anti-amphi and *cis-trans* Isomerisms in Some

Bis(dioximato)nickel(II) Complexes

SØREN BOLS PEDERSEN and ERIK LARSEN

*Chemistry Department I and II, The H. C. Ørsted Institute, University of Copenhagen,
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark*

Nickel(II) complexes of *vic*-dioximes, particularly camphorquinone dioximes, have been isolated and studied by ^{1}H NMR in $CDCl_3$ solution. Generally the Ni-complexes of *anti* dioximes are more stable than those of *amphi* dioximes, but it is found that for bis(2,3-bornane-dione dioximato)nickel(II) this is not the case. The isomerization of Ni(*anti* dioxime)$_2$ to Ni(*amphi* dioxime)$_2$ is shown to be accelerated by acid. The *cis-trans* isomerism is studied by ^{1}H NMR and for a BF_2 derivative of a bis-*anti* complex by ^{19}F NMR. It is concluded that only *trans* isomers are present in measurable quantities.

T he analytically important dioxime complexes of nickel(II) have been
investigated to some degree in the past.[1] However, the low solubility of
the red compounds like bis(dimethylglyoximato)nickel(II) has made it dif-
ficult to study these complexes in solution. In the present paper an investiga-
tion is reported on soluble dioxime complexes, which exist in several isomers.

The dioxime of an α-diketone may take the *anti*, *syn*, and *amphi* configura-
tions, and if the diketone is unsymmetric two *amphi* forms may exist. Of these
the *syn* form is known to be unable to form metal complexes.[1] The *anti* isomer
gives the "usual" red complex, exemplified by the well known bis(dimethyl-
glyoximato)nickel(II). The *amphi* isomers are known to react with nickel(II),
but the complexes formed have not been well characterized, and metal:ligand
ratios of 1:1 as well as 1:2 have been reported.[1–12] The symbols β, α, and δ will
in the following designate the *anti*, and the two *amphi* forms, respectively.

The possibility of *cis-trans* isomerism exists for nickel(II) complexes of un-
symmetric *vic*-dioximes. Both forms may have a twofold axis of symmetry.
In the *cis* isomer this axis lies in the coordination plane, and in the *trans*
complex the symmetry axis is perpendicular to the coordination plane through
the nickel atom.

In the case of unstrained dioximes, the bis(β-dioximato)nickel(II) complex
seems to be more stable than the bis(α- or δ-dioximato) complexes. Both more
favourable ring size (5 membered *vs.* 6 membered ring) and intramolecular

hydrogen bonding in the complex may stabilize the bis β-complex, which furthermore is often insoluble. Isomerization of bis(δ-dioximato)nickel(II) complexes to the bis β-complexes have been observed. The conversion can be accomplished by boiling with dilute acetic acid.[1-10]

In bis(4-iminopentane-2,3-dione 3-oximato)nickel(II) one of the oxime groups coordinates *via* nitrogen and the other *via* oxygen giving a five- and a six-membered ring in the same molecule.[13,14] For bis(2,3-bornanedione dioximato)nickel(II) we find evidence for a similar behavior (a $\beta\delta$-complex) and the conditions for isomerization have been studied by PMR. Nuclear magnetic resonance was also used to establish which *cis-trans* isomers of bis(2,3-bornanedione dioximato)nickel(II) were isolated. ^{19}F NMR of the compounds in which the hydroxy hydrogens are replaced by BF_2 groups bridging the two ligands was found useful to decide whether a *cis* or a *trans* complex was present.

cis-trans Isomerism was suggested by Sugden when two forms of bis-(benzylmethylglyoximato)nickel(II) was isolated.[15,16] Jensen *et al.* held the opinion that the two forms were a crystalline and an amorphous modification of the same *trans* isomer.[17] Thus there has been no unambiguous demonstration of the existence of *cis-trans* isomerism for bis(dioximato)nickel(II) complexes.

The choice of bis(2,3-bornanedione dioximato)nickel(II) for these investigations was decided partly by the possibility that this complex could behave as an optically active model for bis(dioximato)nickel(II) complexes in general with the purpose to get information about the electronic properties by examining the circular dichroism spectrum. However, bis(β-(1R,4S)-2,3-bornanedione dioximato)nickel(II) only exhibits barely detectably Cotton effects. The chiroptical properties are commented on in the last part of the paper.

