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Novel transition metal complexes with camphorquinoneoxime ligands

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NOVEL TRANSITION METAL COMPLEXES WITH CAMPHORQUINONEOXIME LIGANDS

Iowa State University PH.D. 1979

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Novel transition metal complexes with camphorquinoneoxime ligands

by

Man Sheung Ma

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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For the Graduate College

Iowa State University
Ames, Iowa

1979

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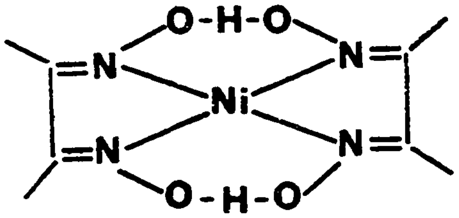
GENERAL INTRODUCTION

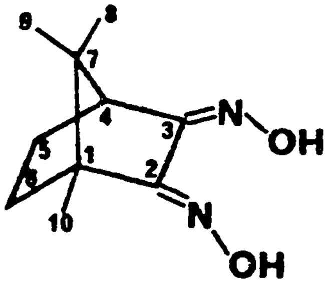
Since the Russian chemist Chugaev[1] discovered the reaction of Ni(II) with dimethylglyoxime (H_2DMG) as shown in eq. 1, the chemistry of the metal dioximes has been

$Ni^{2+} + 2H_2DMG \longrightarrow$  $+ 2H^+$ (1)

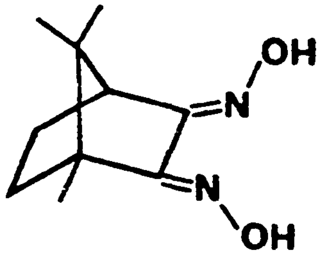
studied extensively. In almost all of the metal dioxime complexes, the deprotonated dioxime acts as a bidentate ligand coordinating to the metal through both nitrogen atoms.

In the past decade interest in the use of α-dioximes as selective analytical reagents[2] has shifted to areas where other applications of the metal dioximes are emphasized. These new areas include studies of these metal complexes as catalysts for asymmetric hydrogenation,[3] as models[4] for vitamin B_{12}, as anti-tumor agents[5] and as semi-conducting materials.[6]

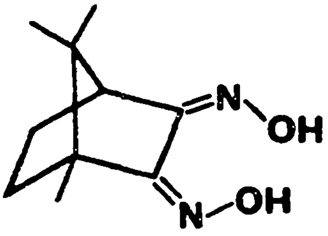
Our interest in this area evolved from previous studies of optically active ligands[7] and a desire to prepare complexes with optically active α-dioxime ligands. Such a ligand is camphorquinonedioxime H_2CQD. It can exist in four stable isomeric forms α, β, γ and δ[8] as shown below:



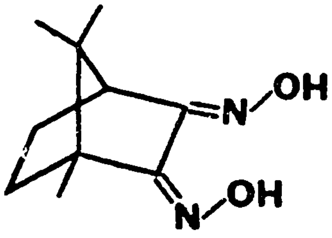
α



β



γ



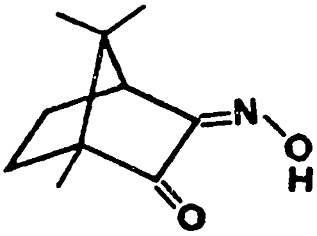
δ

These isomers differ from one another by the orientation of the OH groups at the N atoms. One of the major concerns of the present work is the syntheses and characterizations of transition metal complexes of all isomers of H_2CQD.

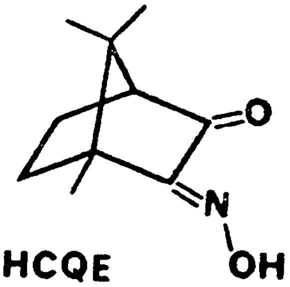
While our work was in progress Nakamura et al.[9] reported that cobalt(II) complexes of α, β and δ-isomers of H_2CQD catalyzed the cyclopropanation of olefins. More recently, they suggested that N,N as well as N,O coordination[10] of these ligands occurred with Co(II), Ni(II) and Pd(II) metal ions. The varieties of H_2CQD metal complex formation have been much more fully explored as described in this dissertation.

We also observed an unusual reaction of $M(HCQD)_2$ complexes of Ni and Pd with Ag(I) to give cluster complexes. Previously Fe(III) was reported to react with methyl-(aquo)cobaloxime[11] to replace one bridging H atom in the planar $Co(HDMG)_2^+$ unit. We find that Ag(I) yields cluster of six metal atoms supported by the $HCQD^-$ ligands.

Since carbonyl-oxime ligands are usually poor coordinating agents[12] for Ni(II), another direction of the present work extends to the study of the coordination chemistry of isonitrosocamphor (HCQM) and isonitroso-epicamphor (HCQE) with Ni(II). In addition, the possible formation of Schiff base ligands of HCQE, HCQM and camphorquinone upon reaction with diaminopropane and metal ions was examined. These studies give further insight into the coordination behavior of this bicyclic type of ligand.



HCQM



HCQE

Throughout the present work, the techniques employed include X-ray crystallography, ^{1}H and ^{13}C NMR, IR, ultraviolet-visible and esr spectroscopy as well as magnetic moments and ionic conductivities, with X-ray crystallography being the most informative.

Explanation of Dissertation Format

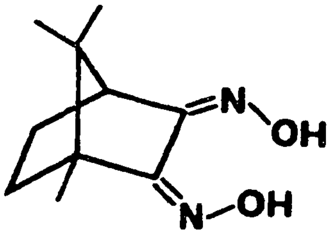
This dissertation is written so that each section represents an article in a publishable form. For this reason the numbering scheme adopted for the figures and tables is independent in each section. References cited in the General Introduction and in the Summary will appear at the end under the heading Literature Cited.

SECTION I. UNUSUAL COORDINATION OF THE α-DIOXIME LIGAND IN BIS(CAMPHORQUINONE DIOXIMATO)NICKEL(II)

INTRODUCTION

Metal complexes[1] of the dimethylglyoximate ligand ($HDMG^-$) have served as models for vitamin B_{12},[2] have been shown to have some one-dimensional metallic properties,[3] and have long been of importance in analytical chemistry.[4] In all of the known structures, the $HDMG^-$ ligand behaves as a bidentate ligand coordinating to the metal through both nitrogen atoms.

Our interest in these compounds evolved from previous studies of optically active ligands[5] and a desire to prepare complexes with optically active α-dioxime ligands. We expected these complexes to have catalytic properties similar to those known for $Co(HDMG)_2$.[6] The chosen ligand, γ-camphorquinone dioxime (H_2CQD), was prepared from d-camphor according to the procedures of Forster.[7] Proton NMR studies[8] and an X-ray structural study[9] indicate that this γ-isomer has a syn structure with the following OH group orientations at the N atoms:



H_2CQD

Recently, complexes of the α, β, and δ isomers of camphorquinone dioxime were reported to catalyze the cyclopropanation of olefins, and it was suggested that these complexes had structures involving N,O as well as N,N ligand bonding.[10]

EXPERIMENTAL SECTION

The nickel(II) complex was prepared by mildly refluxing a MeOH solution of 0.64 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.28 mmol of H_2CQD for 10 minutes. After adding 1.28 mmol of NaOMe in MeOH, the solution was refluxed for an additional 2 hours. Following filtration while warm, the solution was evaporated under vacuum to a green solid, which was dissolved in a minimum volume (~10 ml) of CH_3CN. The solution was filtered immediately and allowed to stand overnight whereupon reddish brown tetrahedral crystals of $Ni(HCQD)_2$ formed in 20% yield. Anal. ($C_{20}H_{30}N_4O_4Ni$) C,H,N.

A single tetrahedral crystal of $Ni(HCQD)_2$ about 0.4 mm on an edge was chosen for the X-ray diffraction study. The observed Laué symmetry and extinctions correspond to the orthorhombic space group $P2_12_12_1$ with a = 13.175(1), b = 13.652(2), c = 12.031(3)Å, Z = 4 and ρcalc = 1.378 g/ml. Four octants of data were collected on a four-circle diffractometer designed and built in the Ames Laboratory[11] using graphite monochromated Mo-Kα X-rays (λ = 0.70954Å) up to a 2θ limit of 60°. Of the 11,562 measured intensities 7,923 were judged observed ($I > 3.0\ \sigma_I$). Correction for Lorentz and polarization effects and averaging of equivalent data yielded 2,253 independent reflections. No correction was applied for absorption and an extinction correction was made with $g = 4.5 \times 10^{-7}$. The heavy atom was readily located on a Patterson map.[12] Full matrix least squares refinement[13] of the structure with anisotropic thermal parameters and fixed hydrogen positions yielded a conventional residual $R = 0.066$ and a weighted residual $R = 0.085$. A computer-generated perspective view of the essential configuration of the ligand and the coordination sphere around the nickel atom is shown in Figure 1.

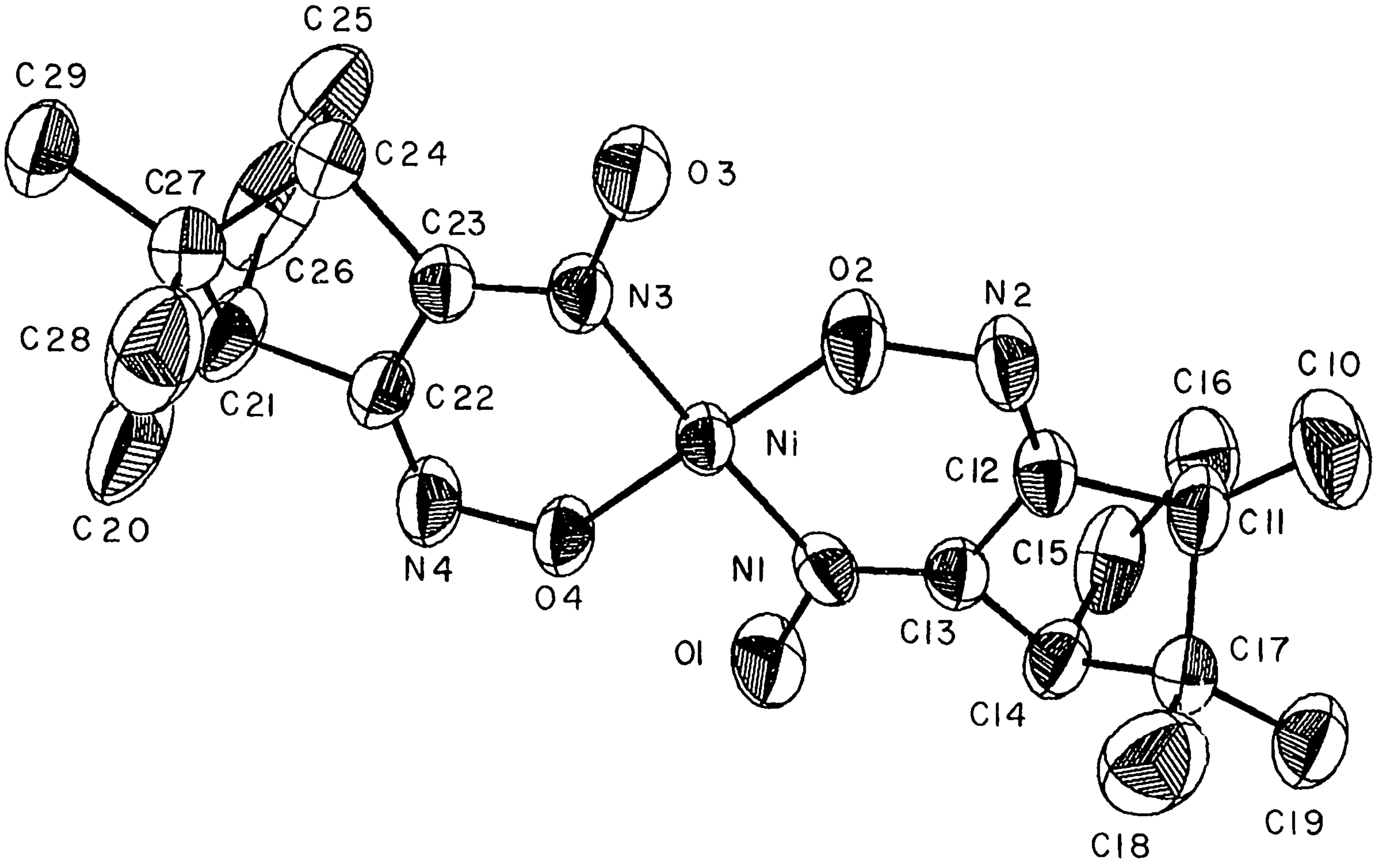


Figure 1. Computer-generated perspective drawing of $Ni(HCQD)_2$.

RESULTS AND DISCUSSION

The 6-membered rings give the Ni atom an almost square planar configuration. The distances from Ni to O2, O4, N1, and N3 are 1.820(4), 1.840(3), 1.859(4), and 1.851(4) Å, respectively. The HCQD$^-$ ligand coordinates to the Ni via N and O donor atoms rather than the common N,N coordination characteristic of other α-dioxime ligands. We believe the reason for this coordination is the bicyclic nature of the ligand which causes the C-C-C angles at C12, C13, C22 and C23 to be 106.6(4), 105.1(4), 104.9(4) and 107.4(4)°, respectively, which are substantially smaller than found (121 and 124°) for the corresponding angles of $Ni(HDMG)_2$.[14]

The small magnitude of these angles presumably increases the C-C-N angles in the chelate ring to the point where formation of a larger ring by N,O coordination becomes more favorable. However, even in the 6-membered ring there appears to be some strain due to the sharp angle (94.2(2) and 93.9(2)°) at the Ni in the chelate ring. Thus all the following angles in the ring are larger than corresponding angles in $Ni(HDMG)_2$: (the given angle is listed first followed by the corresponding angle in the other ring) N3-C23-C22, 122.1(5), 122.9(5); N4-C22-C23, 132.0(5), 129.6(4); Ni-N3-C23, 124.8(4), 126.3(3)°. These unusually large angles suggest that the 6-membered chelate rings may also be strained. The delicate balance between N,O and N,N coordination in $HCQD^-$ complexes is supported by the fact that we find the ligand to be N,N-coordinated in $Cu(HCQD)_2$. The now known existence of these two modes of bonding suggests that N,O-bonded forms may be present as intermediates in reactions of complexes of other α-dioxime ligands.

Although the O1-O4 and O2-O3 distances (2.49 and 2.50Å) are not as short as those (2.40Å)[14] in $Ni(HDMG)_2$, it appears that some hydrogen bonding does occur. There are no short distances which permit intermolecular hydrogen bonding. The molecules pack in the unit cell such that the closest distance between Ni atoms in parallel complexes is one unit cell length (12.031Å) along the c axis. Thus there is no Ni-Ni interaction such as occurs in $Ni(HDMG)_2$.[14]

The infrared spectrum of $Ni(HCQD)_2$ taken in a KBr pellet shows a medium intensity absorption at 1690 cm^{-1}, an unusually high frequency uncharacteristic of N-bonded α-dioxime ligands.[15] Deuteration studies indicate that the band is not associated with the OH group but presumably arises from a vibration which has considerable C=N stretching character. This absorption may allow easy identification of other complexes which contain α-dioxime ligands coordinated <u>via</u> their N and O atoms.

Table I. Final atomic parameters

(a) Final positional parameters and their estimated standard deviations (in parentheses)[a]

Atom	X	Y	Z
Ni	-5.6(4)	-19.8(4)	59.1(4)
N1	887(3)	1003(2)	-229(4)
O1	631(3)	1944(2)	124(4)
O2	816(3)	-944(3)	-554(4)
N2	1778(3)	-872(3)	-1020(4)
N3	-842(3)	-1053(3)	449(4)
O3	-589(3)	-2000(2)	160(4)
O4	-858(3)	919(2)	632(4)
N4	-1734(4)	812(4)	1220(5)
C11	3207(4)	215(4)	-1488(5)
C12	2172(3)	0(3)	-1047(4)
C13	1747(4)	931(4)	-682(5)
C14	2566(4)	1675(4)	-901(5)
C15	3387(5)	1450(5)	-11(5)
C16	3836(4)	448(5)	-391(6)
C17	3048(4)	1271(4)	-1959(5)
C18	2305(6)	1246(6)	-2933(6)
C19	3991(5)	1802(5)	-2303(6)
C10	3713(5)	-546(5)	-2219(7)
C21	-3011(4)	-293(5)	2068(6)
C22	-2053(4)	-50(4)	1369(4)
C23	-1673(4)	-970(4)	1024(5)

---

[a] The positional parameters are presented in fractional unit cell coordinates ($\times 10^4$).

Table I. (continued)

Atom	X	Y	Z
C24	-2355(4)	-1752(4)	1522(5)
C25	-2145(6)	-1733(7)	2781(7)
C26	-2498(7)	-794(8)	3170(6)
C27	-3353(5)	-1217(4)	1492(5)
C28	-3741(5)	-1048(7)	309(6)
C29	-4212(4)	-1768(5)	2138(7)
C20	-3747(6)	520(6)	2233(11)

(b) Final thermal parameters (X 10^4) and their estimated standard deviations (in parentheses)[b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	32.6(3)	42.0(3)	66.4(4)	-1.2(3)	3.0(3)	-5.1(3)
N1	44(3)	44(2)	84(4)	9(2)	1(3)	-8(3)
O1	83(3)	41(2)	176(5)	4(2)	45(4)	-24(3)
O2	42(2)	59(2)	142(4)	-14(2)	25(3)	-28(3)
N2	50(3)	50(3)	131(5)	0(2)	33(3)	-22(3)
N3	39(2)	45(2)	95(4)	-5(2)	8(3)	-9(3)
O3	65(3)	43(2)	168(5)	-5(2)	41(3)	-21(3)
O4	51(2)	46(2)	112(4)	0(2)	32(3)	-5(2)
N4	52(3)	60(3)	119(5)	0(3)	25(3)	-13(3)

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[b] The βij are defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

Table I. (continued)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C11	46(3)	62(4)	101(5)	-7(3)	23(3)	-10(4)
C12	37(2)	54(3)	76(4)	-5(3)	5(3)	-14(3)
C13	46(3)	43(3)	78(4)	-1(2)	8(3)	-2(3)
C14	68(4)	49(3)	99(5)	-8(3)	31(4)	-2(3)
C15	66(4)	102(5)	92(5)	-29(4)	18(4)	-39(5)
C16	40(3)	101(5)	130(7)	-7(3)	-2(4)	-4(5)
C17	54(4)	62(4)	78(4)	4(3)	18(3)	3(3)
C18	118(7)	123(7)	97(6)	-5(6)	3(6)	17(6)
C19	81(4)	73(4)	125(7)	-11(4)	41(5)	0(5)
C10	94(5)	82(5)	145(7)	17(4)	42(6)	-42(5)
C21	72(4)	64(4)	137(7)	-11(3)	63(5)	-14(4)
C22	51(3)	53(3)	86(4)	-4(3)	18(3)	2(4)
C23	40(3)	51(3)	72(4)	-1(2)	2(3)	-3(3)
C24	50(3)	59(4)	102(5)	-3(3)	12(4)	13(4)
C25	86(5)	125(7)	112(7)	-40(5)	-15(5)	44(7)
C26	133(8)	180(10)	69(5)	-81(8)	12(5)	-19(6)
C27	54(3)	63(4)	100(5)	1(3)	10(4)	9(4)
C28	75(5)	171(8)	105(7)	-36(6)	-21(5)	34(7)
C29	53(4)	75(4)	161(8)	-10(3)	29(5)	4(5)
C20	113(7)	68(5)	431(21)	-13(5)	155(11)	-23(9)

Table II. Interatomic distances (Å)

Ni - N1	1.859(4)	C11 - C16	1.590(9)
Ni - O2	1.820(4)	C11 - C17	1.563(8)
Ni - N3	1.851(4)	C14 - C17	1.525(8)
Ni - O4	1.840(3)	C17 - C18	1.527(10)
N1 - O1	1.396(5)	C17 - C19	1.497(8)
N2 - O2	1.388(6)	C11 - C10	1.517(8)
N3 - O3	1.380(5)	C21 - C22	1.553(7)
N4 - O4	1.362(6)	C22 - C23	1.414(7)
N1 - C13	1.261(6)	C23 - C24	1.519(7)
N2 - C12	1.300(6)	C24 - C25	1.540(10)
N3 - C23	1.301(6)	C25 - C26	1.442(12)
N4 - C22	1.264(7)	C21 - C26	1.639(11)
C11- C12	1.492(6)	C21 - C27	1.507(8)
C12- C13	1.457(7)	C24 - C27	1.505(7)
C13- C14	1.505(7)	C27 - C28	1.530(9)
C14- C15	1.553(9)	C27 - C29	1.565(8)
C15- C16	1.559(9)	C21 - C20	1.488(9)

Table III. Bond angles (degree)

N1 - Ni - O2	93.9(2)	C13 - C14 - C17	101.5(4)
N1 - Ni - N3	175.6(2)	C15 - C14 - C17	102.4(4)
N1 - Ni - O4	86.2(2)	C11 - C17 - C18	110.1(5)
O2 - Ni - N3	85.9(2)	C11 - C17 - C19	115.8(5)
O2 - Ni - O4	178.0(2)	C11 - C17 - C14	95.0(4)
N3 - Ni - O4	94.2(2)	C18 - C17 - C19	109.3(5)
Ni - N1 - O1	118.8(3)	C14 - C17 - C18	112.5(5)
Ni - N1 - C13	126.3(3)	C14 - C17 - C19	113.7(5)

Table III. (continued)

Ni - O2 - N2	131.1(3)	C17 - C11 - C10	118.8(5)
O1 - N1 - C13	114.8(4)	C27 - C21 - C20	119.4(6)
O2 - N2 - C12	116.1(4)	C21 - C22 - C23	104.9(4)
N1 - C13 - C12	122.9(5)	C22 - C23 - C24	107.4(4)
N1 - C13 - C14	131.9(5)	C23 - C24 - C25	105.7(5)
N2 - C12 - C11	123.7(5)	C24 - C25 - C26	106.0(7)
N2 - C12 - C13	129.6(4)	C25 - C26 - C21	103.9(6)
C11 - C12 - C13	106.6(4)	C22 - C21 - C26	101.0(5)
C12 - C13 - C14	105.1(4)	C22 - C21 - C27	100.0(5)
C13 - C14 - C15	104.2(4)	C22 - C21 - C20	116.2(6)
C14 - C15 - C16	103.6(5)	C26 - C21 - C27	98.4(6)
C15 - C16 - C11	102.8(5)	C26 - C21 - C20	118.2(8)
C12 - C11 - C16	102.7(4)	C23 - C24 - C27	99.6(4)
C12 - C11 - C17	100.8(4)	C25 - C24 - C27	99.9(6)
C12 - C11 - C10	118.2(5)	C21 - C27 - C28	113.7(6)
C16 - C11 - C17	100.7(5)	C21 - C27 - C29	113.0(5)
C16 - C11 - C10	112.9(5)	C21 - C27 - C24	97.7(5)
C28 - C27 - C29	107.0(6)	N3 - C23 - C22	122.1(5)
C24 - C27 - C28	112.8(6)	O4 - N4 - C22	117.1(5)
C24 - C27 - C29	112.7(5)	O3 - N3 - C23	114.7(4)
N4 - C22 - C23	132.0(5)	Ni - O4 - N4	129.6(3)
N4 - C22 - C21	123.1(5)	Ni - N3 - C23	124.8(4)
N3 - C23 - C24	130.3(5)	Ni - N3 - O3	120.4(3)

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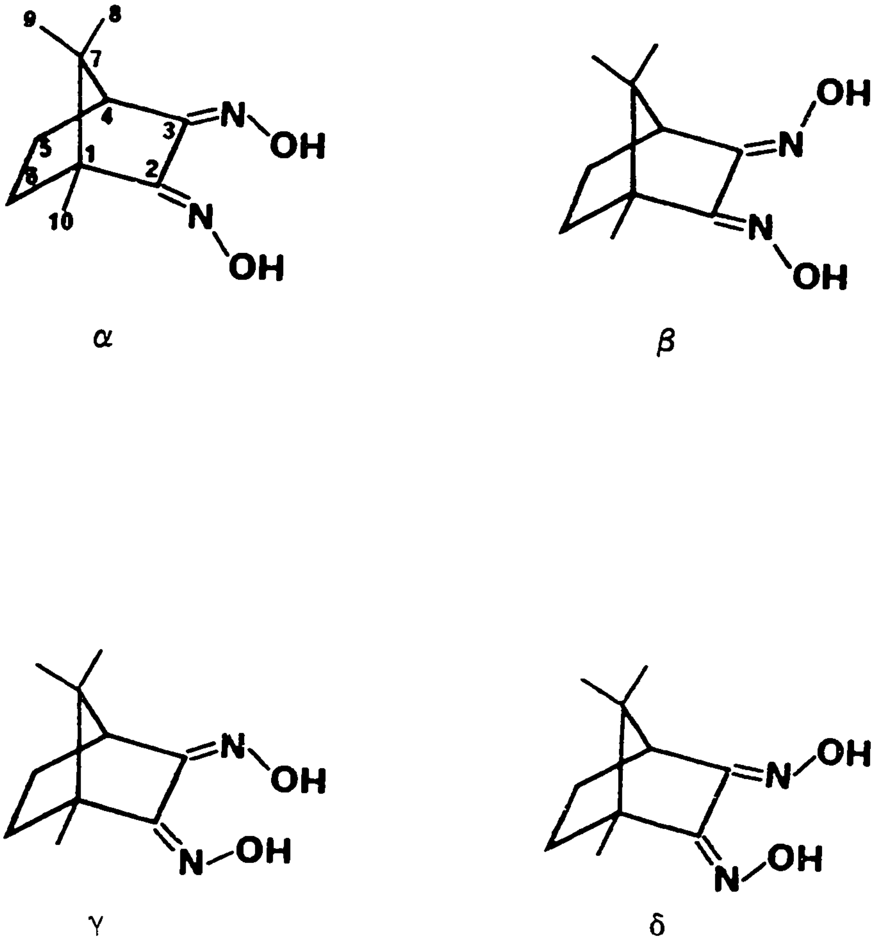
SECTION II. NOVEL TRANSITION METAL COMPLEXES OF CAMPHORQUINONEDIOXIME LIGANDS

INTRODUCTION

The chemistry of transition metal complexes with α-dioxime ligands has been well studied and is the subject of several reviews.[1-5] Yet little was known about the coordination chemistry of transition metals with the camphorquinonedioxime ligands, H_2CQD, until last year when work in this laboratory[6] and in Osaka University[7-9] was reported.

