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

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Abstract—In the research for a selective extractant for nickel a strained dioxime, β-nopinoquinone dioxime, has been studied in its extraction properties for copper(II) and nickel(II). Spectroscopic investigations (ESR and NMR) showed that both copper and nickel are extracted as a N,N-coordinated chelate. The extraction studies showed that the use of strained instead of aliphatic dioximes makes the extraction more convenient because of the higher extraction rate, but the selectivity for nickel above copper disappears.

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

Vicinal dioximate ligands usually form stable N,N-chelated complexes containing a conjugated N = C–C = N system (Fig. 1a).

In previous work[1] 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. 1b).

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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. 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.

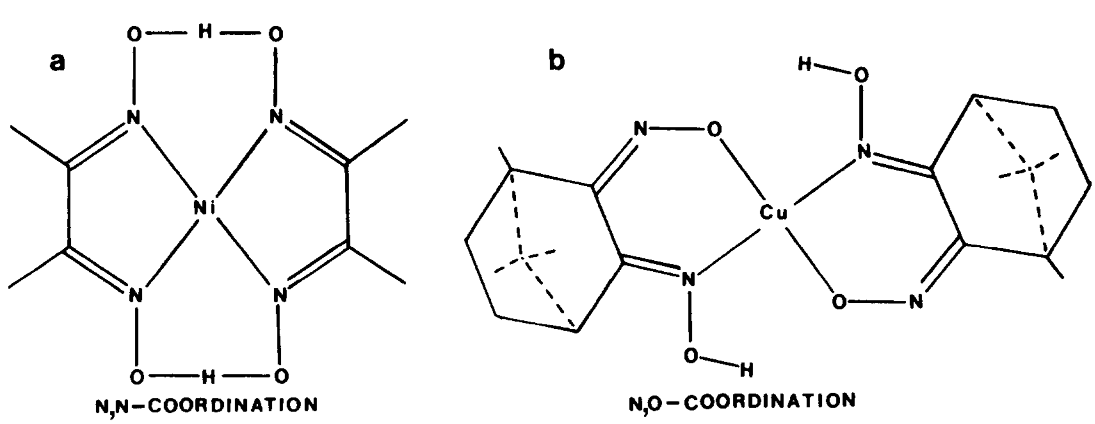
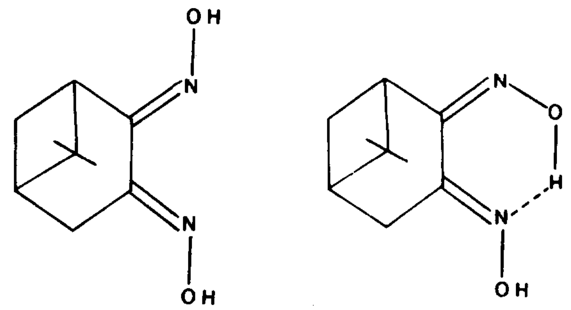


Fig. 1. (a) The N,N-coordinated bis(dimethylglyoximato)nickel(II) chelate. (b) The N,O-coordinated bis(camphorquinonedioximato) copper(II) chelate.



β-H_2NQD δ-H_2NQD

Fig. 2. Two isomeric forms of nopinoquinone dioxime.

EXPERIMENTAL

^1H NMR spectra were obtained at room temperature on a 60 MHz Varian EM 360 A spectrometer, while ESR measurements were done with a Varian E15 spectrometer at room temperature and UV-visible spectra were obtained on a Unicam SP.800D. Aqueous metal ion concentrations were measured with the Perkin–Elmer 300 Atomic Absorption Spectrophotometer.

