

## Metal Complexes with Mixed Ligands

### 1. A Potentiometric, Spectrophotometric and Solubility Study of Copper(II) Imidazoles and Copper(II) Hydroxo-imidazoles in 3.0 M (Na)ClO<sub>4</sub>

STAFFAN SJÖBERG

*Department of Inorganic Chemistry, University of Umeå,  
S-901 87 Umeå, Sweden*

Equilibria between copper(II), imidazole, (C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>), and OH<sup>-</sup> have been studied in 3.0 M (Na)ClO<sub>4</sub> medium at 25°C by means of potentiometric (glass electrode) and spectrophotometric measurements. Both emf and spectrophotometric measurements (treated separately) gave clear evidence for the five mononuclear species Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sup>2+</sup>, Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>2+</sup>, Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>3</sub><sup>2+</sup>, Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>4</sub><sup>2+</sup> and Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>5</sub><sup>2+</sup>. Data also indicated small amounts of one or more mixed polynuclear complexes, and tentatively we have proposed one complex with the formula Cu<sub>2</sub>(OH)<sub>2</sub>(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>3</sub><sup>2+</sup>. The equilibrium constants determined are collected in Table 4. Molar absorbancies have been calculated for the different species at nine different wavelengths from 500 to 900 nm (Table 5).

Three different solid phases Cu<sub>5</sub>(OH)<sub>8</sub>(ClO<sub>4</sub>)<sub>2</sub>, Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>, and Cu<sub>3</sub>(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>8</sub>(ClO<sub>4</sub>)<sub>4</sub> have been identified, and their X-ray and solubility characteristics are given in Table 6.

The literature concerning aqueous copper imidazoles seems to indicate the existence of only mononuclear complexes, and the species Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sup>2+</sup>, Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>2+</sup>, Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>3</sub><sup>2+</sup>, and Cu(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>4</sub><sup>2+</sup> are frequently reported and discussed. The main conclusions from these previous studies are given in Table 1. In connection with preparation of copper imidazole crystals for X-ray diffraction studies<sup>1</sup> it was found that a series of crystals with different compositions could be obtained by means of only small changes of the composition of the solutions used. In order to relate, if possible, the aqueous species and the complexes in the crystals, it was found necessary to study carefully the equilibria in solution. This was the main purpose of the present investigation which forms part of a broader project, dealing with the ability of copper(II) to form mixed complexes with ligands H<sub>2</sub>O, C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub>, OH<sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>.

Table I. Earlier studies on copper(II) imidazoles.

| Ref. No.     | Temp. °C | Medium                                   | Method  | $pK_a$ | $\log k_1$ | $\log k_2$                   | $\log k_3$     | $\log k_4$                   |
|--------------|----------|--|---------|--------|------------|------------------------------|----------------|------------------------------|
| 10           | 25       | $I=0.16$                                 | Pot(gl) |        | 4.33       | 3.54                         | 2.82           | 2.03                         |
| 11           | 25       | $I=0.16$                                 | Pot(gl) | 7.08   | 4.20       | 3.42                         | 2.88           | 2.05                         |
| 12           | 4.5      | 0.16 NaNO <sub>3</sub>                   | Pot(gl) | 7.50   | 4.60       | 3.81                         | 3.09           | 2.30                         |
|              | 22.5     | »  | »       | 7.11   | 4.36       | 3.57                         | 2.85           | 2.00                         |
| 13           | 0        | 0.135 KCl                                | Pot(gl) | 7.63   | 4.72       | 3.90                         | 3.28           | 2.3                          |
|              | 25       | »  | »       | 7.09   | 4.20       | 3.47                         | 2.84           | 2.0                          |
| 14           | 20       | 0.15 NaClO <sub>4</sub>                  | Pot(gl) | 7.20   | 4.26       | 3.61                         | 2.86           | 2.25                         |
| 15           | 25       | $I=0.10$                                 | Pot(gl) | 7.01   | 4.33       | 3.28                         | 2.7            | 1.9                          |
| 16           | 25       | $I=0.16$                                 | Pot(gl) |        | 4.31       | 3.53                         | 2.92           | 2.14                         |
| 17           | 25       | 0.15 KNO <sub>3</sub>                    | Pol     |        |            |                              | $\beta_4=12.6$ |                              |
| Present work | 25       | 3 M (Na)ClO <sub>4</sub><br>in addition: | Pot(gl) | 7.91   | 4.66       | 3.98                         | 3.30           | 2.66                         |
|              |          |  |         |        |            | $\log \beta_{-523} = -21.22$ |                |                              |
|              |          |  |         |        |            |                              |                | $\log \beta_{-616} = -30.00$ |

## EXPERIMENTAL

*Chemicals and analysis.* Stock solutions of sodium perchlorate were prepared by neutralizing strong perchloric acid (Merck *p.a.*) with solid Na<sub>2</sub>CO<sub>3</sub> (Merck *p.a.*). After the acid had been neutralized, a slight excess of sodium carbonate was added. This slightly alkaline solution (pH ≈ 8) was then allowed to stand for about a week. If Fe-, Al-, and Si-impurities were present, they usually precipitated during this time as silicates or hydroxides. These precipitated impurities were filtered off, using a Jena G4 glass-filter. The filtered solution was acidified with a slight excess of perchloric acid and then boiled to expel the carbonate as CO<sub>2</sub>. After boiling, the solution was neutralized to pH ≈ 6. Neither Cl<sup>-</sup> nor CO<sub>3</sub><sup>2-</sup> or Fe<sup>3+</sup> could be detected in the solution prepared in this way. The sodium perchlorate stock was analysed for NaClO<sub>4</sub> by evaporating a known weight of solution at 120°C and drying to a constant weight.

The dilute perchloric acids were standardized against KHCO<sub>3</sub> or tris(hydroxymethyl)-aminomethane (TRISMA-base).

Dilute sodium hydroxide was prepared from "oljelut" (50 % NaOH and 50 % H<sub>2</sub>O) and standardized against acid or hydrazine sulfate.

Imidazole, C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>, (Merck *p.a.*), with melting point 88–90°C (lit. 90°C),<sup>18</sup> was used without further purification after drying for several days over phosphorus pentoxide.

Stock solutions of C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup> were prepared by dissolving C<sub>3</sub>N<sub>2</sub>H<sub>4</sub> in HClO<sub>4</sub>. The "C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup>"-content was determined potentiometrically using the Gran extrapolation method.<sup>3</sup> The titrated amount was always about 0.3 % higher than that expected from the amount weighed. The value from titration has been assumed to be correct.

Sodium chloride (Merck *p.a.*) was dried at 200°C and used without further purification.

Stock solutions of Cu(ClO<sub>4</sub>)<sub>2</sub> were prepared by dissolving CuCl<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> (Merck *p.a.*) in excess HClO<sub>4</sub>. The HCl was expelled by heating on a water bath until no Cl<sup>-</sup> could be detected. These stock solutions were filtered through a Jena G4 glass-filter in order to remove dust particles and then carefully tested for impurities, especially SO<sub>4</sub><sup>2-</sup> and Fe<sup>3+</sup>. Test for these ions were negative. The Cu<sup>2+</sup>-content (≈ 1 M) of the stock-solutions was exactly determined by electro deposition according to Kolthoff-Sandell.<sup>2</sup> The H<sup>+</sup>-concentration was determined potentiometrically using a Gran plot. The ClO<sub>4</sub><sup>-</sup>-content was estimated from the sum [H<sup>+</sup>] + 2[Cu<sup>2+</sup>].

All solutions were prepared using boiled distilled water.

*Apparatus.* All emf-measurements were made at 25.00 ± 0.05°C. The cell arrangement, which was immersed in an oil thermostat, was similar to that described by Forsling *et al.*<sup>19</sup> The emf was measured with a compensator (Methrom E 388).

The Ag,AgCl electrodes were prepared according to Brown.<sup>20</sup> Glass electrodes, Beckman type 40498, were employed, giving constant and reproducible potentials within ± 0.2 mV.

A stream of nitrogen was always passed through the solutions during the measurements. Nitrogen from a cylinder was purified from acid and alkaline impurities by means of 10 % NaOH and 10 % H<sub>2</sub>SO<sub>4</sub>. Finally, before the gas came into contact with the equilibrium solution, it passed through a pure ionic medium.

*Spectrophotometric measurements* were carried out at 25.0 ± 0.5°C using a Hitachi-Perkin-Elmer 139 Spectrophotometer, equipped with a multilog unit, type Optron multilog 801, for digital recording of the measured absorbance. For the measurements, we have used cells (type 100-OS HELLEMA) of 1.001 cm length, matched against each other. The wave length accuracy was within 0.5 nm, and the 656.3 nm spectral line of the hydrogen lamp was used as a wave-length check.

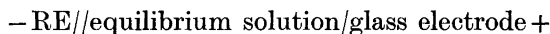
#### METHOD

The present study has been carried out through a series of titrations at 25°C. In order to avoid activity coefficient variations, a constant and "inert" ionic medium of 3.0 M (Na)ClO<sub>4</sub> has been used. In most of the titrations, the total concentrations of copper, *B*, and C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup>, *C*, have been kept constant, and [H<sup>+</sup>] = *h* has been varied by addition of OH<sup>-</sup> or H<sup>+</sup>. The total concentrations of *B* and *C* have been varied within the limits 0.0008 M < *B* < 0.020 M, and 0.010 M < *C* < 0.516 M. The "pH" ranges have been limited to pH < 6.5 for *B* > 0.005 M, and pH < 8.0 for *B* ≤ 0.005 M. This upper limit is determined by the fact that precipitation of crystalline metalimidazoles and copper hydroxide is obtained.

The lower pH-limits in the present study were mainly determined by the onset of the complex formation. However, in most of our titrations, the starting solutions were of even higher acidity. This was necessary to provide a range for calibration.

In one series of measurements, the H<sup>+</sup>-concentrations were measured using an emf method; in another series, the light absorbance of the solutions was measured spectrophotometrically.

*Emf determinations.* The free H<sup>+</sup>-concentration was determined by measuring the emf of the cell



where RE = Ag, AgCl/0.01 M Cl<sup>-</sup>, 2.99 M ClO<sub>4</sub><sup>-</sup>, 3.00 M Na<sup>+</sup>//3.00 M NaClO<sub>4</sub>.

