The extraction of copper(II) and nickel(II) by strained dioximes and trioximes

Citation for published version (APA):
Paping, L. R. M. (1983). *The extraction of copper(II) and nickel(II) by strained dioximes and trioximes*. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Technische Hogeschool Eindhoven. https://doi.org/10.6100/IR52432

DOI:
10.6100/IR52432

Document status and date:
Published: 01/01/1983

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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THE EXTRACTION OF COPPER(II) AND NICKEL(II) BY STRAINED DIOXIMES AND TRIOXIMES

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS PROF. DR. S.T.M. ACKERMANS, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VAN DECANEN IN HET OPENBAAR TE VERDEDIGEN OP VRIJDAG 9 SEPTEMBER 1983, TE 16.00 UUR

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DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOREN

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Aan Lenny en Kasper

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

1.1 LIQUID-LIQUID EXTRACTION

From being a curiosity in the late 19th century liquid-liquid extraction (in this thesis called extraction) has developed into a highly sophisticated process. It is useful in analytical chemistry, in radiochemistry, in the oil and heavy organic chemical industries, in pharmaceutical chemistry, in nuclear fuel reprocessing and most recently in hydrometallurgical processing. In hydrometallurgy liquid-liquid extraction has enjoyed considerable attention since the successful introduction of the hydroxy-oximes, known as the LIX-series (1), into the refining of copper. This success demonstrated that extraction for common metals like copper can be economically applied on a large scale. The tendency of nickel to form complexes is almost as strong as that of copper, but no similar reagent has been found for nickel. If such a selective reagent for nickel could be found, nickel could be separated from mixed-metal solutions in one step.

Economic deposits of nickel are scattered throughout the world, but occur mainly in Canada and the U.S.S.R.

Leaching of the ore with ammonia or acid produces an aqueous solution of mainly nickel ions and some other metal ions. Liquid-liquid extraction with a selective reagent for nickel would remove the impurities in one step. The final nickel products can be obtained by a few generally accepted methods, such as electrolysis crystallization and hydrogen reduction under elevated temperature and pressure.

Another application of selective liquid-liquid extraction can be found in the recovery of nickel from wastes containing heavy metals. The dumping of these wastes has caused growing environmental problems. One of the possibilities for the prevention of dumping is recycling. Nickel might be regained pure from these wastes by liquid-liquid extraction if a selective extractant could be found.

The development of a selective reagent for nickel that can be used in liquid-liquid extraction is therefore of great significance. In this dissertation a report is given of our research to find such a reagent.

1.2 SELECTIVE EXTRACTION

In this paragraph a brief explanation will be given of the term selective extraction. Leaching of an ore or an inorganic mass, containing heavy metals produces an aqueous solution with a variety of metal ions. To this solution an organic extraction agent dissolved in a water-immiscible organic solvent is added. The organic extraction agent is more soluble in the organic solvent than in water and forms complexes with one or more metal ions. These complexes too, are better soluble in the organic solvent than in water. The extraction reaction is accelerated by vigourously stirring. After the reaction has taken place the organic phase and the aqueous phase are separated. The general reaction equation for the extraction of a metal(II) ion by a chelating extractant is:

$$M^{2+} + \overline{2HA} \rightleftarrows \overline{MA_2} + 2H^+ \qquad (1)$$

where M^{2+} represents the aquated metal ion, HA the organic reagent and MA_2 the extractable metal complex and bars indicate the organic layer. The complex formed must be a neutral species to be soluble in the organic phase. As a net result of the reaction the metal is transferred to the organic layer, while H^+ is transferred to the aqueous layer. The reaction will therefore be pH dependent and this pH dependency will be different for a variety of metals as can be seen in fig. 1.1 for the extractant 8-hydroxyquinoline (2).

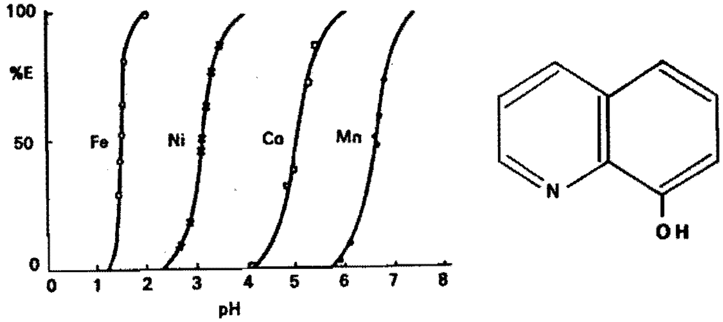


Fig. 1.1 The effect of pH on the extraction of Fe^{3+}, Ni^{2+} Co^{2+} and Mn^{2+} by 8-hydroxyquinoline.

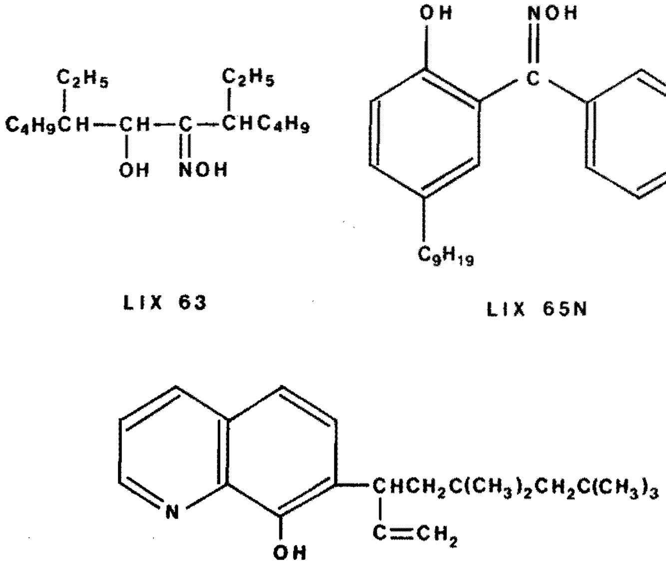
From fig. 1.1 it becomes clear that Fe^{3+} can be separated using 8-hydroxyquinoline from Co^{2+}, Ni^{2+} and Mn^{2+} in one step at pH = 2. The nickel can only be separated from this mixture by 8-hydroxyquinoline in two steps. First an extraction at pH = 2 to remove the iron and then extraction at pH = 4 to extract the nickel. It should be noted that many so-called selective reagents are in fact reagents for which the desired metal extracts at the lowest pH. The pH$_{½}$ value can be defined as the pH at which 50% of the metal is extracted. For example the pH$_{½}$ value of Ni^{2+} in fig. 1.1 is 3.1.

After extraction the organic phase, containing the desired metal in the form of a neutral metal coordination compound, is stripped with an aqueous solution containing a strong mineral acid such as sulphuric acid or hydrochloric acid. The metal values are thus transferred in the form of metal salts to the aqueous stripping solution (equation 1 is an equilibrium reaction) from which they can be isolated as salts by evaporating the water, or as the pure metal by electrolysis, while the organic phase containing the released organic extraction agent is advantageously used again for the extraction of further quantities of metal.
To be commercially attractive a selective organic extraction agent for nickel must give high extraction yields within reasonably short extraction time. Furthermore the pH$_{½}$ value

for nickel must be considerable lower than the pH½ values of other metals.

1.3 SELECTIVE NICKEL EXTRACTION

The development of the LIX-series of chelating extractants by General Mills (1) Inc., U.S.A. and KELEX by Ashland Chemical (3) Co., U.S.A. (see fig. 1.2) as commercial extractants selective for copper has shown that extraction can provide an economic alternative to existing methods for metal recovery.



LIX 63

LIX 65N

KELEX 100

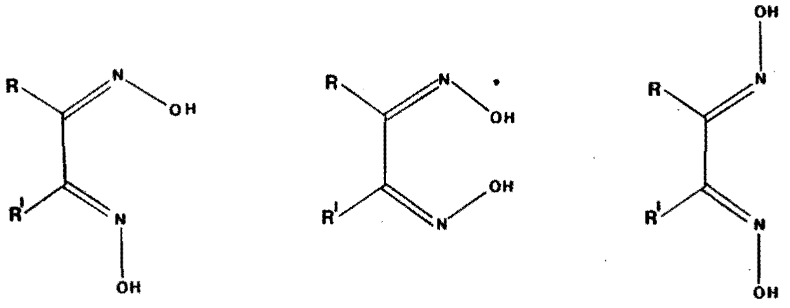
Fig. 1.2 Some commercially-used chelating copper extractants.

Because copper is one of the most versatile of the transition metals, it seems appropriate that it has been the first metal for which a chelating extractant was used on a large scale. The tendency of nickel to form chelates is almost as strong as that of copper, but no selective extractant for nickel has been developed yet.

The stabilities of complexes of related structures formed with transition metals usually follow the Irving-Williams (4) series:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}.$$

To obtain a selective reagent for nickel this Irving-Williams order of stability must be broken with respect to copper and nickel. This is only possible if nickel forms a different kind of chelate than copper. Aliphatic dioximes of the type R-C(NOH)-C(NOH)-R', in which R and R' represent an alkyl group did indeed extract nickel at lower pH than copper (5, 6), in contrast with the Irving-Williams order. This was explained (5) by assuming that nickel forms a square planar chelate with a low-spin d^8 configuration, while copper forms an octahedral chelate by binding two additional water molecules. However, equilibrium was not established within days and this extremely low rate of extraction makes this system unsuited for commercial use. Van der Zeeuw and Kok (7) found that when using dioximes of the type A-C(NOH)-C(NOH)-R, in which A represents an aromatic group substituted with at



amphi(E,Z;Z,E) **syn(Z,Z)** **anti(E,E)**

Fig. 1.3 The three geometrical isomers of the vicinal dioxime. If R ≠ R' there are two different kind of amphi isomers.

least one organic group, and R represents an optionally substituted hydro carbyl group or an hydrogen atom, equilibrium is established relatively rapid, i.e. within hours instead of within days. Every synthesis of vicinal dioximes affords a mixture of geometrical isomers, syn, anti and amphi (see fig. 1.3).
Considering the aliphatic and aryl-aliphatic dioximes the Ni(II) chelates of the anti-isomers (see fig. 1.4a) are thermodynamically most stable and can be obtained by a catalytic isomerization of the chelates of the amphi-isomers (8) (see fig. 1.4b) (syn-isomers do not form chelates with Ni(II)).

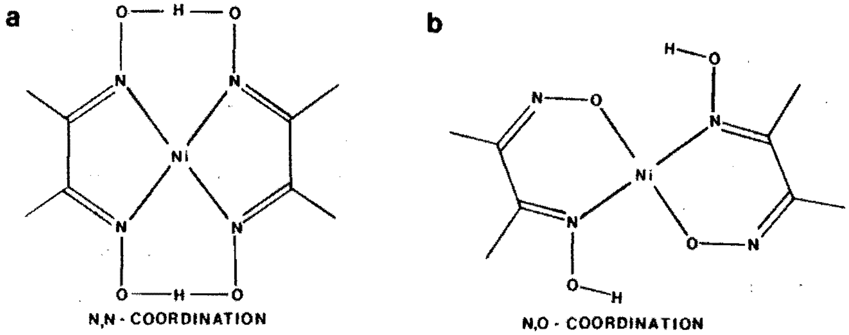


Fig. 1.4 a. The N,N-coordinated chelate formed at the reaction of Ni(II) with the anti-isomer and
b. the N,O-coordinated chelate formed at the reaction of Ni(II) with the amphi-isomer.

Pedersen and Larsen (9) found that when using camphorquinone dioxime (H_2CQD) (fig. 1.5) not the N,N-coordinated nickel chelate but the N,O-coordinated nickel chelate is thermodynamically more stable. The rigid bicyclic structure of the carbon skeleton is responsible for a decrease in the bond angle α (see fig. 1.6). As a consequence the bond angle β is increased (β is roughly equal to $\frac{360^\circ - \alpha}{2}$) which results in an increase of the N-N distance.

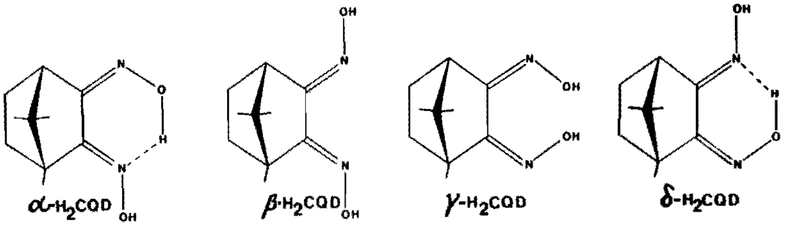


Fig. 1.5 The four isomeric forms of camphorquinone dioxime.

The larger N-N distance causes strain in the N,N-coordinated chelate with the five-membered ring Ni-N-C-C-N- (fig. 1.4a). The N,O-coordination with a six membered ring Ni-N-C-C-N-O- (fig. 1.4b) relieves this strain and becomes more attractive in comparison with the N,N-coordination. Ma and Angelici (10) confirmed that nickel forms N,O-coordinated chelates with H_2CQD, but they also reported (11) that for copper only a N,N-coordinated chelate could be isolated. The two amphi isomers α- and δ-H_2CQD (fig. 1.5) are likely to form N,O-coordinated chelates and if no isomerization takes place into β-H_2CQD it is to be expected that these two isomers should be selective for nickel above copper.

The four isomeric forms of H_2CQD can be isolated pure (12), so camphorquinone dioxime seems to be a good starting point in the search for a selective extractant for nickel.

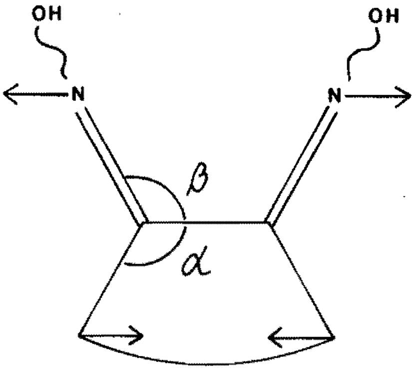


Fig. 1.6 The effect of strain in the carbon skeleton on the dioxime part of the molecule.

1.4 SCOPE OF THIS DISSERTATION

The main theme of this dissertation is the search for a selective extractant for nickel that gives high extraction yields within a reasonably short extraction time. For this purpose the Irving-Williams order of stabilities must be broken. Because of the great affinity of nickel for dioximes (compare for example bis(dimethylglyoximato)nickel(II)) this investigation is limited to organic molecules containing oxime groups or groups related to the oxime group. The cyclic or bicyclic carbon skeleton is used to alter the N-N distance in the dioxime parts and with that the chelating qualities of these dioxime parts.

In chapter 3 the extraction results are presented of α-, β- and δ-camphorquinone dioxime. The bicyclic carbon skeleton increases the N-N distance from 2.4 Å for an unstrained aliphatic dioxime to 3.0 Å. β-Nopinoquinone dioxime is investigated in chapter 4 with an estimated N-N distance of 2.8 Å.

The influence of a third oxime group on the extraction capacities is reported in chapter 5. For this purpose 1,2,3-cyclopentanetrione trioxime and 4-t-butyl-1,2,6-cyclohexanetrione trioxime were synthesized. These two ligands can easily be converted into their furazan oximes, which are also described in chapter 5.

Unstrained aliphatic dioximes of the type R-C(NOH)-C(NOH)-R are tested for their extraction capacities in ammoniacal systems in chapter 6. In this chapter also a kinetic investigation to the rate-determining step of the pH-dependent extraction of nickel by dipentyl dioxime is reported.

In chapter 7 a survey is given of the results presented in this dissertation together with some general remarks.

A brief summary of this dissertation is presented in chapter 8.

Chapter 3 was published already (13), chapter 4, 5 and 6 will soon be published.

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CHAPTER 2

EXPERIMENTAL PART

2.1 EXTRACTION PROCESSES AND EQUIPMENT

The extraction experiments were carried out in a three-stoppered flask with a stirring device and continuous measurement of the pH value. 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 equal, small volumes of the aqueous layer and the organic layer were taken from the system. The aqueous metal-ion concentration was determinated by means of atomic absorption measurements on a Perkin-Elmer 300 Atomic Absorption spectrophotometer, while the chelate concentration in the organic layer could be obtained with the aid of UV-visible spectroscopic measurements on a Unicam SP 800 D. 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 remain constant this method was preferred 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. Organic solvents used were chloroform, 1-pentanol, tri-n-butylphosphate or methylisobutylketone and inorganic salts used were metal chlorides, nitrates or sulfates. NaOH was used as base and HCl, HNO_3 or H_2SO_4 as acids. These chemicals were purchased from E. Merck A.G., Darmstadt (zur analyse).

Kinetic measurements were carried out in a flask provided with a magnetic stirrer. The water layer containing the nickel nitrate was acidified with 4N HNO_3 till the desired pH and then an equal volume (50 ml) of organic phase, in which the ligand was dissolved, was added. Under stirring 10 ml of the mixture was withdrawn after 5, 10, 20 and 30 minutes. The two layers of these withdrawals separated immediately and it appeared that the volumes of both separated layers were equal (5 ml). UV spectroscopy applied to the organic phase gave the absorption at 30.500 cm^{-1}. Since the solvent and the ligand have no absorption below 35.000 cm^{-1} the absorption can be ascribed to the chelate formed during the extraction. According to Lambert Beer's law this absorption is proportional to the chelate concentration. When plotting the absorption against the contact time a straight line was obtained for the first twenty minutes and only a small deviation of the straight line was visible after longer reaction times. This straight line indicates that the initial reaction rate is not, or hardly, inhibited after twenty minutes, so the initial rate could easily be determinated from this straight line.

Optical rotations were obtained at 20°C with a Kreis-Polarimeter 0.01/400 mm from Zeiss Winkel. ^1H NMR spectra were obtained at room temperature on a 60 MHz Varian EM 360 A spectrometer. IR spectra were recorded on a Grubb Parsons IR spectromaster MK-III with the aid of KBr pellets.

2.2 TREATMENT OF EXTRACTION DATA (1)

The extraction is expected to follow equation (1)

$$M^{2+} + \overline{2H_2A} \rightleftarrows \overline{M(HA)_2} + 2H^+ \qquad (1)$$

where M^{2+} represents the aquated metal ion, H_2A the extractant with two acidic hydrogens, $M(HA)_2$ the extractable complex and bars indicate the organic layer. The equilibrium constant (known as the extraction constant) is defined as

$$K_E = \frac{[\overline{M(HA)_2}]\,[H^+]^2}{[M^{2+}]\,[\overline{H_2A}]^2} \qquad (2)$$

The distribution coefficient D of the metal M is defined as the ratio between metal concentrations in the organic and aqueous phases at equilibrium

$$D = \frac{[\overline{M(HA)_2}]}{[M^{2+}]} \qquad (3)$$

Combination of (2) and (3) gives

$$\log D = \log K_E + 2\mathrm{pH} + 2\log\,[\overline{H_2A}] \qquad (4)$$

When using a large excess H_2A, so that the $[\overline{H_2A}]$ is constant, it follows that

$$\left(\frac{\partial \log D}{\partial \mathrm{pH}}\right)_{[\overline{H_2A}]} = 2 \qquad (5)$$

This means that if equation (1) is applicable, plotting log D versus pH will give a straight line with a slope of 2. From this line it is easy to determine the pH½ value as the pH value at which 50% of the metal is extracted (log D = 0). Combination of this pH½ value with equation (4) leads to:

$$\log K_E = -2\log\,[\overline{H_2A}] - 2\mathrm{pH}_{1/2} \qquad (6)$$

From equation (6) it can be seen that the lower the pH½ value the higher the K_E value, which means the higher the stability of the chelate. When a series of metals M_1, $M_2 \ldots M_n$

are extracted by a single extractant and the metal complexes formed have an order in stability of $M_1 > M_2 \ldots . > M_n$ then M_1 will be extracted from solutions of lower pH and M_n from solutions of highest pH or:

$$pH\tfrac{1}{2}(M_1) < pH\tfrac{1}{2}(M_2) < \ldots < pH\tfrac{1}{2}(M_n)$$

Because the pH½ value is dependent on the $\overline{H_2A}$ concentration (eqn. 6) a $(pH\tfrac{1}{2})_{1.0}$ value is defined as the pH½ value at 1.0 M equilibrium concentration of extractant in the organic phase.

$$(pH\tfrac{1}{2})_{1.0} = -\frac{\log K_E}{2} \qquad (7)$$

With this value of $(pH\tfrac{1}{2})_{1.0}$ different kinds of extraction systems can be compared.

The equations derived in this paragraph will be used in subsequent chapters to analyse the experimental extraction results. Equation (5) will be used to check on the stoichiometry of the extraction reaction, while equation (6) will be used to rank the stability order of copper and nickel complexes.

2.3 ESR (2, 3)

Electron Spin Resonance (ESR), also called Electron Paramagnetic Resonance (EPR), is a technique which permits the investigator to detect and in favourable cases to characterize molecules with unpaired electrons.

ESR measurements were done with a Varian E15 spectrometer at room temperature.

Because Cu(II) is a d^9 system with one unpaired electron, this technique is suitable to investigate copper(II) complexes. This unpaired electron gives rise to a doubly degenerate spin energy level. This degeneracy will be removed when a magnetic field is applied (Zeeman effect), because in that case the two possible orientations of the spin (parallel and anti-parallel to the direction of the magnetic field) will have different energies. The energy separation ΔE depends on the strength of the applied magnetic field:

$$\Delta E = g_e \beta H$$

In this equation β is the Bohr magneton, and H is the value of the magnetic field. The electron g factor (g_e) is equal to 2.00232 for a free electron. Transitions between the two Zeeman levels can be induced by an electromagnetic field of the appropriate frequency ν.

$$h\nu = g_{eff} \cdot \beta \cdot H_r$$

In this equation h is the Planck constant and H_r is the external magnetic field at which the resonance condition is met. Alternatively, transitions can be induced by irradiating the sample with a fixed (microwave) frequency ν and changing the magnetic field until the resonance condition is met. The application of an external magnetic field, however, may generate an internal magnetic field in the sample which will add to or substract from the external field. Any local magnetic fields are accounted for by allowing the g factor to vary:

$$g_{eff} = \frac{h\nu}{\beta H_r}$$

The g factor thus can be considered as a quantity characteristic for the molecule in which the unpaired electron is located. The principal source of the local magnetic field, which causes g to deviate from the free-electron value g_e, is an orbital magnetic moment introduced by a mixing in of excited states into the ground state. For most molecules the admixture of excited states is not isotropic (orientation-independent) but is anisotropic (orientation dependent). If the molecule contains axial symmetry (like many copper complexes) $g_{xx} = g_{yy} \neq g_{zz}$.

The copper nucleus possesses a spin angular momentum and the spin of the copper nucleus is characterized by the quantum number I = 3/2. This causes copper hyperfine interaction with the unpaired electron. The copper hyperfine interaction splits each of the electron Zeeman levels into (2I + 1) = 4 levels shown in fig. 2.1. The allowed transitions correspond to $\Delta M_S = \pm 1$ and $\Delta M_I = 0$ (see also fig. 2.1). Note that with ESR the spectra are usually measured with the aid of a phase sensitive technique and as a consequence in fact the derivatives of absorption spectra are obtained.

