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Metal Complexes with Mixed Ligands. 13. A Combined Potentiometric and Spectrophotometric Study of the Systems Cu^{2+}—Imidazole, Cu^{2+}—OH^-—Imidazole and Cu^{2+}—Cl^-—Imidazole in 3.0 M $(Na)ClO_4$,Cl Media

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Equilibria between copper(II), imidazole ($C_3H_4N_2$; L), OH^- and Cl^- were studied at 25 °C by means of a combined potentiometric (glass electrode) and spectrophotometric method. The measurements were performed in media consisting of 3.0 M $(Na)ClO_4$, 3.0 M (Na)Cl and mixtures of these two with $0 \leq [Cl^-] \leq 3.0$ M. Besides pure binary species CuL_n^{2+}, with $n = 1,2,3$ and 4, data could be explained with the ternary complexes $Cu(OH)L^+$, $Cu_2(OH)_2L_2^{2+}$ and $Cu_2(OH)_2L_4^{2+}$ in addition to the ternary chloro species $CuLCl^+$, $CuLCl_2$, CuL_2Cl^+, CuL_2Cl_2 and CuL_3Cl^+. Formation constants as well as molar absorption coefficients for the different species were evaluated within the wavelength range 450 – 750 nm. Data were analyzed with the least squares computer program LETAGROPVRID.

In parts 1 [1] and 7 [2] of this series, equilibria in the system $Cu^{2+} - OH^- -$ imidazole (L) were studied at 25 °C in the media 3.0 M $(Na)ClO_4$, 3.0 M (Na)Cl and 5.0 M (Na)Cl. The results showed that besides a series of mononuclear CuL_n^{2+} complexes with $n = 1,\ldots,6$, the ternary species $Cu(OH)L^+$, $Cu_2(OH)_2L_2^{2+}$, and $Cu_2(OH)_2L_4^{2+}$ were formed. By comparing the results obtained in 3.0 M $(Na)ClO_4$ and 3.0 M (Na)Cl media, indications for the formation of ternary $Cu^{2+} - C_3H_4N_2 - Cl^-$ complexes were also found.

The aim of the present investigation was to confirm the results obtained from these emf-investigations by employing a spectrophotometric method in which both log $[H^+]$ and absorbance values are measured. Furthermore, in an attempt to determine formation of eventual ternary $Cu^{2+} - C_3H_4N_2 - Cl^-$ complexes, measurements were performed in media consisting of mixtures of 3.0 M $(Na)ClO_4$ and 3.0 M (Na)Cl with $0 \leq [Cl^-] \leq 3.0$ M. The results of these investigations are discussed below.

EXPERIMENTAL

Chemicals and analysis. All solutions used were prepared and analyzed as described earlier.[1,2]

Apparatus. The cell arrangement and experimental details of the emf measurements are fully described in Refs. 1 and 2.

The spectrophotometer used was a Heath model 721 single beam instrument with an automatic sample-reference changer combined with an automated potentiometric titrator. A sample cell of flow-through type with a path length of 1.001 cm (HELLMA, type OS) was used. Wavelengths greater than 750 nm were not investigated due to the low sensitivity of the photo cell within this wavelength range. A detailed description of the automated potentiometric and spectrophotometric titration system will be given in a forthcoming paper by Ginstrup, Lyhamn and Ingri.[3]

Method. The present study was carried out as a series of titrations in which both emf and absorbance values were measured. The measurements were performed at 25 °C and were divided into series in which the ionic medium consisted of 3.0 M $(Na)ClO_4$, 3.0 M (Na)Cl or mixtures of these two. In the titrations the total concentrations of copper(II), B, and imidazole, C, were either kept constant or varied, while the ratio C/B was always held constant. The total concentration of hydrogen

ions, H, was calculated over the zero level Cu^{2+}, $C_3H_5N_2^+$ and H_2O and the free hydrogen ion concentration, h, was varied by addition of H^+ and measured with a glass electrode. h was determined according to the relation:

$$E = E_0 + 59.157 \log h + E_j \quad (1)$$

where E_0 is a constant determined in acid solutions where complex formation could be neglected. In some cases E_0 was determined in solutions of known Z-values ($Z = (h-H)/B$). The liquid junction potential, $E = -16.7h$ mV was used in 3.0 M $(Na)ClO_4$,[4] 3.0 M (Na)Cl [2] as well as in mixtures of these two media. It has earlier been shown [5] that within the concentration range $0 \leq X \leq 3.0$ M with $[ClO_4^-] + X = 3.0$ M the concentration scale for H^+ remains constant. No change in E_0 could be found on replacing ClO_4^- by Cl^- or *vice versa*. X stands for the total concentration of chloride ions.

