

## Metal Complexes with Mixed Ligands

### 7. An Emf-Investigation of the Complex Formation between Binuclear Dihydroxo-bridged Copper(II) Cations and Imidazole Ligands

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Equilibria between copper(II), imidazole ( $C_3H_4N_2$ ) and  $OH^-$  have been studied in the three media 3.0 M (Na)ClO<sub>4</sub>, 3.0 M (Na)Cl, and 5.0 M (Na)Cl. The measurements have been performed as potentiometric (glass electrode) titrations at 25°C. Besides pure binary hydrolytic species  $CuOH^+$  and  $Cu_2(OH)_2^{2+}$  and unhydrolyzed copper-imidazole complexes  $Cu(C_3H_4N_2)_n^{2+}$ ,  $n = 1, 2, 3, 4$ , all data could be explained with the ternary complexes  $Cu(OH)C_3H_4N_2^+$  and  $Cu_2(OH)_2(C_3H_4N_2)_4^{2+}$ . In 3.0 M (Na)ClO<sub>4</sub> medium  $Cu_2(OH)_2(C_3H_4N_2)_3^{2+}$  also seems to be formed. The equilibrium constants determined are given in Tables 4 and 6.

Data have been analyzed with the least squares computer program LETAGROPVRID.

In part 1<sup>1</sup> of this series equilibria in the system  $Cu^{2+} - OH^- - imidazole$  were studied at 25°C in 3.0 M (Na)ClO<sub>4</sub>. It was found that for ratios  $C/B \geq 8$  ( $C$  = total imidazole concentration and  $B$  = total copper concentration) all data could be explained by a series of stepwise binary complexes  $Cu(C_3H_4N_2)_n^{2+}$  with  $n = 1, 2, 3, 4$ , and 6 (possibly also small amounts of a complex with  $n = 5$ ). For  $C/B < 8$  the data also indicated formation of ternary complexes and the effects found were tentatively explained by a single complex  $Cu_2(OH)_2(C_3H_4N_2)_3^{2+}$ .

Using solely the data available from the part 1 investigation it was impossible to decide whether the composition  $Cu_2(OH)_2(C_3H_4N_2)_3^{2+}$  really corresponded to a single complex or if it instead was a mean composition of a number of complexes. To clarify the situation it is necessary to collect data where the steps between different  $C/B$  ratios lie much closer together than in the earlier investigation. Supplementary data were therefore collected and a new detailed mathematical analysis was performed. Special attention was paid to the possibility of formation of stepwise binuclear copper-complexes of the type  $Cu_2(OH)_2(C_3H_4N_2)_n^{2+}$ . The results of this analysis will be reported below.

## PREVIOUS STUDIES ON BINARY AND TERNARY HYDROLYZED COPPER(II)-SPECIES

*Binary hydrolytic  $Cu_q(OH)_p$ -species.* The main complex in hydrolyzed  $Cu^{2+}$ -solutions,  $Cu_2(OH)_2^{2+}$  was first reported by Hagisawa<sup>2</sup> in 1939. Since then this complex has been confirmed and more accurately determined especially through the investigations of Pedersen,<sup>3</sup> Berecki-Biedermann<sup>4</sup> (3.0 M (Na)ClO<sub>4</sub>, 25°C) and Ohtaki<sup>5</sup> (dioxane-water mixture, 3.0 M (Li)ClO<sub>4</sub>, 25°C).

Perrin<sup>6</sup> claimed that the hydrolysis of  $Cu^{2+}$  proceeds by a "core- and links" mechanism to form di-, tri-, and polynuclear complexes of the type  $Cu_n(OH)_{2n-2}^{2+}$ . However, neither Berecki-Biedermann nor Ohtaki found any evidence for the formation of trinuclear or higher complexes. The existence of a mononuclear,  $CuOH^+$ , complex has also been reported and is formed in appreciable amounts only at low concentrations of copper.

*Ternary hydrolytic  $Cu_q(OH)_pL_n$ -species.* Both mononuclear ( $q=1$ ) and polynuclear ( $q>1$ ) complexes have been described. In the systems studied the ligands used have been predominantly bidentate in character. Hitherto only two systems with monodentate nitrogen containing ligands appear to have been investigated. In the system  $Cu^{2+} - OH^- - NH_3$ , it has been proposed that a series of complexes  $Cu(OH)_n(NH_3)_{4-n}$  with  $n=1, 2$ , and  $3$  is formed.<sup>8,29</sup> Other species such as  $Cu(OH)NH_3^+$  have also been reported.<sup>29</sup> The other system studied, was the system  $Cu^{2+} - OH^- -$  pyridine. It was proposed<sup>9</sup> that the main complex is  $Cu_2(OH)_2(pyridine)_4^{2+}$  with  $\log K(2 Cu^{2+} + 2OH^- + 4L \rightleftharpoons Cu_2(OH)_2L_4^{2+}) = 24.71$ . However, mononuclear ternary complexes of the type  $Cu(OH)L_n^+$ , with  $n=1, 2, 3$  have also been reported.<sup>10</sup> Information concerning complexes with bidentate ligands may be found in the editions of Stability Constants.<sup>11</sup> The most frequently reported complexes are  $Cu(OH)L$  and  $Cu_2(OH)_2L_2$  [the complex  $Cu_2(OH)_2L_2$  is supposed to be formed by dimerization of  $Cu(OH)L$ ]. Other types of complexes have also been described; e.g. Vacca<sup>12</sup> in an investigation of the system  $Cu^{2+} - OH^- - N,N,N',N'$ -tetramethylethylenediamine found evidence for the formation of trinuclear complexes. The complete set of ternary complexes necessary for explaining his data were:  $Cu(OH)L^+$ ,  $Cu_2(OH)_2L_2^{2+}$ ,  $Cu_2(OH)_2L_2^{2+}$ ,  $Cu_3(OH)_4L_2^{2+}$ , and  $Cu(OH)_2L$ . The choice of this chemical model was, however, a matter of personal judgement. Vacca's computer calculations indicated that four other models were also possible.