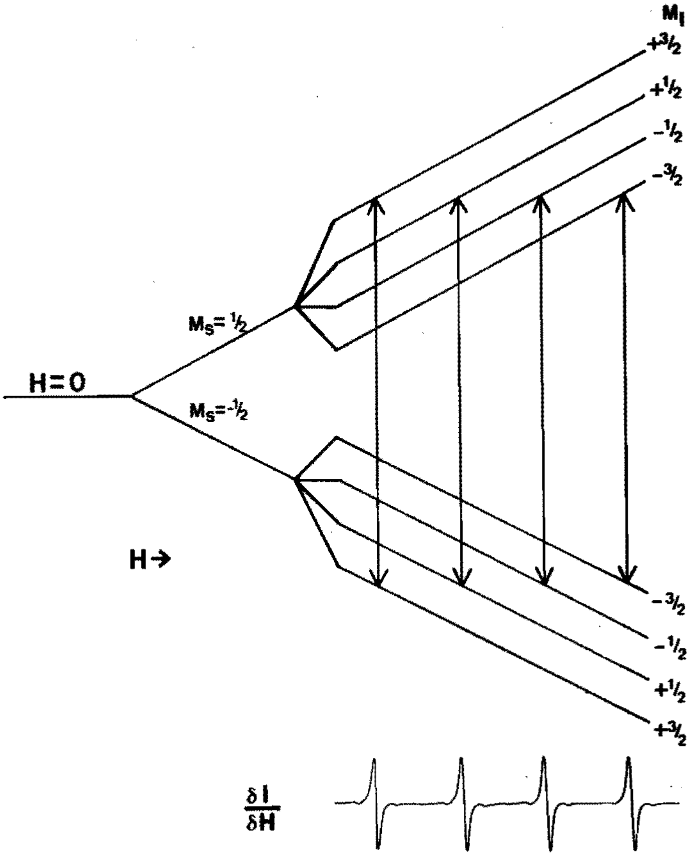

Fig. 2.1 Energy levels as a function of magnetic field at constant microwave frequency for an isotropic system with S = ½ and I = 3/2. There are four resonant fields.

For distorted octahedral Cu^{2+} compounds with the unpaired electron in the $d(x^2-y^2)$ orbital superhyperfine couplings are expected to occur to the ligand atoms in the plane only and not to the axial ligands. This orbital coupling with a ligand atom that possesses a magnetic moment will split the Zeeman levels in the same way as the copper nucleus did. The patterns obtained with a coupling of one, two, three or four equivalent nitrogen atoms (^{14}N:I = 1) are respectively 1:1:1, 1:2:3:2:1, 1:3:6:7:6:3:1 and 1:4:10:16:19:16:10:4:1. If A_N, the superhyperfine coupling constant, is much smaller than A_{Cu}, the copper hyperfine coupling constant, all four lines in fig. 1 are expected to be split according to one of these superhyperfine splitting pattern. In this way the total number of nitrogen atoms attached to copper can be determinated, which can help to elucidate the way in which copper is coordinated by the ligand. Because of the many interacting nitrogen atoms and because of anisotropy effects it is difficult to detect all the superhyperfine lines, especially in spectra of solid solutions (cf. fig. 2.2).

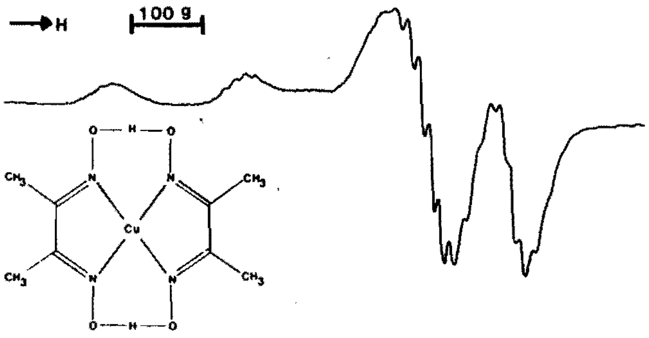

Fig. 2.2 ESR spectrum of a frozen solution of a Cu^{2+} complex exhibiting copper hyperfine structure and nitrogen superhyperfine structure. The sample is Cu^{2+}-dimethylglyoxim dissolved in chloroform containing 0.2 M pyridine (4).

To simplify the spectrum room temperature spectra were taken from the copper complexes in solution. Because in solution anisotropy is averaged out by molecular tumbling only a single isotropic g factor is left:

$$g_{av} = 1/3(g_{xx} + g_{yy} + g_{zz})$$

or when $g_{xx} = g_{yy} = g_{\perp}$ and $g_{zz} = g_{/\!/}$:

$$g_{av} = 1/3(g_{/\!/} + 2g_{\perp}).$$

The anisotropic copper hyperfine coupling constant A_{Cu} is averaged in the same way:

$$(A_{Cu})_{av} = 1/3(A_{/\!/} + 2A_{\perp}).$$

For copper complexes, however, the averaging of the anisotropy usually is not quite complete even at room temperature. This leads to a variation in the linewidth of the copper hyperfine lines (5). An example of an ESR solution spectrum at room temperature is given in fig. 2.3. Because of the difference in linewidth the nitrogen superhyperfine splitting is only clearly visible on the two high-field lines of copper. With the aid of computer simulation the total number of nitrogen atoms attached to copper can be determinated. This computer simulation is a necessity because the copper lines overlap each other significantly, and also because in that way the presence of two copper isotopes ^{63}Cu and ^{65}Cu with slightly different magnetic moments can be taken into account.

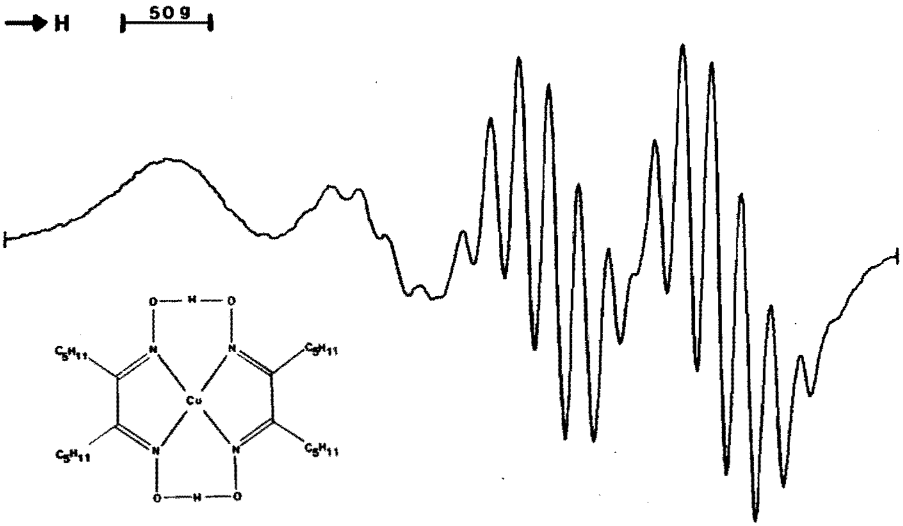

Fig. 2.3 ESR spectrum of a solution of a Cu^{2+} *complex at room temperature exhibiting nitrogen superhyperfine structure. The sample is* Cu^{2+}*-dipentylglyoxim dissolved in chloroform.*

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CHAPTER 3

EXTRACTION OF COPPER(II) AND NICKEL(II) BY CAMPHORQUINONE DIOXIME

3.1 INTRODUCTION

The development of hydroxyoximes as commercial solvent extraction reagents for copper has prompted much research in the chemistry of such systems (1, 2). 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 chelate with the reagent than copper does. Aliphatic *vic*-dioximes (3,4) did indeed extract nickel at lower pH than copper and this was explained (3) by assuming that nickel formed a square planar chelate with a low-spin d^8 configuration, while copper formed an octahedral chelate by binding two additional water molecules. However, the extremely low rate of extraction does not make this system very attractive for commercial use.

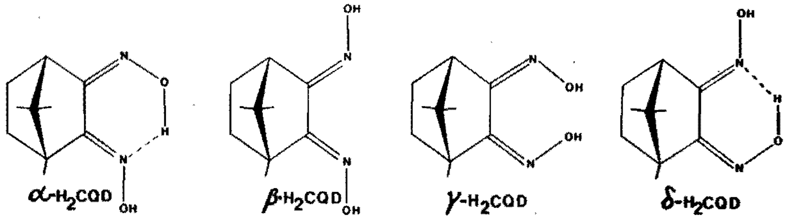

Fig. 3.1 The four isomeric forms of camphorquinone dioxime.

Here we report on the separation properties of another kind of *vic*-dioxime, camphorquinonedioxime H_2CQD(1,7,7-trimethylbicyclo [2.2.1]heptane-2,3-dione dioxime). H_2CQD is known to exist in four isomeric forms (fig. 3.1) which differ by the orientations of the OH groups. The rigid bicyclic skeleton is responsible for a larger N-N distance than in aliphatic *vic*-dioximes. N,N-coordination is the normal mode of coordination for vicinal dioximes but the large N-N distance in H_2CQD makes this kind of coordination less attractive. Recently it was reported (5) that for copper only a N,N-coordinated H_2CQD chelate could be isolated: $Cu(\beta\text{-}HCQD)_2.H_2O.\frac{1}{2}$ dioxane (Fig. 3.2b).

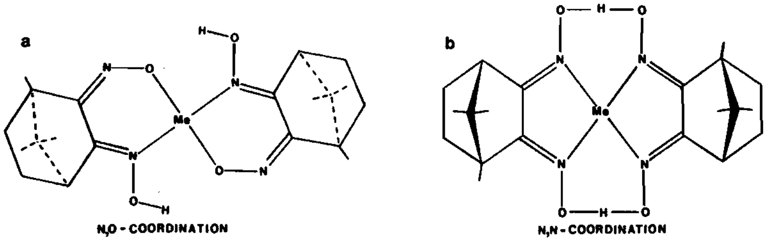

Fig. 3.2 Two possible ways of coordination of camphorquinone dioxime with copper or nickel.

In contrast to this it was published (5-8) that nickel forms stable N,O-coordinated chelates with α-, γ- and δ-H_2CQD (fig. 3.2a) and an unstable N,N-coordinated chelate with β-H_2CQD. α- and δ-H_2CQD are likely to form N,O-coordinated chelates (fig. 3.1) and if no isomerization takes place into β-H_2CQD 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 chelates which are responsible for the extraction.

3.2 SYNTHESIS

3.2.1 Isonitrosocamphor

Following the conventional method (15) using n-butyl nitrite, isonitroso camphor was obtained from d(+) camphor (E. Merck A.G., Darmstadt, zur analyse). This product was not purified but used directly for further preparation.

3.2.2 β-Camphorquinone dioxime

100 gr. Crude isonitroso camphor (0.55 mol) was dissolved in ethanol and treated with an aqueous solution of 80 gr. $NH_2OH.HCl$(1.15 mol) and 160 gr. crystalline NaOAc (1.18 mol) under reflux. The product was washed with ethanol and extracted with boiling ethanol. Recrystallization from boiling methanol gave colourless prisms having $[\alpha]_D = -25.7^0$ in 2% aqueous sodium hydroxide (literature (9) -24.1^0) IR(KBr):3380 and 3190 cm^{-1} (O-H); 1630 and 1580 cm^{-1} (C=N)

3.2.3 α-Camphorquinone dioxime

The combined filtrates from the above reaction were evaporated and diluted with water. The solid thus obtained was extracted four times with cold ethyl acetate to remove the δ-fraction. Recrystallising with ethyl acetate and concentrating the filtrate <u>in vacuo</u> to one half of the original volume to discard the first crop (mixture α and β) gave the pure α-isomer, having $[\alpha]_D = -99.1^0$ in 2% aqueous sodium hydroxide (literature (9) -98.3^0) IR(KBr) 3180 and 3055 cm^{-1} (O-H); 1670 and 1620 cm^{-1} (C=N).

3.2.4 δ-Camphorquinone dioxime

This compound can be isolated from the cold ethyl acetate extracts (α synthesis) by evaporating the solvent, recrystallising the residue from alcohol and then extracting the product with boiling water. Cold ethyl acetate removes a small quantity of the δ fraction giving $[\alpha]_D$ = +85.2° in 2% aqueous sodium hydroxide (literature (9) +83.6°) IR(KBr) 3415 and 3200 cm^{-1} (O-H); 1680 and 1640 cm^{-1} (C=N).

3.3 RESULTS

3.3.1 Extraction of Ni^{2+} with H_2CQD

Figure 3.3 shows the results for the extraction of Ni^{2+} with δ-H_2CQD.

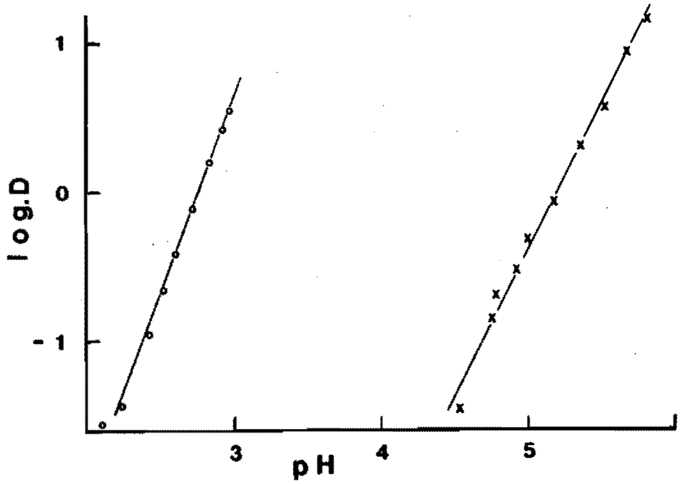

Fig. 3.3 Log D as a function of pH for the extraction of Cu(II)(O) or Ni(II)(X) with δ-camphorquinone dioxime. Concentration of δ-H_2CQD in 1-pentanol 0.025 M. Initial aqueous metal sulfate concentration 0.001 M.

The pH½ value of 5.20 means a $(pH½)_{1.0}$ value of 3.60. The slope (1.93) of the log D-pH curve agrees with the theoretical expected value of 2 for the $Ni(HCQD)_2$ chelate. The H_2CQD recovered after the extraction experiment did not show a significant change in specific rotation (table 3.1).

Equilibrium was reached during the extraction experiments within one hour. The extraction properties of α-H_2CQD for

Table 3.1 Specific rotation

H_2CQD	fresh solution	after 7 days	after 45 days	after Cu extraction	after Ni extraction
α^a	-63.8	-64.3	-63.3	+51.9	+47.1
β^b	+ 3.7	+21.2	+23.9	+59.4	+45.5
δ^a	+78.6	+71.1	+70.2	+67.5	+67.8

a: 1-pentanol as solvent   b TBP as solvent

Ni^{2+} are quite analogous to those of δ-H_2CQD (fig. 3.4) with a pH½ value of 5.03 and a slope of 1.96. The recovered H_2CQD had a specific rotation of +47.1 (table 3.1) indicating that isomerization had taken place.

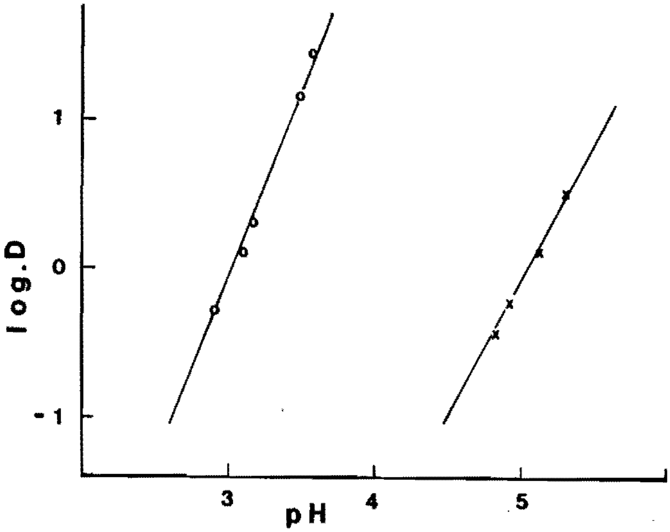

Fig. 3.4 Log D as a function of pH for the extraction of Cu(II)(O) or Ni(II)(X) with α*-camphorquinone dioxime. Concentration of* α-H_2CQD *in 1-pentanol 0.025 M. Initial aqueous metal sulfate concentration 0.001 M.*

The only solvent that we could find which dissolves β-H_2CQD and is not soluble in water was tri-n-butylphosphate (TBP). In fig. 3.5 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.

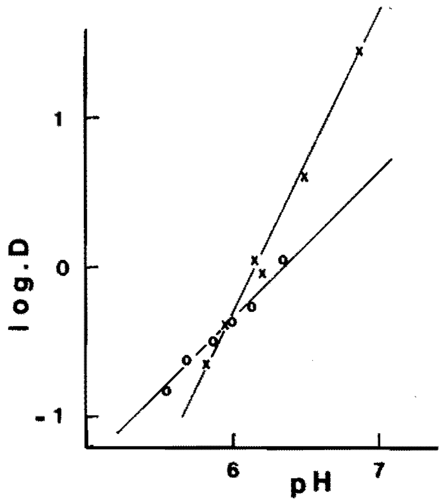

Fig. 3.5 Log D as a function of pH for the extraction of Ni(II) with β-camphorquinone dioxime. Concentration of β-H_2CQD in tri-n-butyl phosphate 0.025 M. Initial aqueous nickel chloride concentration 0.001 M O: fresh solution X: after two days of contact.

In the latter case the results correspond to those of the Ni δ-H_2CQD system: pH½ = 6.16, slope 1.99 and the recovered H_2CQD showed a specific rotation of +45.5^0, indicating that isomerization had occurred. Fresh solutions, however, show a slope of 0.97 and a slightly higher pH½ value of 6.33.

3.3.2 Extraction of Cu^{2+} with H_2CQD

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) of chapter 2) for the slope of the extraction curve for copper with δ-H_2CQD (fig. 3.3). A clearly lower pH½ value of 2.75 - leading to a $(pH½)_{1.0}$ of 1.15 - is found. Also for copper no significant change in the specific rotation of δ-H_2CQD could be noted (table 3.1).

As with the Ni α-H_2CQD system the Cu α-H_2CQD system gives almost the same figures as found for Cu δ-H_2CQD (fig. 3.4). In this case also isomerization had taken place (table 3.1) a pH½ value of 3.08, a slope of 2.76 and a change in specific rotation from -63.8^0 to $+51.9^0$ are found.

With a fresh solution of β-H_2CQD in TBP (fig. 3.6) a pH½ value of 4.21 is obtained for the copper extraction, quite larger than with the Cu δ-H_2CQD pentanol system. The slope of 1.47 indicates that the extraction chemistry

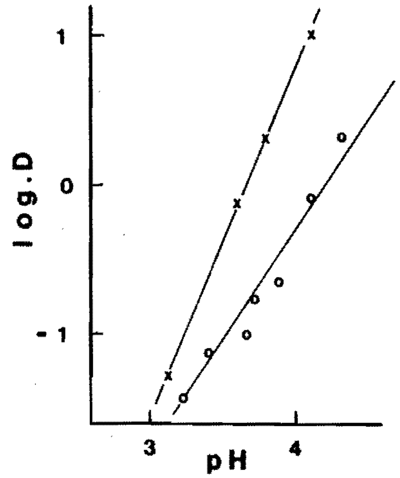

Fig. 3.6 Log D as a function of pH for the extraction of Cu(II) with β-camphorquinone dioxime. Concentration of β-H_2CQD in tri-n-butyl phosphate 0.025 M. Initial aqueous copper chloride concentration 0.001 M. O: fresh solution X: after two days of contact.

must deviate considerably from that represented by the extraction eqn. (1) of chapter 2. Just as in the experiment with nickel and β-H_2CQD, after two days the picture had dramatically changed. The pH½ value was lowered to 3.66 and the slope had increased to 2.37. Specific rotation measurement from the recovered H_2CQD showed that most of the β-H_2CQD had isomerized. This isomerization was more pronounced than the isomerization that occurred without contact with the aqueous copper solution (table 3.1).

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) of chapter 2. To find out which stoichiometry the copper camphorquinone dioxime chelate had during extraction an experiment was carried out with equivalent moles of copper and δ-H_2CQD.

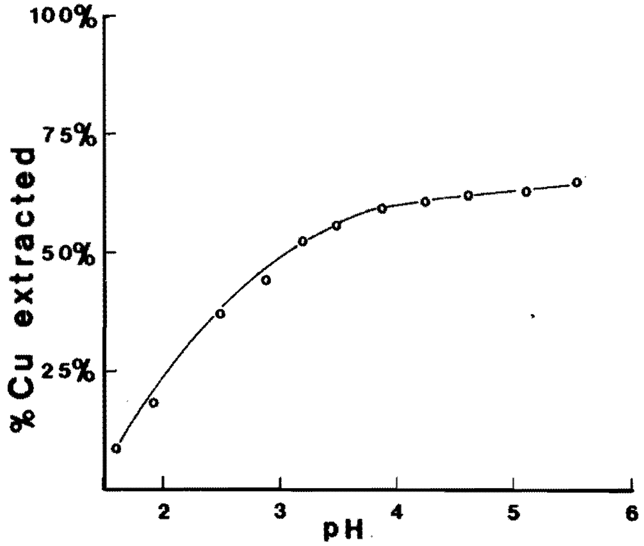

Fig. 3.7 % copper extraction as a function of pH for the extraction of Cu(II) with δ-camphorquinone dioxime. The initial concentration of δ-H_2CQD in chloroform and the initial copper nitrate concentration in H_2O are both 0.002 M.

If $Cu(HCQD)_2$ would be the only extraction chelate at most 50% of the copper can be extracted. Figure 3.7 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.

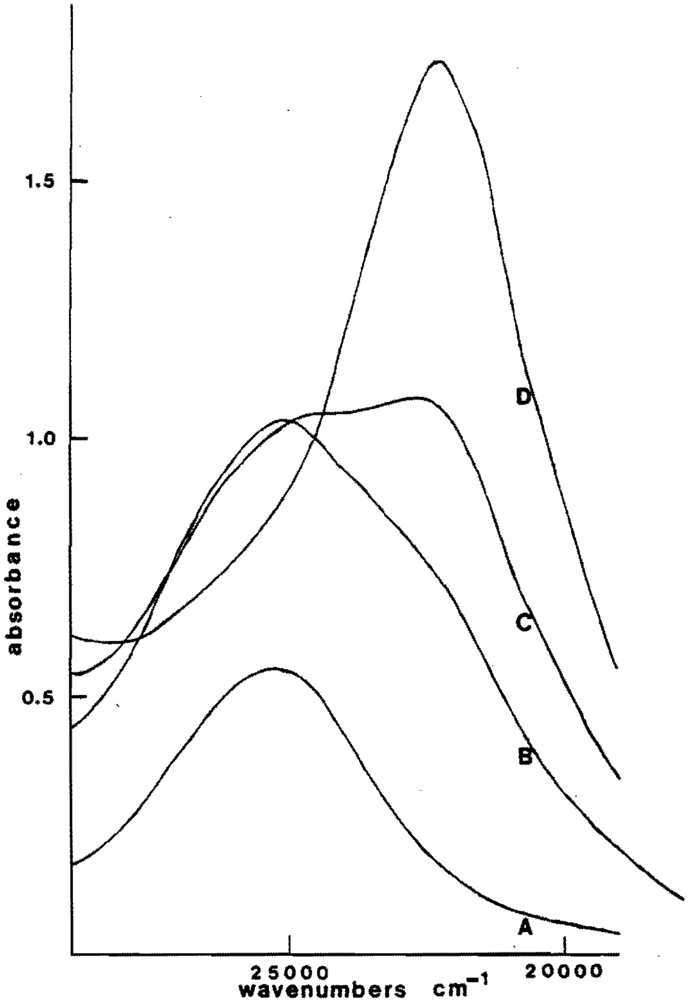

Fig. 3.8 VIS spectra of the organic phase for the extraction of copper(II) with δ-camphorquinone dioxime. A: pH = 1.93; B: pH = 2.87; C: pH = 3.20; D: pH = 5.00. For initial concentrations: see fig. 3.7.

VIS-spectroscopy (fig. 3.8) shows that two different copper chelates are present in the organic phase after extraction. When the pH is relatively low a chelate is formed with a maximum absorbance at 25,300 cm^{-1}. At higher pH's a new band appears with a maximum at 22,400 cm^{-1} and the corresponding chelate becomes prevalent at pH is 3.20.

Also ESR measurements, correlated with the two different Cu-HCQD chelates are carried out. The ESR spectrum of the chelate with λ_{max} 25,300 cm^{-1} is presented in fig. 3.9.