The isomer distributions and the abbreviations used in the following are summarized in Table 1.

EXPERIMENTAL

Complexes. The bis(dioximato)Ni(II) complexes were prepared by three methods:

1. Nickel acetate and *vic*-dioxime (1:2 mol) were refluxed in ethanol or dimethyl sulfoxide for about $\frac{1}{2}$ h. On the addition of water a product precipitated. This product was extracted with chloroform or diethyl ether. The resulting solution was washed with water, dried with sodium sulphate, filtered and evaporated to dryness. The remaining solid was recrystallized from ethanol or hexane.

2. Nickel acetate and *vic*-dioxime (1:2 mol) were mixed in a two-phase system of water-chloroform with stirring at room temperature for about 1 h. The chloroform phase was separated, washed and dried as above.
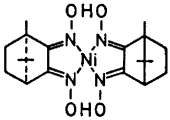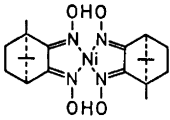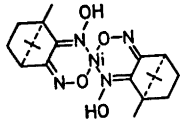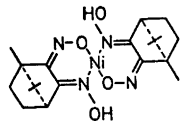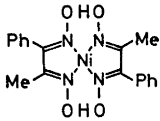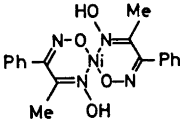
3. *Vic*-dioxime (2 mol) was suspended in dilute sodium hydroxide containing equivalent amount of base, and nickel nitrate (1 mol) was added. The product was extracted with chloroform and isolated as above.

By all three methods $Ni(\alpha\text{-cdo})_2$ and $Ni(\delta\text{-cdo})_2$ could be obtained pure. Both compounds are yellowish green. Yields about 50 % after recrystallization from ethanol.

$Ni(\alpha\text{-cdo})_2$. Found: C 53.50; H 6.88; N 12.48; Ni 12.75. Calc. for $NiC_{20}H_{30}N_4O_4$: C 53.47; H 6.73; N 12.47; Ni 13.07.

$Ni(\delta\text{-cdo})_2$. Found C 53.55; H 6.87; N 12.38; Ni 12.85. The compounds showed similar behavior on heating: Around 240°C there was a slow transformation or destruction with colour change to brown without real melting. No melting was observed below 340°C.

Table 1.

Formulae	Configuration	Abbreviation
	cis-anti	$(cis)\text{Ni}(\beta\text{-cdo})_2$
	trans-anti	$(trans)\text{Ni}(\beta\text{-cdo})_2$
	trans-amphi	$\text{Ni}(\alpha\text{-cdo})_2$
	trans-apmhi	$\text{Ni}(\delta\text{-cdo})_2$
	trans-anti	$\text{Ni}(\beta\text{-PhMeG})_2$
	trans-amphi	$\text{Ni}(\alpha\text{-PhMeG})_2$

Ni(β-cdo)$_2$ was prepared only by methods 2 and 3 in order to avoid contamination with the α- and δ-isomers. Attempts to obtain Ni(β-cdo)$_2$ free from isomers by recrystallization were unsuccessful. It was then purified by column chromatography (2 × 35 cm column, packed with basic silica gel, 0.2 – 0.5 mm particle size) using soda treated chloroform as eluent. The temperature was kept at 5°C. Ni(δ-cdo)$_2$ had a slightly higher mobility than (Ni(α-cdo)$_2$, Ni(β-cdo)$_2$, and Ni(β-cdo)(δ-cdo) in order. The mobilities were so close that it was necessary to repeat the chromatography on the red fraction. The solvent was distilled off under reduced pressure at 10°C. In this way Ni(β-cdo)$_2$ was obtained as a red powder, which contained chloroform of crystallization. This was given off by prolonged heating at $\sim$ 80°C *in vacuo*. Yield approx. 25 % (variable) of Ni(β-cdo)$_2$. (Found: C 53.30; H 6.68; N 12.40; Ni 12.95). When heated it was converted around 165°C with

colour change from red to yellowish brown without melting. There was a further slow transformation or destruction around 230°C, where the compound turned darker brown. It did not melt below 340°.
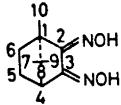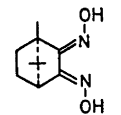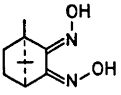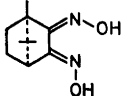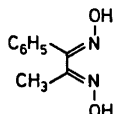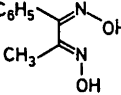
All three isomers are relatively soluble in common organic solvents.