The combined emf and spectrophotometric measurements were performed so that for each titration point the emf was measured until equilibrium was obtained and then the transmittance, T, was recorded at a number of different wavelengths ($N\lambda$). As reference a 3.0 M $NaClO_4$ or 3.0 M NaCl solution was used. The relation between the absorbance, OD, and the concentrations, c_i, of the various absorbing species is given by the equation: $OD = l\sum \varepsilon_i c_i$ where ε_i is the molar absorption coefficient for the absorbing species i at the wavelength λ. The spectrophotometric measurements thus give data (OD, log h, H, B, C, $X)_{N\lambda}$, (after recalculating T to OD).

We assume the presence of four-component equilibria of the general form:

$$pH^+ + qCu^{2+} + rHL^+ + sCl^- \rightleftharpoons H_pCu_q(HL)_rCl_s^{(p+2q+r-s)+};\ \beta_{pqrs} \quad (2)$$

It is convenient to write complexes where $-p = r$ as $Cu_qL_nCl_s$ and the stability constants as β_{nqs}. This terminology is used throughout this paper whenever possible.

Besides the four-component equilibria in (2) we have:

(i) the complex formation between Cu^{2+} and Cl^-:

$$Cu^{2+} + sCl^- \rightleftharpoons CuCl_s^{(2-s)+} \quad (3)$$

(ii) the imidazole equilibria, which within the concentration range $0 \leq X \leq 3.0$ M with $[ClO_4^-] + X = 3.0$ M are [5]

$$HL^+ \rightleftharpoons L + H^+;\ K_a \quad (4)$$

$$HL^+ + Cl^- \rightleftharpoons LCl^- + H^+;\ \beta_{101} \quad (5)$$

$$HL^+ + 2Cl^- \rightleftharpoons LCl_2^{2-} + H^+;\ \beta_{102} \quad (6)$$

with log $K_a = -7.940$, log $\beta_{101} = -8.641$ and log $\beta_{102} = -9.279$.

(iii) the copper(II) imidazole equilibria

$$pH^+ + qCu^{2+} + rHL^+ \rightleftharpoons H_pCu_q(HL)_r^{(2q+p+r)+} \quad (7)$$

with equilibrium constants given in Table 1. In the present study hydrolytic equilibria of the copper(II) ion could be neglected.

Equilibria (3) – (7) were determined in separate investigations and are assumed to be known in calculations concerning the four-component equilibria.

Data treatment. In the evaluation of the experimental data, the LETAGROP [6] version ETITR [7] was applied to the emf-data, and the error squares sum $U = \sum(Z_{calc} - Z_C)^2$, where $Z_C = (h - H)/C$ was minimized. In calculations on the combined emf and spectrophotometric data, the LETAGROP version TITRERSPEFO [8] was used, and $U = \sum(OD_{calc} - OD)^2$ was minimized.

At the present time this program is unable to treat a four-component system. However, it will be possible to reduce the four-component system $H^+ - Cu^{2+} - C_3H_5N_2^+ - Cl^-$ to the three-component system $C_3H_4N_2 - Cu^{2+} - Cl^-$ under the assumption that $-p = r$ in (2) *i.e.* only complexes of the type $Cu_qL_nCl_s^{(2q-s)+}$ are formed. With this assumption [L] can be calculated using the relation

$$[L] = k_a h^{-1}[HL^+] = k_a h^{-1}[C - (h - H)] \quad (8)$$

Thus as input to the program data in the form (OD, log[L], B, $X)_{N\lambda}$ are given instead of (OD, log h, B, C, $X)_{N\lambda}$.

The different standard deviations given, $3\sigma(\log\beta)$ and $\sigma(\varepsilon)$, were defined and calculated according to Sillén.[9] The computation was performed on a CD 3300 computer.

DATA, CALCULATIONS AND RESULTS

The complex formation between copper(II) and imidazole has already been investigated in 3.0 M $(Na)ClO_4$ and 3.0 M (Na)Cl media, by using the emf-titration method. Results of these measurements are found in Refs. 1 and 2. In an attempt to confirm the different binary $Cu^{2+} - L$ as well as ternary $Cu^{2+} - OH^- - L$ complexes proposed, spectrophotometric measurements in which both log h and absorbance were measured, were performed. In addition the formation of ternary $Cu^{2+} - L - Cl^-$ complexes was investigated by employing this combined emf and spectrophotometric method. The results obtained in the different investigations are given below.

(i) *Copper(II) imidazoles in 3.0 M $(Na)ClO_4$ medium.* In all 11 different titrations, including

186 titration points, were performed. As 16 different wavelengths, ranging from 450 to 750 nm, with 20 nm interval were investigated 2976 measured absorbance values were collected. The following concentration ranges were investigated: $0.004 \leq B \leq 0.020$ M, $0.025 \leq C \leq 0.320$ M, $3.0 \leq -\log h \leq 6.7$ with $C/B = 2.5$, 3.5, 8, 16, 32, and 64. With $C/B \geq 8$ a series of mononuclear CuL_n^{2+} species was found to predominate, while with $C/B < 4$ the ternary complexes $Cu(OH)L^+$, $Cu_2(OH)_2L_2^{2+}$ and $Cu_2(OH)_2L_4^{2+}$ are formed in addition. A part of the experimental data is visualized as $\bar{n}(\log[L])$ plots [2] in Fig. 1.