The extraction experiments were carried out in a three stoppered flask with a stirring device and continuous pH measurements. The starting volumes of water and organic solvent were both 250 cm^3. Stirring was stopped when no further change of the pH was noticed, indicating that equilibrium was reached. For analysis equally small volumes of water layer and organic layer were withdrawn from the system. To measure the distribution coefficient as a function of pH thereafter a small quantity of 4N acid or base was added, and the process of stirring until equilibrium and withdrawal of small portions of the aqueous and organic solutions was repeated at a different pH. Care was taken to keep the volumes of the aqueous and organic solutions equal. Although in this procedure the electrolyte concentration does not stay constant we preferred this method because it is convenient to execute and because in a separate experiment it was shown that in the applied concentration range the influence of the electrolyte concentration was negligible. Pentanol was used as organic solvent and as inorganic salt we used metal nitrate. We used NaOH as base and HNO_3 as acid.

SYNTHESIS

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.[2] 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[3] using *n*-butyl nitrite, isonitrosonopinone was obtained in 30% yield from nopinone. Following the procedures of Nakamura[4], crude isonitrosonopinone (0.18 mol) dissolved in 50 cm^3 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 *in vacuo* 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. Found: C,59.3; H,7.9; N,15.5. Calc.: C,59.3; H,7.7; N,15.4%. IR: OH stretching vibrations at 3360 and 3180 cm^{-1} C = N absorptions at 1585 and 1615 cm^{-1}. These values are in perfect agreement with Nakamura.[5] ^1H 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.[4]

The furazan of nopinoquinone dioxime (Fig. 3)

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. Found: C,65.5; H,7.5; N,16.9. Calc. for $C_9H_{12}N_2O$: C,65.8; H,7.3; N,17.1%. ^1H NMR (DMSO-d6): see Fig. 4.

Bis(β-nopinoquinonedioximato)nickel(II)

$Ni(\beta\text{-}HNQD)_2$ 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.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 and 1560 cm^{-1} (shoulder) (C=N) Found: C,51.9; H,6.26; N,13.51. Calc. for $NiC_{18}H_{26}N_4O_4$: C,51.35; H,6.25; N.13.31%.

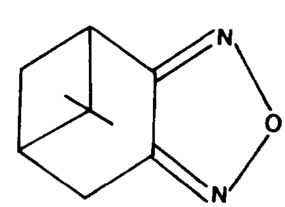


Fig. 3. The structure of the furazan derived from nopinoquinone dioxime.