*Crystal structures.* Numerous crystal structures of  $Cu_2(OH)_2L_n$ -complexes are described in the literature. In all of these the central unit of the complex consists of two copper atoms bonded together through two OH-bridges with the ligands occupying the available coordination sites around the copper atoms. Structures with both monodentate and bidentate ligands have been reported. The following structures with bidentate ligands have been described:  $Cu_2(OH)_2(2,2'$ -bipyridyl)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>,<sup>13</sup>  $Cu_2(OH)_2(2,2'$ -bipyridyl)<sub>2</sub>SO<sub>4</sub>·5H<sub>2</sub>O,<sup>14</sup>  $Cu_2(OH)_2(N,N,N',N'$ -tetramethylethylenediamine)<sub>2</sub>Br<sub>2</sub>,<sup>15</sup> and  $Cu_2(OH)_2(2-(2$ -ethylaminoethyl)pyridine)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub><sup>30</sup> and for monodentate ligands,  $Cu_2(OH)_2(methylamine)_4$ SO<sub>4</sub>·H<sub>2</sub>O.<sup>16</sup> No crystal structure determinations of any  $Cu(OH)_pL_n$  complexes have yet been made. This is probably due to the difficulties involved in preparing crystals.

## EXPERIMENTAL

*Chemicals and analysis.* The perchlorate solutions used were prepared and analyzed as described earlier.<sup>1</sup> Stock solutions of  $\text{CuCl}_2$  were prepared by dissolving recrystallized  $\text{CuCl}_2 \cdot (\text{H}_2\text{O})_2$  (Merck *p.a.*) in water and analyzed for copper as earlier described.<sup>1</sup> Hydrochloric acid (Merck *p.a.*) was used without further purification.

*Apparatus.* The thermostat, cell arrangement, and electrodes used were the same as described earlier. The potentiometric titrations were performed with an automatic system for precise emf-titrations, a system constructed and built at this institute by O. Gintstrup.<sup>17</sup>

*Method.* The measurements were carried out as a series of potentiometric titrations. In general the total copper(II) concentration,  $B$ , and the total imidazole concentration,  $C$ , were kept constant in each of the titrations. The free hydrogen ion concentration,  $h$ , was varied by adding hydroxide ions and measured with a glass electrode. Calibrations and assumptions in connection with the use of the glass electrode were the same as described earlier.<sup>1</sup> The liquid junction potentials used were  $E_j = -16.3 h$ ,  $-17.0 h$ ,  $-3.8 h$  mV in 3.0 M  $(\text{Na})\text{ClO}_4$ , 3.0 M  $(\text{Na})\text{Cl}$ , and 5.0 M  $(\text{Na})\text{Cl}$ , respectively. The reversibility of the equilibria was tested by making back titrations (addition of  $\text{H}^+$ ) to hydrolyzed solutions. However, for the  $C/B$  ratios  $< 2.5$  this was impossible due to the precipitation of  $\text{Cu}(\text{OH})_{1.6}(\text{ClO}_4)_{0.4}$ , which occurred on the  $\text{H}^+$  additions. For testing equilibria at these ratios dilution experiments were carried out. (Solutions of different  $Z$ -values were diluted with pure medium.) It was found that the equilibria were reversible at all the ratios studied. The precipitate obtained for  $C/B < 2.5$  was always of the type  $\text{Cu}(\text{OH})_{1.6}\text{X}_{0.4}$  ( $\text{X} = \text{Cl}, \text{ClO}_4$ ) whereas at higher ratios copper-imidazole complexes were precipitated. In perchlorate solutions this precipitate was either the trinuclear imidazole-imidazolone complex  $\text{Cu}_3(\text{C}_3\text{H}_4\text{N}_2)_3(\text{C}_3\text{H}_5\text{N}_2)_2(\text{ClO}_4)_4$  or  $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_4(\text{ClO}_4)_2$  or a mixture of both. In both cases precipitation causes an increase in acidity and limits the available  $-\log h$  range approximately to  $-\log h < 8$ .

*Data treatment.* The mathematical analysis of data was made with the least squares program LETAGROPVRID<sup>18</sup> (version ETITR<sup>19</sup>). On treating the emf data the error squares sum  $U = \sum (Z_{\text{calc}} - Z_{\text{exp}})^2$  was minimized. The standard deviations were defined and calculated according to Sillén.<sup>20</sup> The computation was performed on a CD 3200 computer.

