The Solution Chemistry of Copper and Nickel Complexes with Dimethylglyoxime

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The distribution of $^{64}\text{Cu}(\text{II})$ at $25^\circ\text{C}$ between chloroform and 0.1 M perchlorate solutions has been studied as a function of $\text{H}^+$ and $\text{HA}$ (dimethylglyoxime) in the aqueous phase and of $B$ (quinoline or dodecylamine) in the organic phase. From the data the following constants have been calculated:

- $\text{CuA}_4 \rightleftharpoons \text{CuA}_3 + \text{A}^-$; $\log K_1 = 0.93 \pm 0.05$
- $\text{Cu}^{2+} + 2\text{A}^- \rightleftharpoons \text{CuA}_4$; $\log K_2K_3 = 19.24 \pm 0.06$
- $\text{CuA}_4$ (in CHCl$_3$) + $B$ (in CHCl$_3$) $\rightleftharpoons \text{CuA}_3B$ (in CHCl$_3$); $\log x_B = 2.04$ (quinoline) and 3.36 (dodecylamine). The data give no evidence of CuA$^+$; we conclude that $\log K_1 \leq \log K_2 - 1.2$.

The solubility of CuA$_4$ in 0.1 M NaClO$_4$ and chloroform has been determined. The solutions were saturated by slow filtration through columns packed with solid radioactive CuA$_4$. Results: $7.9_1 \times 10^{-3}$ M (0.1 M NaClO$_4$), $1.05_3 \times 10^{-3}$ M (wet chloroform) and $1.02_2 \times 10^{-3}$ M (dry chloroform). From a study of the solubility of CuA$_3$ in 0.1 M Na(OH)$_2$ClO$_4$ the hydrolysis constant of CuA$_4$ was determined: $\log x_H = -10.60$. The solubility of NiA$_4$ in chloroform solutions of quinoline or dodecylamine was studied and no reaction between NiA$_4$ and B was found.

These results are compared with previous data$^4$ on NiA$_4$ and it is concluded that the large differences between NiA$_4$ and CuA$_4$ are due to the fact that Cu$^{2+}$ in CuA$_4$ has a tendency to be five-coordinated while Ni$^{2+}$ in NiA$_4$ has only the coordination number of four.

An important contribution to the understanding of the differences of properties between Ni and Cu-complexes with dimethylglyoxime (HA) has recently been made by Frasson, Bardi and Bezzi$^1$ by their X-ray determination of the crystal structure of the copper salt, CuA$_4$. This, together with the determination of the structure of NiA$_3$ by Godycki and Rundle$^2$, means that we are now well-informed about the structures of the two compounds in the solid state and can make some guesses about the linkages that determine the lattice energy. In the case of copper, Cu$_2$A$_4$ dimers are formed in the crystal, while in the case of nickel NiA$_4$ monomers are formed. These units are probably linked with each other in the crystal by van der Waals’ forces, but in the case...
of NiA₂ there may also exist long Ni—Ni bonds (3.245 Å against 2.492 Å in the metal³ and 3.084 Å in NiF₃, which has a rutile lattice⁴).

In the solid medium with its rather high density of bond-forming atoms (N and O) nickel has a coordination number of four in NiA₂, except for the two rather long and probably weak metal bonds, while copper forms an additional coordinate link with an oxygen atom in the neighboring CuA₂ molecule and therefore has a coordination number of five in the crystal state. Consequently, Cu does not lie in the same plane as the four metalbonding N atoms of dimethylglyoxime, while Ni does.

It is thus quite possible that the forces between the NiA₂ or Cu₃A₃ molecules in the solid state (lattice energy) may be of the same order of magnitude and that the solubilities in inert non-solvating solvents may therefore also be about the same for the two salts. A more complete understanding of the differences between NiA₂ and Cu₃A₃ may therefore be obtained from a study of the solution chemistry of the two complexes.

The work reported here includes the determination of the complexity constants for the reaction M²⁺ + 2A⁻ ⇌ MA₂ by the distribution technique (cf. Dyrsen, Krasovec, and Sillén⁵ for nickel), of the distribution constants of MA₂ between chloroform and water, and of the solubilities of MA₂ in chloroform. Furthermore, the reaction MA₂ + B ⇌ MA₂B (B = quinoline or n-dodecylamine) was studied in chloroform.

**EXPERIMENTAL**

**Chemicals.** Chloroform ("Merck's p.a. für Chromatographie") was washed with distilled water to remove the 1% abs. alcohol and to saturate the solvent with water. Dimethylglyoxime (Kebo's p.a. reagent for nickel) was not further purified or recrystallized. n-Dodecylamine (two white crystallized products from Fluka and Light & Co) had a melting point of 26—28°C and was not further purified. Care was taken to avoid contact with CO₂ when handling the amine or its solution in chloroform. Quinoline (synthetic product, Kebo puriss., b.p. 233—237°C) and triethanolamine (Fluka, Switzerland, colorless puriss. quality) were also used without further purification. The NaClO₄ was made according to a technique used in this laboratory⁶. Other chemicals (HClO₄, NH₃, alcohol, etc.) were of analytical grade.