In titrating from acid to alkaline solutions, the total concentrations *B* and *C* were usually kept constant by simultaneously adding equal volumes of solutions T<sub>1</sub> and T<sub>2</sub>. These solutions were of the following general compositions: T<sub>1</sub> = 2 *B* M [Cu<sup>2+</sup>]<sub>tot</sub>, 2 *C* M [C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup>]<sub>tot</sub>, *H* M [H<sup>+</sup>]<sub>tot</sub> over the zero level H<sub>2</sub>O, C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup>, Cu<sup>2+</sup>, (3.0 - 4*B* - 2*C* - *H*) M [Na<sup>+</sup>]<sub>tot</sub> and 3.0 M ClO<sub>4</sub><sup>-</sup>. T<sub>2</sub> = *H* M (negative in this case with OH<sup>-</sup>-excess), (3.0 - *H*) M [Na<sup>+</sup>]<sub>tot</sub> and 3.0 M ClO<sub>4</sub><sup>-</sup>. For reversed titrations only "one-burette-technique" was used. Assuming the activity coefficients to be constant, the following expression is valid for the measured emf *E*:

$$E = E_0 + 59.157 \log h + E_j$$

where *E*<sub>0</sub> is a constant determined in acid (H<sup>+</sup>, Cu<sup>2+</sup>, C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup>)-solutions of known composition. For the liquid junction potential we have used *E*<sub>j</sub> = -16.3 *h* + 8.0 *kw* *h*<sup>-1</sup> mV,<sup>4</sup> where *kw* = 6.03 × 10<sup>-15</sup> M<sup>2</sup><sup>5</sup> is the ionic product of water

in 3.0 M NaClO<sub>4</sub>. From the analytical composition of the solutions and from the measured emf, the concentration of reacted or bound OH<sup>-</sup>, *A*, over the 0-level, can be calculated from the relation

$$A = h - H \quad (1)$$

Thus the emf measurements give the data  $H(\log h)_{BC}$ .

*Spectrophotometric measurements.* The spectrophotometric titrations were also carried out, mainly with constant total *B* and *C*, whilst that of the hydrogen ion was varied by addition of OH<sup>-</sup> or H<sup>+</sup>. For each point in a titration, the absorbancy, *E*, has been measured at 50 nm intervals within the wavelength range 500–900 nm, *i.e.* at 9 different wavelengths. As reference solution we have used an acid solution containing pure ionic medium. The data obtained from the spectrophotometric measurements may thus be written

$$H(E)_{B, C, \lambda_1, \lambda_2, \dots, \lambda_9}$$

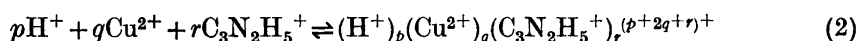
The *B* range has been restricted to 0.002 M < *B* < 0.005 M, but the *C* and pH ranges were as quoted above.

*Solubility measurements.* Preliminary solubility measurements were carried out in an attempt to determine the solubility products of the precipitates. Solutions with known *B*, *C*, and *H* were prepared (all solutions were 3.00 M in [ClO<sub>4</sub><sup>-</sup>]). These solutions were firstly treated with OH<sup>-</sup> until precipitation occurred, and then stored in a thermostated room at 25°C. The containers were shaken occasionally to promote equilibration. After 3–4 weeks, the solid phase was filtered off using a Jena G4 glass-filter maintained at the temperature of equilibration. Three different solid phases were found, of which two were identified from X-ray powder photographs. *H* and log *h* were determined for the filtrates from potentiometric titrations using HClO<sub>4</sub>. The copper content was also determined in some instances through electro deposition.

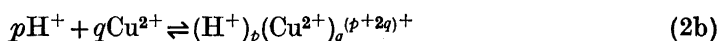
### CALCULATIONS AND RESULTS

Emf and spectrophotometric data will be treated separately, in order to assess their consistency. The emf data are given in Table 2, and the spectrophotometric data in Table 3. For the calculations, the least-squares program LETAGROPVRID<sup>6</sup> has been used; for the emf data, the version ETTR,<sup>7</sup> and for the spectrophotometric data, the version SPEFO.<sup>8</sup>

Considering a number of general 3-component equilibria



besides the 2-component equilibria



the law of mass action and the conditions for the concentrations give:

$$B = b + \sum \sum q \beta_{pq} h^p b^q + \sum \sum \sum q \beta_{pqr} h^p b^q c^r \quad (3)$$

Table 2. Experimental emf data.  $H_{\text{calc}}$  values calculated, using the proposed constants (Table 4).

$B = 0.00512 \text{ M}$ ,  $C = 0.01001 \text{ M}$ ;  $H \times 10^3 \text{ M}$ ,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3 \text{ M}$ ; 2.85, 2.526, 0.12; 2.34, 2.630, -0.01; 1.86, 2.733, -0.02; 1.39, 2.860, -0.03; 0.92, 3.029, -0.01; 0.48, 3.288, -0.02; 0.28, 3.482, -0.04; 0.07, 3.712, -0.02; -0.12, 3.984, -0.04; -0.32, 4.186, -0.03; -0.52, 4.351, -0.02; -0.71, 4.473, 0.01; -1.09, 4.676, 0.03; -1.45, 4.831, 0.04; -1.81, 4.953, 0.07; -2.47, 5.158, 0.10; -3.11, 5.330, 0.12; -3.71, 5.479, 0.14; -4.26, 5.614, 0.13; -5.03, 5.798, 0.11; -5.98, 6.015, 0.08; -6.83, 6.218, -0.08; -7.62, 6.397, -0.29;

$B = 0.00512 \text{ M}$ ,  $C = 0.02003 \text{ M}$ ;  $H \times 10^3 \text{ M}$ ,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3 \text{ M}$ ; 5.25, 2.282, -0.04; 4.53, 2.343, -0.01; 3.84, 2.415, -0.01; 3.17, 2.499, -0.02; 2.53, 2.598, -0.03; 1.91, 2.723, -0.05; 1.32, 2.882, -0.05; 0.73, 3.082, 0.03; 0.18, 3.509, -0.05; -0.36, 3.984, -0.05; -0.88, 4.285, -0.03; -1.37, 4.515, -0.08; -1.88, 4.662, -0.01; -2.33, 4.776, 0.04; -2.79, 4.887, 0.06; -3.23, 4.975, 0.12; -3.66, 5.076, 0.08; -4.49, 5.235, 0.11; -5.27, 5.379, 0.11; -6.00, 5.506, 0.13; -6.68, 5.628, 0.10; -7.33, 5.732, 0.12; -8.55, 5.935, 0.08; -9.11, 6.033, 0.03; -9.90, 6.175, -0.07; -10.63, 6.311, -0.18; -11.10, 6.385, -0.16; -11.54, 6.463, -0.18; -11.96, 6.527, -0.14; -12.37, 6.605, -0.18; -12.76, 6.677, -0.19; -13.14, 6.730, -0.11; -13.84, 6.870, -0.15; -14.50, 6.997, -0.15; -15.10, 7.122, -0.17; -15.67, 7.237, -0.16; -16.21, 7.348, -0.16; -16.70, 7.467, -0.20;

$B = 0.00500 \text{ M}$ ,  $C = 0.04000 \text{ M}$ ;  $H \times 10^3 \text{ M}$ ,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3 \text{ M}$ ; 4.22, 2.372, -0.00; 3.96, 2.399, -0.00; 3.47, 2.457, -0.01; 2.39, 2.618, -0.02; 1.65, 2.779, -0.05; 0.42, 3.262, -0.07; -0.33, 3.744, -0.06; -0.56, 3.873, -0.06; -0.78, 3.976, -0.05; -1.18, 4.138, -0.04; -1.70, 4.309, -0.02; -2.16, 4.436, -0.01; -2.44, 4.503, -0.01; -2.93, 4.615, 0.00; -3.55, 4.740, 0.01; -3.98, 4.821, 0.02; -4.35, 4.889, 0.01; -4.67, 4.943, 0.02; -4.94, 4.990, 0.02; -5.19, 5.031, 0.03; -5.41, 5.068, 0.02; -5.60, 5.092, 0.07; -5.78, 5.126, 0.03;

$B = 0.00500 \text{ M}$ ,  $C = 0.04000 \text{ M}$ ;  $H \times 10^3 \text{ M}$ ,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3 \text{ M}$ ; 10.51, 1.977, 0.02; 8.22, 2.081, 0.07; 7.12, 2.157, -0.18; 6.08, 2.212, 0.05; 5.07, 2.286, 0.08; 4.10, 2.385, -0.00; 2.25, 2.639, 0.00; 0.53, 3.212, -0.10; -1.07, 4.124, -0.11; -1.84, 4.377, -0.12; -2.59, 4.573, -0.16; -3.31, 4.722, -0.14; -4.01, 4.854, -0.13; -4.70, 4.971, -0.11; -5.35, 5.082, -0.12; -6.63, 5.276, -0.08; -7.82, 5.451, -0.05; -8.93, 5.613, -0.06; -9.99, 5.763, -0.05; -11.01, 5.902, -0.01; -11.97, 6.037, -0.03; -12.89, 6.159, -0.00; -13.79, 6.286, -0.03; -15.36, 6.497, -0.05; -16.84, 6.696, -0.13; -18.20, 6.866, -0.15; -19.45, 7.018, -0.22; -20.60, 7.119, -0.19; -22.17, 7.298, -0.20; -23.58, 7.434, -0.27; -25.25, 7.574, -0.26; -26.36, 7.667, -0.30; -28.31, 7.816, -0.27; -29.43, 7.903, -0.29;

$B = 0.00501 \text{ M}$ ,  $C = 0.08013 \text{ M}$ ;  $H \times 10^3 \text{ M}$ ,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3 \text{ M}$ ; 6.64, 2.168, 0.12; 5.36, 2.278, -0.13; 4.13, 2.380, -0.02; 2.96, 2.521, -0.02; 1.80, 2.710, 0.03; 0.70, 3.042, -0.04; -1.35, 3.936, -0.12; -2.33, 4.180, -0.05; -3.28, 4.389, -0.10; -4.20, 4.555, -0.09; -5.09, 4.705, -0.11; -5.53, 4.773, -0.11; -5.95, 4.841, -0.12; -6.37, 4.900, -0.11; -6.79, 4.961, -0.11; -7.20, 5.016, -0.09; -7.60, 5.074, -0.10; -8.37, 5.179, -0.08; -9.13, 5.284, -0.08; -9.87, 5.383, -0.08; -10.59, 5.476, -0.07; -11.29, 5.564, -0.04; -11.96, 5.652, -0.05; -12.61, 5.735, -0.05; -13.25, 5.814, -0.04; -14.45, 5.967, -0.08; -15.62, 6.112, -0.13; -16.73, 6.244, -0.15; -18.76, 6.470, -0.21; -19.72, 6.572, -0.27; -20.61, 6.656, -0.28;

$B = 0.01000 \text{ M}$ ,  $C = 0.01000 \text{ M}$ ;  $H \times 10^3 \text{ M}$ ,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3 \text{ M}$ ; 9.78, 2.014, -0.10; 9.07, 2.041, 0.02; 8.39, 2.035, 0.01; 7.67, 2.114, 0.01; 7.10, 2.145, 0.06; 6.49, 2.186, 0.02; 5.90, 2.226, 0.03; 4.78, 2.321, 0.02; 4.25, 2.369, 0.01; 3.74, 2.421, 0.03; 3.25, 2.487, -0.01; 2.77, 2.562, -0.05; 1.85, 2.731, -0.03; 0.99, 3.002, -0.05; 0.18, 3.519, -0.06; -0.21, 3.864, -0.05; -0.59, 4.157, -0.06; -0.96, 4.346, -0.05; -1.31, 4.497, -0.06; -1.65, 4.615, -0.06; -1.98, 4.720, -0.08; -2.63, 4.889, -0.07; -3.24, 5.031, -0.06; -3.82, 5.149, -0.03; -4.38, 5.257, 0.01; -4.90, 5.355, 0.05; -5.87, 5.538, 0.12; -6.77, 5.697, 0.25;

Table 2. Continued.