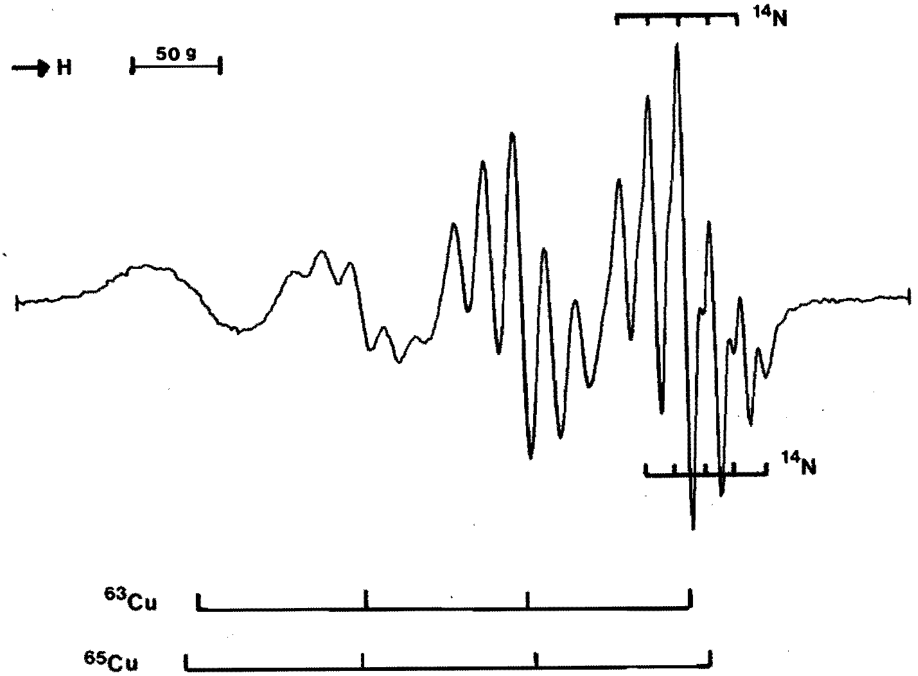

Fig. 3.9 ESR spectrum of copper H_2CQD *chelate (*λ_{max} *25300 cm*$^{-1}$*) in chloroform at room temperature.*

It is exactly the same as that found by Ma (5) for Cu(β-HCQD)$_2$.H$_2$O.½ dioxane. For the chelate with λ_{max} at 22,400 cm^{-1} no ESR signal could be observed.

3.4 DISCUSSION

3.4.1 The isomerization of H_2CQD

From table 3.1 it can be clearly seen that under extraction conditions isomerization takes place when α- or β-H_2CQD are used.

Without contact with an aqueous solution containing metal ions α-H_2CQD does not isomerize at all and β-H_2CQD 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_2CQD is the only isomer which possesses hydrogen bridge stabilization and no steric repulsion (table 3.2). Therefore it is not surprising that it is the most stable isomer.

Pedersen and Larsen (6) found isomerization of Ni(α-$HCQD)_2$ in chloroform to an equilibrium mixture of 85-90% Ni(δ-$HCQD)_2$ 5-10% Ni(α-$HCQD)_2$ and 5% Ni(β-HCQD)(δ-HCQD). This means that after recovering of H_2CQD 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 3.1 it is seen that after extraction with α-, β- or δ-H_2CQD the specific rotation had changed into the direction of this figure, but apparently equilibrium had not been reached.

Table 3.2 Stabilization and repulsion of the four different H_2CQD isomers.

H_2CQD	OH... CH_3 repulsion	OH... OH repulsion	OHO stabilization
α	yes	no	yes
β	yes	no	no
γ	no	yes	no
δ	no	no	yes

3.4.2 The structure of $Cu(HCQD)_2$

The expected selectivity of δ-H_2CQD could not be established. On the contrary, copper was extracted at a much lower pH than nickel (fig. 3.3). This result is surprising because if copper forms a N,N-coordinated chelate as suggested by Ma (5) then rotation around the CN double bond is necessary. Furthermore it might have been expected that copper extraction with β-H_2CQD, for which no rotation is needed would have a lower pH½ value than copper extraction with δ-H_2CQD. However, in fig. 3.6 it can be seen that after a contact time of two days, in which isomerization from β- to δ-H_2CQD has taken place, the pH½ value is lowered and not raised.

These results can only be explained if we assume that copper does not form a N,N-coordinated chelate, but a N,O-coordinated chelate just like nickel.

To investigate this possibility we took a closer look at the ESR spectrum of the extracted chelate, which is completely identical with the ESR spectrum found by Ma (5) for $Cu(\beta\text{-}HCQD)_2.H_2O.\frac{1}{2}$ dioxane. Ma has interpreted the ESR spectrum of $Cu(\beta\text{-}HCQD)_2$ 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 (0.70904×10^{-4} vs 0.75958×10^{-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. 3.9) two overlapping hyperfine splitting patterns with intensity 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 70:30 (see fig. 3.10).

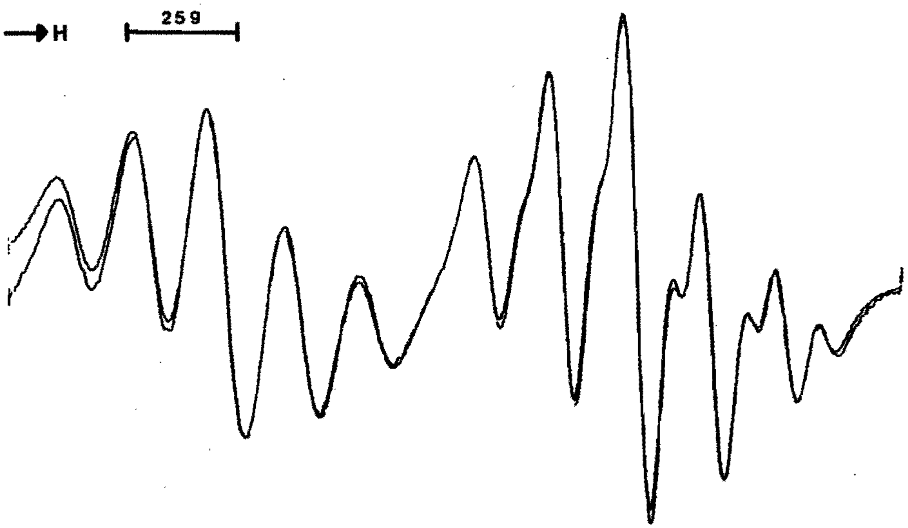

Fig. 3.10 The two high field copper bands from the ESR spectrum of fig. 3.9 together with the computer simulation for a CuN_2O_2 *chromophore. The input values for the simulation are* A_{Cu} *= 90 gauss,* A_N *= 16.6 gauss, linewidth = 9.2/6.2 gauss, modulation = 2.5 gauss, lineform = Lorentz;* ^{63}Cu *= 70% and* ^{65}Cu *= 30%.*

From the complete ESR spectrum a hyperfine splitting of 90 gauss is obtained for ^{63}Cu. The copper hyperfine splitting for ^{65}Cu can now be calculated to be 0.75958/0.70904 x 90 = 96.4 gauss. The predicted separation between ^{63}Cu and ^{65}Cu of the nitrogen superhyperfine splitting on the high field side of the ESR spectrum is 3/2(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 ^{65}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 ½(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 interpretation 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. Computer simulation for a CuN_4 chromophore did not give a picture that resembled the observed spectrum. To confirm this interpretation the ESR spectrum of bis(dipentylglyoximato) copper(II) was also examined. Dipentylglyoxime is an unstrained dioxime which is likely to form N,N-coordinated chelates. Figure 3.11 shows the two high-field copper bands of this spectrum together with the computer simulation assuming a CuN_4 chromophore. The simulated ESR spectrum does not fit completely with the experimental one because we were not able to simulate the overlap between the copper bands. This overlap is caused by the large linewidth of the copper bands. But it is clearly seen that the intensities of the nitrogen superhyperfine lines in the simulation are in very good agreement with the experimental intensities. If we compare the $Cu(HCQD)_2$ spectrum with this CuN_4 spectrum the difference in nitrogen splitting pattern is striking. We therefore 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 $Cu(\beta\text{-HCQD})_2$ chelate of Ma and the extracted chelate with λ_{max} at 25,300 cm^{-1} do not have the N,N structure but just like nickel a N,O structure (fig. 3.2).

The results found in the extraction experiments are in good agreement with this interpretation. For, if copper

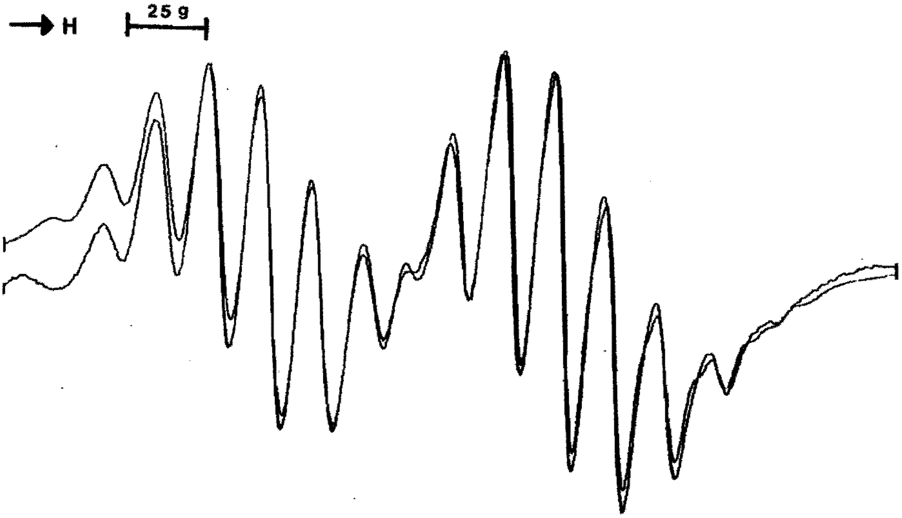

Fig. 3.11 The two high field copper bands from the ESR spectrum of bis(dipentylglyoximato) copper(II) in $CHCl_3$ at room temperature, together with the computer simulation for a CuN_4 chromophore. The input values for the simulation are A_{Cu} = 92 gauss, A_N = 16.2 gauss, modulation = 5 gauss, linewidth = 10.5/8.5 gauss, lineform = Lorentz, ^{63}Cu = 70% and ^{65}Cu = 30%.

and nickel form the same kind of chelate with H_2CQD, copper will have a lower pH½ value than nickel according to the Irving and Williams law.

3.4.3 Slope analysis of the extraction

The low values of the slopes of the log D vs pH curves found in the extraction of copper and nickel by fresh β-H_2CQD (1.47 for Cu and 0.97 for Ni) can now also be explained if we assume that β-H_2CQD is not active in the extraction. Only the small portion of the δ-H_2CQD

that is present will be active. As a consequence the extractant concentration in eqn. (4) of chapter 2 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 β-H_2CQD is isomerized to δ-H_2CQD, excess δ-H_2CQD 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 δ-H_2CQD. Also the change of the pH½ value (4.21-3.66 for Cu and 6.33-6.16 for Ni) can be explained by the fact that isomerization of β-H_2CQD to δ-H_2CQD increases the extractant concentration. For according to eqn. (6) of chapter 2 an increase in the extractant concentration leads to a decrease in the pH½ value. For α-H_2CQD such a phenomenon was not observed. This is not surprising because α-H_2CQD itself can form a N,O coordinated chelate and thus is active in the extraction. As a consequence, during isomerization of α-H_2CQD to δ-H_2CQD the extractant concentration does not change.

The result of the slope analysis of 1.93 for the extraction of nickel(II) by δ-H_2CQD is consistent with the theoretically expected value of 2 (eqn. (5) of chapter 2 and thus the extraction equation can be represented by

$$Ni^{2+} + 2H_2CQD \rightleftarrows Ni(HCQD)_2 + 2H^+.$$

With copper(II), on the contrary, a deviating value of 2.50 was found for the extraction by δ-H_2CQD.
To find out why this value deviated, a closer look will be taken at the extraction of Cu^{2+} by δ-H_2CQD in the next paragraph.

3.4.4 Chelates responsible for the Cu^{2+} extraction by δ-H_2CQD

According to Fig. 3.8 it was shown that two different chelates are involved during the extraction: chelate A with λ_{max} = 25,300 cm^{-1} and chelate B with λ_{max} = 22,400 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, chelate A may be assumed to be $Cu(HCQD)_2$.

Fig. 3.7 shows that at pH = 5, 65% of the copper is extracted and from fig. 3.8 it can be concluded that at this pH chelate B is almost exclusively responsible for the extraction. The value of about 65% extraction at high pH can be explained if a chelate with a copper:H_2CQD = 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 chelates accurate values of the intensities of both (overlapping) bands 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 $y = a(1 + bx^2 + cx^4)^{-1}$ as used by Baker *et al.* (12) for IR band simulation. A strong absorption near 35,000 cm^{-1} with some overlap around 25,000 cm^{-1} has been taken into account. In fig. 3.12 one of the simulations is shown, and the excellent fit is noteworthy. In this way the real intensities of the bands at λ_{max} could be obtained and these values are according to Beer's law proportional to the concentrations of chelate A (25,300 cm^{-1}) and B(22,400 cm^{-1}). By using the trial and error method the best extinction coefficients for A and B could be determined. These extinction coefficients are 4940 for A and 8700 for B. In fig. 3.13 it is shown what happens with the different species as a function of pH.

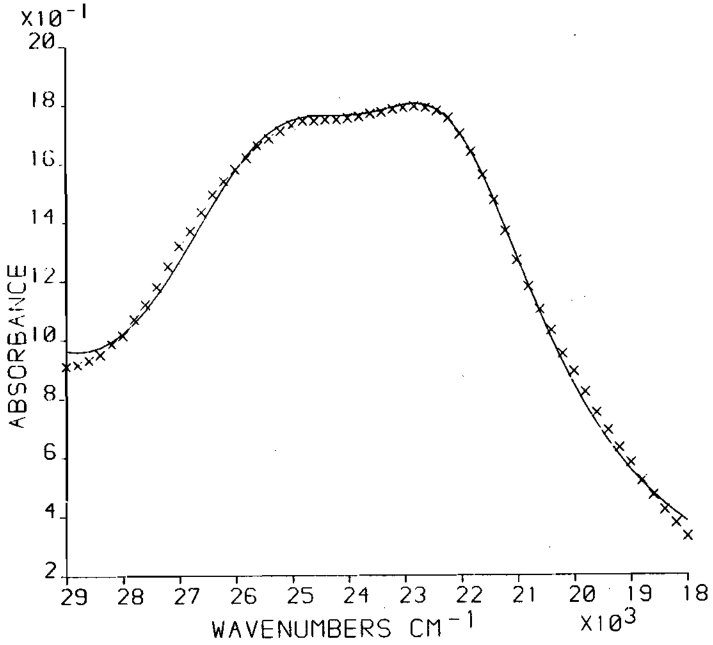

Fig. 3.12 VIS spectrum of the organic phase after the extraction of copper(II) with δ-camphorquinone dioxime at pH 3.20. X: experimental, —: calculated by computer simulation. For initial concentrations see fig. 3.7.

For chelate A we assume that the same reaction equation applies as used in eqn. (1) of chapter 2 and k_A is then given by eqn. (8):

$$k_A = \frac{[Cu(HCQD)_2][H^+]^2}{[Cu^{2+}][H_2CQD]^2} = \frac{[A][H^+]^2}{[Cu^{2+}][H_2CQD]^2} . \qquad (8)$$

The composition of chelate B is more complicated. It is very likely that chelate B is neutral in the organic phase, and in combination with the results of fig. 3.7 this suggests its formula to be $Cu_2(HCQD)_2CQD$. In that case

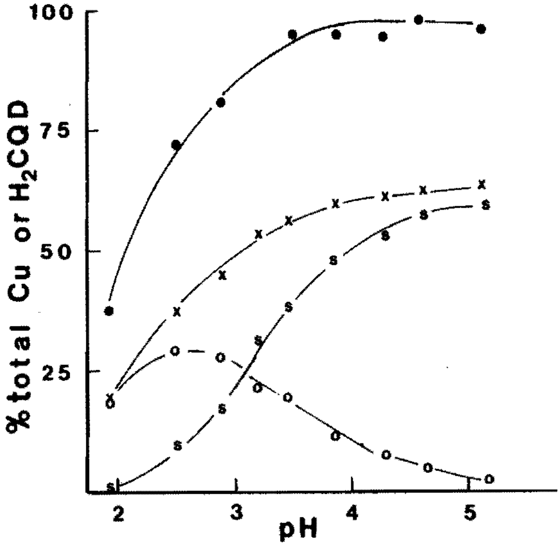

Fig. 3.13 Extraction of copper(II) with δ-camphorquinone dioxime as a function of pH. ● *:% reacted δ-H_2CQD, X: % Cu extracted into the organic phase, O: % Cu extracted by chelate A with λ_{max} 25.300 cm^{-1}; S: % Cu extracted by chelate B with λ_{max} 22.400 cm^{-1}. For initial concentrations see fig. 3.7.*

the reaction equation is

$$2Cu^{2+} + 3H_2CQD \rightleftarrows Cu_2(HCQD)_2CQD + 4H^+ \qquad (9)$$

with an equilibrium constant k_B:

$$k_B = \frac{[Cu_2(HCQD)_2CQD][H^+]^4}{[Cu^{2+}]^2[H_2CQD]^3} = \frac{[B][H^+]^4}{[Cu^{2+}]^2[H_2CQD]^3} \qquad (10)$$

In eqns. (8) and (10) all concentrations can be measured ($[H^+]$ with pH measurements $[Cu^{2+}]$ with atomic absorption, [A] and [B] with UV/visible spectroscopy) with the exception of $[H_2CQD]$. To eliminate $[H_2CQD]$ we combine (8) and (10)

$$\frac{[k_A]^3}{[k_B]^2} = \frac{[A]^3[Cu^{2+}]}{[B]^2[H^+]^2} \tag{11}$$

resulting in

$$\frac{\delta(2\ \log[B]\ -\ 3\log\ [A]\ -\ \log\ [Cu^{2+}])}{\delta pH} = 2\ . \tag{12}$$

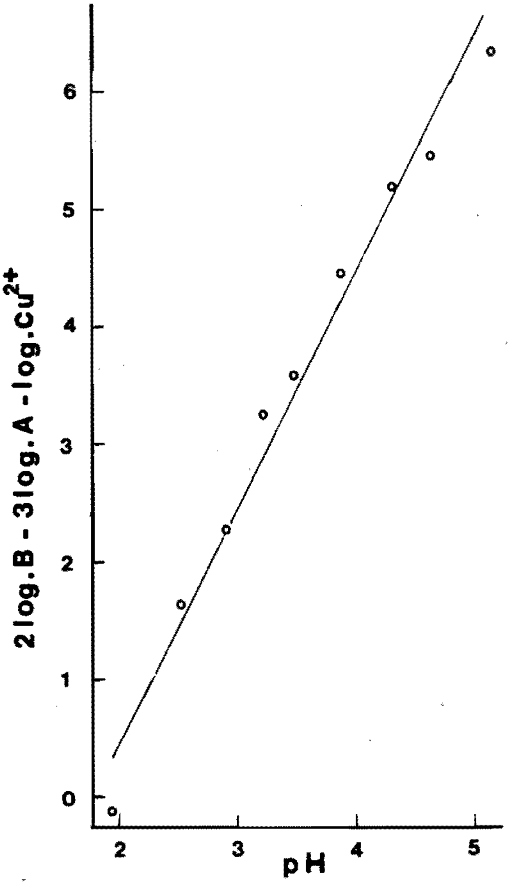

Fig. 3.14 2log[B]- 3log[A]- log [Cu^{2+}] as a function of the pH for the extraction of copper(II) with δ-camphorquinone dioxime. A and B are the calculated values of the maxima of the chelate with λ_{max} = 25.300 cm^{-1} and of the chelate with λ_{max} = 22.400 cm^{-1} respectively For initial concentrations see fig. 3.7.

In fig. 3.14 we see that a plot of 2 log[B] - 3log[A] - log $[Cu^{2+}]$ vs pH indeed gives a straight line with a slope of 1.99 confirming our assumptions concerning chelate B. However, the requirements of a neutral chelate with a copper ligand ratio of 2/3 are also fulfilled with the assumption of the chelate $Cu_2(HCQD)_3OH$, replacing the double negative charge of CQD by $HCQD^-$ plus OH^-:

$$2Cu^{2+} + 3H_2CQD + H_2O \rightleftarrows Cu_2(HCQD)_3OH + 4H^+ \ . \qquad (13)$$

Because H_2O can be assumed to be constant, replacing (9) by (13) gives no difference in expressions (11) and (12) so chelate B might also be represented by $Cu_2(HCQD)_3OH$.

If OH^- is replaced by another anion, for example NO_3^- (to adjust pH HNO_3 is used), elimination of H_2CQD from the expressions for k_A and k_B gives:

$$\frac{k_A{}^3}{k_B{}^2} = \frac{[A]^3}{[B]^2}[NO_3{}^-]^2[Cu^{2+}] \ . \qquad (14)$$

This would mean that $[A]^3/[B]^2$ would be independent from the pH, which does not fit with fig. 3.13. 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 chelate, we checked if a 1:1 chelate could explain the extraction results

$$Cu^{2+} + H_2CQD \rightleftarrows Cu(CQD) + 2H^+ \ . \qquad (15)$$

In combination with eqn. (8) and by eliminating the $[H_2CQD]$ we obtain:

$$\frac{k_A}{k_B{}^2} = \frac{[A]}{[B]^2} \cdot \frac{[Cu^{2+}]}{[H^+]^2} \qquad (16)$$

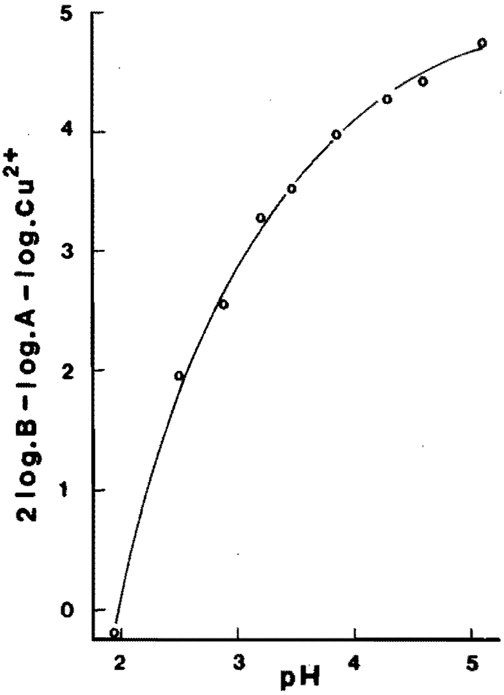

Fig. 3.15 $2\log[B] - \log[A] - \log[Cu^{2+}]$ *as a function of the pH for the extraction of copper(II) with δ-camphorquinone dioxime. A and B are the calculated values of the maxima of the chelate with* λ_{max} *= 25.300* cm^{-1} *and of the chelate with* λ_{max} *= 22.400* cm^{-1} *respectively. For the initial concentrations see fig. 3.7.*

Therefore a plot of $2\log[B] - \log[A] - \log\ [Cu^{2+}]$ vs pH must give a straight line with slope 2. From fig. 3.15 it is clear that this is not the case so we may safely reject eqn (15). Also $Cu(HCQD)(NO_3)$ can be rejected by this way of analysis. Because of all these arguments for chelate B we conclude that chelate B must have the composition $Cu_2(HCQD)_2CQD$ or $Cu_2(HCQD)_3OH$.

In agreement with this conclusion no ESR signal could be observed for chelate B. This is not an unknown phenomenon

(13, 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 chelate B must be $Cu_2(HCQD)_3OH$ or $Cu_2(HCQD)_2CQD$.

