

# Formation of Cu(I) compounds in the Cu|Cu(II) – maleic acid system

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Electrochemical quartz crystal microgravimetry was applied to study the interactions between copper electrode and Cu(II) solutions containing maleic acid (LH<sub>2</sub>). The electrode mass was found to decrease under open-circuit conditions in sufficiently acidic solutions (pH ≤ 5) due to the heterogeneous reaction  $\text{Cu} + \text{Cu}^{2+} \rightleftharpoons 2 \text{Cu}$ . Its rate falls into the region from 0.4 to 0.8 nmol cm<sup>-2</sup> s<sup>-1</sup> depending on pH. Conditions favorable for Cu<sub>2</sub>O formation emerge in less acidic media (5.5 < pH < 6.0); the rate of this process accounts for some nmol cm<sup>-2</sup> s<sup>-1</sup>.

Simulations based on the material balance equations show that deep chemical changes are possible in the system with a 90% transformation of Cu(II) into Cu(I). Formation of Cu<sub>2</sub>O at the electrode surface enhances this process.

Spectrophotometric investigations were carried out with solutions subjected to pre-electrolysis. Actually, complete saturation with intermediate Cu(I) compounds can be achieved, if a sufficiently large charge passes through the solution. According to the simulated data, a neutral CuLH complex should predominate in the final state.

**Key words:** copper, maleic acid, complexes, quartz crystal microgravimetry, spectrophotometry

## INTRODUCTION

It is well known that the electrochemical reduction of Cu(II) complexes proceeds via the consecutive transfer of two electrons with the formation of stable Cu(I) compounds. In the absence of ligand, the equilibrium concentration of Cu<sup>+</sup> aqua-complexes is rather low. Therefore, the formation of this intermediate under open-circuit conditions is often treated as inconsequential and is not taken into account. However, properly selected ligands are capable of shifting the equilibria towards Cu(I) formation, increasing its content to a considerable degree. Thus, a system containing several co-existing redox couples can emerge. Some properties of such objects have been analysed theoretically [1], but less attention has been paid to their experimental investigations.

Our previous experiments have shown that such system can be composed of Cu(II) and maleic (cis-butenedioic) acid HOOC–CH = CH–COOH (LH<sub>2</sub>) as a ligand. Some equilibrium characteristics of Cu(II) – maleic acid solutions have been determined by us [2, 3] and other authors [4]. However,

we found only two articles dealing with the stability characteristics of Cu(I) – maleic acid complexes. Data on the solubility of cuprous chloride in maleic acid solutions have been interpreted by Andrews and Keefer [5] assuming that LH<sub>2</sub>CuCl and LHCuCl<sup>-</sup> complexes are formed. Later, the same authors have found [6] that two other complexes, viz. CuLH and CuLH<sub>2</sub><sup>+</sup>, can also exist. It was considered that π-orbitals in the double bond are responsible for the coordination with Cu<sup>+</sup> ions. Similar experiments with some other unsaturated acids have shown [7] that the stability of the copper–carbon bond depends on steric influences of other groups attached to the double bond.

Results of the further investigations of Cu(II)-maleic acid solutions are reported in the present paper. Attention focused on the effects of re-distribution of complex species resulting from Cu<sup>+</sup> formation in the system.

## EXPERIMENTAL

Reakhim (Russia) reagents KOH, K<sub>2</sub>SO<sub>4</sub> (high purity) and CuSO<sub>4</sub> · 5 H<sub>2</sub>O (analytical grade) as well as pure maleic acid (Fluka) were used for preparation of the solutions. Copper

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sulfate was recrystallized from thrice-distilled water which was also used for preparation of solutions. Maleic acid (>99%, Fluka) was used as received. Cu(II) concentration in the stock solution was controlled by complexometric titration. Besides, solutions under investigation contained 0.3 M  $K_2SO_4$  as a background electrolyte.

