Chiral Metal Complexes. Part 5.[1] Cobalt(II) and Some Other Transition-metal Complexes of Chiral *vic*-Dioximate Ligands derived from D-Camphor and L-β-Pinene

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Chiral bis(*vic*-dioximato)-complexes of Fe^{II}, Co^{II}, Ni^{II}, and Pd^{II} have been prepared from three geometrical isomers (α, β, and δ) of D-camphorquinone dioxime (Hcqd) and two (β and δ) of L-nopinoquinone dioxime (Hnqd). The co-ordination geometry has been investigated by ^1H and ^{13}C n.m.r., i.r., and electronic spectroscopy to reveal a novel *NO*-chelation of the metal with the (*E,Z*)-dioximate isomers (α- and δ-cqd and δ-nqd). The (*E,E*)-dioximate isomers (β-cqd and β-nqd) co-ordinate to a metal with the usual *NN*-chelation. The c.d. spectra of the free ligands and the corresponding metal complexes are utilized to investigate the chirality of the chromophores at the unco-ordinated and co-ordinated dioximate moiety. Opposite Cotton effects around 20 000 cm^{-1} have been observed for $[Co(\alpha\text{-cqd})_2]\cdot H_2O$ and $[Co(\delta\text{-nqd})_2]\cdot H_2O$ indicating their ' quasi-enantiomeric ' stereochemistries.

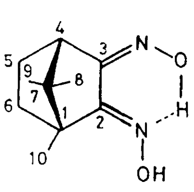
VICINAL dioximate ligands usually form stable *NN*-chelated metal complexes containing a conjugated N=C–C=N system. We have been interested in the utilization of chiral dioximato-complexes for asymmetric reactions. A remarkably successful application is seen in the enantioselective cyclopropanation catalyzed by bis(camphorquinone α-dioximato)cobalt(II) (maximum 88% enantiomer excess).[2]

Vicinal dioximes give rise to several geometrical isomers. For example, camphorquinone dioxime forms four isomers (see below). The geometrically isomeric ligands would give a series of metal complexes in which the chiral environment around the metal varies depending on the particular isomer structure. Thus, the (*E,E*)-dioximate ligands will co-ordinate to a metal with *NN*-chelation similar to dimethylglyoximate, while the (*E,Z*)-dioximate ligands co-ordinate with *NO*-chelation. Further, two co-ordination structures are possible for each of these two types of camphorquinone dioximato-complexes. In addition to these geometrical and co-ordination isomerisms, the camphor skeleton has an interesting strained structure which would reflect the *NN*- or *NO*-bite angles, a stereochemical effect which has received little attention. Thus in this paper we describe new aspects of the co-ordination chemistry of vicinal dioximatometal complexes.

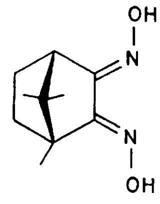
RESULTS AND DISCUSSION

Ligands.—As previously described,[2] camphorquinone dioximes (Hcqd) and nopinoquinone dioximes (Hnqd) were prepared from (+)-camphor and (–)-β-pinene, respectively. Four geometrical isomers denominated as α-, β-, γ-, and δ-Hcqd were separated by recrystallization of the former *vic*-dioximes. We were able to separate two isomers, β- and δ-Hnqd, from the latter.

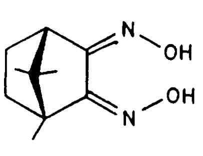
The stereochemistries of four Hcqd isomers have been assigned by Daniel and Pavia with the aid of the ^1H n.m.r. spectra.[3] The principle is based on the anisotropic shielding effect caused by the nitrogen lone pair. The higher chemical shift of the C^4 methine-proton signal or of C^{10} methyl protons reflects the proximity of the nitrogen lone pair. For example, the α-isomer shows a high methine doublet and low C^{10} methyl-proton signal. Both the corresponding signals of β-Hcqd appear at lower field. By the same token the geometries of γ- and δ-Hcqd can be determined.



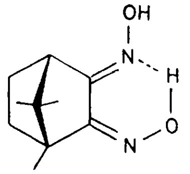
α- Hcqd
(2*E* ,3*Z*)



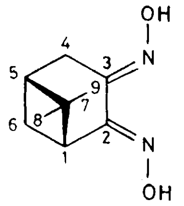
β- Hcqd
(2*E* ,3*E*)



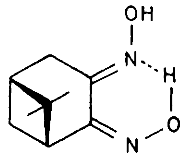
γ- Hcqd
(2*Z* ,3*Z*)



δ - Hcqd
(2*Z* , 3*E*)



β - Hnqd
(2*E* ,3*E*)



δ - Hnqd
(2*Z* , 3*E*)

Their i.r. spectra were found to be consistent with the assigned structures. Thus, the broad absorption at 3 060 cm^{-1} for α-Hcqd or 3 120 cm^{-1} for δ-Hcqd is assignable to the intramolecular hydrogen-bonded OH stretchings, while the OH absorptions of the β-isomer occur at a higher-frequency region (3 200 and 3 390 cm^{-1}). The α-isomer shows two distinct bands of low intensities at 1 670 and 1 615 cm^{-1} assignable to the C=N stretching The C=N absorption of δ-Hcqd is not well resolved and appears as ill defined, weak, broad bands around 1 680 and 1 610 cm^{-1}. The corresponding absorptions of γ-Hcqd appear at 1 645 and 1 605 cm^{-1}. The i.r. spectrum of β-Hcqd shows similar weak broad absorptions around 1 600 cm^{-1}. Such low-intensity C=N absorptions are not unusual for mono- and di-oximes.[4] Each isomer shows four or five strong absorptions in the N–O stretching region (900—1 100 cm^{-1}), and no attempt was made at assignment.