Our interest in this area evolved from previous studies of optically active ligands[10,11] and a desire to prepare complexes with optically active α-dioxime ligands. Unlike dimethylglyoxime, H_2DMG, or cyclohexanedionedioxime, H_2CHD, camphorquinonedioxime has been isolated in four isomeric forms which, henceforth, are referred to as α-, β-, γ-, and δ-H_2CQD as shown in Figure 1. In the present paper, we describe transition metal complexes of all of these isomers, as well as the diverse and novel ways in which these ligands coordinate to metal ions.



α β

γ δ

Figure 1. Isomers of H_2CQD.

EXPERIMENTAL SECTION

Spectral data Proton NMR spectra were obtained on a Varian HA-100 spectrometer using TMS as internal reference. IR spectra (4000-200 cm^{-1}) were obtained as KBr pellets using a Beckman IR-4250 spectrophotometer. Electronic spectra were recorded on a JASCO-ORD/UV-5 or Cary 14 instrument with $CHCl_3$ as solvent.

Conductivity measurement The molar conductivity of $Pd(\gamma\text{-}H_2CQD)_2Cl_2$ in MeOH was measured to be 33.25 $cm^2ohm^{-1}M^{-1}$ by employing a conductivity bridge model RC16-B2. The cell constant was 0.3712, and the concentration of $Pd(\gamma\text{-}H_2CQD)_2Cl_2$ was 1.79×10^{-3} M.

Starting materials The $Pd(PhCN)_2Cl_2$[12] and $Pt(PhCN)_2Cl_2$[13] were prepared according to published procedures. The optically active isomeric H_2CQD ligands were prepared by the procedures of Forster.[14] Deuterium exchange reactions of the camphorquinonedioxime ligands and $Ni(\delta\text{-}HCQD)_2$ were carried out by refluxing the compounds for 10 hours in CH_3OD and then reisolating them by subsequent removal of the solvent under vacuum.

Preparation of $Ni(\delta\text{-}HCQD)_2$ Single crystals of $Ni(\delta\text{-}HCQD)_2$ were prepared by dissolving 0.62 mmol of $Ni(NO_3)_2{\cdot}6H_2O$ in 10 ml of MeOH at 50° C. Then 1.24 mmol of $\gamma\text{-}H_2CQD$ was added. While stirring, 1.24 mmol of NaOMe in 10 ml of MeOH was added. The resulting green solution was refluxed for 2-3 hours. This solution was filtered while still hot. The solvent was removed under vacuum. The crude solids obtained were dissolved in CH_3CN and filtered. Upon standing overnight at room temperature in a stoppered flask, the filtrate yielded brown tetrahedral crystals of $Ni(\delta\text{-}HCQD)_2$. Yield 20%. Anal. Calcd. for $Ni(C_{10}H_{15}N_2O_2)_2$: C, 53.46; H, 6.74; N, 12.47. Found: C, 53.28; H, 6.60; N, 12.55.

Preparation of $Ni(\alpha\text{-}HCQD)_2$ This compound was prepared by dissolving 0.32 mmol of $\alpha\text{-}H_2CQD$ in MeOH containing 0.16 mmol of $Ni(OAc)_2 \cdot 4H_2O$. The resulting solution was filtered. Upon allowing the filtrate to stand overnight fine green needlelike crystals of $Ni(\alpha\text{-}HCQD)_2$ deposited. Yield 50%. Anal. Calcd. for $Ni(C_{10}H_{15}N_2O_2)_2$: C, 53.47; H, 6.75; N, 12.47. Found: C, 53.51; H, 6.75; N, 12.72.

Preparation of $Ni(\delta\text{-}HCQD)_2(\delta\text{-}H_2CQD)_2$ This complex was prepared by dissolving 0.96 mmol of $\gamma\text{-}H_2CQD$ and 0.32 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 10 ml of MeOH, and the resulting solution was refluxed for only one hour in the presence of 0.64 mmol of NaOMe. The green solution was then evaporated to dryness under vacuum and the solid was dissolved in 15 ml of anhydrous CH_3CN which was dried by refluxing over CaH_2 for 8 hours and distilling under anhydrous conditions. The green CH_3CN solution was filtered. The final filtrate was stored in a stoppered flask and cooled to about -25° C. Within an hour fine green needlelike crystals of the product deposited at the bottom of the flask. Yield 23%. Anal. Calcd. for $Ni(C_{10}H_{15}N_2O_2)_2(C_{10}H_{16}N_2O_2)_2$: C, 57.07; H, 7.44; N, 13.32; Ni, 6.97. Found: C, 56.95; H, 7.35; N, 13.28; Ni, 6.86.

Preparation of $Cu(\beta\text{-}HCQD)_2\cdot H_2O\cdot 1/2$ dioxane This compound was obtained by dissolving 0.32 mmol of $Cu(OAc)_2\cdot H_2O$ in 10 ml of MeOH containing 0.64 mmol of $\gamma\text{-}H_2CQD$. The dark brown solution was refluxed for 2-3 hours. After vacuum evaporation the black oily residue was dissolved in 10 ml of dioxane; the resulting solution was filtered and approximately 5 ml of H_2O was added. After several days dark brown needlelike crystals of the compound covered the bottom of the flask. The dioxane in the complex was also detected by GC with $CHCl_3$ as solvent and using an SE-52 column. Yield 80%. Anal. Calcd. for $Cu(C_{10}H_{15}N_2O_2)_2\cdot H_2O\cdot 1/2(C_4H_8O_2)$: C, 51.19; H, 7.04; N, 10.86. Found: C, 51.02; H, 6.99; N, 10.54.

Preparation of $Cu(\beta\text{-}H_2CQD)Cl_2$ This complex was prepared by mixing 0.32 mmol of $CuCl_2\cdot 2H_2O$ with 0.32 mmol of $\gamma\text{-}H_2CQD$ in 10 ml of absolute EtOH. After stirring overnight the green solution was evaporated to dryness. The solid was dissolved in 15 ml of CH_3CN from which green needlelike crystals were obtained. Yield 60%. Anal. Calcd. for $Cu(C_{10}H_{16}N_2O_2)Cl_2$: C, 36.32; H, 4.89; N, 8.47; Cl, 21.44. Found: C, 36.29; H, 4.72; N, 8.35; Cl, 21.57.

Preparation of $Pd(\beta\text{-HCQD})_2$ This Pd(II) complex was prepared by suspending 0.32 mmol of $\beta\text{-}H_2CQD$ in 25 ml of MeOH at 50° C. Then an equivalent amount of NaOMe was added so that a clear solution was obtained. Immediately 0.16 mmol of $Pd(PhCN)_2Cl_2$ in 10 ml of $CHCl_3$ was mixed into the solution. After warming the resulting yellow solution at 70° C in a hot H_2O bath for about 15 minutes, it was filtered into a flask containing 5 ml of H_2O. The filtrate totalling about 40 ml was left standing for a period of several days after which a crop of yellow needlelike crystals of $Pd(\beta\text{-HCQD})_2$ was obtained. Yield 45%. Anal. Calcd. for $Pd(C_{10}H_{15}N_2O_2)_2$: C, 48.34; H, 6.10; N, 11.28. Found: C, 48.48; H, 6.30; N, 11.19.

Preparation of $Pd(\delta\text{-HCQD})_2$ Yellow $Pd(PhCN)_2Cl_2$ (0.32 mmol) was added to 10 ml of MeOH containing 0.64 mmol of $\delta\text{-}H_2CQD$ and an equivalent amount of Et_3N. After stirring at 50° C for 2 hours, the yellow solution was filtered, and the filtrate was cooled to -25° C. Yellow crystals of $Pd(\delta\text{-HCQD})_2$ crystallized out after 24 hours in 45% yield. Anal. Calcd. for $Pd(C_{10}H_{15}N_2O_2)_2$: C, 48.34; H, 6.10; N, 11.28. Found: C, 48.41; H, 6.17; N, 11.45.

Preparation of Pt(β-HCQD)$_2$ Dark brown crystals of Pt(β-HCQD)$_2$ were prepared in the same manner as Pd(β-HCQD)$_2$. Yield 18%. Anal. Calcd. for Pt($C_{10}H_{15}N_2O_2$)$_2$: C, 41.02; H, 5.17; N, 9.57. Found: C, 40.89; H, 5.56; N, 9.15.

Preparation of Pd(γ-H$_2$CQD)$_2$Cl$_2$ Upon mixing 10 ml $CHCl_3$ solutions of γ-H$_2$CQD (0.32 mmol) and Pd(PhCN)$_2$Cl$_2$ (0.16 mmol) at room temperature, yellow crystals of Pd(γ-H$_2$CQD)$_2$Cl$_2$ almost immediately started to crystallize out of the solution. The reaction was complete within 15-30 minutes in 80% yield. Anal. Calcd. for Pd($C_{10}H_{16}N_2O_2$)$_2$Cl$_2$: C, 42.15; H, 5.67; N, 9.83; Cl, 12.44. Found: C, 42.08; H, 5.40; N, 9.75; Cl, 12.63.

Preparation of Pd(δ-H$_2$CQD)$_2$Cl$_2$ This compound was prepared in the same manner as Pd(γ-H$_2$CQD)$_2$Cl$_2$. Yield 80%. Anal. Calcd. for Pd($C_{10}H_{16}N_2O_2$)$_2$Cl$_2$: C, 42.15; H, 5.67; N, 9.83; Cl, 12.44. Found: C, 42.13; H, 5.96; N, 9.53; Cl, 13.76.

Preparation of Pd(α-H$_2$CQD)$_2$Cl$_2$ This complex was prepared in the same manner as Pd(γ-H$_2$CQD)$_2$Cl$_2$. Yield 80%. Anal. Calcd. for Pd($C_{10}H_{16}H_2O_2$)$_2$Cl$_2$: C, 42.15; H, 5.67; N, 9.83; Cl, 12.44. Found: C, 42.86; H, 5.75; N, 9.64; Cl, 13.12.

Preparation of Pd(β-H$_2$CQD)Cl$_2$ This complex was prepared by mixing a boiling 2:1 MeOH/$CHCl_3$ solution of β-H$_2$CQD (0.32 mmol) and 10 ml of a $CHCl_3$ solution of

$Pd(PhCN)_2Cl_2$ (0.32 mmol). After filtration, the filtrate upon cooling to room temperature gave a crop of orange crystals of Pd(β-H_2CQD)Cl_2. Yield 30%. Anal. Calcd. for $Pd(C_{10}H_{16}N_2O_2)Cl_2$: C, 32.15; H, 4.33; N, 7.50; Cl, 18.98. Found: C, 32.38; H, 4.42; N, 7.60; Cl, 18.72.

Preparation of Pt(β-H_2CQD)Cl_2 The preparation of this complex was the same as above except $Pt(PhCN)_2Cl_2$ was used. Yield 30%. It was shown by its IR spectrum to be the desired product.

Preparation of Pd(H_2CHD)Cl_2 The same procedure as the preparation of Pd(β-H_2CQD)Cl_2 was used. Yield 70%. Anal. Calcd. for $Pd(C_6H_{10}N_2O_2)Cl_2$: C, 22.56; H, 3.16; N, 8.77; Cl, 22.19. Found: C, 22.60; H, 3.22; N, 8.87; Cl, 22.52.

Preparation of Pd(H_2DMG)Cl_2 This complex was prepared in the same manner as Pd(β-H_2CQD)Cl_2. Yield 60%. Anal. Calcd. for $Pd(C_4H_8N_2O_2)Cl_2$: C, 16.37; H, 2.75; N, 9.55; Cl, 24.16. Found: C, 16.34; H, 2.87; N, 9.49; Cl, 24.05.

Preparation of [Pt(γ-HCQD)(γ-H_2CQD)Cl$]_2$ Pink K_2PtCl_4 (0.32 mmol) was dissolved in 5 ml of H_2O at 60° C and 0.64 mmol of γ-H_2CQD in 10 ml of 1:1 H_2O/MeOH was added. The resulting yellow solution was then allowed to cool to room temperature. The orange-yellow product which precipitated out was filtered and air dried. Yield 60%. Anal. Calcd. for $Pt(C_{10}H_{15}N_2O_2)(C_{10}H_{16}N_2O_2)Cl$: C, 38.61;

H, 5.03; N, 9.01; Cl, 5.69. Found: C, 38.55; H, 5.14; N, 8.90; Cl, 5.22. The molecular weight determination of Pt(γ-HCQD)(γ-H_2CQD)Cl in acetone using osmometry gave 1,278 g/mol while the calculated value for dimeric Pt(γ-HCQD)(γ-H_2CQD)Cl is 1,250.2 g/mol.

Preparation of Pt(HCQD)$_2$·H_2O When an equivalent amount of NaOMe was added to [Pt(γ-HCQD)(γ-H_2CQD)Cl]$_2$ in methanol, an orange solution was obtained. After stirring for 15 minutes, it was evaporated to dryness under vacuum. The solid was dissolved in 15 ml of CH_3CN. After filtration, diethyl ether was added to precipitate out the product which was dried under vacuum overnight. Yield 60%. Anal. Calcd. for Pt($C_{10}H_{15}N_2O_2$)$_2$·H_2O: C, 39.79; H, 5.35; N, 9.28. Found: C, 39.94; H, 5.37; N, 9.23.

Preparation of Pd(HCQD)$_2$·H_2O This complex was prepared in the same manner as Pt(HCQD)$_2$·H_2O except Et_3N was used as the base and acetone was the solvent and starting with Pd(γ-H_2CQD)$_2Cl_2$. After stirring for 15 minutes, the solution was evaporated to dryness. The orange solid was washed with hot H_2O, filtered and then washed again with acetone and methanol. It was then dried under vacuum. Yield 70%. Anal. Calcd. for Pd($C_{10}H_{15}N_2O_2$)$_2$·H_2O: C, 46.64; H, 6.28; N, 10.88. Found: C, 46.88; H, 6.36; N, 10.83.

RESULTS AND DISCUSSION

Camphorquinonedioxime ligands, H_2CQD The four isomers of H_2CQD were first prepared by Forster.[14] However, not until 1967 when Daniel and Pavia[15] conducted ^1H NMR studies on these isomers were their structures established. Our X-ray structural study[16] of γ-H_2CQD also indicated that it has the syn structure. A computer-generated perspective view of γ-H_2CQD is shown in Figure 2 in which the oxime O atoms are directed towards each other.

The IR spectrum of γ-H_2CQD in a KBr pellet gives three bands of medium intensity at 1600, 1640, and 1540 cm^{-1}. In $CHCl_3$ solution, only the band at 1600 cm^{-1} is observed, plus two other intense bands at 960 and 980 cm^{-1}. These latter two bands are assigned as N-O stretching vibrations. Deuterium substitution of the oxime protons causes the 1640 and 1540 cm^{-1} bands to decrease in intensity and two new bands to appear at 1150 and 1090 cm^{-1}, respectively. They are probably associated with the OH deformation vibration of the N-OH.[17] Therefore, we assign the band at 1600 cm^{-1} to a C=N stretching vibration.

The $CHCl_3$ solution IR spectra of α- and δ-H_2CQD give $\nu(C{=}N)$ absorptions at 1655, 1600 cm^{-1} and 1670, 1605 cm^{-1}, respectively, in good agreement with those reported by Nakamura et. al.[9] Finally, the $\nu(C{=}N)$ absorptions of

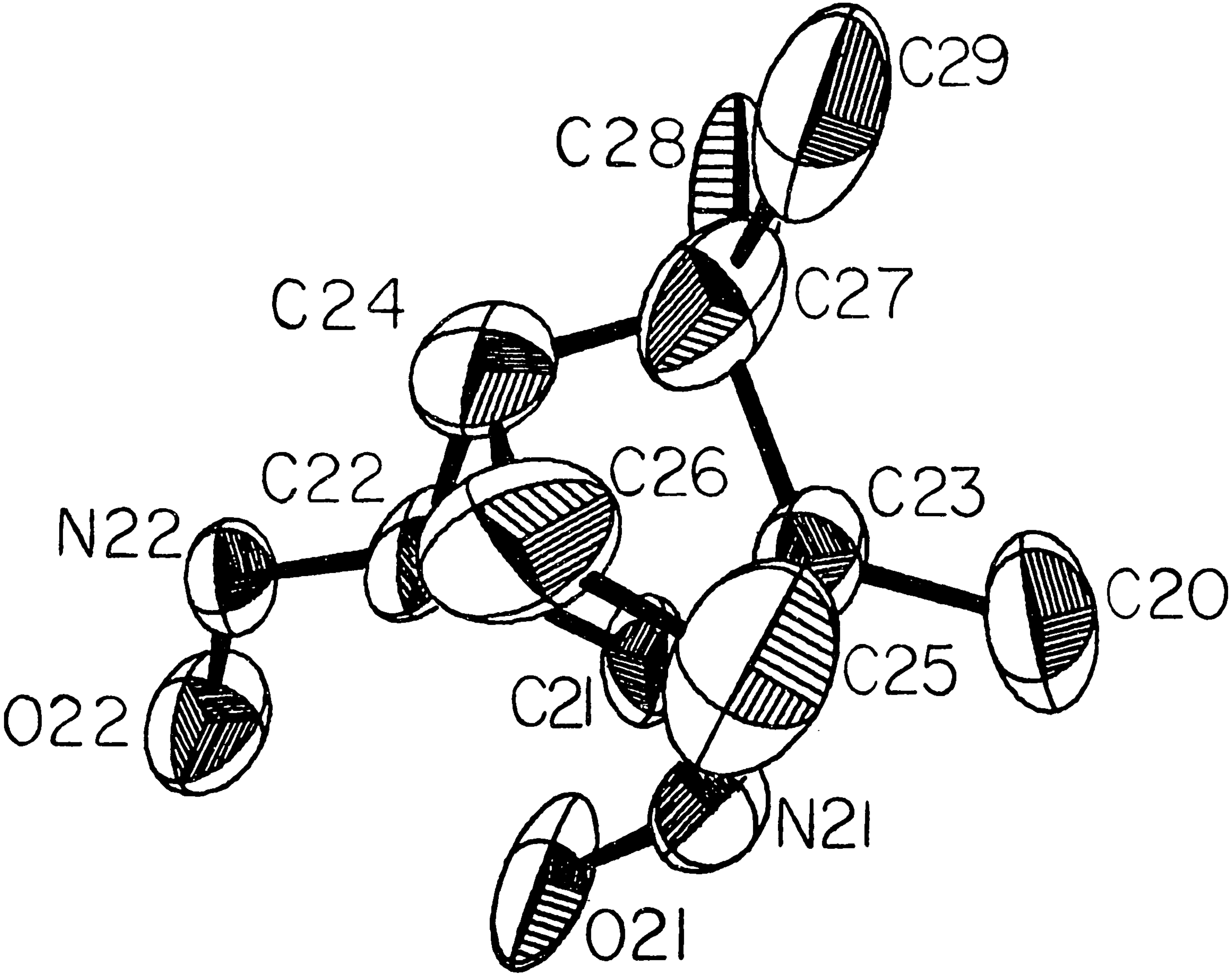
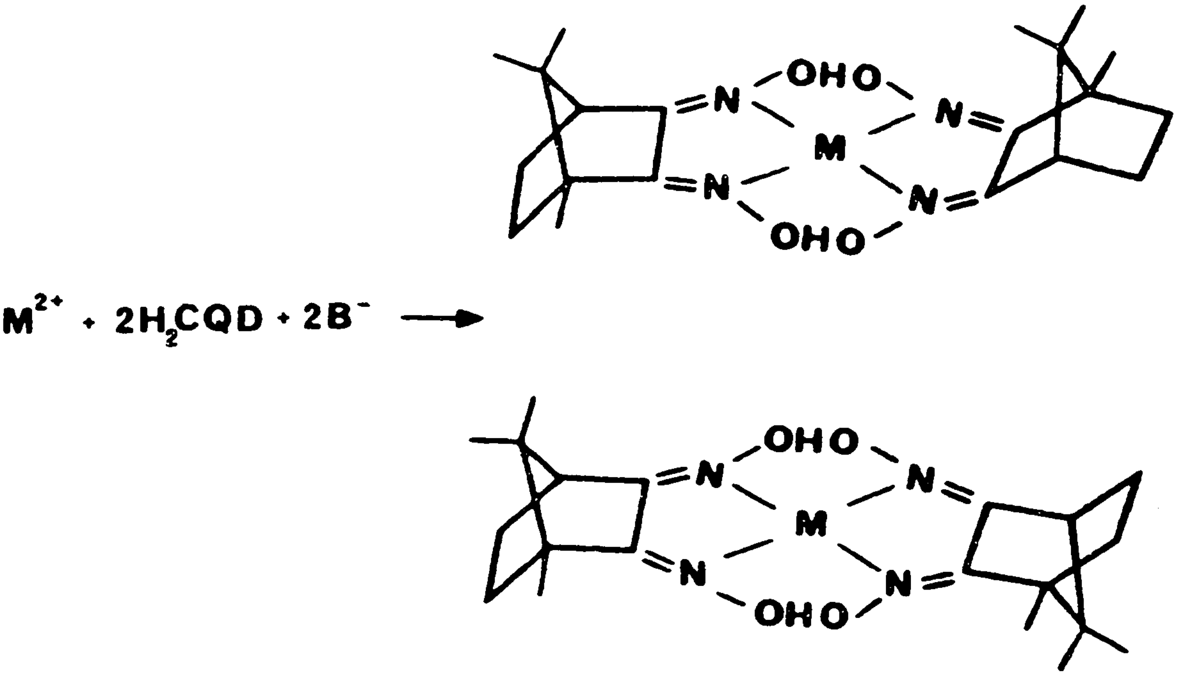


Figure 2. Computer generated perspective view of γ-H_2CQD.

β-H_2CQD are not readily observed due to extensive H-bonding which broadens the region between 1600-1700 cm^{-1}. However, substituting deuterium for the oxime protons causes the disappearance of the broad band at 1600 cm^{-1} and reveals two bands of medium intensity at 1670 and 1615 cm^{-1}. They are therefore assigned as the ν(C=N) absorptions. The N-O vibrations of β-, α-, and δ-H_2CQD are generally observed between 900-1100 cm^{-1}[18] as intense bands.

Bis(β-Camphorquinonedioximato)Cu(II)·H_2O·1/2 dioxane, Cu(β-HCQD)$_2$·H_2O·1/2 dioxane H_2CQD might be expected to react with metal ions in the presence of base according to equation 1:



Two isomeric products are possible. When Cu(OAc)$_2$·H_2O was reacted with γ-H_2CQD in MeOH, only a dark brown product,

$Cu(\beta\text{-HCQD})_2 \cdot H_2O \cdot 1/2$ dioxane, was obtained. The IR spectrum of the complex exhibits $\nu(C{=}N)$ absorptions at 1610 and 1560 cm^{-1} as was previously found for $Cu(HDMG)_2$[19,20] and $Cu(HCHD)_2$[21]; this suggests that the $HCQD^-$ ligand is N,N-coordinated to Cu(II). Further evidence for square planar N,N-coordination comes from the ESR spectrum shown in Figure 3. By analogy with results reported by Wiersema and Windle[22] for $Cu(HDMG)_2$, $Cu(\beta\text{-HCQD})_2$ should have four lines due to copper (Cu^{63}, Cu^{65}, I=3/2) nuclear hyperfine interaction plus extra lines due to nitrogen (N^{14}, I=1) hyperfine interactions which can be accounted for as nine nitrogen hyperfine lines per line of copper. Because of line broadening on the low field side of the spectrum, they are not readily observed; however, nitrogen hyperfine splitting is observed on the high field side. The $CHCl_3$ solution spectrum (Figure 3) of $Cu(\beta\text{-HCQD})_2$ is nearly identical to that of $Cu(HDMG)_2$.[22] Although $Cu(HDMG)_2$ is known to exist as a dimer[23] in the solid state, little is known about the structure of solid $Cu(\beta\text{-HCQD})_2 \cdot H_2O \cdot 1/2$ dioxane; however, the presence of H_2O and dioxane seems to be important for the formation of crystals. Its UV-VIS spectrum in $CHCl_3$ gives a broad absorption band with a maximum at 445 nm ($E = 7.9 \times 10^3$ $cm^{-1}M^{-1}$) most likely due to a d-d transition while its charge transfer band is observed at 266 nm, comparable to that of $Cu(HDMG)_2$.[24]

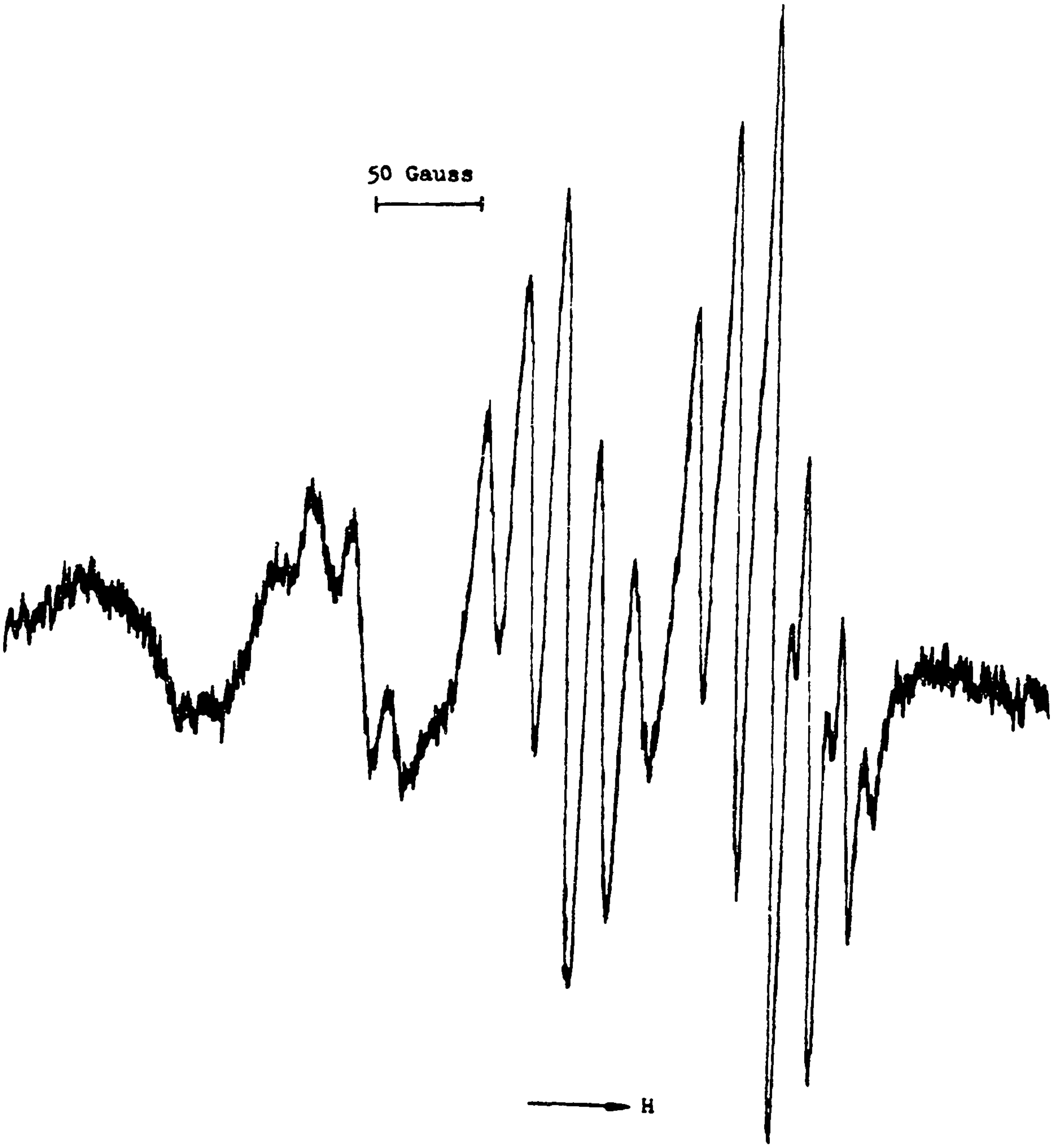


Figure 3. ESR spectrum of Cu(β-HCQD)$_2$ in CHCl$_3$ at room temperature recorded on a Varian E-3 ESR spectrometer. g value = 2.08 measured by comparison with perylene radical cation.