In the LETAGROP (TITRERSPEFO) calculations data with $C/B \geq 8$ were at first treated. The calculations were started with formation constants for the species CuL_n^{2+}, with $n = 1$, 2, 3 and 4 taken from Ref. 2. Molar absorption coefficients ε_{n1n} for each of the different copper(II) species were then calculated and it was found that a satisfactory fit to the experimental data was obtained. In the subsequent calculations, data with $0 \leq \bar{n} \leq 1.5$ were treated and β_{-111}, β_{-212}, ε_{-111} and ε_{-212} were covaried, while β_{-313}, β_{-414}, ε_{-313}, and ε_{-414} were kept constant. The results of this calculation are given in Table 1. In a similar way data with $1.5 \leq \bar{n} \leq 3.5$ were treated: β_{-313}, β_{-414}, ε_{-313} and ε_{-414} were covaried while the new refined values of β_{-111}, β_{-212}, ε_{-111} and ε_{-212} were kept constant.

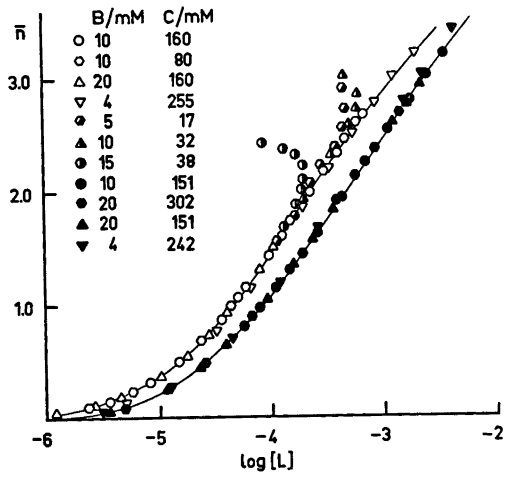


Fig. 1. Parts of experimental data plotted as curves $\bar{n}(\log[L])$ in 3.0 M $(Na)ClO_4$ (left) and (Na)Cl (right) media. The full curves were calculated with the set of constants given in Table 1 (emf+spect.).

As can be seen from Table 1 the values of the different β_{n1n} constants were obtained with very low errors $[3\sigma(\log \beta_{n1n}) \leq 0.03]$ and they are in agreement with those obtained from the emf-investigation.

Data with $C/B < 4$, where the ternary $Cu^{2+} - L - OH^-$ complexes are formed, were treated as follows: With knowledge of the formation constants of these species molar absorption coefficients at each wavelength investigated could be calculated. As the amounts of $Cu(OH)L^+$, $Cu_2(OH)_2L_2^{2+}$ are less than 10 % of B within the C/B ratios studied, ε_{-211} and ε_{-422} were obtained with relatively high errors and no attempts were made to refine their formation constants. However, the formation constant of $Cu_2(OH)_2L_4^{2+}$ was varied in one calculation giving $\log \beta_{-624} = -27.08 \pm 0.07$ which can be compared with the value -27.18 ± 0.02 obtained in the emf-investigation.

Molar absorption coefficients of the different $Cu^{2+} - L$ and $Cu^{2+} - L - OH^-$ complexes are given in Table 2.

(ii) *Copper(II) imidazoles in 3.0 M (Na)Cl medium.* 5 different titrations yielding 77 titrations points were performed, the following $B(C)$ combinations were investigated 4(242), 10(151), 20(151), 20(302), 42(302) mM, respectively, with $3.0 \leq -\log h \leq 6.7$. These experimental data are visualized as an $\bar{n}(\log[L])$ plot in Fig. 1. The same wavelength ranges as in (i) were covered, thus yielding 1232 absorbance values. The calculations were performed as under (i) and the formation constants are given in Table 1. Molar absorption coefficients are visualized in Fig. 2b. Formation constants as well as molar absorption coefficients determined in this medium are "conditional" as in the different species chloride ions most probably are coordinated. This is strongly indicated by comparing the spectra for the different mononuclear $Cu^{2+} - L$ species given in Figs 2a and 2b. As can be seen from these figures the chloride medium appears to cause a shift of the absorption maximum to higher wavelengths and an increase of the molar absorbance for each of the species Cu^{2+}, CuL^{2+}, CuL_2^{2+} and CuL_3^{2+} was found, while the spectrum of CuL_4^{2+} was almost identical in the two media.

Table 1. Results of LETAGROP calculations concerning the equilibria: $pH^+ + qCu^{2+} + rC_3H_5N_2^+ \rightleftharpoons H_pCu_q(C_3H_5N_2^+)_r^{(p+2q+r)+}$.