Among four possible isomers of Hnqd, two isomers, m.p. 211 and 215 °C, were separated in pure states.[2] The OH stretching vibrations of the isomer of low m.p. occur at 3 360 and 3 180 cm^{-1}, while those of the other appear at a lower-frequency region (3 120 and 3 080 cm^{-1}), assignable to the intramolecular hydrogen-bonded OH stretchings. Consistently, the latter isomer shows relatively separated C=N absorptions (1 650 and 1 580 cm^{-1}) compared to the former (1 610 and 1 585 cm^{-1}). These aspects suggest that the latter isomer should be either the α-(2*E*,3*Z*)- or δ-isomer(2*Z*,3*E*) and the former the β-isomer.[2] In the complex ^1H n.m.r. spectrum of the β-isomer (m.p. 211 °C), we were able to discern the methine-proton triplet at δ 3.47 p.p.m. (1 H). The corresponding signals of the Hnqd isomer (m.p. 215 °C) unfortunately overlapped with the methylene-proton signals centred around δ 2.6 p.p.m. The high chemical shift of the methine signals is apparently due to the shielding effect of the lone pair of the proximal nitrogen atom. Therefore we assign the δ structure to the isomer of high m.p. Support for these assignments is obtained from ^1H n.m.r. spectra of $[Ni(\beta\text{-nqd})_2]$ and $[Ni(\delta\text{-nqd})_2]$ which exhibit well separated signals (see below).

The circular dichroism (c.d.) spectra of several chiral dioximes are compared in Table 1. The spectral patterns of α-Hcqd and δ-Hcqd are in an essentially mirror-image relation. Those of the two δ-dioximes resemble each other, in particular in the 35 000—40 000 cm^{-1} region. These spectra should be compared with the known c.d. pattern of camphorquinone. The non-coplanarity of two carbonyls groups in D-camphorquinone caused by a steric interaction with the methyl group at the bridgehead creates a specific helicity which determines the c.d. pattern.[5] A current theory of this sort of helicity predicts a negative Cotton effect at the lowest-energy transition (*b* symmetry) and a positive Cotton effect at the higher one (*a* symmetry).[5] The helicity of the dioxime moiety in β-Hcqd may be regarded as the same as that of the dicarbonyl moiety in D-camphorquinone.

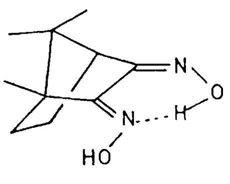
TABLE 1

Circular dichroism spectral data in EtOH

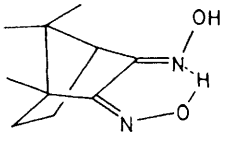
Compound	$10^{-3}\ \nu/cm^{-1}$	$\Delta\varepsilon_{max.}/$ $dm^3\ mol^{-1}\ cm^{-1}$
(+)-Camphorquinone	20.9	−0.32
	21.5	−0.33
	37.6 *	+0.41
(+)-α-Hcqd	45.5	−1.53
	40.7	+3.58
(+)-β-Hcqd	45.6	−0.59
	40.7	+2.75
	38.8	−2.07
(−)-δ-Hcqd	41.7	−2.87
	36.4	+2.65
(+)-δ-Hnqd	46.7	−0.83
	38.9	+3.12
	34.2	−0.36

* The highest maximum with a vibrational fine structure (spacing *ca.* 1 560 cm^{-1}); see ref. 5.

The conformations of the N=C–C=N moiety of the dioxime groups in α- and δ-Hcqd should be similar. However, opposite c.d. patterns are observed. The explanation for this remarkable phenomenon must be sought in the difference in chelate structure as a whole. The locations of the nitrogen lone pair and of the OH group not involved in the intramolecular hydrogen-bonded ring of α-Hcqd are exchanged in δ-Hcqd. If this situation is assumed to cause a reversal in the direction of the transition dipole in the lowest-energy transition *n*–π*, opposite c.d. spectra would be expected.



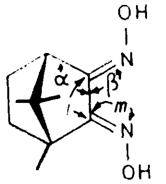
α-Hcqd



δ-Hcqd

Preparation of Metal(II) *Complexes*.—Complexes of Fe^{II}, Co^{II}, Ni^{II}, and Pd^{II} of several chiral *vic*-dioximes were prepared by treating metal(II) acetates or halides in ethanol or methanol with the dioximes in the presence of a base such as Na[OH] or pyridine. Since the preparation of the air-sensitive cobalt(II) complexes has previously been described,[2] only typical examples of preparations of other metal complexes are given in the Experimental section. Analytical data, colours, melting points, and molecular weights of the new complexes are listed in Table 2. The γ-cqd ligand does not form stable chelates with any metal ions so far examined, an expected result in view of the ligand geometry.

In contrast to the well known stability of $[Ni(dmg)_2]$ [dmg = dimethylglyoximate(1−)] attempted preparation of $[Ni(\beta\text{-cqd})_2]$ from nickel(II) acetate, halide, or perchlorate results in yellow solid amorphous products which on recrystallization or column chromatography lead to only ill defined compounds. This failure may be ascribed to the large bite angle of the ligand which could be semiquantitatively assessed from the N • • • N distance. The required molecular parameters for the assessment are bond angles α and β and distances *l* and *m*; the angle 108° for α was taken from $[PdCl_2(nbd)]$ [6] (nbd = norbornadiene) and β is set equal to (360 − α)/2. The distances *l* (1.53 Å) and *m* (1.25 Å) are taken from data for $[Ni(dmg)_2]$.[7] The calculated N • • • N distance of this Hcqd molecule is 3.0 Å which should be compared with that (2.4 Å) of $[Ni(dmg)_2]$. The rigid bicyclic skeleton of Hcqd is thus responsible for the larger N • • • N distance. If the N–Ni–N angle is taken as 80° as in $[Ni(dmg)_2]$, the Ni–N distance is expected to be 2.3 Å. This larger value implies weaker co-



ordination of β-cqd to Ni^{II} than the dmg ligand which is more flexible.

Characterization of Complexes.—NN-*Chelation.* The ability of dimethylglyoxime (Hdmg) to form quantitatively a stable chelate co-ordination with Ni^{2+} or Pd^{2+} is well known. The insolubility of $[Ni(dmg)_2]$ is due to the metal–metal-bonded polymeric structure.[7] The (2*E*,3*E*)-dioximate (β-cqd or β-nqd) is expected to form a similar five-membered chelate with two nitrogen atoms. $[Ni(\beta\text{-nqd})_2]$. In contrast to $[Ni(dmg)_2]$, the title complex is soluble in ethanol, diethyl ether, benzene, chloroform, and even slightly in n-hexane, precluding a polymeric structure. This is apparently due to the bulky nopinone skeleton which prevents association. The i.r. absorptions ascribed to the intramolecular hydrogen-bonded OH stretching and bending vibrations (around 2 300 and 1 750 cm^{-1}, respectively) are broad and weak. The C=N absorptions (1 585, 1 565 cm^{-1}) are lowered, compared to those of free β-Hnqd (1 610, 1 585 cm^{-1}).