The radioactive copper, 12.8 h ⁶⁵Cu, was obtained by irradiation of weighed pieces (about 200 mg) of pure sheet-copper in the Swedish reactor R 1; the neutron flux used was between 5 and 20 × 10¹¹ n cm⁻² sec⁻¹. After irradiation the copper was dissolved in conc. HNO₃. This solution was evaporated to dryness and the copper nitrate was dissolved in 25 ml of 0.1 M HClO₄. This stock solution was then further diluted with 0.1 M NaClO₄. The purity of the ⁶⁵Cu nuclide was checked by following the decay over a week.

The radioactive Cu₃A₃ was synthesized according to Tschugaeff⁷. However, his method was slightly modified as follows: 10 mmoles of dimethylglyoxime (HA) were dissolved in a hot solution of 2 ml of conc. NH₃ × 20 ml of abs. alcohol. 5 ml of a hot solution of 1 M CuSO₄ with radioactive ⁶⁵Cu was added. On chilling, Cu₃A₃ crystallized out of the dark solution. The crystals were washed with alcohol and dried on filter paper at room temperature.

NiA₂ was simply precipitated from a saturated solution of dimethylglyoxime in water with a solution of NiCl₂.

**Analytical procedures.** For the analysis of dimethylglyoxime in 0.1 M NaClO₄ and in chloroform solutions, the dimethylglyoxime was reacted with an excess of nickel chloride in an alcohol-chloroform mixture using triethanolamine as a proton-acceptor. The UV light absorption of the NiA₂ formed was measured at 365 mµ. At this wave-length the absorption did not seem to vary with the conc. of quinoline in the chloroform solution. The extinction coefficient of NiA₂ at 365 mµ is 3 356 M⁻¹ cm⁻¹. The same wave-length

was used for the determination of the solubility of NiA₄ in chloroform solutions of quinolone or dodecylamine.

The analysis of the conc. of copper was made radiometrically utilizing the annihilation radiation of the positrons formed in the decay of ⁶⁴Cu. The gamma quanta were counted in a Tracerlab SC-57 low background well scintillation counter connected with a Tracerlab SC-18A Superscaler or SC-73 Versatime II scaler.

**Solubility experiments.** Solutions of quinoline or n-dodecylamine in chloroform were saturated with dimethylglyoxime or its nickel and copper salts, NiA₄ and CuA₄, by filtering the solutions through columns with a bed 7-10 cm thick at a flow rate of about 1 cm min⁻¹. It is an experience at our laboratory that solutions that flow from such columns are saturated. This was checked in our case by filtering some solutions twice through a column (or back-washing), and by variation of the flow rate and column height. The results agreed also with experiments where equilibrium was obtained by shaking the solutions over night. These experiments confirm that the diffusion layer outside the surface of the solid phase is much more effectively broken down in a filtering column than in a shaking process. Solutions of 0.1 M NaClO₄ + 0.0001 M HClO₄ were saturated with dimethylglyoxime in a similar manner and the solubility of CuA₄ in 0.1 M NaOH, ClO₄ was studied by the same technique.

**Distribution experiments.** The two phases (15 ml of each) were made up as follows. The organic phase was either pure chloroform or a solution of quinoline or n-dodecylamine in chloroform. Dimethylglyoxime was added as a saturated solution (0.005 M) in 0.1 M NaClO₄ (+ 0.0001 M HClO₄). The hydrogen ion concentration of the aqueous layer ([H⁺]) was adjusted with three solutions: 0.09 M NaClO₄ + 0.01 M HClO₄, 0.09 M NaClO₄ + 0.01 M Na-acetate, and 0.09 M NaClO₄ + 0.01 M NaOH. The final volume of the aqueous phase (15 ml) was made up with 0.1 M NaClO₄ after addition of radioactive copper (see above).

The two phases were shaken for 1-18 h and centrifuged. No heating of the solutions was observed after 10 min centrifugation. The value of -log [H⁺] was measured with a glass electrode standardized against a solution of 0.01 M HClO₄ + 0.09 M NaClO₄ (-log [H⁺] = 2.00). The copper concentration of each phase was measured radiometrically as described above. Care was taken not to contaminate the sample of the chloroform layer with the more active aqueous layer. No difficulties were met in obtaining material balance; the sum of intensities of the two phases was constant for each sample of irradiated copper when corrected for the decay of ⁶⁴Cu.

All experiments were carried out at 25°C in constant temperature rooms and the ionic strength of the aqueous solutions was kept constant at 0.1 M using mainly NaClO₄.

**SYMBOLS AND EQUILIBRIUM CONSTANTS**

HA = dimethylglyoxime, CH₃C(:NOH)C(:NOH)CH₃
B = quinoline, C₇H₇N, or n-dodecylamine, C₁₅H₃₂NH₂
HAc = acetic acid, CH₃COOH

\[ K_a = \frac{[H^+][A^-][HA]^{-1}}{[HA]} \]
\[ K_d = \frac{[HA]_{org}[HA]^{-1}}{[HA]} \]
\[ K_B = \frac{[HAB]_{org}[HA]_{org}[B]_{org}}{[HAB]_{org}[HA]_{org}[B]_{org}^{-1}} \]
\[ K_{n2} = \frac{[HAB]_{org}[HA]_{org}[B]_{org}^{-1}}{[HAB]_{org}[HA]_{org}[B]_{org}^{-1}} \]