3.4.5 The influence of the N-N distance

The bicyclic character of the carbon skeleton of H_2CQD enlarges the N-N distance from 2.4 Å in a normal unstrained aliphatic dioxime to 3.0 Å. This increase causes some remarkable changes in the extraction properties. In the first place the chelates formed do not have normal N,N-coordination but have N,O-coordination to relieve the strain. Secondly, the rank of stabilities for copper and nickel is reversed with respect to unstrained aliphatic dioximes. Thirdly, extraction equilibrium for nickel is reached much quicker. With H_2CQD equilibrium was established within an hour while for unstrained aliphatic dioximes equilibrium was not yet reached even after several days. These three changes make it very interesting to investigate other strained dioximes, expecially those with a N-N distance between 2.4 and 3.0 Å.

3.5 CONCLUSIONS

The expected selectivity of δ-H_2CQD for the extraction of nickel above copper has not been confirmed. On the contrary, copper was found to have a pH½ 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 $Cu(\beta\text{-}HCQD)_2.H_2O.\frac{1}{2}$ dioxane, had a N,N-coordination around copper.

Our analysis of the ESR spectrum showed, however, that this product does not have a N,N-coordination but a N,O-coordination like nickel. With the knowledge that there is no difference in coordination of H_2CQD around copper and nickel, it is not surprising that δ-H_2CQD 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 α- and β-H_2CQD into δ-H_2CQD. Without contact with metal ions or protons the α-H_2CQD is stable in solution. We therefore conclude that metal ions or protons attache to the nitrogen atoms and lower the double bond character of the CN bond, thus making rotation around this bond more easily.

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

With copper two different chelates are involved in the extraction which is clearly seen by UV spectroscopy. Computer simulation showed that these two chelates are $Cu(HCQD)_2$, with an absorption at 25,300 cm^{-1} and $Cu_2(HCQD)_2CQD$ or $Cu_2(HCQD)_3OH$ with an absorption at 22,400 cm^{-1}. ESR spectroscopy proved the $Cu(HCQD)_2$ chelate to have an N,O structure. For the Cu:HCQD = 2:3 chelate no ESR signal could be observed, which is not uncommon for binuclear copper(II) complexes with a very strong antiferromagnetic coupling.

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CHAPTER 4

EXTRACTION OF COPPER(II) AND NICKEL(II) BY NOPINOQUINONE DIOXIME

4.1 INTRODUCTION

Vicinal dioximate ligands usually form stable N,N-chelated complexes containing a conjugated N=C-C=N system (fig. 4.1a).

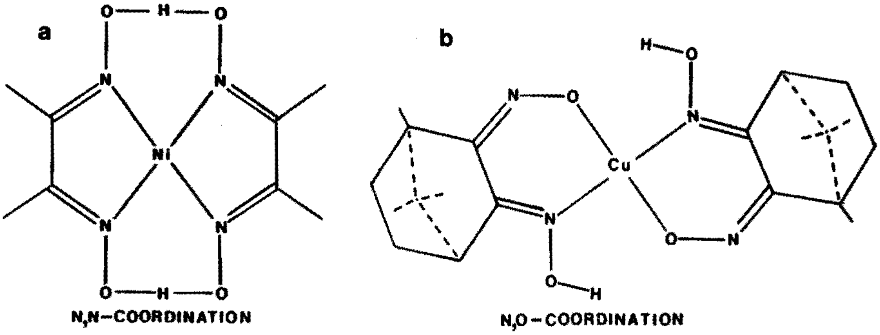
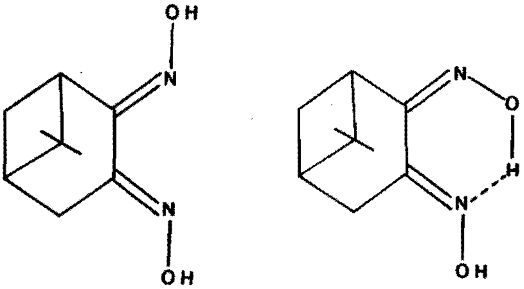


Fig. 4.1(a) The N,N-coordinated bis(dimethylglyoximato)-nickel(II) chelate.
(b) The N,O-coordinated bis(camphorquinonedioximato)-copper(II) chelate.

In chapter 3 it became clear that camphorquinone dioxime cannot form a stable N,N-coordinated chelate with copper and nickel. The rigid bicyclic skeleton is responsible for a larger N-N distance than in aliphatic α-dioximes and makes the N,O-coordination, with a six-membered ring metal-N=C-C=N-O- more attractive (fig. 4.1b).

Nopinoquinone dioxime H_2NQD(6,6-dimethylbicyclo[3.1.1]-heptane-2,3-dione dioxime), also a bicyclic molecule, is therefore of interest because the strain in this structure is somewhat less and so the N-N distance will be shorter than in camphorquinone dioxime. This may have consequences for the way of coordination and may lead to different complexes for copper and nickel. By using the right isomer (fig. 4.2) there might be a chance that a selective ligand will be found for nickel. For this reason we tried to synthesize β- and δ-nopinoquinone dioxime, studied the extraction properties and tried to determine the structure of the chelates formed during the extraction.



β-H_2NQD δ-H_2NQD

Fig. 4.2 Two isomeric forms of nopinoquinone dioxime

4.2 SYNTHESIS

4.2.1 β-Nopinoquinonedioxime

Nopinone(6,6-dimethylbicyclo [3.1.1]heptane-2-one) was prepared by ozonolysis of β-pinene (J.T. Baker chemicals B.V. Deventer, Baker grade) according to a published method. The decrease in intensity of the sharp C-H band of alkenes at 3070 cm^{-1} in the IR spectrum was a useful indication how much pinene was converted. Following the conventional method using n-butyl nitrite, isonitrosonopinone was obtained in 30% yield from nopinone. Following the procedures of Nakamura (3), crude isonitrosonopinone (0.18 mol) dissolved in 50 ml ethanol was treated with an aqueous solution of $NH_2OH.HCl$ (0.48 mol) and NaOAc (0.51 mol) at 90°C for 3 days.
A solid white inorganic product precipitated. The mother liquid was concentrated <u>in vacuo</u> to 50% of the original

volume and filtered. Further concentration, removing ethanol completely gave the crude β-isomer. Extraction with boiling ethyl acetate removed the δ-isomer completely and gave the pure β-H_2NQD.

Expected C59.3 H7.7 N15.4 O17.6. Found C59.3 H7.9 N15.5.

IR: OH stretching vibrations at 3360 cm^{-1} and 3180 cm^{-1} C=N absorptions at 1585 cm^{-1} and 1615 cm^{-1}. These values are in perfect agreement with Nakamura (4).

^{1}H NMR (DMSO-d6):δ0.74 (s, 3H), 1.03 (s, 3H), 2.05 (m.c, 1H), 2.41(t, 1H), 2.64 (d, 1H), 3.41 (t, 1H), 10.74 (s, 1H), 11.18 (s, 1H) confirms the β structure (3).

4.2.2 The furazan of nopinoquinone dioxime (fig. 4.3)

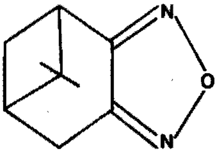


Fig. 4.3 The structure of the furazan derived from nopinoquinone dioxime

The yellow oil, which was obtained in the above synthesis by the evaporation of the ethylacetate from the extract, was treated with 1N NaOH and extracted with ether. The ether layer was dried and evaporated. A yellow pleasantly smelling oil was obtained. After distillation a white powder was produced with a melting point of 30°C. IR: 1510 cm^{-1} (furazan) 1550 and 1615 cm^{-1} (C=N); no OH stretchings present. Expected $C_9H_{12}N_2O$, C65.8 H7.3 N17.1 O9.8. Found C65.5 H7.5 N16.9 ^{1}H NMR (DMSO-d6): see fig. 4.4.

4.2.3 Bis(β-nopinoquinonedioximato)nickel(II).

Ni(β-NHQD)$_2$ was synthesized by the reaction of β-nopinoquinone dioxime and $NiCl_2.6H_2O$ in ethanol with NaOH in a minimum amount of water. After stirring for two hours water was added and the orange-red chelate precipitated.

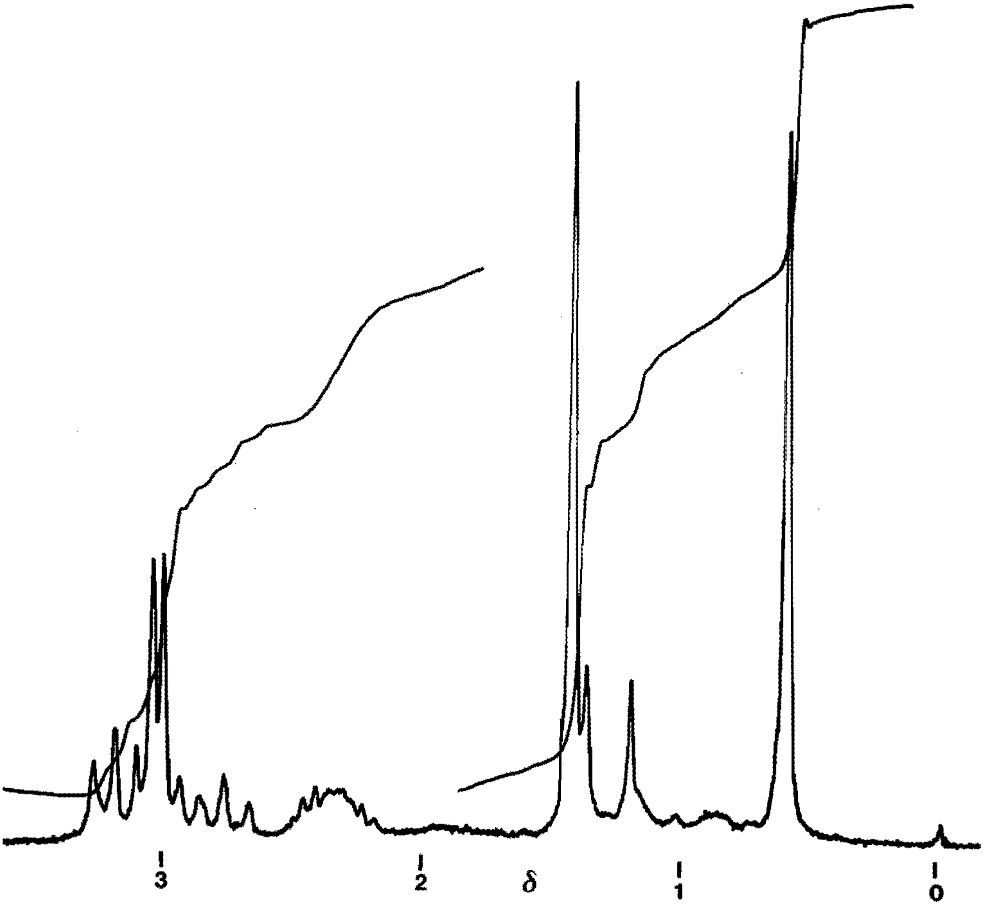


Fig. 4.4 60 MHz ^{1}H NMR spectrum of the furazan of nopinoquinone dioxime in DMSO-d6.

The chelate was washed with water and dried at 50°C in the presence of silica.

IR: No absorption in the 3100-3600 cm^{-1} region.

1585 cm^{-1} and 1560 cm^{-1} (shoulder)(C=N)

Expected $NiC_{18}H_{26}N_4O_4$: C51.35 H6.25 N13.31 O15.21 Ni13.95.

Found C51.09 H6.26 N13.51.

4.3 RESULTS

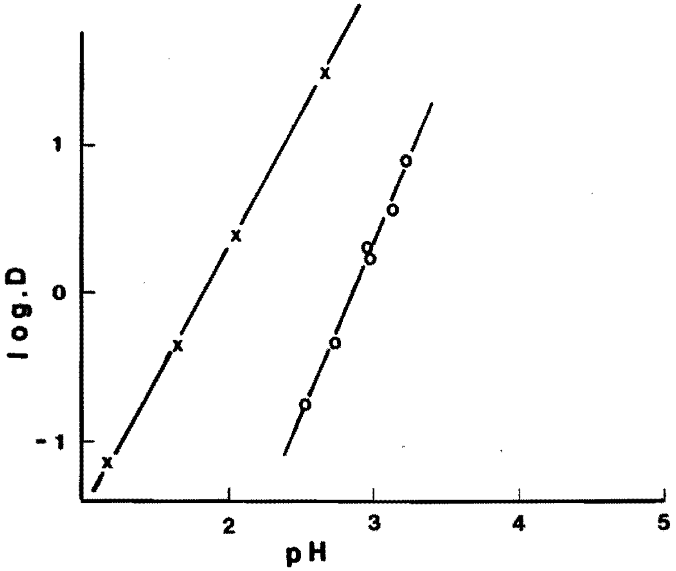


Fig. 4.5 Log D as a function of pH for the extraction of Cu(II)(X) and Ni(II)(O) with β-nopinoquinone dioxime. Concentration of β-H_2NQD in pentanol 0.025 M. Initial aqueous metal nitrate concentration 0.001 M.

Figure 4.5 shows the results for the extraction of Cu^{2+} and Ni^{2+} with an excess of β-H_2NQD. The pH½ value of 1.85 for Cu^{2+} corresponds with $(pH½)_{1.0}$ = 0.25. For Ni^{2+} these values are somewhat higher: pH½ = 2.88 and $(pH½)_{1.0}$ = 1.28. For the nickel extraction equilibrium was reached within ten minutes.

The slopes of the log D-pH curves are 1.75 for copper and 2.22 for nickel, both values slightly deviate from the theoretically expected value of 2 for a metal: ligand ratio of 1:2. No change in the extraction behaviour of β-H_2NQD could be observed after two days of contact.

To find out if copper only forms a 1:2 chelate with β-H_2NQD an experiment was done with equimolair amounts of copper and β-H_2NQD (fig. 4.6). Maximum copper extraction was 50%, in excellent agreement with the formation of Cu:β-H_2NQD = 1:2. The shape of the UV/visible spectrum of the pentanol solution with the extracted chelate did not change during this experiment. The spectrum showed two maxima below 37.500 cm^{-1}, one at 35.700 cm^{-1} (ε = 9000) and the other at 27.000 cm^{-1} (ε = 2300).

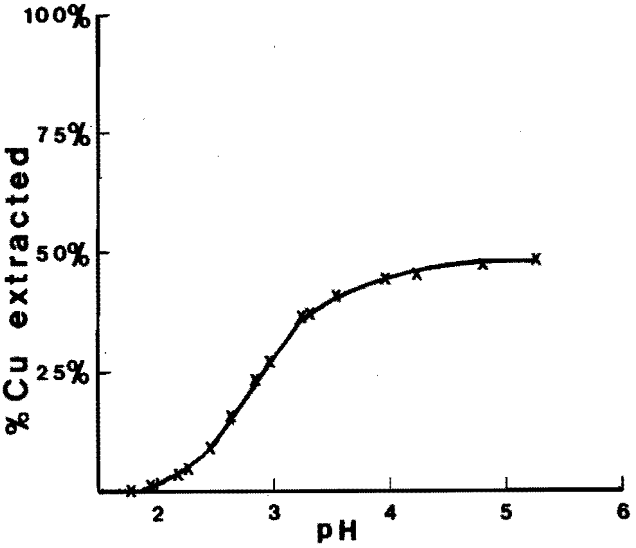


Fig. 4.6 % Copper extraction as a function of pH for the extraction of Cu(II) with β-nopinoquinone dioxime. The initial concentration of β-H_2NQD in pentanol and the initial copper nitrate concentration in water are both 0.002 M.

The elemental analysis from the isolated chelate is C48.61 H6.32 N11.29 Cu12.98 O20.8. This leads to a chelate with $CuC_{20}H_{31}N_4O_6$ indicating that the chelate has two additional water molecules and that also some pentanol is left behind. The expected elemental analysis from $Cu(HNQD)_2 \cdot 2H_2O$ containing 6½% pentanol ($C_5H_{11}OH$) is C48.19 H6.96 N11.34 Cu12.88 O20.63. The ESR spectrum of the chelate in $CHCl_3$ is presented in fig. 4.7.

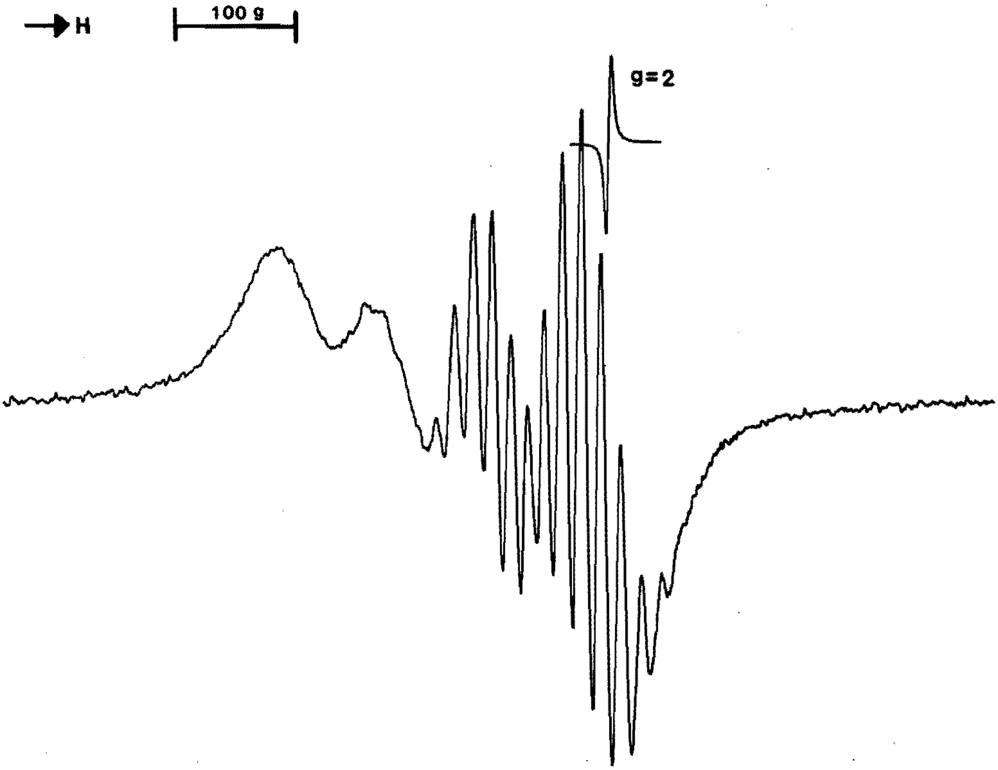


Fig. 4.7 ESR spectrum of the copper chelate formed during the extraction of Cu^{2+} by β-H_2NQD in chloroform at room temperature.

The nickel H_2NQD chelate isolated from the extraction was examined with NMR (fig. 4.8). The elemental analysis gave C54.4% H7.0% N12.6% Ni11.7% which was somewhat different from the expected Ni(HNQD)$_2$: C51.3% H6.2% N13.3% Ni13.9%. The IR spectrum was almost identical with that from the synthesized Ni(β-HNQD)$_2$. Only one extra absorption appeared at 3400 cm^{-1}, probably due to the OH from pentanol that was not completely removed at 60°C.

The furazan of nopinoquinone dioxime did not have any extraction capacities at all.

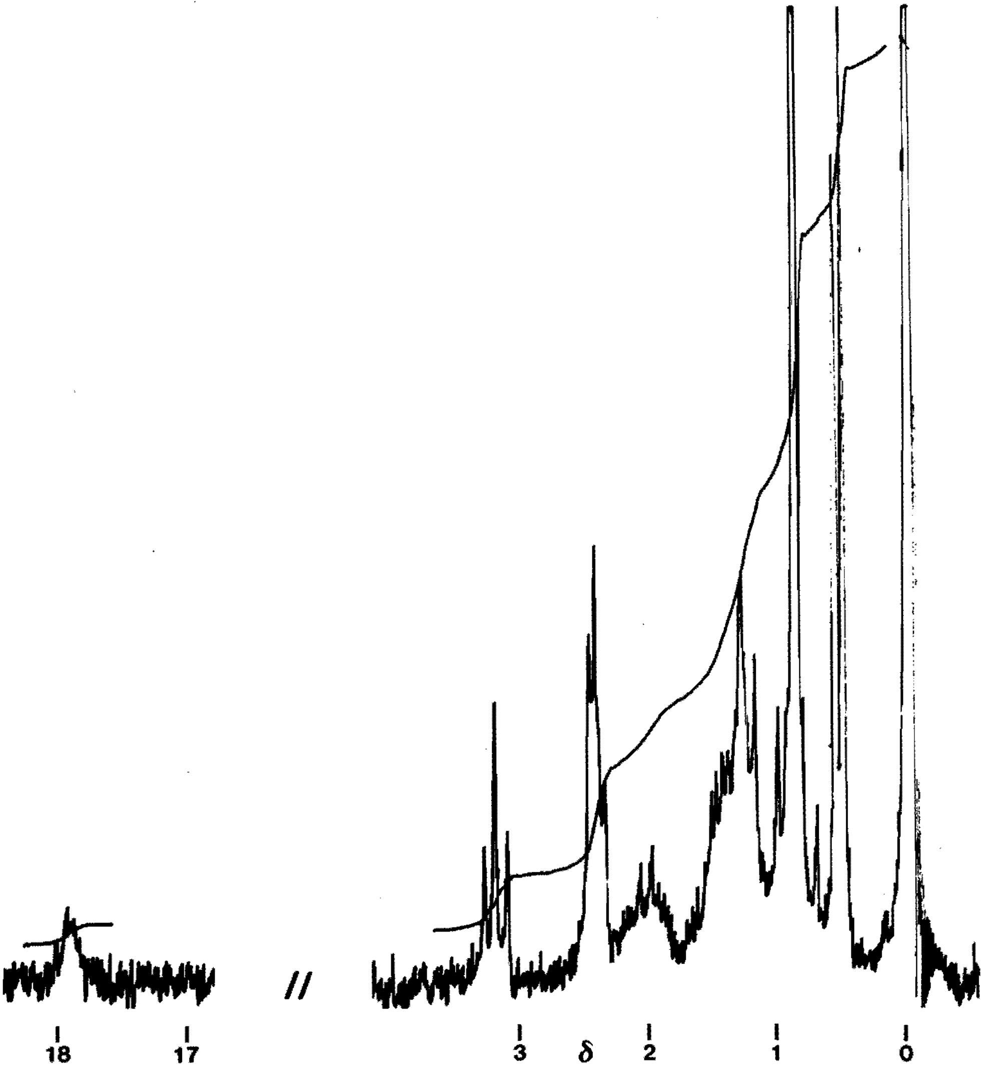


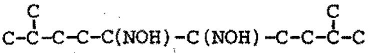
Fig. 4.8 60 MHz ^1H spectrum of the nickel chelate formed during the extraction of Ni^{2+} by β-H_2NQD in benzene at room temperature.

4.4 DISCUSSION

4.4.1 Extraction

If we compare the extraction results of β-H_2NQD with those of β-H_2CQD clearly a lowering of the $(pH½)_{1.0}$ value for both copper and nickel is observed (table 4.1).

Table 4.1 Extraction of copper(II) and nickel(II) by some vic-dioximes

Compound	solvent	$(pH½)_{1.0}$ Cu	$(pH½)_{1.0}$ Ni	reference
α-H_2CQD*	pentanol	+1.48	+3.43	chapter 3 (5)
β-H_2CQD*	t.b.p.	+2.61	+4.73	chapter 3 (5)
δ-H_2CQD	pentanol	+1.15	+3.60	chapter 3 (5)
β-H_2NQD	pentanol	+0.25	+1.28	this chapter
$C_5H_{11}-C(NOH)-C(NOH)-C_5H_{11}$	toluene	+0.62	-0.42	Burkin (6)
$C_7H_{15}-C(NOH)-C(NOH)-C_7H_{15}$	toluene	+0.54	-0.36	Burkin (6)
 $C-\overset{C}{C}-C-C-C(NOH)-C(NOH)-C-C-\overset{C}{C}-C$	toluene	+0.59	-0.14	Burkin (6)

*Isomerization occurs to δ-H_2CQD under extraction conditions.