Six MHz quartz crystals covered with a 0.5 cm<sup>2</sup> gold sub-layer were used in electrochemical quartz crystal microgravimetry (EQCM). For 5 min they were coated with copper at 10 mA cm<sup>-2</sup> in a 50 cm<sup>3</sup> EQCM cell containing (g dm<sup>-3</sup>)  $CuSO_4 \cdot 5 H_2O - 250$  and  $H_2SO_4 - 50$ . At the same time, the frequency of quartz oscillation was measured using a potentiostat-galvanostat PAR Model 2273, equipped with a frequency analyzer. The EQCM constant  $k$  (see below) was calculated from the latter data. Thereafter, the initial solution was replaced by the solution under investigation. Electrode potentials were controlled using an Ag|AgCl|KCl(sat) reference electrode and were converted to the standard hydrogen scale.

Pre-electrolysis of deaerated solutions was used in some experiments. For this purpose, a 50 cm<sup>3</sup> hermetic cell containing two 16 cm<sup>2</sup> copper electrodes was utilized. To saturate the solutions with Cu(I), 1 mA direct current was passed over a controlled time. According to the estimations, the whole Cu(II) in the cell undergoes electrochemical transformations during ~14 hours of electrolysis.

UV-visible spectra were recorded in 0.1 cm path length quartz cells using a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. The reference cell contained pure water. All experiments were carried out with deaerated solutions at 20 °C.

## RESULTS AND DISCUSSION

$Cu^+$  generation in the system under investigation might be performed in some different ways. One of them consists in the electrolysis of Cu(II) solutions with formation of stable Cu(I) compounds. These intermediates are capable of leaving the reaction zone and diffusing into the bulk solution. The same result is also obtained under open-circuit conditions when Cu(II) solution comes into contact with the Cu electrode. In both cases, the law of charge conservation should hold true or, to put it otherwise, the stoichiometry of the reversible process should be obeyed.

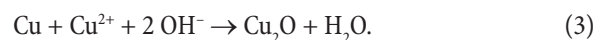


A complete saturation of the system with  $Cu^+$  ions is possible when the equilibrium state of the above process is achieved, provided that the concentration of  $Cu^+$  ions does not exceed the maximal quantity determined by the condition [8]:

$$\log [Cu^+]_{\max} = -0.84 - pH. \quad (2)$$

Otherwise, the formation of unstable intermediate CuOH originates with its following decomposition into  $Cu_2O$ . Thus,

the net process of  $Cu_2O$  formation may be written as follows:



It is remarkable that the first reaction offers a loss of electrode mass, whereas process (3) gives rise to the opposite effect. Keeping this in mind, the EQCM seems to be the most preferable technique to detect the occurrence of both heterogeneous processes.

It is common knowledge that the change in quartz crystal mass ( $\Delta m$ ) is related to its oscillation frequency ( $\Delta f$ ) according to the relationship:

$$\Delta m = -k\Delta f. \quad (4)$$

Then, the rate of the heterogeneous process may be given by the relation

$$v = \frac{k}{M} \left| \frac{d\Delta f}{dt} \right|, \quad (5)$$

where  $M$  is the molar mass of the chemical element responsible for the occurrence of  $\Delta m$ . As regards processes (1) and (3), these elements are copper and oxygen, respectively.

Typical EQCM data obtained for a quartz crystal covered with ~2  $\mu m$  Cu layer are shown in Fig. 1. Variations of oscillation frequency were recorded under open-circuit conditions at electrode potentials ( $E_{oc}$ ) falling into the range between 0.233 and 0.238 V (pH 4–6). The main changes of  $E_{oc}$  were observed at  $t < 3$  min, whereupon  $E_{oc}$  remained actually at the same level.

Two types of EQCM plots may be distinguished. The first group concerns  $pH \leq 5$  and is characterized by a positive slope of the curves, which clearly demonstrates the loss of electrode mass throughout the entire experiment. In contrast, at  $pH > 5$ , the plots acquire a negative slope at a certain time.