\[ \beta_1 = \frac{[MA^+][M₂^+]^{-1}[A^-]^{-1}}{[MA]_{org}[M₂]_{org}^{-1}}; M = Ni \text{ or } Cu \]
\[ \beta_2 = \frac{[MA][M₂^+]^{-1}[A^-]^{-2}}{[MA]_{org}[M₂]_{org}^{-1}}; \beta_1 = K_4; \beta_2 = K_4K_2 \]
\[ \lambda_2 = \frac{[MA]_{org}[MA]_{org}}{[MA]_{org}[MA]_{org}^{-1}} \]
\[ \kappa_B = \frac{[MAB]_{org}[MA]_{org}[B]_{org}^{-1}}{[MA]_{org}[MA]_{org}[B]_{org}^{-1}} \]
\[ \kappa_H = \frac{[H^+][MA]_{org}[OH^-][MA]_{org}^{-1}}{[MA]_{org}[MA]_{org}^{-1}} \]

\[ q = \text{net distribution ratio (org/aq)} \]

\[ [HA]_{tot} = \text{initial total conc. of HA in the aqueous phase} \]
\[ [Cu]_{tot} = \text{initial total conc. of copper in the aqueous phase} \]

Fig. 1. Distribution of nickel (upper curve) and copper between chloroform and 0.1 M NaClO₄ as a function of log [HA]−log [H⁺]. Normalised curves 𝑌 = −log (1 + 𝑝𝑣 + 𝑠), 𝑋 = −log 𝑣 in position of best fit, for 𝑝 = 0 (full-drawn) and 𝑝 = 1 (dotted). The thin lines are the asymptotes.

COMPLEX FORMATION OF CuA₄

Recently it has been shown by Dyrssen, Krašovec, and Sillén that the complex formation of nickel with dimethylglyoxime could be studied by the distribution method with reasonably good accuracy. This method is also used here for the determination of β₂ and λ₂ for the copper-dimethylglyoxime-chloroform system. The general equations in our previous paper will not be repeated here. The distribution data are given in Table 1 and plotted as log q against log [HA][H⁺]⁻¹ in Fig. 1.

[HA], the free conc. of dimethylglyoxime in the aqueous phase, was calculated from the initial conc. of HA, [HA]₀, with the following two equations, which allow for the amount of free HA in the organic phase, [HA]₀, and the small amount bound to Cu as CuA₄ both in the organic and aqueous phase (equal volumes of each phase):

\[
[CuA₄] = \frac{[Cu]₀}{1 + λ₂ + 10^{−4.84}[H⁺][HA]₀⁻²}
\]

\[
[HA]₀ = \frac{[HA]₀ − 2(1 + λ₂)[CuA₄]}{1 + Kₐ}
\]

Table 1. Distribution of Cu\textsuperscript{2+} between chloroform and 0.1 M perchlorate solutions at 25°C. The concentrations refer to the initial total concentrations in the aqueous phase. The data are plotted in Fig. 1 as log q against log [HA] - log [H\textsuperscript{+}].

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<th>[Ac\textsubscript{tot}] (10^{-4}) M</th>
<th>[HA\textsubscript{tot}] (10^{-3}) M</th>
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* λ\(_2\) was calculated from these experiments by dividing the sum of counts per minute of the organic layers (23 778) with the corresponding value of the aqueous layers (201 800).

The constants λ\(_2\) = 10\(^{-5.93}\) and 10\(^{4.42}\) were obtained from a plot log q against log [HA]$_{tot}$[H\textsuperscript{+}]$^{-1}$. $K_d$ = 0.0786 was obtained by dividing the solubility of dimethylglyoxime in CHCl\(_3\) (saturated with water), 3.94 × 10$^{-4}$ M, by that in 0.1 M NaClO\(_4\) + 0.0001 M HClO\(_4\), 5.01 × 10$^{-3}$ M. In most experiments (see Table 1) [Cu\textsubscript{tot}] is considerably smaller than [HA]$_{tot}$. It can therefore not be a serious error to neglect the amount of A bound as CuA\textsuperscript{2+}.

The influence of the acetate ions on the distribution is greater in the case of copper than in the case of nickel as λ\(_2\)\(_B\) and λ\(_2\) for MA\(_4\) are smaller and the constants for the formation of MA\(_2^+\) and MA\(_4\) are larger than for nickel. However, at low values of [A\textsuperscript{2+}] (low pH) the formation of acetic acid will predominate over the formation of copper acetate complexes, and at high values of [A\textsuperscript{2+}] the dominating complex will be CuA\(_4\). If one uses the stability constants for the copper-acetate system given by Pedersen \* and corrected with Kielland's 10\(^{th}\) activity factors, it can be calculated for the acetate concentrations used, that the lowering of log q is less than 0.05 in the most sensitive region. This

was confirmed experimentally by varying the amount of acetate buffer in the aqueous phase; no systematic deviations can be observed. As the acetate ion concentration must be kept below 0.005 M, the buffering capacity of the aqueous phase is not very large. We therefore believe that the scattering of the data in Fig. 1 is due in part to errors in the measurement of \(-\log [H^+]\) of the sampled aqueous layers. This error is of course not serious for the horizontal part of the curve.

