the solutions was monitored by spectrophotometry.<sup>7</sup> 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.

<sup>‡</sup> 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  $\text{Mn}^{2+}$ -doped MgO as a standard. The values of spin Hamiltonian parameters were calculated by known recommendations.<sup>11</sup> Amounts of paramagnetic centres were determined with respect to the standard  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  single crystal with a known amount of paramagnetic centres. The relative accuracy of the determination of paramagnetic particle concentrations was  $\pm 10\%$ .



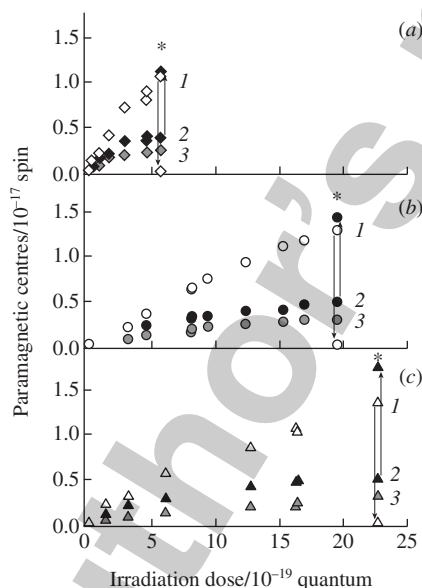


**Table 1** The quantum yields ( $\varphi \times 10^3$ ) of consumption of total number of paramagnetic centres and  $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  and formation of paramagnetic products of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  photolysis.

Compound	Concentration of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}/\text{mol dm}^{-3}$		
	$3.1 \times 10^{-3}$	$4.2 \times 10^{-3}$	$5.2 \times 10^{-3}$
$N_{\Sigma}$	0.1	0.1	0.1
$[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$	3.9	1.4	1.2
<b>1-Cu</b>	1.1	0.4	0.4
<b>2-Cu</b>	2.5	0.9	0.8
<b>R'</b>	0.5	0.2	0.2

dependences are often observed under photolysis of metal complexes in solid matrices.<sup>14</sup> Breaks of dose dependences of product formation and  $N_{\Sigma}$  decrease correspond to nearly equal  $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  conversion degrees. The largest value of  $N_{\Sigma}$  is recorded in the case of the lowest  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  concentration. As it was early supposed, this fact may be explained by various degrees of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  self-association.<sup>3</sup> As is well known, the photochemical properties of light-absorbing metal complexes can change because of their local concentration and permolecular organization.<sup>15</sup> 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  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  concentration of  $5.2 \times 10^{-3}$  mol  $\text{dm}^{-3}$ . 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.<sup>7</sup> In addition,  $N_{\Sigma}$  reduces on heating to 100 K for the samples with initial concentrations of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  equal to  $3.1 \times 10^{-3}$  and  $4.2 \times 10^{-3}$  mol  $\text{dm}^{-3}$ . Most likely this peculiarity as well as unusual concentration dependences of photochemical transformations of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  relate to the effect of self-association of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  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



**Figure 4** Dependences of the amounts of (1) **2-Cu**, (2) **1-Cu**, and (3) **R'** upon the absorbed light dose in the low-temperature matrices of 2-chlorobutane. The initial concentrations of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  were (a)  $3.1 \times 10^{-3}$ , (b)  $4.2 \times 10^{-3}$  and (c)  $5.2 \times 10^{-3}$  mol  $\text{dm}^{-3}$ . 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.

of copper(II).<sup>8</sup> Note that the formation of **1-Cu** with the participation of **R'** and **Cu** complexes, as observed earlier,<sup>2</sup> 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.

In summary, the photolysis of  $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$  (concentration  $\leq 5 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) 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.

This study was supported in part by the Russian Foundation for Basic Research (project no. 10-03-00603a). We are grateful to A. Kh. Vorobiev for providing us with computer programs for modeling the EPR spectra.

