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CHEMISTRY

On the Stability of Copper(II) Organic Compounds with the σ Bond Cu–C: A Quantum-Chemical Study

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Until recently, it was assumed that stable organic compounds of copper(II) with the Cu(II)–C σ bond were nonexistent [1]. However, in a later obtained crystalline complex with nitrogen-containing ligands, the existence of such a bond was suggested [2]. At the same time, there is reliable experimental evidence of the formation of analogous labile complexes on photolysis and radiolysis of Cu(II) compounds as well as by the reaction of Cu^{2+} ions with organic radicals in water and organic solvents [3–6]. In particular, the electronic absorption spectra of the products of photochemical and thermal reactions of copper chloride complexes in organic solvents show new bands at 430–450 nm, which can be assigned to $n \longrightarrow d$ transitions [5, 6]. The corresponding EPR spectrum also shows a new signal. In particular, for the product of photolysis of quaternary ammonium tetrachlorocuprate, the *g* values and HFC tensors *A*(Cu) are as follows: $g_1 = 2.082 \pm 0.003$, $g_2 = 2.033 \pm 0.001$, and $g_3 = 2.024 \pm 0.001$; $A_1(^{63}Cu) = 4.1 \pm 0.2$ mT, $A_2(^{63}Cu) = 3.8 \pm 0.1$ mT, and $A_3(^{63}Cu) = 11.02 \pm 0.2$ mT. The half widths for these signals are as follows: $\Delta H_1 = 10.0$, $\Delta H_2 = 3.7$, and $\Delta H_3 = 6.6$ mT. These values are typical of copper(II) complexes [6]. However, these compounds are stable in frozen solvent matrices only below 100 K and their lifetime under common conditions is 10^{-6}–10^{-8} s. Therefore, it is accepted that copper(II) organic compounds are unstable and readily decompose with cleavage of the Cu–C bond. However, in our opinion, the rapid disappearance of such complexes in solutions can be due to their high reactivity in various bimolecular processes, the rate of which in solids is diffusion-controlled.

It was of interest to perform quantum-chemical calculations of some model copper(II) organic compounds with the Cu(II)–C σ bond, as well as of the energies of possible reactions involving these compounds in order to confirm the possibility of their formation and predict

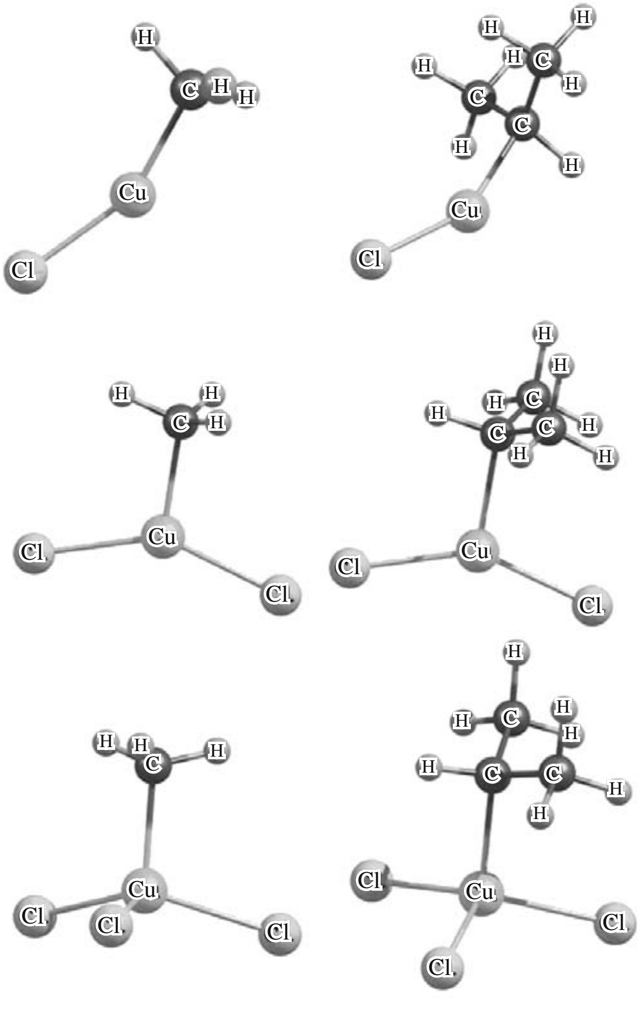

Fig. 1. Calculated structures of $Cl_nCu(II)R^{1-n}$ complexes.

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Calculated Cu–C bond dissociation energies, Cu–Cl and Cu–C distances, charges and spin density on atoms and fragments of $Cl_nCu(II)R^{1-n}$ complexes