In the least squares calculations use was made of the quantity  $Z$ , which is defined as the average number of  $\text{OH}^-$  bound or reacted per  $\text{Cu}^{2+}$ -ion. This quantity can be determined from the analytical excess of  $\text{OH}^-$  over the zero level of  $\text{Cu}^{2+}$ ,  $\text{C}_3\text{H}_5\text{N}_2^+$ ,  $\text{H}_2\text{O}$  and from the measured  $h$  with the relationship

$$Z = (h - H - K_w h^{-1})/B \quad (1)$$

where  $K_w$  is the ionic product of water. In the present study the term  $K_w h^{-1}$  can be neglected. Another quantity that will be used in the present paper is  $\bar{n}$ , which in the part 1<sup>1</sup> investigation was denoted as  $Z_n$ .  $\bar{n}$  is given by the relationship

$$\bar{n} = (h - H - [\text{C}_3\text{H}_4\text{N}_2])/B \quad (2)$$

For the case when only complexes of the type  $\text{Cu}_q(\text{C}_3\text{H}_4\text{N}_2)_r^{2q+}$  are formed,  $[\text{C}_3\text{H}_4\text{N}_2]$  can be calculated from the relationship

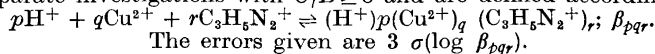
$$[\text{C}_3\text{H}_4\text{N}_2] = K_a h^{-1} [\text{C}_3\text{H}_5\text{N}_2]^+ = K_a h^{-1} (C + H - h) \quad (3)$$

where  $K_a$  is the acidity constant of  $\text{C}_3\text{H}_5\text{N}_2^+$ . In this particular case  $\bar{n}$  is the average number of imidazole molecules bound per copper atom. In all other cases  $[\text{C}_3\text{H}_4\text{N}_2]$  must be considered as a calculated quantity, which is used only for testing how well or how poorly a set of experimental data fits a series of complexes  $\text{Cu}_q(\text{C}_3\text{H}_4\text{N}_2)_r^{2q+}$ .

## DATA, CALCULATIONS AND RESULTS

*Binary data.* The mononuclear complexes of the series  $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_n^{2+}$  were accurately determined by making separate calculations with data for  $C/B \geq 8$  only. The results of these calculations with complexes and best equilibrium

Table 1. The acidity constant of  $C_3H_5N_2^+$  and equilibrium constant for the mononuclear complexes  $Cu(C_3H_4N_2)_n^{2+}$  with  $n=1,2,3,4$ . The constants have been determined in separate investigations with  $C/B \geq 8$  and are defined according to:



$\log \beta_{pqr}$	3.0 M (Na)ClO <sub>4</sub> <sup>a</sup>	3.0 M (Na)Cl	5.0 M (Na)Cl
$\log \beta_{-101}$	$-7.913 \pm 0.002$	$-7.637 \pm 0.001$	$-8.118 \pm 0.002$
$\log \beta_{-111}$	$-3.27 \pm 0.03$	$-3.238 \pm 0.015$	$-3.610 \pm 0.019$
$\log \beta_{-212}$	$-7.23 \pm 0.03$	$-7.209 \pm 0.014$	$-7.920 \pm 0.016$
$\log \beta_{-313}$	$-11.82 \pm 0.04$	$-11.85 \pm 0.02$	$-12.98 \pm 0.03$
$\log \beta_{-414}$	$-17.04 \pm 0.04$	$-17.17 \pm 0.02$	$-18.43 \pm 0.03$

<sup>a</sup> From the part 1<sup>1</sup> investigation with  $C/B \geq 8$ .

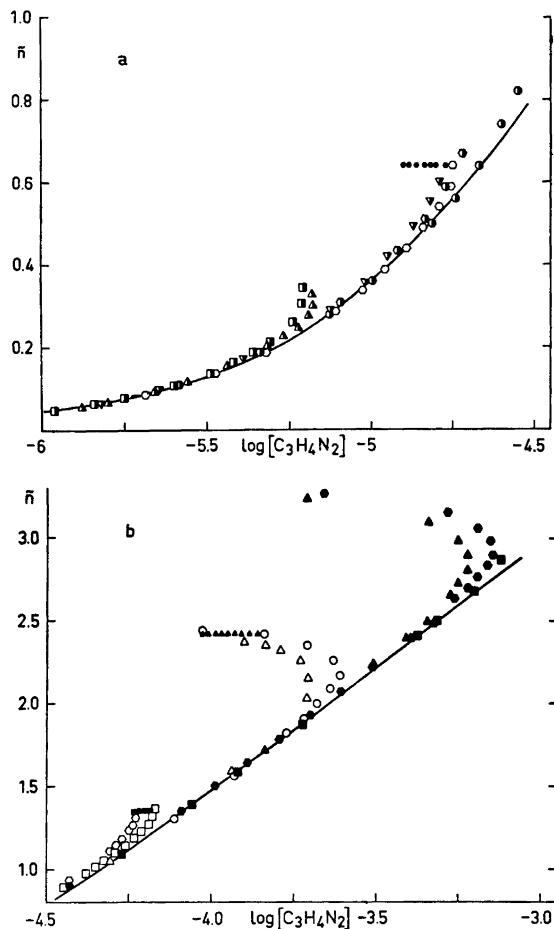
constants are collected in Table 1. For the binary hydrolytic complexes  $Cu_q(OH)_p$  we have used the results of Berecki-Biedermann's emf-investigation<sup>4</sup> (3.0 M (Na)ClO<sub>4</sub>, 25°C) and it has been assumed that the main complexes are  $Cu(OH)^+$  and  $Cu_2(OH)_2^{2+}$  with the equilibrium constants  $\beta_{-110} = 1.0 \times 10^{-8}$  M and  $\beta_{-220} = 2.5 \times 10^{-11}$  M.