## References

- (a) B. G. Jeliakova, G. Ch. Sarova and S. N. Doneva, *Inorg. Chim. Acta*, 1998, **273**, 403; (b) N. D. Yordanov, B. G. Jeliakova, D. Roussanova, G. Ch. Sarova, P. O'Brien and M. A. Malik, *Polyhedron*, 2000, **19**, 2177; (c) J. Sýkora, *Coord. Chem. Rev.*, 1997, **159**, 95; (d) E. Cervone, F. Diomedei Camassei, I. Giannini and J. Sýkora, *J. Photochem.*, 1979, **11**, 321; (e) E. Cervone and F. Diomedei Camassei, *J. Photochem.*, 1981, **15**, 203; (f) N. Armadori, G. Accorsi, F. Cardinali and A. Listorti, in *Photochemistry and Photobiology*, ed. V. Balzani, Springer, Berlin, Heidelberg, New York, 2007, p. 69.
- V. F. Plyusnin, N. M. Bazhin and O. B. Kiseleva, *Zh. Khim. Fiz.*, 1980, **54**, 672 (in Russian).
- (a) E. N. Golubeva, A. V. Lobanov, V. I. Pergushov, N. A. Chumakova and A. I. Kokorin, *Dokl. Akad. Nauk*, 2008, **421**, 630 [*Dokl. Chem. (Engl. Transl.)*, 2008, **421**, 171]; (b) E. N. Golubeva, A. V. Lobanov and A. I. Kokorin, *Khim. Fiz.*, 2009, **28**, 9 (*Russ. J. Phys. Chem. B.*, 2009, **3**, 179).
- (a) B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 533; (b) *Modern Organocopper Chemistry*, ed. N. Krause, Wiley-VCH, Weinheim, 2001.
- (a) R. Miyamoto, R. Santo, T. Matsushita, T. Nishioka, A. Ichimura, Y. Teki and I. Kinoshita, *Dalton Trans.*, 2005, 3179; (b) H. Maeda, A. Osuka, Y. Ishikawa, I. Aritome, Y. Hisaeda and H. Furuta, *Org. Lett.*, 2003, **5**, 1293; (c) P. J. Chmielewski, L. Latos-Grażyński and I. Schmidt, *Inorg. Chem.*, 2000, **39**, 5475.
- G. Ferraudi, *Inorg. Chem.*, 1978, **17**, 2506.
- A. V. Lobanov, E. N. Golubeva, E. M. Zubanova and M. Ya. Mel'nikov, *Khim. Vys. Energ.*, 2009, **43**, 438 [*High Energy Chem.*, 2009, **43**, 384].
- E. N. Golubeva, G. M. Zhidomirov and A. I. Kokorin, *Dokl. Akad. Nauk*, 2009, **426**, 766 [*Dokl. Chem. (Engl. Transl.)*, 2009, **426**, 143].
- V. V. Saraev and F. K. Schmidt, *Elektronnyi paramagnitnyi rezonans metallokompleksnykh katalizatorov (Electron Spin Resonance of Metal Complex Catalysts)*, Irkutsk University, Irkutsk, 1985 (in Russian).
- Yu. A. Karyakin and I. I. Angelov, *Chistye khimicheskie veshchestva (Pure Chemicals)*, Khimiya, Moscow, 1974 (in Russian).
- Eksperimental'nye metody khimii vysokikh energii (Experimental Methods of High Energy Chemistry)*, ed. M. Ya. Mel'nikov, Izd. MGU, Moscow, 2009 (in Russian).
- E. I. Solomon, *Inorg. Chem.*, 2006, **45**, 8012.
- N. Ya. Shteinshneider, G. M. Zhidomirov and K. I. Zamaraev, *Zh. Strukt. Khim.*, 1972, **13**, 795 (in Russian).
- A. Kh. Vorobiev and V. S. Gurman, *J. Photochem.*, 1982, **20**, 123.
- S. S. Dudar', E. B. Sveshnikova, A. V. Shablya and V. L. Ermolaev, *Khim. Vys. Energ.*, 2007, **41**, 189 [*High Energy Chem. (Engl. Transl.)*, 2007, **41**, 156].

Received: 15th April 2010; Com. 10/3507