TABLE 2

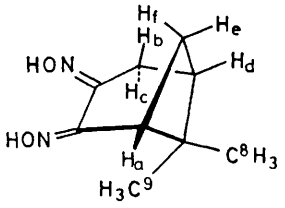
Colours, melting points, analytical data, and molecular weights of bis(*vic*-dioximato)metal(II) complexes

Complex	Colour	M.p. (θ_c/°C)	Analysis (%) [a] C	H	N	*M* [a,b]
$[Fe(\beta\text{-cqd})_2]\cdot 2\,py$	Orange-red	177—179	59.25	7.00	13.75	
			(59.60)	(6.65)	(13.90)	
$[Fe(\beta\text{-nqd})_2]\cdot 2\,py$	Orange-red	125—127	58.00	6.35	14.25	
		(decomp.)	(58.35)	(6.30)	(14.60)	
$[Co(\alpha\text{-cqd})_2]\cdot H_2O$	Brown	240—241	50.85	6.75	11.80	863 [c]
			(51.40)	(6.90)	(12.00)	(467)
$[Co(\beta\text{-cqd})_2]\cdot H_2O$	Brown	295—296	51.0	7.00	11.85	
			(51.40)	(6.90)	(12.00)	
$[Co(\delta\text{-cqd})_2]\cdot H_2O$	Dull yellow	252—253	51.75	6.55	11.85	
			(51.40)	(6.90)	(12.0)	
$[Co(\beta\text{-nqd})_2]\cdot 2H_2O$	Orange-brown	256—257	47.20	6.60	12.20	
			(47.25)	(6.60)	(12.25)	
$[Co(\delta\text{-nqd})_2]\cdot H_2O$	Brown	250	49.55	6.00	12.75	836 [c]
		(decomp.)	(49.20)	(6.40)	(12.75)	(439)
$[Ni(\alpha\text{-cqd})_2]$	Yellow-green	260	53.45	6.80	12.50	441 [d]
		(decomp.)	(53.50)	(6.75)	(13.45)	(449)
$[Ni(\delta\text{-cqd})_2]$	Yellow-green	222	53.35	6.70	12.55	446 [d]
		(decomp.)	(53.50]	(6.75)	(12.45)	(449)
$[Ni(\delta\text{-nqd})_2]$	Yellow-orange	211	51.45	6.30	13.35	452 [d]
			(51.35)	(6.25)	(13.30)	(421)
$[Ni(\beta\text{-nqd})_2]$	Orange	248—249	51.35	6.15	13.40	
			(51.35)	(6.25)	(13.30)	
$[Pd(\beta\text{-cqd})_2]$	Yellow	265—266	48.20	6.15	11.20	
			(48.35)	(6.10)	(11.30)	
$[Pd(\beta\text{-nqd})_2]$	Yellow	270	45.90	5.70	11.80	
			(46.10)	(5.60)	(11.95)	

[a] Calculated values are given in parentheses. [b] Value for monomer. [c] Measured cryoscopically in benzene. [d] Measured by vapour-pressure osmometry.

TABLE 3

Hydrogen-1 n.m.r. spectra [a] of bis(chiral *vic*-dioximato)metal(II) complexes



Hnqd

(*a*) Camphorquinone dioximato(cqd)-complexes

Complex	C^8H_3	C^9H_3	$C^{10}H_3$	CH	OH
$[Ni(\alpha\text{-cqd})_2]$	[0.89 (s)	0.92 (s)] [b]	1.40 (s)	2.61 (d)	11.07 (s)
$[Ni(\delta\text{-cqd})_2]$	[0.82 (s)	0.97 (s)] [b]	1.12 (s)	3.16 (d)	10.80 (s)
$[Pd(\beta\text{-cqd})_2]$	[0.91 (s)	1.00 (s)] [b]	1.47 (s)	2.95 (d)	11.82 (s)

(*b*) Nopinoquinone dioximato(nqd)-complexes

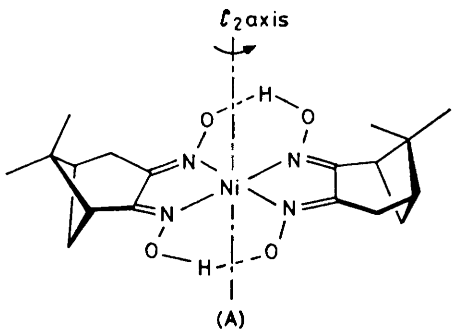
Complex		C^9H_3	C^8H_3	H	H_c	H_d	H_b, H_c	H_a	OH
$[Fe(\beta\text{-nqd})_2]\cdot 2\,py$ [c]		0.10 (s)	1.28 (s)	0.98 (d)	2.13 (mc)	2.52 (mc)	2.88 (mc) [d]	3.60 (mc)	
$[Ni(\delta\text{-nqd})_2]$		0.80 (s)	1.35 (s)	1.21 (d)	2.16 (mc)	2.60 (mc)	2.82 (mc) [d]		11.16 (s)
$[Ni(\beta\text{-nqd})_2]$	[e]	0.90 (s)	1.38 (s)	1.27 (d)	2.12 (mc)	2.62 (mc)	2.68 (mc) [d]	3.31 (t)	16.88 (s)
		0.87 (s)	1.38 (s)	1.27 (d)	2.12 (mc)	2.62 (mc)	2.68 (mc) [d]	3.31 (t)	17.10 (s)
	[e,f]	0.56 (s)	0.94 (s)	1.17 (d)	1.52 (mc)	2.20 (mc)	2.45 (mc) [d]	3.29 (t)	17.90 (s)
		0.63 (s)	0.94 (s)	0.86 (d)	1.52 (mc)	2.09 (mc)	2.38 (mc) [d]	3.29 (t)	18.14 (s)
$[Pd(\beta\text{-nqd})_2]$		0.88 (s)	1.43 (s)	1.63 (d)	2.18 (mc)	2.63 (mc)	2.72 (mc) [d]	3.35 (t)	12.11 (s)

s = Singlet, d = doublet, t = triplet, mc = multiplet centre.