In the search for ternary complexes it was assumed that the binary equilibria in the three-component system were completely explained with the above mentioned complexes and no attempts were made to adjust their equilibrium constants or to introduce new binary species. Only in the very last steps of the refinements was a covariation of the binary constants together with the ternary constants made. The purpose of this variation was to determine whether this covariation affected the ternary complexes found (by changing their equilibrium constants or in the worst case by rejecting one or more of them).

*Ternary data.* Experimental data were collected covering the following concentration ranges:  $5 \text{ mM} \leq B \leq 160 \text{ mM}$ ,  $5 \text{ mM} \leq C \leq 166 \text{ mM}$  and  $1 < -\log h < 8$ . All experimental data from the 3.0 M (Na)ClO<sub>4</sub> medium are collected in Table 2. In order to separate and accurately determine for instance setwise polynuclear complexes of the type  $Cu_2(OH)_2(C_3H_4N_2)_n^{2+}$ , it was found necessary to keep the  $C/B$  ratios studied rather close to each other, thus in 3.0 M (Na)ClO<sub>4</sub> we have used the ratios: 0.5, 0.8, 1, 1.7, 2.5, 3.3, in 3.0 M (Na)Cl 0.5, 1, 1.5, 2, 2.5, 3, 4, and in 5.0 M (Na)Cl 0.125, 0.25, 0.5, 1, 2, 4, respectively. In order to visualize the magnitudes of the effects which must be explained and also to illustrate how poorly (or well) the present data conform with solely  $Cu(C_3H_4N_2)_n^{2+}$ -complexes, we have constructed Bjerrum-plots,  $\bar{n}(\log[C_3H_4N_2])$  for the 3.0 M (Na)ClO<sub>4</sub> medium. The plots are shown in Fig. 1. It can be seen that for  $C/B < 8$  there are pronounced effects which must be due to complexes other than  $Cu(C_3H_4N_2)_n^{2+}$ . It was also found that the data available for the 3.0 M perchlorate medium were considerably greater than for the chloride media. This arises from the fact that the precipitated  $Cu(OH)_{1.6}(ClO_4)_{0.4}$  is more soluble than the corresponding chloride compound.







**Fig. 1.** Experimental data (3.0 M (Na)ClO<sub>4</sub>) plotted as curves  $\bar{n}$  ( $\log [C_3H_4N_2]$ ) for  $C/B$  ratios 0.5, 0.8, 1.0, 1.7, 2.5, and 3.3. Half-filled symbols mark titrations where  $B$  and  $C$  have been kept constant. All other symbols represent starting concentrations. The full curve has been calculated with the set of mononuclear complexes  $Cu(C_3H_4N_2)_n^{2+}$  given in Table 1. The symbols stand for the following  $B$  and  $C$  (in mM): (a)  $\square$  10-5,  $\triangle$  20-10,  $\circ$  38-32,  $\bullet$  30-25,  $\nabla$  5-5,  $\diamond$  20-20,  $\ominus$  80-80, (b)  $\circ$  15-25,  $\blacksquare$  26-44,  $\square$  38-64,  $\circ$  38-95,  $\blacktriangle$  22-55,  $\triangle$  15-38,  $\blacktriangle$  7-25,  $\bullet$  15-51,  $\blacksquare$  38-127.

the data. For the two regions Data 1 ( $0.5 \leq C/B \leq 1.7$ ) and Data 2 ( $1.7 \leq C/B \leq 3.3$ ),  $\sigma(Z)$  values were 0.0035 and 0.0058, respectively. (See Table 3.)

Even though this model explained the data rather well, further tests were carried out. The mononuclear complexes  $Cu(OH)L^+$ ,  $Cu(OH)L_2^+$ , and  $Cu(OH)L_3^+$  were systematically tested. Table 3 shows that the addition of the complex  $Cu(OH)L^+$  causes a replacement of the two complexes  $Cu_2(OH)_2L_2^{2+}$  and  $Cu_2(OH)_2L_3^{2+}$ . The calculations also show that the ternary complex

Table 3. Results of LETAGROP calculations for some different assumptions concerning the ternary complexes formed in 3.0 M (Na)ClO<sub>4</sub> medium. In the calculations, the binary constants given in Table 1 together with the hydrolysis constants given by Berecki-Biedermann, have not been varied. The constants  $\beta_{qr}$  are defined as in Table 1 and the errors  $3\sigma(\log \beta_{qr})$  are given when the corresponding equilibrium constant has been varied. Ranges 1 and 2 refer to data with  $0.5 \leq C/B \leq 1.7$  and  $1.7 \leq C/B \leq 3.3$ , respectively. R denotes a rejected complex.