(β-Camphorquinonedioxime)Cu(II)Cl_2, Cu(β-H_2CQD)Cl_2

This complex can be prepared by reacting $CuCl_2$ with γ-H_2CQD in the absence of added base in absolute EtOH. Unlike Cu(H_2DMG)Cl_2, it is very stable in air. Svedung[25] reported that the structure of Cu(H_2DMG)Cl_2 consists of double chains of Cu(H_2DMG)Cl_2 dimers linked together by intermolecular O-H-O bonds. Since Cu(β-H_2CQD)Cl_2 has an IR spectrum very similar to that of Cu(H_2DMG)Cl_2, we believe that it probably has a similar dimeric structure as shown in Figure 4. The two molecules are bridged by Cl atoms, and the structure is probably further stabilized by intramolecular O-H-Cl bonding.

The intense IR band at 1450 cm^{-1}, presumably due to the ν(C=N) absorption, was observed in Cu(H_2DMG)Cl_2 and is also observed in similar Pt(II) and Pd(II) compounds (see below). Svedung was unable to account for such a low frequency for a ν(C=N) vibration, although Mikhelson and Evtushenko[19] assigned it to the ν(C=N) vibrational mode.

Bis(δ-Camphorquinonedioximato)Ni(II), Ni(δ-HCQD)$_2$

This brown complex was prepared by addition of NaOMe to a methanol solution of $Ni(NO_3)_2 \cdot 6H_2O$ and γ-H_2CQD. Our earlier single crystal X-ray structural study[6] established that the ligand forms a 6-membered chelate ring by coordinating to the Ni through the N and O atoms in a trans manner as shown in Figure 5.

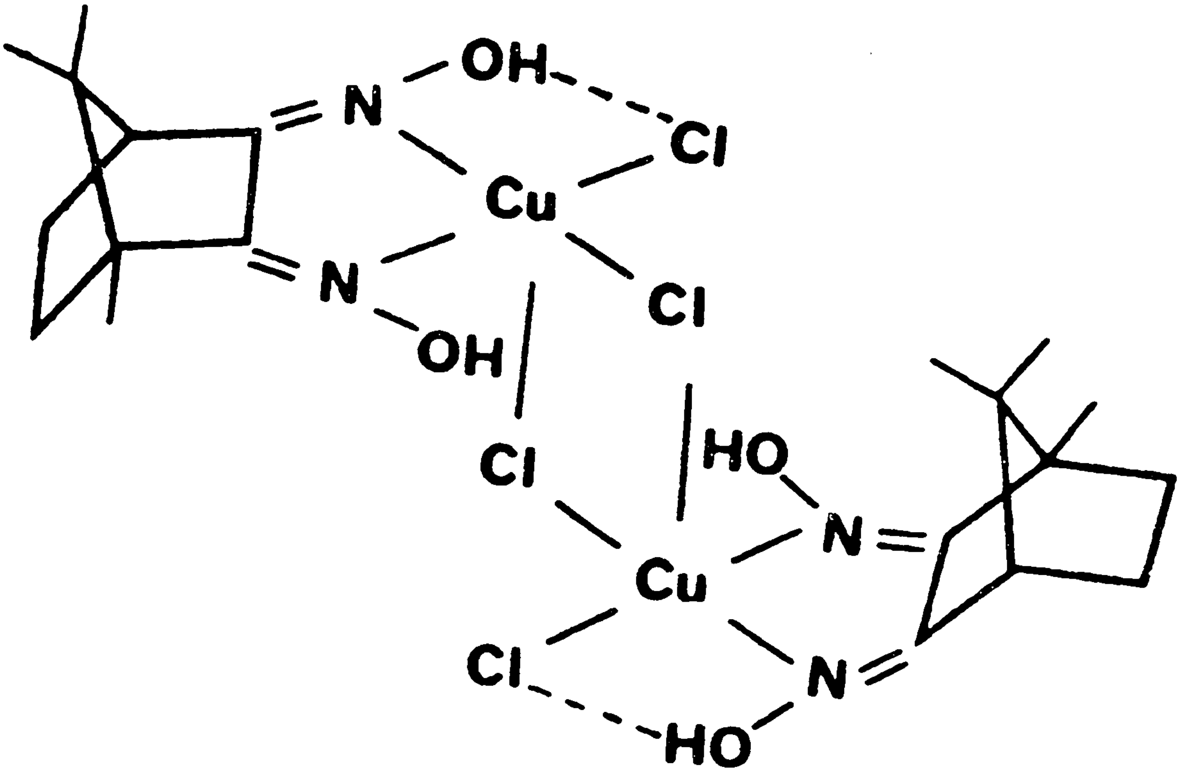


Figure 4. Cu(β-H_2CQD)Cl_2 dimer.

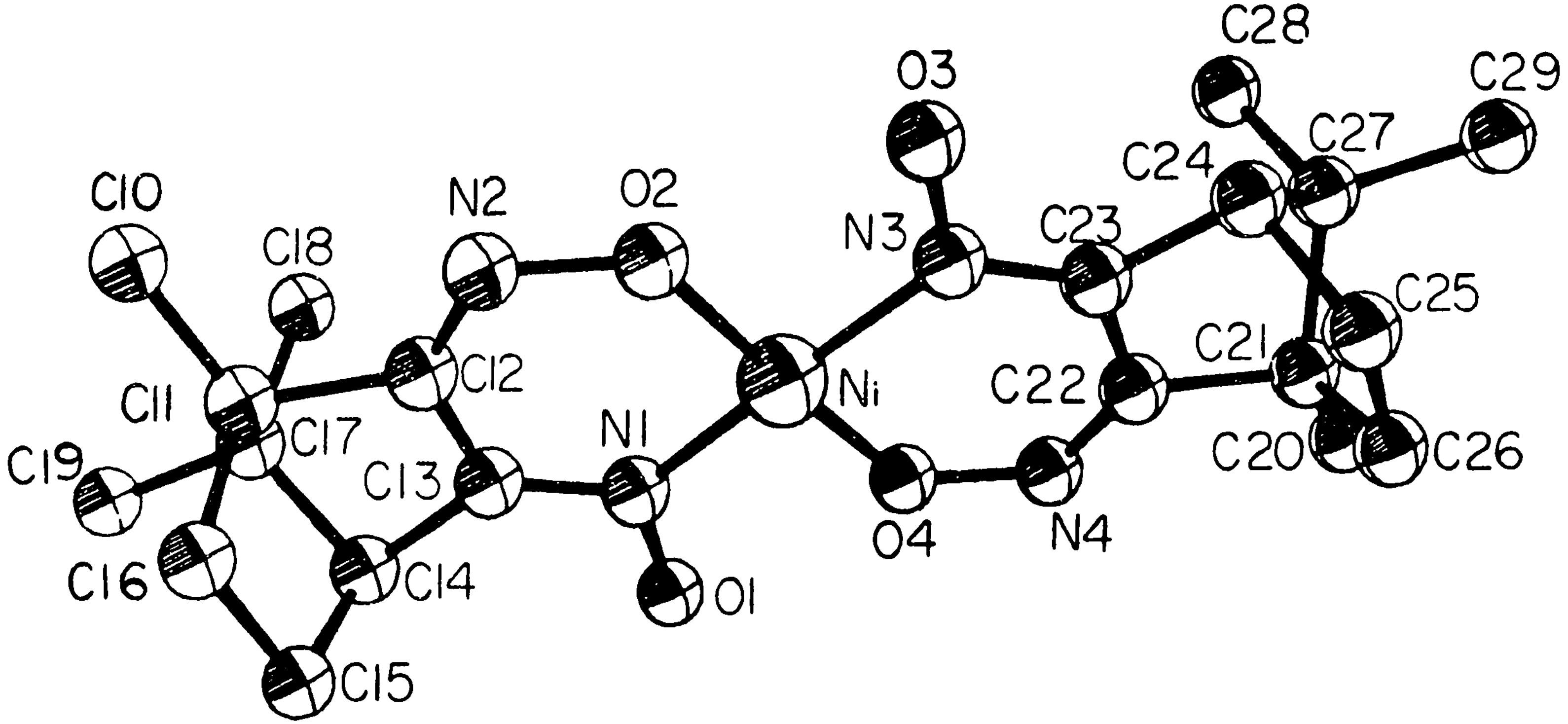


Figure 5. Computer generated perspective view of Ni(δ-HCQD)$_2$.

The reason for this unusual coordination is believed to be the bicyclic nature of the ligand which increases the C-C-N angles in the chelate ring to the point where formation of a larger ring by N,O rather than N,N coordination becomes more favorable. The IR spectrum of $Ni(\delta\text{-}HCQD)_2$ shows an absorption band of medium intensity at 1690 cm^{-1}. Deuterium substitution studies indicate that this absorption is not associated with the OH group but presumably arises from a vibration which has considerable C=N stretching character. The other $\nu(C{=}N)$ absorption occurs at 1560 cm^{-1}.

Bis(α-Camphorquinonedioximato)Ni(II), $Ni(\alpha\text{-}HCQD)_2$ This green complex was prepared by adding $\alpha\text{-}H_2CQD$ to a methanol solution of $Ni(OAc)_2\cdot 4H_2O$. It also probably has trans-N,O coordination around the Ni as in the case of $Ni(\delta\text{-}HCQD)_2$. This assumption is supported by the presence of two different $\nu(C{=}N)$ absorptions at 1675 and 1560 cm^{-1} in the IR spectrum. In a recent paper, Nakamura et al.[9] reported the preparation of the same Ni(II) and Pd(II) complexes of $HCQD^-$. Our spectral data for $Ni(\delta\text{-}HCQD)_2$ and $Ni(\alpha\text{-}HCQD)_2$ were in good agreement with theirs.

Although the coordination around Ni is very similar in both $Ni(\alpha\text{-}HCQD)_2$ and $Ni(\delta\text{-}HCQD)_2$ complexes, $Ni(\alpha\text{-}HCQD)_2$ is observed to be less stable. Recrystallization of

Ni(α-HCQD)$_2$ in boiling (1:3:1) $CHCl_3$/MeOH/H_2O partially converts Ni(α-HCQD)$_2$ into Ni(δ-HCQD)$_2$. It is possible that the repulsion of the oxime O with the bridgehead methyl (see structure of α-H_2CQD) destabilizes the Ni(α-HCQD)$_2$ complex relative to that of Ni(δ-HCQD)$_2$.

The mixed ligand complex Ni(α-HCQD)(δ-HCQD) has not been isolated; nor has any Ni complex with cis N,O coordination (Figure 6) around Ni been detected. Such a complex would presumably be less stable due to the lack of hydrogen bonding which is present in the other Ni complex. Also in the reaction of Ni(II) with β-H_2CQD, only Ni(δ-HCQD)$_2$ was isolated.

^{1}H NMR spectra of Ni(δ-HCQD)$_2$ and Ni(α-HCQD)$_2$ are summarized in Table I. The chemical shifts of the methyl proton signals in each complex are very close to those of the free ligands (Table I). The oxime protons are downfield at 10.94 and 11.10 ppm, respectively.

The UV-VIS spectra of the two complexes (Figure 7) are almost identical; their absorption maxima and ϵ values are summarized in Table II.

Bis(δ-Camphorquinonedioximato)-bis(δ-camphorquinonedioxime)Ni(II), Ni(δ-HCQD)$_2$(δ-H_2CQD)$_2$ This unstable complex was prepared using a 3 to 1 ratio of γ-H_2CQD to $Ni(NO_3)_2 \cdot 6H_2O$ and crystallized from anhydrous CH_3CN at -25° C. Once the

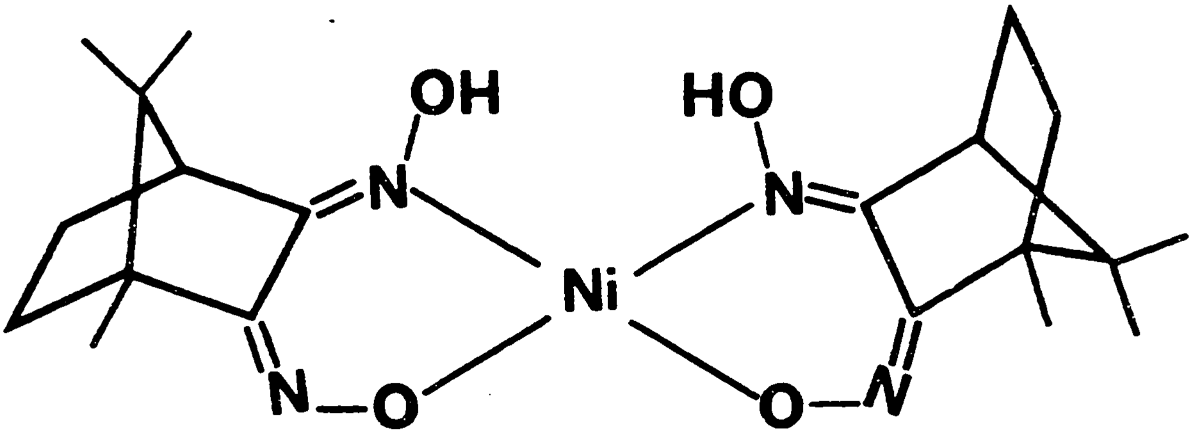


Figure 6. Cis isomer of Ni(δ-HCQD)$_2$.

Table I. ^1H NMR spectra of $M(HCQD)_2$ complex

Complex	Solvent	O-H	C_4-H	Methyl-H					
Ni(α-HCQD)$_2$	-[a]	11.10[b]	2.62	0.88		0.90			1.39[c]
	-[d]	e	2.62	0.88		0.94			1.39
Ni(δ-HCQD)$_2$	-[a]	10.94[b]	3.20	0.82		0.96			1.12[c]
	-[d]	e	3.20	0.82			1.00		1.12
Ni(δ-HCQD)$_2$(δ-H_2CQD)$_2$	-[d]	e	3.25	0.82	0.86	0.96	1.01	1.09	1.12
δ-H_2CQD	-[d]	e	3.10		0.86		1.01	1.09[c]	
Pd(β-HCQD)$_2$	-[a]	12.35[f]	2.90	0.82			1.00		1.38[c]
Pd(δ-HCQD)$_2$	d_6-DMSO	e	3.24	0.80		0.95			1.12[c]
Pt(β-HCQD)$_2$	-[a]	12.56[f]	3.0	0.82		0.98			1.42[c]

[a] d-$CHCl_3$.

[b] Sharp singlet.

[c] C_{10}-Methyl.

[d] d_6-acetone.

[e] Not observed.

[f] Broad and asymmetrical.

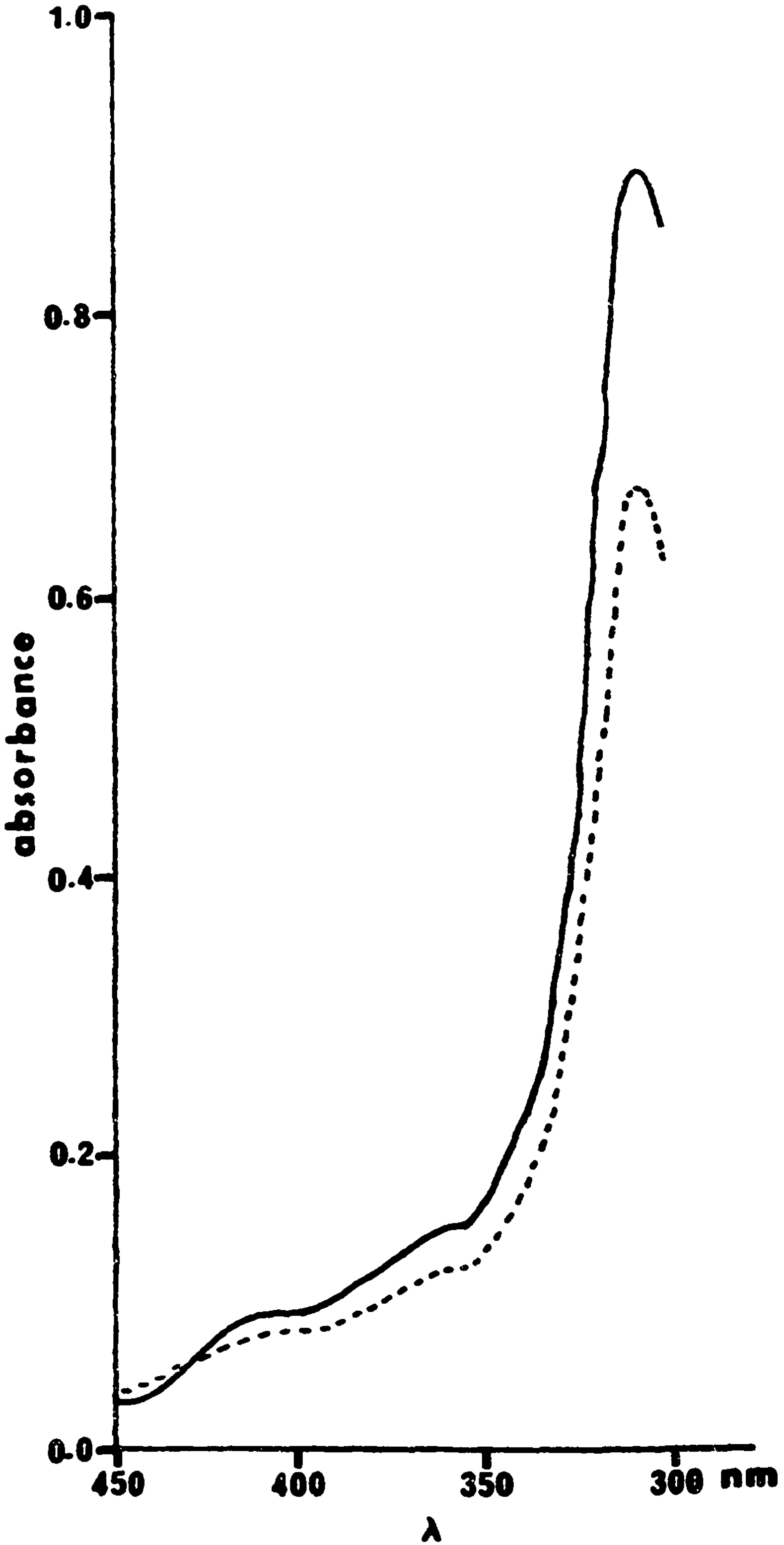


Figure 7. UV-visible spectra of Ni(δ-HCQD)$_2$ (———) and Ni(α-HCQD)$_2$ (-----) in CHCl$_3$.

Table II. UV-Visible spectra of Ni complexes

Complex	λ max.(nm)	ε($cm^{-1}M^{-1}$)
Ni(δ-HCQD)$_2$[a]	576	3.5 X 10
	413 sh[b]	1.6 X 10^3
	360 sh	3.3 X 10^3
	308	1.8 X 10^4
Ni(α-HCQD)$_2$[a]	576	3.3 X 10
	405 sh	8.8 X 10^2
	359 sh	1.6 X 10^3
	306	1.3 X 10^4
Ni(δ-H_2CQD)$_2$(δ-HCQD)$_2$[c]	413	
	359	
	304	

[a] In $CHCl_3$.

[b] Shoulder.

[c] As KBr pellet.

complex crystallized out, further attempts to recrystallize it led only to Ni(δ-HCQD)$_2$.

Proton NMR studies established that all four ligands in Ni(δ-HCQD)$_2$(δ-H_2CQD)$_2$ have the δ- structure. In d_6-acetone, 6 methyl proton signals of equal intensity are observed (Table I). The signals at 0.86, 1.01, 1.09 ppm can be assigned to the free δ-H_2CQD ligand while those at 0.82, 0.96, 1.12 ppm belong to Ni(δ-HCQD)$_2$. The entire ^{1}H NMR spectrum can be reproduced by mixing a 1:2 ratio of Ni(δ-HCQD)$_2$ and δ-H$_2$CQD in d$_6$-acetone. This result implies that Ni(δ-HCQD)$_2$(δ-H$_2$CQD)$_2$ exists as Ni(δ-HCQD)$_2$ and δ-H$_2$CQD in solution, which is consistent with the fact that recrystallization of the complex gives only Ni(δ-HCQD)$_2$.

The observation of ν(C=N) absorptions of the free ligand at 1670 and 1605 cm^{-1} and of Ni(δ-HCQD)$_2$ at 1690 and 1560 cm^{-1} in the IR spectrum of Ni(δ-HCQD)$_2$(δ-H$_2$CQD)$_2$ in CHCl$_3$ solvent further supports the presence of these species in solution. However, the IR spectrum of the solid complex in KBr gives only a medium intense band with slight splittings at 1565 cm^{-1} which can be assigned to ν(C=N) of N-coordinated oxime. A weak band is observed at 1690 cm^{-1} which is due to the O-coordinated ν(C=N). The difference in the solution and solid state IR spectra implies that in the crystalline state, all four ligands are coordinated to the metal; the structure is probably stabilized by hydrogen bonding as indicated by the intense absorption band between 3260-3100 cm^{-1}[26] in the solid state IR spectrum.

The UV-VIS absorption spectrum (Figure 8) of the solid complex pressed into a KBr pellet is very similar to solution spectra of Ni(δ-HCQD)$_2$ and Ni(α-HCQD)$_2$. Such a similarity suggests that there are also two N and two O donor groups in the coordination sphere of Ni(δ-HCQD)$_2$-(δ-H$_2$CQD)$_2$. Steric considerations favor a trans arrangement

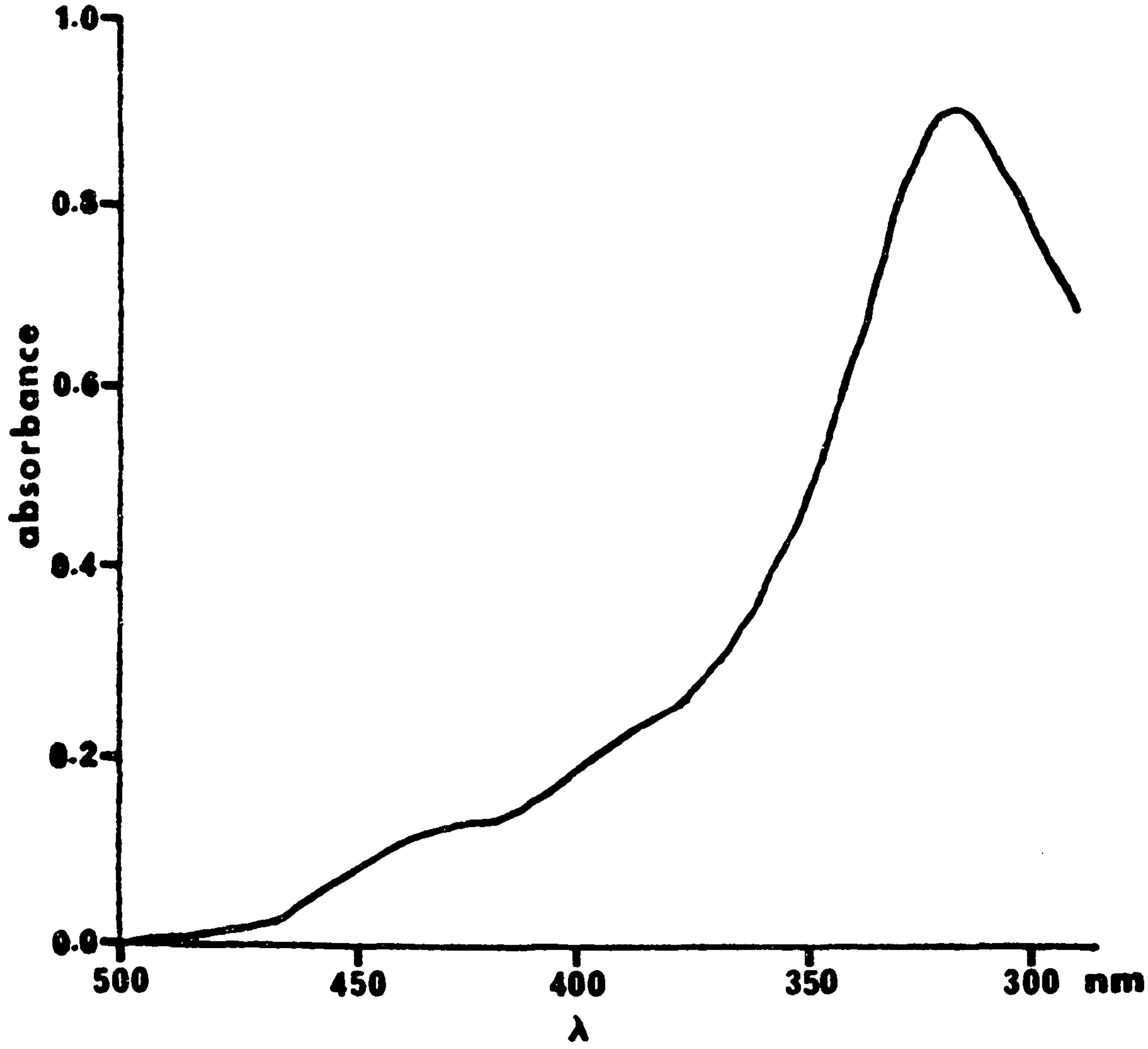


Figure 8. UV-visible spectrum of $Ni(\delta\text{-}H_2CQD)_2(\delta\text{-}HCQD)_2$ as KBr pellet.

of these donors around the Ni as shown in Figure 9. This structure is consistent with a facile solution dissociation of two δ-H_2CQD ligands followed by ring closure of the δ-$HCQD^-$ ligands to give Ni(δ-HCQD)$_2$.