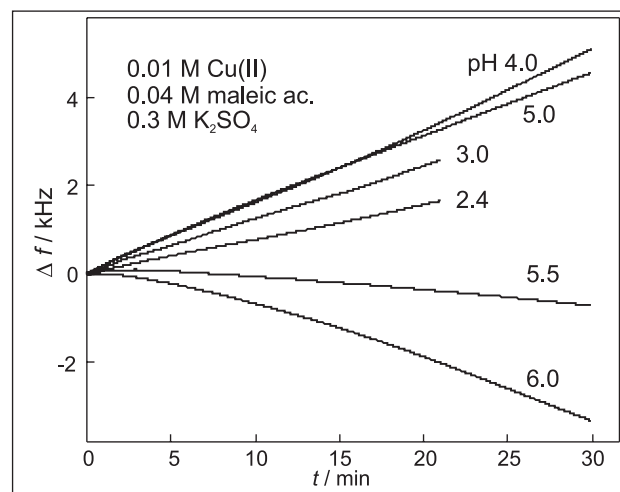


Fig. 1. EQCM data obtained for copper electrode in 0.01 M Cu(II) solutions containing 0.04 M of maleic acid at indicated pH. Open-circuit conditions

This suggests that process (3) resulting in an increase in electrode mass becomes possible.

Fitting procedures applied to EQCM plots have shown that the experimental data can be described quantitatively with a high accuracy using the second degree polynomials. This made it possible to determine the derivative  $d\Delta f / dt$  analytically, whereupon the rate of heterogeneous processes was obtained by Eq (5). In so doing, the required  $k$  value was found to be equal to  $19.8 \text{ ng cm}^{-2} \text{ Hz}^{-1}$ , using special experiments described above (see Experimental). The results obtained are shown in Fig. 2.

The rates of both processes are approximately of the same order and are measured in  $\text{nmol cm}^{-2} \text{ s}^{-1}$ . It is worth noting that the initial rate of copper corrosion grows with solution pH, despite the fact that the concentration of  $\text{Cu}^{2+}$  ions decreases in this case due to the rise in the complexation degree. Consequently, the activity of copper surface should be considered as the main factor that controls the kinetics of heterogeneous process (1). On the other hand,  $\text{Cu}_2\text{O}$  formation also accelerates with pH, what is evident from scheme (3).

The depth of Cu(II) transformation into Cu(I) may be analyzed theoretically using procedures reported in [9]. They are based on material balance equations and involve respective stability constants ( $\beta$ ). The  $\beta$  values concerning Cu(II) and maleic acid solutions were taken from our previous reports [2, 3]; similar characteristics of Cu(I) complexes were

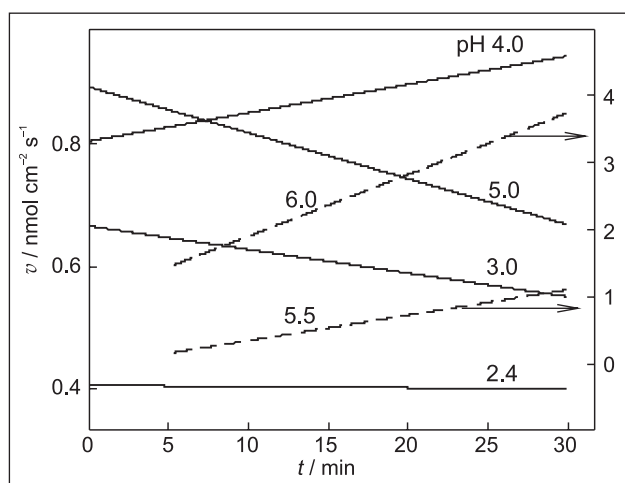


Fig. 2. Rate of generation of  $\text{Cu}^+$  ions (solid lines, ordinate to the left) and that of  $\text{Cu}_2\text{O}$  formation (dashed lines, ordinate to the right) at the surface of copper electrode. The results were obtained from the EQCM data shown in Fig. 1

Table. Cumulative stability constants used in simulations

Equilibrium	$\log \beta$	Ref.
$\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{LH}^-$	5.75	[2]
$2 \text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{LH}_2$	7.3	[2]
$\text{Cu}^{2+} + \text{L}^{2-} \rightleftharpoons \text{CuLH}$	2.2	[3]
$\text{Cu}^+ + \text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{CuLH}$	9.9	[6]
$\text{Cu}^+ + 2 \text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{CuLH}_2^+$	10.3	[6]
$\text{Cu}^{2+} + \text{Cu} \rightleftharpoons 2 \text{Cu}^+$	-6.4	[4]

obtained from data given in [6]. All the quantities used are listed in the Table. The activity coefficient of hydronium ions  $\gamma_{\text{H}} = 0.7$  was taken from [2]. In the following, a certain solution containing Cu(II) and maleic acid is treated as the initial state of the system. When it comes into contact with the Cu electrode, the described above chemical processes occur and a new equilibrium state (the final state of the system) is established.

