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EXTRACTION OF Cu(II) AND Ni(II) BY CAMPHORQUINONE DIOXIME

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Abstract—The extraction properties of three geometrical isomers (α-, β- and δ-) of D-camphorquinone dioxime (H₂CQD) with copper and nickel are described. Under extraction conditions isomerization occurred from α- and β-H₂CQD into δ-H₂CQD. The expected selectivity of δ-H₂CQD for nickel could not be established. On the contrary, copper formed complexes with lower pHₐₜ values than nickel. An ESR study showed that this was due to the fact that copper did not form a NN coordinated complex, but just like nickel a NO coordinated complex. UV spectroscopy proved that besides the Cu(HCQD)₂ complex a Cu₂(HCQD)₂(COD) complex is involved in copper extraction.

INTRODUCTION

The development of hydroxyoximes as commercial solvent extraction reagents for copper has prompted much research in the chemistry of such systems. Many attempts have been made to find a reagent that is selective for nickel above copper. In order to form stronger complexes with nickel than with copper, a reagent must be found that does not follow the normal Irving-Williams order of stabilities. This is only possible if nickel forms a different kind of complex with the reagent than copper does. Aliphatic α-dioximes did indeed extract nickel at lower pH than copper and this was explained by assuming that nickel formed a square planar complex with a low spin d⁸ configuration, while copper formed an octahedral complex by binding two additional water molecules. However, the extremely low rate of extraction does not make this system very attractive for commercial use.

Here we report on the separation properties of another kind of α-dioxime, camphorquinonedioxime H₂CQD. H₂CQD is known to exist in four isomeric forms (Fig. 1) which differ by the orientations of the OH groups. The rigid bicyclic skeleton is responsible for a larger NN distance than in aliphatic α-dioximes. NN coordination is the normal mode of coordination for vicinal dioximes but the large N . . . N distance in H₂CQD makes this kind of coordination less attractive. Recently it was reported that for copper only a NN coordinated H₂CQD complex could be isolated: Cu₂(HCQD)₂·H₂O·2 COD (Fig. 2b).

In contrast to this it was published that nickel forms stable NO coordinated complexes with α- and δ-H₂CQD (Fig. 2a) and an unstable NN coordinated com-

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Fig. 1. The four isomeric forms of camphorquinone dioxime.

Fig. 2. Two possible ways of coordination of camphorquinone dioxime with copper or nickel.
plex with $\beta$-H$_2$CQD. $\alpha$- and $\delta$-H$_2$CQD are likely to form NO coordinated complexes (Fig. 1) and if no isomerization takes place into $\beta$-H$_2$CQD it is to be expected that these two isomers react better with nickel than with copper. In this way the Irving-Williams order of stabilities might be broken.

For this reason we have studied the extraction properties of the camphorquinone dioxime isomers for copper and nickel and the kind of complexes which are responsible for the extraction.

**EXPERIMENTAL**

The optically active camphorquinone dioxime ligands were prepared from (+) camphor according to the procedures of Forster.

$$\alpha$-H$_2$CQD: $[\alpha]_D = 25.7$° ($-24.1°$); $\gamma$-H$_2$CQD could not be isolated pure. $\delta$-H$_2$CQD: $[\alpha]_D = +85.2$° ($+83.6°$).

Optical rotations were obtained at 20°C with a Kreis-Polarimeter 0.01/400 mm from Zeiss Winkel, while ESR measurements were done with a Varian E15 spectrometer at room temperature and UV-visible spectra were obtained on a Unicam SP.800D.

**RESULTS**

Figure 3 shows the results for the extraction of Ni$^{2+}$ with $\delta$-H$_2$CQD. The pH$_{II}$ value of 5.20 means a (pH$_{II}$,c) value of 3.60. The slope (1.93) of the log D-pH curve agrees with the theoretical expected value of 2 for the Ni(HCQD)$_2$ complex. The H$_2$CQD recovered after the extraction experiment did not show a significant change in specific rotation (Table 1).