Bis(β-Camphorquinonedioximato)Pd(II), Pd(β-HCQD)$_2$ The yellow complex, Pd(β-HCQD)$_2$ was prepared in H_2O/MeOH/$CHCl_3$ (1:3:1) from Pd(PhCN)$_2$Cl$_2$, β-H_2CQD and NaOMe. This is a different method from the one reported by Nakamura, et al.[9] and the product is believed to be a mixture of two isomers with structures shown in equation 1.

The IR spectrum of the complex clearly indicates N,N chelation of the ligands around the Pd atom. The ν(C=N) band appears at 1550 cm^{-1}, and the H-bonded ν(OH) absorption at 2380 cm^{-1} is comparable to the reported value for Pd(HCHD)$_2$.[21] The UV-VIS absorption spectrum exhibits a shoulder at 362 nm ($\epsilon = 2.0 \times 10^3$ cm^{-1}M^{-1}) and a charge transfer band at 274 nm ($\epsilon = 1.4 \times 10^4$ cm^{-1}M^{-1}).

In its ^{1}H NMR spectrum (Table I) taken in d-$CHCl_3$, the oxime proton with a chemical shift of 12.35 ppm downfield from TMS is observed as a broad asymmetric peak. Although Marov et al.[27] who studied the H-bonding of Ni(II) α-dioximates by ^{1}H NMR suggested that an asymmetric peak indicates the presence of isomers, there is no

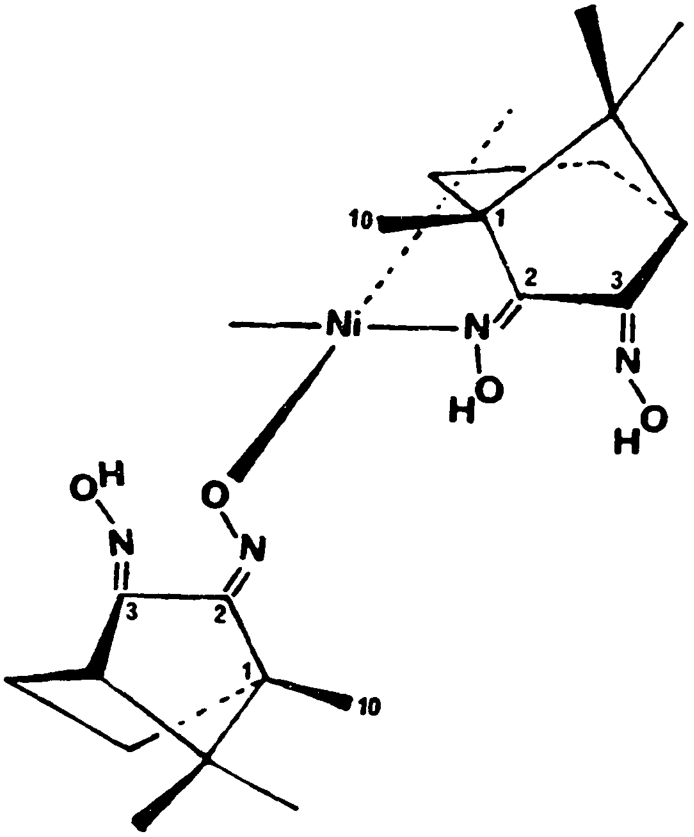


Figure 9. Ni(δ-H_2CQD)$_2$(δ-HCQD)$_2$ square planar coordination with trans N_2O_2. Two other ligands are omitted for clarity.

independent evidence for their presence in this system. However, a ^{13}C NMR study by Nakamura et al.[9] has shown that isomers are indeed present in this complex.

Bis(δ-Camphorquinonedioximato)Pd(II), Pd(δ-HCQD)$_2$ Yellow crystals of Pd(δ-HCQD)$_2$ could be obtained by reacting Pd(PhCN)$_2$Cl$_2$ with δ-H$_2$CQD in MeOH in the presence of Et$_3$N. This procedure is different from the one reported by Nakamura et al.[9] and gave crystals of Pd(δ-H$_2$CQD)$_2$ so that elemental analyses and ^1H NMR spectrum of the complex could be obtained.

It is believed to have the same N,O-coordinated structure as Ni(δ-HCQD)$_2$ because its ^1H NMR spectrum (Table I) in d$_6$-DMSO is almost identical to that of Ni(δ-HCQD)$_2$. Its IR absorptions appear at 1560 and 1620 cm^{-1} corresponding to the N-coordinated and O-coordinated oxime ν(C=N) frequencies, respectively. Free ν(OH) and H-bonded ν(OH) are observed at 3400 and 2600 cm^{-1}, respectively.

Bis(β-Camphorquinonedioximato)Pt(II), Pt(β-HCQD)$_2$ This complex was prepared by reacting Pt(PhCN)$_2$Cl$_2$ with NaOMe and β-H$_2$CQD in a 1:3:1 CHCl$_3$/MeOH/H$_2$O solution. The brown crystalline product has the structures shown in equation 1. The UV-VIS spectrum unequivocally established N,N-coordination of the β-HCQD$^-$ ligands by comparison with spectra of Pt(HDMG)$_2$[28] and Pt(HCHD)$_2$. Maxima for Pt(β-HCQD)$_2$ occur at 411 nm (ϵ = 1.3 X 10^3 cm^{-1}M^{-1}) and 340 nm (ϵ = 4.0 X 10^3 cm^{-1}M^{-1}). Absorptions at 305 nm (ϵ = 1.09 X 10^4 cm^{-1}M^{-1}) and 273 nm (1.14 X 10^4 cm^{-1}M^{-1}) are probably charge transfer bands. In the IR spectrum, the ν(C=N) absorption appears at 1570 cm^{-1} as a broad but intense band, and H-bonded ν(OH) bands at 3400 and 2380 cm^{-1} are observed. Its ^{1}H NMR spectrum (Table I) resembles that of Pd(β-HCQD)$_2$ showing an asymmetric peak for the oxime protons at 12.56 ppm possibly indicating the presence of both isomers (eq. 1).

Trans-Bis(γ-Camphorquinonedioxime)PdCl$_2$, trans-Pd(γ-H$_2$CQD)$_2$Cl$_2$ A CHCl$_3$ solution of Pd(PhCN)$_2$Cl$_2$ in the presence of γ-H$_2$CQD gives large yellow needlelike crystals of Pd(γ-H$_2$CQD)$_2$Cl$_2$. Spectra and a conductivity measurement on this complex suggest that the γ-H$_2$CQD ligands are monodentate and coordinate to the Pd in positions trans to each other. The trans geometry is supported by the presence of only one Pd-Cl absorption band at 345 cm^{-1} in the IR spectrum of the complex in KBr. By comparing its IR spectrum with that of the free ligand, the coordinated oxime ν(C=N) vibration may be assigned to the band at 1535 cm^{-1} while the uncoordinated oxime ν(C=N) is at 1615 cm^{-1} (Table III). The ^{1}H NMR spectrum of Pd(γ-H$_2$CQD)$_2$Cl$_2$

Table III. IR[a] absorption frequencies (cm^{-1}) of metal H_2CQD dichloride complexes

Complex	$\nu(C{=}N{\rightarrow}M)$[b]	$\nu(C{=}N)$[c]	$\nu(M{-}Cl)$
$Pd(\gamma\text{-}H_2CQD)_2Cl_2$	1535	1615	345
$Pd(\delta\text{-}H_2CQD)_2Cl_2$	1555	1680	300-350[d]
$Pd(\alpha\text{-}H_2CQD)_2Cl_2$	1560	1680	300-350[d]
$[Pt(\gamma\text{-}H_2CQD)(\gamma\text{-}HCQD)Cl]_2$	1560	1610	330

[a] As KBr pellet

[b] Coordinated $\nu(C{=}N)$

[c] Uncoordinated $\nu(C{=}N)$

[d] Several $\nu(M{-}Cl)$ are observed in this region

is summarized in Table IV. The presence of other isomers is not observed. The downfield shift of the C_4-H from 2.65 ppm of the free ligand to 4.34 ppm of the complex seems to indicate that coordination through the N-atom of the C_3-oxime is more favorable. Although coordination at the C_2-N (Figure 10) is possible, this position is less favorable because of the steric interaction of the remainder of the metal complex with the C_{10}-methyl group. Attempts to make $Pd(\beta\text{-}HCQD)_2$ out of $Pd(\gamma\text{-}H_2CQD)_2Cl_2$ in methanol by adding an equivalent amount of base led to the formation of $Pd(HCQD)_2{\cdot}H_2O$, an orange solid of unknown structure

Table IV. ^{1}H NMR of metal camphorquinonedioxime (H_2CQD)dichloride complexes

Complex	Solvent	Methyl-H				
Pd(γ-H_2CQD)$_2$Cl$_2$	d_6-acetone	0.92	1.1	1.12		
	d_6-DMSO	0.76	0.91	1.02		
γ-H_2CQD	d_6-DMSO	0.76	0.91	1.02		
Pd(α-H_2CQD)$_2$Cl$_2$	d-MeOH/d_6-acetone	0.92	0.95	1.02	1.41	
	d_6-DMSO	0.84	1.33			
α-H_2CQD	d_6-DMSO	0.84	1.33			
Pd(δ-H_2CQD)$_2$Cl$_2$	d-MeOH/d_6-acetone	0.84	0.87	0.98	1.06	
	d_6-DMSO	0.74	0.88	0.98		
δ-H_2CQD	d_6-DMSO	0.74	0.88	0.98		
Pd(β-H_2CQD)Cl$_2$	d_3-CH_3CN	0.98	1.04	1.34		
	d_6-DMSO	0.84	0.90	0.94	1.30	1.34
β-H_2CQD	d_6-DMSO	0.83			1.31	
[Pt(γ-HCQD)(γ-H_2CQD)Cl]$_2$	d_6-acetone	0.90	1.00	1.07	1.10	1.12
	d_6-DMSO	0.74	0.90	0.98	1.04	

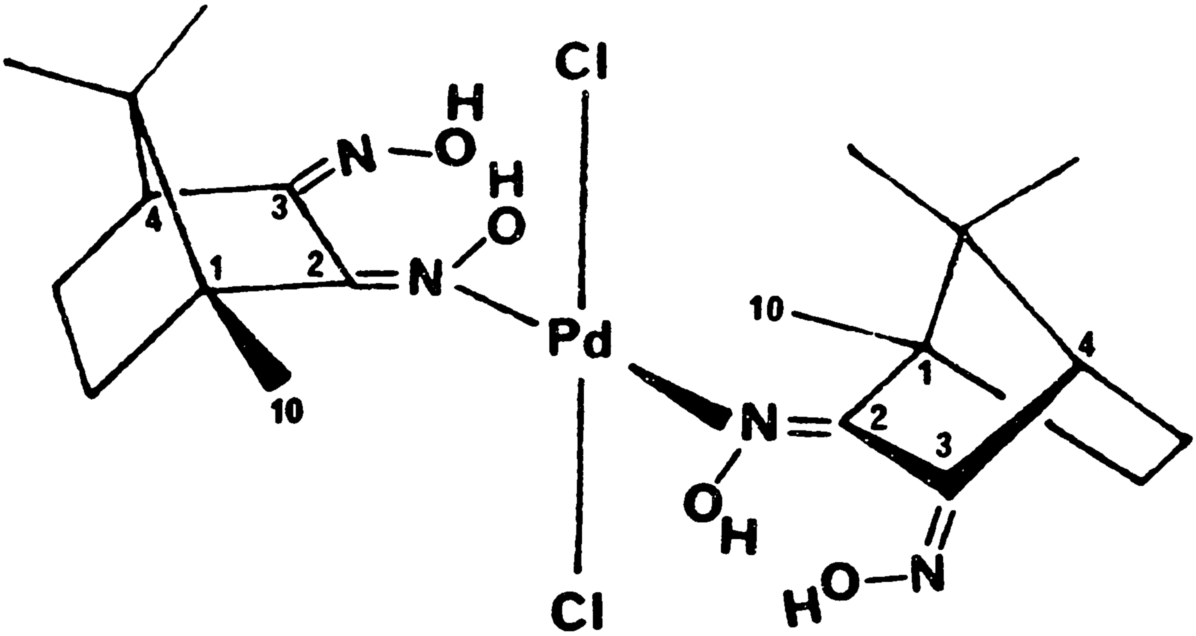


Figure 10. Trans-Pd(γ-H_2CQD)$_2$$Cl_2$.

insoluble in common organic solvents such as $CHCl_3$, methanol or H_2O.

When a strongly coordinating solvent such as DMSO is added to a MeOH solution of the complex, DMSO displaces the γ-H_2CQD ligands which were identified by their characteristic ^1H NMR spectrum (Table IV).

Bis(δ-Camphorquinonedioxime)$PdCl_2$, Pd(δ-H_2CQD)$_2Cl_2$ This complex prepared in the same way as Pd(γ-H_2CQD)$_2Cl_2$ may exist as a mixture of cis and trans isomers as indicated by several ν(Pd-Cl) bands between 300-350 cm^{-1} in its IR spectrum (Table III). A possible structure of Pd(δ-H_2CQD)$_2Cl_2$ is shown in Figure 11. The coordinated and uncoordinated oxime C=N absorption bands appear at 1555 and 1680 cm^{-1}, respectively. The complex is slightly soluble in acetone, and its ^1H NMR spectrum exhibits four methyl proton signals (Table IV) consistent with the assumption that more than one isomer is present. When excess DMSO is added to a solution of the complex, the free δ-H_2CQD is regenerated.

Bis(α-Camphorquinonedioxime)$PdCl_2$, Pd(α-H_2CQD)$_2Cl_2$ Pd(α-H_2CQD)$_2Cl_2$ can be prepared in a manner similar to that of Pd(δ-H_2CQD)$_2Cl_2$ and probably exists as cis and trans isomers. Its possible structure is shown in Figure 12. Its ^1H NMR and IR spectra are summarized in Tables III and IV.

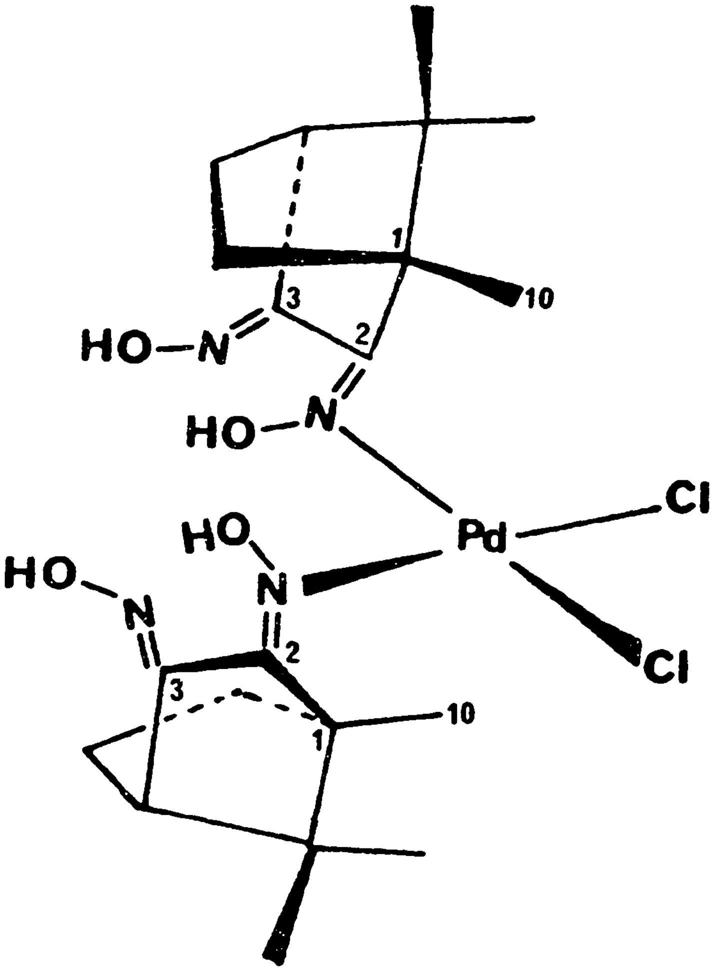


Figure 11. Cis-Pd(δ-$H_2CQD)_2Cl_2$.

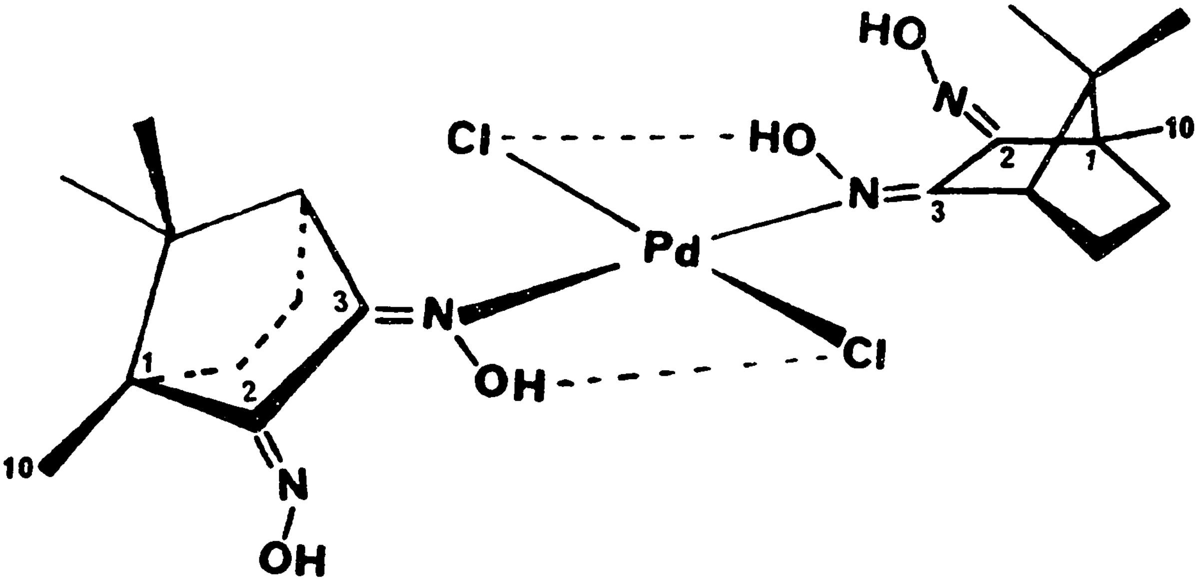


Figure 12. Trans-Pd(α-H_2CQD)$_2$$Cl_2$.

Four methyl proton signals appear at 0.92, 0.95, 1.02 and 1.41 ppm. Coordinated and uncoordinated ν(C=N) are observed at 1560 and 1680 cm^{-1}, respectively. Since the ligand coordinates through its less sterically hindered oxime-N, intramolecular H-bonding is possible between the Cl atoms and the ligands, as shown in the trans complex (Figure 12).

Bis(β-Camphorquinonedioxime)PdCl$_2$, Pd(β-H$_2$CQD)Cl$_2$ When a CH$_3$CN solution of Pd(γ-H$_2$CQD)$_2$Cl$_2$ was allowed to stand for a period of 1-2 weeks at room temperature, Pd(β-H$_2$CQD)Cl$_2$ began to crystallize out. In this reaction, the γ-H$_2$CQD ligand is transformed into the β-isomer. A nearly quantitative yield of the Pd(β-H$_2$CQD)Cl$_2$ complex can be obtained by direct reaction between the ligand and Pd(PhCN)$_2$Cl$_2$.

As in the case of Cu(β-H$_2$CQD)Cl$_2$, an intense, sharp band at 1430 cm^{-1} may be assigned to the ν(C=N) frequency. Sharp bands of medium intensity also appear at 3270 and 3220 cm^{-1} corresponding to intermolecular and intramolecular H-bonding,[25] respectively. The similarity of their IR spectra (Table V) implies that Pd(β-H$_2$CQD)Cl$_2$ and Cu(β-H$_2$CQD)Cl$_2$ have similar square planar structures with possible intermolecular bridging as suggested in Figure 4.

Table V. IR[a] absorption frequencies (cm^{-1}) of $M(dioxime)Cl_2$ complexes

Complex	ν(C=N)	ν(OH)	ν(M-Cl)
$Cu(H_2DMG)Cl_2$	1400	3310, 3220	
$Cu(\beta\text{-}H_2CQD)Cl_2$	1450	3310, 3260	
$Pd(\beta\text{-}H_2CQD)Cl_2$	1430	3270, 3220	350, 325
$Pt(\beta\text{-}H_2CQD)Cl_2$	1440	3300, 3260	345, 320
$Pd(H_2DMG)Cl_2$	1400	3300, 3200	350, 310
$Pd(H_2CHD)Cl_2$	1400	3300, 3230	350, 310

[a] As KBr pellet.

The β-H_2CQD ligand is not displaced when the complex is dissolved in DMSO, but formation of other Pd complexes occurs as indicated by the appearance of new signals in the ^1H NMR spectrum (Table IV).

The method for the preparation of $Pd(\beta\text{-}H_2CQD)Cl_2$ can also be used to prepare $Pd(H_2CHD)Cl_2$, and $Pd(H_2DMG)Cl_2$, all having the same characteristic band at about 1410 cm^{-1}. The compound $Pd(H_2CHD)Cl_2$ has not been reported in the literature, but Busch et al.[29] prepared $Pd(H_2DMG)Cl_2$ by reaction of $Pd(HDMG)_2$ with acetyl chloride. Their IR spectra are summarized in Table V.

[(γ-Camphorquinonedioxime)(γ-camphorquinonedioximato)-Pt(II)Cl]$_2$, [Pt(γ-HCQD)(γ-H$_2$CQD)Cl]$_2$ This dimeric complex was prepared by the reaction of K_2PtCl_4 and γ-H$_2$CQD. A possible structure is shown in Figure 13. This particular structure requires the two ligands to be cis to each other. Steric considerations favor coordination at the less hindered oxime N. Such an arrangement also provides for substantial intramolecular H-bonding.

The absorption bands at 1560 and 1610 cm^{-1} in the IR spectrum may be assigned to the ν(C=N) vibrations of the coordinated and uncoordinated oxime groups. The broad ν(OH) absorptions at 3100 and 2800 cm^{-1} resemble those of γ-H$_2$CQD, suggesting that γ-H$_2$CQD and γ-HCQD$^-$ are present in the complex. As in the case of Pd(γ-H$_2$CQD)$_2$Cl$_2$, addition of base to a methanol solution of [Pt(γ-HCQD)(γ-H$_2$CQD)Cl]$_2$ yielded the highly insoluble complex, Pt(HCQD)$_2$·H$_2$O of unknown structure. Attempts to isolate pure Pt(α-H$_2$CQD)$_2$Cl$_2$ and Pt(δ-H$_2$CQD)$_2$Cl$_2$ were unsuccessful.

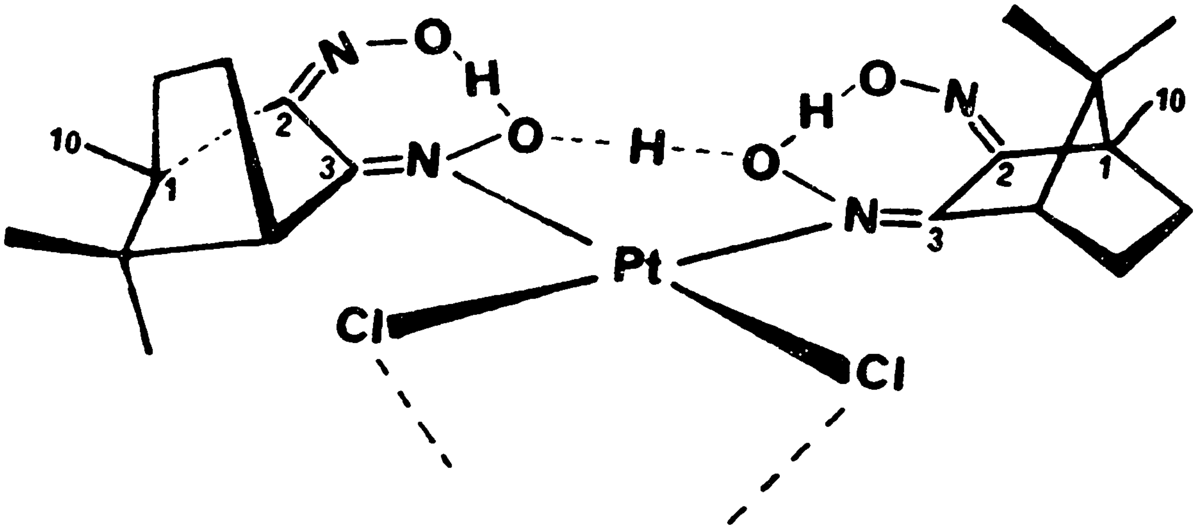


Figure 13. $[Pt(\gamma\text{-}H_2CQD)(\gamma\text{-}HCQD)Cl]_2$.