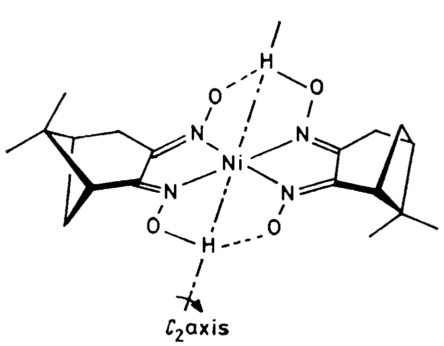
[a] Chemical shifts are in p.p.m. from $SiMe_4$ at 100 MHz in $CDCl_3$. [b] Unassignable. [c] Chemical shifts of pyridine; 6.93 (mc), 7.34 (mc), and 8.52 (mc) p.p.m. [d] Unresolvable. [e] In two geometric isomers. [f] In C_6D_6.

The i.r. and ^1H n.m.r. data are consistent with a five-membered *NN*-co-ordination of β-nqd to the metal as in $[Ni(dmg)_2]$. There are, however, two possible ligand alignments, *anti* (A) and *syn* (B). The different C_2

axes are to be noted. In each isomer two inequivalent methyl-proton signals should be observed. The ^{1}H n.m.r. data with provisional assignments are summarized in Table 3. These assignments are based on the known coupling scheme in bicyclo[2.1.1]hexane [8] and decoupling experiments. By virtue of the relative intensity of two signals of, *e.g.* the H$_f$ protons, the isomer ratio is assessed to be *ca.* 4:6. It was not possible, however, to assign the spectrum to each of these two isomers.



(A)



(B)

The ^{13}C n.m.r. spectra (Table 4) also indicate the presence of two isomers. The tertiary (C^6) and secondary carbon (C^1, C^5) resonances could readily be assigned by the multiplicity appearing upon partial ^{1}H decoupling. The lower-field doublet is assigned to C^1 proximal to the C=N double bond. The other resonances are assignable as a pair. Separation of the two isomers was not possible.

[Pd(β-cqd)$_2$]. This thermally stable diamagnetic complex can be prepared without difficulty in contrast to the nickel analogue. This is understandable in view of the larger ionic size of Pd^{II}. The solubility in most organic solvents is as good as that of [Ni(β-nqd)$_2$]. Although full assignments of the complex ^{1}H and ^{13}C n.m.r. spectra could not be made, there are some assignable signals (Tables 3 and 4). The broad i.r. absorptions around 1 570 cm^{-1} ascribable to C=N stretching vibrations are lower than those of the free ligand and are consistent with the *NN*-chelate co-ordination.

Although the ^{1}H n.m.r. spectrum shows no indication of the existence of two isomers, this is clearly shown by the ^{13}C n.m.r., in particular the C^2 and C^3 resonances (Table 4). The electronic spectrum shows a shoulder at 26 500 at cm^{-1} (ε 2.38 × 10^3 dm^3 mol^{-1} cm^{-1}) and extrema of the c.d. spectrum appear at 28 200 (Δε −1.00) and 24 500 cm^{-1} (Δε +0.20). No c.d. intensity was gained in the 14 000—21 000 cm^{-1} region.

[Pd(β-nqd)$_2$]. The solubility of this complex is similar to that of [Pd(β-cqd)$_2$]. The C=N stretching frequencies, at 1 550 and 1 525 cm^{-1}, are lower than those of [Ni(β-nqd)$_2$] (1 585, 1 565 cm^{-1}), a feature expected from their d_π-donating properties, *i.e.* Ni^{II} < Pd^{II}.[9] Other spectral features resemble those of [Ni(β-nqd)$_2$]. However, neither the ^{1}H nor ^{13}C n.m.r. spectrum reveals splitting due to the isomers. It is to be noted that in [Pd(β-cqd)$_2$] two isomers exist as indicated by two resonances each for C^2 and C^3 (Table 4). It is not defined whether the [Pd(β-nqd)$_2$] obtained consists of two geometrical isomers or only one. The electronic spectrum shows a maximum at 27 000 cm^{-1} (ε 2.1 × 10^3 dm^3 mol^{-1} cm^{-1}) and extrema of the c.d. spectrum at 30 000 (Δε +0.89), 26 300 (Δε +1.04), and 23 300 cm^{-1} (Δε −0.06).

[Co(β-cqd)$_2$]·H$_2$O. This air-sensitive, brown, paramagnetic complex is soluble in ethanol and chloroform and slightly soluble in benzene and n-hexane. The molecular weight could not be measured due to the sensitivity to air and poor solubility. The presence of a

TABLE 4

Carbon-13 n.m.r. spectra [a] of bis(chiral *vic*-dioximato)metal(II) complexes

(*a*) Camphorquinone dioximato(cqd)-complexes

Complex		C^8	C^9	C^{10}	C^5	C^6	C^4	C^7	C^1	C^2	C^3
[Ni(α-cqd)$_2$]		(12.6	17.3	20.4) [b]	(25.2	31.0) [b]	48.9	50.6	56.2	(146.7	151.9) [b]
[Ni(δ-cqd)$_3$]		(10.7	17.0	19.8) [b]	(23.1	32.4) [b]	48.8	49.0	52.1	(146.3	153.2) [b]
[Ni(β-cqd)$_2$]	c	(18.7	25.0	28.8 [b]	(32.1	40.4) [b]	55.3	60.6	61.6	(168.2	171.5) [b]
		(18.7	25.0	28.8) [b]	(32.1	40.4) [b]	55.3	60.6	61.4	(169.5	170.4) [b]

(*b*) Nopinoquinone dioximato(nqd)-complexes

Complex		C^8	C^9	C^7	C^4	C^6	C^5	C^1	C^2	C^3
[Ni(δ-nqd)$_2$]		(21.5	21.4) [b]	(30.3	30.5) [b]	37.6	40.1	46.4	(139.4	147.2) [b]
[Ni(β-nqd)$_2$]	c	(21.5	25.5) [b]	27.8	29.9	37.7	42.1	42.3	(149.3	159.3) [b]
		(21.5	25.5) [b]	27.9	30.5	37.7	42.1	41.9	(150.7	157.5) [b]
[Pd(β-nqd)$_2$]		(21.5	25.6) [b]	27.7	29.3	37.9	42.1	42.4	(147.3	162.5) [b]