The loss of total Cu(II) occurring at different concentrations of ligand ( $c_L$ ) is shown in Fig. 3. Solid lines represent the results of simulations that ignore the formation of  $\text{Cu}_2\text{O}$ . All they pass a certain maximum, the height of which increases with  $c_L$ . Since Cu(I) complexes are much stronger than Cu(II) maleates, the quantity of Cu(II) transformed into Cu(I) is rather large and can range up to ~90%. According to the analysis,  $\text{Cu}_2\text{O}$  becomes thermodynamically stable at a certain pH equal to 3.48, 3.61 and 3.85 at  $c_L$  equal to 0.02, 0.04 and 0.08 M, respectively. When pH exceeds this critical value, the final state of the system is shown by a dashed line. Some more details illustrating the redistribution of the system components are given in Fig. 4. In the region of  $\text{Cu}_2\text{O}$  instability, the main diminution of total Cu(II) is conditioned by the decay of "free"  $\text{Cu}^{2+}$  ions (aqua-complexes), whereas the content of CuL complexes varies weakly (cf. solid and dotted lines in Fig. 4). It is necessary to emphasize that the formation of cuprous oxide requires large amounts of Cu(II).

The data presented above characterize the states when all redox processes attain their own self-coordinated equilibria. However, the establishment of such states in practical situations is controlled by a number of factors such as the kinetics of the processes, mass transport in the diffusion layer and others. To take an illustration of some kinetic aspects, let us

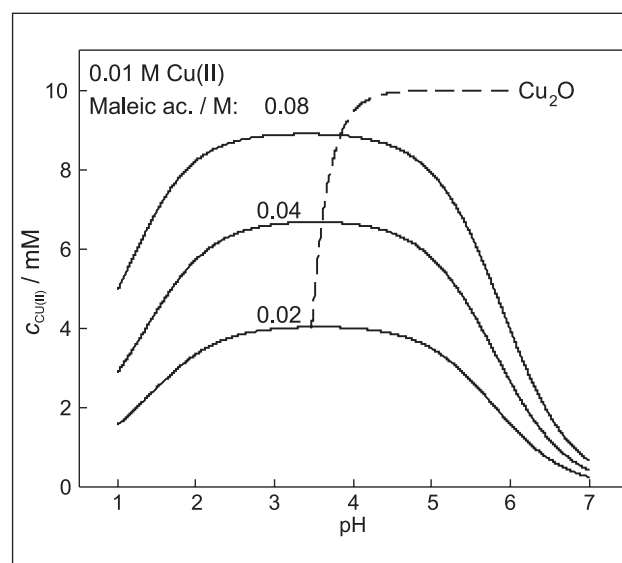


Fig. 3. Amount of Cu(II) transformed into Cu(I) at different pH in 0.01 M Cu(II) solutions containing indicated amounts of maleic acid. The dashed line represents simulation data considering  $\text{Cu}_2\text{O}$  formation

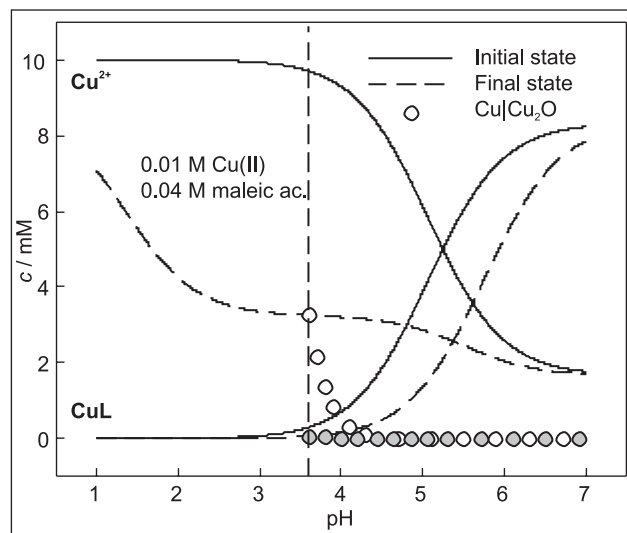


Fig. 4. Distribution of Cu(II) species in 0.01 M Cu(II) solutions containing 0.04 M of maleic acid at different pH in the initial (solid lines) and final states (dashed lines). The case of Cu<sub>2</sub>O formation is presented by circles