The variation of \(\log q\) with \(\log [HA][H^+]^{-1}\) plotted in Fig. 1 is ascribed to reactions between \(Cu^{2+}\) and HA and we may compare the data with those in the study of the complex formation with nickel\(^5\) (cf. p. 57, Fig. 2 in that work; the signs of the two axes have there been reversed to simplify the comparison with solubility data). It may then be seen that the data can be fitted to the normalized curve\(^6\):\(^11\) \(Y = -\log (1 + pv + v^2)\), \(X = -\log v\) with \(p = 0\) (full-drawn curve in Fig. 1), but not with \(p = 1\) (dotted). Thus no evidence is found of CuA\(^+\) in appreciable amounts just as in the case with nickel\(^5\), and the same conclusion may be drawn about the parameter \(p = \sqrt{K_1/K_2} \leq 0.25\). Using the value of the horizontal asymptote of the distribution curve, \(\log \lambda_2 = -0.93\), calculated from the data in Table 1, we find from the position of the best fit with the other data for the reaction

\[ Cu^{2+} + \frac{1}{4}2 HA \rightleftharpoons CuA_2 + 2 H^+ \]

the equilibrium constant

\[ \log \beta_2 + 2 \log K_a = -2(0.84 \pm 0.03) \]

from the point of intersection between the asymptotes in Fig. 1. Using \(K_a = -10.46\) calculated from solubility data\(^5\):\(^12\) we obtain \(\log \beta_2 = 19.24 \pm 0.06\).

We have thus determined the following set of equilibrium constants for the \(CHCl_3\) -- 0.1 M NaClO\(_4\) system at 25°C:

\[ \begin{align*}
\log \lambda_2: & \quad 2.51 \pm 0.10 \text{ (Ni)} \quad \text{and} \quad -0.93 \pm 0.05 \text{ (Cu)} \\
\log \beta_2: & \quad 17.24 \pm 0.07 \text{ (Ni)} \quad \text{and} \quad 19.24 \pm 0.06 \text{ (Cu)}
\end{align*} \]

The distribution curves determined by these constants and log \(K_a = -10.46\) are shown as full-drawn curves in Fig. 1. It may be seen that, at all values of

log [HA][H⁺]⁻¹, the extraction of Ni is much larger than the extraction of Cu, the larger value of β₂ for Cu being unable to counterbalance the large difference in log λ₂. Fig. 2 shows the percentage extraction for the two metals as a function of log [HA][H⁺]⁻¹. The fact that nickel is readily extracted with dimethylglyoxime and chloroform while copper is not, is well-known to analytical chemists even if the explanations given hitherto have been based on insufficient experimental data.

The values of λ₂ and β₂ will be further discussed below.

FORMATION OF MIXED COMPLEXES WITH QUINOLINE AND DODECYLAMINE

The reason why λ₂ is so low for CuA₂ in comparison with NiA₂ is probably that Cu³⁺ in CuA₂ has a tendency to coordinate with H₂O and to be linked thereby with the water lattice. NiA₂ on the other hand does not form any strong bonds with water, so it will have a fairly large value of λ₂. Dimethylglyoxime itself (HA) can form hydrogen bonds both as an acceptor and donor and consequently K₆ is rather small.

If Cu²⁺ in CuA₂ can be five-coordinated also in solution it should be possible to form a mixed complex (adduct) CuA₂B in the organic phase with a hydrophobic uncharged ligand B (base) and thus increase the distribution ratio q for copper:

\[ q = \frac{[CuA_2]_\text{org} + [CuA_2B]_\text{org}}{[Cu^{+2}] + [CuA_2]} \]

If we carry out the experiment in the range where \([Cu^{2+}] \ll [CuA_2]\) the expression for q is simplified:

\[ q = \lambda_2 + \lambda_2 x_{B[B]_\text{org}} \]

Table 2. Distribution of Cu³⁺ between solutions of quinoline in chloroform and 0.1 M perchlorate solutions buffered with acetate. The concentrations refer to the initial conc. in the aqueous (copper, dimethylglyoxime and acetate) or organic phase (quinoline).

The data are plotted in Fig. 2 as log q against log [B]org.

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<th>[Cu]_\text{org}</th>
<th>[Ac]_\text{org}</th>
<th>[HA]_\text{org}</th>
<th>[B]_\text{org}</th>
<th>-log [H⁺]</th>
<th>log q₂</th>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>1.58 10⁻⁴ M</td>
<td>4.20 10⁻⁴ M</td>
<td>-0.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>5.88 10⁻⁴ M</td>
<td>-0.03</td>
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</tr>
<tr>
<td>1.58 10⁻⁴ M</td>
<td>6.03 10⁻⁴ M</td>
<td>+ 0.28</td>
<td></td>
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<tr>
<td>1.58 10⁻⁴ M</td>
<td>6.34 10⁻⁴ M</td>
<td>+ 0.55</td>
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</tr>
<tr>
<td>1.58 10⁻⁴ M</td>
<td>6.34 10⁻⁴ M</td>
<td>+ 0.79</td>
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<td></td>
</tr>
<tr>
<td>1.58 10⁻⁴ M</td>
<td>5.37 10⁻⁴ M</td>
<td>+ 1.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Table 3. Distribution of Cu\(^{2+}\) between solutions of n-dodecylamine in chloroform and 0.1 M perchlorate solutions buffered with 0.1 mmole NH\(_3\) per 15 ml. The initial total conc. of dimethylglyoxime in the aqueous phase was 1.66 \times 10^{-3} M and the value of $-\log [H^+]$ varies between 8.6—8.9.