This lowering cannot completely be explained by the fact that different solvents are used. In chapter 3 it is proven that β-H_2CQD isomerizes to δ-H_2CQD and that this is coupled with a lowering of the pH½ value. So pH½(β-H_2CQD) > pH½(δ-H_2CQD). In table 4.1 it is observed that the pH½ value of δ-H_2CQD is larger than that of β-H_2NQD in pentanol. The conclusion can be drawn that the pH½ value of β-H_2NQD is smaller than that of β-H_2CQD. Another difference between β-H_2NQD and β-H_2CQD is that with the former compound no change in the extraction behaviour is seen after a contact time of two days. Isomerization of β-H_2NQD is therefore very unlikely. To confirm this the isolated copper chelate was investigated with ESR spectroscopy (see 4.4.2) and the isolated nickel chelate was examined with NMR spectroscopy (see 4.4.3).

4.4.2 The structure of the copper H_2NQD chelate

Figure 4.6 shows that copper forms a 1:2 chelate with β-H_2NQD under extraction conditions. From the elemental analysis of the extracted $Cu(\beta\text{-}HNQD)_2$ it became clear that the chelate is extracted with two additional water molecules. It is reasonable to expect that these two water molecules are weakly bound in the axial position of a distorted octahedron. Cu^{2+} is a d^9 system with one unpaired electron which will be located in the $d(x^2-y^2)$ orbital to minimize the electronic repulsion of the other electrons with the ligand electrons. The ESR spectrum (fig. 4.7) shows four main lines which are due to copper (^{63}Cu, ^{65}Cu:I = 3/2) and extra lines superimposed on it due to the nitrogen (^{14}N:I = 1) superhyperfine interaction. If copper forms a CuN_4 species then the $d(x^2-y^2)$ orbital will have overlap with 4N's which results in a superhyperfine structure with nine equidistant lines with an intensity ratio of 1:4:10:16:19:16:10:4:1. If on the other hand copper forms a CuN_2O_2 chromophore, only 2 N's are coupled to copper, and given the fact that O does not have a magnetic moment, five equidistant lines with an intensity ratio of 1:2:3:2:1 are expected. In figure 4.7 it is hard to see how many lines are superimposed on one copper line because there is some overlap between the two copper lines on which nitrogen superhyperfine splitting is noticable. In contrast with the spectrum of $Cu(\beta\text{-}HCQD)_2$ (chapter 3 fig. 3.9) there are now no equidistant extra lines with strange intensities due to ^{65}Cu, visible on the high field side of the spectrum. This can be explained in two ways. Firstly, the $Cu(\delta\text{-}HCQD)_2$ spectrum has more narrow lines as deduced from the fact that the nitrogen superhyperfine splitting is clearly visible on the second low-field copper line. Furthermore, the ^{63}Cu splitting is smaller in $Cu(\beta\text{-}HNQD)_2$:77.5 gauss instead of 90.5 gauss. The splitting of ^{65}Cu can now be calculated from the difference in magnetic moment (0.70904×10^{-4} for ^{63}Cu versus 0.75958×10^{-4} rad sec^{-1} $gauss^{-1}$ for ^{65}Cu). The expected separation between ^{63}Cu

and ^{65}Cu on the high field side of the ESR spectrum is $3/2.(\frac{0.75958}{0.70904}-1).77.5 = 8.3$ gauss instead of the 9.6 gauss for Cu(δ-HCQD)$_2$. In fig. 4.9 the two high-field lines of copper are seen, and the nitrogen superhyperfine lines are numbered.

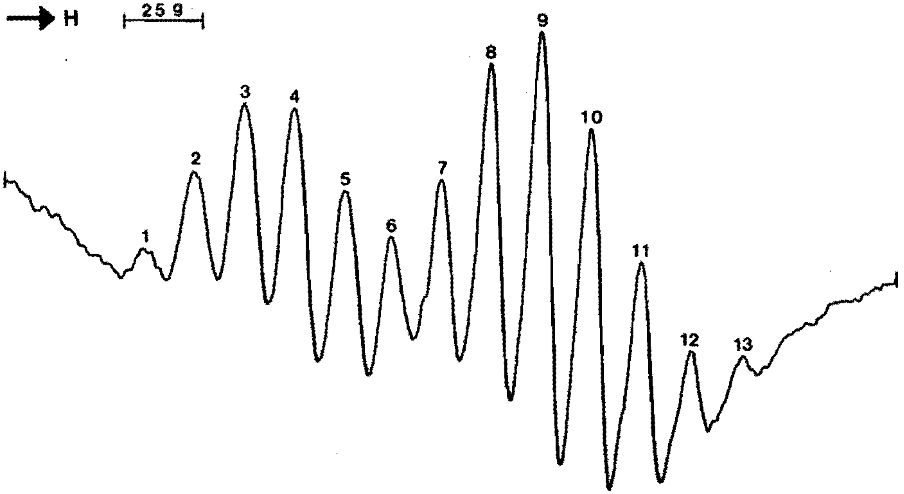


Fig. 4.9 The two high-field lines of copper from fig. 4.7.

The intensities cannot be measured exactly, because of the superposition on the copper lines. The rough values can be obtained by taking the so-called up-down distance, but these values are too low if the copper line goes up and too high if the copper line goes down.

Table 4.2 Up-down values of the nitrogen superhyperfine splittings of fig. 4.9 and the expected values for CuN$_4$ and CuN$_2$O$_2$ chromophores.

line number	up-down value	CuN$_4$ expection	CuN$_2$O$_2$ expection
1	1.2	2.3	0
2	4.4	5.8	3.7
3	9.1	9.3	7.4
4	11.1	11.1	11.1
5	8.4	9.3/1.0*	7.4
6	4.4	5.8/4.1*	3.7
7	8.1	2.3/10.3*	6.5
8	15.2	0.6/16.4*	13.0
9	19.5	19.5	19.5
10	15.7	16.4	13.0
11	9.6	10.3	6.5
12	3.2	4.1	0
13	0.8	1.0	0

*The superhyperfine splitting of the two copper lines are overlapping in this region.

Table 4.2 shows that the intensities are in reasonably good correlation with a CuN_4 chromophore, especially the lines 8-13 where no overlap occurs with the other nitrogen superhyperfine splitting. The CuN_2O_2 chromophore can be rejected because the lines 1, 12 and 13 cannot be explained. Furthermore the calculated intensities of the lines 7, 8, 10 and 11 are quite deviating from the observed intensities. The conclusion that can be drawn from the ESR spectrum is that $Cu(\beta\text{-}HNQD)_2$ has N,N-coordination.

4.4.3 The structure of the nickel H_2NQD chelate

The elemental analysis of $Ni(\beta\text{-}HNQD)_2$ from extraction is somewhat deviating from the expected values, while the synthesized $Ni(\beta\text{-}HNQD)_2$ had a very good elemental analysis. Nevertheless the IR spectra of these two species are identical, except for an extra absorption of the extracted chelate at 3400 cm^{-1}, probably due to the OH group of pentanol that was not completely removed at 60°C. That is why the C and H percentages are raised and as a consequence the N and Ni percentages are lowered. No additional water molecules are found by the elemental analysis. This makes a square planar structure the most probable configuration as is often seen for Ni^{2+} d^8 systems. This system will therefore have a low-spin state, which means that the electrons are paired in the $d(z^2)$ orbital - the orbitals d(xy), d(xz) and d(yz) are also filled with paired electrons - and the $d(x^2-y^2)$ orbital, which has a large electron repulsion with the ligand electrons, is empty. As a consequence $Ni(\beta\text{-}HNQD)_2$ is diamagnetic so ESR spectroscopy gives no information, while NMR spectroscopy might give information in this case.

The NMR spectrum of $Ni(\beta\text{-}HNQD)_2$ is of a bad quality probably due to the presence of some paramagnetic traces. This is not strange for such a strong complexant as $\beta\text{-}H_2NQD$. According to Nakamura (4) $Ni(\beta\text{-}HNQD)_2$ can have two possible ligand alignments, anti and syn. This can also be observed in the NMR spectrum of the extracted $Ni(\beta\text{-}HNQD)_2$. The values of the chemical shift are given in table 4.3 together with the literature values. The proton numbering can be found in fig. 4.10.

Table 4.3 ^1H NMR spectra of β- and δ-nopinoquinone dioxime and their nickel(II) chelates.

compound	C^9H_3	C^8H_3	Hf	He	Hd	Hb,c	Ha	OH	solvent	reference
Ni(δ-HNQD)$_2$	0.80	1.35	1.21	2.16	2.60	2.82		11.16	$CDCl_3$	4
Ni(β-HNQD)$_2$	0.56	0.94	1.17	1.52	2.20	2.45	3.29	17.90	C_6D_6	4
	0.63	0.94	0.86	1.52	2.09	2.38	3.29	18.14		
Ni(β-HNQD)$_2$	0.53	0.89	1.16	*	2.15	*	3.28	17.87	C_6H_6	this chapter
extraction	0.60	0.89	0.82	*	2.05	*	3.28			
β-H$_2$NQD	0.74	1.30	1.07	2.05	2.48 -	2.74	3.47	11.09/10.72	DMSO-d_6	3
δ-H$_2$NQD	0.74	1.31	1.20	2.10	2.44 -------		2.78	12.30/12.08	DMSO-d_6	3
β-H$_2$NQD	0.74	1.30	1.03	2.05	2.40 -	2.80	3.41	11.18/10.74	DMSO-d_6	this chapter

The chemical shifts are given in ppm from $SiMe_4$.

*The chemical shifts of these protons could not be determined because of the presence of some pentanol.

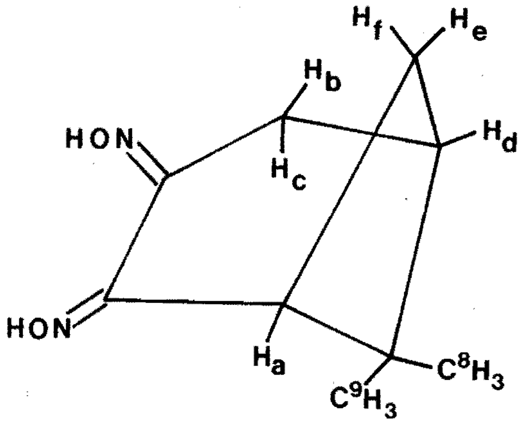


Fig. 4.10 The nopinoquinone dioxime molecule with hydrogen numbering.

Daniel and Pavia (7, 8) have studied in detail the effect of the oxime group on the chemical shift of the neighbouring proton. If the oxime group is anti, as is the case in Ni(β-HNQD)$_2$ the chemical shift of Ha will move to higher field. The origin of this effect is not known with certainty. Phillips (9) explains the shift by the interaction of the hydroxylgroup with the Ha proton. Saitō (10) suggests an interference of the free electron pair of nitrogen in the syn structure. The observed δ of 3.28 for the extracted Ni(β-HNQD)$_2$ proves that the neighbouring oxime group has the anti configuration. Furthermore, the observed δ of 17.87 of the OH group is in very good agreement with the synthesized Ni(β-HNQD)$_2$ compound of Nakamura.

In N,O-coordination another kind of hydrogen bridging occurs (see fig. 4.1) and this leads to a different chemical shift, such as Ni(δ-HNQD)$_2$:δ = 11.16, Ni(α-HCQD)$_2$ (4):δ = 11.07 and Ni(δ-HCQD)$_2$ (4):δ = 10.80. The conclusion drawn from this NMR study is that the extracted nickel chelate indeed has N,N-coordination. The spectrum gives some extra lines in the δ = 1.4 region because of the presence of some pentanol. From the NMR integral the quantity of pentanol is calculated to be about 6%, which is in good agreement with the deviation found in the elemental analysis.

4.4.4 The influence of the N-N distance

The fact that both Cu^{2+} and Ni^{2+} form a N,N-bonding chelate with β-H_2NQD confirms the theory that the N-N distance is an important factor in the chelation. Camphorquinone dioxime H_2CQD, an analogous molecule with a N-N distance of about 3.0 Å instead of the 2.8 Å of H_2NQD, cannot form stable N,N-coordinated chelates. From the fact that copper and nickel have smaller pH½ values with β-H_2NQD than with δ-H_2CQD (see table 4.1) the conclusion may be drawn that N,N-coordinated chelates are thermodynamically more stable, but that with H_2CQD the critical boundary for the N-N distance is passed.

Comparing β-H_2NQD with the unstrained aliphatic

dioximes in table 4.1 it is remarkable that the order of stability for copper and nickel is reversed. For copper it does not seem to matter that the N-N distance is enlarged and even a slight decrease of the pH½ value can be observed. For nickel the greater N-N distance is coupled with a striking increase of the pH½ value. Furthermore, the nickel extraction rate is raised enormously. Equilibrium is reached within ten minutes using β-H_2NQD as extractant instead of several days, when using unstrained aliphatic dioximes.
To understand this difference the crystal structure of some known copper and nickel dioxime chelates have to be discussed. If we compare the results of the crystal structure analysis of bis(methylethylglyoximato)nickel(II) of Bowers *et al.* (11) with the crystal structure analysis of bis(dimethylglyoximato)copper(II) from Vaciago and Zambonelli (12) there are some clear differences. Nickel forms a square planar structure with a nickel to nitrogen distance of 1.86 Å and a dioxime N-N distance of 2.426 Å, while copper is five coordinated in a square-pyramidal configuration with a copper to nitrogen distance of 1.95 Å and a dioxime N-N distance of 2.52 Å. Shannon (13) has calculated the ionic radii for different kinds of configurations. The values for copper(II) are 0.57 Å for a four coordinated square complex, 0.65 Å for a five coordinated complex and 0.73 Å for a six coordinated complex. For nickel(II) these values are 0.49 Å for a four coordinated square complex, 0.63 Å for a five coordinated complex and 0.69 Å for a six coordinated complex. The difference between the copper and nickel radius in the structure analysis of the glyoxime chelate, however, is 0.09 Å. In the unstrained glyoxime chelate the N-N distance will be determinated by the metal ion radius. That elucidates the difference in N-N distance between the two complexes in the crystal structure. In the β-H_2NQD complex the N-N distance is determinated by the strained carbon skeleton to be about 2.8 Å. This is far from the ideal N-N distance for a NiN_4 chromophore which is 2.426, so the chelate will be destabilized and the pH½ value will rise. For Cu(β-HNQD)$_2$ elemental analysis shows

that there are two additional water molecules associated to the chelate. It is not unlikely that these water molecules are located in the axial position of octahedral copper ($d(z^2)$) so that a (distorted) octahedral configuration exists. The six coordinated copper has according to Shanon a much greater ionic radius than the four coordinated nickel: 0.73 Å versus 0.49 Å. Furthermore the copper coordination sphere possesses some plasticity (22) *i.e.* the stronger the axial ligands are bonded, the weaker the equatorial ligands are bonded (which means in this case the larger the Cu-N distance). So less destabilization is to be expected for copper.

Good kinetics of nickel(II) extraction are to be expected whenever substitution of water takes place within an octahedral paramagnetic complex, which is directly followed by the elimination of the surplus monodentate ligands to a square planar diamagnetic complex (14). No octahedral complexes of the type $Ni(H_2O)_2(L\cap L)_2$ are formed by unstrained aliphatic dioximes. The weakening of the ligand by enlargement of the N-N distance makes it energetically more favourable to form this kind of paramagnetic octahedral intermediate. This could explain why β-H_2NQD has such good kinetics relative to unstrained aliphatic dioximes.

4.4.5 The furazan of nopinoquinone dioxime

The yellow oil which was obtained in the synthesis of β-H_2NQD (paragraph 4.2) by evaporation of ethylacetate probably consists for the major part of δ-H_2NQD. To remove the impurities the oil was treated with 1N NaOH and extracted with ether. Acidifying of the water layer did not give much product, but evaporation of the ether layer gave a compound that is probably the dehydrated form of nopinoquinone dioxime. Wolff (15) made such a furazan - also called 1,2,5-oxadiazole - by refluxing dimethylglyoxime with sodium hydroxide in water. This compound had a low melting point -7°C and a sweet smell. Also other furazans could be synthesized from dioximes. Behr (16) found that especially the amphi forms (δ-H_2NQD is amphi) are most easily dehydrated. To prove whether the compound really is the furazan the NMR spectrum (fig. 4.4) was studied in detail. The compound gives a very clear spectrum. Chemical shifts and coupling constants are given in table 4.4.

Table 4.4 The chemical shifts in ppm and the coupling constants in cps from the furazan of nopinoquinone dioxime. NMR spectrum see fig. 4.7. Protonnumbering see fig. 4.10.

Ha	= 3.20	triplet	^2J(He, Hf)	= 10.5
Hb,c	= 3.04	doublet	^3J(Ha, He)	= 5.0
Hd	= 2.35	multiplet	^3J(Ha, Hf)	= 0
He	= 2.87	doublet	^3J(Hd, He)	= 5.0
Hf	= 1.27	multiplet	^3J(Hd, Hf)	= 0
C^9H_3	= 0.58	singlet	^3J(Hd, Hb,c)	= 2.5
C^8H_3	= 1.42	singlet	^4J(Ha, Hd)	= 5.0

Because furazan is a six electron system, 4π electrons from the two CN double bonds and two from the oxygen, the five membered ring is aromatic. The field of this aromatic ring causes a deshielding effect for the protons on the pinene skeleton. Comparing the chemical shifts of β-H_2NQD with those of the furazan it is notable that almost all chemical shifts are shifted downfield. This confirms the aromatic character of the furazan ring. The chemical shift of Ha is somewhat smaller, which was to be expected because in the furazan no anti OH group exists. The chemical shift of C^9H_3 is changed in the opposite direction because the methyl group is placed partly above the aromatic ring where the field lines of the induced field are opposite to the applied field.

It is known that theoretical treatments of the magnitude of coupling constants such as the Karplus (17) equation (vicinal couplings) must be treated with reserve (18). Nevertheless the use of the equation of Karplus:

$$^3J(H, H) = 4.22 - 0.5\cos \phi + 4.5\cos 2\phi$$

in which ϕ is the dihedral angle between the two H's, gives dihedral angles which are in good agreement with the scale model made from the furazan of nopinoquinone dioxime. $^3J(Ha, He) = 5.0$ cps leads to an angle of 37^0 between Ha and He. The expected angle between Ha and Hf now is $120^0 - 37^0 = 83^0$. A dihedral angle of 83^0 leads to a coupling constant $^3J(Ha, Hf) = -0.21$ cps, a coupling that will not be observed. The same holds for $^3J(Hd, Hf)$. The coupling constants are almost equal to the values found by Abraham (19) for some other pinane derivatives. The long-range coupling $^4J(Ha, Hd)$ is remarkable but not unknown in bicyclic molecules (19, 20). Meinwald (20) explained this long-range interaction by assuming a fairly extensive overlap between the small lobes of the orbitals directed 180^0 away from the direction of the CH bonds, which are pointed towards each other. This explanation appears reasonable when a scale model is examined. This proves that the pinane skeleton is still preserved. Elemental analysis also leaves no doubt on the compound being the furazan of nopinoquinone dioxime.

The furazan of nopinoquinone dioxime shows no extraction capacities at all. The main reason for this is that there is no acidic H atom present. Also no hydrogen bridge stabilization of the complex can occur. Furthermore the bidentate character of the ligand is lost. Driessen (21) did make some metal furazan complexes with $SbCl_6^-$ as anion. All the complexes decomposed when in contact with water which means that furazan is a rather weak ligand.

The aromaticity of the furazan ring makes the molecule very stable. It is therefore not possible to convert the furazan into β- or δ-H_2NQD.

4.5 CONCLUSIONS

In contrast to β-H_2CQD, β-H_2NQD forms stable N,N-coordinated chelates with both copper and nickel. The pH½ values of β-H_2NQD are lower than those for δ-H_2CQD. This implicates that N,N-chelation is more favourable than N,O-chelation. The large N-N distance makes this way of coordination unattractive for δ-H_2CQD and δ-H_2CQD therefore has chelation through N and O.

Comparing β-H_2NQD as an extractant for nickel with unstrained aliphatic dioximes, two differences are noticable. Firstly, the $(pH½)_{1.0}$ value is raised from -0.4 to +1.28 and secondly, the extraction rate is increased enormously. For copper the $(pH½)_{1.0}$ value does not change much, +0.6 to +0.25. This results in a reverse of the stabilities for copper and nickel. The reason is, that nickel easily forms low-spin d^8 square planar species and in such configurations the nickel ion has a very small ionic radius. The copper ion, on the other hand, tends to form octahedral complexes and then has much larger ionic radii.

The conclusion can be drawn from our work that the use of strained instead of aliphatic dioximes will make the extraction of nickel more convenient because of the higher extraction rate, but the selectivity for nickel above copper will disappear.

δ-H_2NQD is easily converted in the furazan of nopinoquinone dioxime by treatment with 1N NaOH. This furazan is a rather weak ligand without significant extraction capacities.

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CHAPTER 5

EXTRACTION OF COPPER(II) AND NICKEL(II) BY CYCLIC TRIOXIMES AND CYCLIC FURAZAN OXIMES

5.1 INTRODUCTION

From chapter 3 and 4 it became clear that enlargement of the N-N distance of aliphatic dioximes on one hand makes the extraction of nickel more convenient because of the higher extraction rate, but that on the other hand the selectivity for nickel above copper disappears. In this chapter two new kinds of ligands will be examined, viz. the cyclic trioximes (fig. 5.1) and the cyclic furazan oximes (fig. 5.2).

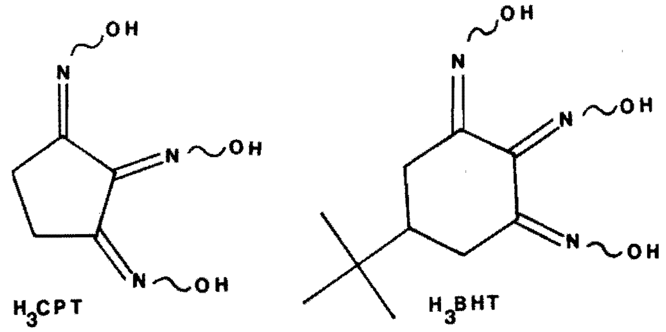

Fig. 5.1 Schematic structures of 1,2,3-cyclopentanetrione trioxime (H_3CPT) and 4-t-butyl-1,2,6-cyclohexanetrione trioxime H_3BHT.

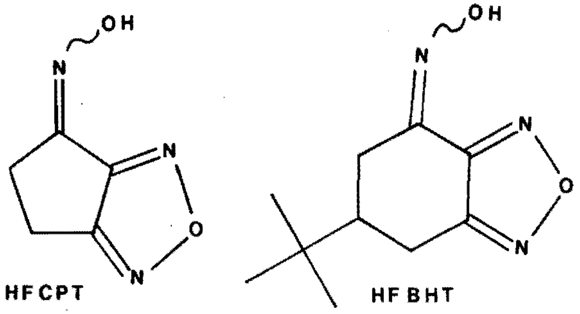

Fig. 5.2 Schematic structures of the furazan derived from 1,2,3-cyclopentanetrione trioxime (HFCPT) and the furazan derived from 4-t-butyl-1,2,6-cyclohexanetrione trioxime (HFBHT).

Frierson and Marable (1) discovered that 1,2,3-cyclohexanetrione trioxime instantaneously forms a NiL_2 chelate with nickel(II) salts in an ethanol/water mixture. They did not investigate the extraction capacities, however. They postulated, without prove, a NiN_2O_2 chromophore to be formed which is unexpected because there is not much strain in the cyclic hexane ring. Furthermore, it is unknown what the influence will be of the third oxime group on the stability of the copper and nickel chelates, because now additional hydrogen bridging is possible. This makes the cyclic trioximes very interesting to study. Besides, the cyclic trioxime is a precursor of the cyclic furazan oxime. In chapter 4 it was found that nopinoquinone dioxime could easily be converted into a furazan, but this furazan was not active in extraction, probably because no acidic hydrogen atom is present. The cyclic furazan oxime has such an acidic hydrogen and furthermore this molecule can react as a bidentate ligand.