Range	$\sigma(z)$ $\times 1000$	$\text{Cu}(\text{OH})_2\text{L}$ $\log(\beta_{-211} \pm 3\sigma)$	$\text{Cu}_2(\text{OH})_2\text{L}$ $\log(\beta_{-321} \pm 3\sigma)$	$\text{Cu}_2(\text{OH})_2\text{L}_2$ $\log(\beta_{-422} \pm 3\sigma)$	$\text{Cu}_2(\text{OH})_2\text{L}_3$ $\log(\beta_{-523} \pm 3\sigma)$	$\text{Cu}_2(\text{OH})_2\text{L}_4$ $\log(\beta_{-624} \pm 3\sigma)$	$\log(\beta_{pqr} \pm 3\sigma)$	$p,q,r$
1 (215 points)	3.48		-14.10 ± 0.07	-17.72 ± 0.06				
	2.69	-10.42 ± 0.11	-15.15 ± 0.60	-17.88 ± 0.08				
	2.69	-10.42 ± 0.05		-17.87 ± 0.07			R	-3,1, 1
	2.69	-10.42 ± 0.05		-17.87 ± 0.07			-8.95 ± 0.30	-2,2, 1
	2.47	-10.47 ± 0.08		-17.88 ± 0.08			-12.35 ± 0.25	-3,2, 2
	2.60	-10.44 ± 0.05		-17.92 ± 0.08			-16.22 ± 0.31	-4,2, 3
	2.66	-10.41 ± 0.05		-18.02 ± 0.19			R	-6,3, 2
	2.69	-10.40 ± 0.05		-17.89 ± 0.07			-16.04 ± 0.26	-4,3, 2
	2.62	-10.43 ± 0.06		-17.91 ± 0.08				
	5.75	-10.42		-17.87	-22.71 ± 0.15	-27.28 ± 0.07		
2 (177 points)	3.51	-10.42		-17.89 ± 0.04	R	-27.20 ± 0.02		
	3.23	-10.42		-17.91 ± 0.04		-27.30 ± 0.06	-15.70 ± 0.22	-3,1, 2
	3.48	-10.42		-17.88 ± 0.05		-27.23 ± 0.09	-21.34 ± 0.52	-4,1, 3
	3.51	-10.42		-17.89 ± 0.04		-27.19 ± 0.02	R	-12,3,10
	3.50	-10.42		-17.90 ± 0.04		-27.19 ± 0.02	R	-5,2, 4
	3.50	-10.42		-17.90 ± 0.04		-27.19 ± 0.02	-26.37 ± 1.32	-6,2, 5
	3.51	-10.42		-17.90 ± 0.05		-27.20 ± 0.03	R	-8,3, 6



Table 4. Results of final covariations of binary and ternary constants in the three media investigated. When no  $3\sigma(\log pqr)$  is given the formation constant has not been varied. R denotes a rejected complex.

Medium	Range	$\sigma(Z)$ $\times 1000$	$\text{CuL}^{2+}$ $\log(\beta_{-111})$ $\pm 3\sigma$	$\text{CuL}_2^{2+}$ $\log(\beta_{-212})$ $\pm 3\sigma$	$\text{CuL}_3^{2+}$ $\log(\beta_{-313})$ $\pm 3\sigma$	$\text{CuL}_4^{2+}$ $\log(\beta_{-414})$ $\pm 3\sigma$	$\text{Cu}_2(\text{OH})_2^{2+}$ $\log(\beta_{-220})$ $\pm 3\sigma$	$\text{Cu}(\text{OH})\text{L}^+$ $\log(\beta_{-211})$ $\pm 3\sigma$	$\text{Cu}_2(\text{OH})_2\text{L}_2^{2+}$ $\log(\beta_{-422})$ $\pm 3\sigma$	$\text{Cu}_2(\text{OH})_2\text{L}_4^{2+}$ $\log(\beta_{-624})$ $\pm 3\sigma$
3.0 M(Na)ClO <sub>4</sub>	$1/2 \leq C/B \leq 7/2$ (350 points)	2.91	-3.261 $\pm 0.003$	-7.219 $\pm 0.003$	-11.816 $\pm 0.006$	-17.035 $\pm 0.013$	-10.59 $\pm 0.04$	-10.44 $\pm 0.06$	-17.90 $\pm 0.07$	-27.18 $\pm 0.02$
3.0 M(Na)Cl	$1/2 \leq C/B \leq 4$ (204 points)	3.21	-3.218 $\pm 0.003$	-7.187 $\pm 0.005$	-11.827 $\pm 0.008$	-17.17	R	-10.37 $\pm 0.04$	R	-28.01 $\pm 0.03$
5.0 M(Na)Cl	$1/8 \leq C/B \leq 4$ (229 points)	3.68	-3.588 $\pm 0.003$	-7.917 $\pm 0.009$	-12.96 $\pm 0.02$	-18.43	R	-10.23 $\pm 0.04$	R	-27.80 $\pm 0.07$

$\text{Cu}(\text{CH})\text{L}_2^+$  may be present in small amounts. However, calculations which included this complex gave a rather high value of  $3\sigma(\log \beta_{-311}) = 0.22$ . Similar calculations were made assuming complexes of the type  $\text{Cu}(\text{OH})_2\text{L}_n$ ,  $\text{Cu}_2(\text{OH})\text{L}_n^{3+}$ ,  $\text{Cu}_3(\text{OH})_2\text{L}_n^{4+}$ , and  $\text{Cu}_3(\text{OH})_4\text{L}_n^{2+}$ . Table 3 indicates that none of these complexes give any appreciable improvement.