<table>
<thead>
<tr>
<th>[Cu](_{\text{tot}}) (10^{-4}) M</th>
<th>[B](_{\text{tot}}) M</th>
<th>log q</th>
<th>log q $-\log[B]_{\text{org}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.479</td>
<td>0.005</td>
<td>0.19</td>
<td>2.49</td>
</tr>
<tr>
<td>0.958</td>
<td>0.0133</td>
<td>0.59</td>
<td>2.47</td>
</tr>
<tr>
<td>0.0271</td>
<td>0.0133</td>
<td>0.56</td>
<td>2.44</td>
</tr>
<tr>
<td>0.479</td>
<td>0.02</td>
<td>0.75</td>
<td>2.45</td>
</tr>
<tr>
<td>0.271</td>
<td>0.02</td>
<td>0.74</td>
<td>2.44</td>
</tr>
<tr>
<td>0.958</td>
<td>0.04</td>
<td>1.04</td>
<td>2.44</td>
</tr>
<tr>
<td>0.958</td>
<td>0.05</td>
<td>1.17</td>
<td>2.47</td>
</tr>
<tr>
<td>0.271</td>
<td>0.06</td>
<td>1.14</td>
<td>2.36</td>
</tr>
<tr>
<td>0.479</td>
<td>0.1</td>
<td>1.40</td>
<td>2.40</td>
</tr>
<tr>
<td>0.0271</td>
<td>0.1</td>
<td>1.43</td>
<td>2.43</td>
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<td>2.05</td>
</tr>
<tr>
<td>0.271</td>
<td>1</td>
<td>1.47</td>
<td>1.47</td>
</tr>
</tbody>
</table>

The mean value of $\log q \left[\text{[B]}^{-1}\right]_{\text{org}}$ for \([B]_{\text{tot}} \leq 0.22\) M is $2.43 \pm 0.05$, which is equal to $\log \lambda_{W_{\text{org}}}$ (see text).

Quinoline and n-dodecylamine were chosen as B-ligands of different basicity. The hydrocarbon parts of these molecules are so large that the amount of B in the aqueous phase is negligible *, and the formation of CuA\(_2\)B in the aqueous phase may therefore be neglected. The pH of the aqueous phase was so high that the amount of BH\(^+\) could be neglected too.

The value of $\lambda_{\text{org}}$ for Ni is so large ($\log \lambda_{\text{org}} = 2.51$) that the distribution method is not very suitable for a study of a complex formation between NiA\(_2\) and quinoline and dodecylamine. We therefore chose to study the solubility of NiA\(_3\) in chloroform solutions of quinoline and dodecylamine. The same method was also used to study reactions between HA and B (see below the results with CuA\(_2\) and NiA\(_3\)).

Results. The data are given in Tables 2 (CuA\(_2\)-quinoline), 3 (CuA\(_2\)-dodecylamine), 4 (HA-quinoline), and 5 (HA-dodecylamine). The copper data are plotted in Fig. 3 and the HA-data in Fig. 5 as $log q$ and $log S$ against $log [B]_{\text{org}}$.

The data with quinoline in Fig. 3 can be fitted with the normalized curve $Y = \log (1 + v)$; $X = \log v$, which indicates that in addition to CuA\(_2\)(H\(_2\)O)\(_x\) (x is not determined in these experiments where the activity of H\(_2\)O is constant) a 1:1 complex is formed with quinoline and that Cu\(^{2+}\) can attain a coordination number of at least five in CuA\(_2\). No experiments with dodecylamine were made with [B]\(_{\text{org}}\) between 0 and 0.005 M since it was feared that the correction for the amount of dodecylamine bound to HA would be too large (see below). For this reason we did not obtain the part of

* The distribution constant of quinoline between chloroform and 0.1 M NaClO\(_4\) was determined as 471 ± 3 by S. Ekberg.

the curve, where appreciable amounts of both CuA₂ and CuA₂B are present in the organic phase. Deviations at \([B]_{\text{org}} > 0.22\ \text{M}\) are probably due to the self-association of dodecylamine in chloroform (cf. Fig. 5).

The equilibrium constant \(k_a\) of the reaction CuA₂ (in CHCl₃) + B (in CHCl₃) = CuA₂B (in CHCl₃) is obtained from the intercept of the two asymptotes, \(\log q = \log \lambda_2 (Y=0)\) and \(\log q = \log \lambda_2 k_B[B]_{\text{org}} (Y=X)\), to the curve (Fig. 3):

\[
\begin{align*}
\log k_B &= 2.04 \quad (B = \text{quinoline}) \\
\log k_B &= 3.36 \quad (B = \text{dodecylamine})
\end{align*}
\]

Fig. 4 shows that the solubility of NiA₂ is very little increased by the addition of quinoline or dodecylamine to the chloroform phase; the decrease at high \([B]_{\text{org}}\) is probably due to self-association of B. From the experiments we conclude that Ni²⁺ is four-coordinated in NiA₂. The value of the solubility of NiA₂ in chloroform, saturated with water, obtained by us is \(4.75 \times 10^{-4}\ \text{M}\), which agrees very well with the value of \(4.8 \times 10^{-4}\ \text{M}\) determined by Christopherson and Sandell [12], who saturated their solutions by shaking for 6 hours.