Medium	Method	$\log(\beta_{pqr} \pm 3\sigma)$							
		−111	−212	−313	−414	−211	−422	−624	Remark
3.0 M	emf	−3.27(3)	−7.23(3)	−11.82(4)	−17.04(4)	−10.44(6)	−17.90(7)	−27.18(2)	Ref. 2
$(Na)ClO_4$	emf+spect.	−3.28(3)	−7.24(3)	−11.82	−17.04	–	–	–	$0 \leq \bar{n} \leq 1.5$ [a]
	emf+spect.	−3.28	−7.24	−11.80(2)	−17.18(1)	–	–	–	$1.5 \leq \bar{n} \leq 3.2$ [a]
	emf+spect.	−3.28	−7.24	−11.80	−17.18	−10.44	−17.90	−27.08(7)	$C/B < 4$ [a]
3.0 M	emf	−3.24(2)	−7.21(1)	−11.85(2)	−17.17(2)				Ref. 2
(Na)Cl	emf+spect.	−3.21(1)	−7.20(2)	−11.85	−17.17				$0 \leq \bar{n} \leq 1.5$ [a]
	emf+spect.	−3.21	−7.20	−11.84(2)	−17.13(1)				$1.5 \leq \bar{n} \leq 3.5$ [a]

[a] This work.

Table 2. Molar absorption coefficients for different copper(II) complexes in 3.0 M $(Na)ClO_4$ medium ($L = C_3H_4N_2$).

λ/nm	Cu^{2+}	CuL^{2+}	CuL_2^{2+}	CuL_3^{2+}	CuL_4^{2+}	$Cu(OH)L^+$	$Cu_2(OH)_2L_2^{2+}$	$Cu_2(OH)_2L_4^{2+}$	$\sigma(OD) \times 10^3$
450	0.1(1)	0.1(1)	0.0(4)	0.6(2)	2.4(11)	–	–	–	1
470	0.1(1)	0.1(1)	0.1(1)	1.0(2)	9.6(10)	–	–	–	1
490	0.1(1)	0.1(1)	0.6(1)	2.9(2)	20.2(10)	–	–	–	1
510	0.1(1)	0.1(1)	1.7(2)	6.5(2)	34.8(10)	–	–	–	1
530	0.2(2)	0.4(1)	3.2(2)	13.1(2)	48.7(14)	0.0(9)	18.5(14)	49.2(21)	2
550	0.3(2)	0.9(1)	6.0(2)	21.6(2)	59.4(16)	0.0(11)	33.9(11)	65.8(17)	2
570	0.5(3)	1.9(1)	10.1(2)	30.9(3)	61.9(20)	0.0(11)	54.6(11)	80.3(17)	2
590	0.8(3)	3.4(1)	15.5(2)	38.1(3)	62.2(20)	6.6(13)	57.2(32)	97.2(22)	3
610	1.3(2)	5.7(1)	21.0(1)	43.4(3)	55.7(19)	16.6(20)	52.3(48)	108.0(33)	2
630	1.9(1)	8.3(1)	26.2(1)	44.9(3)	49.4(22)	19.5(21)	57.5(49)	107.7(33)	3
650	3.0(1)	11.5(1)	29.9(2)	43.7(3)	42.9(22)	23.1(16)	68.1(38)	94.5(26)	2
670	4.3(1)	14.5(1)	32.1(1)	40.8(3)	38.3(19)	32.6(20)	53.0(47)	88.1(32)	2
690	5.9(1)	17.0(1)	32.8(1)	37.4(3)	32.2(19)	30.7(17)	51.4(41)	77.2(28)	2
710	7.5(1)	18.7(1)	32.3(1)	33.3(3)	27.2(17)	30.5(24)	46.3(58)	67.6(40)	2
730	9.0(1)	19.9(1)	30.6(2)	29.7(3)	24.4(19)	31.2(14)	32.6(32)	47.2(40)	2
750	10.3(2)	20.2(1)	29.0(1)	26.4(3)	19.6(16)	24.9(24)	20.6(58)	39.7(22)	2

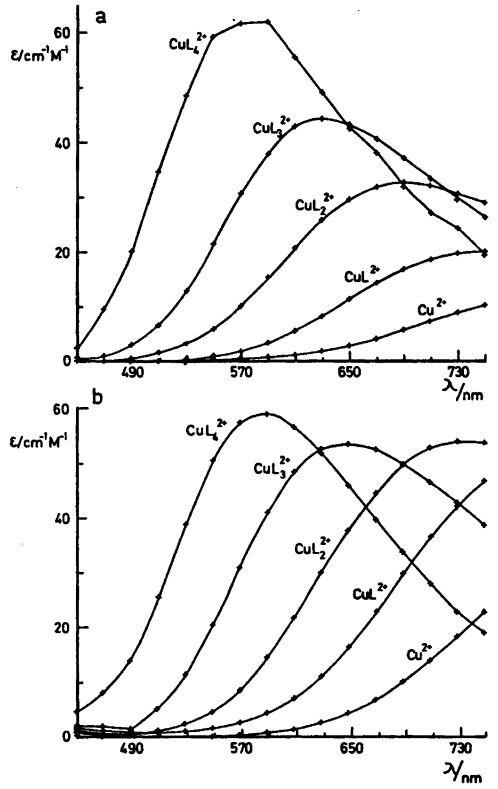


Fig. 2. Molar absorption coefficients, ε cm^{-1} M^{-1}, as a function of the wavelength, λ nm, plotted for the mononuclear complexes CuL_n^{2+} with $n = 0$, 1, 2, 3 and 4. (a) 3.0 M $(Na)ClO_4$ and (b) 3.0 M (Na)Cl medium.