The extraction properties of $\alpha$-H$_2$CQD for Ni$^{2+}$ are constant, it follows that

$$\left(\frac{\partial \log D}{\partial \text{pH}}\right)_{\text{[H}_2\text{CQD]}} = 2.$$

Introducing pH$_{1/2}$ as the pH value at which 50% of the metal is extracted (log D = 0) eqn (4) leads to:

$$\log K_{Fe} = 2 \log \text{[H}_2\text{CQD]} - 2 \text{pH}_{1/2}.$$

Finally the value of pH$_{1/2}$ at 1.0 M equilibrium concentration of extractant in the organic phase, denoted by (pH$_{1/2}$)$_{1}$ can be obtained from eqn (6) as

$$\text{(pH}_{1/2})_{1} = -\frac{\log K_{Fe}}{2}.$$

**EXPERIMENTAL**

The optically active camphorquinone dioxime ligands were prepared from (+) camphor according to the procedures of Forster.

$$\alpha$-H$_2$CQD: $[\alpha]_D = -99.1$° ($-98.3°$); $\beta$-H$_2$CQD: $[\alpha]_D = -25.7$° ($-24.1°$); $\gamma$-H$_2$CQD could not be isolated pure. $\delta$-H$_2$CQD: $[\alpha]_D = +85.2$° ($+83.6°$).

Optical rotations were obtained at 20°C with a Kreis-Polarimeter 0.01/400 mm from Zeiss Winkel, while ESR measurements were done with a Varian E15 spectrometer at room temperature and UV-visible spectra were obtained on a Unicam SP.800D. Aqueous metal ion concentrations were measured with the Perkin-Elmer 300 Atomic Absorption Spectrophotometer.

The extraction experiments were carried out in a three stoppered flask with a stirring device and continuous pH measurements. The starting volumes of water and organic solvent were both 250 ml. Stirring was stopped when no further change of the pH was noticed, indicating that equilibrium was reached. For analysis equally small volumes of water layer and organic layer were withdrawn from the system. To measure the distribution coefficient as a function of pH thereafter a small quantity of 4N acid or base was added, and the process of stirring until equilibrium and withdrawal of small portions of the aqueous and organic solutions was repeated at a different pH. Care was taken to keep the volumes of the aqueous and organic solutions equal. Although in this procedure the electrolyte concentration does not stay constant we referred this method because it is convenient to execute and because in a separate experiment it was shown that in the applied concentration range the influence of the electrolyte concentration is negligible. As organic solvents used were chloroform, pentanol and tributylphosphate and inorganic salts used were metal chlorides, nitrates or sulphates. NAOH was used as base and HCl, HNO$_3$, or H$_2$SO$_4$, as acids.

**TREATMENT OF EXTRACTION DATA**

The extraction is expected to follow eqn (1):

$$M^{2+} + 2H_2CQD \rightleftharpoons M(HCQD)_2 + 2H^+$$

(1)

where $M^{2+}$ represents the aquo metal ion, $M(HCQD)_2$ the extractable complex and bars indicate the organic layer. The equilibrium constant $K_E$ and the distribution coefficient D are defined as:

$$K_E = \frac{[M(HCQD)_2][H^+]^2}{[M^{2+}][H_2CQD]^2}$$

(2)

$$D = \frac{[M(HCQD)_2]}{[M^{2+}]}.$$  

(3)

Combination of (2) and (3) gives

$$\log D = \log K_E + 2\text{pH} + 2 \log [H_2CQD].$$

(4)

When taking a large excess $H_2CQD$, so that $H_2CQD$ is constant, it follows that

$$\left(\frac{\partial \log D}{\partial \text{pH}}\right)_{\text{[H}_2\text{CQD]}} = 2.$$

Introducing pH$_{1/2}$ as the pH value at which 50% of the metal is extracted (log D = 0) eqn (4) leads to:

$$\log K_{Fe} = 2 \log \text{[H}_2\text{CQD]} - 2 \text{pH}_{1/2}.$$

Finally the value of pH$_{1/2}$ at 1.0 M equilibrium concentration of extractant in the organic phase, denoted by (pH$_{1/2}$)$_{1}$ can be obtained from eqn (6) as

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**RESULTS**

Figure 3 shows the results for the extraction of Ni$^{2+}$ with $\delta$-H$_2$CQD. The pH$_{1/2}$ value of 5.20 means a (pH$_{1/2}$)$_{1}$ value of 3.60. The slope (1.93) of the log D-pH curve agrees with the theoretical expected value of 2 for the Ni(HCQD)$_2$ complex. The H$_2$CQD recovered after the extraction experiment did not show a significant change in specific rotation (Table 1).