Formula	E(Cu–C), kJ/mol	r, Å		q			Mulliken spin density	
		Cu–Cl	Cu–C	Cu	Cl	C_nH_{2n+1}	Cu	C_nH_{2n+1}
CuCl	–	2.06	–	0.67	−0.67	–	0	–
$CuCl_2^-$	–	2.13	–	0.58	−0.79	–	0	–
$CuCl_3^{2-}$	–	2.33	–	0.70	−0.90	–	0	–
CH_3•	–	–	–	–	–	0	–	1
C_3H_7•	–	–	–	–	–	0	–	1
$ClCuCH_3$	149	2.10	1.92	0.86	−0.57	−0.29	0.49	0.34
$Cl_2CuCH_3^-$	61	2.20	2.00	0.91	−0.75	−0.41	0.38	0.42
$Cl_3CuCH_3^{2-}$	83	2.40	2.01	1.01	−0.86	−0.43	0.50	0.41
$ClCuC_3H_7$	137	2.10	1.95	0.79	−0.64	−0.15	0.41	0.48
$Cl_2CuC_3H_7^-$	36	2.20	2.04	0.87	−0.76	−0.35	0.34	0.58
$Cl_3CuC_3H_7^{2-}$	72	2.39	2.04	0.99	−0.86	−0.41	0.40	0.50

potential paths of their loss. Numerous previous quantum-chemical calculations of copper(I) complexes (d^{10} configuration) with chloride ions and organic substituents [7, 8] provided an accurate description of their geometric and electronic structures and spectral properties and made it possible to interpret data on their reactivity and catalytic activity. The electronic structure of copper(II) (d^9) chloride complexes was calculated by both the extended Huckel method [9] and modern density functional theory (DFT) [10] and multiconfigurational (CASSCF, CASPT2) methods [11]. All these methods provided qualitative description of the Cu(II) complex geometry, including Jahn–Teller distortions and assignments of transitions in electronic spectra. However, only recent quantum-chemical computations gave values quantitatively consistent with the experiment [11].

In this paper, we report the results of quantum-chemical calculations of the structure and properties of copper(II) organic compounds with the aim to demonstrate the possibility of their existence by the example of $Cl_nCu(II)R^{1-n}$, where R is $CH_3^{\bullet}$ and $C_3H_7^{\bullet}$, and determine their geometric parameters and the Cu–C bond energy. In addition, it was important to calculate the energies of possible mono- and bimolecular reactions involving $Cl_nCu(II)R_{1-n}$ and justify the most probable mechanism of $Cl_nCu(II)R^{1-n}$ transformations.

Calculations were performed with the Gaussian 03 program package [12] by the unrestricted DFT method with the PBE exchange-correlation functional [13] using the 6–311G^{++}(3*df*,3*pd*) basis set. The complex geometries were completely or partially optimized, and location of minima on the potential energy surface (PES) was checked by calculation of normal mode frequencies. The reaction energies were calculated as the difference between the sums of the total energies of final and initial states, introducing the zero-point energy corrections. The charges on atoms were determined by the natural bond orbital (NBO) method [14].

Our calculations show that, in all cases, the PESs have minima corresponding to the formation of neutral and anionic alkylcopper chloride complexes. Their geometric structures are shown in Fig. 1. The calculations predict that all known mononuclear Cu(I) chloride complexes can react with alkyl radicals to form stable σ complexes. As expected, the lowest formation energy was found for complexes based on $CuCl_2^-$, the most stable copper(I) chloride complex. The structural and electronic characteristics of these complexes and their isolated fragments are presented in the table. A considerable variation of these characteristics upon complexation, for example, emergence of spin density on the copper nucleus and a change in charges on all atoms, points to the formation of new individual compounds. The equilibrium Cu–C distance (1.92–2.04 Å) is evidence of the formation of a strong bond between these atoms.

On the whole, the DFT calculations support the hypothesis that stable alkyl copper(II) complexes can exist. Calculation with partial geometry optimization at fixed Cu–C distances shows that formation of these complexes is an activationless process (Fig. 2).

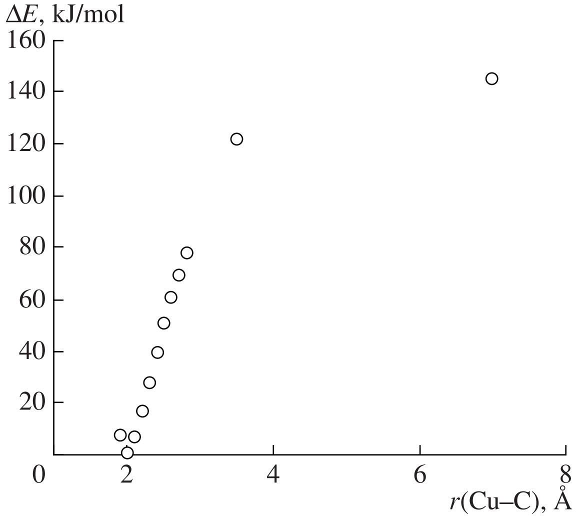

Fig. 2. Relative energy of the $ClCu–CH_3$ system vs. the Cu–C distance.

Thus, short lifetimes of copper(II) organic compounds at room temperature are not due to a low Cu–C bond strength; most likely, the cause is in their high reactivity in various bimolecular reactions with analogous complexes, organic radicals, and hydrogen chloride. Examples of such reactions and their energies (ΔE, kJ/mol) are listed below:

	ΔE, kJ/mol
$2CuClCH_3 \longrightarrow 2CuCl + C_2H_6$	63
$2CuCl_2CH_3^- \longrightarrow 2CuCl_2^- + C_2H_6$	242
$2CuCl_3CH_3^{2-} \longrightarrow 2CuCl_2^- + C_2H_6$	200
$CuClCH_3 + CH_3 \longrightarrow CuCl + C_2H_6$	220

High values of reaction heats indicate that they can proceed even at low temperatures; however, exact conclusions can be drawn only after calculations of transition state energies.

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