For these reasons 1,2,3-cyclopentanetrione trioxime (H_3CPT) and 4-t-butyl-1,2,6-cyclohexanetrione trioxime

(H_3BHT) were synthesized and examined. In addition, these two trioximes were converted into the furazan of 1,2,3-cyclopentanetrione trioxime (HFCPT) and the furazan of 4-t-butyl-1,2,6-cyclohexanetrione trioxime (HFBHT).

5.2 SYNTHESIS

5.2.1 1,2,3-cyclopentanetrione trioxime (H_3CPT)

Following the method of Ferris (2) using n-butylnitrite crude 1,2,3-cyclopentanetrione 1,3-dioxime was obtained as a brown compound from cyclopentanone (E. Merck A.G., Darmstadt, zur synthese).
IR: 1725 cm^{-1} (C=O); and new bands at 1625 cm^{-1} (C=N) and 3250 cm^{-1} broad (OH).

The crude trione dioxime was dissolved in ethanol and treated with an aqueous solution of $NH_2OH.HCl$ and NaOAc under reflux. The product was washed with ethanol and extracted with boiling ethanol and after that washed with water. A brown product was obtained in small quantity (because of the good solubility in water) which could not be decolourized. Elemental analysis: expected $C_5H_7N_3O_3$: C38.22 H4.49 N26.74 O30.55, found C36.67 H4.23 N27.06.
IR: 1725 cm^{-1} (C=O) disappeared; 1625 cm^{-1} broad absorption (C=N) and 3300 cm^{-1} broad absorption.

5.2.2 The furazan of 1,2,3-cyclopentanetrione trioxime (HFCPT)

Crude 1,2,3-cyclopentanetrione 1,3-dioxime (0.07 mol) (see synthesis H_3CPT) dissolved in a solution of 0.3 mol NaOH in 50 ml water was treated with a solution of $NH_2OH.HCl$ (0.18 mol) in 75 ml water during several days at 60°C. After filtration the filtrate was acidified till pH = 2 and filtered. The filtrate was extracted with ether and evaporating the ether layer after drying (Na_2SO_4) gave 1 gram of a yellow solid.
Elemental analysis: expected $C_5H_5N_3O_2$ C43.17 H3.62 N30.21 O23.00, found C43.22 H3.90 N30.11.

IR 3300 cm^{-1} sharp (OH), 1520 cm^{-1} (furazan) 1600-1650 cm^{-1} broad (C=N).

5.2.3 4-t-butyl-1,2,6-cyclohexanetrione trioxime (H_3BHT)

Following the method of Ferris (2) using n-butylnitrite crude 4-t-butyl-1,2,6-trione-2,6-dioxime was obtained as a light brown compound from 4-t-butylcyclohexanon (Janssen Chimica, Beerse, Belgium, 95+%).
Elemental analysis: expected $C_{10}H_{16}N_2O_3$: C56.60 H7.55 N13.21 O22.64, found C56.19 H7.51 N12.92.
IR: 3230 cm^{-1} broad (OH), 1620 and 1590 cm^{-1} (C=N) as new absorptions, 1710 cm^{-1} (C=O).

Crude 4-t-butyl-1,2,6-trione 2,6-dioxime was converted into H_3BHT by the same method as for H_3CPT. The reaction mixture was filtered and the filtrate was evaporated. The solid thus obtained was washed with ethylacetate resulting in a white product.
Elemental analysis $C_{10}H_{17}N_3O_3$ expected C52.86 H7.49 N18.50 O21.05, found C53.00 H7.66 N18.77.
IR: 3230 cm^{-1} broad (OH), 1650, 1610, 1580 cm^{-1} weak (C=N); the C=O absorption at 1710 cm^{-1} had disappeared.
^{1}H NMR DMSO-d6: δ0.9 (s, 9H), δ1.6-3.2 (m.c, 5H), δ11.4, 11.7 en 12.6 (s, OH).

5.2.4 The furazan of 4-t-butyl-1,2,6-cyclohexanetrione trioxime (HFBHT)

Crude 4-t-butyl-1,2,6-cyclohexanetrione-2,6-dioxime (see synthesis H_3BHT) was converted into the furazan of H_3BHT by using the same method as for the synthesis of HFCPT. The reaction mixture was filtered and acidified till pH = 7. The solid thus obtained was filtered, washed with water and dried with silica to yield a white product.
Elemental analysis: expected $C_{10}H_{15}N_3O_2$: C57.42 H7.18 N20.10 O15.30, found C57.15 H7.33 N19.93.
IR: 3290 cm^{-1} sharp (OH); 1635 and 1582 cm^{-1} (C=N), 1510 cm^{-1} (furazan). ^{1}H NMR DMSO-d6: δ0.9 (s, 9H),

δ1.6-3.5 (m.c, 5H), δ12.1 (s, OH).

5.3 RESULTS

H_3CPT appeared to be fairly soluble in water. The only organic solvent in which we could dissolve H_3CPT was tri-n-butyl phosphate (tbp) but when this solution was mixed with water the H_3CPT was transported to the water layer. When adding metal sulfates the copper and nickel chelates formed were not transported to the organic layer, but precipitated in the water layer. The isolated brown copper chelate had an elemental analysis of C27.26 H2.55 N17.69 Cu19.34. The isolated red brown nickel chelate had an elemental analysis of C28.78 H3.02 N18.48 Ni17.21.
No ESR signal could be measured for this copper chelate, while the NMR spectrum of the nickel chelate could not be obtained because of its insolubility in organic solvents. These results will be discussed in paragraph 5.4.1.

HFCPT dissolved very well in tbp, pentanol, ether and water. However, also HFCPT possessed no extraction capacity for Cu(II) and Ni(II).

H_3BHT dissolved very well in pentanol and only slightly in water. Extraction experiments in pentanol with Ni(II) gave a fine red precipitate in the organic layer. At pH = 2.86 99.4% of the nickel was extracted, when using 0.025 mol/l H_3BHT in pentanol and 0.002 mol/l $Ni(NO_3)_2$ in water with equal volumes. Equilibrium was reached in about one hour. Back extraction could not be observed down to pH = 1. The isolated nickel chelate had an elemental analysis of C47.74 H6.52 N16.60 Ni10.67 which points in the direction of a $Ni(H_2BHT)_2$ chelate: expected $NiC_{20}H_{32}N_6O_6$, C46.99 H6.50 N16.45 Ni11.49 O18.57.

The extraction of a 0.001 mol/l $Cu(NO_3)_2$ solution in water by 0.025 mol/l H_3BCT in pentanol gave the same results as with Ni^{2+}: a light brown suspension in the organic layer at pH = 2.91 and no back extraction till pH = 1. The isolated copper chelate had an elemental analysis of C45.41 H6.12 N15.91 Cu12.15 which is in good

agreement with a $Cu(H_2BHT)_2.2H_2O$ chelate.
Expected $CuC_{20}H_{36}N_6O_8$: C44.99 H6.37 N15.75 Cu11.90 O20.99.

No proper solvent could be found to enable an ESR solution spectrum to be measured. A "Powder" ESR spectrum from this compound was not recorded. In that case the anisotropy will not be averaged out (see paragraph 2.3) and therefore it is unlikely that the total number of nitrogen atoms coordinated to the copper can be established.

An extraction experiment with excess Cu^{2+} gave a surprising effect. The organic layer became dark brown and the suspension disappeared. The filtered organic layer was evaporated which yielded a dark brown solid with an elemental analysis of C40.07 H5.25 N17.74 Cu19.04, which is not completely in agreement with a $Cu_n(HBHT)_n.2nH_2O$ chelate: expected Cu2072 C39.15 H5.55 N13.70 O20.88. No ESR signal could be detected for this chelate in solution at room temperature.

HFBHT was very soluble in organic solvents, but did not possess extraction capacities for Cu(II) or Ni(II).

5.4 DISCUSSION

5.4.1 1,2,3-cyclopentanetrione trioxime (H_3CPT)

H_3CPT is fairly soluble in water. The origin of this behaviour is that the three oxime groups, which can form hydrogen bridges with water, are making the molecule hydrophilic, and the relative small organic part ($-CH_2-CH_2-$) causes only a small hydrophobic effect. The relative small organic part and the large polarity, caused by the three oxime groups, are making this ligand almost unsoluble in organic solvents, which do not form homogeneous solutions with water. The H_3CPT ligand will therefore be of limited value as an extractant, because most of the H_3CPT will be transported to the water layer, which will lead to undesired ligand losses. Furthermore, the chelates formed with Cu(II) and Ni(II) are not transported to the organic layer but precipitate in the water layer. It is therefore recommended to use branched cyclic rings to enlarge the organic hydrophobic part. In that way the resulting ligand will be more soluble in organic solvents and less in water. The elemental analysis of the copper H_3CPT chelate shows that if a Cu:H_3CPT = 1:2 chelate is formed at all, it is not the only chelate. The Cu:C = 1:7.5 ratio and the Cu:N = 1:4.15 ratio point in the direction of Cu:L = 2:3 chelate.

The fact that no ESR spectrum is observed, which can be explained by a copper-copper interaction, confirms the hypothesis that at least one copper ion is present nearby each copper(II). For the nickel H_3CPT chelate almost the same values are observed as for Cu: Ni:C = 1:8.2 and Ni:N = 1:4.5. So here also a Ni:L = 2:3 molecule is the most probable chelate. The C:N = 5:2.78 ratio in both chelates shows that some oxime must be lost. Too low hydrogen values (2.55 and 3.02) and the high rest values (100%-Cu-C-H-N = 33.16%, 100%-Ni-C-H-N = 32.51%) are pointing in the direction of some inorganic part. Therefore no great significance must be given to the composition of these chelates in relation to extraction chemistry.

5.4.2 The furazan of 1,2,3-cyclopentanetrione trioxime (HFCPT)

HFCPT can also be called 3,4-trimethylene furazan-6-oxime in analogy with the furazan oxide of Barnes (3). This ligand is better soluble in organic solvents than H_3CPT because two of the three polar oxime groups have now formed an organic aromatic furazan ring. The fact that no extraction capacities are found for this ligand is not surprising when we look at a molecular model of the ligand. The extimated N-N distance is about 3.2 Å, which is far too large for N,N-coordination and also makes N,O-coordination unattractive.

This result therefore does not exclude the possibility that furazan oximes may be good extractants. If we compare HFCPT with H_3CPT we can conclude that the solubility capacities have improved, but that the chelating capacities have disappeared.

5.4.3 4-t-butyl-1,2,6-cyclohexanetrione trioxime (H_3BHT)

The solubility properties of H_3BHT for extraction have much improved compared to H_3CPT. Differences between H_3BHT and H_3CPT are the increase of the carbon ring by one carbon atom and the t-butyl group. We suggest that most of the increased solubility originates from the large t-butyl group which makes the molecule hydrophobic. It is unlikely that enlargement of the ring with only one atom can cause such a change. H_3CPT has a good extraction capacity (99.4% extraction at pH = 2.86) for nickel, but the extracted chelate was not soluble in the organic layer and precipitated in this phase. The reason for the precipitation in the organic layer (the pentanol layer is the upper phase, the water layer the under phase) instead of in the water layer must be the strong hydrophobic effect of the t-butyl group. Because no such insolubility has been found for the bis(cyclohexaneglyoximato) nickel (II) chelate (4) the reason for the precipitation must be the third oxime group of H_3BHT. Elemental analysis showed that presumably a $Ni(H_2BHT)_2$ chelate is formed, which means that the third oxime group is likely to be involved in intermolecular coordination or hydrogen bridge formation between chelate molecules. As a result the chelate molecules agglomerate and precipitate. This precipitation also means that the extraction reaction is no longer an equilibrium reaction, but a termination reaction. The back extraction is blocked, so the only way to free the nickel ions again is to break the chelate with strong acids, but these acids will also attack and possibly distroy the ligand. As a result this ligand is unattractive for use in a continous process.

The estimated N-N distance of 2.8 Å for H_3BHT is comparable with that of β-H_2NQD (chapter 4), which formed N,N-coordinated chelates. The red color of $Ni(H_2BHT)_2$ is also found for unstrained aliphatic dioxime nickel chelates and Ni(β-HNQD)$_2$, while N,O-coordinated chelates, like Ni(α-HCQD)$_2$ and Ni(δ-HCQD)$_2$, are green (5, 6). This makes N,N-coordination the most reasonable structure, rather than N,O-coordination as suggested by Frierson and Marable (1). In figure 5.3 some possible structures are presented.

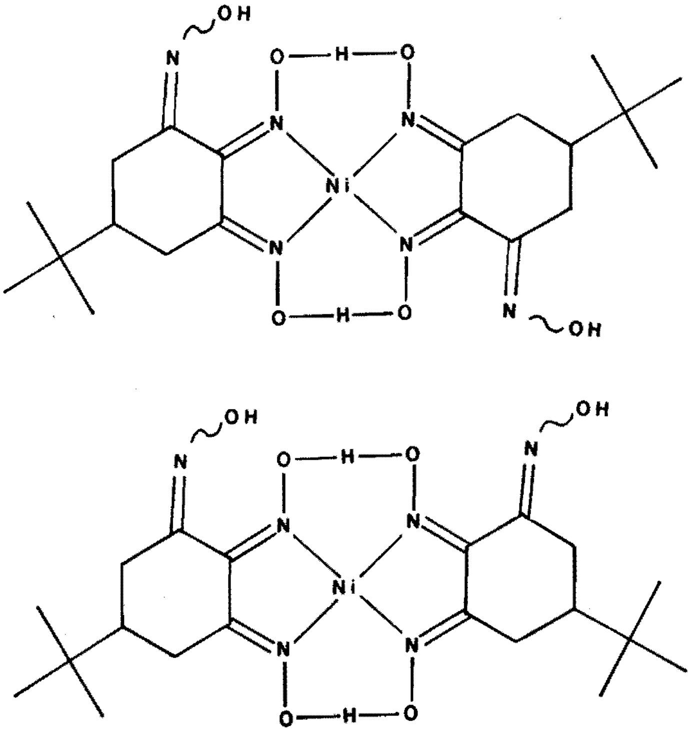

Fig. 5.3 Two possible structures of the Ni(H$_2$BHT)$_2$ chelate assuming N,N-coordination.

The copper extraction by H$_3$BHT in pentanol gives the same picture as the nickel extraction when excess H$_3$BHT is used. Elemental analysis showed that Cu(H$_2$BHT)$_2$2H$_2$O precipitated in the organic layer. This means that probably copper forms a distorted octahedral chelate with two additional waters in the axial position, while nickel forms a square planar chelate. This is in analogy with β-H$_2$NQD chelates (see chapter 4). "Powder" ESR spectrscopy can perhaps confirm that the copper ion has an octahedral environment (14).

When using excess copper in the extraction a new chelate is formed that is soluble in the organic layer. From the elemental analysis of the isolated chelate the ratio's Cu:C = 1:11.1 and Cu:N = 1:3.51 are calculated. This means that no longer a Cu:L = 1:2 chelate is formed but that a Cu:L = 1:1 chelate is formed (Cu:C = 1:10 and C:N = 1:3) presumably with some organic impurities. The solubility of this chelate in the organic layer can now be explained by the fact that the third oxime group is involved in the chelation with copper, and therefore is no longer available for intermolecular hydrogen bridge formation or intermolecular coordination. The fact that no ESR spectrum can be found for this chelate points in the direction of a strong antiferromagnetic coupling between at least two copper ions, which is not unknown for binuclear copper complexes (7, 8, 12, 13). The chelate must be of the type Cu_nL_n with n = even.

The phenomenon that with excess copper different chelates are formed was also observed with δ-H_2NQD (see chapter 3) where a Cu:L = 2:3 chelate was formed.

5.4.4 The furazan of 4-t-butyl-1,2,6-cyclohexanetrione trioxime (HFBHT)

HFBHT can also be called 6-t-butyl-4-hydroxyimino-4,5,6,7-tetrahydrobenzofurazan in analogy with Lewis (9) (the same molecule without t-butyl group) or 6,7-dihydro-6-t-butylbenzofurazan-4(5H)-one oxime in similarity with Calleri (10) (the same molecule with a dimethyl group instead of a t-butylgroup). Other names for this compound could use a 1,2,5-oxadiazole ring as basis.

HFBHT is not very soluble in water, but dissolves very well in organic solvents like ethanol and ether. This can be explained by the hydrophobic t-butyl group and by the fact that two of the three polar oxime groups are now transformed in an organic furazan ring. The N-N distance between the nitrogen of the oxime group and the nitrogen of the furazan can be calculated from the values of the atomic coordinates found by Calleri (10) for a similar molecule. The N-N distance is calculated to be 2.835 Å and such a distance makes N,N-coordination the most likely one. Furthermore Calleri's X-ray analysis showed that the oxime group is anti in respect to the furazan. Nevertheless no extraction properties are found for this ligand. The reason for this is, most likely, that the furazan possesses such a poor complexing capacity - Driessen (11) found indeed poor complexing capacities for furazans - that even with a strong complexing neighbour as the oxime group no bidentate reaction with metal ions takes place under extraction conditions. Another reason may be that a furazan oxime chelate cannot have hydrogen bridge stabilization, like dioxime chelates, because the oxime group will be deprotonated by the extraction reaction:

$$M^{2+} + 2HFBHT \rightleftarrows M(FBHT)_2 + 2H^+ \; .$$

The conclusion that can be drawn from these results is that furazan oximes are of no use for extraction of Cu(II) and Ni(II).

5.5 CONCLUSIONS

H_3CPT is better soluble in water than in organic solvents, which makes this compound of no use as an extractant. This ligand is able to form chelates with copper and nickel which precipitate in the water layer. The introduction of a large hydrophobic group into the aliphatic ring, like t-butyl in H_3BHT, provides an answer to this solubility problem.

Ni(II) was extracted by H_3BHT as $Ni(H_2BHT)_2$, but this chelate precipitated in the organic layer and therefore blocked the back extraction. This is caused by intermolecular hydrogen bridge formation and/or coordination of the third oxime group, which is not primarily involved in the chelation with nickel. The Cu(II) extraction by excess H_3BHT showed the same picture with the precipitation of Cu$(H_2BHT)_2 \cdot 2H_2O$. When the extraction is performed with excess copper ions a Cu:H_3BHT = 1:1 chelate is formed which is soluble in the organic layer. The third oxime group is now directly involved in the chelation with copper and no intermolecular hydrogen bridge formation can occur. These results show that the use of trioximes for the extraction of Cu(II) and Ni(II) is not an improvement with respect to the dioximes but, on the contrary, is a step backwards because new problems, like precipitation and blocked back extraction, are introduced.

The experiments with the two furazan oximes confirm the conclusion that a large hydrophobic group like t-butyl changes the solubility properties in the desired direction. Furthermore, it is shown that this type of ligand is not suitable for extraction of copper and nickel ions because under extraction conditions no chelates with copper and nickel are formed. The reasons for this are that furazan is a too weak ligand and that no hydrogen bridge stabilization is possible after chelation.

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CHAPTER 6

EXTRACTION OF COPPER(II) AND NICKEL(II) BY LONG-CHAIN ALIPHATIC DIOXIMES

6.1 INTRODUCTION

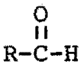
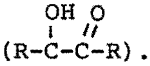
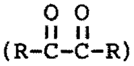
From analytical chemistry it is well-known that nickel ions react with dimethylglyoxime to form quantitatively the red bis(dimethylglyoximato)nickel(II) chelate. The relatively low solubility of dimethylglyoxime in organic solvents makes this compound unattractive for extraction. Burkin and Preston (1) investigated some aliphatic *vic.*-dioximes with a total carbon number of 12 to 16 and found extremely low extraction rates for nickel especially with compounds containing secondary alkyl groups. Navtanovich and co-workers (2) discovered that the extraction of Cu(II) and Ni(II) from ammoniacal solutions is dependent on the total number of carbon atoms. Equilibrium was not established in the extraction and re-extraction of nickel. The extraction of copper(II) and nickel(II) from ammoniacal solutions is not identical in character with the pH dependent extraction from acidic solutions. Although the pH is larger than 7, which is caused by the ammonia, no precipitation of metal hydroxides occurs because metal ammine complexes are formed in the water layer. The expected extraction equation is:

$$M(NH_3)_n^{2+} + 2H_2A \rightleftarrows M(HA)_2.xNH_3 + 2NH_4^+ + n\text{-}x\text{-}2\ NH_3$$

In this chapter the extraction properties of dialkyldioximes of the type C_nH_{2n+1}-C(NOH)-C(NOH)-C_nH_{2n+1} are described. The ammoniacal extraction is compared with the pH dependent extraction from acidic solutions.

6.2 SYNTHESIS OF DIALKYLDIOXIMES R-C(NOH)-C(NOH)-R

All dioximes were prepared as described in the following general procedure.

Under nitrogen 0.39 mol freshly distilled alkylaldehyde  $R-\overset{\overset{O}{\|}}{C}-H$ was dissolved in 120 ml ethanol. 0.02 mol 3-benzyl-5-(2-hydroxy-ethyl)-4-methyl-1,3-thiazolium chloride was added and subsequently 0.12 mol triethyl amine was added dropwise under vigorous stirring (Stetter synthesis (3, 4)). After refluxing for two hours the reaction mixture was poured out into ice, filtered, washed with water and extracted with chloroform. The organic layer was washed with aqueous $NaHCO_3$, dried with Na_2SO_4 and distilled to give the dialkylhydroxy ketone  $(R-\overset{\overset{OH}{|}}{C}-\overset{\overset{O}{\|}}{C}-R)$. This dialkylhydroxy ketone was dissolved in 100 ml 2-ethoxyethanol with 30 ml glacial acetic acid. To this solution, heated at 80°C, 0,044 mol Bi_2O_3 was added fast. After that the reaction mixture was heated for one and a half hour at 105°, filtered and the residue was extracted with chloroform. The organic layer was washed with water till free from acid, dried and distilled to give the dialkyldiketone  $(R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R)$.

0.4 mol $NH_2OH.HCl$ and 0.32 mol NaOAc were dissolved in 25 ml water and 50 ml ethanol. To this 0.135 mol dialkyldiketon was added. The reaction mixture was refluxed for half an hour, cooled, and the residue filtered and washed with hot water. Recrystallization from diluted alcohol gave the pure dialkyldioxime (R-C(NOH)-C(NOH)-R) in an overall yield of about 25%. The results of elemental analysis are presented in table 6.1.

Table 6.1 Synthesized dialkyl dioximes with analytical results

Compound	expected			found		
	%C	%H	%N	%C	%H	%N
C_3H_7-C(NOH)C(NOH)C_3H_7	55.8	9.4	16.3	55.6	9.3	16.1
C_5H_{11}-C(NOH)C(NOH)C_5H_{11}	63.1	10.6	12.3	63.1	10.7	12.4
C_7H_{15}-C(NOH)C(NOH)C_7H_{15}	67.6	11.1	9.8	67.5	11.2	9.9
C_9H_{19}-C(NOHC(NOH)C_8H_{19}	70.5	11.8	8.2	70.9	12.1	7.9
$C_{11}H_{23}$-C(NOH)C(NOH)$C_{11}H_{23}$	72.7	12.2	7.1	73.7	12.5	6.9

6.3 RESULTS

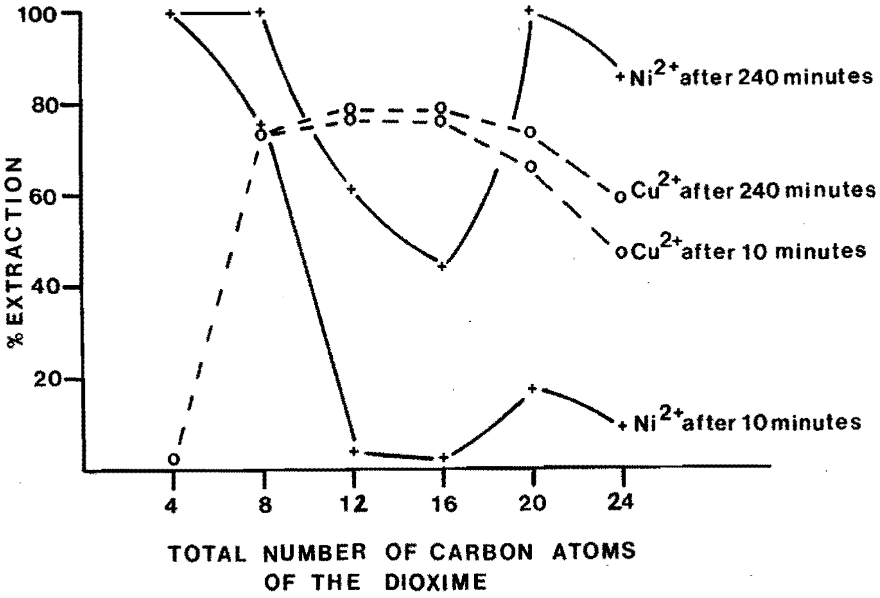


Fig. 6.1 Extraction of Cu(II) and Ni(II) by dialkyldioximes R-C (NOH)-C(NOH)-R as a function of the total number of carbon atoms in the dioxime. Initial aqueous metal nitrate concentration 0.05 M. Initial dioxime concentration in methylisobutylketone (MIBK) 0.3M. Initial NH_3 concentration 1.33 M. Initial NH_4NO_3 concentration 0.33 M.