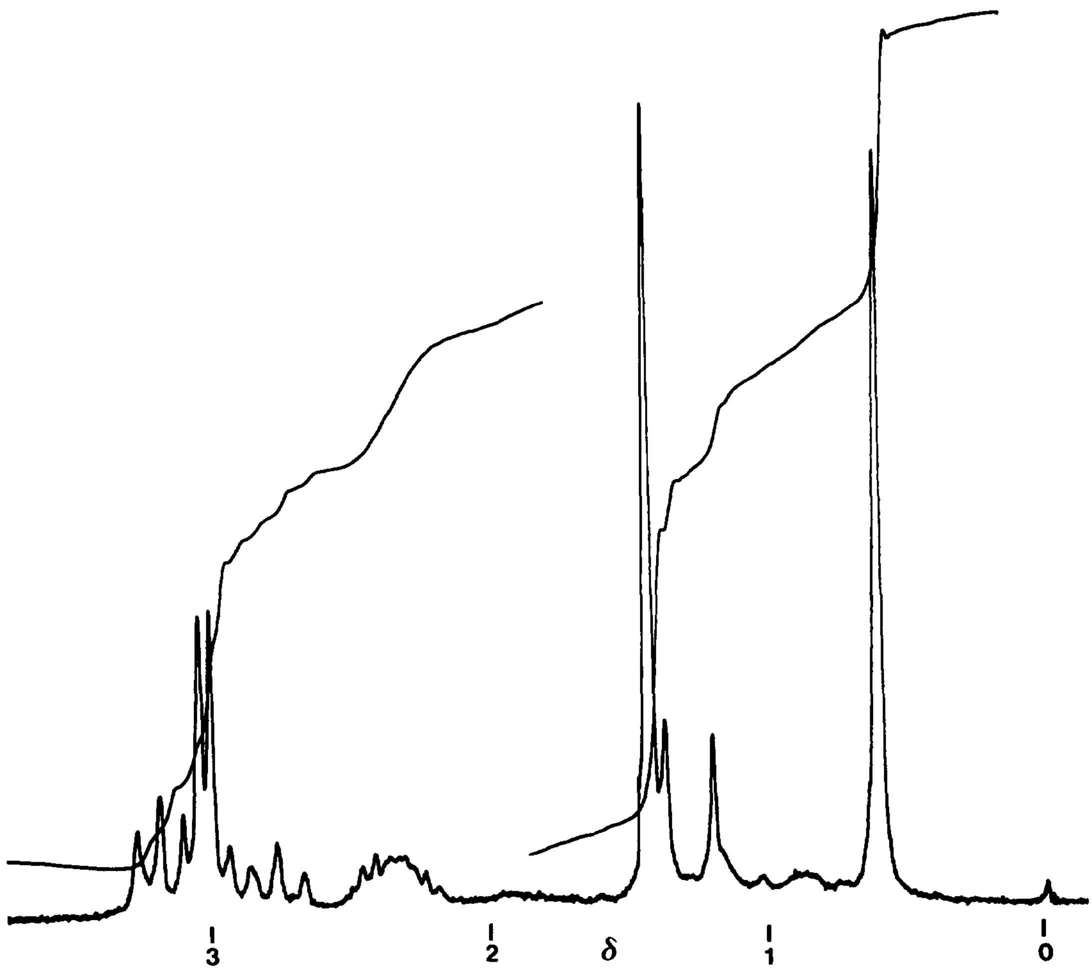


Fig. 4. 60 MHz ^{1}H NMR spectrum of the furazan of nopinoquinone dioxime.

TREATMENT OF EXTRACTION DATA

The extraction is expected to follow eqn (1):

$$Me^{2+} + \overline{2H_2NQD} \rightleftharpoons \overline{Me(HNQD)_2} + 2H^+ \quad (1)$$

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

$$K_E = \frac{[Me(HNQD)_2][H^+]^2}{[Me^{2+}][H_2NQD]^2} \quad (2)$$

$$D = \frac{[Me(HNQD)_2]}{[Me^{2+}]}. \quad (3)$$

Combination of (2) and (3) gives

$$\log D = \log K_E + 2pH + 2\log[H_2NQD]. \quad (4)$$

When taking a large excess H_2NQD, so that H_2NQD is constant, it follows that

$$\left(\frac{\partial \log D}{\partial pH}\right)_{[H_2NQD]} = 2. \quad (5)$$

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

$$\log K_E = -2\log[H_2NQD] - 2pH_{\frac{1}{2}}. \quad (6)$$

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

$$(pH_{1/2})_{1.0} = -\frac{\log K_E}{2}. \quad (7)$$

Figure 5 shows the results for the extraction of Cu^{2+} and Ni^{2+} with an excess of β-H_2NQD. The $pH\frac{1}{2}$ value of 1.85 for Cu^{2+} corresponds with

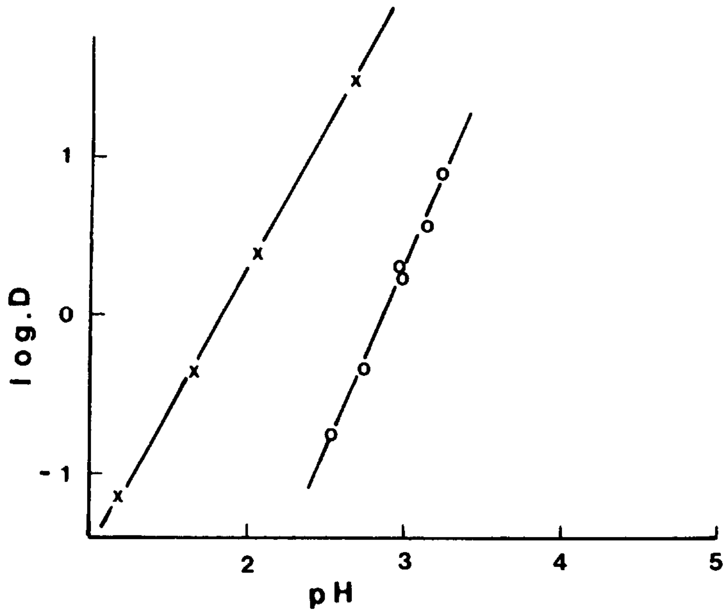


Fig. 5. Log D as a function of pH for the extraction of Cu(II) (X) and Ni(II) (O) by nopinoquinone dioxime. Concentration of β-H_2NQD is pentanol 0.025 M. Initial metal nitrate concentration 0.001 M.