CONCLUSION

Camphorquinonedioxime has been shown to be capable of being either a bidentate or monodentate ligand. As a bidentate ligand in the complexes Ni(α-HCQD)$_2$, Ni(δ-HCQD)$_2$ and Pd(δ-HCQD)$_2$, α-HCQD$^-$ or δ-HCQD$^-$ coordinates to the metal ion via N,O chelation. This mode of coordination is characterized by the presence of both the N-coordinated and O-coordinated ν(C=N) absorptions in the IR spectrum.

In the complexes Pd(β-HCQD)$_2$, Pt(β-HCQD)$_2$ and Cu(β-HCQD)$_2$$\cdot$H$_2O\cdot$1/2 dioxane, β-HCQD$^-$ coordinates to the metal ion by N,N chelation. In this case, only N-coordinated ν(C=N) absorptions are observed in their IR spectra. The failure to obtain Ni(β-HCQD)$_2$ is believed to be due to the bicyclic nature of the ligand which increases the C-C-N angles so that formation of 5-membered chelate rings around Ni(II) becomes less favorable. This is supported by our earlier crystal structure determination of Ni(δ-HCQD)$_2$.[6] The isolation of Cu(β-HCQD)$_2$$\cdot$H$_2O\cdot$1/2 dioxane with N,N-coordination of the β-HCQD$^-$ ligand was somewhat surprising because Cu(II) has the smallest ionic radius of the four metal ions used in these studies. Therefore the strain in the chelate ring should be greatest.

This result might be understood, however, by considering the M-N bond strength in the $M(HDMG)_2$ complexes, they are reported[20] to decrease in the order Pt(II)>Pd(II)>Cu(II)>Ni(II). The higher Cu-N bond strength presumably more than compensates for the strain in the 5-membered rings of $Cu(\beta\text{-}HCQD)_2 \cdot H_2O \cdot 1/2$ dioxane.

In the complexes $Pd(\beta\text{-}H_2CQD)Cl_2$, $Pt(\beta\text{-}H_2CQD)Cl_2$ and $Cu(\beta\text{-}H_2CQD)Cl_2$, the neutral $\beta\text{-}H_2CQD$ ligand also chelates through both N atoms. This type of compound exhibits a strong infrared absorption for coordinated $\nu(C{=}N)$ between 1450-1400 cm^{-1}.

In the complexes $Pd(\gamma\text{-}H_2CQD)_2Cl_2$, $Pd(\delta\text{-}H_2CQD)_2Cl_2$ and $Pd(\alpha\text{-}H_2CQD)_2Cl_2$, the H_2CQD ligand coordinates through only one of its N atoms. Since our attempts to synthesize similar Pd complexes from H_2DMG and H_2CHD were unsuccessful, the $Pd(H_2CQD)_2Cl_2$ complexes are the first reported examples of a monodentate α-dioxime ligand. This type of complex is probably stabilized to some extent by the formation of inter- or intramolecular H-bonding as in the case of bis(cyclohexanone oxime)palladium dichloride.[30] Finally, in $[Pt(\gamma\text{-}HCQD)(\gamma\text{-}H_2CQD)Cl]_2$ and $Ni(\delta\text{-}HCQD)_2(\delta\text{-}H_2CQD)_2$, the ligands also appear to coordinate as monodentate ligands but in the unusual proposed structures shown in Figures 9 and 13.

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SECTION III. COORDINATION CHEMISTRY OF BIS(δ-CAMPHORQUINONEDIOXIMATO)Ni(II) AND Pd(II). REACTIONS AND STRUCTURAL STUDIES OF SOME M_3Ag_3 CLUSTER COMPLEXES OF CAMPHORQUINONEDIOXIME

INTRODUCTION

Our earlier work,[1,2] as well as that of Nakamura et al.,[3] showed that α- and δ-camphorquinonedioximes (H_2CQD) form square planar Ni(II) and Pd(II) complexes by chelating the metal ions using nitrogen and oxygen donor atoms. The structure[1] of Ni(δ-HCQD)$_2$ is shown in Figure 1.

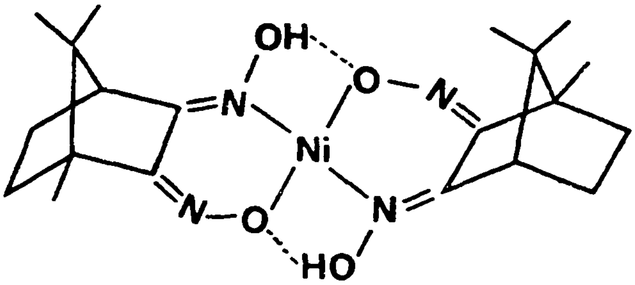

Figure 1. Structure of Ni(δ-HCQD)$_2$.

In the present paper, we report the reactions of Ni(δ-HCQD)$_2$ and Pd(δ-HCQD)$_2$ with $AgNO_3$ to form hexanuclear clusters of the composition [M(δ-HCQD)$_2$Ag]$_3$, where M is Ni(II) or Pd(II). Results of crystallographic studies on both of these complexes are described. It has also been found that Ni(δ-HCQD)$_2$ reacts with pyridine to give an adduct whose proposed structure is related to that of the clusters.

EXPERIMENTAL SECTION

Spectral data Proton NMR spectra were obtained using a Varian HA-100 spectrometer with TMS as the internal reference and $CDCl_3$ as the solvent. The ^{13}C NMR spectra were recorded on a Jeol FX-90Q ^{13}C NMR/^{1}H NMR spectrometer. Infrared spectra were obtained on KBr pellets using a Beckman IR-4250 (4000-200 cm^{-1}) spectrophotometer. Electronic spectra were recorded on a JASCO-ORD/UV-5 or Cary 14 spectrophotometer.

Starting materials The complexes $Pd(\delta\text{-}HCQD)_2$, $Ni(\delta\text{-}HCQD)_2$ and $Ni(\alpha\text{-}HCQD)_2$ were prepared according to published procedures.[2] The $Pd(PhCN)_2Cl_2$ was prepared by the method of Doyle, et al.[4]

Preparation of $[Ni(\delta\text{-}HCQD)_2Ag]_3 \cdot 2\ 1/2CHCl_3$ To 3 ml of a $CHCl_3$ solution containing 0.05 g (0.11 mmol) of $Ni(\delta\text{-}HCQD)_2$, approximately 5 ml of 0.05 M aqueous $AgNO_3$ solution was added. The two solution layers were mixed together by adding MeOH (15 ml) until a homogeneous solution was obtained. The resulting green solution was allowed to evaporate overnight at room temperature. After 24 hrs. green needlelike crystals were obtained. Yield 90%. IR(KBr): $\nu(C=N)$ at 1615 cm^{-1}, 1560. ^{1}H NMR($CDCl_3$): δ3.20(m), C4-H; 1.12(s), 0.86(s), 0.78(s), Me. ^{13}C NMR-($CDCl_3$): 153.76, 153.49, 147.42, 147.31, oxime C; 20.0, 17.35, 11.99, Me. UV-VIS maxima ($CHCl_3$): 620 nm(5.3×10 $cm^{-1}M^{-1}$), 402 (1.2×10^3), 305 (1.5×10^4). Anal. $[Ni(C_{20}H_{29}N_4O_4)Ag]_3 \cdot 2\ 1/2CHCl_3$, C, H, N, Cl; Ag: Calcd., 16.50; found, 17.13. m.p. > 300° C.

Preparation of $[Pd(\delta\text{-HCQD})_2Ag]_3 \cdot 2CHCl_3$ Yellow crystals of $[Pd(\delta\text{-HCQD})_2Ag]_3 \cdot 2CHCl_3$ were prepared using the same procedure for $[Ni(\delta\text{-HCQD})_2Ag]_3 \cdot 2\ 1/2CHCl_3$ substituting $Pd(\delta\text{-HCQD})_2$ for $Ni(\delta\text{-HCQD})_2$. Yield 80%. IR(KBr): ν(C=N) at 1605 cm^{-1}, 1550. ^1H NMR($CDCl_3$): δ3.31(m), C4-H; 1.24(s), 0.90(s), 0.78(s), Me. ^{13}C NMR-($CDCl_3$): 153.70, 142.49, oxime C; 20.05, 17.40, 12.58, Me. UV-VIS maxima ($CHCl_3$): 362 nm(1.8×10^3 $cm^{-1}M^{-1}$). Anal. $[Pd(C_{20}H_{29}N_4O_4)Ag]_3 \cdot 2CHCl_3$, C, H, N, Ag; Cl: Calcd., 10.36; found, 7.22. m.p. > 300° C.

Preparation of $Ni(\alpha\text{-HCQD})_2Ag \cdot 1/2AgNO_3$ This complex was prepared in the same manner as $[Ni(\delta\text{-HCQD})_2Ag]_3 \cdot 2\ 1/2CHCl_3$ substituting $Ni(\alpha\text{-HCQD})_2$ for $Ni(\delta\text{-HCQD})_2$. Yield 90%. IR(KBr): ν(C=N) at 1615 cm^{-1}, 1550. UV-VIS maxima ($CHCl_3$): 402 nm, 302. Anal. $Ni(C_{20}H_{29}N_4O_4)Ag \cdot 1/2AgNO_3$, C, H, N, Ag.

Preparation of $Pd(\alpha\text{-HCQD})_2Ag \cdot 1/2AgNO_3$ To 20 ml of MeOH containing 0.32 mmol of α-H_2CQD, an equivalent amount of Et_3N (0.32 mmol) was added, followed by 0.16 mmol of $Pd(PhCN)_2Cl_2$. After stirring at 50° C for 2-3 hrs., the yellow solution was filtered and cooled to room temperature.

Then aqueous $AgNO_3$ (0.05 M) was added until no further precipitation of AgCl was observed. The solution was then filtered into a flask containing 10 ml of $CHCl_3$. Upon allowing the solution to stand overnight, the product $Pd(\alpha\text{-HCQD})_2Ag \cdot 1/2AgNO_3$ crystallized out as pale yellow microcrystals. Yield 80%. IR(KBr): $\nu(C{=}N)$ at 1600 cm^{-1}, 1550. UV-VIS maximum ($CHCl_3$): 362 nm. Anal. $Pd(C_{20}H_{29}N_4O_4)Ag \cdot 1/2AgNO_3$, C, H, N; Ag: Calcd., 23.35; found, 22.59.

Preparation of $[Ni(\delta\text{-HCQD})_2(Py)_2] \cdot CHCl_3$ This complex was prepared by dissolving 0.05 g (0.11 mmol) of $Ni(\delta\text{-HCQD})_2$ in 20 ml of $H_2O/MeOH/CHCl_3$ (1:3:1) to which 1 ml of pyridine (Py) was added. After allowing the solution to stand at room temperature for several days, green crystals of $[Ni(\delta\text{-HCQD})_2(Py)_2] \cdot CHCl_3$ were obtained. Yield 80%. IR(KBr): $\nu(C{=}N)$ at 1610 cm^{-1}, 1558. UV-VIS maxima ($CHCl_3$): 614 nm(5.8 X 10 $cm^{-1}M^{-1}$), 296 (1.4 X 10^4). $\Lambda(CH_3CN)$: 0.534 $cm^2 ohm^{-1} M^{-1}$ at 25° C.

Crystal data $[Ni(\delta\text{-HCQD})_2Ag]_3 \cdot 1/2H_2O \cdot 1.3CHCl_3$: mol. wt. 1832.40, orthorhombic $P2_12_12_1$, a = 15.990(5), b = 38.44(1), c = 13.437(5) Å, V = 8260.97 Å^3, P_c = 1.474 g/cm^3, Z = 4, μ = 8.36 cm^{-1} for Mo-K_α. $[Pd(\delta\text{-HCQD})_2Ag]_3 \cdot 1.1CHCl_3$: mol. wt. 1945.62, orthorhombic $P2_12_12_1$, a = 16.110(6), b = 38.92(1), c = 13.393(3) Å,

$V = 8395.55$ Å^3, $P_c = 1.540$ g/cm^3, $Z = 4$, $\mu = 17.7$ cm^{-1} for Mo-K_α. Both complexes are formulated according to the results of their X-ray structure studies. The $[Ni(\delta\text{-HCQD})_2Ag]_3 \cdot 1/2H_2O \cdot 1.3CHCl_3$ cluster will be referred to as Ni-Ag, while $[Pd(\delta\text{-HCQD})_2Ag]_3 \cdot 1.1CHCl_3$ will be designated Pd-Ag in the discussion below.

A 0.36 X 0.19 X 0.16 mm single crystal of Ni-Ag and a 0.30 X 0.08 X 0.10 mm crystal of Pd-Ag were used in the collection of X-ray intensity data. In each case, 12-15 independent reflections taken from four preliminary ω-oscillation photographs at various χ and ϕ settings were input to the automatic indexing program ALICE.[5] The resulting reduced cell and reduced cell scalars indicated $P2_12_12_1$ (orthorhombic) symmetry in both cases. This was confirmed by inspection of axial ω-oscillation photographs which showed mmm symmetry in both Ni-Ag and Pd-Ag. The final lattice constants were obtained using least squares refinement based on the precise $\pm 2\theta$ measurement of 13 independent reflections with $|2\theta| > 20^\circ$ for Ni-Ag and 15 independent reflections with $|2\theta| > 30^\circ$ for Pd-Ag.

Collection and reduction of X-ray intensity data

The data were collected at 25° C using graphite monochromated Mo-K_α radiation on an automated four circle diffractometer designed and built at the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[6] All data (4412 reflections for Ni-Ag and 6524 reflections for Pd-Ag) within a 2θ sphere of 40° in the case of Ni-Ag and 60° in the case of Pd-Ag in the hkℓ octant were measured using an ω-stepscan technique.

As a general check on electronic and crystal stability, the intensities of three standard reflections were measured every seventy-five reflections. These standard reflections were not observed to vary significantly throughout the data collection period (~6 days) for the Pd-Ag complex but indicated considerable decay for the Ni-Ag complex in the last 1025 reflections. The decay as measured from the standard reflections was found to fit a quadratic polynomial by least squares method: $y(x) = 5979 + (-0.2615)x + (-0.0007267)x^2$. Subsequently all reflections after the first 3375 in the Ni-Ag complex were divided by $\frac{y(x)}{y(o)} = 1.0 + (-0.4374 \text{ X } 10^{-5})x + (-1.216 \text{ X } 10^{-7})x^2$ to account for the decay correction.

Examination of data revealed systematic absences of h00, 0k0, 00ℓ reflections for $h = 2n + 1$, $k = 2n + 1$, $\ell = 2n + 1$ in the Ni-Ag and Pd-Ag structures, thus uniquely defining the space group $P2_12_12_1$ in both cases. The intensity data were corrected for Lorentz and polarization effects. An absorption correction was applied to the data of the Pd-Ag complex, but no such correction was necessary for the Ni-Ag complex. The estimated error in each intensity was calculated by $\sigma_I{}^2 = C_T + K_t C_B + (0.03\ C_T)^2 + (0.03\ C_B)^2$, where C_T, K_t, and C_B represent the total count, a counting time factor and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite difference method.[7] Since only one octant of data was collected in each case, no averaging of data was required. While 3021 reflections with $I_o > 3\sigma(I)$ from Ni-Ag were retained for structural solution and refinement, 6112 reflections from Pd-Ag were retained.

Solution and refinement of the structures The positions of the heavy atoms in the asymmetric unit were obtained from an analysis of a standard sharpened three dimensional Patterson map.[7] The remaining non-hydrogen atoms were found by successive structure factor and electron density map calculation.[8] A block matrix least squares procedure[9] was used to refine the atomic positional parameters with anisotropic thermal parameters for the heavy atoms but isotropic thermal parameters for the remaining non-hydrogen atoms to conventional discrepancy factors of $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ = 10.7 and 11.4 and weighted R values of 12.7 and 15.0 for the Ni-Ag and Pd-Ag structures, respectively, using weights of $\frac{1}{(\sigma_F)^2}$. There appeared to be two regions for $CHCl_3$ and one site for H_2O in the Ni-Ag structure, but three regions for $CHCl_3$ were observed in the structure of Pd-Ag. The $CHCl_3$ molecules in both structures were disordered with respect to positions and occupation, and the C-Cl bond distances varied from 1.34-2.05 Å. Therefore occupation and thermal parameters for the solvent sites were estimated from successive electron density difference maps. Hydrogen positions in the terminal methyl groups and in the bicyclic rings were calculated using a 1.07 Å C-H bond distance and tetrahedral H-C-H angles in both Ni-Ag and Pd-Ag. They were included but not refined during the last least squares refinement cycles. The scattering factors for non-hydrogen atoms were those of Hanson et al.,[10] modified by the real and imaginary parts of anomalous dispersion.[11] Scattering factors for Ni(II), Pd(II) and Ag(I) were those of Thomas and Umeda.[12] Hydrogen scattering factors were those of Stewart, et al.[13] The final positional and thermal parameters for the Ni-Ag and Pd-Ag structures are listed in Tables I and II, respectively.

Table I. Final atomic parameters of the Ni-Ag structure

(a) Final positional parameters and isotropic thermal parameters (B) of the light atoms and their estimated standard deviations (in parentheses)

	X	Y	Z	B
Ag1	0.2093(2)	0.1705(1)	-0.0952(3)	
Ag2	0.3188(2)	0.1124(1)	-0.1801(3)	
Ag3	0.4230(2)	0.0530(1)	-0.2658(3)	
Ni1	0.4713(4)	0.1239(2)	0.0159(5)	
Ni2	0.1326(4)	0.0568(2)	-0.1905(5)	
Ni3	0.3937(4)	0.1704(2)	-0.3759(4)	
1O1	0.4422(18)	0.0951(7)	-0.0944(23)	5.0(7)
1O2	0.6331(19)	0.1170(8)	0.1003(25)	6.2(8)
1O3	0.5524(21)	0.1625(9)	0.1716(26)	7.4(9)
1O4	0.3700(19)	0.1418(8)	-0.0279(23)	5.3(7)
1N1	0.4795(23)	0.0620(10)	-0.1228(29)	5.4(9)
1N2	0.5747(25)	0.1038(9)	0.0399(29)	5.6(9)
1N3	0.4795(23)	0.1588(9)	0.1187(29)	5.0(9)
1N4	0.3152(22)	0.1676(9)	0.0088(26)	5.2(8)
1C10	0.5666(37)	0.0005(15)	-0.1742(46)	7.9(16)
1C11	0.5987(27)	0.0218(11)	-0.0934(34)	5.0(10)
1C12	0.5451(29)	0.0515(13)	-0.0769(36)	4.9(12)
1C13	0.5972(27)	0.0710(11)	0.0084(32)	4.6(10)
1C14	0.6786(33)	0.0491(14)	0.0180(40)	6.3(13)
1C15	0.6392(35)	0.0198(14)	0.0848(44)	7.7(15)
1C16	0.5909(32)	0.0020(13)	0.0047(39)	6.4(13)
1C17	0.6834(38)	0.0359(15)	-0.0830(48)	7.5(16)
1C18	0.7012(34)	0.0579(14)	-0.1699(43)	7.3(14)
1C19	0.7529(33)	0.0062(13)	-0.0904(40)	6.9(13)

Table I. (continued)

	X	Y	Z	B
1C20	0.1959(34)	0.2097(14)	0.1276(42)	6.9(14)
1C21	0.2937(33)	0.2093(13)	0.1471(39)	6.3(13)
1C22	0.3422(28)	0.1816(12)	0.0903(36)	5.9(11)
1C23	0.4188(27)	0.1793(10)	0.1414(30)	4.3(10)
1C24	0.4175(31)	0.2034(12)	0.2243(36)	5.2(12)
1C25	0.4248(35)	0.2382(14)	0.1791(43)	8.4(14)
1C26	0.3418(29)	0.2432(12)	0.1119(37)	5.5(12)
1C27	0.3221(28)	0.2037(12)	0.2568(34)	4.8(11)
1C28	0.2953(32)	0.1685(14)	0.2991(39)	6.4(13)
1C29	0.2920(42)	0.2307(17)	0.3259(53)	9.4(19)
2O1	0.2441(17)	0.0572(7)	-0.2207(20)	4.2(6)
2O2	0.0350(24)	0.0006(10)	-0.2628(30)	7.5(10)
2O3	-0.0342(22)	0.0353(9)	-0.1395(27)	8.4(10)
2O4	0.1677(16)	0.1016(7)	-0.1442(20)	4.5(7)
2N1	0.2948(22)	0.0339(9)	-0.2699(28)	5.2(9)
2N2	0.1167(20)	0.0143(8)	-0.2601(25)	5.5(9)
2N3	0.0271(23)	0.0614(10)	-0.1374(28)	3.9(8)
2N4	0.1224(23)	0.1269(9)	-0.1081(29)	4.9(9)
2C10	0.3948(33)	-0.0268(13)	-0.3559(39)	6.3(13)
2C11	0.2986(31)	-0.0229(12)	-0.3757(38)	6.0(12)
2C12	0.2535(28)	0.0089(11)	-0.3081(36)	4.5(11)
2C13	0.1661(28)	-0.0011(12)	-0.3125(38)	5.0(11)
2C14	0.1602(30)	-0.0351(12)	-0.3694(37)	5.3(12)
2C15	0.1790(34)	-0.0217(14)	-0.4662(42)	7.6(14)
2C16	0.2642(39)	-0.0143(15)	-0.4752(48)	8.7(17)
2C17	0.2388(37)	-0.0522(16)	-0.3372(46)	8.4(16)
2C18	0.2574(42)	-0.0868(16)	-0.4012(53)	9.2(18)
2C19	0.2474(34)	-0.0628(14)	-0.2316(42)	7.4(15)

Table I. (continued)

	X	Y	Z	B
2C20	0.0064(33)	0.1843(13)	-0.0426(41)	6.4(14)
2C21	-0.0207(34)	0.1459(14)	-0.0266(41)	6.8(14)
2C22	0.0456(30)	0.1213(13)	-0.0818(38)	5.7(12)
2C23	-0.0004(26)	0.0882(11)	-0.0871(33)	4.1(10)
2C24	-0.0959(29)	0.0944(11)	-0.0466(35)	5.0(11)
2C25	-0.0732(38)	0.0948(14)	0.0663(45)	8.5(16)
2C26	-0.0207(35)	0.1328(14)	0.0836(43)	6.8(14)
2C27	-0.1014(34)	0.1357(13)	-0.0798(41)	6.1(14)
2C28	-0.1003(32)	0.1389(12)	-0.1850(39)	6.2(13)
2C29	-0.1834(37)	0.1483(15)	-0.0230(45)	8.5(16)
3O1	0.4007(18)	0.1247(7)	-0.3379(21)	4.8(7)
3O2	0.5043(19)	0.1934(8)	-0.5306(24)	5.7(8)
3O3	0.4149(22)	0.2343(8)	-0.4723(25)	6.8(8)
3O4	0.3154(18)	0.1706(8)	-0.2693(22)	5.2(7)
3N1	0.4524(22)	0.0974(9)	-0.3632(28)	5.2(9)
3N2	0.4751(20)	0.1645(8)	-0.4718(24)	3.7(8)
3N3	0.3720(19)	0.2162(8)	-0.4004(24)	3.2(7)
3N4	0.2671(23)	0.1947(10)	-0.2356(28)	4.7(9)
3C10	0.5395(34)	0.0397(14)	-0.4584(42)	6.7(14)
3C11	0.5639(28)	0.0762(11)	-0.4849(33)	4.5(10)
3C12	0.4991(28)	0.1057(12)	-0.4437(36)	4.9(11)
3C13	0.5107(36)	0.1379(14)	-0.4916(43)	6.5(15)
3C14	0.5769(30)	0.1313(11)	-0.5723(34)	5.2(11)
3C15	0.6617(31)	0.1254(13)	-0.5082(38)	6.1(13)
3C16	0.6442(33)	0.0913(14)	-0.4515(41)	5.9(14)
3C17	0.5593(36)	0.0953(14)	-0.5972(46)	7.7(15)
3C18	0.4772(33)	0.0913(13)	-0.6463(40)	7.4(14)
3C19	0.6206(32)	0.0758(13)	-0.6605(39)	6.4(13)

Table I. (continued)

	X	Y	Z	B
3C20	0.1713(38)	0.2504(16)	-0.1438(45)	9.4(17)
3C21	0.2108(26)	0.2565(10)	-0.2434(32)	3.9(10)
3C22	0.2678(27)	0.2237(11)	-0.2734(34)	4.9(11)
3C23	0.3136(30)	0.2354(12)	-0.3633(36)	5.6(12)
3C24	0.2921(30)	0.2748(12)	-0.3695(37)	5.6(12)
3C25	0.2035(41)	0.2728(16)	-0.4115(52)	9.8(18)
3C26	0.1468(30)	0.2599(12)	-0.3211(38)	5.9(12)
3C27	0.2739(33)	0.2838(13)	-0.2640(41)	6.6(14)
3C28	0.3526(36)	0.2812(15)	-0.1931(45)	7.8(15)
3C29	0.2323(33)	0.3215(14)	-0.2598(42)	7.4(14)
1Cℓ1[a](0.4)[b]	0.5515(27)	0.2176(12)	-0.2676(34)	7.0
1Cℓ2(0.4)	0.6120(22)	0.1534(9)	-0.2148(26)	7.0
1Cℓ3(0.4)	0.5810(24)	0.2004(9)	-0.0690(28)	7.0
1Cℓ4(0.25)	0.6242(31)	0.1758(13)	-0.1071(40)	7.0
1Cℓ5(0.25)	0.5138(32)	0.2174(13)	-0.0980(41)	7.0
1Cℓ6(0.25)	0.5787(34)	0.2081(14)	-0.2846(40)	7.0
1CS1(0.4)	0.5533(73)	0.1934(30)	-0.1930(95)	7.0
1CS2(0.25)	0.5731(132)	0.2042(55)	-0.2743(167)	7.0
2Cℓ1(0.4)	0.2510(21)	0.1022(9)	-0.4902(26)	7.0
2Cℓ2(0.4)	0.1438(21)	0.1527(9)	-0.4040(26)	7.0
2Cℓ3(0.4)	0.1095(21)	0.0815(9)	-0.4340(26)	7.0
2Cℓ4(0.25)	0.0774(34)	0.1022(13)	-0.3785(41)	7.0
2Cℓ5(0.25)	0.2171(37)	0.0922(15)	-0.4421(45)	7.0
2Cℓ6(0.25)	0.1878(36)	0.1528(14)	-0.4734(43)	7.0

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[a] Only 1.3 CHCl$_3$ rather than 2 1/2 CHCl$_3$ as indicated by elemental analyses was observed on an electron density difference map.