$B = 0.01024$  M,  $C = 0.02002$  M;  $H \times 10^3$  M,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3$  M; 5.86, 2.226, 0.06; 5.17, 2.281, 0.04; 4.52, 2.342, 0.00; 3.88, 2.408, -0.00; 3.27, 2.486, -0.04; 2.68, 2.569, -0.03; 2.12, 2.675, -0.06; 1.56, 2.816, -0.11; 1.03, 2.970, -0.07; 0.52, 3.220, -0.11; 0.03, 3.541, -0.13; -0.44, 3.815, -0.11; -0.90, 4.023, -0.09; -1.35, 4.169, -0.04; -1.79, 4.297, 0.03; -2.21, 4.392, 0.02; -2.62, 4.475, 0.07; -3.40, 4.629, 0.07; -4.17, 4.743, 0.17; -5.50, 4.941, 0.18; -6.71, 5.100, 0.21; -7.80, 5.227, 0.29; -8.79, 5.347, 0.30; -9.70, 5.453, 0.30; -10.52, 5.545, 0.35; -11.64, 5.675, 0.34; -12.63, 5.795, 0.27; -13.79, 5.932, 0.20; -14.80, 6.059, 0.00; -15.68, 6.177, -0.30; -16.45, 6.263, -0.44;

$B = 0.01022$  M,  $C = 0.03999$  M;  $H \times 10^3$  M,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3$  M; 8.01, 2.101, -0.11; 6.95, 2.160, -0.07; 5.95, 2.223, -0.00; 4.96, 2.304, -0.05; 4.02, 2.393, -0.03; 3.12, 2.510, -0.10; 2.24, 2.643, 0.07; 1.40, 2.826, -0.06; 0.58, 3.092, -0.05; -0.21, 3.438, -0.03; -0.97, 3.753, -0.04; -1.70, 3.966, -0.03; -2.41, 4.132, -0.04; -3.10, 4.263, -0.06; -3.77, 4.372, -0.06; -4.42, 4.473, -0.13; -5.05, 4.551, -0.10; -6.26, 4.688, -0.06; -7.41, 4.811, -0.06; -9.48, 5.011, -0.04; -11.35, 5.166, 0.12; -13.81, 5.389, 0.01; -15.97, 5.575, -0.05; -17.81, 5.724, 0.00; -19.46, 5.873, -0.14; -21.38, 6.037, -0.17; -23.05, 6.184, -0.20; 24.83, 6.351, -0.28;

$B = 0.01000$  M,  $C = 0.08000$  M;  $H \times 10^3$  M,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3$  M; 12.63, 1.898, -0.03; 10.44, 1.982, -0.06; 8.32, 2.069, 0.17; 6.25, 2.201, -0.03; 4.28, 2.366, -0.08; 2.39, 2.594, -0.02; 0.56, 2.995, 0.02; -1.21, 3.518, 0.16; -2.93, 3.924, 0.02; -4.58, 4.179, -0.11; -6.17, 4.357, -0.08; -9.18, 4.669, -0.38; -10.63, 4.783, -0.29; -13.39, 4.996, -0.21; -16.01, 5.183, -0.07; -18.48, 5.379, -0.25; -20.84, 5.528, 0.07; -22.96, 5.699, -0.17; -25.01, 5.844, -0.14; -27.01, 5.995, -0.21; -28.82, 6.110, 0.00; -31.43, 6.301, -0.01;

$B = 0.01024$  M,  $C = 0.1604$  M;  $H \times 10^3$  M,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3$  M; 12.14, 1.913, 0.00; 10.10, 1.995, -0.07; 8.16, 2.080, 0.05; 6.26, 2.188, 0.08; 4.44, 2.331, 0.03; 2.70, 2.529, -0.05; 1.01, 2.808, -0.03; -0.63, 3.191, -0.05; -2.21, 3.509, -0.03; -3.72, 3.761, -0.18; -5.19, 3.931, -0.15; -6.60, 4.092, -0.33; -7.97, 4.202, -0.17; -9.30, 4.327, -0.33; -10.60, 4.422, -0.22, -11.85, 4.523, -0.31; -13.07, 4.611, -0.28; -14.26, 4.707, -0.44; -15.40, 4.785, -0.41; -17.61, 4.925, -0.22; -19.68, 5.061, -0.14; -21.61, 5.192, -0.18; -23.47, 5.311, -0.11; -25.23, 5.433, -0.19; -26.89, 5.536, -0.10; -28.48, 5.639, -0.08; -31.42, 5.842, -0.22;

$B = 0.00080$  M,  $C = 0.01275$  M;  $H \times 10^3$  M,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3$  M; -7.96, 7.922, 0.07; -7.37, 7.827, 0.03; -6.82, 7.742, -0.03; -6.19, 7.631, -0.04; -5.61, 7.523, -0.04; -5.08, 7.413, -0.03; -4.58, 7.299, -0.03; -4.12, 7.183, -0.02; -3.71, 7.063, -0.01; -3.39, 6.972, -0.04; -3.10, 6.863, -0.02; -2.89, 6.789, -0.04; -2.68, 6.701, -0.04; -2.42, 6.579, -0.03; -2.18, 6.449, -0.02; -1.94, 6.316, -0.03; -1.72, 6.177, -0.02; -1.51, 6.033, -0.02; -1.30, 5.883, -0.02; -1.11, 5.727, -0.02; -0.92, 5.572, -0.02; -0.75, 5.406, -0.02; -0.58, 5.230, -0.02; -0.41, 5.029, -0.01; -0.26, 4.782, -0.01; -0.18, 4.629, -0.01; -0.11, 4.459, -0.01; -0.03, 4.255, -0.01; 0.04, 4.045, -0.01; 0.11, 3.863, -0.02; 0.18, 3.716, -0.02; 0.25, 3.601, -0.02; 0.38, 3.425, -0.02; 0.57, 3.251, -0.02; 0.75, 3.127, -0.02; 1.02, 2.988, -0.01; 1.38, 2.858, -0.00; 1.78, 2.748, 0.00; 1.98, 2.703, 0.00; 2.16, 2.664, 0.00; 2.34, 2.630, 0.00;

$B \times 10^3$  M,  $C \times 10^3$  M,  $H \times 10^3$  M,  $-\log h$ ,  $(H_{\text{calc}} - H) \times 10^3$  M; 5.13, 163.6, 17.45, 1.757, 0.02; 5.08, 162.0, 16.77, 1.781, -0.24; 4.98, 158.8, 15.47, 1.807, 0.12; 4.75, 151.5, 12.38, 1.904, 0.07; 4.54, 144.8, 9.57, 2.014, 0.06; 4.42, 141.0, 7.99, 2.093, 0.05; 4.27, 136.2, 6.00, 2.217, 0.02; 4.14, 132.0, 4.17, 2.362, 0.11; 4.01, 127.9, 2.42, 2.596, 0.00; 3.89, 123.9, 0.79, 2.997, -0.04; 3.86, 123.0, 0.40, 3.160, -0.07; 3.83, 122.1, 0.01, 3.336, -0.08; 3.80, 121.2, -0.36, 3.510, -0.07; 3.77, 120.3, -0.74, 3.677, -0.08; 3.74, 119.4, -1.11, 3.822, -0.05; 3.72, 118.5, -1.46, 3.941, -0.06; 3.69, 117.7, -1.83, 4.064, -0.08; 3.64, 116.0, -2.53, 4.260, -0.07; 3.59, 114.4, -3.20, 4.434, -0.07; 3.54, 112.8, -3.86, 4.588, -0.03; 3.49, 111.3, -4.50, 4.737, -0.02; 3.44, 109.8, -5.14, 4.882, -0.01; 3.37, 107.6, -6.07, 5.087,

Table 2. Continued.

0.03; 3.29, 104.9, -7.20, 5.330, 0.10; 3.21, 102.3, -8.29, 5.576, 0.11; 3.13, 99.8, -9.34, 5.807, 0.11; 3.05, 97.4, -10.35, 6.022, 0.08; 2.98, 95.1, -11.30, 6.211, 0.06; 2.91, 93.0, -12.20, 6.395, -0.14; 2.85, 90.9, -13.08, 6.532, -0.16; 2.77, 88.4, -14.11, 6.674, -0.20; 2.70, 86.1, -15.08, 6.791, -0.25; 2.62, 83.5, -16.19, 6.908, -0.31; 2.49, 79.4, -17.88, 7.065, -0.43; 2.38, 75.7, -19.43, 7.187, -0.44;

$B \times 10^3 M, C \times 10^3 M, H \times 10^3 M, -\log h, (H_{\text{calc}} - H) \times 10^3 M$ ; 4.78, 515.6, 4.720, 1.325, 0.05; 4.74, 511.3, 42.28, 1.373, 0.04; 4.69, 505.9, 37.03, 1.432, -0.08; 4.64, 500.5, 31.88, 1.498, -0.14; 4.60, 496.2, 26.94, 1.573, -0.27; 4.56, 491.9, 21.98, 1.664, -0.35; 4.51, 486.5, 17.03, 1.773, -0.25; 4.47, 482.2, 12.26, 1.916, -0.21; 4.45, 477.9, 7.58, 2.123, -0.20; 4.39, 473.5, 2.98, 2.500, -0.17; 4.37, 469.2, -1.53, 3.397, -0.19; 4.33, 465.0, -5.96, 4.201, -0.17; 4.29, 460.9, -10.22, 4.832, -0.06; 4.25, 456.9, -14.50, 5.405, -0.04; 4.22, 452.8, -18.78, 5.833, 0.24; 4.07, 437.5, -34.87, 6.541, 0.65; 3.94, 423.2, -49.91, 6.835, 0.05; 3.82, 409.8, -63.92, 7.021, 0.07; 3.70, 397.3, -77.15, 7.165, 0.11; 3.59, 385.4, -95.53, 7.333, 0.79;