$(pH\frac{1}{2})_{1.0} = 0.25$. For Ni^{2+} these values are somewhat higher: $pH\frac{1}{2} = 2.88$ and $(pH\frac{1}{2})_{1.0} = 1.28$. 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 deviate from the theoretically expected value of 2 for a meatal:ligand ratio of 1:2. No change in the extraction behaviour of β – H_2NQD could be observed after 2 days of contact.

To find out if copper only forms a 1:2 chelate with β-H_2NQD an experiment was done with equimolar amounts of copper and β-H_2NQD (Fig. 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} ($\epsilon = 9000$) and

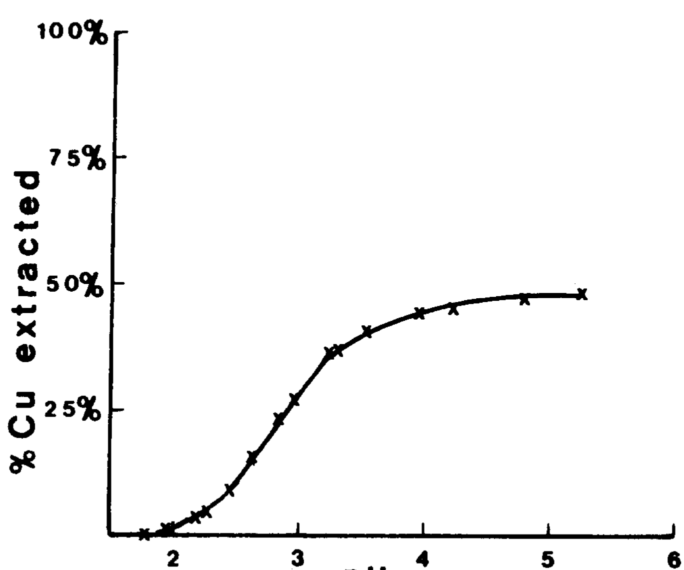


Fig. 6. % Copper extraction as a function of pH for the extraction of Cu(II) by β- nopinoquinone dioxime. The initial concentration of β-H_2NQD in pentanol and the initial copper concentration in water are both 0.002 M.