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Fig. 5. The solubility of dimethylglyoxime in chloroform as a function of the conc. of quinoline (full-drawn curve) or dodecylamine (dashed curve). The normalised curve \( Y = \log (1 + pv + v^2) \), \( X = \log v \) is fitted to the data. The best fit was obtained with \( p = 2 \).

Table 4. Solubility of dimethylglyoxime in wet chloroform solutions of quinoline at 25°C. Values of \( S \) in mmole per liter and molar conc. of quinoline: 0.392 (0), 0.391 (0.0025), 0.405 (0.005), 0.389 (0.01), 0.583 (0.025), 0.769 (0.05), 1.383 (0.1), 1.430 (0.14), 3.20 (0.2), 5.36 (0.3), 6.79 (0.4), 11.98 (0.5), 11.47 (0.6), 10.64 (0.6), 15.53 (0.7), 19.58 (0.8), 22.4 (0.9), 32.0 (1).

Table 5. Solubility of dimethylglyoxime in wet chloroform solutions of dodecylamine at 25°C. Values of \( S \) in mmole per liter and molar conc. of dodecylamine: 0.403 (0.0098), 0.439 (0.00196), 0.534 (0.0049), 0.638 (0.0098), 0.823 (0.0196), 1.86 (0.049), 3.97 (0.098), 7.42 (0.196).

Table 6. Distribution of Cu^{2+} between chloroform and aqueous solutions containing dimethylglyoxime and NH_3. Values of log \( g \) and molar conc. of NH_3 in the aqueous phase: \( -0.91 \) (0.0067), \( -0.81 \) (0.0333), \( -0.91 \) (0.107), \( -1.31 \) (0.6).

That also B can react with dimethylglyoxime itself is obvious from Tables 4 and 5 and Fig. 5, which shows the increase of the solubility of HA with \([B]_{org}\). The data seem to approach a line with slope 2, which corresponds to the formation of HAB; each hydrogen in the oxime groups seems to form a hydrogen bond with the acceptor molecule B. Using the technique of curve-fitting \(^{14,15}\) it was found that a curve \( Y = \log (1 + 2v + v^2) \), \( X = \log v \) fitted the data reasonably well except for dodecylamine concentrations above 0.1 M where probably self-association occurs (cf. Fig. 3). The equation of the curves can be derived as follows.

\[
S = [HA] + [HAB] + [HAB_2] = [HA][1 + K_B[B]_{org} + K_{B_2}[B]_{org}^2]
\]

The equations of the two asymptotes to the curve \( \log S \) vs \( \log [B]_{org} \) are

\[
\log S = \log [HA] = \log S_0
\]

\[
\log S = \log S_0 K_B[B]_{org}^2
\]

The parameters \( S_0 \) and \( K_B \) are obtained from the point of intercept of the asymptotes: \( S_0 = 3.94 \times 10^{-4} \) M and \( K_B = 1.80 \) (quinoline) and 2.74 (dodecylamine). From the difference between \( S \) and \( S_0 \) at this point we obtain \( K_B; \log K_B = 1.20 \) (quinoline) and 1.67 (dodecylamine) (cf. Ref.\(^{12}\)). The value of \( S_0 \) agrees fairly well with Christopherson and Sandell’s value \(^{13} 4.5 \times 10^{-4} \) M and very well with the value of Babko and Mikkelson \(^{14} 3.96 \times 10^{-4} \) M.

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The reactions between HA and B lower the value of [HA] in the aqueous phase, and will disturb an investigation of the complex formation of MA₄ and B if the value of log [HA][H⁺]⁻¹ is not sufficiently high. With quinoline the correction in the calculation of the conc. of free B, [B]₀/Q, is small as the total conc. of HA is always below 0.0021 M. This is not quite true with dodecylamine, which reacts more readily with HA.

REATIONS BETWEEN Cu₄ AND NH₃

The investigations with quinoline and dodecylamine showed clearly that Cu₄ could react with a base in chloroform and it was therefore thought worthwhile to see if the distribution ratio of copper could be lowered by the addition of NH₃ to the aqueous phase. Such an experiment might indicate the existence of a five-coordinated copper complex, Cu₄NH₃. The data in Table 6 show, however, that q is very little affected by the addition of NH₃ at pH where the hydrolysis of Cu₄ may be neglected (see below). We therefore conclude that for NH₃-concentrations less than 0.2 M, Cu₄(H₂O) is the dominating complex in the aqueous phase. This is in agreement with the fact that the equilibrium constant for the reaction Cu(NH₃)₄⁺ + NH₃ ⇌ Cu(NH₃)₃⁺ is small. It can then be concluded that the method of removing Cu₄ from the chloroform layer by shaking the chloroform with dilute ammonia, is an effect due to a low value of λ₂ and not due to the formation of a Cu₄NH₃ complex. In this procedure the nickel content in the organic phase is not appreciably lowered if the pH is sufficiently high.