$B \times 10^3 M, C \times 10^3 M, H \times 10^3 M, -\log h, (H_{\text{calc}} - H) \times 10^3 M$ ; 4.92, 311.0, 23.69, 1.625, 0.01; 4.83, 305.4, 20.03, 1.698, -0.04; 4.74, 299.7, 16.51, 1.780, 0.02; 4.66, 294.6, 13.12, 1.881, -0.03; 4.57, 288.9, 9.88, 2.000, 0.04; 4.49, 283.9, 6.69, 2.169, -0.01; 4.42, 279.1, 3.61, 2.425, -0.03; 4.34, 274.3, 0.63, 2.921, 0.04; 4.27, 269.7, -2.24, 3.736, -0.02; 4.20, 265.3, -4.99, 4.290, -0.05; 4.13, 261.1, -7.63, 4.726, 0.05; 4.07, 256.9, -10.18, 5.135, 0.08; 4.00, 252.9, -12.76, 5.518, 0.15; 3.94, 249.0, -15.18, 5.859, 0.06; 3.88, 245.2, -17.55, 6.119, 0.08; 3.82, 241.5, -19.82, 6.302, 0.24; 3.76, 238.0, -22.03, 6.451, 0.22; 3.71, 234.6, -24.16, 6.569, 0.12; 3.66, 231.2, -26.24, 6.665, 0.04; 3.61, 228.0, -28.27, 6.747, -0.04; 3.56, 224.8, -30.24, 6.816, -0.09; 3.51, 221.7, -32.16, 6.880, -0.25; 3.46, 218.7, -34.02, 6.936, -0.34; 3.41, 215.8, -35.87, 6.988, -0.45; 3.33, 210.1, -39.34, 7.080, -0.30; 3.20, 202.3, -44.25, 7.191, -0.30; 3.01, 190.4, -51.30, 7.345, -0.56; 2.84, 179.8, -58.29, 7.475, -0.47; 2.69, 170.3, -64.19, 7.588, -0.17; 2.56, 161.8, -69.49, 7.693, 0.06;

$B \times 10^3 M, C \times 10^3 M, H \times 10^3 M, -\log h, (H_{\text{calc}} - H) \times 10^3 M$ ; 20.47, 10.02, 12.37, 1.902, 0.16; 19.31, 9.45, 10.21, 1.987, 0.08; 18.28, 8.95, 8.29, 2.080, 0.01; 17.35, 8.49, 6.56, 2.182, 0.00; 16.51, 8.08, 4.99, 2.304, -0.05; 15.75, 7.71, 3.58, 2.447, -0.02; 15.06, 7.37, 2.28, 2.643, -0.04; 14.42, 7.06, 1.10, 2.955, -0.04; 13.75, 6.73, -0.16, 3.864, -0.06; 13.65, 6.68, -0.33, 4.011, -0.05; 13.56, 6.64, -0.50, 4.145, -0.05; 13.47, 6.59, -0.67, 4.260, -0.06; 13.39, 6.55, -0.83, 4.355, -0.05; 13.30, 6.51, -1.00, 4.446, -0.06; 13.21, 6.47, -1.15, 4.525, -0.06; 13.13, 6.43, -1.31, 4.593, -0.04; 13.05, 6.39, -1.47, 4.662, -0.04; 12.96, 6.34, -1.62, 4.725, -0.04; 12.88, 6.30, -1.77, 4.784, -0.04; 12.80, 6.27, -1.92, 4.840, -0.03; 12.72, 6.23, -2.07, 4.892, -0.02; 12.64, 6.19, -2.22, 4.941, 0.00; 12.57, 6.15, -2.36, 4.990, 0.02; 12.49, 6.11, -2.51, 5.038, 0.03; 12.34, 6.04, -2.79, 5.132, 0.06; 12.19, 5.97, -3.06, 5.224, 0.09; 12.05, 5.90, -3.33, 5.308, 0.14; 11.91, 5.83, -3.59, 5.386, 0.21; 11.77, 5.76, -3.84, 5.443, 0.35; 11.51, 5.63, -4.33, 5.555, 0.63;

$B \times 10^3 M, C \times 10^3 M, H \times 10^3 M, -\log h, (H_{\text{calc}} - H) \times 10^3 M$ ; 20.00, 20.00, 16.60, 1.777, 0.09; 19.60, 19.60, 15.77, 1.799, 0.09; 19.04, 19.04, 14.58, 1.832, 0.13; 18.34, 18.34, 13.46, 1.868, 0.08; 18.01, 18.01, 12.41, 1.903, 0.07; 17.53, 17.53, 11.40, 1.941, 0.04; 16.95, 16.95, 10.14, 1.992, 0.03; 16.38, 16.38, 8.94, 2.046, 0.03; 15.87, 15.87, 7.86, 2.102, 0.02; 15.15, 15.15, 6.34, 2.198, -0.01; 14.29, 14.29, 4.50, 2.347, -0.03; 13.51, 13.51, 2.87, 2.542, -0.03; 12.82, 12.82, 1.40, 2.853, -0.06; 12.50, 12.50, 0.72, 3.114, -0.07; 12.20, 12.20, 0.08, 3.548, -0.08; 12.05, 12.05, -0.24, 3.792, -0.08; 11.91, 11.91, -0.54, 3.998, -0.08; 11.76, 11.76, -0.84, 4.157, -0.08; 11.63, 11.63, -1.13, 4.287, -0.07; 11.36, 11.36, -1.69, 4.495, -0.04; 11.11, 11.11, -2.22, 4.669, -0.05; 10.87, 10.87, -2.73, 4.813, -0.03; 10.64, 10.64, -3.22, 4.945, -0.02; 10.42, 10.42, -3.69, 5.049, 0.08; 10.10, 10.10, -4.36, 5.235, 0.03; 9.80, 9.80, -4.99, 5.394, 0.08; 9.52, 9.52, -5.58, 5.546, 0.16; 9.26, 9.26, -6.14, 5.697, 0.24;

Table 2. Continued.

$B \times 10^3 \text{ M}, C \times 10^3 \text{ M}, H \times 10^3 \text{ M}, -\log h, (H_{\text{calc}} - H) \times 10^3 \text{ M}; 20.47, 40.00, 11.51, 1.943, -0.14; 20.07, 39.22, 10.28, 1.987, -0.02; 19.69, 38.47, 9.10, 2.040, -0.02; 19.28, 37.67, 7.86, 2.101, 0.02; 18.89, 36.91, 6.66, 2.170, 0.03; 18.43, 36.01, 5.36, 2.265, -0.00; 17.97, 35.11, 3.83, 2.416, -0.09; 17.51, 34.21, 2.42, 2.613, -0.12; 17.07, 33.35, 1.08, 2.936, -0.20; 16.52, 32.28, -0.60, 3.577, -0.20; 16.13, 31.52, -1.79, 3.907, -0.10; 15.88, 31.03, -2.56, 4.069, -0.05; 15.65, 30.56, -3.30, 4.203, -0.01; 15.39, 30.08, -4.05, 4.307, 0.15; 15.12, 29.54, -4.89, 4.432, 0.19; 14.84, 28.99, -5.76, 4.559, 0.17; 14.59, 28.50, -6.53, 4.669, 0.12; 14.33, 28.00, -7.31, 4.754, 0.29; 14.04, 27.42, -8.21, 4.863, 0.34; 13.66, 26.70, -9.36, 5.002, 0.41; 13.48, 26.34, -9.91, 5.073, 0.39; 13.14, 25.67, -10.96, 5.197, 0.52; 12.81, 25.03, -11.97, 5.333, 0.47; 12.50, 24.42, -12.92, 5.469, 0.42; 12.20, 23.84, -13.83, 5.590, 0.49; 11.92, 23.29, -14.70, 5.722, 0.43; 11.65, 22.75, -15.53, 5.859, 0.30; 11.39, 21.76, -16.32, 5.989, 0.19; 11.14, 21.31, -17.10, 6.128, -0.06; 10.91, 20.87, -17.80, 6.246, -0.23; 10.68, 20.44, -18.50, 6.321, 0.08;$

$B \times 10^3 \text{ M}, C \times 10^3 \text{ M}, H \times 10^3 \text{ M}, -\log h, (H_{\text{calc}} - H) \times 10^3 \text{ M}; 20.45, 80.00, 16.88, 1.777, -0.23; 19.67, 76.95, 14.26, 1.845, -0.05; 18.93, 74.05, 11.84, 1.922, 0.05; 18.26, 71.43, 9.59, 2.016, -0.03; 17.63, 68.97, 7.50, 2.119, 0.01; 16.49, 64.51, 3.71, 2.428, -0.13; 15.98, 62.51, 1.97, 2.686, -0.18; 15.49, 60.60, 0.36, 3.109, -0.24; 15.26, 59.70, -0.41, 3.355, -0.25; 14.82, 57.98, -1.87, 3.724, -0.20; 14.40, 56.33, -3.26, 3.981, -0.18; 14.20, 55.55, -3.93, 4.084, -0.17; 14.01, 54.81, -4.57, 4.172, -0.13; 13.82, 54.06, -5.20, 4.255, -0.11; 13.63, 53.32, -5.82, 4.334, -0.11; 13.45, 52.62, -6.42, 4.404, -0.07; 13.28, 51.95, -6.99, 4.471, -0.06; 13.11, 51.29, -7.56, 4.536, -0.04; 12.94, 50.62, -8.11, 4.596, -0.01; 12.78, 49.99, -8.65, 4.661, -0.04; 12.63, 49.41, -9.17, 4.716, -0.01; 12.47, 48.78, -9.69, 4.772, 0.01; 12.32, 48.20, -10.19, 4.826, 0.04; 12.17, 47.61, -10.69, 4.880, 0.05; 12.03, 47.06, -11.17, 4.934, 0.05; 11.75, 45.97, -12.09, 5.036, 0.09; 11.49, 44.95, -12.97, 5.141, 0.04; 11.36, 44.43, -13.39, 5.190, 0.05; 11.23, 43.95, -13.81, 5.235, 0.10; 10.99, 43.00, -14.61, 5.333, 0.09; 10.76, 42.10, -15.38, 5.428, 0.10; 10.54, 41.23, -16.12, 5.523, 0.09; 10.33, 40.40, -16.83, 5.617, 0.08; 10.22, 40.00, -17.17, 5.663, 0.10; 10.03, 39.22, -17.84, 5.751, 0.15; 9.83, 38.46, -18.48, 5.844, 0.15; 9.65, 37.74, -19.09, 5.935, 0.15; 9.47, 37.04, -19.69, 6.030, 0.16; 9.27, 36.36, -20.27, 6.123, 0.20;$

$B \times 10^3 \text{ M}, C \times 10^3 \text{ M}, H \times 10^3 \text{ M}, -\log h, (H_{\text{calc}} - H) \times 10^3 \text{ M}; 20.49, 320.9, 24.68, 1.605, -0.02; 18.79, 294.3, 8.47, 2.049, 0.11; 18.45, 288.9, 5.25, 2.241, -0.03; 18.30, 286.6, 3.87, 2.368, -0.27; 17.81, 278.9, -0.84, 2.930, -0.19; 17.51, 274.1, -3.74, 3.287, -0.18; 17.21, 269.5, -6.53, 3.546, -0.15; 16.93, 265.1, -9.23, 3.749, -0.12; 16.65, 260.7, -11.87, 3.918, -0.01; 16.38, 256.5, -14.43, 4.075, -0.01; 16.12, 252.4, -16.90, 4.226, -0.12; 15.63, 244.8, -21.56, 4.486, -0.01; 15.16, 237.4, -26.02, 4.735, 0.15; 14.73, 230.2, -30.16, 4.973, 0.28; 14.33, 224.2, -34.08, 5.203, 0.50; 13.93, 218.1, -37.78, 5.439, 0.54; 13.56, 212.4, -41.26, 5.681, 0.47; 13.39, 209.6, -42.95, 5.811, 0.31; 13.21, 206.9, -44.59, 5.931, 0.37; 13.05, 204.3, -46.19, 6.062, 0.25;$

Table 3. Experimental spectrophotometric data. For each composition in  $H, B, C$ , is given the absorbance,  $E$ ,  $1000 \times (E_{\text{calc}} - E)$ , for each wavelength ranging from 500 to 900 nm with 50 nm intervals.  $E_{\text{calc}}$  is calculated using the set of proposed constants from the spectrophotometric calculations.