$Ni(\beta\text{-}PhMeG)_2$ could be prepared by all of the three methods. Recrystallization from ethanol gave red crystals, melting point: 248 — 250°C. Yield 60 %. (Found: C 52.50; H 4.45; N 13.62; Ni 14.47. Calc. for $NiC_{18}H_{18}N_4O_4$: C 52.34; H 4.39; N 13.56; Ni 14.21.)

$Ni(\alpha\text{-}PhMeG)_2$ was prepared by methods 2 and 3. Recrystallization from hexane gave yellow crystals, which decompose around 200°C. Yield 45 %. (Found: C 52.60; H 4.41; N 13.38; Ni 14.45).

$Ni(\beta\text{-}PhMeGBF_2)_2$ was prepared by analogy with Schrauzers' method,[18] by the reaction of $Ni(\beta\text{-}PhMeG)_2$ and $BF_3.OEt_2$. The compound was recrystallized from acetone,

Table 2. ¹H NMR spectra of isomeric *vic*-dioximes represented as δ-values recorded at 60 MHz with TMS as internal standard.

		H-4	CH₃-10	CH₃-7 (or 9)	CH₃-9 (or 7)	OH	
β-cdoH	a	e 2.99	d 1.32	d 0.82	d 0.82	d 10.5	
α-cdoH	a	e 2.38	d 1.31	d 0.83	d 0.83	d 11.1,	d 11.2
δ-cdoH	a	e 3.07	d 0.99	d 0.88	d 0.75	d 10.9,	d 11.1
	b	e 3.15	d 1.08	d 0.94	d 0.86	d 8.42,	d 11.3

$C_6H_5C(NOH)C(NOH)CH_3$

		CH₃	C₆H₅	OH	
β-PhMeGH	a	d 2.05	d 7.22	d 11.35,	d 11.37
α-PhMeGH	a	d 2.02	f 7.37	d 11.1,	d 11.4

a (CD₃)₂SO. *b* CDCl₃. *c* Ref. 19. *d* Singlet. *e* Average doublet. *f* Multiplet.

giving yellow crystals, which decompose at around 340°C. Yield 50 %. (Found: C 42.42; H 3.40; N 10.87; Ni 11.26. Calc. for $NiC_{18}H_{16}N_4O_4B_2F_4$: C 42.49; H 3.17; N 11.0; Ni 11.54.)

Bis(benzylmethylglyoximato)nickel(II) (α and β) and other bis(dioximato)Ni(II) complexes were kindly supplied by professor K. A. Jensen. They were identified by melting points and elemental analyses.

NMR spectra were recorded on Varian A-60A and 100A spectrometers. Circular dichroism measurements were performed with Roussel-Jouan Dichrographs (type I and II). The absorption spectra were measured with Cary 14 and Unicam spectrophotometers.

RESULTS AND DISCUSSION

The preparation and identification of the vic-dioxime isomers was achieved by published methods.[1] The ligands and the complexes were isolated and isomeric purity ascertained by chromatography. ^{1}H NMR served to identify the isomers.

In Table 2 are shown the chemical shifts, which are most easily used for the dioximes. The assignments for the camphor derivatives are the same as those proposed by Daniel and Pavia.[19] The H-4 signal occurs as a doublet for these camphor derivatives, as it does [20] in a series of derivatives such as formylcamphor and its enamines. This suggests that ring strain produces a dihedral angle of approximately 90° between H-4 and one of the two H-5 protons, thus giving a very small coupling constant between these two protons. The chemical shift differences between the isomers are quite substantial and make identification easy.

Table 3 contains the ^{1}H NMR signals for the nickel(II) complexes isolated from the dioximes. Chemical shift differences are also big enough in the complexes to ascertain assignments. For the hydroxy protons there is a variation from ca. 17 to ca. 10 ppm (vs. TMS). The former value is characteristic for the bis-β-complexes, where the OH protons participate in strong and probably nearly symmetric hydrogen bonds. This feature also manifests itself in the

Table 3. ^{1}H NMR spectra recorded at 60 MHz in $CDCl_3$ with TMS as internal standard, given as δ-values.