[b] Multiplier used.

Table I. (continued)

	X	Y	Z	B
2CS2(0.25)	0.1883(121)	0.1171(51)	-0.4164(152)	7.0
1OS(0.55)	0.5187(37)	0.3270(16)	-0.3466(44)	7.0

(b) Anisotropic thermal parameters (X 10^5) of the heavy atoms and their estimated standard deviations (in parentheses)[c]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag1	396(18)	69(3)	805(29)	3(6)	-48(20)	18(9)
Ag2	400(16)	58(3)	718(26)	0(6)	24(19)	32(8)
Ag3	411(17)	67(3)	793(29)	0(7)	-41(21)	24(8)
Ni1	390(30)	58(5)	709(47)	-6(11)	8(34)	-2(14)
Ni2	404(30)	55(5)	676(45)	-7(10)	-44(33)	18(14)
Ni3	429(31)	57(5)	633(44)	13(11)	-55(31)	-2(14)

[c] The βij are defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

Table II. Final atomic parameters of the Pd-Ag structure

(a) Final positional parameters and isotropic thermal parameters (B) of the light atoms and their estimated standard deviations (in parentheses)

Atom	X	Y	Z	B
Ag1	0.29459(13)	0.32877(5)	0.40075(20)	
Ag2	0.18500(12)	0.38870(5)	0.30904(19)	
Ag3	0.07899(13)	0.44983(5)	0.21672(20)	
Pd1	0.02627(13)	0.37629(5)	0.49885(20)	
Pd2	0.37097(12)	0.44287(4)	0.29997(19)	
Pd3	0.10885(13)	0.33064(5)	0.11501(19)	
1O1	0.0538(11)	0.4079(5)	0.3827(17)	4.5(4)
1O2	-0.1388(12)	0.3859(5)	0.5920(17)	5.7(4)
1O3	-0.0548(13)	0.3389(5)	0.6592(18)	6.1(5)
1O4	0.1379(11)	0.3573(4)	0.4567(15)	4.6(4)
1N1	0.0174(14)	0.4387(6)	0.3597(20)	4.4(5)
1N2	-0.0812(15)	0.4000(6)	0.5254(20)	5.2(5)
1N3	0.0151(15)	0.3414(6)	0.6090(21)	4.8(5)
1N4	0.1784(13)	0.3339(5)	0.5103(17)	3.8(4)
1C10	-0.0710(24)	0.5017(10)	0.3055(34)	7.1(9)
1C11	-0.1012(22)	0.4808(9)	0.3946(31)	6.9(8)
1C12	-0.0516(17)	0.4463(7)	0.4056(24)	4.8(6)
1C13	-0.0987(17)	0.4291(7)	0.4849(24)	5.3(6)
1C14	-0.1820(19)	0.4494(8)	0.4961(27)	5.2(7)
1C15	-0.1500(18)	0.4783(7)	0.5686(26)	5.9(6)
1C16	-0.1018(24)	0.4983(10)	0.4895(34)	6.0(9)
1C17	-0.1916(17)	0.4646(7)	0.3893(24)	5.1(6)
1C18	-0.2584(28)	0.4938(10)	0.3913(35)	7.9(9)
1C19	-0.2074(21)	0.4408(8)	0.3138(30)	5.9(8)

Table II. (continued)

Atom	X	Y	Z	B
1C20	0.2931(21)	0.2897(8)	0.6230(28)	6.2(7)
1C21	0.1966(19)	0.2900(8)	0.6360(27)	5.5(7)
1C22	0.1513(15)	0.3186(6)	0.5801(21)	3.8(5)
1C23	0.0704(17)	0.3194(6)	0.6344(22)	3.7(6)
1C24	0.0667(19)	0.2956(7)	0.7120(26)	5.6(7)
1C25	0.0635(25)	0.2599(10)	0.6574(33)	7.9(9)
1C26	0.1491(23)	0.2557(9)	0.6086(33)	6.6(11)
1C27	0.1582(20)	0.2966(8)	0.7466(28)	6.8(7)
1C28	0.1851(28)	0.2655(11)	0.8196(40)	9.1(10)
1C29	0.1890(25)	0.3314(10)	0.7868(35)	8.6(10)
2O1	0.2493(11)	0.4438(4)	0.2654(14)	4.2(3)
2O2	0.4695(14)	0.5007(6)	0.2286(19)	6.5(5)
2O3	0.5397(14)	0.4623(5)	0.3444(19)	6.4(5)
2O4	0.3324(11)	0.3972(4)	0.3522(15)	4.3(4)
2N1	0.2095(14)	0.4679(5)	0.2114(20)	4.4(5)
2N2	0.3946(14)	0.4872(5)	0.2307(19)	5.2(5)
2N3	0.4820(14)	0.4380(5)	0.3530(20)	4.6(5)
2N4	0.3833(14)	0.3734(5)	0.3950(19)	4.6(5)
2C10	0.1141(20)	0.5273(8)	0.1258(28)	6.3(7)
2C11	0.2009(22)	0.5229(9)	0.1225(31)	7.6(8)
2C12	0.2487(18)	0.4946(7)	0.1793(22)	3.3(6)
2C13	0.3384(17)	0.5032(7)	0.1835(24)	4.4(6)
2C14	0.3457(19)	0.5374(7)	0.1285(27)	5.1(7)
2C15	0.3389(23)	0.5248(9)	0.0164(33)	9.1(9)
2C16	0.2388(26)	0.5142(9)	0.0145(36)	8.4(11)
2C17	0.2665(19)	0.5540(7)	0.1484(26)	5.0(7)
2C18	0.2593(21)	0.5650(8)	0.2586(29)	8.0(8)
2C19	0.2433(27)	0.5889(10)	0.0930(40)	9.2(11)

Table II. (continued)

Atom	X	Y	Z	B
2C20	0.4863(20)	0.3178(8)	0.4807(22)	5.9(7)
2C21	0.5108(20)	0.3544(7)	0.4792(26)	5.2(7)
2C22	0.4556(18)	0.3788(7)	0.4193(24)	5.0(6)
2C23	0.5007(16)	0.4105(6)	0.4028(23)	4.4(6)
2C24	0.5904(22)	0.4043(9)	0.4445(31)	6.1(8)
2C25	0.5799(26)	0.4074(11)	0.5594(37)	9.3(11)
2C26	0.5201(23)	0.3698(9)	0.5794(31)	7.5(11)
2C27	0.5891(17)	0.3652(7)	0.4299(23)	5.5(6)
2C28	0.6009(24)	0.3537(9)	0.3285(33)	6.4(9)
2C29	0.6710(21)	0.3482(8)	0.4723(29)	6.6(8)
3O1	0.1044(11)	0.3797(4)	0.1497(14)	4.3(4)
3O2	-0.0055(12)	0.3075(4)	-0.0418(16)	4.8(4)
3O3	0.0807(13)	0.2640(5)	0.0248(17)	5.8(4)
3O4	0.1923(12)	0.3334(5)	0.2219(16)	5.4(4)
3N1	0.0535(15)	0.4037(6)	0.1110(22)	5.0(6)
3N2	0.0226(14)	0.3360(5)	0.0113(19)	4.6(5)
3N3	0.1271(14)	0.2803(5)	0.0880(19)	4.8(5)
3N4	0.2423(15)	0.3059(6)	0.2600(20)	4.7(5)
3C10	-0.0294(21)	0.4603(8)	-0.0069(29)	6.1(8)
3C11	-0.0523(19)	0.4229(8)	-0.0055(27)	5.5(7)
3C12	0.0084(17)	0.3964(7)	0.0450(24)	3.8(6)
3C13	-0.0131(18)	0.3631(7)	-0.0104(25)	4.7(6)
3C14	-0.0791(19)	0.3680(7)	-0.0824(25)	5.2(6)
3C15	-0.1574(21)	0.3756(8)	-0.0252(28)	7.3(8)
3C16	-0.1415(24)	0.4096(10)	0.0297(35)	6.1(11)
3C17	-0.0594(19)	0.4078(8)	-0.1209(28)	5.4(7)
3C18	-0.1196(22)	0.4251(9)	-0.1782(31)	7.4(8)
3C19	0.0282(24)	0.4066(9)	-0.1674(33)	5.8(9)

Table II. (continued)

Atom	X	Y	Z	B
3C20	0.3304(23)	0.2486(9)	0.3504(32)	6.2(8)
3C21	0.2868(20)	0.2450(8)	0.2503(27)	6.4(7)
3C22	0.2355(15)	0.2751(6)	0.2164(21)	4.0(5)
3C23	0.1806(20)	0.2640(8)	0.1393(27)	5.3(7)
3C24	0.2027(21)	0.2254(8)	0.1267(30)	6.7(7)
3C25	0.2923(24)	0.2262(9)	0.0765(32)	8.7(9)
3C26	0.3535(28)	0.2368(10)	0.1631(39)	8.9(11)
3C27	0.2208(17)	0.2163(7)	0.2324(23)	5.4(6)
3C28	0.1461(22)	0.2176(9)	0.3047(32)	6.6(8)
3C29	0.2689(26)	0.1818(10)	0.2386(36)	9.1(11)
C1(0.5)[a]	0.4331(58)	0.1914(23)	0.7051(83)	7.0
C2(0.5)	0.0674(101)	0.1194(38)	0.0101(134)	7.0
C3(0.5)	0.3183(99)	0.3863(39)	0.0533(132)	7.0
1Cℓ1[b](0.3)	0.3849(26)	0.1535(10)	0.7298(35)	7.0
1Cℓ2(0.3)	0.4417(26)	0.2198(10)	0.7784(36)	7.0
1Cℓ3(0.3)	0.4131(27)	0.2016(10)	0.5840(35)	7.0
1Cℓ4(0.2)	0.4698(39)	0.2153(15)	0.6025(54)	7.0
1Cℓ5(0.2)	0.4110(39)	0.2101(15)	0.7906(55)	7.0
1Cℓ6(0.2)	0.3655(39)	0.1840(16)	0.6142(54)	7.0
2Cℓ1(0.3)	0.1124(26)	0.1054(10)	0.0956(36)	7.0
2Cℓ2(0.3)	0.1146(26)	0.1545(10)	0.9719(35)	7.0

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[a] Multiplier used.

[b] Only 1.1 $CHCl_3$ rather than 2 $CHCl_3$ as indicated by elemental analyses was observed on an electron density difference map.

Table II. (continued)

Atom	X	Y	Z	B
2Cℓ3(0.3)	0.1121(25)	0.0879(10)	0.9116(36)	7.0
3Cℓ1(0.3)	0.3716(27)	0.4213(10)	0.0355(36)	7.0
3Cℓ2(0.3)	0.3964(26)	0.3616(10)	0.1439(36)	7.0
3Cℓ3(0.3)	0.2984(27)	0.3633(10)	-0.0138(36)	7.0

(b) Anisotropic thermal parameters (X 10^4) of the heavy atoms and their estimated standard deviations (in parentheses)^c

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag1	37.0(9)	6.5(1)	80.2(18)	-0.3(3)	-3.7(12)	3.0(5)
Ag2	35.2(8)	5.8(1)	71.8(16)	-1.3(3)	-2.9(11)	7.9(4)
Ag3	35.2(8)	6.1(1)	80.3(19)	-0.9(3)	-5.3(11)	2.7(5)
Pd1	33.5(8)	5.6(1)	70.2(16)	-2.1(3)	-3.4(11)	1.9(4)
Pd2	34.4(9)	6.6(1)	67.9(16)	-0.5(3)	5.0(11)	0.3(5)
Pd3	41.4(9)	6.1(1)	64.2(16)	0.1(3)	-6.0(11)	-0.8(5)

^{c}The βij are defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

RESULTS AND DISCUSSION

Description of the structure [Ni(δ-HCQD)$_2$Ag]$_3$·1/2H$_2$O·1.3CHCl$_3$, Ni-Ag   The unit cell (Figure 2) of Ni-Ag consists of four hexanuclear molecules with CHCl$_3$ and H$_2$O molecules occupying interstitial sites. Each hexanuclear molecule (Figure 3) in turn consists of three individual Ni(δ-HCQD)$_2^-$ ligands coordinated to a linear chain of three silver atoms. The δ-HCQD$^-$ ligands form two 6-membered chelate rings with each of the three Ni(II) atoms. The observed coordination of the ligands to Ni *via* N and O rather than N,N atoms was established previously in Ni(δ-HCQD)$_2$[1] and probably is caused by the bicyclic nature of the ligand which increases the size of the C-C-N angles and thus favors 6-membered chelate ring formation. There are two types of Ag atoms in the cluster. Coordinated to the center Ag are six oxygen atoms, while there are three nitrogen atoms coordinated to each of the terminal silver atoms. Several interesting features of the structure are discussed below.

Coordination around Ni   While the crystal structure[1] of Ni(δ-HCQD)$_2$ was found to have trans N$_2$O$_2$ square planar coordination around Ni (Figure 1), the δ-HCQD$^-$ ligands in Ni-Ag coordinate to the Ni with a cis N$_2$O$_2$ geometry

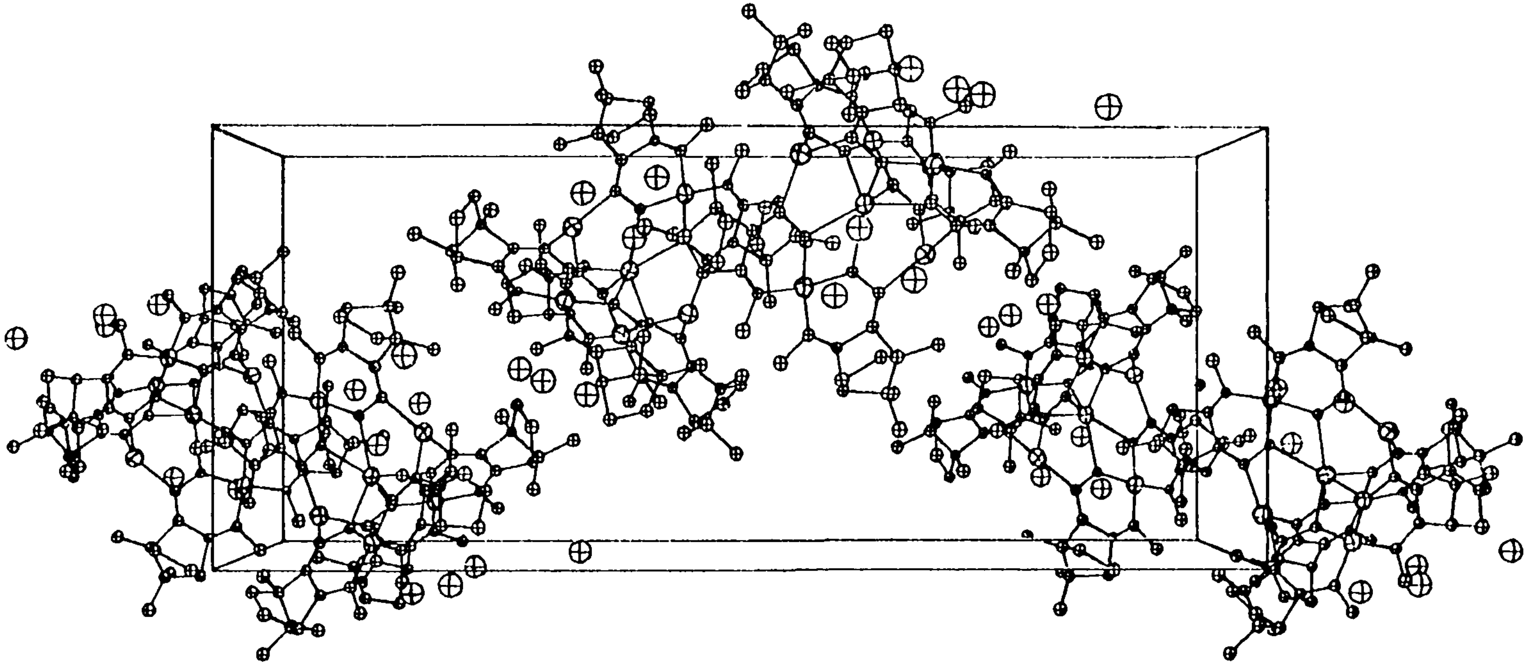

Figure 2. The unit cell of $[Ni(\delta\text{-}HCQD)_2Ag]_3 \cdot 1/2H_2O \cdot 1.3CHCl_3$ with the *a* axis vertical and the *b* axis horizontal.

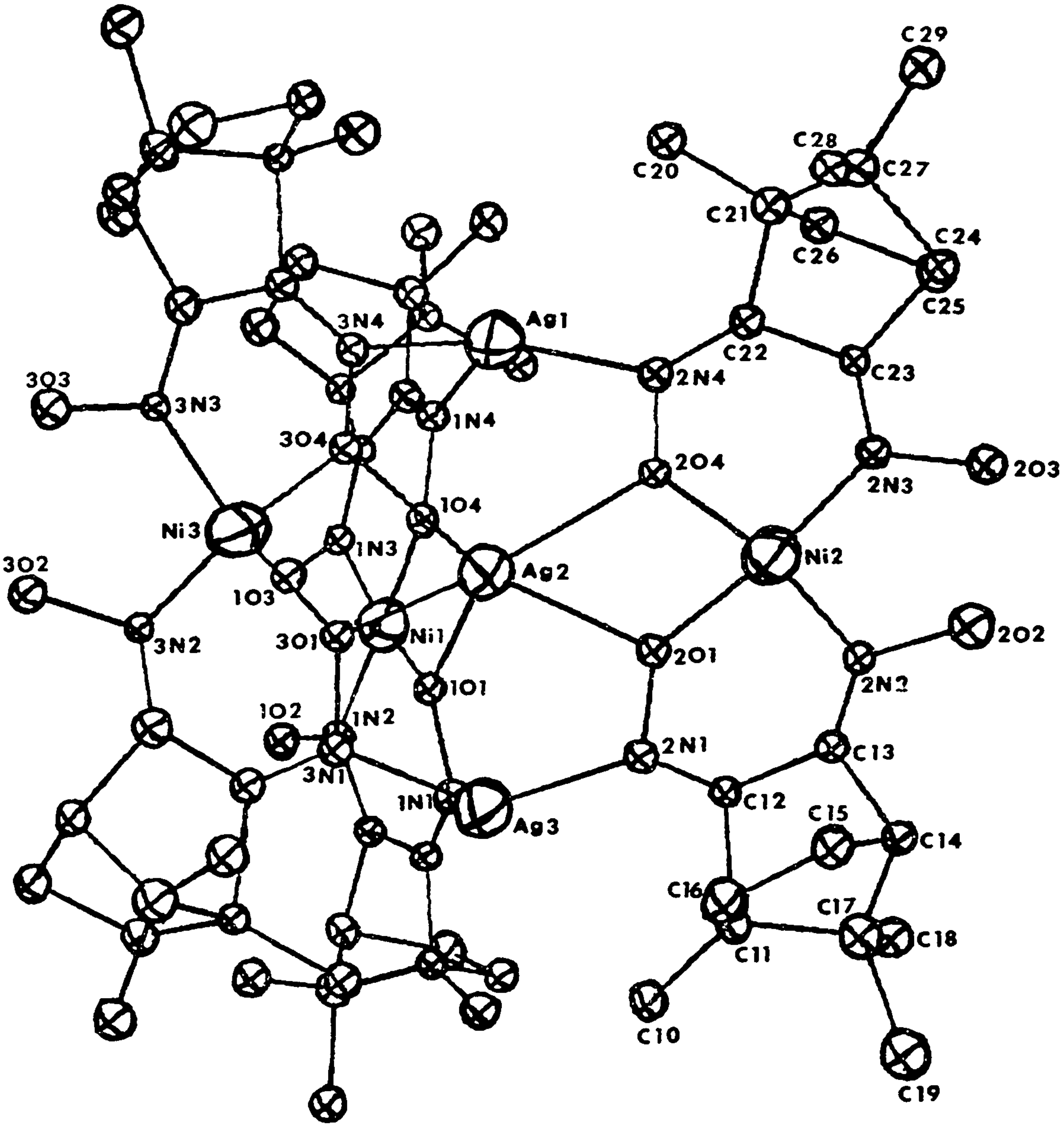

Figure 3. Molecular structure of $[\mathrm{Ni}(\delta\text{-HCQD})_2\mathrm{Ag}]_3$ with 50% probability ellipsoids for heavy atoms but 10% for light atoms. For clarity only the C atoms of the Ni2 unit are labelled but the adopted numbering scheme is also applied to the other two units.

(Figure 3). Thus, the addition of Ag^+ to Ni(δ-HCQD)$_2$ has caused one ligand in Ni(δ-HCQD)$_2$ to rotate such that the structure around the Ni changes from trans N_2O_2 to cis N_2O_2.

The important bond distances and bond angles of the three Ni(δ-HCQD)$_2^-$ units in Ni-Ag are summarized in Tables III and IV. The average Ni-N distance of 1.86(4) Å is comparable to 1.855(3) Å reported in the Ni(δ-HCQD)$_2$ complex.[1] However, the average Ni-O distance of 1.87(3) Å is considerably longer than the 1.830(3) Å observed in Ni(δ-HCQD)$_2$. This lengthening is presumably due to coordination of the Ag(I) to these O atoms. Also such coordination seems to affect the O_4-Ni-O_1 angles (75.9(1), 77.2(1) and 80.5(1)°) so that they are consistently smaller than the other angles, O_4-Ni-N_3, N_3-Ni-N_2 and N_2-Ni-O_1, which are all greater than 90° in the three nickel anion ligands. The distances of the Ni atoms from the least squares planes (Table V) defined by Ni-O_1-O_4-N_2-N_3 are small, being only 0.04, 0.006 and 0.01 Å for the three units. The average C-C (1.53 Å), C=N (1.28 Å) and N-O (1.38 Å) distances of the ligands correspond well with those observed in the structures of Ni(δ-HCQD)$_2$[1] and γ-H_2CQD.[14]

Table III. Interatomic distances (Å) and their estimated standard deviations (in parentheses) for the Ni-Ag and Pd-Ag structures

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
Ag1-N4	2.198(35)	2.184(36)	2.298(38)	2.386(22)	2.249(21)	2.250(26)
Ag1-O4	2.939(31)	2.809(27)	2.890(30)	2.858(18)	2.808(16)	2.912(21)
Ag2-O4	2.476(31)	2.498(26)	2.539(31)	2.445(19)	2.466(18)	2.450(20)
Ag2-O1	2.379(29)	2.495(27)	2.537(29)	2.449(18)	2.454(16)	2.450(20)
Ag3-O1	2.834(30)	2.929(27)	2.942(27)	2.787(20)	2.830(18)	2.902(16)
Ag3-N1	2.154(39)	2.178(35)	2.200(36)	2.199(26)	2.217(22)	2.325(26)
M[a]-O1	1.908(30)	1.828(28)	1.833(28)	2.033(19)	2.014(18)	1.967(16)
M-O4	1.856(31)	1.915(28)	1.902(30)	2.024(18)	2.009(16)	1.968(21)
M-N2	1.853(40)	1.900(32)	1.846(33)	1.994(24)	1.996(21)	1.976(23)
M-N3	1.930(38)	1.840(37)	1.824(32)	2.014(26)	1.933(23)	2.015(20)
O1-N1	1.456(47)	1.377(45)	1.378(45)	1.369(28)	1.346(30)	1.346(30)
O4-N4	1.412(46)	1.306(45)	1.288(48)	1.332(27)	1.365(28)	1.435(31)
N2-O2	1.337(50)	1.409(50)	1.441(44)	1.399(33)	1.317(32)	1.396(29)

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[a] Corresponds to the metal ions labelled on the top of each column.