$B = 5.00 \text{ mM}, C = 5.00 \text{ mM};$   
 $H = -0.52 \text{ mM}; -; -; 0.003, 0; 0.020, 0; 0.041, -0; 0.058, -0; 0.060, 1; 0.059, 0; 0.045, 1;$   
 $H = -1.05 \text{ mM}; -; -; 0.005, 1; 0.024, 1; 0.047, 0; 0.063, 0; 0.065, 0; 0.061, 0; 0.046, 1;$   
 $H = -1.56 \text{ mM}; -; -; 0.008, 2; 0.030, 0; 0.052, 1; 0.068, 0; 0.067, 1; 0.064, -0; 0.048, 1;$   
 $H = -2.04 \text{ mM}; -; -; 0.010, 3; 0.034, 1; 0.057, 1; 0.073, 0; 0.070, 1; 0.065, -1; 0.050, 0;$   
 $H = -2.50 \text{ mM}; -; 0.002, 2; 0.014, 3; 0.039, 1; 0.064, 0; 0.077, -1; 0.073, 0; 0.067, 1;$   
 $0.050, 1;$   
 $H = -2.92 \text{ mM}; -; 0.003, 1; 0.017, 2; 0.045, 0; 0.069, -1; 0.081, -2; 0.075, 0; 0.069, -2;$   
 $0.051, 0;$   
 $H = -3.34 \text{ mM}; 0.001, 0; 0.005, 1; 0.021, 2; 0.048, 1; 0.072, 0; 0.082, 0; 0.076, 0; 0.069,$   
 $-2; 0.051, 1;$



Table 3. Continued.

$B = 5.12$  mM,  $C = 20.03$  mM;

$H = -1.39$  mM; 0.001, 0; 0.003, -1; 0.014, -5; 0.032, -2; 0.054, -1; 0.069, -1; 0.070, -1; 0.063, 1; 0.052, -2;  
 $H = -2.01$  mM; 0.001, 0; 0.003, -0; 0.016, -3; 0.037, -1; 0.060, 0; 0.074, 1; 0.074, -1; 0.065, 1; 0.054, -2;  
 $H = -3.12$  mM; 0.001, 0; 0.006, -1; 0.023, -2; 0.050, 0; 0.074, 0; 0.084, 1; 0.081, -1; 0.070, 1; 0.057, -2;  
 $H = -4.12$  mM; 0.002, 0; 0.009, -1; 0.030, -1; 0.061, 1; 0.085, 1; 0.093, 1; 0.086, 0; 0.073, 1; 0.059, -1;  
 $H = -5.01$  mM; 0.002, 0; 0.012, -1; 0.038, -1; 0.073, 0; 0.096, 0; 100, 1; 0.091, 0; 0.076, 1; 0.060, 0;  
 $H = -5.81$  mM; 0.003, 0; 0.015, -1; 0.046, -1; 0.083, 0; 0.105, 0; 0.108, 0; 0.094, 1; 0.078, 1; 0.061, 0;  
 $H = -6.87$  mM; 0.004, 0; 0.021, -2; 0.058, -2; 0.099, -2; 0.117, -1; 0.114, 0; 0.099, 0; 0.080, 1; 0.062, 1;  
 $H = -7.80$  mM; 0.005, 0; 0.026, -1; 0.069, -2; 0.112, -1; 0.127, -1; 0.121, 0; 0.102, 0; 0.081, 1; 0.062, 1;  
 $H = -8.61$  mM; 0.008, -1; 0.031, 0; 0.080, -1; 0.122, 0; 0.135, -1; 0.124, 0; 0.103, 0; 0.082, 0; 0.061, 2;  
 $H = -9.33$  mM; 0.009, -1; 0.038, -0; 0.091, -0; 0.133, -0; 0.142, -1; 0.128, -1; 0.105, 0; 0.082, 0; 0.060, 1;  
 $H = -9.97$  mM; 0.010, 0; 0.044, 0; 0.102, -1; 0.143, -1; 0.148, -1; 0.130, 0; 0.105, 0; 0.081, 0; 0.059, 1;  
 $H = -10.55$  mM; 0.012, 0; 0.050, -0; 0.112, -1; 0.151, 0; 0.152, 0; 0.132, 0; 0.105, 0; 0.080, 0; 0.057, 1;  
 $H = -11.23$  mM; 0.015, 0; 0.057, 1; 0.123, 0; 0.160, 1; 0.157, 0; 0.134, 0; 0.105, 0; 0.078, 0; 0.056, 0;  
 $H = -12.09$  mM; 0.017, 1; 0.068, 1; 0.137, 2; 0.171, 1; 0.162, 1; 0.135, 0; 0.103, 0; 0.076, 0; 0.054, -2;

$B = 5.00$  mM,  $C = 40.00$  mM;

$H = -8.45$ ; 0.005, 1; 0.027, 2; 0.071, 5; 0.113, 5; 0.128, 3; 0.121, 1; 0.103, -1; 0.082, -1; 0.066, -3;  
 $H = -11.09$ ; 0.013, -1; 0.056, -2; 0.118, -2; 0.156, -2; 0.153, -1; 0.131, -1; 0.105, 0; 0.080, -1; 0.060, -1;  
 $H = -15.88$  mM; 0.038, -0; 0.120, -1; 0.188, -2; 0.195, -1; 0.161, 1; 0.123, 1; 0.089, 1; 0.062, 1; 0.042, 1;  
 $H = -18.06$  mM; 0.052, 0; 0.150, -2; 0.210, -1; 0.200, 0; 156, 1; 0.112, 1; 0.078, 2; 0.052, 2; 0.034, 2;  
 $H = -20.11$  mM; 0.066, -2; 0.173, -1; 0.226, -1; 0.202, -1; 0.151, -1; 0.105, -2; 0.073, -3; 0.049, -3; 0.031, -1;  
 $H = -27.24$  mM; 0.087, -0; 0.214, -2; 0.247, -2; 0.198, -2; 0.133, -1; 0.084, -1; 0.053, -1; 0.033, 0; 0.021, 0;  
 $H = -30.27$  mM; 0.089, 2; 0.214, 4; 0.243, 5; 0.192, 3; 0.127, 2; 0.079, 1; 0.049, 1; 0.032, 0; 0.021, -1;

$H = -11.93$  mM,  $B = 4.07$  mM,  $C = 257.2$  mM; 0.021, 2; 0.074, 5; 0.131, 4; 0.148, 2; 0.133, 0; 0.105, 0; 0.079, 0; 0.057, -1; 0.041, -1;

$H = -17.09$  mM,  $B = 3.94$  mM,  $C = 249.3$  mM; 0.053, 1; 0.141, 0; 0.179, 1; 0.157, 1; 0.116, -0; 0.078, 0; 0.051, 1; 0.033, 1; 0.021, 1;

$H = -21.95$  mM,  $B = 3.83$  mM,  $C = 241.9$  mM; 0.065, 0; 0.162, -1; 0.189, -2; 0.153, -2; 0.104, -2; 0.065, 0; 0.041, 0; 0.027, -1; 0.018, -1;

$H = -40.66$  mM,  $B = 3.38$  mM,  $C = 213.4$  mM; 0.071, -1; 0.164, -2; 0.181, -2; 0.137, 0; 0.086, 1; 0.050, 1; 0.030, 1; 0.018, 1; 0.012, 1;

Table 3. Continued.

$H = -45.94$  mM,  $B = 3.25$  mM,  $C = 205.3$  mM; 0.069, 1; 0.159, 1; 0.175, 0; 0.132, 0; 0.083, 1; 0.048, 1; 0.028, 1; 0.018, 1; 0.012, 0;

$H = -58.27$  mM,  $B = 2.95$  mM,  $C = 186.5$  mM; 0.065, -1; 0.147, -1; 0.163, -1; 0.123, -0; 0.079, -2; 0.045, -1; 0.027, -0; 0.017, -1; 0.011, 0;

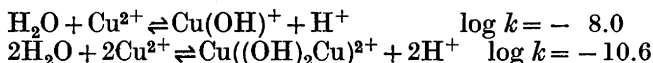
$H = -68.53$  mM,  $B = 2.70$  mM,  $C = 170.9$  mM; 0.057, 2; 0.133, 2; 0.149, 1; 0.114, -1; 0.073, -1; 0.042, -1; 0.025, -1; 0.016, -1; 0.011, -1;

$$C = c + k_a h^{-1}c + \sum \sum \sum r \beta_{pqr} h^p b^q c^r \quad (4)$$

$$H = h - k_a h^{-1}c + \sum \sum p \beta_{pq} h^p b^q + \sum \sum \sum p \beta_{pqr} h^p b^q c^r \quad (5)$$

where  $h = [H^+]$ ,  $b = [Cu^{2+}]$ ,  $c = [C_3N_2H_5^+]$ ;  $\beta_{pqr}$ ,  $\beta_{pq}$  and  $k_a$  are the equilibrium constants for the reactions (2), (2b), and (2a), respectively.

In a separate study we found the equilibrium (2a) to be the predominating one in the system  $C_3N_2H_5^+ \cdot H^+$ , and the acidity constant  $k_a \pm 3\sigma$  was determined to  $k_a = (1.222 \pm 0.005) \times 10^{-8} M$ .<sup>21</sup> The 2-component hydrolysis equilibria according to eqn. (2b) have also earlier been carefully studied,<sup>9</sup> and the following complexes and equilibrium constants have thereby been proposed.



These results on the 2-component equilibria will in the following calculations be considered as known, and no attempt will be made to adjust the equilibrium constants  $\beta_{pq}$ .