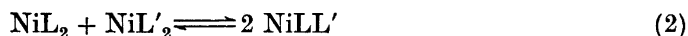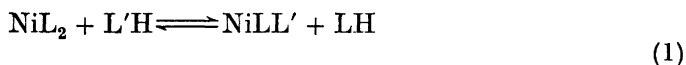|	H-4	CH_3-10	CH_3-7 (or 9)	CH_3-9 (or 7)	OH
Ni(β-cdo)$_2$	2.83[a]	1.31[b]	1.00[b]	0.89[b]	16.8[b]
Ni(α-cdo)$_2$	2.58[a]	1.37[b]	0.88[b]	0.87[b]	11.0[b]
Ni(δ-cdo)$_2$	3.20[a]	1.11[b]	0.94[b]	0.81[b]	10.8[b]
	CH_3	C_6H_5	OH		
Ni(β-PhMeG)$_2$	1.99[b]	7.35[c]	17.6[b]		
Ni(α-PhMeG)$_2$	2.06[b]	7.30[c]	11.2[b]		

[a] App. doublet. [b] Singlet. [c] App. singlet.

infrared spectra of the complexes of *anti-vic*-dioximes by the characteristic band at approximately 2300 cm^{-1}.

As already mentioned the H-4 and CH$_3$-10 signals are also in the complexes quite sensitive to the anisotropy of the neighbouring oxime groups. For the two isomers of Ni(PhMeG)$_2$ the differences in chemical shifts of C$_6$H$_5$ and CH$_3$ protons are smaller, but still in accordance with the anisotropy.

^{1}H NMR is thus applicable for the identification of the different isomers of bis(dioximato)nickel(II) complexes that have been isolated. The outlined assignments will later be utilized to identify isomers observed only in solution and not isolated.

Exchange reactions. Nickel(II) complexes are known to be rather labile in aqueous solution.[21] Also planar, four-coordinated complexes such as Ni(CN)$_4$$^{2-}$ exchange ligands very rapidly. In aprotic organic solvents the exchange may become very slow, and this has been shown to be the case for chloroform solutions of bis(dioximato)Ni(II) complexes under certain conditions (acid-free chloroform, *vide infra*). The following reactions have been studied:

$$NiL_2 + L'H \rightleftharpoons NiLL' + LH$$

$$\tag{1}$$

$$NiLL' + L'H \rightleftharpoons NiL'_2 + LH$$

$$NiL_2 + NiL'_2 \rightleftharpoons 2\ NiLL' \tag{2}$$

The equilibrium (1) can be established by mixing Ni(δ-cdo)$_2$ and β-PhMeGH ($=$ L'H) in CDCl$_3$. The reaction was followed by ^{1}H NMR, and the equilibrium composition of NiL$_2$:NiLL':NiL'$_2$ was found to be 1:2.7:1.9 at 35°C, when the solution was saturated with both LH and L'H. Equilibrium constants of the order of 250 and 70 were found for the two reactions. The time for half conversion is about 80 min at 35°C at usual NMR concentrations. The mixed complex Ni(δ-cdo)(β-PhMeG) differ in chemical shifts from the "pure" complexes; see Table 4.

Table 4. ^{1}H NMR spectra of mixed complexes recorded at 60 MHz in CDCl$_3$ with TMS as internal standard, given as δ-values.

	H-4	CH$_3$-10	CH$_3$-7 (or 9)	CH$_3$-9 (or 7)	OH	CH$_3$	C$_6$H$_5$
Ni(δ-cdo) (β-PhMeG)	3.29	1.16	0.93^a	0.77	10.5 17.8	2.01	7.35^a
Ni(δ-cdo) (β-cdo)	3.23 2.81^a	1.12^a 1.31^a	0.93^a 0.99^a	0.77 0.90^a	9.3 18.2		
Ni(α-PhMeG) (β-PhMeG)					10.3 18.3	2.07^a 1.92	7.28^a 7.40^a

^{a} These signals are positioned very near the corresponding signals in the unmixed complexes and have only been visible as shoulders or broadening of the signals; *cf*. Table 3.