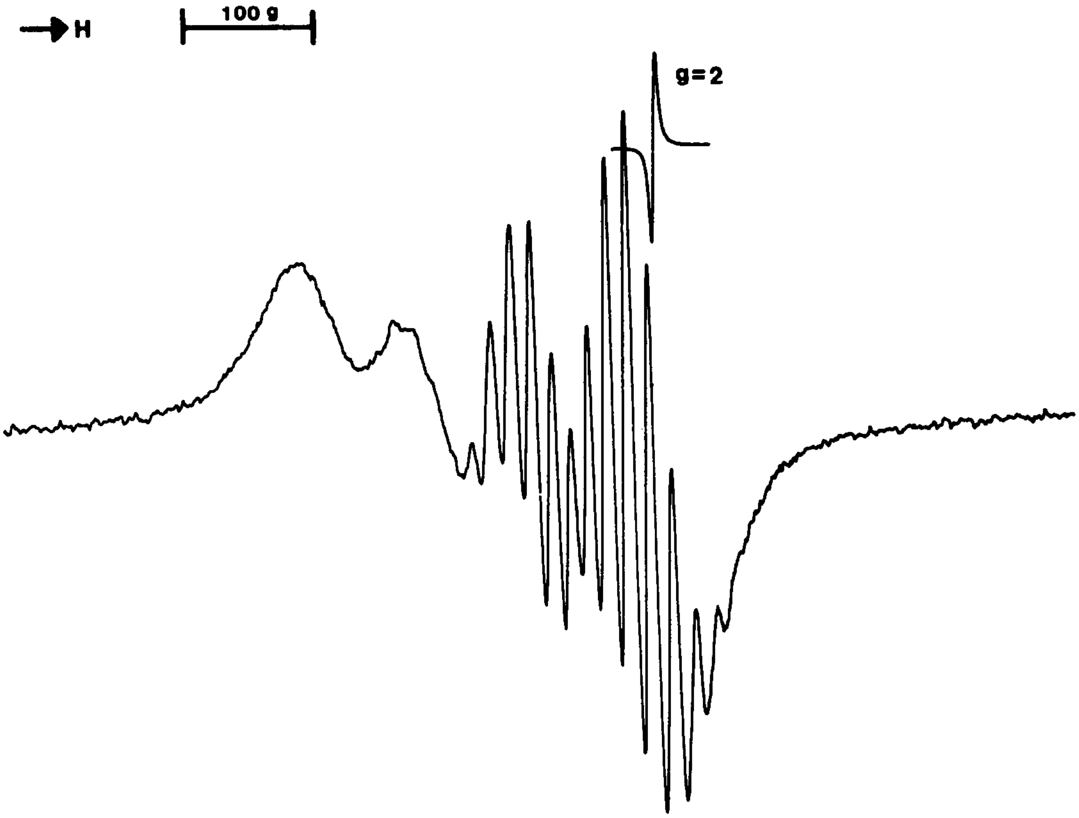


Fig. 7. ESR spectrum of the copper chelate formed during the extraction of Cu^{2+} by β-H_2NQD in chloroform at room temperature.

the other at 27.000 cm^{-1} ($\epsilon = 2300$). The elemental analysis from the isolated chelate is: C,48.61; H,6.32; N,11.29; Cu,12.98; O,20.8%. This leads to a chelate with formula $CuC_{20}H_{31}N_4O_6$ indicating that the chelate has two additional water molecules and also that some pentanol is retained. The expected elemental analysis for $Cu(HNQD)_2.2H_2O$ containing $6\frac{1}{2}$% pentanol ($C_5H_{11}OH$) is: C,48.19; H,6.96; N,11.34; Cu,12.88; O,20.63%. The ESR spectrum of the chelate in $CHCl_3$ is presented in Fig. 7.

The nickel H_2NQD chelate isolated from the extraction was examined by NMR (Fig. 8). The elemental analysis gave: C,54.4; H,7.0; N,12.6; Ni,11.7% which was different from the expected for $Ni(HNQD)_2$: C,51.3; H,6.2; N,13.3; Ni,13.9%. 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.

DISCUSSION

Extraction

If we compare the extraction results of β-H_2NQD with those of β-H_2CQD clearly a lowering of the $(pH\frac{1}{2})_{1.0}$ value for both copper and nickel is observed (Table 1). This lowering cannot completely be explained by the fact that different solvents are used. In previous work[1] it was proven that β-H_2CQD isomerizes to δ-H_2CQD and that this is coupled with a lowering of the $pH\frac{1}{2}$ value. So $pH\frac{1}{2}(\beta\text{-}H_2CQD) > pH\frac{1}{2}(\delta\text{-}H_2CQD)$. In Table 1 it is observed that the $pH\frac{1}{2}$ value of δ-H_2CQD is larger than that of β-H_2NQD in pentanol. The conclusion can be drawn that the $pH\frac{1}{2}$ 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 and the isolated nickel chelate was examined with NMR spectroscopy.