[a] Chemical shifts are in p.p.m. from CDCl$_3$ (77.0 p.p.m.) at 25.05 MHz in CDCl$_3$. [b] Unassignable. [c] In two geometrical isomers.

co-ordinated water molecule is shown by the broad OH absorption at 3 200 cm^{-1} and the elemental analysis agrees with this composition. The C=N absorptions appear at 1 615 and 1 575 cm^{-1}. The electronic spectrum shows a maximum at 477 nm (ε 3 100 dm^3 mol^{-1} cm^{-1}, in EtOH) emerging from the charge-transfer band and tailing into the visible region. The n.m.r. spectrum is heavily broadened due to the paramagnetism, so the presence of isomers is uncertain. The magnetic moment (3.6 μ_B at 292 K) is intermediate between the values for typical low-spin (1.8 μ_B) and high-spin (4.8—5.1 μ_B) cobalt(II) complexes (Table 5), suggesting either a distorted square-pyramidal or a trigonal-bipyramidal structure. The e.s.r. spectra show only very broad signals with low intensity.

TABLE 5

Magnetic moments (μ_B) of cobalt(II) complexes

Complex	Solution at 308 K	Solid [a] 292 K	Solid [a] 78 K
$[Co(\alpha\text{-cqd})_2]\cdot H_2O$	3.4 [b]	3.5	2.9
$[Co(\beta\text{-cqd})_2]\cdot H_2O$	3.4 [c]	3.6	3.1
$[Co(\delta\text{-cqd})_2]\cdot H_2O$	3.7 [b]		
$[Co(\beta\text{-nqd})_2]\cdot 2\,H_2O$	2.3 [c]	2.0	1.9
$[Co(\delta\text{-nqd})_2]\cdot H_2O$	4.1 [b]	3.9	3.4

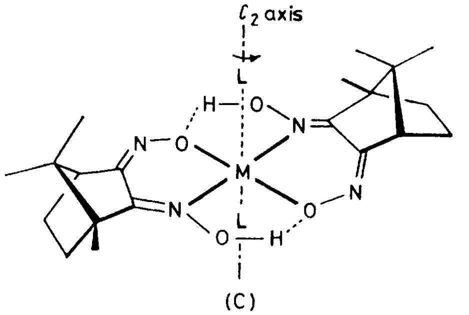
[a] Measured by the Faraday method. [b] Measured in toluene by use of the n.m.r. shifts.[19] [c] Measured in ethanol by use of n.m.r. shifts.[19]

$[Co(\beta\text{-nqd})_2]\cdot 2H_2O$. This complex is air-sensitive, but a little less so than $[Co(\beta\text{-cqd})_2]\cdot H_2O$; it is stable in air for a few hours. It is soluble in chloroform and only slightly in ethanol and benzene, precluding cryoscopic measurement of the molecular weight. A strong broad i.r. absorption of the co-ordinated water appears around 3 200 cm^{-1}. The C=N absorptions (1 565, 1 535 cm^{-1}) are lower than those of $[Ni(\beta\text{-nqd})_2]$ (1 585, 1 565 cm^{-1}). This complex shows a distinct maximum at 476 nm (ε 3 460 dm^3 mol^{-1} cm^{-1}, in EtOH), overlapping the tail of the charge-transfer band. The water molecule in the orange-brown complex can be removed by heating at 80 °C *in vacuo* to give an anhydrous dark brown complex. The presence of isomers is also uncertain. The magnetic moment is virtually constant over a range of temperature (78—292 K) in the solid state (Table 5).

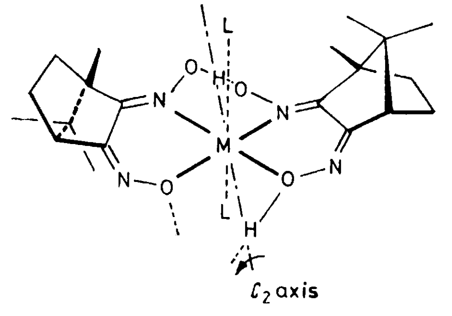
$[Fe(\beta\text{-cqd})_2]\cdot 2py$ *and* $[Fe(\beta\text{-nqd})_2]\cdot 2py$. The solubilities of these diamagnetic complexes are similar to that of $[Ni(\beta\text{-nqd})_2]$. The iron(II) complexes in the solid state may be stable for a while (a few minutes) in air presumably due to the six-co-ordination. The ^{1}H n.m.r. spectrum of $[Fe(\beta\text{-nqd})_2]\cdot 2py$ (py = pyridine) does not show any splitting due to the isomers (Table 3). A definite n.m.r. spectrum was not obtained for $[Fe(\beta\text{-cqd})_2]\cdot 2py$ due to paramagnetic impurities in its solution.

NO-*Chelation*. The geometry of (*E*,*Z*)-dioximate ligands, α- and δ-cqd and δ-nqd, allows a six-membered chelation with their N and O atoms. As was the case with the β-dioximes, two molecular structures are possible for bis(chelate) complexes. These are shown for a six-co-ordinate complex, $[M(\alpha\text{-cqd})_2]\cdot 2L$, in (C) and (D). Structure (C), involving two *trans* co-ordinating N atoms, is characterized by two stereochemically equivalent, hydrogen-bonded, five-membered chelate rings, $\overline{\mathrm{O{-}M{-}NO \cdots H}}$, while in structure (D), where the two N atoms, are *cis*, only one intramolecular hydrogen-bonded chelate ring is involved, since a four-membered hydrogen-bonded chelation on the *cis*-O,O side is geometrically impossible. Thus, (D) is stabilized in a dimeric structure linked by two intermolecular hydrogen bonds.