A number of systems (including the above mentioned complexes) have been examined to see whether ligand exchange could occur in CDCl$_3$ according to (2) above. However, in all cases it was found that no such reaction takes place within a few days, even in the presence of acid. For this reason the complexes are considered robust in chloroform.

cis-trans Isomerization. The earlier reported [15] attempt to isolate *cis-trans* isomers of unsymmetric *vic*-bis(dioximato) complexes was shown by Jensen *et al.*[17] to be inconclusive. However, in view of the above found robust character of these complexes, it might seem likely that both isomers could be present. The two samples of bis(*anti*-benzylmethylglyoximato)nickel(II) used by K. A. Jensen have identical PMR spectra. Therefore, we conclude that only one form is present rather than assuming the *cis* and *trans* forms to have the same chemical shifts for corresponding protons.

For this complex, as for the other *anti*-complexes, we should expect the two bridging protons to be non-equivalent in the *cis* isomer, but equivalent in the *trans* isomer, provided the hydrogen bonds are symmetric. The PMR signal for the two OH protons in Ni(β-cdo)$_2$, Ni(β-PhMeG)$_2$, and bis(*anti*-benzylmethylglyoximato)Ni(II) splits into three components of unequal intensity at low temperature (in the range $-40°$C to $-20°$C). This is taken as evidence for the presence of different tautomers. For all other protons there is an effective twofold axis in the molecule. Although these results present evidence for the *trans* isomers, it was believed that the complex obtained by introducing BF$_2$ groups instead of H in the $O-H-O$ bridge would give more conclusive results. The configuration of this product is certainly locked, and tautomerization of the molecule is not likely. The ^{19}F NMR is known to exhibit large chemical shift differences, and since for this complex a *cis* isomer would produce two non-equivalent fluorine nuclei and a *trans* isomer equivalent nuclei, a conclusive result was anticipated. The ^{19}F NMR of Ni (β-PhMeGBF$_2$)$_2$ in CH$_3$NO$_2$ at 70°C consisted of a single broad signal at 7058 Hz to higher field from external CF$_3$COOH (recorded at 94.1 MHz).

The ^{1}H NMR spectra (see Tables 1 and 3) of the *amphi* complexes also indicate that only the *trans* forms are present in measurable quantities. All the signals are unsplit and the OH signal appears as a sharp singlet over the temperature interval $-40°$ to 30°C.

All our experiments indicate that only *trans* isomers of the complexes with unsymmetric ligands have been isolated. Neither on steric nor on electronic grounds can this finding be rationalized. Instead crystal packing forces may be important in the isolation from solvents in which nickel(II) complexes are labile, and thus all complex is precipitated in the most insoluble form.

amphi-anti Isomerization for Ni(cdo)$_2$. As mentioned in the experimental section the preparation of Ni(β-cdo)$_2$ from the corresponding ligand isomer, β-cdoH, yields products containing different fractions of Ni(β-cdo)$_2$, Ni(α-cdo)$_2$, Ni(δ-cdo)$_2$, and "mixed" complexes. Method of preparation, *i.e.* choice of solvent, pH in the aqueous phase, temperature and length of time for interaction seem to be important for the relative amounts of isomers isolated. No systematic studies were carried out to investigate the conditions. The isomers were isolated by means of column chromatography and identified by PMR. During this work great irreproducibility was noted with respect to both the chro-

matographic separations and the PMR spectra. These circumstances were related to the use of $CHCl_3$ or $CDCl_3$ as solvent and the acid content of the chloroform. The PMR spectra of the $Ni(cdo)_2$ complexes were found to be constant with time only when the $CDCl_3$ used as solvent was carefully treated with Na_2CO_3. The following results were obtained with a $CDCl_3$ sample of convenient "natural" acid content. Similar results have been obtained with purified $CDCl_3$ solutions to which were added known amounts of CF_3COOD.

The PMR spectra of $Ni(\beta\text{-cdo})_2$, $Ni(\alpha\text{-cdo})_2$, and $Ni(\delta\text{-cdo})_2$, in the above mentioned $CDCl_3$ of suitable acidity, were recorded as a function of time, temperature, and concentration of complex. The change with time is most spectacular for $Ni(\beta\text{-cdo})_2$, where the colour also changes from red to yellow. Fig. 1 shows how $Ni(\beta\text{-cdo})_2$ present at $t = 0$ is isomerized via at least one
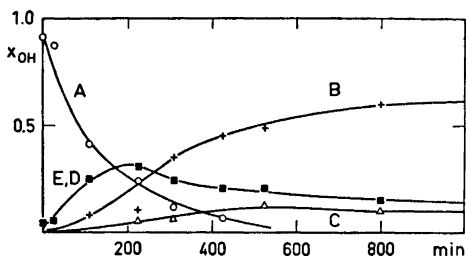