The structure of the copper H_2NQD *chelate*

Figure 6 shows that copper forms a 1:2 chelate with β-H_2NQD under extraction conditions. From the elemental analysis of the extracted Cu(β-HNQD$)_2$ it became clear that the chelate is extracted with two additional water molecules. It

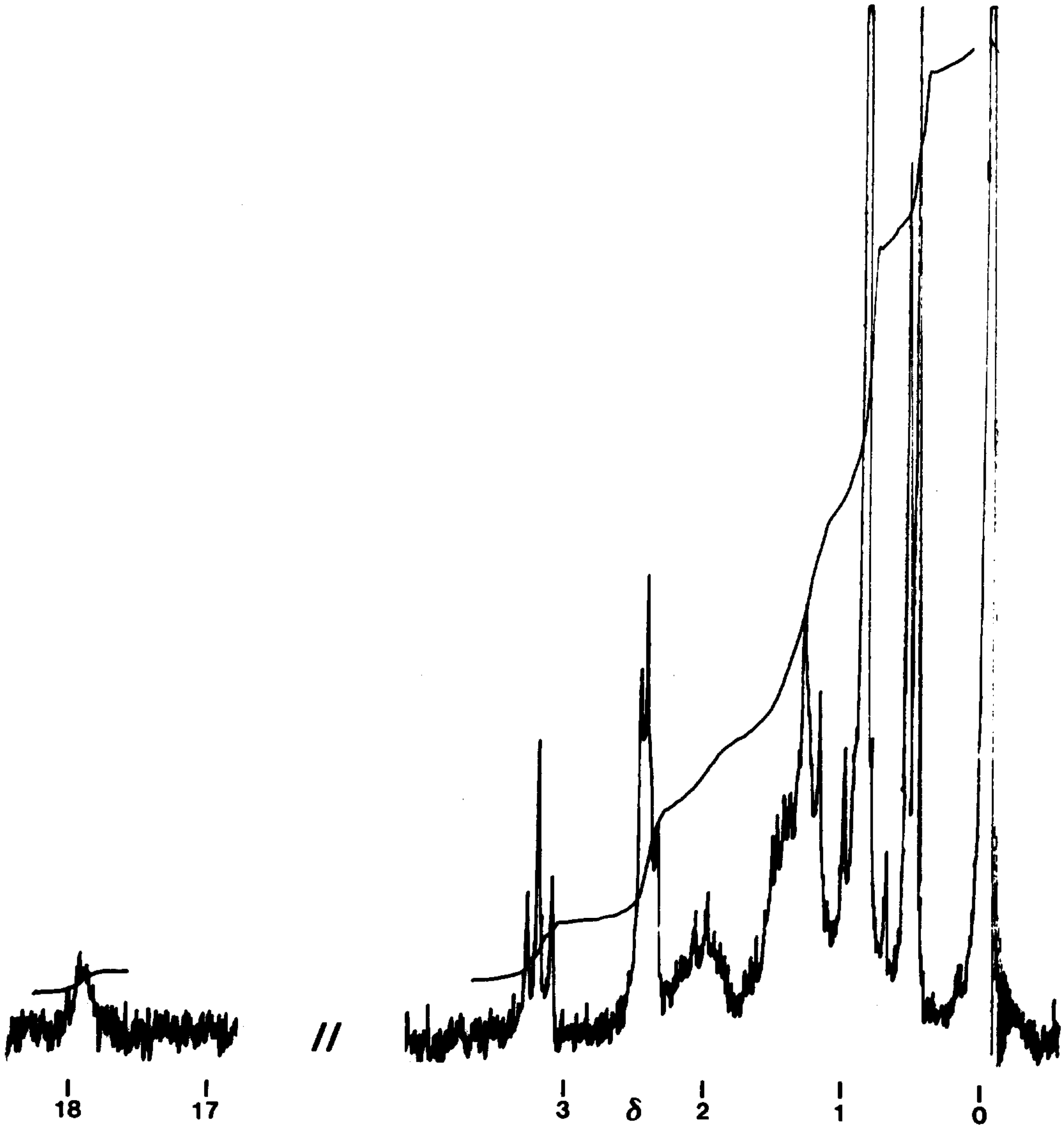


Fig. 8. 60 MHz ^1H spectrum of the nickel chelate formed during the extraction of Ni^{2+} by β-H_2NQD in benzene at room temperature.