The extraction properties of $\alpha$-H$_2$CQD for Ni$^{2+}$ are
Extraction of Cu(I1) and Ni(I1) by camphorquinone dioxime

Table 1. Specific rotation

<table>
<thead>
<tr>
<th></th>
<th>H2CQD fresh solution</th>
<th>after 7 days</th>
<th>after 45 days</th>
<th>after Cu extraction</th>
<th>after Ni extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-63.8</td>
<td>-64.3</td>
<td>-63.3</td>
<td>+51.9</td>
<td>+47.1</td>
</tr>
<tr>
<td>b</td>
<td>+3.7</td>
<td>+21.2</td>
<td>+23.9</td>
<td>+59.4</td>
<td>+45.5</td>
</tr>
<tr>
<td>c</td>
<td>+78.6</td>
<td>+71.1</td>
<td>+70.2</td>
<td>+67.5</td>
<td>+67.8</td>
</tr>
</tbody>
</table>

Table 1: Specific rotation

<table>
<thead>
<tr>
<th></th>
<th>a: pentanol as solvent</th>
<th>b: t.b.p. as solvent</th>
</tr>
</thead>
</table>

The only solvent that we could find which dissolves β-H2CQD and is not soluble in water was tributylphosphate (TBP). In Fig. 5 a pronounced difference is seen between results from experiments with fresh solutions and results from extractions performed with solutions after contact times of two days. In the latter case the results correspond to those of the Ni δ-H2CQD system: pH<sub>H2</sub> = 6.16, slope 1.99 and the recovered H2CQD showed a specific rotation of +45.5, indicating that isomerization had occurred. Fresh solutions, however, show a slope of 0.97 and a slightly higher pH<sub>H2</sub> value of 6.33.

In contrast to the results obtained in the extraction of nickel a value of 2.50 is found (2 was expected on ground of eqn 1) for the slope of the extraction curve for copper with δ-H2CQD (Fig. 3). A clearly lower pH<sub>H2</sub> value of 2.75—leading to a (pH<sub>H2</sub>)<sub>0</sub> of 1.15—is found. Also for copper no significant change in the specific rotation of δ-H2CQD could be noted (Table 1).

As with the Ni α-H2CQD system the Cu α-H2CQD system gives almost the same figures as found for Cu δ-H2CQD (Fig. 4). In this case also isomerization had taken place (Table 1) a pH<sub>H2</sub> value of 3.08, a slope of 2.67 and a change in specific rotation from -63.8 to +51.9 are found.

With a fresh solution of β-H2CQD in TBP (Fig. 6) a pH<sub>H2</sub> value of 4.21 is obtained for the copper extraction, quite larger than with the Cu δ-H2CQD pentanol system. The slope of 1.47 indicates that the extraction chemistry must deviate considerably from that represented by the extraction eqn (1). Just as in the experiment with nickel and β-H2CQD, after two days the picture had dramatically changed. The pH<sub>H2</sub> value was lowered to 3.66 and the slope had increased to 2.37. Specific rotation measurement from the recovered H2CQD showed that most of the β-H2CQD had isomerized. This isomerization was more pronounced than the isomerization that occurred without contact with the aqueous copper solution (Table 1).

The slopes of the log D-pH curves for the copper extraction deviate from 2 and point to an extraction chemistry which is different from that assumed in eqn (1). To find out which stoichiometry the copper camphorquinone dioxime complex had during extraction an experiment was carried out with equivalent moles of copper and δ-H2CQD. If Cu(HCQDb would be the only extraction complex at most 50% of the copper can be extracted. Figure 7 shows that definitely more than 50% of the copper can be extracted, but that even at high pH 100% extraction is not reached. At pH 5.0 65% of the copper was extracted.

VIS-spectroscopy (Fig. 8) shows that two different copper complexes are present in the organic phase after extraction. When the pH is relatively low a complex is formed with a maximum absorbance at 25,300 cm<sup>-1</sup>. At higher pH's a new band appears with a maximum at 22,400 cm<sup>-1</sup> and the corresponding complex becomes prevalent at pH is 3.20. Also ESR measurements, correlated with the two different Cu-HCQD complexes are carried out. The ESR spectrum of the complex with λ<sub>max</sub> 25,300 cm<sup>-1</sup> is presented in Fig. 9. It is exactly the same as that found.
Fig. 7. % copper extraction as a function of pH for the extraction of Cu(II) with β-camphorquinone dioxime. The initial concentration of δ-H$_2$CQD in chloroform and the initial copper nitrate concentration in H$_2$O are both 0.002 M.

by Ma$^5$ for Cu(β-HCQD)$_2$·H$_2$O₄½ dioxane. For the complex with λ$_{max}$ at 22,400 cm⁻¹ no ESR signal could be observed.