These pronounced spectral changes indicate that ternary complexes, in which up to three imidazole molecules are coordinated, are formed.

(iii) *Copper(II) chlorides in mixtures of 3.0 M $(Na)ClO_4$ and 3.0 M (Na)Cl media.* In an attempt to determine formation constants of different $Cu^{2+} - Cl^-$ equilibria, titrations were performed at a constant acidity level ($[H^+] = 0.01$ M), where eventual hydrolysis reactions could be neglected. 5 different titrations were performed yielding 66 titrations points and 1056 absorbance values. The concentration ranges investigated were $0.010 \leq B \leq 0.040$ M and $0 \leq X \leq 3.0$ M. The calculations showed that within the concentration ranges investigated formation of the complexes $CuCl^+$ and $CuCl_2$ could be established. $K(Cu^{2+} + Cl^- \rightleftharpoons CuCl^+) = 0.99 \pm 0.15$ M^{-1} and $K(CuCl^+ + Cl^- \rightleftharpoons CuCl_2) = 0.40 \pm 0.06$ M^{-1} are values in good agreement with those reported by Bjerrum,[10] Lister *et al.*[11] and McConell *et al.*[12] The standard deviation $\sigma(OD)$ at the different wavelengths ranged from 0.001 to 0.003, thus a good fit to experimental data at each wavelength studied was obtained.

(iv) *Copper(II) imidazoles in mixtures of 3.0 M $(Na)ClO_4$ and 3.0 M (Na)Cl.* For determining the formation of ternary $Cu^{2+} - C_3H_4N_2 - Cl^-$ complexes measurements were performed in the four-component system $H^+ - Cu^{2+} - C_3H_5N_2^+ - Cl^-$. In the measurements the concentration ranges $0.003 \leq B \leq 0.02$ M, $0.04 \leq C \leq 0.3$ M, $0 \leq X \leq 3.0$ M and $3.9 \leq -\log h \leq 6.5$ were investigated. The measurements were performed at different constant levels of Z ($Z = 0.5$, 1.3, 1.5, 2.5 and 4.2) and X was varied by the addition of a solution where $X = 3.0$ M to a solution where $[ClO_4^-] = 3.0$ M or *vice versa*. In this way it was possible to cover the range $0 \leq X \leq 3.0$ M. H, B and C were either kept constant or varied in the measurement. The experiments thus give data $(OD, \log h, H, B, C, X)_{N\lambda}$. In the LETAGROP calculations the two data sets ($\log h$, H, B, C, X) and $(OD, \log[L], B, X)_{N\lambda}$ were treated separately in order to assess their consistency. In these calculations equilibria (3) – (7) were assumed to be known and no attempts were made to adjust their equilibrium constants.

($\log h$, H, B, C, X) data. 13 different titrations including 197 experimental points were treated in the LETAGROP calculations. The ternary complexes $CuLCl^+$, $CuLCl_2$, CuL_2Cl^+, CuL_2Cl_2 and CuL_3Cl^+ were included in the equilibrium model. A final covariation of formation constants for all these species, showed that a very good fit to experimental data was obtained giving $\sigma(Z_C) \times 1000 = 1.8$ (*cf.* Table 3). In one calculation formation constants for $CuCl^+$ and $CuCl_2$ were covaried with β_{111} and β_{112} on data with $Z \leq 1.3$. This calculation gave $\beta_{011} = 1.20 \pm 0.03$ M^{-1} and $\beta_{012} = 0.25 \pm 0.005$ M^{-2}, values which can be compared with 0.99 ± 0.15 M^{-1} and 0.40 ± 0.06 M^{-2}, respectively, obtained from the spectrophotometric investigation.

$(OD, log[L], B, X)_{N\lambda}$ data. To confirm formation of the different ternary species, the combined emf and spectrophotometric data were treated. 9 different titrations including 164 titration points and 1312 absorbance values

Table 3. Results of LETAGROP calculations concerning formation of ternary $Cu^{2+}-L(C_3H_4N_2)-Cl^-$ complexes. The equilibria are defined according to: $Cu^{2+}+nHL^+ + sCl^- = CuL_nCl_s^{(2-s)+} + nH^+$; β_{n1s}. The errors $3\sigma(\log \beta_{n1s})$ are given when the corresponding equilibrium constant has been varied.