return to EQCM data shown in Fig. 1. As has been pointed above, the critical pH for Cu<sub>2</sub>O formation in such solutions is estimated at 3.61; however, no increase in the electrode mass is observed right up to pH 5. Besides, to form a stable oxide at pH 4, Cu(II) concentration should fall at least to 0.007 M (see Fig. 4). Accounting for the rate of copper dissolution that does not exceed 1 nmol cm<sup>-2</sup> s<sup>-1</sup> (Fig. 2) and keeping in mind some details given above in Experimental, one can conclude that the equilibrium Cu<sub>2</sub>O phase can be formed only in 40 hours. The thickness of dissolved copper coating therewith should approach ~10 μm. Accounting for local concentrations at the electrode surface can somewhat diminish these quantities, but the duration of the experiment remains too short for Cu<sub>2</sub>O formation.

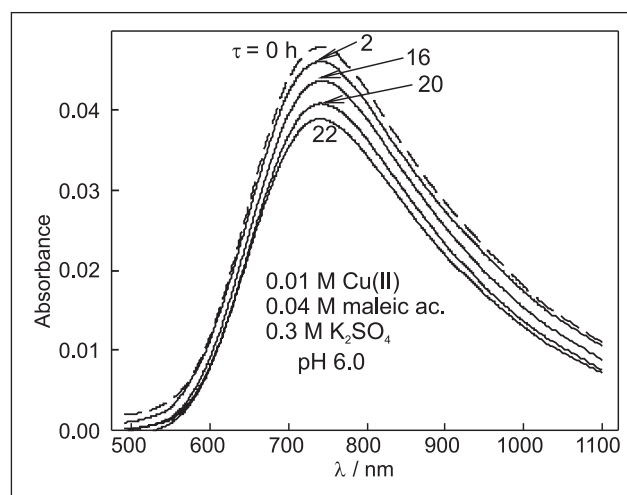


Fig. 5. Absorption spectra of pre-electrolyzed 0.01 M Cu(II) solutions containing 0.04 M of maleic acid at pH 6. Duration of pre-electrolysis (hours) is given at the curves

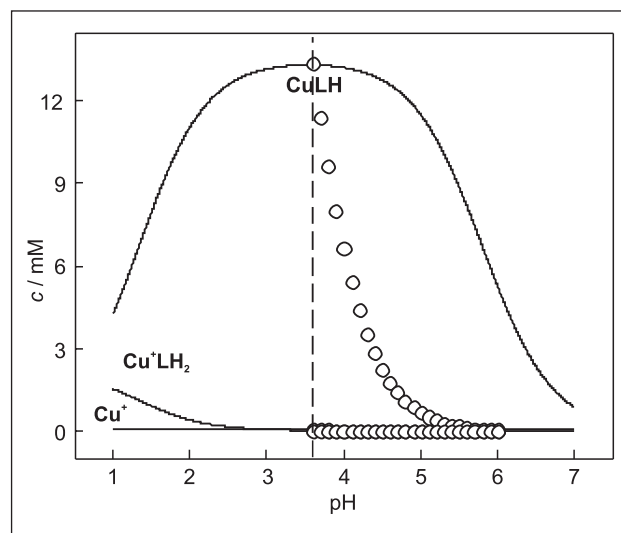


Fig. 6. Distribution of Cu(I) in the final state. The case of Cu<sub>2</sub>O formation is presented by circles