**DISCUSSION**

From Table 1 it can be clearly seen that under extraction conditions isomerization takes place when α- or β-H$_2$CQD are used.

Without contact with an aqueous solution containing metal ions α-H$_2$CQD does not isomerize at all and β-H$_2$CQD isomerizes only to a certain extent.

This phenomenon can be readily explained by the bonding of metal ions or protons to the dioxime; by this interaction the double bond character of the CN bond will be weakened and thus the rotation barrier of this bond will be lowered. δ-H$_2$CQD is the only isomer which possesses hydrogen bridge stabilization and no steric repulsion (Table 2). Therefore it is not surprising that it is the most stable isomer.

Pedersen and Larsen$^6$ found isomerization of Ni(α-H$_2$CQD)₂ in chloroform to an equilibrium mixture of 85–90% Ni(δ-H$_2$CQD)₂ 5–10% Ni(α-H$_2$CQD)₂ and 5% Ni(β-H$_2$CQD) (δ-H$_2$CQD). This means that after recovering of H$_2$CQD a specific rotation is expected of $0.90 \times (+78.6) + 0.075 \times (-63.8) + 0.025 \times (+3.7) = +66.0$.

In Table 1 it is seen that after extraction with α-, β- or

Fig. 8. VIS spectra of the organic phase for the extraction of copper(II) with β-camphorquinone dioxime. A: pH = 1.93; B: pH = 2.87; C: pH = 3.20; D: pH = 5.00. For initial concentrations: see Fig. 7.