$\sigma(Z)\times 10^3$	$CuCl^+$ $\log(\beta_{011}\pm 3\sigma)$	$CuCl_2$ $\log(\beta_{012}\pm 3\sigma)$	$CuLCl^+$ $\log(\beta_{111}\pm 3\sigma)$	$CuLCl_2$ $\log(\beta_{112}\pm 3\sigma)$	CuL_2Cl^+ $\log(\beta_{211}\pm 3\sigma)$	CuL_2Cl_2 $\log(\beta_{212}\pm 3\sigma)$	CuL_3Cl^+ $\log(\beta_{311}\pm 3\sigma)$	Remark
1.8	0.00 [a]	−0.40 [a]	−3.19(3)	−3.88(11)	−7.50(5)	−7.54(3)	−11.56(2)	$0\leq Z\leq 4.3$
0.3	0.08(1)	−0.60(3)	−3.16(1)	−3.88(1)	−7.50	−7.54	−11.56	$0\leq Z\leq 1.3$
0.002 [c]	0.000	−0.40	−3.15(1)	−3.92(7)	−7.50	−7.54	−11.56	[b]

[a] Values from a separate spectrophotometric investigation. [b] A calculation based upon (OD, log $[C_3H_4N_2]$, B, $X)_{NA}$ data. [c] $\sigma(OD)$.

were treated in the calculations. As the addition of chloride ions to a copper(II) imidazole solution was found to displace the absorption spectra to higher wavelengths, 8 different wavelengths ranging from 610 to 750 nm were investigated. The concentrations ranges were mainly the same as given under (iv) except that solutions with $Z=1.3$ and 4.2 were not investigated.

By assuming the different $Cu^{2+}-Cl^-$ and $Cu^{2+}-L$ equilibria with formation constants and molar absorption coefficients as obtained under (iii) and (i) to be known the following calculations were performed: the different ternary $Cu^{2+}-L-Cl^-$ complexes, with their formation constants as obtained from calculations on the emf data, were included in the equilibrium model. This calculation showed that a satisfactory fit to experimental data was obtained. $\sigma(OD)$ at each wavelength varied between 0.001 and 0.003 and any discrepancies within the wavelength range investigated could not be found, which is in support of the equilibrium model proposed.

The molar absorption coefficients of the ternary complexes are given in Table 4.

DISCUSSION

The combined emf and spectrophotometric titration technique, in which both log h and absorbance values were measured, was found to yield accurate and extensive experimental data in a convenient way. In this study 30 different titrations, including 527 titration points and approximately 6500 absorbance values, were treated. As approximately 250 different parameters (molar absorption coefficients for each absorbing species at each wavelength plus a number of formation constants) were determined, it seems necessary to collect this vast data amount. Unless automated titration procedures are available this collecting of data is unrealistic.*

With regard to the results of the different investigations, there is very good agreement between formation constants of the different CuL_n^{2+} complexes with $n=1$, 2, 3 and 4, as

* A complete list of the experimental data, including the spectrophotometric data, is available from this Department.

Table 4. Molar absorption coefficients for different $Cu^{2+} - C_3H_4N_2 - Cl^-$ complexes obtained in a LETAGROP calculation ($L = C_3H_4N_2$).

λ/nm	$\varepsilon \pm \sigma(\varepsilon)$/cm^{-1} M^{-1} $CuCl^+$	$CuCl_2$	$CuLCl^+$	$CuLCl_2$	CuL_2Cl^+	CuL_2Cl_2	CuL_3Cl^+	$\sigma(OD) \times 10^3$
610	1.4(0)	1.4(0)	6.6(3)	3.8(9)	11.4(19)	23.1(7)	45.7(6)	3
630	2.7(0)	2.4(0)	10.6(4)	11.3(2)	17.7(25)	30.0(10)	49.5(8)	3
650	4.4(1)	4.4(1)	14.7(3)	20.0(7)	24.5(16)	37.7(6)	50.1(5)	2
670	6.9(0)	7.2(0)	18.8(2)	34.1(7)	30.7(15)	44.4(6)	48.0(5)	2
690	9.9(0)	11.3(1)	22.7(2)	49.8(7)	32.4(14)	50.7(6)	44.9(5)	2
710	13.4(1)	16.5(1)	25.5(2)	66.8(7)	31.8(15)	55.5(6)	41.7(5)	2
730	16.8(1)	22.6(1)	27.6(3)	83.3(8)	30.7(16)	57.6(6)	37.6(5)	2
750	19.9(1)	29.2(1)	28.4(3)	95.8(9)	30.5(20)	58.2(8)	34.1(7)	3

evaluated in this study compared with those reported from the emf investigations [1,2] (*cf.* Table 1). The standard deviations of the constants valid in 3.0 M $(Na)ClO_4$ and 3.0 M (Na)Cl media are less than 0.03 logarithmic units, values which are of the same magnitude as those obtained in the emf investigations. Thus it may be concluded that the combined emf and spectrophotometric measurements strongly support the complexes and complex constants earlier proposed.