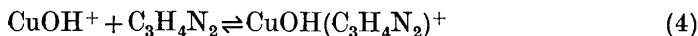
Thus it may be concluded that the main ternary complexes are  $\text{Cu}(\text{OH})\text{L}^+$ ,  $\text{Cu}_2(\text{OH})_2\text{L}_2^{2+}$ , and  $\text{Cu}_2(\text{OH})_2\text{L}_4^{2+}$ . In a covariation of binary constants against ternary constants it was found that none of the complexes was rejected and that the standard deviations  $3\sigma(\log \beta_{pqr})$  for the ternary complexes were less than 0.07. The values of the binary equilibrium constants did not change significantly; see Table 4.

*Analysis of (Na)Cl data.* Because of the restricted data range available for these two media no separate mathematical analysis of the data was made as for the 3.0 M (Na)ClO<sub>4</sub> medium. Instead the "best" model found for the 3.0 M (Na)ClO<sub>4</sub> medium was tested. The results of this test are given in Table 4. It is seen that in both media the data can be explained well with the complexes  $\text{Cu}(\text{OH})\text{L}^+$  and  $\text{Cu}_2(\text{OH})_2\text{L}_4^{2+}$  only. (The equilibrium constants for  $\text{Cu}_2(\text{OH})_2^{2+}$  and  $\text{Cu}_2(\text{OH})_2\text{L}_2^{2+}$  were always zero).

A final covariation of binary constants and ternary constants gave satisfactory results. The standard deviations  $3\sigma(\log \beta_{pqr})$  for the ternary complexes also in these media were less than 0.07; see Table 4.

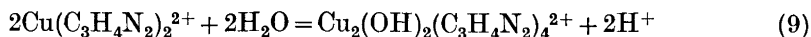
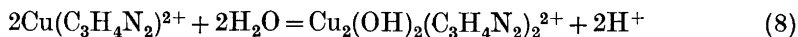
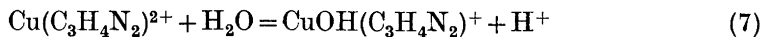
## DISCUSSION

The present investigation has given the intermediate hydrolytic species formed when imidazole is added successively to hydrolyzed Cu(II)-solutions. The main species in hydrolyzed pure Cu(II)-perchlorate solutions are  $\text{Cu}_2(\text{OH})_2^{2+}$  and  $\text{CuOH}^+$ . Our results seem to indicate that these hydroxo ions and imidazole molecules form complexes in the solution and in 3.0 M (Na)ClO<sub>4</sub> medium the following equilibria could be established



with  $\log K = 5.47$ ,  $8.53$ , and  $16.06$  for reactions (4), (5), and (6), respectively.

In the chloride media equilibrium (5) could not be detected. Alternatively the results may be interpreted as a series of hydrolysis reactions of Cu(II)-imidazoles where the equilibria present may be written



with equilibrium constants given in Table 5.

It is perhaps necessary to point out that we have assumed that we really have  $\text{OH}^-$  in the complexes. However, an  $\text{OH}^-$ -group together with a  $\text{C}_3\text{H}_4\text{N}_2^-$

Table 5. Acidity and dimerization constants of some hydrolyzed copper(II)-complexes. The constants are defined according to the equilibria given. For brevity the charges of the complexes have been omitted.

Equilibria	H <sub>2</sub> O (n = 0)	Imidazole (n = 1)	(n = 2)	Histamine (n = 1)	Histidine (n = 1)
$\text{CuL}_n + \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})\text{L}_n + \text{H}^+$	-8 <sup>a</sup>	-7.18 <sup>b</sup> -7.15 <sup>c</sup> -6.64 <sup>d</sup>	-8.5 <sup>b</sup>	-7.0 <sup>e</sup> -7.1 <sup>f</sup>	-7.39 <sup>g</sup> -7.18 <sup>h</sup> -6.63 <sup>i</sup> -8.00 <sup>j</sup>
$2\text{CuL}_n + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{OH})_2\text{L}_{2n} + 2\text{H}^+$	-10.6 <sup>a</sup>	-11.37 <sup>b</sup>	-11.75 <sup>b</sup> -13.63 <sup>c</sup> -11.97 <sup>d</sup>	-11.8 <sup>e</sup> -11.99 <sup>h</sup>	-12.15 <sup>g</sup> -12.44 <sup>j</sup>
$2\text{Cu}(\text{OH})\text{L}_n \rightleftharpoons \text{Cu}_2(\text{OH})_2\text{L}_{2n}$	5.4 <sup>a</sup>	3.0 <sup>b</sup>	4.2 <sup>b</sup>	2.2 <sup>e</sup>	2.63 <sup>j</sup> 3.76 <sup>g</sup>