It should be noted that the latter process involves the origination and development of a new phase; therefore it requires special conditions which are more favourable at the electrode surface than in the bulk of solution. If the formation of Cu<sub>2</sub>O germs are retarded, the restriction (2) becomes inoperative and does not bind the Cu(I) concentration. Such a situation seems to arise in the course of pre-electrolysis of Cu(II) – maleic acid solutions. Spectrophotometric investigations of such solutions have shown [3] that addition of maleic acid into Cu(II) solutions results in a significant rise of the absorption maximum ( $A_{\max}$ ) and its shift towards shorter wavelengths from 806 up to 722 nm. Therefore,  $A_{\max}$  may serve as a measure of Cu(II) concentration which decreases in the course of pre-electrolysis (Fig. 5). It follows from the data given in Fig. 4 at pH 6 that Cu<sup>2+</sup> concentration can fall down from 2.6 (final state) to 2.05 mM (initial state), if Cu<sub>2</sub>O is not formed. The respective concentrations of CuL complexes are 7.4 and 5.3 mM. The employment of these data and the correlations established in [3] show that  $A_{\max}$  should reach ~0.035 in the process. According to the experimental data (Fig. 6),  $A_{\max}$  diminishes from 0.048 to 0.039 in 22 hours of pre-electrolysis. Consequently, a nearly complete saturation of the solution with Cu(I) complexes can be attained under such conditions.

The distribution of Cu(I) species in final states is shown in Fig. 6. Although the quantitative accuracy of the concentrations depends on the reliability of stability constants presented in [6], there is a good reason to believe that neutral CuLH complexes predominate at pH > 2.5.

## CONCLUSIONS

1. It follows from EQCM data that the Cu electrode mass decreases under open-circuit conditions in sufficiently

acidic Cu(II) – maleic acid solutions ( $\text{pH} \leq 5$ ) due to the heterogeneous reaction  $\text{Cu} + \text{Cu}^{2+} \rightleftharpoons 2 \text{Cu}$ . Its rate falls into the region from 0.4 to 0.8  $\text{nmol cm}^{-2} \text{s}^{-1}$  depending on pH.

2. Conditions favourable for  $\text{Cu}_2\text{O}$  formation emerge in less acidic media ( $5.5 < \text{pH} < 6.0$ ); the rate of this process accounts for some  $\text{nmol cm}^{-2} \text{s}^{-1}$ .

3. Simulations based on the material balance equations show that deep chemical changes are possible in the system with a 90% transformation of Cu(II) into Cu(I). Formation of  $\text{Cu}_2\text{O}$  at the electrode surface enhances this process.

4. Spectrophotometric investigations of the solutions subjected to pre-electrolysis show that actually complete saturation with intermediate Cu(I) compounds can be achieved, if a sufficiently large charge passes through the solution. According to the simulated data, the neutral complex  $\text{CuLH}$  should predominate in the final state.

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## Cu(I) JUNGINIŲ SUSIDARYMAS SISTEMOJE Cu|Cu(II) – MALEINO RŪGŠTIS

### Santrauka

Elektrocheminės kvarco kristalo mikrogravimetrijos (EKKM) metodu ištirta vario elektrodo sąveika su Cu(II) ir maleino rūgšties ( $\text{LH}_2$ ) tirpalu atviros grandinės sąlygomis. Nustatyta, kad pakankamai rūgščiuose tirpaluose ( $\text{pH} \leq 5$ ) elektrodo masė mažėja dėl heterogeninės reakcijos  $\text{Cu} + \text{Cu}^{2+} \rightleftharpoons 2 \text{Cu}$ , kurios greitis priklauso nuo pH ir yra lygus 0,4–0,8  $\text{nmol cm}^{-2} \text{s}^{-1}$ . Sumažėjus tirpalų rūgštingumui ( $5,5 < \text{pH} < 6,0$ ) palankiomis sąlygomis gali susidaryti  $\text{Cu}_2\text{O}$ . Pastarojo proceso greitis yra keli  $\text{nmol cm}^{-2} \text{s}^{-1}$ .

Skaičiavimai pagal materialaus balanso lygtis parodo, kad šioje sistemoje galimi gilūs virsmai, kurių metu iki 90% Cu(II) gali pereiti į Cu(I). Paviršinio  $\text{Cu}_2\text{O}$  susidarymas skatina Cu(I) generaciją.

Spektrofotometriškai ištirti Cu(II) tirpalai, kuriuose buvo atliekama elektrolizė. Nustatyta, kad praleidus pakankamą elektros krūvį, tirpalus galima įsotinti tarpinio oksidacijos laipsnio junginiais. Skaičiavimai rodo, kad galutinėje būsenoje turėtų vyrauti neutralus kompleksas  $\text{CuLH}$ .