Table 1. Extraction of copper(II) and nickel(II) by some vic-dioximes

compound	solvent	$(pH_{1/2})_{1.}$ Cu	$(pH_{1/2})_{1.}$ Ni	reference
α-H_2CQD*	pentanol	+1.48	+3.43	(1)
β-H_2CQD*	t.b.p.	+2.61	+4.73	(1)
δ-H_2CQD	pentanol	+1.15	+3.60	(1)
β-H_2NQD	pentanol	+0.25	+1.28	this study
C_5H_{11}-C(NOH)-C(NOH)-C_5H_{11}	toluene	+0.62	-0.42	(6)
C_7H_{15}-C(NOH)-C(NOH)-C_7H_{15}	toluene	+0.54	-0.36	(6)
C C C-C-C-C-C(NOH)-C(NOH)-C-C-C-C	toluene	+0.59	-0.14	(6)

*Isomerization occurs to δ-H_2CQD under extraction conditions.

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. 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 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 Fig. 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 noticeable. In contrast with the spectrum of Cu(δ-HCQD)$_2$ (Ref. 1 Fig. 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 days. Firstly, the Cu(δ-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(β-HNQD)$_2$: 77.5 G instead of 90.5 G. The splitting of ^{65}Cu can now be calculated from the difference in magnetic moment (0.70904×10^{-4} for ^{63}Cu vs 0.75958×10^{-4} rad sec^{-1} G^{-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. ((0.75958/0.70904) − 1).77.5 = 8.3 G instead of the 9.6 G for Cu(δ-HCQD)$_2$. In Fig. 9 the two high-field lines of copper are seen, and the nitrogen superhyperfine lines are numbered. 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 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 deviate from the observed intensities. It is concluded from the ESR spectrum that Cu(β-HNQD)$_2$ has N,N-coordination.

The structure of the nickel H_2NQD *chelate*

The elemental analysis of Ni(β-HNQD)$_2$ from extraction deviates from the expected values, while the synthesized Ni(β-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 were 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

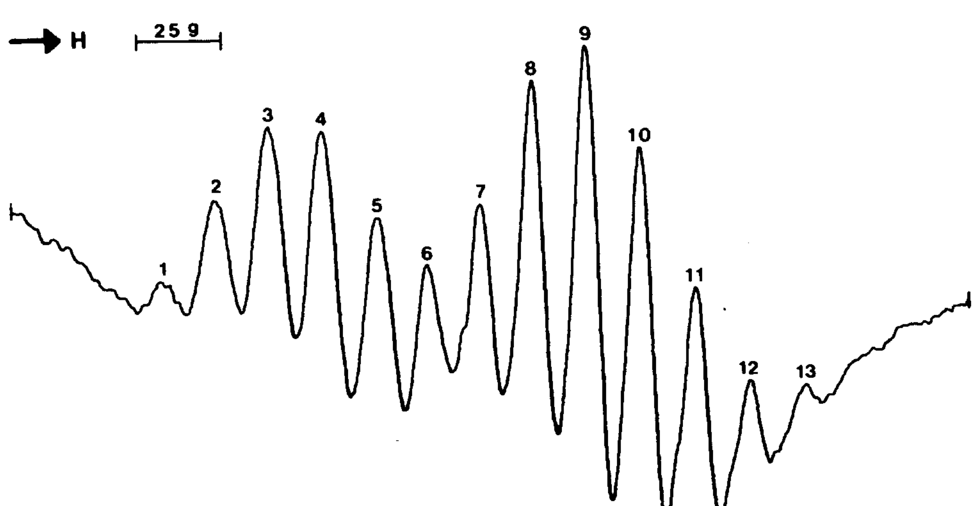


Fig. 9. The two high-field lines of copper from Fig. 7.