Table III. (continued)

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
N3-O3	1.373(50)	1.403(51)	1.374(46)	1.315(33)	1.332(31)	1.293(31)
N1-C12	1.282(60)	1.274(56)	1.352(60)	1.304(37)	1.289(35)	1.178(41)
N4-C22	1.294(59)	1.296(61)	1.225(57)	1.199(34)	1.227(37)	1.335(34)
N2-C13	1.378(55)	1.212(57)	1.200(63)	1.286(37)	1.268(36)	1.236(35)
N3-C23	1.287(55)	1.308(57)	1.290(56)	1.280(35)	1.296(35)	1.271(40)
C10-C11	1.453(75)	1.568(72)	1.499(69)	1.525(57)	1.409(48)	1.506(44)
C11-C12	1.445(65)	1.685(66)	1.633(63)	1.571(42)	1.546(45)	1.573(43)
C11-C16	1.527(68)	1.483(82)	1.479(69)	1.440(59)	1.607(62)	1.599(50)
C11-C17	1.465(74)	1.565(77)	1.680(75)	1.588(45)	1.642(45)	1.655(51)
C12-C13	1.603(64)	1.451(63)	1.407(72)	1.467(42)	1.485(40)	1.534(41)
C13-C14	1.555(68)	1.517(67)	1.536(74)	1.564(41)	1.524(41)	1.447(44)
C14-C15	1.572(78)	1.431(75)	1.622(69)	1.575(44)	1.584(56)	1.506(47)
C14-C17	1.451(83)	1.483(76)	1.451(69)	1.556(48)	1.454(41)	1.665(42)
C15-C16	1.491(77)	1.397(82)	1.542(74)	1.525(52)	1.535(52)	1.603(53)
C17-C18	1.470(84)	1.612(89)	1.477(79)	1.567(51)	1.541(51)	1.411(50)
C17-C19	1.596(78)	1.483(84)	1.499(78)	1.395(47)	1.593(52)	1.545(51)
C20-C21	1.586(76)	1.553(74)	1.498(74)	1.565(46)	1.478(42)	1.520(54)
C21-C22	1.522(69)	1.602(73)	1.607(58)	1.517(41)	1.527(43)	1.504(40)
C21-C26	1.585(69)	1.564(79)	1.468(65)	1.580(48)	1.478(53)	1.619(60)

Table III. (continued)

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
C21-C27	1.557(69)	1.526(77)	1.482(65)	1.626(50)	1.610(43)	1.560(42)
C22-C23	1.407(62)	1.471(65)	1.482(65)	1.493(37)	1.450(37)	1.427(43)
C23-C24	1.449(62)	1.638(62)	1.555(65)	1.394(42)	1.570(45)	1.553(44)
C24-C25	1.474(72)	1.560(76)	1.527(82)	1.570(47)	1.552(64)	1.593(53)
C24-C27	1.587(67)	1.651(66)	1.488(74)	1.546(45)	1.536(46)	1.488(50)
C25-C26	1.617(74)	1.701(78)	1.595(84)	1.535(56)	1.772(54)	1.578(64)
C27-C28	1.529(70)	1.419(76)	1.582(79)	1.617(57)	1.431(53)	1.545(48)
C27-C29	1.473(82)	1.592(80)	1.596(74)	1.540(51)	1.491(44)	1.554(48)
O2-O3	2.375(46)	2.398(53)	2.265(45)	2.447(29)	2.433(33)	2.363(27)
O1-O4	2.314(42)	2.337(38)	2.413(41)	2.587(24)	2.537(24)	2.487(26)

Table IV. Bond angles (deg) and their estimated standard deviations (in parentheses) for the Ni-Ag and Pd-Ag structures

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
O1-Ag2-O4	56.88(99)	55.80(89)	56.78(90)	63.82(59)	62.09(56)	60.00(60)
Ag2-O4-M[a]	112.4(14)	111.7(12)	109.7(13)	108.64(73)	109.56(75)	111.23(84)
Ag2-O1-M	114.6(13)	115.2(13)	112.3(13)	108.15(70)	109.87(70)	108.41(73)
O1-M-O4	75.9(13)	77.2(12)	80.5(13)	79.22(68)	78.19(69)	78.41(78)
O1-M-N2	96.4(15)	91.6(13)	91.9(13)	92.63(86)	93.60(80)	92.14(78)
O4-M-N3	91.6(15)	93.2(14)	90.4(14)	92.15(86)	94.13(88)	94.87(87)
N2-M-N3	96.0(16)	98.7(16)	97.3(14)	96.0(10)	94.50(97)	94.56(88)
O1-M-N3	167.4(14)	168.3(15)	170.7(15)	171.40(86)	170.47(88)	172.93(89)
O4-M-N2	171.3(16)	166.5(13)	172.0(14)	171.96(90)	170.38(86)	170.63(80)
M-O1-N1	127.6(24)	132.4(23)	134.2(24)	127.5(16)	126.9(14)	127.1(16)
M-O4-N4	133.7(25)	128.9(23)	131.4(27)	122.3(15)	124.2(14)	126.9(16)
M-N2-O2	124.8(27)	177.3(25)	121.1(23)	120.5(17)	122.0(18)	120.1(15)
M-N3-O3	120.0(27)	124.3(28)	121.4(24)	120.0(18)	123.0(18)	120.6(17)

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[a] Corresponds to the metal ions labelled on the top of each column.

Table IV. (continued)

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
M-N2-C13	124.1(31)	128.2(31)	126.4(35)	121.5(21)	121.3(19)	125.7(20)
M-N3-C23	123.0(31)	125.7(31)	128.3(30)	125.6(21)	119.0(18)	119.1(20)
O1-N1-C12	119.0(38)	112.3(34)	110.4(32)	117.2(23)	120.4(23)	120.0(24)
N1-C12-C13	128.5(43)	135.7(43)	130.2(44)	132.8(26)	130.3(25)	134.8(27)
N1-C12-C11	131.3(45)	122.8(39)	117.2(37)	125.7(27)	119.7(26)	123.4(27)
N2-C13-C12	120.8(38)	118.3(42)	125.8(52)	126.4(26)	127.0(26)	120.1(28)
N2-C13-C14	133.5(40)	132.3(42)	128.6(48)	126.3(27)	127.9(25)	127.6(27)
O2-N2-C13	110.6(35)	114.0(36)	112.4(38)	118.0(23)	116.6(23)	114.1(24)
C11-C12-C13	99.8(36)	101.4(36)	111.8(40)	101.2(24)	109.9(23)	101.6(24)
C12-C13-C14	104.0(36)	108.0(38)	105.6(42)	106.4(24)	104.8(23)	112.2(23)
C13-C14-C15	95.7(38)	97.8(40)	103.0(38)	98.0(23)	100.5(24)	107.5(28)
C14-C15-C16	97.1(43)	110.9(49)	103.3(38)	95.9(27)	99.1(29)	107.8(27)
C15-C16-C11	110.6(41)	103.8(50)	110.0(42)	112.1(30)	107.6(32)	101.5(29)
C12-C11-C16	102.3(38)	99.5(39)	100.1(36)	108.9(31)	95.9(26)	100.4(25)
C12-C11-C17	104.0(40)	94.7(38)	88.5(33)	97.5(23)	95.7(24)	102.3(24)
C12-C11-C10	110.5(41)	113.4(38)	113.8(38)	111.6(29)	124.4(31)	119.1(26)
C16-C11-C17	100.7(41)	103.4(43)	98.0(38)	102.8(29)	95.8(26)	99.9(25)
C16-C11-C10	109.6(40)	122.6(45)	121.4(42)	116.2(30)	115.5(33)	121.5(28)
C17-C11-C10	127.3(46)	118.3(42)	127.7(40)	118.0(31)	122.9(28)	110.4(28)

Table IV. (continued)

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
C13-C14-C17	99.0(42)	100.5(41)	100.8(41)	100.9(25)	103.3(25)	100.8(23)
C15-C14-C17	107.7(45)	104.3(44)	98.7(38)	109.0(25)	104.5(27)	97.6(22)
C11-C17-C14	99.8(46)	95.9(43)	101.6(42)	91.1(24)	101.5(23)	93.1(24)
C18-C17-C19	103.1(46)	105.5(48)	106.0(46)	111.6(28)	98.1(28)	115.0(32)
O4-N4-C22	112.4(34)	120.2(36)	120.2(38)	126.2(22)	124.4(22)	118.0(23)
N4-C22-C23	132.6(42)	127.2(43)	128.2(42)	133.0(24)	125.6(26)	129.7(25)
N4-C22-C21	123.0(41)	130.9(44)	127.2(40)	125.3(24)	125.7(26)	121.4(25)
N3-C23-C22	125.4(39)	122.5(40)	119.9(40)	119.9(25)	131.7(26)	131.3(28)
N3-C23-C24	125.8(41)	126.8(37)	134.1(43)	127.8(28)	121.7(24)	125.3(30)
O3-N3-C23	117.0(36)	109.8(35)	110.1(33)	114.2(25)	117.9(23)	120.1(23)
C21-C22-C23	104.0(39)	101.7(38)	104.3(34)	101.7(22)	108.5(24)	108.8(24)
C22-C23-C24	108.8(38)	108.9(35)	103.3(37)	112.3(23)	105.9(23)	103.3(26)
C23-C24-C25	105.2(40)	96.2(37)	100.1(40)	104.1(28)	103.9(29)	103.6(26)
C24-C25-C26	105.8(41)	104.8(41)	105.2(48)	105.2(28)	98.3(29)	105.1(33)
C25-C26-C21	97.7(37)	98.5(41)	100.0(40)	104.3(28)	104.6(30)	99.6(31)
C22-C21-C26	100.3(38)	104.4(41)	106.7(35)	105.3(26)	106.6(25)	107.5(28)
C22-C21-C27	103.2(39)	101.0(41)	97.0(34)	98.7(23)	97.6(23)	97.8(23)
C28-C27-C29	107.3(43)	117.5(46)	111.6(42)	111.2(31)	103.9(27)	112.5(28)
C26-C21-C27	104.7(39)	111.1(44)	106.2(38)	99.3(26)	100.2(25)	101.6(25)

Table IV. (continued)

	Ni1	Ni2	Ni3	Pd1	Pd2	Pd3
C27-C21-C20	116.4(42)	114.5(40)	124.4(42)	118.7(28)	119.4(25)	121.1(28)
C25-C24-C27	100.5(39)	105.4(37)	100.5(43)	101.2(25)	102.3(29)	103.2(27)
N2-O2-O3	98.3(24)	101.7(25)	98.1(22)	99.3(15)	99.6(17)	100.7(15)
N3-O3-O2	100.1(25)	95.1(25)	101.9(22)	103.3(17)	99.6(17)	103.7(15)

Table V. Equations of least squares planes[a]

Atom	D[b]	Atom	D
Plane 1: Ni1-1O1-1O4-1N2-1N3 $0.4553x + 0.6283y + 0.6308z - 6.3268 = 0$			
Ni1	-0.0377	1N2	0.0261
1O1	-0.0102	1N3	-0.0064
1O4	0.0283		
Plane 2: Ni2-2O1-2O4-2N2-2N3 $-0.2591x + 0.4619y + 0.8482z - 2.636 = 0$			
Ni2	-0.0059	2N2	0.0986
2O1	-0.1165	2N3	-0.0924
2O4	0.1163		
Plane 3: Ni3-3O1-3O4-3N2-3N3 $0.7150x + 0.2574y - 0.6500z - 2.9148 = 0$			
Ni3	-0.0102	3N2	0.0245
3O1	-0.0225	3N3	-0.0191
3O4	0.0274		

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[a] Planes are defined as $C_1x + C_2y + C_3z + C_4 = 0$ where x, y, and z are cartesian coordinates.

[b] D = distance (Å) of the given atom from the fitted plane.

Table V. (continued)

Atom	D	Atom	D
Plane 4: Ni1-Ni2-Ni3-Ag2			
$0.5494x - 0.7432y + 0.3818z - 0.5180 = 0$			
Ni1	0.0013	Ni3	0.0012
Ni2	0.0016	Ag2	-0.0043
Plane 5: Ag2-104-1Ni1-101			
$0.5202x + 0.6249y + 0.5821z - 6.7340 = 0$			
Ag2	0.0265	Ni1	0.0382
104	-0.0319	101	-0.0328
Plane 6: Ag2-204-Ni2-201			
$-0.2305x + 0.3763y + 0.8974z - 2.6079 = 0$			
Ag2	0.0145	Ni2	0.0220
204	-0.0176	201	-0.0189
Plane 7: Ag2-304-Ni3-301			
$0.7617x + 0.2871y - 0.5808z - 3.6753 = 0$			
Ag2	0.0423	Ni3	0.0665
304	-0.0529	301	-0.0559
Plane 8: Pd1-101-104-1N2-1N3			
$-0.24045x + 0.46758y + 0.85061z - 10.0 = 0$			
Pd1	-0.0040	1N2	-0.0783
101	0.0914	1N3	0.0814
104	-0.0904		

Table V. (continued)

Atom	D	Atom	D
Plane 9: Pd2-201-204-2N2-2N3			
$0.45919x + 0.62615y + 0.63013z - 13.6 = 0$			
Pd2	-0.0009	2N2	0.0061
201	-0.0065	2N3	-0.0056
204	0.0070		
Plane 10: Pd3-301-304-3N2-3N3			
$0.70502x + 0.21164y - 0.67686z - 2.93391 = 0$			
Pd3	-0.0165	3N2	-0.0117
301	0.0227	3N3	0.0199
304	-0.0144		
Plane 11: Pd1-Pd2-Pd3-Ag2			
$-0.53741x + 0.74438y - 0.39633z - 8.02520 = 0$			
Pd1	0.0021	Pd3	0.0015
Pd2	0.0017	Ag2	-0.0054
Plane 12: Ag2-104-Pd1-101			
$-0.24227x + 0.39028y + 0.88824z - 8.88979 = 0$			
Ag2	-0.0311	Pd1	-0.0420
104	0.0364	101	0.0366
Plane 13: Ag2-204-Pd2-201			
$0.48246x + 0.63531y + 0.60299z - 13.6 = 0$			
Ag2	-0.0233	Pd2	-0.0310
204	1.6807	201	1.4880

Table V. (continued)

Atom	D	Atom	D
Plane 14: Ag2-304-Pd3-301			
$0.75923x + 0.27875y - 0.58809z - 4.12457 = 0$			
Ag2	-0.0787	Pd3	-0.1118
304	0.0976	301	-0.0930

Since intramolecular H-bonding is of interest in almost all metal dioxime complexes, it is worthwhile to mention the O_2-O_3 distances (2.38(5), 2.40(5) and 2.27(4) Å) for the three nickel anion complexes. They are considered to be short as compared to the 2.40 Å reported for the dimethylglyoximato complex $Ni(HDMG)_2$[15] and other related oxime metal complexes.[16] Since the O_2-O_3 bond distances are not equal in the three $Ni(\delta\text{-}HCQD)_2^-$ ligands, they appear to be affected by crystal packing forces, which may also be the reason for the different Ag-O and Ag-N bond lengths in the three $Ni(\delta\text{-}HCQD)_2^-$ units.

Configuration of the metal cluster The geometry of the metal atoms in the molecule can be best described as a trigonal bipyramid as shown in Figure 4. The deviation of Ag2 from the least squares plane (Table V) defined by Ni1-Ni2-Ni3-Ag2 is only 0.004 Å. The Ag1-Ag2-Ag3 chain is almost linear 178.1(2)°. The angle between the Ag1-Ag2-Ag3 line and the Ni1-Ni2-Ni3 least squares plane is 89.7° indicating that the chain of silver atoms is nearly perpendicular to the plane.

It is worthwhile to note that Ag1 and Ag3 are about equidistant (~4.7 Å) from the three nickel atoms. However they are too far for direct interaction. The center Ag2 is closer to the nickel atoms, about 3.6 Å away but are

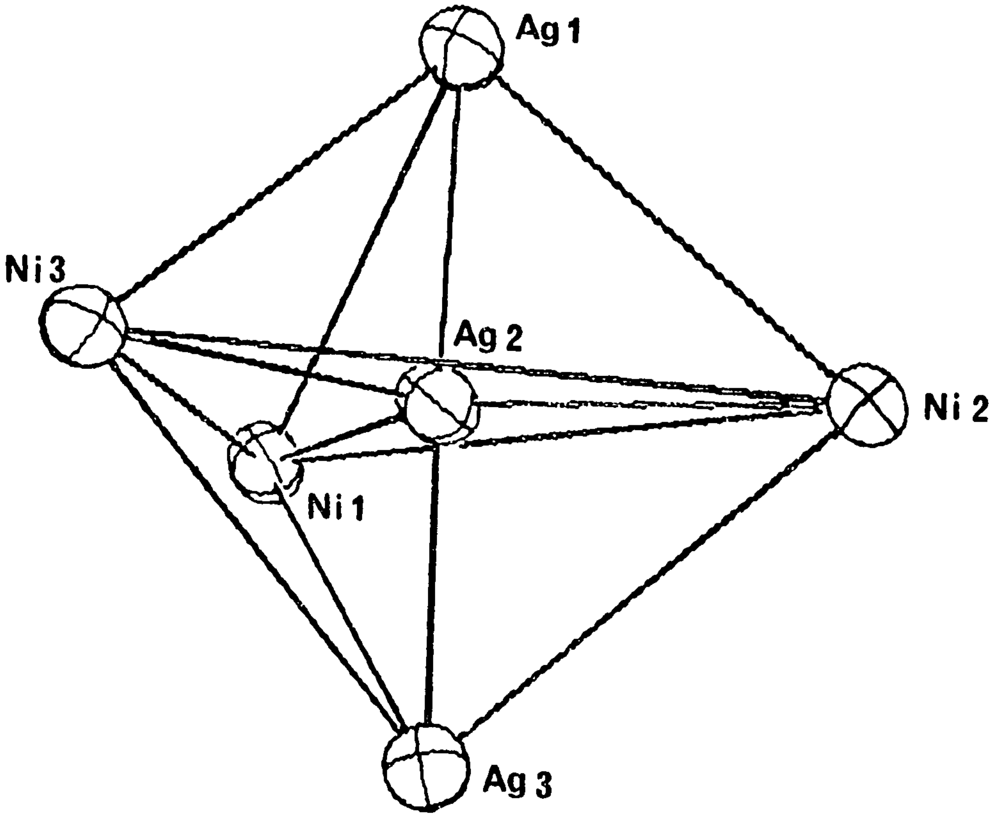

Figure 4. The trigonal bipyramid configuration of the Ni-Ag cluster.

still too far for M-M interactions to occur. The distances between the nickel atoms are listed in Table VI with Ni1 and Ni3 closer to each other. Most interesting are the short Ag1-Ag2 (3.059(5) Å) and Ag2-Ag3 (3.052(5) Å) distances. By comparison the Ag-Ag distance in metallic silver is 2.89 Å.[17] Since a Ni-Ni distance of 3.25 Å is sufficient to indicate M-M interaction in the stacked $Ni(HDMG)_2$[15] complex, it seems likely that there are strong interactions between the Ag atoms in the Ni-Ag cluster. The tendency of Ag(I) ions to form linear bonds may also contribute to the linear arrangement of the atoms.

Coordination around Ag The Ag2 atom in the center of the chain is also coordinated to six O atoms of three $Ni(\delta\text{-HCQD})_2^-$ units which act as bidentate ligands coordinating to Ag2 via their O1 and O4 oxime oxygen atoms, forming three 4-membered chelate rings around Ag2 (Figure 3). The average Ag-O bond length is 2.49(3) Å, well within the range of Ag-O bonds (2.15-2.88 Å) reported in the literature.[18-21] The three $Ni(\delta\text{-HCQD})_2^-$ are not arranged symmetrically around Ag2 at 120° angles with respect to each other, but rather the dihedral angles formed between the three least squares planes Ag2-104-Ni1-101, Ag2-204-Ni2-201 and Ag2-304-Ni3-301 are 130.2, 126.7 and 104.3°, respectively.

Table VI. Distances between heavy atoms (Å) and their estimated standard deviations (in parentheses)

Ni-Ag		Pd-Ag	
Ni1-Ni2	6.609(9)	Pd1-Pd2	6.682(3)
Ni1-Ni3	5.697(9)	Pd2-Pd3	6.561(3)
Ni2-Ni3	6.535(10)	Pd1-Pd3	5.600(4)
Ag1-Ag2	3.059(5)	Ag1-Ag2	3.173(3)
Ag2-Ag3	3.052(7)	Ag2-Ag3	3.179(3)
Ag1-Ni1	4.795(7)	Ag1-Pd1	4.882(3)
Ag1-Ni2	4.717(8)	Ag1-Pd2	4.802(3)
Ag1-Ni3	4.787(6)	Ag1-Pd3	4.858(3)
Ag2-Ni1	3.616(7)	Ag2-Pd1	3.638(3)
Ag2-Ni2	3.668(8)	Ag2-Pd2	3.666(3)
Ag2-Ni3	3.651(8)	Ag2-Pd3	3.656(3)
Ag3-Ni1	4.728(9)	Ag3-Pd1	4.816(3)
Ag3-Ni2	4.755(7)	Ag3-Pd2	4.842(3)
Ag3-Ni3	4.772(11)	Ag3-Pd3	4.859(3)

In contrast to Ag2, only N atoms (N_1 or N_4) from the Ni(δ-HCQD)$_2^-$ ligands are coordinated to Ag1 and Ag3 to give a trigonal pyramidal configuration in each case (Figure 3). The average Ag-N bond length is 2.20(4) Å comparable to other Ag-N bonds (2.11-2.51 Å) reported in the literature.[19-23] The oxime oxygen atoms O_1 and O_4 are too far (> 2.8 Å) from Ag1 or Ag3 to form Ag-O bonds. The distance of Ag1 and Ag3 from the least squares planes defined by 1N4-2N4-3N4 and 1N1-2N1-3N1, respectively, are 0.523 Å in both cases.

Within the unit cell (Figure 2) of Ni-Ag, no intermolecular H-bonding is observed. However, molecules tend to pair up through Van der Waals interactions between molecules along the 2-fold screw parallel to the C axis. There are also two sites for $CHCl_3$ near each hexanuclear molecule. The molecule $CHCl_3$ distances (> 3.4 Å) indicate interactions of only the Van der Waals type. A stereoscopic view of the Ni-Ag molecule is shown in Figure 5.

Description of the structure [Pd(δ-HCQD)$_2$Ag]$_3$·1.1$CHCl_3$, Pd-Ag A single crystal of the Pd-Ag complex prepared by adding aqueous $AgNO_3$ to a MeOH/$CHCl_3$ solution of Pd(δ-HCQD)$_2$ was chosen for the X-ray structural study. The results of that study showed that Pd-Ag has the same structure as

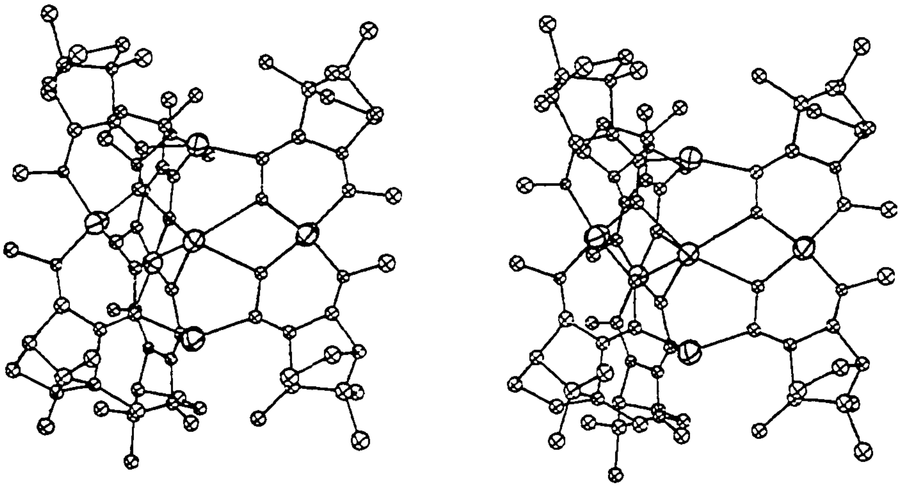

Figure 5. The stereoscopic view of the molecule of $[Ni(\delta\text{-HCQD})_2Ag]_3$.

Ni-Ag with $Pd(\delta\text{-HCQD})_2^-$ units acting as multidentate ligands. The average Pd-N bond length is 1.99(2) Å which corresponds well with literature values (1.96-2.03 Å) for Pd oxime complexes.[15,24,25] The average Pd-O bond distance of 2.00(2) Å is also comparable to those (2.00-2.03 Å) observed in other palladium oxime compounds.[25] While the average Ag-O (2.45(2) Å) and Ag-N (2.27(3) Å) bond distances are comparable to those of the Ni-Ag structure the distances between Ag1-Ag2 (3.173(3) Å) and Ag2-Ag3 (3.179(3) Å) are significantly longer. This arises from the larger size of the Pd(II) ions which move the $\delta\text{-HCQD}^-$ ligands further away from each other in

$Pd(\delta\text{-}HCQD)_2^-$ as compared to $Ni(\delta\text{-}HCQD)_2^-$, resulting in longer Ag-Ag distances. Since the Ag1-Ag2-Ag3 angle is almost linear, 178.6(4)° (Table VII) the short Ag-Ag distances (~3.17 Å) in the present case would also suggest M-M interaction. The angle between the Ag chain and the least squares plane defined by Pd1-Pd2-Pd3-Ag2 is 89.5°, very close to the value in the Ni-Ag structure.

The average intramolecular H-bonding distance (2.41(3) Å) is shorter than the 2.59 Å reported for $Pd(HDMG)_2$,[15b] but it is longer than that (2.35(3) Å) in the Ni-Ag structure. However, this is not unexpected because the H-bonding distance in $M(HDMG)_2$ complexes[26,27] is directly proportional to the size of the metal ion. Other bond distances and angles are summarized in Tables III and IV.

<u>$[Ni(\delta\text{-}HCQD)_2Ag]_3\cdot 1/2H_2O\cdot 1.3CHCl_3$, Ni-Ag, and $[Pd(\delta\text{-}HCQD)_2Ag]_3\cdot 1.1CHCl_3$, Pd-Ag</u> Both the Ni-Ag and the Pd-Ag complexes can be prepared by adding aqueous $AgNO_3$ to a $CHCl_3/MeOH$ solution of the corresponding $M(\delta\text{-}HCQD)_2$ complex according to the following equation:

$$3M(\delta\text{-}HCQD)_2 + 3Ag^+ \xrightarrow[MeOH/CHCl_3]{H_2O} [M(\delta\text{-}HCQD)_2Ag]_3 + 3H^+ \qquad (1)$$

where $M = Ni^{2+}$ or Pd^{2+}

This Ni-Ag complex is very stable so that the addition of $HgCl_2$ to a solution of the complex will not precipitate AgCl immediately.

Table VII. Related angles (deg) and their estimated standard deviations (in parentheses) for the M_3Ag_3 clusters

	Ni_3Ag_3	Pd_3Ag_3
Ag1-Ag2-Ag3	178.1(2)	178.65(4)
M[a]1-Ag1-M2	88.0(1)	87.25(4)
M1-Ag1-M3	73.0(1)	70.18(4)
M2-Ag1-M3	86.9(1)	85.55(5)
M1-Ag2-M2	130.3(2)	132.38(9)
M1-Ag2-M3	103.2(2)	100.29(6)
M2-Ag2-M3	126.5(2)	127.32(8)
M1-Ag3-M2	88.4(1)	87.55(5)
M1-Ag3-M3	73.7(1)	70.72(5)
M2-Ag3-M3	86.6(1)	85.12(4)

[a] Stands for Ni in column 1 but Pd in column 2.