Fig. 9. ESR spectrum of copper H$_2$CQD complex (λ$_{max}$ 25300 cm⁻¹) in chloroform at room temperature.
The expected selectivity of $\delta$-H$_2$CQD could not be
determined. On the contrary, copper was extracted at a
much lower pH than nickel (Fig. 3). This result is surprising
because if copper forms a NN complex as sug-
gested by Ma$^5$ then rotation around the CN double bond
is necessary. Furthermore it might have been expected
that copper extraction with $\beta$-H$_2$CQD, for which no
rotation is needed would have a lower $\text{pH}_{1/2}$ value than
copper extraction with $\delta$-H$_2$CQD. However, in Fig. 6 it
can be seen that after a contact time of two days, in
which isomerization from $\beta$- to $\delta$-H$_2$CQD has taken
place, the $\text{pH}_{1/2}$ value is lowered and not raised.
These results can only be explained if we assume that
copper does not form a NN complex but a NO complex
just like nickel.
To investigate this possibility we took a closer look at
the ESR spectrum of the extracted complex, which is
completely identical with the ESR spectrum found by
Ma$^5$ for Cu($\beta$-HCQD)$_2$.H$_2$O. Ma has inter-
preted the ESR spectrum of Cu($\beta$-HCQD)$_2$ by assigning
the four main lines to copper ($^{63}$Cu, $^{65}$Cu: I = 3/2) nuclear
hyperfine interactions and the extra lines as being due to
the nitrogen ($^{14}$N: I = 1) superhyperfine interaction. By
counting 9 nitrogen superhyperfine lines he concluded
that four nitrogen atoms are attached to copper. Because
of the line broadening on the low field side of the
spectrum the nitrogen superhyperfine lines are only
clearly observed on the high field side.
Our interpretation of the superhyperfine structure is
completely different from that of Ma. Natural copper is
composed of 69.1% $^{63}$Cu and 30.9% $^{65}$Cu both with spin
3/2 but with a slightly different magnetic moment
(0.70904 x 10$^{-4}$ vs 0.75958 x 10$^{-4}$ rad. sec.$^{-1}$ gauss$^{-1}$).
The ESR signal of most copper compounds in liquid solution
shows four lines with fairly large linewidths and as a
consequence no separate peaks can be observed for the
two Cu isotopes. However, whenever ligand nitrogen
superhyperfine structure is observed one has to take into
account$^{10,11}$ that extra lines may become observable as a
result of the different magnetic moments of $^{63}$Cu and
$^{65}$Cu. At the high field side of the spectrum (see Fig. 9)
two overlapping hyperfine splitting patterns with inten-
sity ratios of 1:2:3:2:1 can be seen with a splitting of
16.5 gauss. Computer simulation gave an excellent fit
with an intensity ratio between $^{63}$Cu and $^{65}$Cu of 76:24.
From the complete ESR spectrum a hyperfine splitting of
90 gauss is obtained for $^{65}$Cu. The copper hyperfine
splitting for $^{63}$Cu can now be calculated to be
0.75958 x 90 = 69.4 gauss. The predicted separa-
tion between $^{63}$Cu and $^{65}$Cu of the nitrogen super-
hyperfine splitting on the high field side of the ESR
spectrum is 3(96.4 - 90) = 9.6 gauss, and is in very
good agreement with the observed separation of 9.5
gauss. With this interpretation it becomes clear why this
extra hyperfine splitting of $^{63}$Cu cannot be seen on the
other copper hyperfine line with nitrogen superhyperfine
structure, because for that line the calculated separation
between $^{63}$Cu and $^{65}$Cu would be 2(96.4 - 90) = 3.2 gauss
and with such a small difference no separate peaks can
be detected. A further argument in favour of our inter-
pretation of the ESR spectrum is the fact that the
nitrogen superhyperfine structure on the high field copper
line does not have an intensity ratio of
1:4:10:16:19:16:10:4:1 and that the superhyperfine
lines are not equidistant either, as would be required if
four nitrogen atoms were bonded to copper. We there-
fore conclude that only two instead of four nitrogen
atoms are bonded to copper, and so an intensity ratio of
1:2:3:2:1 occurs in the nitrogen superhyperfine
structure. As a consequence the Cu($\beta$-HCQD)$_2$ complex of
Ma and the extracted complex with $\lambda_{\text{max}}$ at 25,300 cm$^{-1}$
do not have the NN structure but just like nickel a NO
structure (Fig. 2).
The results found in the extraction experiments are in
good agreement with this interpretation. For, when cop-
per and nickel form the same kind of complex with
H$_2$CQD, copper will have a lower pH$_{1/2}$ value than nickel
according to the Irving and Williams law.
The low values of the slopes of the log D vs pH curves
found in the extraction of copper and nickel by fresh
$\beta$-H$_2$CQD (1.47 for Cu and 0.97 for Ni) can now also be
explained if we assume that $\beta$-H$_2$CQD is not active in
the extraction. Only the small portion of the $\delta$-H$_2$CQD
that is present will be active. As a consequence the
extractant concentration in eqn (4) is not a constant
when the equilibrium is changed by adding acid or base.
This means that the slope of log D vs pH will not give a
value of two, but will give a value which is considerably
lower. After two days, during which most of the
$\beta$-H$_2$CQD is isomerized to $\delta$-H$_2$CQD, excess $\delta$-H$_2$CQD
will be present and indeed the slopes are increased to
values (2.37 for Cu and 1.99 for Ni) which are almost
equal to the values found in the extraction by $\delta$-H$_2$CQD.
Also the change of the pH$_{1/2}$ value (4.21-3.66 for Cu and
6.33-6.16 for Ni) can be explained by the fact that
isomerization of $\beta$-H$_2$CQD to $\delta$-H$_2$CQD increases the
extractant concentration. For according to eqn (6) an
increase in the extractant concentration leads to a
decrease in the pH$_{1/2}$ value. For $\alpha$-H$_2$CQD such a
phenomenon was not observed. This is not surprising
because $\alpha$-H$_2$CQD itself can form a NO complex and
thus is active in the extraction. As a consequence, during
isomerization of $\alpha$-H$_2$CQD to $\delta$-H$_2$CQD the extractant
concentration does not change.
The result of the slope analysis of 1.93 for the extrac-
tion of nickel(II) by $\delta$-H$_2$CQD is consistent with the
theoretically expected value of 2 (eqn 5) and thus the
extraction equation can be represented by

$$\text{Ni}^{2+} + 2\text{H}_2\text{CQD} \leftrightarrow \text{Ni(HCQD)}_2 + 2\text{H}^+.$$  

With copper(II), on the contrary, a deviating value of
2.50 was found for the extraction by $\delta$-H$_2$CQD.
According to Fig. 8 it was shown that two different complexes are involved during the extraction: complex A with \( \lambda_{\text{max}} = 25300 \text{ cm}^{-1} \) and complex B with \( \lambda_{\text{max}} = 22400 \text{ cm}^{-1} \). Their ratio is strongly pH-dependent; at low pH the spectrum is dominated by A, at relatively high pH values B is more important. Since the spectrum of A correlates with the presence of the copper ESR described above, complex A may be assumed to be Cu(HCQD)₂.