Table 2. Up-down values of the nitrogen superhyperfine splittings of Fig. 9 and the expected values for CuN_4 and CuN_2O_2 chromophores

line number	up-down value	CuN_4 expectation	CuN_2O_2 expectation
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 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	$CDCl_3$	(5)
Ni(β-HNQD)$_2$	0.56	0.94	1.17	1.52	2.20	2.45	3.29	17.90	C_6D_6	(5)
	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
extraction	0.60	0.89	0.82	*	2.05	*	3.28			study
β-H_2NQD	0.74	1.30	1.07	2.05	2.48-2.74		3.47	11.09/10.72	DMSO-d_6	(4)
δ-H_2NQD	0.74	1.31	1.20	2.10	2.44- - -		2.78	12.30/12.08	DMSO-d_6	(4)
β-H_2NQD	0.74	1.30	1.03	2.05	2.40-2.80		3.41	11.18/10.74	DMSO-d_6	this study

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.

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(β-HNQD)$_2$ is diamagnetic and NMR spectroscopy might give useful information.

The NMR spectrum of Ni(β-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 β-H_2NQD. According to Nakamura[5] Ni(β-HNQD)$_2$ can have two possible ligand alignments, *anti* and *syn*. This can also be observed in the NMR spectrum of the extracted Ni(β-HNQD)$_2$. The values of the chemical shifts are given in Table 3 together with the literature values. The proton numbering can be found in Fig. 10.

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

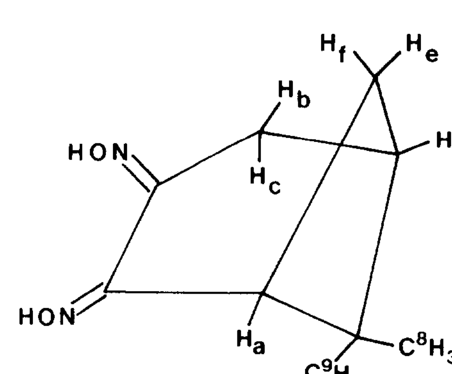


Fig. 10. The nopinoquinone dioxime molecule with hydrogen numbering.

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 hydroxyl group with the Ha proton. Saitô[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 Ni(β-HNQD)$_2$ compound synthesized by Nakamura.

In N,O-coordination another kind of hydrogen bridging occurs (see Fig. 1) and this leads to a different chemical shift, such as Ni(δ-HNQD)$_2$: $\delta = 11.16$, Ni(α-HCQD)$_2$: $\delta = 11.07$[5] and Ni(δ-HCQD)$_2$: $\delta = 10.80$[5]. 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 $\delta = 1.4$ 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 that estimated by elemental analysis.

The influence of the N–N *distance*

The fact that both Cu^{2+} and Ni^{2+} form N,N-bonding chelates 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 pH$\frac{1}{2}$ values with β-H_2NQD than with δ-H_2CQD (see Table 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 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 pH$\frac{1}{2}$ value can be observed. For nickel the greater N–N distance is coupled with a striking increase of the pH$\frac{1}{2}$ value. Furthermore, the nickel extraction rate is raised enormously. Equilibrium is reached within 10 min 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 cooordinated 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 determined 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 determined 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 pH$\frac{1}{2}$ 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 Shannon a much greater ionic radius than the four coordinated nickel: 0.73 Å vs 0.49 Å. Furthermore the copper coordination sphere possesses some plasticity[14] 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.[15] No octahedral complexes of the type $Ni(H_2O)_2$ $(LL)_2$ 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.

Table 4. The chemical shifts in ppm and the coupling constants in *cps* from the furazan of nopinoquinone dioxime. NMR spectrum see Fig. 7. Proton numbering see Fig. 10

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

The furazan of nopinoquinone dioxime

The yellow oil which was obtained in the synthesis of β-H_2NQD 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[16] 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[17] 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) was studied in detail. The compound gave a very clear spectrum. Chemical Shifts and coupling constants are given in Table 4. 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 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[18] equation (vicinal couplings) must be treated with reserve.[19] 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° between H*a* and H*e*. The expected angle between H*a* and H*f* now is $120° - 37° = 83°$. A dihedral angle of 83° 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[20] for some other pinane derivatives. The long-range coupling $^4J(Ha, Hd)$ is remarkable but not unknown in bicyclic molecules.[20,21] Meinwald[21] explained this long-range interaction by assuming a fairly extensive overlap between the small lobes of the orbitals directed 180° 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[22] 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.

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