No six-membered *NO*-chelation has been reported for *vic*-dioximato-complexes. Very recently, an *X*-ray analysis of $[Ni(\delta\text{-cqd})_2]$ confirmed the *NO*-chelation.[10] The distance between the co-ordinated O and N atoms (estimated value for cqd, 2.7 Å) in α- and δ-cqd and δ-nqd appears to be adequate for accommodation of bivalent ions. Complexes of similar six-membered mono-oximate chelates are known, *e.g.* bis(salicylaldoximato)nickel(II).[11]



(C)



(D)

$[Ni(\alpha\text{-cqd})_2]$ *and* $[Ni(\delta\text{-cqd})_2]$. These complexes are as soluble in organic solvents as is $[Ni(\beta\text{-nqd})_2]$ and are monomeric in benzene (Table 2). They are most likely to be square planar as indicated by their diamagnetism. In the case of $[Ni(\alpha\text{-cqd})_2]$ the C=N stretching frequency (1 560 cm^{-1}) of the N-atom-co-ordinated C=N bond is lower than that of free α-Hcqd (1 615 cm^{-1}), whereas that (1 670 cm^{-1}) of the O-atom-co-ordinated C=N group is similar. Similarly, the C=N stretchings in $[Ni(\delta\text{-cqd})_2]$ appear at 1 700 and 1 565 cm^{-1}. In contrast to $[Ni(\beta\text{-nqd})_2]$ and $[Pd(\beta\text{-cqd})_2]$, there is no indication in the ^{1}H and ^{13}C n.m.r. spectra of the existence of two isomers (Table 3 and 4). On the basis of the molecular weights and these n.m.r. data, it is inferred that these complexes assume only structure (C) as confirmed independently by Angelici *et al.*[10]

The c.d. spectra of [Ni(α-cqd)$_2$] and [Ni(δ-cqd)$_2$] (Figure 1) are characterized by two extrema in negative regions around 17 000 and 22 000 cm^{-1} although the latter extremum of [Ni(δ-cqd)$_2$] is hardly discernible. Large $\Delta\varepsilon$ values are observed in the charge-transfer region (above 23 000 cm^{-1}); the magnitude may be due to the rotational strength of the chiral ligand itself since the reversal in sign for the two complexes corresponds to that for the free ligands. In d^8 complexes of D_{4h} symmetry two magnetic dipole-allowed one-electron *d–d* transitions in order of increasing energy are $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$. The contribution of a magnetic dipole-forbidden transition $d_{x^2-y^2} \rightarrow d_{z^2}$ to the electronic spectrum could be ignored.[12–15] In D_{2h} symmetry the degeneracy of d_{xz} and d_{yz} will be lifted. The local symmetry around the metal in the present systems belongs to the D_{2h} symmetry point group. Thus the appearance of two maxima in the electronic spectra in the 21 000—24 000 cm^{-1} region is in accord with this symmetry. These transitions account for the main rotational strength around 22 000 cm^{-1} and the lower-energy *d–d* transition ($d_{x^2-y^2} \rightarrow d_{xy}$) accounts for that observed at 17 000 cm^{-1}. The same signs of the c.d. spectra reflect similar configurations of the chromophores around the metal in these complexes.

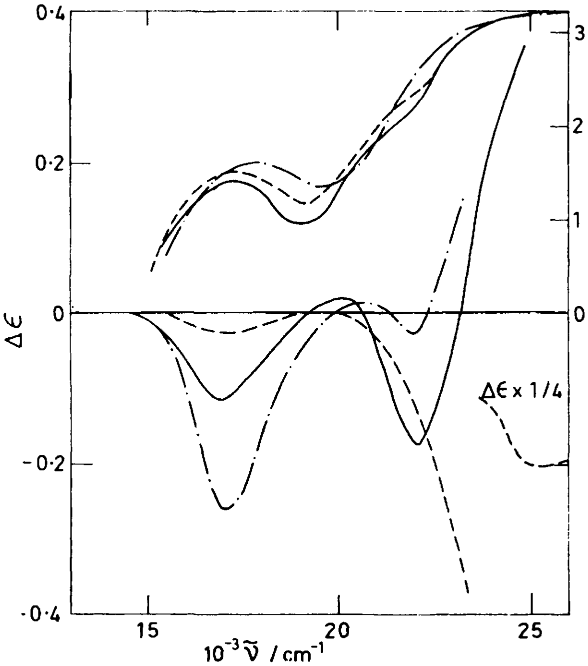


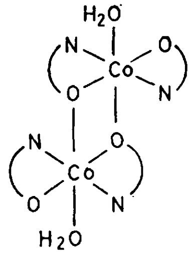
FIGURE 1 Electronic and c.d. spectra of [Ni(α-cqd)$_2$] (——), [Ni(δ-cqd)$_2$] (– – – –), and [Ni(δ-nqd)$_2$] (— · — · — · — · —) $CHCl_3$

[Ni(δ-nqd)$_2$]. The solubility in organic solvents is comparable to that of [Ni(δ-cqd)$_2$]. The complex is monomeric in benzene (Table 3). The two C=N stretching absorptions (1 520 and 1 645 cm^{-1}) are well separated and thus consistent with the *NO*-chelate co-ordination (*cf.* 1 580 and 1 645 cm^{-1} of free δ-Hnqd). The molecular weight and ^{1}H and ^{13}C n.m.r. spectrum (Tables 2—4) indicate the *trans*-N,N alignment as in [Ni(α-cqd)$_2$] and [Ni(δ-cqd)$_2$]. The c.d. spectrum resembles that of [Ni(α-cqd)$_2$] apart from the $\Delta\varepsilon$ values at 17 000 and 22 500 cm^{-1}.

[Pd(δ-cqd)$_2$]. This complex was readily prepared from [Pd(O_2CMe)$_2$] and δ-Hcqd in ethanol. In contrast, attempts to prepare [Pd(α-cqd)$_2$] and [Pd(δ-nqd)$_2$] by the same method have been frustrated by contamination with a considerable amount of impurities which are not readily removed by recrystallization. The i.r. spectrum of [Pd(δ-cqd)$_2$] showed the C=N stretchings at 1 540 cm^{-1} (*N*-co-ordinated) and 1 700 cm^{-1} (*O*-co-ordinated). These values are to be compared with those of [Ni(δ-cqd)$_2$]. In the electronic spectrum a strong band appears at 28 700 cm^{-1} (ε 3 400 dm^3 mol^{-1} cm^{-1}) where the extremum of the c.d. also occurs ($\Delta\varepsilon$ —3.91).