Temperature and medium: <sup>a</sup> 25°C, 3 M(Na)ClO<sub>4</sub>,<sup>4</sup> <sup>b</sup> 25°C, 3 M(Na)ClO<sub>4</sub>, <sup>c</sup> 25°C, 3 M(Na)Cl, <sup>d</sup> 25°C, 5 M(Na)Cl, <sup>e</sup> 25°C, 0.1 (KNO<sub>3</sub>),<sup>22</sup> <sup>f</sup> 36°C, 1.5(K<sub>2</sub>SO<sub>4</sub>),<sup>23</sup> <sup>g</sup> 37°C, 0.15(KNO<sub>3</sub>),<sup>24</sup> <sup>h</sup> 25°C, 0.01,<sup>25</sup> <sup>i</sup> 25°C, 3 M(Na)ClO<sub>4</sub>,<sup>26</sup> <sup>j</sup> 25°C, 0.1(KNO<sub>3</sub>),<sup>27</sup> <sup>k</sup> 20°C, 0.1(KNO<sub>3</sub>).<sup>28</sup>

molecule may equally well be interpreted as an imidazolite group C<sub>3</sub>H<sub>3</sub>N<sub>2</sub><sup>-</sup>; thus the complex proposed could also be Cu(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sup>+</sup>, Cu<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub><sup>2+</sup>, and Cu<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub><sup>2+</sup>. However, for structural reasons the presence of hydroxide groups in the complexes is more probable. With regard to the aqueous structure of the complexes formed, we may tentatively propose that copper is surrounded by ligands including also one or two perchlorate groups in the coordination sphere. It has been found that in the X-ray investigated compound, Cu(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>,<sup>31</sup> the structure is built up of isolated Cu-(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> molecules held together solely by hydrogen and van der Waals bonds.

As can be seen from Table 4 the standard deviations of the proposed complexes are rather low and the complexes may thus be considered as well determined. The strengths of the complexes are illustrated by the distribution diagrams given in Fig. 2. It may be noted that in 3.0 M (Na)ClO<sub>4</sub> for instance the maximum amounts of Cu<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>, Cu(OH)L<sup>+</sup>, Cu<sub>2</sub>(OH)<sub>2</sub>L<sub>2</sub><sup>2+</sup>, and Cu<sub>2</sub>(OH)<sub>2</sub>L<sub>4</sub><sup>2+</sup> as percentages of total copper are estimated to be 3, 10, 10, and 15 respectively.

In Table 5 acidity and dimerization constants are given for some copper(II)-complexes with the ligands H<sub>2</sub>O, imidazole, histamine, and histidine. It can be seen that  $K_a(\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)^{2+})$  is greater than  $K_a(\text{Cu}^{2+})$ . Thus the introducing of a ligand increases the acidity of the copper ion. Furthermore if we compare complexes Cu(OH)L with ligands imidazole, histamine, and histidine we see that the log  $K_a(\text{CuL})$ -values reported usually fall within the ranges  $7.2 \pm 0.2$ . The dimerization constants indicate that there is more extensive dimerization when the ligands are H<sub>2</sub>O-molecules than when they are mixed H<sub>2</sub>O and imidazole, histidine or histamine species. Thus the enolization reac-

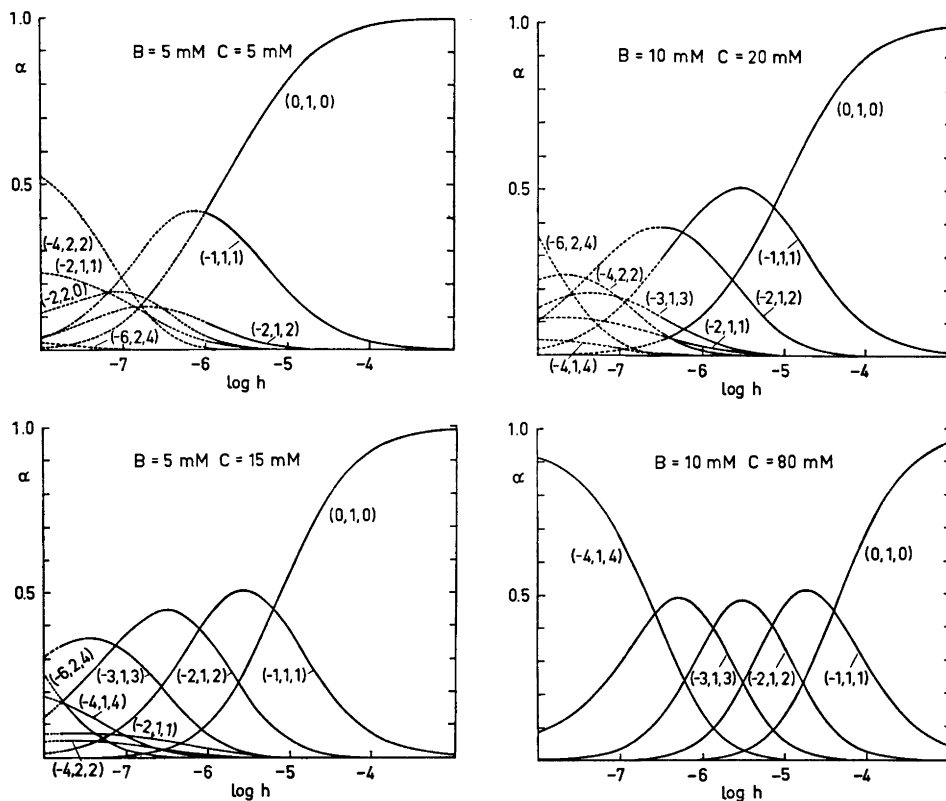
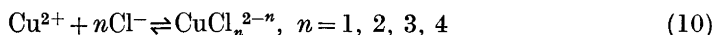