In fig. 6.1 the results are shown for the extraction of Cu(II) and Ni(II) from ammoniacal solutions by solutions of dialkyl dioximes in methylisobutylketone (MIBK) as a function of the total number of carbon atoms at two different extraction times. Equilibrium is not yet reached in the extraction of Ni(II) by dioximes with a total number of carbon atoms of 12, 16 and 24 after 240 minutes.

The dependencies of the extractions of Cu(II) and Ni(II) by dipentyldioxime(dodecane-6,7-dione dioxime) on the NH_3 and NH_4^+ concentration are presented in fig. 6.2 and 6.3.

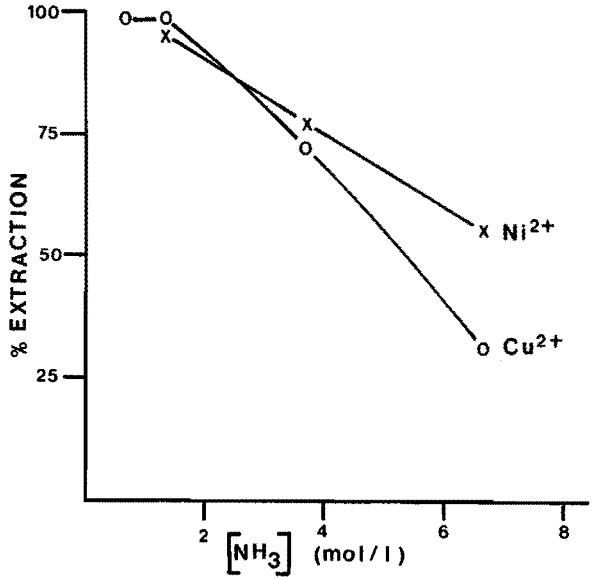


Fig. 6.2 Extraction of Cu(II) and Ni(II) by dipentyldioxime as a function of the initial NH_3 concentration after a contact time of 240 minutes. Initial dioxime concentration in MIBK 0.55 M. Initial NH_4NO_3 concentration 0.33 M.

The pH dependent extraction of Cu(II) from nitrate solutions by a solution of dipentyldioxime in chloroform is shown in fig. 6.4.

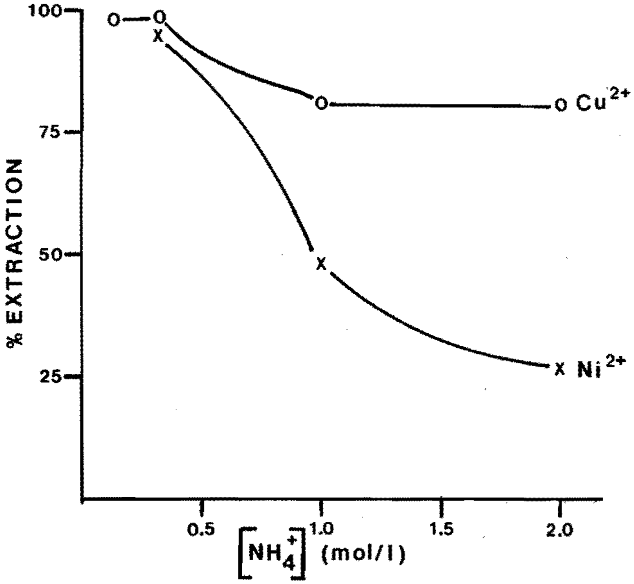


Fig. 6.3 Extraction of Cu(II) and Ni(II) by dipentyldioxime as a function of the initial NH_4NO_3 *concentration after 240 minutes of contact. Initial dioxime concentration in MIBK is 0.55 M. Initial* NH_3 *concentration is 1.33 M.*

It is clear that at pH > 5 more than the theoretically expected 50% for a CuL_2 chelate is extracted. The shape of the UV spectrum also changed at pH > 5. Thus it is clear that two different chelates are involved: chelate A at low pH and chelate B at pH > 5. When using an excess of Cu(II) compared to dioxime, the UV spectrum indicated that the extraction at pH = 4.3 resulted in chelate A with only a slight fraction of chelate B. Evaporation of the organic phase and recrystallization with ethanol and water gave a brown solid which was filtered and dried at 60°C. Elemental analysis of this compound gave Cu13.8 N10.5 C55.2 H8.7 O11.8. After isolation the compound is only slightly soluble in chloroform, in contrast with the extracted chelate A. Further it is found that the extracted chelate A is unstable when the organic layer is dried with Na_2SO_4.

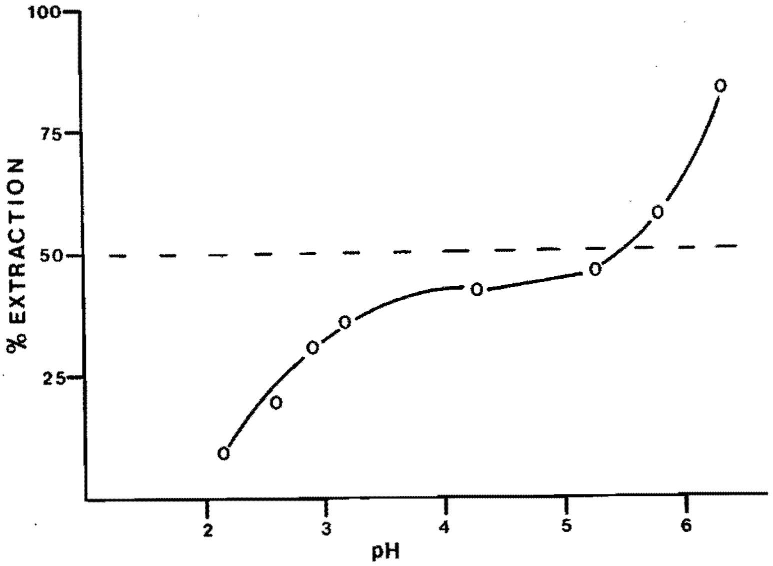


Fig. 6.4 Extraction of Cu(II) by dipentyldioxime as a function of the equilibrium pH. Initial aqueous copper nitrate concentration and the initial dipentyldioxime concentration in chloroform both are 0.001 M.

The ESR spectrum of this chelate A in chloroform is depicted in fig. 6.5.

The extraction of excess Cu(II) at pH = 8.4 resulted, according to the UV spectrum, in an organic solution containing nearly pure chelate B. Evaporation of the organic phase and recrystallization with dioxane and water gave a green solid that was dried at 60°C. Elemental analysis of this compound gave Cu23.5 N8.0 C46.8 H7.5. After redissolving the compound in chloroform the UV spectrum deviated somewhat from that of the extracted chelate B. No ESR spectrum could be observed for this compound in solution at room temperature.

Kinetic measurements were done on the extraction of Ni(II) from a nitrate solution by dipentyldioxime to obtain some information why this reaction is so slow (no equilibrium within days).

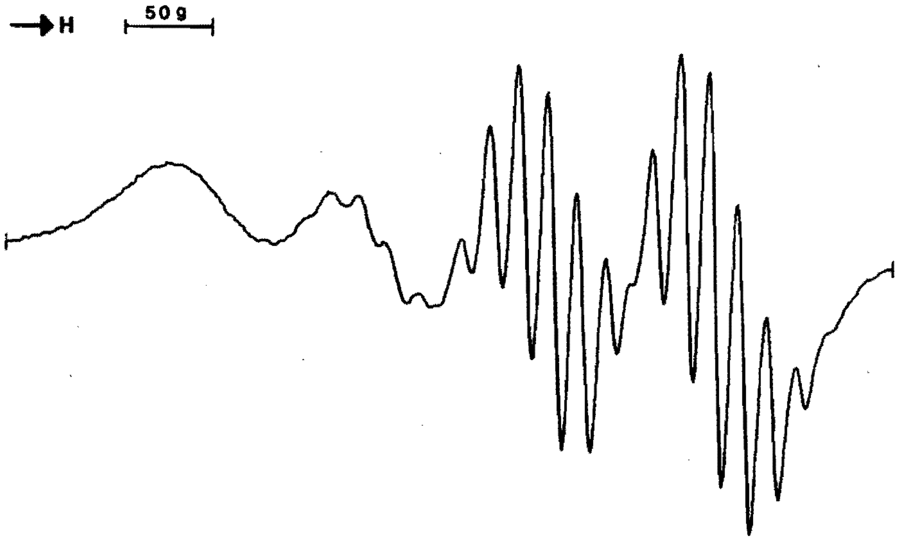


Fig. 6.5 ESR spectrum of the copper(II)-dipentyldioxime chelate (chelate A) in chloroform at room temperature.

In fig. 6.6, 6.7 and 6.8 the initial extraction rate can be seen as a function of some initial concentrations. The order in dipentyldioxime concentration is calculated from the slope in fig. 6.6 as 0.90. The order in Ni^{2+} concentration calculated from the slope of the line in fig. 6.7 is 0.91. The dependence of the hydrogen ion concentration can be seen in fig. 6.7. The order of -0.16 calculated from this figure is not too reliable because only two measurements were done.

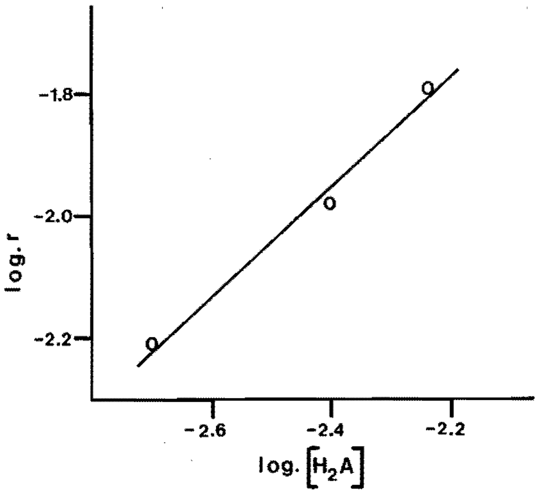


Fig. 6.6 Dependence of the initial rate of extraction of nickel by dipentyldioxime on the concentration of dipentyldioxime in chloroform. Initial pH is 3.52. Initial aqueous nickel nitrate concentration 0.00397 M.

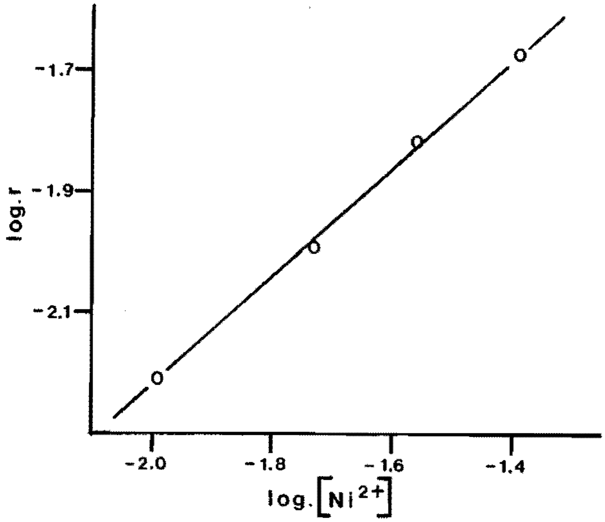


Fig. 6.7 The dependence of the initial rate of extraction of nickel(II) by dipentyldioxime on the concentration of Ni^{2+} in the aqueous phase. Initial dipentyldioxime concentration in chloroform is 0.00612M. Initial pH is 3.65.

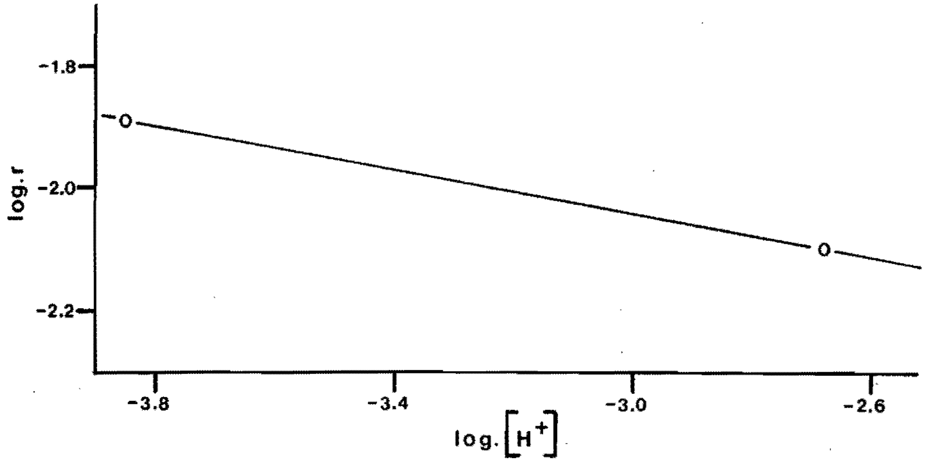


Fig. 6.8 The dependence of the initial rate of extraction of nickel(II) by dipentyldioxime on the concentration of hydrogen ions in the aqueous phase. Initial dipentyldioxime concentration in chloroform is 0.00415 M. Initial aqueous nickel nitrate concentration is 0.003 M.

6.4 DISCUSSION

6.4.1 Extraction of Cu(II) and Ni(II) from ammoniacal solutions by aliphatic dioximes

From fig. 6.1 it can be seen that the only dialkyldioxime which is really selective for nickel above copper in the extraction from ammoniacal solutions is dimethylglyoxime. However, the extracted bis(dimethylglyoximato) nickel(II) chelate precipitates in the organic layer, and the back-extraction is blocked. Caton (5) explains this bad solubility by nickel-nickel interactions which prevent solvation. This bond is possible because of the close packing of molecules in the crystal, a packing that cannot occur with larger alkyl groups according to Sharpe and

Wakefield (6). Dyrssen (7) stated that the bis(dimethylglyoximato)copper(II) chelate possesses two additional water molecules, which makes this chelate to remain preferentially in the aqueous phase. The low percentage extraction of Cu(II) by dimethylglyoxime can also be explained by the formation of such a hydrophilic aqua chelate. When larger alkyl groups are introduced in the dioxime the bulky hydrophobic substituents cause a change in the distribution coefficient of the copper chelate to the advantage of the organic layer. But we must also expect a destabilization of the above aqua chelate. In fig. 6.1 it is clearly seen that from C = 8 till C = 16 these two effects keep each other in balance but with longer alkyl groups the destabilization effect is stronger.

In contrast with copper, nickel does not form octahedral chelates but square planar chelates with dioximes. The lower nickel extraction observed for dioximes with a total number of carbon atoms of 12, 16 and 24 after four hours is not caused by a difference in thermodynamic stability of the chelates formed, but is caused by a difference in extraction rate. If the contact time is taken long enough nickel extraction will also be almost 100%, but from fig. 6.1 it can be seen that four hours is not long enough to reach this point. This difference in extraction rate can be caused by steric hindrance. The steric hindrance from alkyl groups with 5 till 7 atoms is most effective according to fig. 6.1. The reason why longer chains do not produce such a great hindrance is probably that longer chains are causing a greater insolubility of the dioxime in water, which means that the reaction takes place in the interface with the two long carbon chains pointed into the organic phase

Figure 6.2 shows that the extraction of copper and nickel is dependent on the ammonia concentration. The dependence of copper is stronger which can be explained by the fact that copper forms more stable complexes with ammonia than nickel. Figure 6.3 shows that the extraction of copper and nickel also depends on the NH_4^+ concentration.

The expected reaction equation for the extraction is:

$$M(NH_3)_n^{2+} + 2H_2A \rightleftarrows M(HA)_2 + 2NH_4^+ + (n-2)NH_3 \ .$$

The extracted copper chelate will probably have two water or ammonia molecules in the axial position.

A useful selectivity for nickel above copper is not found in the extraction by dialkyldioximes from ammoniacal solutions. At high ammonia concentrations and low NH_4^+ concentrations nickel is favoured but no good separation can be obtained.

6.4.2 The pH dependent extraction of Cu(II) by dipentyldioxime

From fig. 6.4 and UV spectroscopy it becomes clear that two different kinds of chelates are involved in the extraction of Cu(II) by dipentyldioxime. Elemental analysis of chelate A formed at low pH values indicates that a CuL_2 chelate is formed:
$Cu(C_{12}H_{22}N_2O_2)_2$ expected Cu12.3 H8.5 N10.9 O12.4 C55.9, found Cu13.8 H8.7 N10.5 C55.2. The percentage copper observed is somewhat high, probably because of the presence of a small amount of chelate B, which has a higher percentage of copper (23.5%). No additional water molecules are found but it is not excluded that these molecules were present in the extracted chelate and disappeared during heating at 60°C. The presence of water molecules also explains the instability in solution with Na_2SO_4, a water absorber, and the change in solubility properties after drying at 60 C. If Na_2SO_4 absorbs the two axial water molecules, this means that these are fairly weakly coordinated and so it is not surprising that they dissociate at 60°C.

Cu^{2+} is a d^9 system with one unpaired electron, which means that four main lines can be expected in the ESR spectrum because I = 3/2 both for ^{63}Cu and ^{65}Cu. The normal way of coordination for unstrained dioximes is the N,N-configuration. Because I = 1 for nitrogen nine equidistant lines are to be expected on each copper line with intensity ratio of 1:4:10:16:19:16:10:4:1. Furthermore, we must take into account that copper consists for 69.1% of ^{63}Cu and for 30.9% of ^{65}Cu with a slight difference in magnetic moment (0.70904 x 10^{-4} vs 0.75958 x 10^{-4} rad. sec^{-1} $gauss^{-1}$). A computer simulation of the spectrum is shown in fig. 6.9 and an excellent fit is noticable.

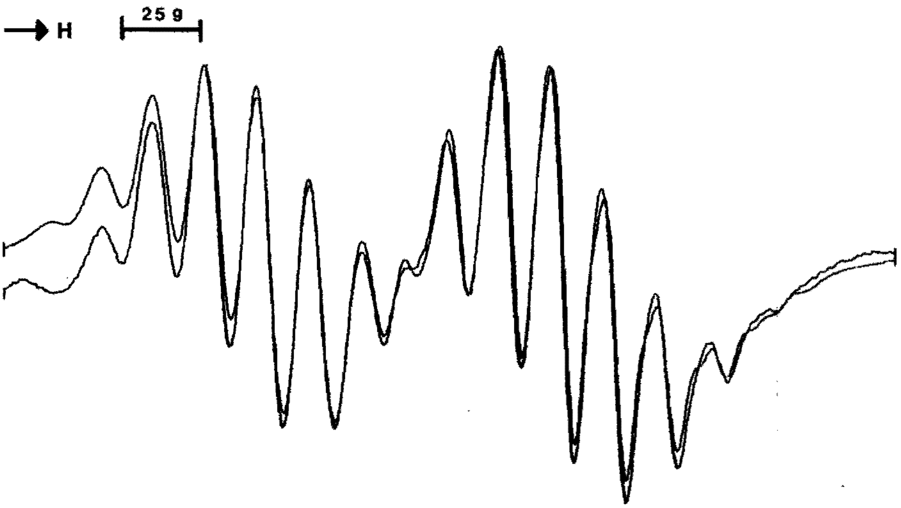


Fig. 6.9 The two high field copper bands from the ESR spectrum of fig. 6.5 together with the computer simulation for a CuN_4 chromophore. The input values for the simulation are A_{Cu} = 92 gauss; A_N = 16.2 gauss; linewidth = 10.5/8.5 gauss; modulation 5 gauss; lineform lorentz; ^{63}Cu = 70% and ^{65}Cu = 30%.

The left part of the simulation is somewhat raised compared to the observed spectrum because the overlap with the third copper band could not be taken in account with our program. This simulation proves that indeed chelate A has N,N-coordination.

Chelate B is formed at high pH values (pH > 5) with an excess of copper. This phenomenon is also seen in the extraction of copper by δ-H_2CQD (chapter 3) and in the extraction of copper by α-benzildioxime (Einaga and Ishii (8)).

The elemental analysis of chelate B can be explained by assuming a $Cu_4(C_{12}H_{22}N_2O_2)_3(OH)_2C_4H_8O_2$ chelate. The expected elemental analysis for this chelate - Cu24.1, N8.0, C45.5, H7.2 and O15.2 - is in reasonable agreement with the observed values : Cu23.5 N8.0 C46.8 H7.5. The dioxane molecule would then be introduced during the recrystallization. This would also explain why the UV spectrum changed after isolation. These results are insufficient to determine the structure of chelate B directly after extraction. The absence of an ESR spectrum points to the direction of a chelate with a strong copper copper coupling as was also found for the Cu:H_2CQD = 2:3 chelate (chapter 3). A composition of $Cu_4(C_{12}H_{22}N_2O_2)_3(OH)_2.xH_2O$ is possible for the extracted chelate but other compositions cannot be excluded. The high copper extraction as observed in fig. 6.4 can readily be explained by such a chelate. The significance of this chelate B for the extraction of copper is very small because when dipentyldioxime is used in practical processes excess ligand will be used and the pH will be kept low (to prevent copper hydroxide precipitation) and under these circumstances no chelate B will be formed.

6.4.3 Kinetic measurements on the pH dependent nickel extraction by dipentyldioxime

To find the rate-determining step kinetic measurements were performed on the extraction of nickel(II) by dipentyldioxime. From fig. 6.6 the order in dipentyldioxime is calculated to be 0.90, which approximates 1 and not 2 as was found by Navtanovich and co-workers for the extraction from ammoniacal solutions. The order in Ni^{2+} is 0.91 (fig. 6.7) in good agreement with the expected order of 1. The order in H^+ is -0.16 (fig. 6.8) which is not far from zero. These orders can be explained when we assume the following reaction scheme

$$(1)\quad \overline{H_2A} \overset{k_1}{\rightleftarrows} H_2A* \qquad\qquad K_1 = \frac{k_1}{k-1} = \frac{[H_2A^*]}{[\overline{H_2A}]}$$

$$(2)\quad Ni^{2+} + H_2A* \overset{k_2}{\rightleftarrows} Ni(HA)^{+}* + H^{+}$$

$$(3)\quad Ni(HA)^{+}* + H_2A \overset{k_3}{\rightleftarrows} Ni(HA)_2* + H^{+}$$

$$(4)\quad Ni(HA)_2* \overset{k_4}{\rightleftarrows} \overline{Ni(HA)_2}$$

The compounds marked with an asterisk are in the interface or in the water layer and bars indicate the organic layer.

If reaction two is the rate-determining step the initial extraction rate will be given by

$$(5)\quad r = k_2[H_2A^*][Ni^{2+}] = k_2.K_1\ [\overline{H_2A}][Ni^{2+}]$$

This would explain the first order in H_2A and in Ni^{2+} and the zero order in H^+. It is not known whether the reaction takes place in the interface or in the water layer but the zero order in H^+, which means that H_2A is not ionized before the reaction, points to the direction of the interface because ionization of H_2A in the water layer is likely to occur. The acidic water layer does not make it very attractive for the dioxime part of the ligand (which is acidic too) to appear at the interface. Because of this low interfacial dioxime concentration equation (2) will be the rate-determining step. In ammoniacal solutions Navtanovich and co-workers (2) found a second-order rate dependence in H_2A which means that in that case the reaction of Ni^{2+} with the second H_2A molecule is rate-determining. The ammonia causes a high pH value and it is reasonable to assume that the acidic dioxime part of the ligand is pulled to the interface for being ionized. This causes a high interfacial dioxime concentration and as a result the normally expected second order in H_2A is found.