[Co(α-cqd)$_2$]·H_2O *and* [Co(δ-cqd)$_2$]·H_2O. These air-sensitive complexes are quite soluble in ethanol, diethyl ether, chloroform, and benzene and even slightly soluble in n-hexane. In contrast to the nickel(II) complexes (see above) they are dimeric (Table 2). The presence of a co-ordinated water molecule is indicated by their elemental analyses and i.r. OH_2-stretching band at 3 300 cm^{-1}. The expected OH stretching and bending vibrations around 2 200 and 1 700 cm^{-1}, respectively, were very broad and weak. The C=N stretchings, 1 630 and 1 540 cm^{-1} for [Co(α-cqd)$_2$]·H_2O and 1 670 and 1 560 cm^{-1} for [Co(δ-cqd)$_2$]·H_2O, are considered to be consistent with the *NO*-chelating co-ordination. The co-ordinated water molecule is not removed by heating at 60 °C *in vacuo*. The ^{1}H n.m.r. spectra are broadened due to the paramagnetism and are not informative. The broad and weak e.s.r. spectra (78—300 K) are also uninformative. The static magnetic moments were measured in toluene and the solid state (Table 5). These moments depend on temperature. A structurally related distorted five-co-ordinate cobalt(II) complex, [Co(salen)(py)] [salen = *NN'*-ethylenebis(salicylideneiminate)] also shows a temperature-dependent magnetic moment (2.22 μ_B at 297 K and 1.68 μ_B at 95 K).[16] The magnetic moments (Table 5) are intermediate between those of typical low-spin (1.8 μ_B) and high-spin (4.8—5.1 μ_B) cobalt(II) ion suggesting a distortion from a square-pyramidal to a trigonal-bipyramidal structure. Failure to obtain single crystals of these complexes prevented *X*-ray analyses.

Consistent with its dimeric structure, [Co(α-cqd)$_2$]·H_2O shows antiferromagnetic behaviour (Table 5). Obviously the molecular association of [Co(α-cqd)$_2$]·H_2O in an axial direction as depicted below is prevented by the ligand bulk. Further, six-co-ordination is incompatible with the ready dioxygen absorption by [Co(α-cqd)$_2$]·H_2O. Similar six-co-ordinate complexes, *e.g.* [Co(dmg)$_2$]·2py, do not absorb O_2. The dimer formation would then be achieved by two intermolecular hydrogen bonds leading to structure (D). This should also be the case for [Co(δ-cqd)$_2$]·H_2O since the two complexes resemble each other in every spectral property except their chiroptics (see below).



The c.d. and electronic spectra in ethanol are shown in Figure 2. The electronic spectra are characterized by featureless intense charge-transfer bands (*e.g.* ε 3 000 dm^3 mol^{-1} cm^{-1} at 25 000 cm^{-1}) tailing into the visible region. The c.d. patterns for [Co(α-cqd)$_2$]$\cdot$H$_2$O and [Co(δ-nqd)$_2$]$\cdot$H$_2$O are mirror-image relationships in the range 15 000—22 000 cm^{-1}. The reversed sign of the Cotton effect of [Co(α-cqd)$_2$]$\cdot$H$_2$O and [Co(δ-nqd)$_2$]$\cdot$H$_2$O indicates an enantiomeric configuration at the metal chromophore. This stereochemical correlation is reflected in the olefin cyclopropanation catalyzed by these two complexes.[2] The identity of the donor ligand at the fifth apical co-ordination site appears not to influence the signs of the c.d. in 20 000 cm^{-1} region since the pyridine adduct, [Co(α-cqd)$_2$]$\cdot$py, shows a similar c.d. spectrum with an extremum at 18 300 cm^{-1} ($\Delta\varepsilon$ —0.91) and a shoulder at 21 700 cm^{-1} ($\Delta\varepsilon$ —0.57).[2] The molecular model of [Co(α-cqd)$_2$]$\cdot$H$_2$O indicates the λ conformation at the hydrogen-bonded ring to be one of the stable configurations, a situation arising from the proximity of two O atoms in the chelate ring and the relative bulkiness of the two chiral camphor skeletons. It should be noted that the chiral configuration is induced even in the absence of chiral centres within the chelate ring.

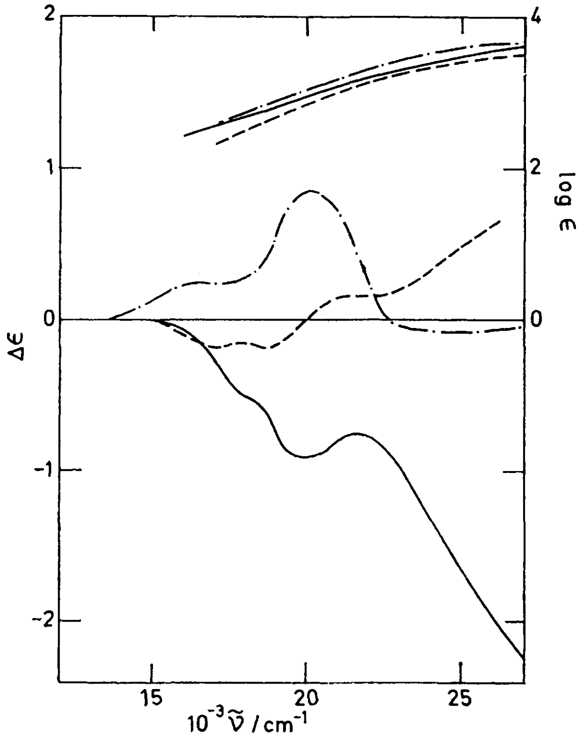


FIGURE 2 Electronic and c.d. spectra of [Co(α-cqd)$_2$]$\cdot$H$_2$O (——), [Co(δ-cqd)$_2$]$\cdot$H$_2$O (– – – – –), and [Co(δ-nqd)$_2$]$\cdot$H$_2$O (— • — • —) in EtOH

The c.d. pattern for [Co(δ-cqd)$_2$]$\cdot$H$_2$O in the 15 000—22 000 cm^{-1} region is complicated by the three peaks of different signs. The configuration at the metal chromophore is apparently different, but is not completely the mirror image of that of [Co(α-cqd)$_2$]$\cdot$H$_2$O. In the cyclopropanation catalysis these two [Co(cqd)$_2$]$\cdot$H$_2$O complexes work as ' quasi-enantiomeric ' catalysts.[2] The assignment of the c.d. patterns of these labile distorted cobalt(II) complexes[17] remains to be elucidated since their spectra reflect the dynamically equilibrated stereochemistry at the metal.