Fig. 2. Distribution diagrams  $\alpha(\log h)_{B,C}$ .  $\alpha$  is defined as the ratio between copper(II) in a species and total copper(II). The computer program HALTAFALL<sup>21</sup> was used for the calculations with the constants given in Table 4 [3.0 M (Na)ClO<sub>4</sub>]. Broken lines denote ranges where no measurements have been performed due to precipitation (extrapolated range).

tion seems to be hindered when the ligands imidazole, histamine, or histidine are introduced around the copper ion.

For complex formation in the two chloride media, the formation of chloro complexes must be taken into consideration. Many workers<sup>11</sup> have reported that copper(II) ions form weak complexes with chloride ions. Bjerrum,<sup>32</sup> in a spectrophotometric investigation, has shown that the species  $\text{CuCl}^+$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}_3^-$ , and  $\text{CuCl}_4^{2-}$  are formed with  $K_1 < 1$ ,  $K_2 \approx 0.1 - 0.4$ ,  $K_3 \approx 0.02 - 0.06$ , and  $K_4 \approx 0.003 - 0.001 \text{ M}^{-1}$ , respectively.

The stability constants given in Tables 1 and 4, calculated from the experimental data in the two chloride media, are not true stability constants but rather "conditional" constants. This is because it is assumed that no complex formation has taken place between copper and chloride ions. However, by assuming the equilibria



to be known (with equilibrium constants given by Bjerrum) it is possible to calculate new conditional constants  $\beta_{pqr}'$  which are corrected for the equilibria (10) through the relation

$$\beta_{pqr}' = \beta_{pqr}(1 + \beta_{010})^q \quad (11)$$

$$\text{where } \beta_{010} = K_1[\text{Cl}^-] + K_1K_2[\text{Cl}^-]^2 + K_1K_2K_3[\text{Cl}^-]^3 + K_1K_2K_3K_4[\text{Cl}^-]^4 \quad (12)$$

$\beta_{010}$  is a constant provided  $[\text{Cl}^-]$  remains constant during the titrations.

The values of  $\beta_{pqr}'$  from the two chloride media are given in Table 6. As is seen from this table the values of the  $\beta_{pqr}'$  constants are usually greater than those in the perchlorate medium, thus indicating that  $(\text{H}^+)_p(\text{Cu}^{2+})_q(\text{C}_3\text{H}_5\text{N}_2^+)_r(\text{Cl}^-)_s$  complexes are also formed. However, in order to determine the formation constants of these mixed complexes, it is necessary to perform measurements in perchlorate media containing varying amounts of chloride, e.g.  $[\text{ClO}_4^-] + [\text{Cl}^-] = 3.0 \text{ M}$ . Further studies in this direction are planned.

Table 6. "Conditional stability constants"  $\beta_{pqr}'$  defined according to  $p\text{H}^+ + q\text{Cu}^{2+} + r\text{C}_3\text{H}_5\text{N}_2^+ \rightleftharpoons (\text{H}^+)_p(\text{Cu}^{2+})_q(\text{C}_3\text{H}_5\text{N}_2^+)_r(2q+p)$  and calculated from the relation  $\beta_{pqr}' = \beta_{pqr}(1 + \beta_{010})^q$ . The values of  $\beta_{pqr}'$  are calculated from constants given in Table 4. Approximate values of  $\beta_{010}$  have been calculated (see eqn. 12) by assuming  $K(\text{CuCl}^+) = 1$ ,  $K(\text{CuCl}_2) = 0.2$ ,  $K(\text{CuCl}_3^-) = 0.004$ ,  $K(\text{CuCl}_4^{2-}) = 0.006$  and  $[\text{Cl}^-] = 3$  and  $5 \text{ M}$  in each chloride media, respectively.

	$\text{CuL}^{2+}$	$\text{CuL}_2^{2+}$	$\text{CuL}_3^{2+}$	$\text{CuL}_4^{2+}$	$\text{Cu}(\text{OH})\text{L}^+$	$\text{Cu}_2(\text{OH})_2\text{L}_4^{2+}$
Medium	$\log \beta_{011}'$	$\log \beta_{012}'$	$\log \beta_{013}'$	$\log \beta_{014}'$	$\log \beta_{-111}'$	$\log \beta_{-224}'$
3.0 M (Na)ClO <sub>4</sub>	4.652	8.607	11.92	14.62	-2.53	4.47
3.0 M (Na)Cl	5.197	8.865	11.86	14.16	-1.95	4.10
5.0 M (Na)Cl	5.610	9.399	12.48	15.13	-1.04	6.83

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