THE SOLUBILITIES OF Ni₄ AND Cu₄

It is a well-known fact that the Ni²⁺ but not Cu²⁺ may be precipitated from aqueous solutions with dimethylglyoxime. Following Godycki and Rundle, Sharpe and Wakefield suggested that the forces in the solid state and especially the Ni—Ni bond offered an explanation of the great difference in solubility between the copper and nickel complex. The new X-ray data on Cu₄ and the fact that Cu₄ is known to be less extractable than Ni₄ in spite of the fact that Cu²⁺ forms stronger complexes, suggested, however, that solvation effects should be much more important.

If this was true the solubility of the two salts in an organic non-solvating solvent should not be very different. We obtained the following results for chloroform, which presumably does not coordinate with the central atom:

For Ni₄:
\[ 4.75 \times 10^{-4} \text{ M (wet)} \]
\[ 10.5 \times 10^{-4} \text{ M (wet)} \text{ and } 10.2 \times 10^{-4} \text{ M (dry)} \]

For Cu₄:
\[ 10.7 \times 10^{-4} \text{ M (wet)} \text{ and } 10.2 \times 10^{-4} \text{ M (dry)} \]

The values of the solubilities of the salts in 0.1 M NaClO₄ saturated with chloroform can be estimated by dividing the solubilities in chloroform with λ₂:

For Ni₄:
\[ \lambda_2^{-1} \times 4.75 \times 10^{-4} = (1.5 \pm 0.3) \times 10^{-6} \text{ M} \]

For Cu₄:
\[ \lambda_2^{-1} \times 10.5 \times 10^{-4} = (9 \pm 1) \times 10^{-3} \text{ M} \]

The estimated value for Ni₄ agrees fairly well with a value given by Christopherson and Sandell for 0.05 M NaCl saturated with CHCl₃: 1.23 \times 10^{-6} M and for Cu₄ in 0.1 M NaClO₄ the value measured by us is 7.91 \times 10^{-3} M, which also agrees reasonably well with the estimated value.

From these experiments we conclude that lattice the energies of the two salts are about the same, and that the large difference in water-solubility must be due to solvation of CuA₂, which thereby is linked to the water lattice. Furthermore, we conclude from the solubilities of CuA₂ in dry and wet chloroform, that the complex may be unhydrated in wet chloroform. This conclusion could not be drawn from the distribution experiments.

The crystal structure of CuA₂ and experiments reported above suggest that copper may be five-coordinated in CuA₂ and form a monohydrate, CuA₂(H₂O), in water. The low solubility of NiA₂ in water is then partly due to the forces in the solid state and partly to the fact that it contains hydrophobic groups and no tendency to be five- or six-coordinated (and solvated). The importance of the forces in the solid state (but not necessarily the Ni—Ni bond) is shown by the fact that the ethylmethylglyoxime nickel salt is more soluble in water despite the increased size of the hydrophobic groups. How much the long Ni—Ni bond contributes to the lattice energy is still open to speculation.

THE HYDROLYSIS OF CuA₂H₄O

If it is correct that CuA₂ can coordinate with a water molecule it should be possible to find a complex CuA₂OH⁻ in alkaline solutions provided the hydrolysis of CuA₂H₂O is not too weak.

As chloroform reacts with alkali we preferred to study the hydrolysis of CuA₂H₂O by measuring the solubility of CuA₂ in 0.1 M Na(OH₂ClO₄) as a function of \(-\log [H^+]\). As seen from Fig. 6 the solubility increases with pH \((-\log [H^+])\) and the data could be fitted to the normalized curve \(Y = \log (1 + v)\), \(X = \log v\). In addition to CuA₂ there must then be a complex with one proton less than in CuA₂. Our guess is CuA₂OH⁻, but the proton can equally well come from one of the hydrogen bridges in CuA₂. To explain the experimental curve we shall write the solubility of CuA₂ as

\[
S = [\text{CuA}_2\text{H}_2\text{O}] + [\text{CuA}_2\text{OH}^-] = [\text{CuA}_2\text{H}_2\text{O}](1 + x_H[H^+]^{-1})
\]

In the neutral range (0.1 M NaClO₄)

\[
S = [\text{CuA}_2\text{H}_2\text{O}] = 7.91 \times 10^{-3} \text{ M}
\]

We then obtain

\[
\log S = -2.10 + \log (1 + x_H[H^+]^{-1})
\]
The constant $\kappa_H$ may be found from the position of the asymptotes to the curve at the best fit: $\log \kappa_H = -10.60$.

This value may be compared with $\log K_1 \sim -7$ for the hydrolysis of $\text{Cu(H}_2\text{O)}^{2+}_n$. Obviously, the hydrolysis of $\text{CuA}_2\text{H}_2\text{O}$ is much weaker than the hydrolysis of the charged aqueous complex. Alternatively it can be said that the complex formation with the strong base $\text{OH}^-$ is much weaker. Using $\log [\text{H}^+][\text{OH}^-] = -13.81$ in 0.1 M $\text{NaClO}_4$ we may calculate $\log K_1$ as 3.21 for $\text{CuA}_2 + \text{OH}^- \rightleftharpoons \text{CuA}_2\text{OH}^-$. 

**CONCLUSIONS**

From distribution experiments no evidence is found of the presence of significant amounts of $\text{CuA}^+$, and it is concluded that $\log K_1 \leq \log K_2 - 1.2$ as in the case of nickel.$^5$ As this is not true for either ethylenediamine,$^{15}$ acetylacetone$^{15}$, or $\beta$-isopropyltropolone$^{21,22}$ we conclude that the formation of the second complex is favored by the formation of two hydrogen bonds.