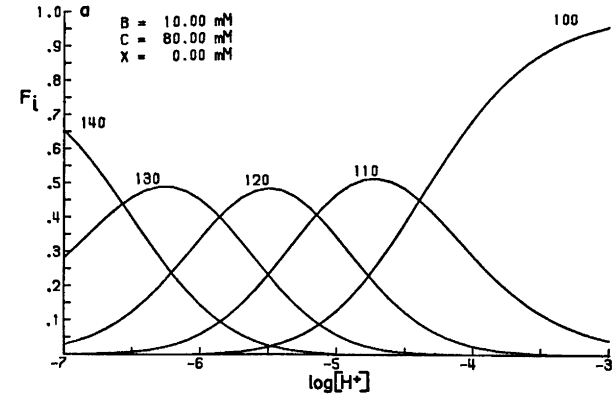
The formation of ternary $Cu^{2+} - L - OH^-$ complexes were also investigated by this spectrophotometric method. The agreement in log β_{-624} as obtained in this study (-27.08 ± 0.07) compared with the value earlier proposed [2] (-27.18 ± 0.02) is satisfactory and confirms the existance of the $Cu_2(OH)_2L_4^{2+}$ complex.

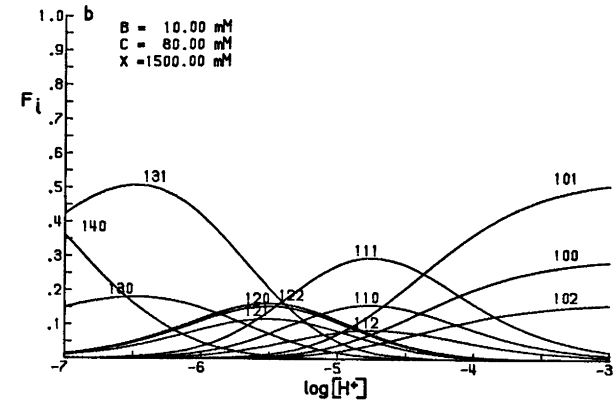
The formation of binary $Cu^{2+} - Cl^-$ and ternary $Cu^{2+} - L - Cl^-$ complexes was also studied. Within the concentration range $0 \leq X \leq 3.0$ M, the binary $CuCl^+$ and $CuCl_2$ as well as the ternary $CuLCl^+$, $CuLCl_2$, CuL_2Cl^+, CuL_2Cl_2 and CuL_3Cl^+ complexes were evaluated with formation constants given in Table 3. According to this Table $3\sigma(\log \beta_{n1s}) \leq 0.05$ and the equilibria must be considered as well-determined. Distributions of the different complexes are visualized in Figs. 3a – 3c. As can be seen from these diagrams the ternary $Cu^{2+} - L - Cl^-$ complexes are formed to about 15 – 60 % of B, with the two- and four-coordinated species dominating.

The results obtained can be interpreted as series of stepwise reactions in which chloride ions are successively coordinated to a CuL_n^{2+}.

Table 5. Some stepwise reactions with constants (K or log K) calculated by means of formation constants given in Ref. 2 and Table 4. The different reactions define the stepwise uptake of ligands (a) $C_3H_4N_2$(L) and (b) Cl^-, and are to be read horizontally. ($CuLCl^+$ 3.62 CuL_2Cl^+ stands for $CuLCl^+ + L \rightleftharpoons CuL_2Cl^+$ with log $K = 3.62$).

(a)	log K		log K		log K	
Cu^{2+}	4.65	CuL^{2+}	3.95	CuL_2^{2+}	3.32	CuL_3^{2+}
$CuCl^+$	4.75	$CuLCl^+$	3.62	CuL_2Cl^+	3.89	CuL_3Cl^+
$CuCl_2$	4.46	$CuLCl_2$	3.98	CuL_2Cl_2		
(b)	K		K			
Cu^{2+}	0.99	$CuCl^+$	0.40	$CuCl_2$		
CuL^{2+}	1.04	$CuLCl^+$	0.40	$CuLCl_2$		
CuL_2^{2+}	0.51	CuL_2Cl^+	0.94	CuL_2Cl_2		
CuL_3^{2+}	1.90	CuL_3Cl^+				





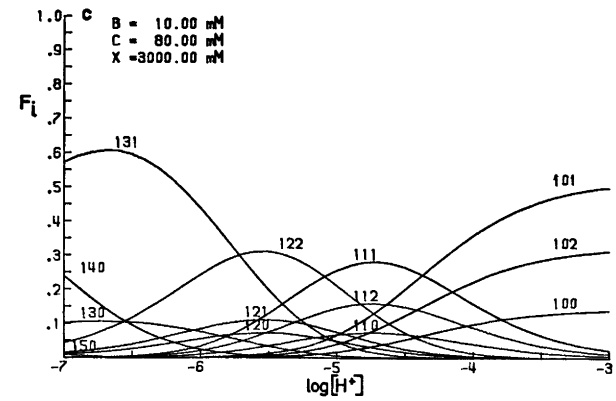


Fig. 3. Distribution diagrams $F_i(\log h)_{B,C,X}$ for the different copper(II) imidazole complexes. The computer program SOLGASWATER [17] was used in the calculations. The figures denote the number of Cu^{2+}, $C_3H_4N_2$ and Cl^- in the complexes.

core with $n = 0$, 1, 2 and 3 or alternatively as imidazole molecules coordinated to a $CuCl_n^{(2-n)+}$ core with $n = 0$, 1, 2. Stepwise constants of these reactions are given in Table 5.