Fig. 1. Isomerization of $Ni(\beta\text{-cdo})_2$. The changes in the mol fractions of the different OH signals as a function of time. Temp. $26.38 \pm 0.02°C$, solvent $CDCl_3$. The chemical shifts are as follows (δ-values with TMS as internal standard) A, ○ 16.8 ppm; B, + 10.9 ppm; C, △ 11.1 ppm; D, ■ 18.2 ppm; E, ■ 9.3 ppm.

intermediate to a mixture of $Ni(\delta\text{-cdo})_2$ and $Ni(\alpha\text{-cdo})_2$. The curve is characteristic for the conversion over the temperature interval $15 - 40°C$. Altogether five different OH proton resonances are observed. More signals may be present, since the detection limit of an isomer was around 5 % of the total. Three of the hydroxyl protons have chemical shifts corresponding to the β_2, α_2, and δ_2 complexes. The remaining two absorb at 18.2 and 9.3 ppm, with a 1:1 intensity relation in all runs. The chemical shifts for the latter two protons and the fact that they have equal concentration indicate that a mixed complex $Ni(\beta\text{-cdo})(\delta\text{-cdo})$ is formed (Table 4). At equilibrium the $CDCl_3$ solution contains $85 - 90$ % of the complex in the form of $Ni(\delta\text{-cdo})_2$, $5 - 10$ % as $Ni(\alpha\text{-cdo})_2$, and about 5 % as $Ni(\beta\text{-cdo})(\delta\text{-cdo})$ over the interval $15°C$ to $40°C$.

$Ni(\alpha\text{-cdo})_2$ isomerizes to the same equilibrium mixture, but the rate is about ten times slower than that of $Ni(\beta\text{-cdo})_2$

The rate of disappearance of the starting isomer was shown to be first order. For $Ni(\beta\text{-cdo})_2$ the halftime for the transformation of complex-bound β-cdo was estimated from the area under the H-4 signal and the CH_3-10 signal as well as from the peak height of CH_3-10. The halftime found in this way agrees fairly well with the halftime of transformation of the total anti OH, meaning x_A plus x_D from Fig. 1. The first order kinetics indicate that the reaction closely follows the ideal case where the rate of isomerization of complex-bound β-cdo is independent of the other ligand. The course of the reaction shown in Fig. 1 further supports this idea, as the time of maximum concentration of the "mixed" complex correspond rather well to two half-

times for conversion of the starting complex, as it would in the ideal case, neglecting the reverse reaction.

In the above mentioned solvent the apparent energy of activation was found to be about 24 kcal mol^{-1} (25°C), and the rate of isomerization corresponds to the rate in a *ca.* 10^{-3} M CF$_3$COOH solution, *vide infra*.

The catalytic effect of acid was demonstrated by following (PMR) solutions of Ni(β-cdo)$_2$ or Ni(α-cdo)$_2$ in soda-treated CDCl$_3$ after the addition of small amounts of CF$_3$COOH (up to 5 mol % with respect to nickel complex). The addition of larger amounts of CF$_3$COOH (*e.g.* equivalent amounts) yields green paramagnetic solutions, which presumably contain ion pairs. No precipitation of free dioxime or nickel trifluoroacetate was noted.

The addition of the weak acid β-cdoH to Ni(β-cdo)$_2$ in acid-free CDCl$_3$ did not catalyze the isomerization, although ligand exchange occurs under these conditions. Thus we conclude that the isomerization reaction is promoted by the formation of protonated complexes such as Ni(β-cdo)(β-cdoH). This explains the preparative method used earlier.

The Ni(α-PhMeG)$_2$ complex behaves qualitatively in the same way as the unstable cdo-complexes and isomerizes in acid chloroform to Ni(β-PhMeG)$_2$. Due
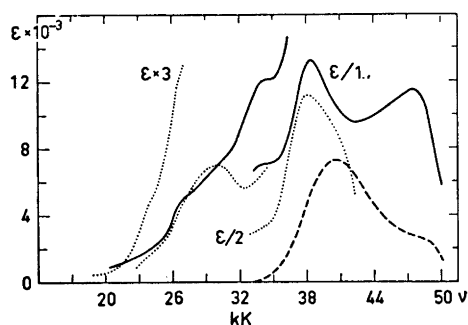