The distribution of copper can be increased by the addition of a base (quinoline or dodecylamine) to the chloroform phase. The reaction, which is an example of the so-called "synergic" effect,$^{24}$ can be written as follows:

$$\text{CuA}_2(\text{org}) + \text{B(organ)} \rightleftharpoons \text{CuA}_2\text{B(organ)}$$

(eq. const. $\kappa_B$)

Dodecylamine is a stronger base than quinoline and consequently gives a higher value of $\kappa_B$. The solubility of $\text{NiA}_2$ in chloroform is very little affected by the addition of quinoline or dodecylamine. From these experiments it is concluded that $\text{Cu}^{2+}$ has a tendency to be five-coordinated in $\text{CuA}_2$ while $\text{Ni}^{2+}$ in $\text{NiA}_2$ has not. From the values of the distribution constants of $\text{NiA}_2$ and $\text{CuA}_2$ it is concluded that the large difference can only be explained by the fact that the $\text{CuA}_2$ complex is solvated in the aqueous phase. As $\text{CuA}_3$ is five-coordinated in the crystal state as well as in chloroform solutions of quinoline or dodecylamine it seems probable that the primary complex in the aqueous phase is $\text{CuA}_2\text{H}_2\text{O}$. This complex is then linked with the water lattice. — For $\beta$-isopropyltropolone$^{22}$ we obtained $\lambda_2(\text{Cu}) > 1000 > \lambda_2(\text{Ni}) > 100$, and the copper salt of tropolone is planar (four-coordinate) in the crystal state$^{23}$. The difference between dimethylglyoxime and $\beta$-isopropyltropolone as chelate-forming ligands may be explained by the smaller tendency of the two dimethylglyoximate ions to fill the electron gaps in the $\text{Cu}^{2+}$ ion. In the $\text{Cu(II)}$ di$\beta$-isopropyltropolonate complex the gaps are probably more effectively filled and no coordination power is left.

The solubilities of $\text{NiA}_2$ and $\text{CuA}_2$ have been determined in wet chloroform, and were found to be not very different. From these experiments it is concluded that the lattice energy is about the same for both complexes and that the long Ni—Ni bonds in $\text{NiA}_2$ are weak. The large difference in water solubility can be explained by the solvation of $\text{CuA}_2$ and is a consequence of the tendency of $\text{Cu}^{2+}$ to be five-coordinated in $\text{CuA}_2$. The low solubility of $\text{NiA}_2$ in water is an effect of the weak tendency of $\text{NiA}_2$ to co-ordinate water molecules.

As pH increases, the solubility of CuA₂ in 0.1 M Na₂(OH,ClO₄) will increase. The data show that one proton comes off, and our guess is that this is not a proton from one of the two strong hydrogen bridges but one from the associated water molecule in Cu₂H₂O.

Note. When our work was completed we obtained a microfilm of a thesis by D. Fleischer with the title "A thermodynamic study of some factors affecting the stability and solubility of metal chelates". This work contains a determination of the solubilities of the nickel and copper salts of dimethylglyoxime in water, chloroform, benzene and n-heptane at various temperatures. The following values were obtained at 25°C (Ni, Cu): 1.05 × 10⁻⁴, 5.68 × 10⁻⁴ M (H₂O); 4.62 × 10⁻⁴, 1.24 × 10⁻⁴ M (CHCl₃); 7.53 × 10⁻⁴, 4.5 × 10⁻⁴ M (C₆H₆); 2.5 × 10⁻⁴, 1.84 × 10⁻⁷ M (C₆H₄). The values for water and chloroform are not very different from our values. The heats of solution (ΔH°) in water were 9.0 kcal (Ni) and 0.0 kcal (Cu). According to Fleischer this difference must be due to larger solvation energy of CuA₂ in water and to the fact that copper can exhibit a coordination number higher than four. Fleischer also states that the addition of n-butylamine permitted quantitative extraction of CuA₂ into chloroform. From the solubilities in benzene and heptane Fleischer concludes that the crystalline CuA₂ is more stable than NiA₂ by about two or three kilocalories. On the whole Fleischer's data and conclusions agree with our results, and as the two investigations have been carried out independently still more reliability can be placed on the present explanation of the chemical differences between NiA₂ and CuA₂.

Note added in proof. The spectra of 5 × 10⁻⁴ M CuA₂ in 0.1 M NaClO₄ with 1.503 × 10⁻⁴ M HA has recently been studied in our laboratory as a function of -log [H⁺] by Mrs. Solveig Ekberg and Mr. Sven Hansson. The light absorption between 350 and 450 μm increases from 10 to 90% between -log [H⁺] = 3 and 4, but the shape of the curve remains unchanged. As neither Cu⁺⁺ nor HA absorbs light in this region, the experiments indicate that below pH = 7 CuA₂ is the only complex formed: Cu⁺⁺ + 2HA ⇄ CuA₂⁻ + 2H⁺. From the data the equilibrium constant of this reaction could be calculated as log β₂K₂ = 2(0.55 ± 0.04). This value is in complete agreement with the result from the extraction work reported above.

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