6.5 CONCLUSIONS

The extraction of copper and nickel from ammoniacal solutions by dialkyldioximes of the type C_nH_{2n+1}-C(NOH)-C(NOH)-C_nH_{2n+1} has been studied. The extraction capacities of the dioximes for nickel and copper have a different dependence on the length of the alkyl chain due to the fact that copper forms octahedral chelates while nickel forms square planar chelates. The dependence of the NH_3 and NH_4^+ concentration is in agreement with a reaction equation:

$$M(NH_3)_n + 2H_2A \rightleftarrows M(HA)_2 + 2NH_4^+ + (n-2)NH_3$$

In the pH dependent extraction of copper by dipentyldioxime two different chelates are involved, chelate A at low pH values and chelate B with excess copper at pH > 5. Elemental analysis showed that chelate A is the normally expected $Cu(HA)_2$ chelate. ESR investigation demonstrated that this chelate has N,N-coordination, which is common for Cu(II) dioxime chelates. The significance of chelate B in the extraction chemistry is small because this chelate is only formed under extreme circumstances. The composition of chelate B could not completely be elucidated but it became clear that the copper:ligand ratio is larger than one and that the chelate contains more than one copper ion (the absence of an ESR spectrum also suggests that there is a copper-copper interaction in chelate B).

Kinetic measurements showed that in the extraction of a nickel nitrate solution by dipentyl dioxime the reaction of Ni^{2+} with the first dioxime molecule is rate-determining, while Navtanovich *et al.* discovered that in ammoniacal solutions the reaction of Ni^{2+} with the second dioxime is rate-determining. These results are explained by assuming that in acidic nitrate solutions the interfacial dioxime concentration is low while in basic ammoniacal solutions the dioxime part of the ligand is pulled to the interface for being ionized.

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CHAPTER 7

GENERAL DISCUSSION

The main objective of the studies presented in this thesis was the search for an extractant which is selective for nickel above copper (which means that the Irving-Williams (1) order of stabilities must be reversed) and which has a commercially attractive extraction rate for nickel. Molecules of the type R_1-C(NOH)-C(NOH)-R_2 were taken as a starting point, because of the known great affinity of nickel for dimethylglyoxime. Aliphatic α-dioximes (2, 3) do indeed extract nickel at lower pH than copper, but the extremely low rate of extraction does not make this system attractive. In this dissertation the influence is examined of small changes in R_1 and R_2 on the extraction capacities of dialkylglyoxime.

In chapter 3 and 4 a bicyclic ring system was taken for R_1 and R_2. By making use of the resulting strain in the dioxime part of the molecule the N-N distance could be varied. The effect of this variation on the so called $(pH\frac{1}{2})_{1.0}$ value of all dioximes studied is presented in fig. 7.1. From this figure it becomes clear that the stability order of nickel and copper is reversed when the N-N distance is larger than 2.6 Å. The increasing N-N distance also influences the rate of nickel extraction. While with the unstrained dioximes equilibrium in the extraction reaction is not reached within days, with nopinoquinone dioxime equilibrium in the extraction reaction is reached within ten minutes. This tendency for an increase in reaction rate is not completely pursued

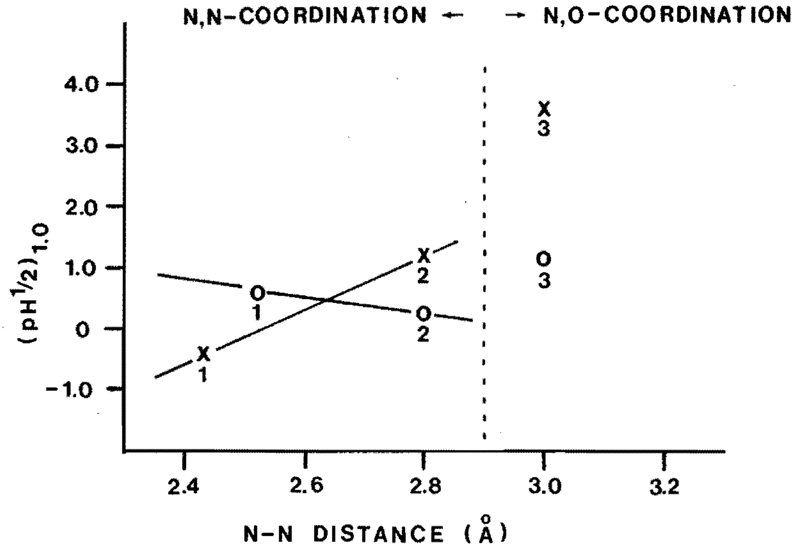


Fig. 7.1 $(\text{pH}\tfrac{1}{2})_{1.0}$ values as a function of the N-N distance in the chelate for the extraction of nickel (x) and copper (o). 1 dipentyldioxime (2) 2 -nopinoquinone dioxime (chapter 4) 3 -camphorquinone dioxime (chapter 3). * The N-N distances were taken from crystal structures of analogous copper (4) and nickel (5) chelates.*

with camphorquinone dioxime (equilibrium in one hour) This molecule can, however, not be compared with nopinoquinone dioxime, because it does not form a N,N-coordinated chelate, but a N,O-coordinated chelate. Given these results it would be of interest to investigate a dioxime molecule with a N-N distance of about 2.6 Å. It might be that such a molecule would have the extraction rate of nopinoquinone dioxime and the $(\text{pH}\tfrac{1}{2})_{1.0}$ value of the unstrained dioxime, but presumably the increase in nickel extraction rate will go parallel with the increase in the $(\text{pH}\tfrac{1}{2})_{1.0}$ value for nickel extraction. It is not easy to find a dioxime molecule with a rigid N-N distance of about 2.6 Å. Bicyclo [3.2.1] octane-2,3-dione dioxime (see fig. 7.2), a derivative of homocamphor, might be important in this respect.

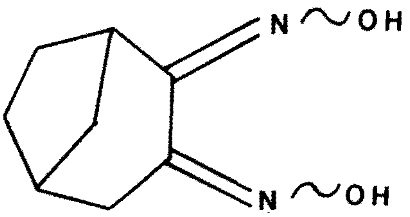


Fig. 7.2 Bicyclo [3.2.1] octane-2,3-dione dioxime

If the bond angles are taken from the crystal structure of carboncamphenilone (6), which has two ketone groups instead of two dioxime groups, and the C-C and C-N distances are taken from the crystal structure of bis(2,3-pentanedionedioximato)nickel(II) (5), the N-N distance in bicyclo [3.2.1] octane-2,3-dione dioxime is calculated to be 2.72 Å.

Also a dioxime molecule with a N-N distance of about 2.9 Å would be of interest. Such a dioxime would perhaps coordinate in a different way with copper than with nickel. However, when looking at fig. 7.1 it is doubtful if such a molecule will be a selective extractant for nickel. Furthermore, when an isomer is used with a special orientation of the OH groups suitable for chelation with nickel and not for chelation with copper it is likely that under extraction conditions isomerization takes place and that as a result also chelation with copper will occur. This isomerization phenomenon was found with the camphorquinone dioxime isomers (see chapter 3).

The second way in which we varied the dioxime molecule was to put an extra oxime group neighbouring to the dioxime part (see chapter 5). This third oxime group makes the organic molecule more hydrophilic, and as a result of that a bulky alkyl group proved necessary to keep the trioxime in the organic layer. The results of chapter 5 show that the trioxime is not suitable for nickel extraction since precipitation caused by intermolecular hydrogen bridge formation and/or coordination of the third oxime group blocks the back extraction

As a third possibility the dioxime part of the trioxime molecule was changed into a furazan ring (see fig. 7.3).

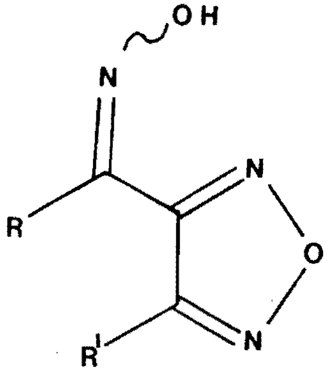
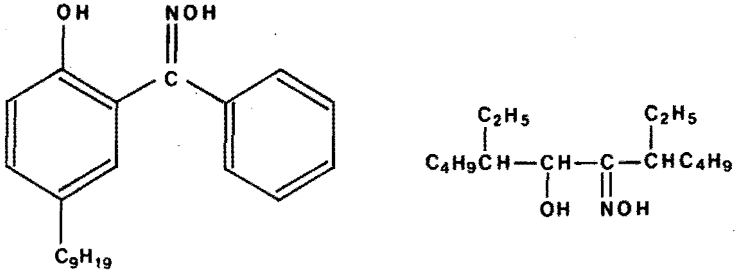


Fig. 7.3 The general structure of a furazan oxime.

This seemed to be a promising kind of ligand because the bidentate character is preserved. Such molecules are easily made by a thermal reaction of a 1,2,3-trione-1,3-dioxime in an aqueous solution of sodium hydroxide (see chapter 5.2). However, the furazan is such a weak ligand (7) that in spite of the vicinal oxime group no reaction occurred with copper(II) and nickel(II) under extraction conditions.

The fourth variation of the dioxime we investigated was the influence of the length of the aliphatic group in the extraction. The length of the aliphatic group did not seem to have much influence on the thermodynamic stability of the formed chelates, but it did have influence on the nickel extraction rate. The use of ammoniacal solution did not constitute an advantage because no good separation could be obtained between nickel and copper, whereas a good separation is possible by pH controlled extraction from acidic nitrate solutions. Because nickel forms chelates with aliphatic dioximes that are more stable than those of copper (2, 3), further investigations with the intention to accelerate the nickel extraction rate might be worthwhile. LIX 64N (8), commercially used for copper extraction, contains an active extractant 2-hydroxy-5-nonylbenzophenon oxime (HA) together with a catalyst compound 5,8-diethyl-7-hydroxydodecan-6-one oxime (HB) (see fig. 7.4) typically in a ratio of 20:1 by weight.



HA **HB**

Fig. 7.4 2-Hydroxy-5-nonylbenzophenone oxime (HA) and 5,8-diethyl-7-hydroxydodecan-6-one oxime (HB).

The initial copper extraction rate is considerably larger than the sum of the separate components under the same conditions. This has been explained (9, 10) by assuming that the high reaction rate for the coordination of compound HB is combined with the high thermodynamic driving force for the coordination of compound HA. The proposed mechanism is (10):

$$Cu^{2+} + HA_* \rightleftarrows CuA_*^+ + H^+ \qquad (1)$$

$$CuA_{*}^{+} + HB_{*} \rightleftarrows CuAB_{*} + H^{+} \tag{2}$$

$$CuAB_{*} \rightleftarrows \overline{CuAB} \tag{3}$$

$$\overline{CuAB} + \overline{HA} \rightleftarrows \overline{CuA_2} + \overline{HB} \tag{4}$$

The compounds marked with an asterisk are supposed to be present in the interface, while the compounds marked with bars are in the organic phase. Because at the end the thermodynamically more stable CuA_2 is formed the $(pH\frac{1}{2})_{1.0}$ value will be determined by HA. It would be of interest to investigate whether or not the extraction of nickel by unstrained aliphatic dioximes (as HA) can be accelerated in a similar way by, for example, nopinoquinone dioxime (as HB).

Finally it can be stated that copper has a more complex extraction chemistry than nickel. Whereas nickel only forms Ni:L = 1:2 chelates, under special conditions copper sometimes also forms chelates with a higher Cu:L ratio. This phenomenon was observed with camphorquinone dioxime (chapter 3), 4-t-butyl-1,2,6-cyclohexanetrione trioxime (chapter 5) and dipentyldioxime (chapter 6).

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CHAPTER 8

SUMMARY

In order to find an extractant that is selective for nickel with respect to copper a number of organic compounds containing oxime groups have been synthesized and studied for their extraction properties.

In chapter 1 a general introduction is presented about the extraction issue.

The experimental details how the extractions were performed and how the results obtained are treated mathematically are described in chapter 2. A brief theoretical study of the application of ESR spectroscopy to copper complexes in solution can also be found in this chapter.

In chapter 3 the properties of three geometrical isomers (α-, β- and δ-) of camphorquinone dioxime (H_2CQD) in the liquid-liquid extraction of copper and nickel are described. Under extraction conditions isomerization occurred from α- and β-H_2CQD into δ-H_2CQD The expected selectivity of δ-H_2CQD for nickel could not be established. On the contrary, copper formed chelates with lower pH½ values than nickel. An ESR study showed that this was due to the fact that copper did not form a N,N-coordinated chelate, but analogously to nickel a N,O-coordinated chelate. UV spectroscopy proved that besides the $Cu(HCQD)_2$ chelate a $Cu_2(HCQD)_2CQD$ chelate is involved in copper extraction.

The extraction properties of β-nopinoquinone dioxime (β-H_2NQD) with copper and nickel are reported in chapter 4. Spectroscopic investigations (ESR and NMR) showed that both copper and nickel are extracted as a N,N-coordinated chelate.

In comparison with aliphatic dioximes β-H_2NQD had a high extraction rate for nickel, but unfortunately the selectivity for nickel above copper was reversed. The furazan of H_2NQD, synthesized by treatment of δ-H_2NQD with 1N NaOH, did not show any extraction capacities for either copper or nickel.

Chapter 5 deals with the extraction properties of 1,2,3-cyclopentanetrione trioxime (H_3CPT) and its furazan, and of 4-t-butyl-1,2,6-cyclohexanetrione trioxime H_3BHT and its furazan. H_3CPT appeared to be too soluble in water. The introduction of a large hydrophobic group like t-butyl in H_3BHT provided an answer to this problem. The extracted copper and nickel chelates of H_3BHT precipitate by agglomeration caused by intermolecular hydrogen bridge formation and/or coordination of the third oxime group. This precipitation blocked the back extraction. The furazan oximes did not form copper or nickel chelates under extraction conditions.

In chapter 6 the extraction properties are presented of some unstrained aliphatic dioximes. Extraction from ammoniacal solutions showed that the extraction of copper and nickel has a different dependence on the length of the alkyl chains of the aliphatic dioximes. From the pH dependent extraction of copper by dipentyldioxime it became clear that two chelates are involved in copper extraction. Kinetic measurements showed that in the extraction of a nickel nitrate solution by dipentyl-dioxime the reaction of Ni^{2+} with the first un-ionized dioxime molecule is rate-determining.

In chapter 7 the most important conclusions from this thesis are summarized and discussed and some recommendations are given for further research.

SAMENVATTING

Met het doel een extractant te vinden dat selectief is voor nikkel ten opzichte van koper zijn een aantal organische verbindingen, die oximgroepen bevatten, gesynthetiseerd en bestudeerd op hun extractie-eigenschappen.

In hoofdstuk 1 is een algemene inleiding gegeven over de extractieproblematiek.

Hoe de extractie-experimenten zijn uitgevoerd en hoe de resultaten zijn verwerkt is beschreven in hoofdstuk 2. Verder staat er in dit hoofdstuk een korte theoretische verhandeling over ESR spectroscopie aan kopercomplexen in oplossing.

De eigenschappen van drie geometrische isomeren (α-, β- en δ-) van kamferchinondioxim (H_2CQD) voor de vloeistof-vloeistof extractie van koper en nikkel zijn beschreven in hoofdstuk 3. Onder extractieomstandigheden vond isomerisatie plaats van α- en β-H_2CQD naar δ-H_2CQD. De verwachte selectiviteit van δ-H_2CQD voor nikkel werd niet waargenomen. Koper vormde daarentegen chelaten met lagere $pH_{\frac{1}{2}}$ waarden dan nikkel. Een ESR-studie liet zien dat dit kwam door het feit dat koper geen N,N-gecoördineerd chelaat, maar net als nikkel een N,O-gecoördineerd chelaat vormt. Uit UV-spectroscopische metingen werd duidelijk dat naast het $Cu(HCQD)_2$ chelaat een $Cu_2(HCQD)_2CQD$ chelaat is betrokken bij de koper-extractie.

Een verslag over de eigenschappen van β-nopinochinondioxim (β-H_2NQD) in de extractie van koper en nikkel is te vinden in hoofdstuk 4. Spectroscopisch onderzoek (ESR en NMR) liet zien dat zowel koper als nikkel worden geëxtraheerd als een N,N-gecoördineerd chelaat. In vergelijking met alifatische dioximmen bezat β-H_2NQD een hoge extractiesnelheid voor nikkel, maar de selectiviteit voor nikkel ten opzichte van koper is helaas verdwenen. Het furazan afgeleid van H_2NQD, dat gesynthetiseerd werd door de behandeling van δ-H_2NQD met loog, bezit in het geheel geen extractie-eigenschappen voor koper en nikkel.

In hoofdstuk 5 worden de extractie-eigenschappen van 1,2,3-cyclopentaantriontrioxim (H_3CPT) met zijn furazan, en die van 4-t-butyl-1,2,6-cyclohexaantriontrioxim met zijn furazan (H_3BHT) behandeld. H_3CPT bleek te goed oplosbaar in water te zijn. Het introduceren van een grote hydrofobe groep, zoals t-butyl in H_3BHT, was een antwoord op dit probleem. De derde oxim groep van H_3BHT, zorgde ervoor dat de geëxtraheerde koper- en nikkelchelaten neersloegen door agglomeratie. Deze agglomeratie werd veroorzaakt door intermoleculaire waterstofbrugvorming en/of coördinatie. Dit neerslaan verhinderde de terugextractie. De furazanoximmen vormden geen koper- of nikkelchelaat onder extractie-omstandigheden.

In hoofdstuk 6 worden de extractie-eigenschappen van een paar niet-cyclische alifatische dioximmen beschreven. Bij de extractie van ammoniakale oplossingen was te zien dat de koper- en de nikkelextractie op een verschillende manier afhangt van de lengte van de alkylketens van de alifatische dioximmen. Uit de pH afhankelijke extractie van koper met dipentyldioxim werd duidelijk dat er twee verschillende chelaten betrokken zijn bij de koperextractie. Kinetische metingen lieten zien dat bij de extractie van een nikkelnitraat-oplossing met dipentyldioxim de reactie van Ni^{2+} met het eerste ongeïoniseerde dioximmolecuul snelheidsbepalend is.

In hoofdstuk 7 worden de belangrijkste conclusies van dit proefschrift nog eens op een rijtje gezet en worden enkele aanbevelingen gedaan voor verder onderzoek.

DANKWOORD

Graag wil ik allen, die op enigerlei wijze hebben bijgedragen aan de totstandkoming van dit proefschrift, bedanken.

In het bijzonder ben ik dank verschuldigd aan dr. ir. T.P.M. Beelen en drs. J.P. Weterings met wie ik vele leerzame discussies heb gevoerd.

Verder ben ik dhr. C.P.J. Rummens zeer erkentelijk voor zijn belangrijke bijdrage aan het onderzoek beschreven in de hoofdstukken 3 en 6. Van zeer groot belang is het werk geweest van de studenten Jan van de Berg, Paul Vriens en Maarten Mols. Veel waardering heb ik ook voor de hulp van drs. J.H.M.C. van Wolput (ESR), mevr. A.M. Elemans-Mehring (analyses) en dhr. W. van Herpen (apparatuur).
Ine van 't Blik-Quax wil ik bedanken voor de verzorging van het typewerk en de lay-out van dit proefschrift.

Tenslotte bedank ik alle collega's, personeelsleden en studenten van de vakgroep Anorganische Chemie voor de plezierige tijd die ik in hun midden heb doorgebracht.

CURRICULUM VITAE

VAN

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1953: 6 januari geboren te Zwolle
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1979-1983: wetenschappelijk assistent aan de Technische Hogeschool Eindhoven bij de vakgroep Anorganische Chemie

Stellingen

behorende bij het proefschrift van L.R.M. Paping

1. De opvatting van Worley et al. dat de verschillen tussen de door hun onderzochte Rh katalysatoren, zoals die blijken uit IR onderzoek aan geadsorbeerd CO, een gevolg zijn van een verschil in reduceerbaarheid, is onjuist.
   S.D. Worley, C.A. Rice, G.A. Mattson, C.W. Curtis, J.A. Guin en A.R. Tarrer, J. Chem. Phys. 1982, 76 (1), 20.
   S.D. Worley, C.A. Rice, G.A. Mattson, C.W. Curtis, J.A. Guin en A.R. Tarrer, J.Phys. Chem. 1982, 86, 2714.

2. De veronderstelling van Skorobogaty en Smith dat het cobalt (II) chelate van 4,4',4",4''' - tetrasulfoftalocyanine (Co(II)TSP) geadsorbeerd op amberlyst bij pH = 12 een monomeer is, gaat zowel voorbij aan de ervaring dat bij hoge pH zeer snel Co-O_2-Co dimeren gevormd worden als aan het feit dat een $\pi \rightarrow \pi^*$ overgang nauwelijks te onderscheiden is in een mengsel van Co(II)TSP monomeren en Co-O_2-Co dimeren.
   A. Skorobogaty en T.D. Smith, J. Mol. Catal. 1982, 16, 131.

3. De methode die Burch en Collins toepassen - het gebruik van een gasinjektiespuit voor het pulsen van zuurstof, het niet in situ verrichten van de metingen en het resulfideren om tot reproduceerbare resultaten te komen - om zuurstofchemisorptie aan sulfidische katalysatoren te meten is dubieus.
   R. Burch en A. Collins, Reprint Fourth International Conference on the chemistry and uses of Molybdenum Colorado, USA 1982.

4. Het doen van uitspraken over de mogelijke formule van kopercomplexen waarbij wel C,H,N analyses zijn verricht, maar waarbij het kopergehalte niet is bepaald, is op zijn minst bedenkelijk.
   M.S. Ma en R.J. Angelici, Inorg. Chem. 1980, 19, 363.

5. Op grond van hun conversiemetingen kunnen Dessau en La Pierre geen uitspraak doen over het alkeen dat hoofdzakelijk betrokken is bij de propagatiereactie van methanol over HZSM-5.
   R.M. Dessau en R.B. La Pierre, J. Catal. 1982, 78, 136.

6. Op grond van ^{57}Fe ENDOR metingen aan het Fe-Mo eiwit van nitrogenase is het niet gerechtvaardigd te concluderen dat de Fe-Mo cofactor zes inequivalente ijzeratomen bevat aangezien het proteïne in staat geacht moet worden in gelijkwaardige ijzeratomen verschillende hyperfijn interactie tensoren te induceren.
   B.M. Hoffman, R.A. Venters en J.E. Roberts,
   J. Am. Chem. Soc. 1982, 104, 4711.

7. De conclusie die Yates et al. uit Transmissie Electronen Mikroskopie metingen aan hoog gedispergeerde rhodium katalysatoren trekken, dat na reductie de rhodium kristalletjes zich als twee dimensionale deeltjes op de drager bevinden, moet ernstig in twijfel worden getrokken.
   D.J.C. Yates, L.L. Murrell en E.B. Prestridge,
   J. Catal. 1979, 57, 41.

8. Gezien het feit dat voor menigeen tegenwoordig geldt dat toename van vrije tijd gepaard gaat met een afname in inkomsten zal in de toekomst een bloei te verwachten zijn van goedkope hobbies zoals kaartspelen.

9. Meesterpunten bij bridge geven niet altijd een juist beeld van iemands speelsterkte. Een periodiek aan te passen "rating", zoals bij schaken te doen gebruikelijk, zou in dit opzicht wellicht meer op zijn plaats zijn.

10. Het feit dat steeds meer mensen zeggen dat zij maar zelden televisie kijken, lijkt geheel in strijd met de door de omroepen opgegeven kijkdichtheidscijfers.