The computational problem involves determination of the set of  $pqr$ -triplets and the corresponding equilibrium constants  $\beta_{pqr}$ , that best fit the emf and spectrophotometric data.

We will start the calculations by testing the hypothesis that only a series of stepwise complexes  $Cu(C_3N_2H_4)_n^{2+}$  is formed. Such an approach has previously been applied to this system (Table 1).

With this hypothesis and assuming that equilibria (2b) can be neglected, eqns. (3), (4), and (5) are simplified to:

$$B = b + \sum \beta_{n1n} b (h^{-1}c)^n \quad (3a)$$

$$C = c + k_a h^{-1}c + \sum n \beta_{n1n} b (h^{-1}c)^n \quad (4a)$$

$$H = h - k_a h^{-1}c - \sum n \beta_{n1n} b (h^{-1}c)^n \quad (5a)$$

It follows that:

$$C + H - h = c = [C_3N_2H_5^+] \quad (6)$$

$$[C_3N_2H_4] = k_a h^{-1}(C + H - h) \quad (7)$$

Furthermore, the average number of  $A$  bound per Cu,  $Z_n$ , is given by the relationship:

$$Z_n = \frac{h - H - k_a h^{-1}(C + H - h)}{B} = \frac{\sum n \beta_{n1n} (h^{-1}c)^n}{1 + \sum \beta_{n1n} (h^{-1}c)^n} \quad (8)$$

Evidently, if  $k_a$  is known,  $Z_n$  and  $\log [C_3N_2H_4]$  can be calculated from available emf data  $H(\log h)_{BC}$  by using eqns. (8) and (7).

According to eqn. (8), a plot of  $Z_n$  against  $\log [C_3N_2H_4]$  will give points falling on a single curve independent of  $B$  and  $C$ . Using present emf data, we have made such a  $Z_n$  ( $\log [C_3N_2H_4]$ )-plot, which is shown in Fig. 1.

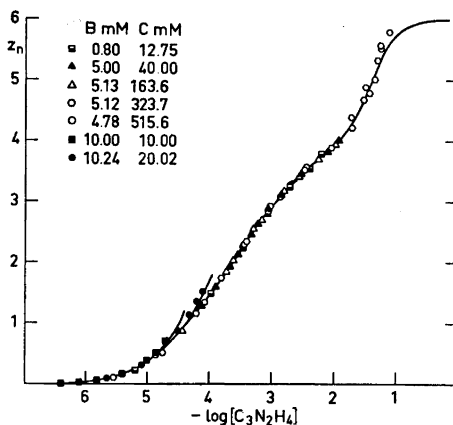


Fig. 1. Experimental data plotted as curves,  $Z_n$  ( $\log [C_3N_2H_4]_{BC}$ ). Open symbols mark titrations where  $B$  and  $C$  have been varied. The  $B$  and  $C$  values represent starting concentrations; half-filled symbols back-titrations (decreasing pH). The full curves have been calculated with the set of proposed constants in Table 4.

If we consider only data-points with  $C/B > 8$ , we see from this plot that the assumed hypothesis appears valid up to  $Z_n \approx 5$ . However, at  $Z_n < 1.5$ , and with  $C/B < 8$ , there are marked systematic deviations. In the following, these two groups of data will be denoted as 1 and 2, respectively. An analysis of data 1 using the least-squares computer program LETAGROPVRID showed that it could be explained employing the complexes  $Cu(C_3N_2H_4)^{2+}$ ,  $Cu(C_3N_2H_4)_2^{2+}$ ,  $Cu(C_3N_2H_4)_3^{2+}$ ,  $Cu(C_3N_2H_4)_4^{2+}$ , and  $Cu(C_3N_2H_4)_6^{2+}$ .

In attempts to add the missing complex  $Cu(C_3N_2H_4)_5^{2+}$ , the equilibrium constant always came out as zero or negative. The refined "best" equilibrium constants  $\beta_{pqr}$  and the corresponding standard deviations  $3\sigma$  ( $\log \beta_{pqr}$ ) obtained are given in Table 4.

The analysis of data 2 was started with a residual calculation, using the result (species and "best"  $\beta_n$ -values) from the calculation on data 1. The residuals indicate clearly that one or more additional complexes, beside those belonging to the series  $Cu(C_3N_2H_4)_n^{2+}$ , must be present. In order to explain these data, we will try the very simple hypothesis that only one additional complex  $(H^+)_P(Cu^{2+})_Q(C_3N_2H_5^+)_R^{(P+2Q+R)+}$  is present. A trial and error procedure with a LETAGROPVRID program was used to determine the composition and equilibrium constant of the complex  $(H^+)_P(Cu^{2+})_Q(C_3N_2H_5^+)_R^{(P+2Q+R)+}$  providing the closest fit to data 2. The principal of this method has been that complexes of different  $pqr$ -compositions have successively been tested one by one, and the complex that gives the lowest error square sum  $U = \sum (H_{calc} - H)^2$  will be considered as the best explanation of the data. The calculations have been carried out in the  $pqr$ -space  $-9 \leq p \leq -1$ ,  $1 \leq q \leq 4$ , and  $0 \leq r \leq 6$ . The error square sums  $U$  obtained for the tested com-

Table 4. Results of LETAGROP calculations for some different assumptions concerning the complexes formed. The errors  $3\sigma$  ( $\log\beta_{pq}$ ) are given when the corresponding equilibrium constant has not been kept constant. Ranges 1 and 2 refer to data 1 and 2, respectively. Range 3 represents an even distribution of data 1 plus data 2.

| Method             | Range              | Number of points | $U$   | $\sigma(H)$<br>mM | $\log\beta_{-101}$<br>$\pm 3\sigma$ | $\log\beta_{-111}$<br>$\pm 3\sigma$ | $\log\beta_{-212}$<br>$\pm 3\sigma$ | $\log\beta_{-313}$<br>$\pm 3\sigma$ | $\log\beta_{-414}$<br>$\pm 3\sigma$ | $\log\beta_{-515}$<br>$\pm 3\sigma$ | $\log\beta_{-616}$<br>$\pm 3\sigma$ | $\log\beta_{-523}$<br>$\pm 3\sigma$ |
|--------------------|--------------------|------------------|-------|-------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Emf                | 1                  | 350              | 481.0 | 1.18              | -7.913                              | -3.28                               | -7.21                               | -11.88                              | -17.03                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.07                                | 0.08                                | 0.18                                | 0.15                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.27                               | -7.32                               | -11.77                              | -17.48                              | -23.49                              |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.07                                | 0.07                                | 0.09                                | 0.14                                | 0.12                                |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.27                               | -7.23                               | -11.82                              | -17.09                              |                                     | -29.93                              |                                     |
|                    |                    |                  |       |                   |                                     | 0.07                                | 0.07                                | 0.09                                | 0.09                                | 0                                   | 0.17                                |                                     |
| Emf                | 2                  | 516              | 54.9  | 0.32              | -7.913                              | -3.27                               | -7.14                               | -11.58                              | -17.09                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.01                                | 0.03                                | 0.10                                |                                     |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.27                               | -7.13                               | -11.86                              | -17.09                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.01                                | 0.02                                | 0.14                                |                                     |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.27                               | -7.13                               | -11.86                              | -17.09                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.01                                | 0.02                                | 0.14                                |                                     |                                     |                                     |                                     |
| Proposed constants | 3                  | 577              | 45.6  | 0.28              | -7.913                              | -3.25                               | -7.18                               | -11.79                              | -17.04                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.02                                | 0.02                                | 0.04                                | 0.04                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.25                               | -7.18                               | -11.79                              | -17.04                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.02                                | 0.02                                | 0.04                                | 0.04                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.25                               | -7.18                               | -11.79                              | -17.04                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.02                                | 0.02                                | 0.04                                | 0.04                                |                                     |                                     |                                     |
| Spec.              | Proposed constants | 9 × 35           | 145.9 | 2.4               | -7.913                              | -3.23                               | -7.85                               | -12.08                              | -17.53                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.20                                | 0.23                                | 0.10                                | 0.25                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.22                               | -7.00                               | -12.36                              | -17.12                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.26                                | 0.20                                | 0.30                                | 0.21                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.23                               | -7.21                               | -12.21                              | -17.11                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.11                                | 0.17                                | 0.15                                | 0.21                                |                                     |                                     |                                     |
| Proposed constants | 9 × 35             | 73.0             | 1.7   | 1.5               | -7.913                              | -3.23                               | -7.21                               | -12.21                              | -17.11                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.26                                | 0.20                                | 0.30                                | 0.21                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.23                               | -7.21                               | -12.21                              | -17.11                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.11                                | 0.17                                | 0.15                                | 0.21                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.23                               | -7.21                               | -12.21                              | -17.11                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.11                                | 0.17                                | 0.15                                | 0.21                                |                                     |                                     |                                     |
| Proposed constants | 9 × 35             | 55.3             | 1.5   | 1.5               | -7.913                              | -3.23                               | -7.21                               | -12.21                              | -17.11                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.26                                | 0.20                                | 0.30                                | 0.21                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.23                               | -7.21                               | -12.21                              | -17.11                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.11                                | 0.17                                | 0.15                                | 0.21                                |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | -3.23                               | -7.21                               | -12.21                              | -17.11                              |                                     |                                     |                                     |
|                    |                    |                  |       |                   |                                     | 0.11                                | 0.17                                | 0.15                                | 0.21                                |                                     |                                     |                                     |