Figure 7 shows that at pH = 5, 65% of the copper is extracted and from Fig. 8 it can be concluded that at this pH complex B is almost exclusively responsible for the extraction. The value of about 65% extraction at high pH can be explained if a complex with a copper:HCQD = 2:3 ratio is assumed to be present during extraction. In that case the maximum concentration of copper in the organic phase is expected to be 66.7%. To check the hypotheses on the stoichiometry of the two copper complexes accurate values of the intensities of the bands (overlapping) were necessary. The separation at different pH values was carried out by means of computer simulation.

The best fit was obtained by using a corrected Lorentz function with the general form \( y = a(1 + bx^2 + cx^4) \) as used by Baker et al., for IR band simulation. A strong absorption near 35000 cm⁻¹ with some overlap around 25000 cm⁻¹ has been taken into account. In Fig. 10 one of the simulations is shown, and the excellent fit is noteworthy. In this way the real intensities of the bands at \( \lambda_{\text{max}} \) could be obtained and these values are according to Lambert-Beer's law proportional to the concentrations of both (overlapping) bands. The separation at different pH values was carried out by means of computer simulation.

For complex A we assume that the same reaction equation applies as used in eqn (1) and \( k_A \) is then given by eqn (8).

\[
k_A = \frac{[\text{Cu(HCQD)₂}] [\text{H}^+]}{[\text{Cu²⁺}] [\text{HCQD}]^2} = \frac{[\text{A}] [\text{H}^+]}{[\text{Cu}^2⁺] [\text{HCQD}]^2}.
\]  

\[k_B = \frac{[\text{Cu(HCQD)₂}][\text{HCQD}][\text{H}^+]}{[\text{Cu²⁺}][\text{HCQD}]^3} = \frac{[\text{B}] [\text{H}^+]^4}{[\text{Cu}^2⁺][\text{HCQD}]^4}.
\]

In eqns (8) and (10) all concentrations can be measured ([H⁺] with pH measurements, [Cu²⁺] with atomic absorption, [A] and [B] with UV/visible spectroscopy) with the exception of [H₂CQD]. To eliminate [H₂CQD] we combine (8) and (10)

\[
3 \text{log } [B] - 3 \text{log } [A] - \text{log } [\text{Cu}^2⁺] = \frac{\text{log } [\text{B}] - \text{log } [\text{A}]}{\text{log } [\text{Cu}^2⁺] - \text{log } [\text{Cu}^2⁺]}.
\]

resulting in

\[
\frac{\text{d}(\text{log } [B]) - 3 \text{log } [A] - \text{log } [\text{Cu}^2⁺]}{\text{d} \text{pH}} = 2.
\]

In Fig. 12 we see that a plot of 2 log B - 3 log A - \text{log } [\text{Cu}^2⁺] vs pH indeed gives a straight line with a slope of 1.99 confirming our assumptions concerning complex B. However, the requirements of a neutral complex with a copper ligand ratio of 2:3 are also fulfilled with the assumption of the complex Cu₂(HCQD)OH, replacing the double negative charge of CQD by HCQD⁻ plus OH⁻:

\[
2\text{Cu}^2⁺ + 3\text{HCQD} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2\text{(HCQD)}_3\text{OH} + 4\text{H}^⁺.
\]

Because [H₂O] can be assumed to be constant, replacing (9) by (13) gives no difference in expressions (11) and
Extraction of Cu(II) and Ni(II) by camphorquinone dioxime

Fig. 12. $2 \log B - 3 \log A - \log [\text{Cu}^{2+}]$ as a function of the pH for the extraction of copper(II) with $\delta$-camphorquinone dioxime. A and B are the calculated values of the maxima of the complex with $\lambda_{\text{max}} = 25300 \text{ cm}^{-1}$ and of the complex with $\lambda_{\text{max}} = 22400 \text{ cm}^{-1}$ respectively. For initial concentrations see Fig. 7.

(12) so complex B might also be represented by $\text{Cu}_2(\text{HCQD})_2\text{OH}$.