[Co(δ-nqd)$_2$]$\cdot$H$_2$O. This air-sensitive complex is also dimeric in benzene (Table 2). The presence of a co-ordinated water molecule is shown by the elemental analysis and the i.r. OH stretching around 3 300 cm^{-1}. The C=N stretchings (1 630, 1 515 cm^{-1}) are lower than those of [Ni(δ-nqd)$_2$] (1 645, 1 520 cm^{-1}). The magnetic moment (Table 5) is slightly larger (0.5 μ_B) at ambient temperature than that of [Co(δ-cqd)$_2$]$\cdot$H$_2$O. Antiferromagnetic coupling is also observed. The electronic spectrum is similar to that of [Co(δ-cqd)$_2$]$\cdot$H$_2$O and featureless (Figure 1). The c.d. spectrum shows two distinct extrema at 16 000 and 20 000 cm^{-1} and one around 18 000 cm^{-1} as a shoulder. The sign identity strongly suggests an enantiomeric configuration with respect to that of [Co(α-cqd)$_2$]$\cdot$H$_2$O.

It may be pertinent to discuss here possible reasons for the observed differences in physical properties between the β-cqd and β-nqd complexes. Since the six-membered ring in nqd is more flexible in comparison to that in cqd, the N • • • N distance could be adjusted in the chelate-ring formation with a smaller metal ion. Similar distortion at the ligand has been observed in the nickel(II) complex of cyclohexane-1,2-dioximate. The ability of β-nqd to accommodate smaller metal ions is manifested in the magnetic moments (Table 5) and in the reactivities of the cobalt(II) complexes which will be described elsewhere. The steric requirement of the two ligands also differs. With respect to the metal accommodation the cqd ligand is more sterically demanding than nqd due to the different location of their methyl groups. The bulkiness should exercise some hindrance to a close approach of the two chelate ligands upon their co-ordination to a metal. This would then affect the strength of the metal–ligand bonding. These factors will influence the extent of distortion from the regular co-ordination geometry around the metal and the resulting difference is manifested in the magnetic moments (see Table 5). The values for [Co(β-cqd)$_2$]$\cdot$H$_2$L (3.4 μ_B in solution and 3.6 μ_B in the solid state) should be compared with those of [Co(β-nqd)$_2$]$\cdot$2H$_2$O (2.3 μ_B in solution and 2.0 μ_B in the solid state). Some of the reactions of these β-type dioximato-complexes also differ and will be reported separately.

In concluding this paper, the chemical consequences of the chiral bulky bicyclic skeletal structure of the dioximate chelates are summarized as follows: (*a*) geometrical isomerism of [M(β-cqd)$_2$] or [M(β-cqd)$_2$] was revealed by careful analysis of the n.m.r. spectra; (*b*) the bite angle of the chelate is controlled by the strained bicyclic skeleton; (*c*) the bite-angle effect is reflected in the strengths of chelation; (*d*) the electronic state of the metal is thus influenced by the bite angle; (*e*) the sign of the c.d. curves of [Co(δ-cqd)$_2$]·H$_2$O or [Co(δ-nqd)$_2$]·H$_2$O is correlated with the configuration at the metal which is dynamic in solution (' dynamic chirality '); (*f*) the sign of some c.d. bands can be utilized to predict the helicity at the co-ordination site; and (*g*) novel *NO*-chelate formation is realized in complexes of α- and δ-cqd and of δ-nqd. This is again a result of the wider bite angles of these chelate ligands.

EXPERIMENTAL

Infrared spectra were obtained on a Hitachi 295 spectrometer in Nujol mulls. The ^{1}H and ^{13}C n.m.r. spectra were recorded on a JEOL MH-100 and a JEOL JNM-FX100 spectrometer, respectively. C.d. spectra were measured with a Jasco J-40 and the electronic-absorption spectra with a Hitachi EPS-3T instrument. The ligand preparations have been described previously.[2] The magnetic susceptibilities of the cobalt(II) complexes were measured in the solid state with the Faraday method and in solution with the n.m.r. technique.[18]

The preparation and physical measurements of cobalt(II) and iron(II) complexes were performed in a pure nitrogen atmosphere with degassed or N$_2$-saturated reagents and solvents. The complexes of Ni^{II} or Pd^{II} can be prepared in air. The preparation of the cobalt(II) complexes has already been reported. Since the preparations were performed by similar methods only typical examples are given below.

Bis(β-*nopinoquinone dioximato*)*iron*(II)-*Pyridine* (1/2), [Fe(β-nqd)$_2$]·2py.—To a methanol suspension (10 cm^3) of iron(II) acetate (0.368 g, 2.12 mmol) were added β-Hnqd (0.772 g, 4.24 mmol) and pyridine (1.5 cm^3). The mixture was stirred for 5 h at room temperature then filtered. Water (30 cm^3) was added to the filtrate to precipitate an orange-red microcrystalline product which was washed three times each with water (20 cm^3) and dried *in vacuo*, yield 0.55 g (45%).

Bis(α-*camphorquinone dioximato*)*nickel*(II), [Ni(α-cqd)$_2$].—Nickel(II) acetate tetrahydrate (0.604 g, 2.42 mmol) was added to an ethanol solution (20 cm^3) of α-Hcqd (0.951 g, 4.85 mmol), and the mixture was stirred at 60—70 °C for 2 h. After cooling, the green precipitate was filtered off, washed with water, and dried *in vacuo*, yield 0.99 g (91%).

[Pd(β-nqd)$_2$].—Palladium(II) acetate (0.510 g, 2.27 mmol) was added to an ethanol solution (20 cm^3) of β-Hnqd (0.828 g, 4.54 mmol) and stirred at 50—60 °C for 3 h. The yellow precipitate was filtered after cooling, washed with water, and dried *in vacuo*, yield, 0.80 g (75%).

[Pd(δ-cqd)$_2$].—This was prepared by a similar method as above. The yellow crude product was purified by continuous extraction with hot n-hexane followed by recrystallization (60%).

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