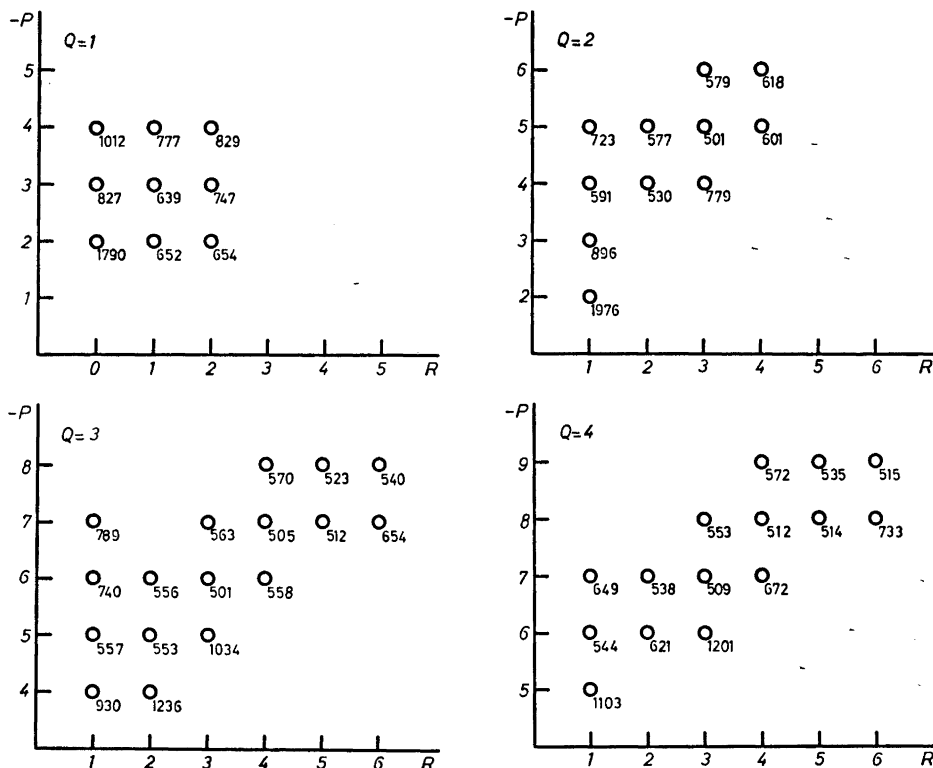


Fig. 2. LETAGROP-search for single  $H_P B_Q C_R$  complexes. The diagrams give error square sums  $U(PR)_Q$  assuming only one complex  $(H^+)_P(Cu^{2+})_Q(C_3N_2H_5^+)_R^{(P+2Q+R)+}$ . The lowest error square sums indicate those  $PQR$ -triplets that provide a "best-fit" to the data. If a mixture of complexes is present, the lowest error square sums give valuable information about the mean composition of possible complexes  $H_P B_Q C_R$ . In the calculations, the species  $CuOH^+$ ,  $Cu_2(OH)_2^{2+}$ ,  $Cu(C_3N_2H_4)_n$ , ( $n=1...4, 6$ ) have been assumed to be known. 69 points, arbitrarily chosen to cover as great range as possible, have been used in the LETAGROP-calculations.

binations are given in Fig. 2. We see here that rather low error square sums are obtained for the complexes  $(H^+)_{-6}(Cu^{2+})_3(C_3N_2H_5^+)_3^{3+}$ ,  $(H^+)_{-7}(Cu^{2+})_3(C_3N_2H_5^+)_4^{3+}$ ,  $(H^+)_{-7}(Cu^{2+})_4(C_3N_2H_5^+)_3^{4+}$ , and  $(H^+)_{-5}(Cu^{2+})_2(C_3N_2H_5^+)_3^{2+}$ . The differences in error square sums between the complexes mentioned are so small that it is impossible to say which of the complexes is the most probable one. Such a decision requires a much greater data range. However, as a working hypothesis, we may assume that  $(H^+)_{-5}(Cu^{2+})_2(C_3N_2H_5^+)_3$  is the main polynuclear complex in the range of data 2. A LETAGROP-refinement with this polynuclear complex added and calculated on data 2, and data 1 + data 2, respectively, gave the results shown in Table 4.

The standard deviations  $3\sigma$  ( $\log \beta_{-523}$ ) and  $\sigma(H)$  were found to be 0.12 and 0.28 mM, respectively. The residuals,  $H_{calc} - H$ , obtained in this calculation (Fig. 3) show no systematic trends.

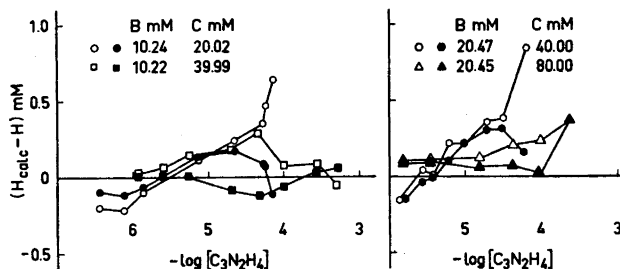


Fig. 3. Residuals ( $H_{\text{calc}} - H$ ) mM versus  $\log [C_3N_2H_4]$  from calculations on data 2. Filled symbols represent residuals with final proposed complexes and complex constants, and unfilled such with the complex  $Cu_2(OH)_2(C_3N_2H_4)_3^{2+}$  omitted (cf. Table 4). In order to make the figure clear only four (representative) titrations have been plotted.

Equilibrium calculations on the *spectrophotometric data* are given in Table 4, and the molar absorbances for the different ions have been calculated, and are given in Table 5 and in Fig. 4.

Table 5. The molar absorbance,  $\epsilon$   $cm^{-1} M^{-1}$ , with the error  $\sigma(\epsilon)$   $cm^{-1} M^{-1}$  as a function of the wavelength for the different ions.  $\epsilon$  has been calculated using the final values of the constants from the spectrophotometric measurements.

| Wavelength (nm) | Molar absorbance   | $Cu^{2+}$ | $Cu(C_3N_2H_4)_3^{2+}$ | $Cu(C_3N_2H_4)_2^{2+}$ | $Cu(C_3N_2H_4)_3^{2+}$ | $Cu(C_3N_2H_4)_2^{2+}$ | $Cu(C_3N_2H_4)_3^{2+}$ | $Cu_2(OH)_2(C_3N_2H_4)_3^{2+}$ |
|-----------------|--------------------|-----------|------------------------|------------------------|------------------------|------------------------|------------------------|--------------------------------|
| 500             | $\epsilon$         | 0.07      | 0.31                   | 1.29                   | 1.27                   | 19.42                  | 22.57                  | 14.14                          |
|                 | $\sigma(\epsilon)$ | 0.32      | 0.43                   | 0.48                   | 0.88                   | 0.24                   | 0.30                   | 2.25                           |
| 550             | $\epsilon$         | 0         | 1.18                   | 6.58                   | 19.24                  | 45.72                  | 51.32                  | 40.02                          |
|                 | $\sigma(\epsilon)$ | 0.53      | 0.38                   | 0.65                   | 1.47                   | 0.44                   | 0.55                   | 4.00                           |
| 600             | $\epsilon$         | 0         | 6.32                   | 16.88                  | 48.50                  | 49.00                  | 57.24                  | 75.90                          |
|                 | $\sigma(\epsilon)$ | 0.39      | 0.44                   | 0.77                   | 1.78                   | 0.53                   | 0.66                   | 4.84                           |
| 650             | $\epsilon$         | 2.68      | 13.99                  | 27.19                  | 55.91                  | 36.83                  | 43.20                  | 82.70                          |
|                 | $\sigma(\epsilon)$ | 0.27      | 0.50                   | 0.64                   | 1.29                   | 0.37                   | 0.45                   | 3.38                           |
| 700             | $\epsilon$         | 6.66      | 20.05                  | 29.30                  | 47.27                  | 23.45                  | 27.07                  | 71.05                          |
|                 | $\sigma(\epsilon)$ | 0.20      | 0.36                   | 0.47                   | 0.94                   | 0.27                   | 0.33                   | 2.48                           |
| 750             | $\epsilon$         | 10.47     | 21.51                  | 26.30                  | 35.67                  | 13.93                  | 15.32                  | 53.76                          |
|                 | $\sigma(\epsilon)$ | 0.15      | 0.28                   | 0.36                   | 0.72                   | 0.20                   | 0.25                   | 1.89                           |
| 800             | $\epsilon$         | 11.44     | 19.10                  | 22.10                  | 24.74                  | 8.34                   | 9.09                   | 34.05                          |
|                 | $\sigma(\epsilon)$ | 0.15      | 0.29                   | 0.37                   | 0.74                   | 0.21                   | 0.26                   | 1.95                           |
| 850             | $\epsilon$         | 11.40     | 15.80                  | 17.40                  | 15.63                  | 5.28                   | 5.74                   | 22.42                          |
|                 | $\sigma(\epsilon)$ | 0.20      | 0.37                   | 0.48                   | 0.96                   | 0.27                   | 0.33                   | 2.52                           |
| 900             | $\epsilon$         | 8.83      | 12.42                  | 13.89                  | 8.60                   | 3.60                   | 3.86                   | 7.91                           |
|                 | $\sigma(\epsilon)$ | 0.22      | 0.40                   | 0.52                   | 1.05                   | 0.30                   | 0.37                   | 2.77                           |

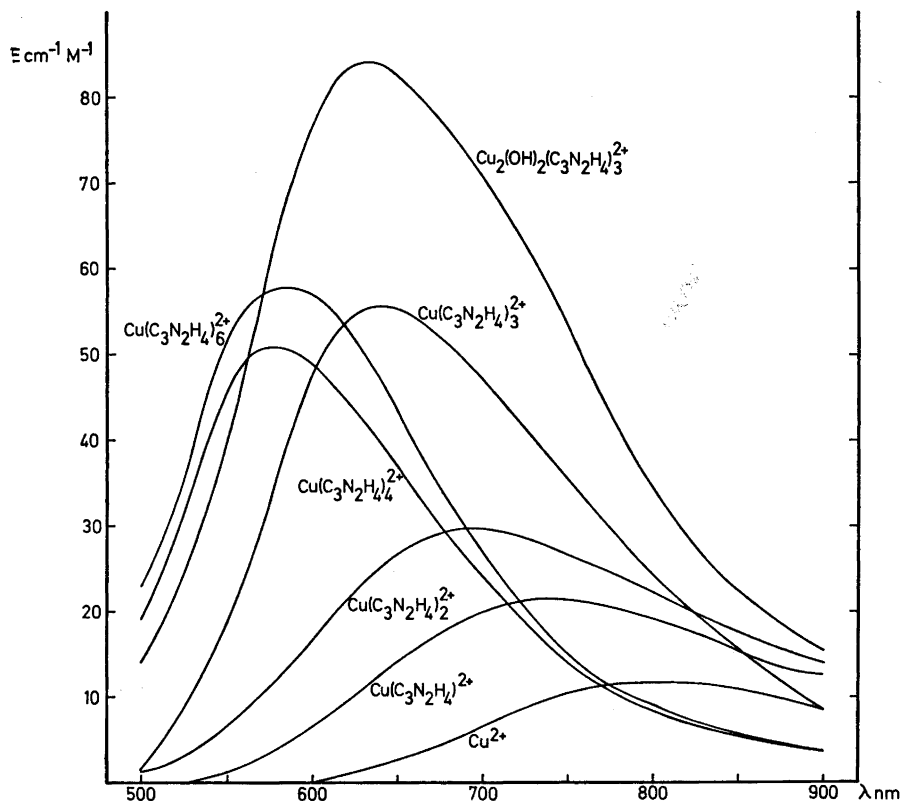


Fig. 4. The molar absorbance,  $\epsilon \text{ cm}^{-1} \text{ M}^{-1}$ , as a function of the wavelength  $\lambda \text{ nm}$  plotted for the different proposed copper species.

The *solubility measurements* indicated the existence of three different phases, I, II, and III. Phase I (light blue in colour) is formed in the alkaline region of the titrations, where the ratio  $C/B \leq 2$ . All attempts to get sharp powder photographs failed, but the composition of the phase was found to be approximately  $\text{Cu}(\text{OH})_{1.6}(\text{ClO}_4)_{0.4}$ . No imidazole could be found in this precipitate. This composition agrees closely with that in solutions without imidazole, reported earlier by Berecki-Biedermann<sup>9</sup>. An approximate solubility product  $\log(k_s \pm 3\sigma)$  has been determined. We found  $[\text{Cu}^{2+}]^5[\text{H}^+]^{-8}[\text{ClO}_4^-]^2 = 10^{33.64 \pm 0.35} \text{ M}^{-1}$ .