If $\text{OH}^-$ is replaced by another anion, for example $\text{NO}_3^-$ (to adjust pH HNO$_3$ is used), elimination of $[\text{H}_2\text{CQD}]$ from the expressions for $k_A$ and $k_B$ gives:

$$k_A^3 = \frac{[\text{A}^3]}{[\text{B}^2] \cdot [\text{NO}_3^-] \cdot [\text{Cu}^{2+}]}. \quad (14)$$

This would mean that $[\text{A}^3]/[\text{B}^2]$ would be independent from the pH, which does not fit with Fig. 11. We therefore conclude that this reaction does not take place.

Although the extraction experiments strongly point to the formation of a 2:3 Cu:HCQD complex, we checked if a 1:1 complex could explain the extraction results

$$\text{Cu}^{2+} + 2 \text{HCQD} \rightleftharpoons \text{Cu(CQD)} + 2\text{H}^+. \quad (15)$$

In combination with eqn (8) and by eliminating the $[\text{H}_2\text{CQD}]$ we obtain

$$k_A^3 = \frac{[\text{A}^3][\text{Cu}^{2+}]}{[\text{B}^2][\text{H}^+][\text{Cu}^{2+}]}.$$

Therefore a plot of $2 \log B - \log A - \log [\text{Cu}^{2+}]$ vs pH must give a straight line with slope 2. From Fig. 13 it is clear that this is not the case so we may safely reject eqn (15). Also Cu(HCQD) (NO$_3$) could be rejected by this way of analysis. Because of all these arguments for complex B we conclude that complex B must have the composition $\text{Cu}_2(\text{HCQD})_2\text{CQD}$ or $\text{Cu}_2(\text{HCQD})_2\text{OH}$.

In agreement with this conclusion no ESR signal could be observed for complex B. This is not an unknown phenomena$^{23,14}$ for binuclear Cu(II) complexes in which the antiferromagnetic coupling between the two copper ions is so large that the singlet ground state has a very pronounced energy difference from the triplet state. As a result the complex is diamagnetic at room temperature. Since only binuclear copper(II) complexes can have such an antiferromagnetic coupling and mononuclear copper(II) complexes always have an unpaired electron, this confirms the conclusion that the composition of complex B must be $\text{Cu}_2(\text{HCQD})_2\text{OH}$ or $\text{Cu}_2(\text{HCQD})_2\text{CQD}$.

CONCLUSIONS

The expected selectivity of $\delta$-H$_2$CQD for the extraction of nickel above copper has not been confirmed. On the contrary, copper was found to have a pH$\text{H}_{1/2}$ value that was much lower (2.75 vs 5.20) than that of nickel. This expected selectivity of camphorquinone dioxime for nickel above copper was based on a publication of Ma, claiming that the dioxime in Cu($\beta$-HCQD)$_2\cdot\text{H}_2\text{O}$-dioxane, had a NN coordination around copper.

Our analysis of the ESR spectrum showed, however, that this product does not have a NN coordination but a NO coordination like nickel. With the knowledge that there is no difference in coordination of H$_2$CQD around copper and nickel, it is not surprising that $\delta$-H$_2$CQD has no selectivity for nickel above copper, and that the normal order of stabilities according to Irving and Williams is followed.

Under extraction conditions isomerization occurred from $\alpha$- and $\beta$-H$_2$CQD into $\delta$-H$_2$CQD. Without contact with metal ions or protons the $\alpha$-H$_2$CQD is stable in solution. We therefore conclude that metal ion or proton attaches on the nitrogen atoms and lowers the double
bond character of the CN bond, thus making rotation around this bond more easy.

Analysis of the slope of log D vs pH confirmed the expected reaction equation for nickel: Ni^{2+} + 2H_2CQD ⇌ Ni(HCQD)_2 + 2H^+.

With copper two different complexes are involved in the extraction which is clearly seen by UV spectroscopy. Computer simulation showed that these two complexes are Cu(HCQD)_2, with an absorption at 23500 cm⁻¹ and Cu_2(HCQD)_2 CQD or Cu_2(HCQD)_2 OH with an absorption at 22400 cm⁻¹. ESR spectroscopy proved the Cu(HCQD)_2 complex to have an NO structure. For the Cu:HCQD = 2:3 complex no ESR signal could be observed, which is not uncommon for binuclear copper(II) complexes with a very strong antiferromagnetic coupling.

REFERENCES