According to this table the successive uptake of an imidazole molecule proceeds easily irrespective of whether the core is Cu^{2+}, $CuCl^+$ or $CuCl_2$. A similar trend was found in the $Hg^{2+} - C_3H_4N_2 - Cl^-$ system,[5] *i.e.* $K(Hg^{2+} + C_3H_4N_2 \rightleftharpoons HgC_3H_4N_2^{2+}) \approx K(HgCl^+ + C_3H_4N_2 \rightleftharpoons HgClC_3H_4N_2)$ and $K(HgCl_2 + C_3H_4N_2 \rightleftharpoons HgCl_2 \cdot C_3H_4N_2) \approx K(HgCl_3^- + C_3H_4N_2 \rightleftharpoons HgCl_3C_3H_4N_2^-)$. In the Ni^{2+}-system [13] this relation was also found concerning formation of $NiC_3H_4N_2^{2+}$ and $NiClC_3H_4N_2^+$.

From Table 5 it can also be seen that chloride ions approximately coordinate the Cu^{2+}-ion as easily as the different $Cu^{2+} - L$ complexes.

These findings indicate that approximate stepwise constants defining formation of these ternary species should be given by the corresponding binary $Cu^{2+} - L$ or $Cu^{2+} - Cl^-$ constants. These findings are also valid in the Hg^{2+}- and Ni^{2+}-systems.

The spectrophotometric investigations not only confirmed results obtained in the different emf investigations, but also provided characteristic optical spectra for each of the different copper(II) species. As the wavelength range was restricted to $\lambda \leq 750$ nm complete optical spectra of all species, especially the ternary $Cu^{2+} - L - Cl^-$ species were not obtained. However, complementary measurements with $\lambda > 750$ nm are planned.

The wavelength (λ_{max}) where absorption maxima (ε_{max}) for some copper(II) complexes were found are given in Table 6. As can be seen from this table the strength of the ligand field increases (λ_{max} decreases) with the number of imidazole molecules coordinated in the different CuL_n^{2+} complexes ($n = 0$, 1, 2, 3 and 4).

Furthermore ε_{max} also increases with n. These findings are consistent with results obtained from other systems in which nitrogen containing ligands are successively coordinated to the copper(II) ion.[12,15]

With regard to the spectra of the different $Cu^{2+} - L - OH^-$ complexes $\lambda_{max} = 610$ nm and $\varepsilon_{max} = 108$ cm^{-1} M^{-1} were found for the $Cu_2(OH)_2L_4^{2+}$ complex. These values are consistent with those reported by Harris *et al.*[16] for $Cu_2(OH)_2L_2^{2+}$ complexes with L = 2,2′-bipyridyl and 1,10-phenanthroline. They found $\lambda_{max} = 620$ nm and $\varepsilon_{max} = 97$ cm^{-1} M^{-1} with 2,2′-bipyridyl and $\lambda_{max} = 630$ nm and $\varepsilon_{max} = 105$ cm^{-1} M^{-1} with 1,10 phenanthroline as ligands.

Some common features may also be derived concerning the spectra of the different $Cu^{2+} - L - Cl^-$ complexes. The uptake of chloride ions to a CuL_n^{2+} complex with $n = 0$, 1, 2, and 3 yields an increase in λ_{max} as well as in ε_{max}. Before a detailed discussion of the spectra of these complexes can be made it is necessary to extend the measurement to include data with $\lambda > 750$ nm. However, it may finally be concluded that the strength of the ligand field increases within the series $C_3H_4N_2 > H_2O > Cl^-$, which is in accordance with the spectrochemical series.

Table 6. The wavelength, λ_{max}, with corresponding molar absorption maximum, ε_{max} for different copper(II) complexes. The uncertainty in λ_{max} and ε_{max} is estimated to 10 nm and 1 cm^{-1} M^{-1}, respectively. $L = C_3H_4N_2$.

Complex	λ_{max}	ε_{max}/cm^{-1} M^{-1}
Cu^{2+}	800 [a]	11
CuL^{2+}	750 [a]	21
CuL_2^{2+}	690	33
CuL_3^{2+}	630	45
CuL_4^{2+}	580	62
$Cu(OH)L^+$	–	–
$Cu_2(OH)_2L_2^{2+}$	650	68
$Cu_2(OH)_2L_4^{2+}$	610	108
$CuLCl^+$	$\gtrsim 750$	29
$CuLCl_2$	–	–
CuL_2Cl^+	700	33
CuL_2Cl_2	$\gtrsim 750$	58
CuL_2Cl^+	650	50

[a] Value taken from Ref. 1.

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