Phase II (dark blue in colour) and phase III (violet in colour) are obtained in the alkaline region of the titrations with  $C/B > 4$ .

Phase II seems to have the formula  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_4(\text{ClO}_4)_2$  and is easily obtained as long as  $4 < C/B < 8$ . At higher ratios with  $B < 0.001 \text{ M}$ , phase III is formed, otherwise a mixture of phase II and III seems to be formed. Phase II has been found to be monoclinic with  $\beta = 126.9^\circ$ ,  $a = 9.50 \text{ \AA}$ ,  $b = 16.40 \text{ \AA}$ , and

Table 6. Solubility and X-ray data for the three different solid phases  $\text{Cu}_5(\text{OH})_8(\text{ClO}_4)_2$ ,  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_4(\text{ClO}_4)_2$ , and  $\text{Cu}_3(\text{C}_3\text{N}_2\text{H}_3)_2(\text{C}_3\text{N}_2\text{H}_4)_8(\text{ClO}_4)_4$ . The solubility product  $k_s$  is defined according to the equation:

$$[\text{H}^+]^p[\text{Cu}^{2+}]^q[\text{C}_3\text{N}_2\text{H}_5^+]^r[\text{ClO}_4^-]^t = k_s$$

| Formula   | $\log(k_s \pm 3\sigma)$ | X-Ray characteristics  |
|---|-------------------------|--|
| $\text{Cu}_5(\text{OH})_8(\text{ClO}_4)_2$  | 33.64<br>0.35           |  |
| $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_4(\text{ClO}_4)_2$                                     | 14.65<br>0.09           | Symmetry: monoclinic with $\beta = 126.9^\circ$ ,<br>$a = 9.5 \text{ \AA}$ , $b = 16.4 \text{ \AA}$ , $c = 8.38 \text{ \AA}$ .                                 |
| $\text{Cu}_3(\text{C}_3\text{N}_2\text{H}_3)_2(\text{C}_3\text{N}_2\text{H}_4)_8(\text{ClO}_4)_4$ |                         | Symmetry: monoclinic with $\beta = 94.68^\circ$ ,<br>$a = 16.644 \text{ \AA}$ , $b = 15.524 \text{ \AA}$ , $c = 9.226 \text{ \AA}$ .<br>Spacegroup: $P2_1/a$ . |

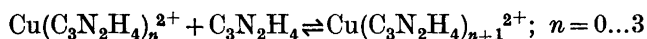
$c = 8.38 \text{ \AA}$ .<sup>1</sup> A determination of the solubility product for this phase gave  $\log(k_s \pm 3\sigma)$ :

$$[\text{Cu}^{2+}][\text{C}_3\text{N}_2\text{H}_5^+]^4[\text{H}^+]^{-4}[\text{ClO}_4^-]^2 = 10^{14.65 \pm 0.09} \text{ M}^3$$

Crystals of phase III were chosen and showed monoclinic symmetry ( $\beta = 94.68^\circ$ ). The composition was found to be  $\text{Cu}_3(\text{C}_3\text{N}_2\text{H}_3)_2(\text{C}_3\text{N}_2\text{H}_4)_8(\text{ClO}_4)_4$  with unit cell dimensions:  $a = 16.644 \text{ \AA}$ ,  $b = 15.524 \text{ \AA}$ , and  $c = 9.226 \text{ \AA}$ . The space group is  $P2_1/a$ .<sup>1</sup> Attempts to determine the solubility product for phase III failed. In order to calculate the solubility products, a special version of the least-squares program LETAGROPVRID (partly also HALTAFALL)<sup>27</sup> was employed.

## DISCUSSION

The emf measurements have given clear indications for the existence of the mononuclear complexes  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)^{2+}$ ,  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_2^{2+}$ ,  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_3^{2+}$ ,  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_4^{2+}$  and  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_6^{2+}$ , and most of the equilibrium constants have been determined with an accuracy better than 0.04 logarithmic units (Table 4). If we compare the value of the stepwise constants with earlier determinations (Table 1), we find that the absolute values of the constants are different, probably due to medium effects. However, the trend between the different steps seems to be similar. Considering the stepwise equilibria



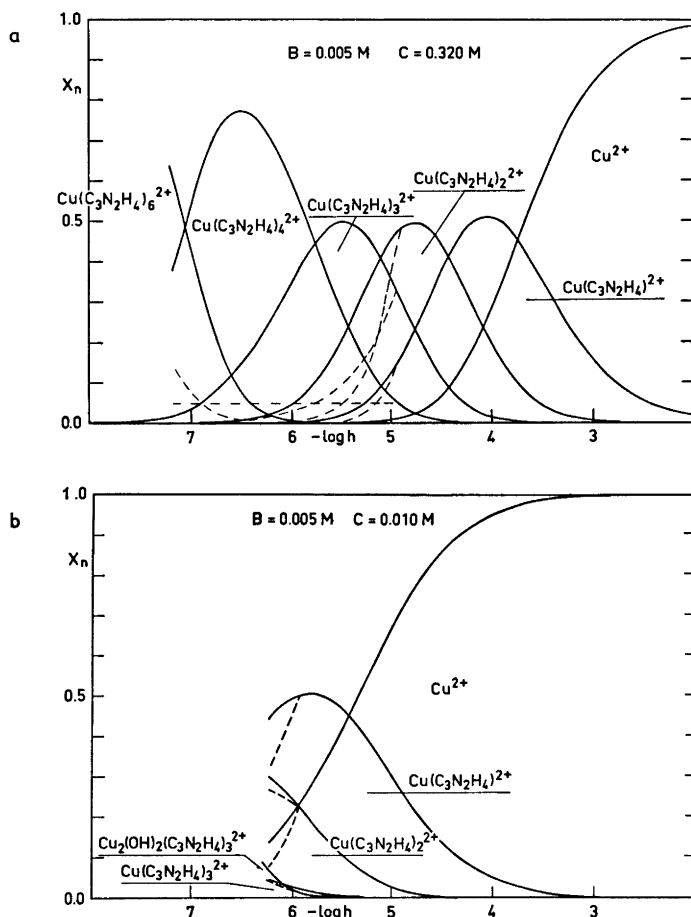
and

$$k_{n+1} = \frac{[\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_{n+1}^{2+}]}{[\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_n^{2+}][\text{C}_3\text{N}_2\text{H}_4]}$$

we find that the stepwise constants can be approximately expressed with the two parameters  $k_0$  and  $k$ ,  $k_{n+1} = k_0 \times k^n$ , where  $k_0 = 10 \exp(4.66) \text{ M}$ , and



$k = 10 \exp(-0.67)$ .  $k$  has been obtained as an mean value of  $10 \exp(-0.70)$ ,  $10 \exp(-0.68)$ , and  $10 \exp(-0.64)$ . Between the first and second step, the difference is  $10 \exp(-0.70)$  compared with  $10 \exp(-0.68)$  and  $10 \exp(-0.64)$  between the last two steps. However, the error may be within the error of the constants, and the differences are probably not significant. This two-parameter behaviour is not specific for copper imidazole, but has also been found in a number of ammonia systems studied by Bjerrum.<sup>22</sup> In the  $\text{Cu}^{2+} - \text{NH}_3$  case, he found  $k_0 = 10 \exp(4.15) \text{ M}$ , and the mean value in  $k = 10 \exp(-0.67)$ . The ease of successive addition of imidazole to copper seems to



*Figs. 5a and 5b.* Distribution curves  $X(\log h)_{BC}$  for the different copper imidazole species. The quantity  $X$  is defined as the fraction of total Cu present in each ion. The final proposed constants given in Table 4 have been used in the calculations. Full curves represent homogeneous equilibria, and broken lines equilibria with solid phases present. In diagram 5a, the solid phase is  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_4(\text{ClO}_4)_2$ , and in 5b,  $\text{Cu}_5(\text{OH})_8(\text{ClO}_4)_2$ . In each of the diagrams, areas with both full and broken curves are given, representing a range of supersaturation.

decrease when the number of imidazole ligands increases. A more detailed discussion concerning this trend in stability would require appropriate enthalpy and entropy data. Further studies in this direction are planned.

In the range  $Z_n > 3.5$ , where effects due to the species  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_6^{2+}$  are obvious, a calculation where a variation in  $k_a$  may be allowed shows that it is possible to get a still better fit to the data used, and that the effects due to  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_6^{2+}$  are remaining. However, it is very difficult to get an accurate value in  $k_6$ , as a change in  $\text{p}k_a$  with 0.01 units will change  $\log k_6$  with 0.5 units (Table 4).

In addition to the mononuclear copper imidazole complexes, we have also found evidence for the formation of one or more mixed polynuclear  $\text{C}_3\text{N}_2\text{H}_4\text{-OH}^- - \text{Cu}^{2+}$ -complexes. We have, as a working hypothesis, proposed the species  $\text{Cu}_2(\text{OH})_2(\text{C}_3\text{N}_2\text{H}_4)_3^{2+}$  to be the main one. Other complexes or complex combinations might also be possible. It is necessary to cover a greater data range before these can be determined exactly. Further studies in this direction are planned.

Curves showing the distribution between the different species and solid phases are given in Figs. 5a and 5b.

The spectrophotometric data were treated separately from the emf data, and here again the best explanation was given by the complexes:  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_n^{2+}$ , ( $n = 1 \dots 6$ ) and  $\text{Cu}_2(\text{OH})_2(\text{C}_3\text{N}_2\text{H}_4)_3^{2+}$ . The absorption peaks are displaced towards shorter wavelengths as the number of imidazole ligands in the complexes increases (from  $n = 1 \dots 4$ ). However, the peak for the ion  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_6^{2+}$  does not follow this trend, but has its maximum at about the same wavelength as  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_4^{2+}$ . This peak displacement agrees with earlier findings in complexes between copper and nitrogen containing ligands.<sup>23-26</sup> Furthermore, the different peaks are not symmetric around a maximum, but are somewhat displaced towards a longer wavelength. It is of interest that the absorption for  $\text{Cu}_2(\text{OH})_2(\text{C}_3\text{N}_2\text{H}_4)_3^{2+}$  is strongest, and that the maximum for the extinction curve corresponding to  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_3^{2+}$  is higher than that corresponding to  $\text{Cu}(\text{C}_3\text{N}_2\text{H}_4)_4^{2+}$ . Otherwise the extinction coefficients seem to increase with increasing number of ligands in the complexes. In the future we hope to be able to discuss these spectra more fully along the lines of ligand field theory.

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