Fig. 2. Molar absorption of β-cdoH (- - -) in methanol, and molar absorption of Ni (β-cdo)$_2$ in methanol (———), and in chloroform (···).
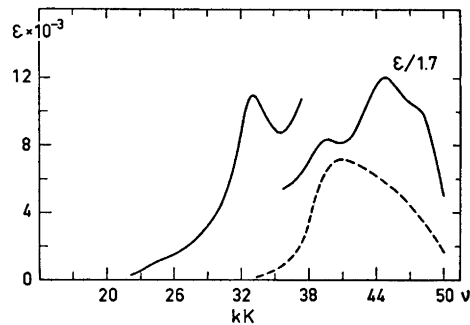
Fig. 3. Molar absorption of α-cdoH (- - -) and of Ni(α-cdo)$_2$ (———) in methanol.

to the low solubility of the latter complex the reaction could only be studied at elevated temperatures. In this case also an intermediate, Ni(α-PhMeG) (β-PhMeG), was clearly detected (see Table 4). At equilibrium only Ni(β-PhMeG)$_2$ could be detected.

The isomerization has not been studied in detail in other solvents. However, isomerization has been observed to occur in several common organic solvents.

Electronic spectra of β, α, and δ-cdoH and their corresponding nickel(II) complexes are shown in Figs. 2, 3, and 4, respectively. The α- and δ-compounds exhibit very similar absorption, as expected. The circular dichroism of the two *amphi* complexes, Ni(α-cdo)$_2$ and Ni(δ-cdo)$_2$, are markedly different

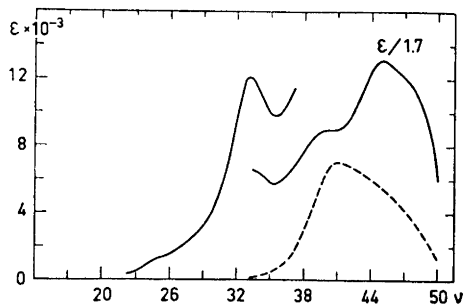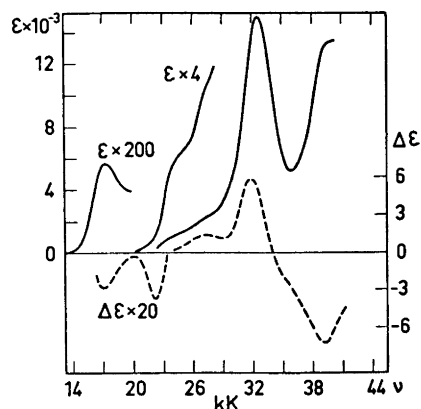*Fig. 4.* Molar absorption of δ-cdoH (– – –) and of Ni(δ-cdo)$_2$ (———) in methanol.

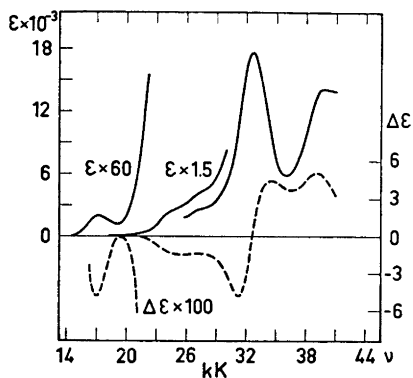*Fig. 5.* Molar absorption (———) and circular dichroism (– – –) of Ni(α-cdo)$_2$ in chloroform.

Fig. 6. Molar absorption (———) and circular dichroism (– – –) of Ni(δ-cdo)$_2$ in chloroform.

(Figs. 5 and 6). The *anti* complex, Ni(β-cdo)$_2$, exhibits only very small Cotton effects. The band at about 24 kK is the only measurable optically active band, with a dissymmetry factor, $\Delta\varepsilon/\varepsilon$, of only -10^{-4}. The low activity indicates that the complex (the chromophore) is very nearly planar on a time average.

Ingraham [22] reported a theoretical investigation on bis(dimethylglyoximato)nickel(II) and calculated that the energy difference between the lowest unfilled orbital ($2b_{1g}$) and the highest filled orbital ($3b_{3g}$) should be about 1 eV. This suggests that the triplet state might be thermally populated in solution. For Ni(β-cdo)$_2$, which is soluble, this is not the case. The PMR gave sharp signals, without contact shift. Also, the chemical shifts were almost temperature-independent.

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