The ^{13}C NMR spectrum of the Ni-Ag complex in $CDCl_3$ solvent exhibits twelve peaks for the C atoms. Following assignments made in the ^{13}C NMR spectrum of Ni(δ-HCQD)$_2$,[3] the four peaks at 153.76, 153.49, 147.42 and 147.31 ppm downfield from TMS may be assigned to those of the oxime C atoms. The solid state structure suggests, however, that only two oxime ^{13}C resonances should be observed. Since the Ag^{107} and Ag^{109} isotopes have a spin of -1/2, spin-spin coupling between C and Ag may occur. However, this possibility may be dismissed because only two peaks at 153.70 and 142.49 ppm are observed for the oxime C atoms in the similar Pd-Ag complex. It therefore appears that Ni-Ag either has a different structure or is a mixture of structures in solution.

The IR spectrum of the Ni-Ag complex in a KBr pellet no longer shows an absorption band at 1690 cm^{-1} corresponding to the oxygen-coordinated oxime ν(C=N) vibration found in Ni(δ-HCQD)$_2$.[2,3] Instead, a new band is observed at 1615 cm^{-1} which is most likely the ν(C=N) frequency of the oxime group coordinated to both the Ag and Ni ions. The other ν(C=N) absorption which probably arises from the oxime which is N-coordinated to Ni remains unchanged at 1560 cm^{-1}, as previously reported for Ni(δ-HCQD)$_2$.[2] Since the IR spectrum of the Pd-Ag complex in a KBr pellet is very similar to that of Ni-Ag, it appears that the 1605 and 1550 cm^{-1} bands are characteristic of this type of hexanuclear cluster.

Products having infrared absorptions at these positions have also been obtained from reactions of Ni(δ-HCQD)$_2$ with Sm(III), La(III), Nd(III) and Hg(II) salts. Although these compounds have not been characterized further, their infrared spectra suggest that they may have cluster structures of the type observed for Ni-Ag and Pd-Ag.

[Ni(α-HCQD)$_2$Ag]·1/2AgNO$_3$ and [Pd(α-HCQD)$_2$Ag]·1/2AgNO$_3$

Both complexes can be prepared by adding aqueous AgNO$_3$ to a MeOH/CHCl$_3$ solution of the corresponding M(α-HCQD)$_2$ complex. The difference between the starting material M(α-HCQD)$_2$ and M(δ-HCQD)$_2$, mentioned in an earlier section, is the isomeric form of the HCQD$^-$ ligand. In Ni(α-HCQD)$_2$, the oxime N atom coordinated to the metal ion is closer to the bridgehead methyl group, as shown in Figure 6 (compare Figure 1). The reaction of M(α-HCQD)$_2$ with AgNO$_3$ proceeds in a manner very similar to that of M(δ-HCQD)$_2$ (eq. 1).

In contrast to the Ni-Ag and Pd-Ag complexes, both of the products [Ni(α-HCQD)$_2$Ag]·1/2AgNO$_3$ and [Pd(α-HCQD)$_2$Ag]·1/2AgNO$_3$ obtained from the reaction of M(α-HCQD)$_2$ with AgNO$_3$ are not soluble in common organic solvents such as

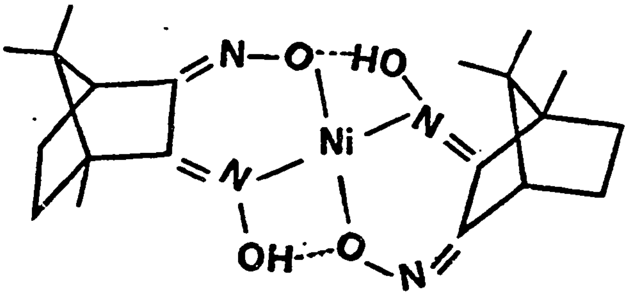

Figure 6. Structure of Ni(α-HCQD)$_2$.

alcohols, $CHCl_3$, CH_3CN and DMSO. This low solubility may be the result of the co-crystallization of a hexanuclear metal cluster similar to those of Ni-Ag or Pd-Ag with $AgNO_3$. The IR spectrum of [Ni(α-HCQD)$_2$Ag]·1/2$AgNO_3$ in a KBr pellet shows absorption bands at 1615 and 1550 cm^{-1} while that of [Pd(α-HCQD)$_2$Ag]·1/2$AgNO_3$ exhibits absorptions at 1600 and 1550 cm^{-1}. These characteristic ν(C=N) vibrational frequencies seem to indicate that hexanuclear metal clusters are indeed present in these compounds as well. Compounds of the type [Ni(α-HCQD)$_2$Ag]$_3$ without $AgNO_3$ have not been isolated.

[Ni(δ-HCQD)$_2$(Py)$_2$]·$CHCl_3$ In a further attempt to understand the coordination chemistry of Ni(δ-HCQD)$_2$, pyridine was added to a H_2O/MeOH/$CHCl_3$ solution of Ni(δ-HCQD)$_2$, from which a green paramagnetic complex, [Ni(δ-HCQD)$_2$(Py)$_2$]·$CHCl_3$ was isolated. The molar conductivity of the complex in CH_3CN shows that it is non-ionic, which suggests that a dipyridine adduct of Ni(δ-HCQD)$_2$ is formed. Its infrared spectrum taken in a KBr pellet shows ν(C=N) absorptions at 1610 and 1550 cm^{-1}. These are indeed very similar to those (1615 and 1560 cm^{-1}) observed in the Ni-Ag complex. Although it is unlikely that a hexanuclear metal cluster is formed, it does suggest that the trans-N_2O_2 coordination around Ni(II) may have changed to cis-N_2O_2.

In an effort to determine if [Ni(δ-HCQD)$_2$(Py)$_2$]·$CHCl_3$ is simply a 2:1 adduct of pyridine with trans N_2O_2 Ni(δ-HCQD)$_2$, the UV-visible spectrum of Ni(δ-HCQD)$_2$ in $CHCl_3$ was studied in the presence and absence of pyridine. In fact, there is no reaction of Ni(δ-HCQD)$_2$ with pyridine since its absorption at 576 nm remains unchanged over a period of several days. Also there is no evidence of the 614 nm absorption characteristic of Ni(δ-HCQD)$_2$(Py)$_2$. Moreover, the pyridine solution remains diamagnetic, which suggests that the Ni(δ-HCQD)$_2$ retains its square planar geometry even in the presence of excess pyridine. These observations strongly indicate that Ni(δ-HCQD)$_2$(Py)$_2$ is not a simple trans adduct of Ni(δ-HCQD)$_2$, Figure 1. A possible structure for this complex is the one shown in Figure 7 in which the (HCQD$^-$)$_2$ coordination around

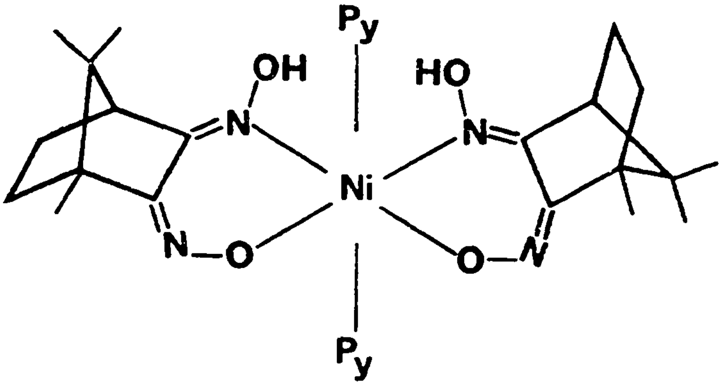

Figure 7. Structure of $[Ni(\delta\text{-HCQD})_2(Py)_2]\cdot CHCl_3$.

the Ni is now cis-N_2O_2 as suggested by the IR results. Further evidence in support of this structure is the fact that addition of $AgNO_3$ to a H_2O/MeOH/$CHCl_3$ solution of $[Ni(\delta\text{-HCQD})_2(Py)_2]\cdot CHCl_3$ readily yields the Ni-Ag cluster.

The solvent (H_2O/MeOH/$CHCl_3$) plays an important role in the preparation of $Ni(\delta\text{-HCQD})_2(Py)_2$. Perhaps its high polarity promotes the isomerization of trans-N_2O_2 $Ni(\delta\text{-HCQD})_2$ to the cis-N_2O_2 isomer which then reacts with pyridine.

Since our attempts to prepare similar Ni-Ag cluster complexes with $Ni(HDMG)_2$ and $Pd(\beta\text{-HCQD})_2$ (in the ternary solvent system) failed, it becomes evident that N,O-chelation of the ligand to the metal is probably a necessary condition for the formation of these hexanuclear cluster complexes.

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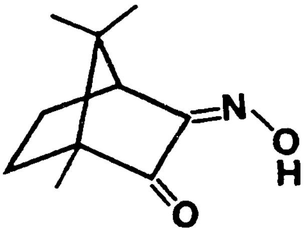
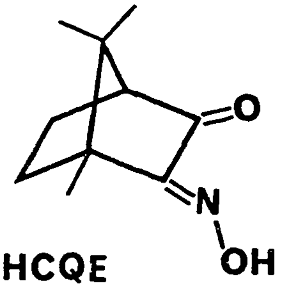
SECTION IV. CAMPHORQUINONE OXIME AND IMINE COMPLEXES OF NICKEL(II) AND ZINC(II)

INTRODUCTION

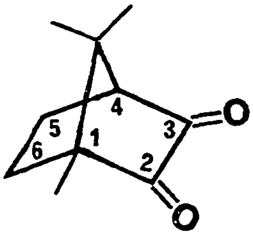
Our recent studies of optically active chelating ligands, particularly those formed from camphorquinonedioxime,[1,2] have led us to investigate Ni(II) complexes of isonitrosocamphor (HCQM) and isonitrosoepicamphor (HCQE). Both HCQM and HCQE are oxime derivatives of camphorquinone (CQ) as shown in Figure 1. Each of them



HCQM



HCQE



CQ

Figure 1. Camphorquinone and its mono-oxime derivatives.

is capable of existing in two isomeric forms[3] with the OH group either syn or anti to the carbonyl oxygen. Unlike the reactions of isomers of camphorquinonedioxime,[1,2,4] the products of reactions with HCQM and HCQE did not depend upon the isomeric form of the reacting ligand. Several Ni(II) complexes of these ligands were isolated. In addition, Zn(II) and Ni(II) imine complexes of CQ were obtained by condensing one of the two amino groups of 1,3-diaminopropane (H_2NdpNH_2) with CQ in the presence of the metal ions. These studies give further insight into the coordination chemistry of this bicyclic type of ligand and also show that carbonyl-oxime ligands which are usually poor coordinating agents[5] for Ni(II) do indeed form stable complexes in the case of HCQM and HCQE.

EXPERIMENTAL SECTION

Spectral data   Proton NMR spectra were obtained on Perkin-Elmer R-20B and A-60 spectrometers using TMS as an internal reference and d-$CHCl_3$ or d_3-CH_3CN as solvents. Infrared spectra (4000-200 cm^{-1}) were obtained on KBr pellets using a Beckman IR-4250 spectrophotometer. Electronic spectra were recorded on a Cary 14 instrument using CH_3CN as the solvent.

Conductivity measurements   Molar conductivities of all metal complexes were obtained in CH_3CN employing an Industrial Instruments conductivity bridge model RC16-B2. The solution concentrations were approximately 2×10^{-3} M based on the formula weights of the analyzed complexes.

Magnetic moments   The values of μ_{eff} (B.M.) for individual complexes were obtained in CH_3CN using the NMR shift method.[6-8] They are corrected for the diamagnetic contributions of the ligand atoms.[9]

Starting materials   Optically active camphorquinone was prepared from (+)-camphor using the procedure of Evans, et al.[10] Also optically active isonitrosocamphor[11] (HCQM) and isonitrosoepicamphor[12] (HCQE) were prepared according to the methods of Forster.

Preparation of $[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$ This compound was prepared by reacting 0.6 mmol of a mixture of syn and anti isomers of HCQM with 0.3 mmol of $NiCl_2 \cdot 6H_2O$ in 20 ml of MeOH at room temperature for 10 min. Then 0.25 g of NH_4PF_6 was added to the light green solution, which was then filtered. Approximately 1 ml of pyridine (Py) was added to the filtrate. Within 2 hrs. at room temperature, brown crystals (90% yield) of $[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$ were obtained. Anal. calcd. for $Ni(C_{25}H_{29}N_4O_2)PF_6 \cdot 2H_2O$: C, 47.86; H, 5.31; N, 8.93; Ni, 9.36. Found: C, 48.09; H, 4.96; N, 8.82; Ni, 9.41. The analogous $B(C_6H_5)_4^-$ salt may be prepared by precipitation with $NaB(C_6H_5)_4$ instead of NH_4PF_6.

Preparation of $[Ni(CQE)(Py)_3(H_2O)]PF_6 \cdot 1/2H_2O$ Isonitrosoepicamphor (0.3 mmol), as a mixture of syn and anti isomers, was reacted with $NiCl_2 \cdot 6H_2O$ (0.3 mmol) according to the procedure for the preparation of $[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$ mentioned above. Yield 70%. Anal. calcd. for $Ni(C_{25}H_{29}N_4O_2)PF_6 \cdot 1\ 1/2H_2O$: C, 48.56; H, 5.22; N, 9.06. Found: C, 48.24; H, 4.85; N, 8.98.

Preparation of $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$ This greenish-blue crystalline complex was prepared by refluxing a mixture of 3 mmol of CQ, 1.5 mmol of 1,3-diaminopropane (H_2NdpNH_2), and 1.5 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 20 ml of abs.

EtOH for 6 hrs. The resulting green solution was filtered, and approximately 0.5 g of $NaB(C_6H_5)_4$ in 10 ml of MeOH was mixed into the filtrate. After 15 min. the product began to crystallize out of the solution. It was collected and recrystallized again in CH_3CN/MeOH to give greenish-blue crystals of the product (60% yield). Anal. calcd. for $NiB_2C_{74}H_{84}N_4O_2$: C, 77.83; H, 7.42; N, 4.91. Found: C, 78.06; H, 7.59; N, 4.94.

Preparation of $Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2 \cdot CH_3CN$ This complex was prepared in the same manner as $Ni(CQdpNH_2)_2$-$[B(C_6H_5)_4]_2$ substituting $Zn(NO_3)_2 \cdot 6H_2O$ for $Ni(NO_3)_2 \cdot 6H_2O$. After the yellow product precipitated, it was collected and recrystallized in CH_3CN/MeOH to give yellow crystals (75% yield). Anal. calcd. for $ZnB_2C_{74}H_{84}N_4O_2 \cdot CH_3CN$: C, 76.72; H, 7.38; N, 5.89. Found: C, 76.31; H, 7.59; N, 5.70.

Preparation of $Ni[(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$ This complex was prepared by gradually bringing a 10 ml diisopropyl ether solution of 3 mmol of HCQE and 1.5 mmol of H_2NdpNH_2 to reflux and then allowing it to cool to room temperature. After filtration, the solvent was removed by vacuum evaporation. The yellow oily residue was dissolved in 10 ml of MeOH. Another 10 ml MeOH solution containing 1.5 mmol of $NiCl_2 \cdot 6H_2O$ and 0.5 g of

$NaB(C_6H_5)_4$ was mixed into it. A dark brown solution resulted immediately, followed by precipitation of the product which was recrystallized in CH_3CN as brick red crystals. Yield 50%. Anal. calcd. for $NiBC_{47}H_{55}N_4O_2\cdot 2CH_3CN$: C, 71.24; H, 7.17; N, 9.78. Found: C, 71.16; H, 6.91; N, 9.78.

Preparation of $(HCQM)_2(H_2NdpNH_2)$ This solid was prepared by the procedure of Uhlig and Friedrich.[13] To 20 ml of diisopropyl ether containing 6 mmol of HCQM was added 3 mmol of H_2NdpNH_2. The solution was gently brought to boiling and then allowed to cool to room temperature gradually. Yellow crystals of $(HCQM)_2(H_2NdpNH_2)$ crystallized out after 30 min. Yield 95%. Anal. calcd. for $C_{23}H_{40}N_4O_4$: C, 63.26; H, 9.25; N, 12.83. Found: C, 63.20; H, 8.97; N, 12.45.

Preparation of $[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4\cdot MeOH\cdot H_2O$ This nickel complex was prepared by adding a 15 ml MeOH solution containing 0.3 mmol of $(HCQM)_2(H_2NdpNH_2)$ to a MeOH solution (approximately 10 ml) of 0.3 mmol of $NiCl_2\cdot 6H_2O$. The dark brown solution was then filtered into a flask containing 0.5 g of $NaB(C_6H_5)_4$. After 30 min. the green solid which precipitated was collected and recrystallized in CH_3CN/MeOH to give the product. Yield 60%. Anal. calcd. for $Ni_2C_{48}H_{65}BN_4O_7$: C, 61.43; H, 6.99; N, 5.97; Ni, 12.51. Found: C, 62.01; H, 7.28; N, 6.19; Ni, 12.18.

RESULTS AND DISCUSSION

$[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$ This complex was prepared by reacting $Ni(NO_3)_2 \cdot 6H_2O$ with HCQM in the presence of excess pyridine (eq. 1). No identifiable compounds could

$$Ni^{2+} + H_2O + HCQM + 4Py \xrightarrow{MeOH} [Ni(CQM)(Py)_3(H_2O)]^+ + PyH^+ \quad (1)$$

be isolated in the absence of pyridine. When precipitated as the PF_6^- salt, the dark brown paramagnetic crystalline product was obtained. The molar conductivity (Table I) of the complex in CH_3CN[14] is consistent with its formulation as a 1:1 electrolyte, and suggests that the oxime group is probably deprotonated. It does not, however, distinguish between monomeric and dimeric structural types. By comparing the IR spectrum (Table II) of the complex with that of HCQM[3], which has its $\nu(C=N)$ and $\nu(C=O)$ frequencies at 1653 and 1751 cm^{-1}, respectively, a new band of strong intensity at 1540 cm^{-1} can be assigned to the $\nu(C=N)$ mode of the coordinated oxime. Another band of equally strong intensity is found at 1670 cm^{-1}. Based on IR studies of organic carbonyls coordinated to Ni(II) by Ablov et al.,[15,16] this latter band may be attributed to the $\nu(C=O)$ mode of the coordinated CQM^- ligand.

The anion PF_6^- gives a characteristic broad, intense absorption between 820 and 860 cm^{-1}. The coordination of

Table I. Physical properties of the complexes

Compound	Color	Molar Conductance[a]	μ (B.M.)
$[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$	brown	122	3.04[b]
$[Ni(CQE)(Py)_3(H_2O)]PF_6 \cdot 1/2H_2O$	brown	129	3.14[b]
$Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$[c]	green	155	3.50[b]
$Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2$[c]	yellow	174	diamagnetic
$[Ni(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$[c]	brown	113	3.27[d]
$[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4 \cdot MeOH \cdot H_2O$[c]	green	83	2.28[d,e]

[a] At 25° C in $cm^2ohm^{-1}M^{-1}$.

[b] At 35° C.

[c] The presence of $B(C_6H_5)_4^-$ usually lowers molar conductance values in CH_3CN.[14]

[d] At 25° C.

[e] Value per Ni.

Table II. IR[a] absorption spectra (cm^{-1}) of the complexes

Compound	ν(N-H)	ν(C=O)	ν(C=N)	ν(M-Py)
$[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$		1670	1540	235
$[Ni(CQE)(Py)_3(H_2O)]PF_6 \cdot 1/2H_2O$		1675	1520	230
$Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$	3300, 3260	1720	1675	
$Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2$	3290, 3250	1740	1680	
$[Ni(HCQEdpCQE)(CH_3CN)_2] \cdot B(C_6H_5)_4$	3340, 3280[b]		1650, 1615	
$[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4 \cdot MeOH \cdot H_2O$	3350, 3290	1670	1540	

[a] Taken on KBr pellets.

[b] Probably either ν(O-H) or ν(N-H) modes.

pyridine to Ni(II) is evidenced by the vibrational frequencies of pyridine at 626, 426 cm^{-1} and also the ν(M-Py) absorption at 236 cm^{-1} in agreement with those reported by Nakamoto.[17] The IR spectral and the molar conductivity results are consistent with either a dimeric or monomeric formulation for the complex.

A possible dimeric structure for $[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$ is shown in Figure 2, in which CQM^- bridges two

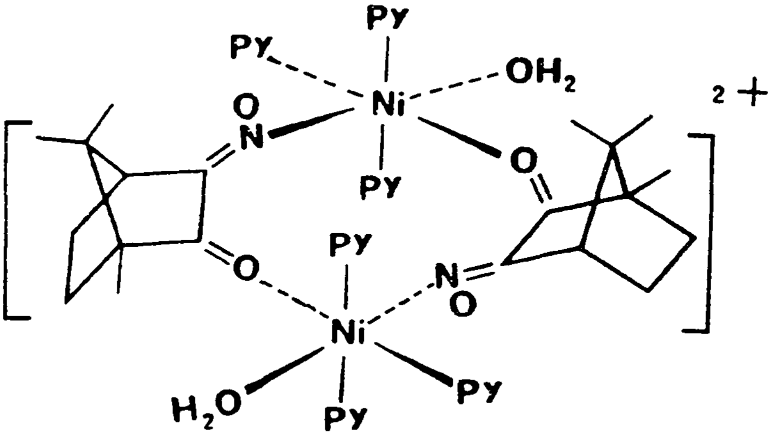


Figure 2. The dimeric structure of $[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$.

Ni atoms through its oxime N and carbonyl O atoms. The pyridine molecules occupy positions above and below the CQM^- plane of coordination and away from the bridgehead methyl of the CQM^- ligand. The small water molecules occupy the remaining sites to complete the octahedral coordination of Ni(II). Charalambous, et al.,[18] proposed a similar type of oxime-carbonyl bridge between Ni atoms in Ni complexes of the mono-oximes of ortho-benzoquinones. In the case that the complex is monomeric, both the carbonyl O and oxime N atoms of the CQM^- ligand would probably coordinate to the same Ni atom. The magnetic moment of the complex is 3.04 B.M., and its electronic spectrum exhibits a broad asymmetric absorption with a maximum at 980 nm(ϵ = 9.8 $cm^{-1}M^{-1}$); both of these results are consistent[19] with octahedral Ni(II) in either a monomeric or dimeric structure.

$[Ni(CQE)(Py)_3(H_2O)]\cdot PF_6\cdot 1/2H_2O$ As expected, this complex can be prepared in a manner similar (eq. 1) to that of the nickel complex of CQM^-, and probably has the same type of structure because its electronic absorption spectrum (Table III) and magnetic moment (3.14 B.M.) are comparable to those of $[Ni(CQM)(Py)_3(H_2O)]PF_6\cdot H_2O$. Coordination of the CQE^- ligand to Ni(II) is indicated by the positions of the ν(C=O) and ν(C=N) absorptions at 1675 and 1520 cm^{-1}, respectively, in its infrared spectrum.

Although carbonyl-oxime compounds are known[5] to be poor coordinating ligands for Ni(II), the mono-oxime of ortho-benzoquinone forms Ni(II) complexes, which are perhaps stabilized by delocalization through the highly conjugated ligand system. In the present studies of

Table III. Visible and near IR absorption bands in CH_3CN solvent

Compound	Maximum Absorption (nm)[a]		
$[Ni(CQM)(Py)_3 \cdot H_2O]PF_6 \cdot H_2O$	825(sh)[b]	980(9.3)	1125(sh)
$[Ni(CQE)(Py)_3 \cdot H_2O]PF_6 \cdot 1/2H_2O$	800(sh)	975(8.9)	1050(sh)
$Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$	587(26)	975(9.8)	
$[Ni(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$	775(sh)	810(sh)	840(3.6)
$[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4 \cdot MeOH \cdot H_2O$	585(45.5)[c]	1020(10)[c]	

[a] Extinction coefficients ($cm^{-1}M^{-1}$) are given in parentheses.

[b] Sh means shoulder.

[c] Extinction coefficient per Ni.

isonitrosocamphor and isonitrosoepicamphor where there is no such conjugation, stable Ni(II) complexes can still be obtained provided pyridine is used to complete the octahedral coordination sphere.

<u>$[Ni(CQdpNH_2)_2][B(C_6H_5)_4]_2$</u> In an attempt to prepare the complex bis-(camphorquinone-diimine-1,3-propane)Ni(II) tetraphenylborate (Figure 3), a green compound was isolated

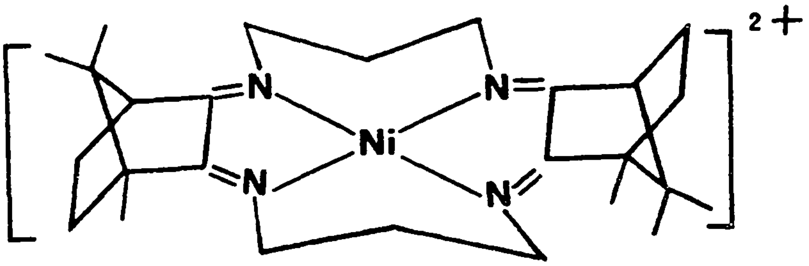


Figure 3. Bis-(camphorquinone-diimine-1,3-propane)Ni(II) ion.

when a mixture of $Ni(NO_3)_2 \cdot 6H_2O$, CQ and H_2NdpNH_2 in abs. EtOH was refluxed for several hours, followed by subsequent exchange of NO_3^- for $B(C_6H_5)_4^-$. Elemental analysis of the product indicated that the reaction proceeded according to the following equation:

$$Ni^{2+} + 2\ CQ + 2\ H_2NdpNH_2 \xrightarrow{MeOH} [Ni(CQdpNH_2)_2]^{2+} + 2H_2O \qquad (2)$$

A conductivity measurement showed that the product is a 2:1 electrolyte in CH_3CN. The $CQdpNH_2$ ligand is the

Schiff base resulting from the condensation of the C3 carbonyl group with one amino group of H_2NdpNH_2. Its presence in the complex is supported by the KBr infrared spectrum of the complex which shows two ν(N-H) absorptions at 3300 and 3250 cm^{-1}. The sharp, intense band at 1675 cm^{-1} may be assigned to the ν(C=N) mode of the Schiff base. The carbonyl ν(C=O) absorption occurs at 1720 cm^{-1}, which is shifted somewhat to lower frequency from values of 1780 and 1765 cm^{-1} for free CQ in $CHCl_3$ solution. The small shift of the ν(C=O) frequency suggests that the carbonyl group is either weakly coordinated to the metal ion or hydrogen bonded to a coordinated amino group.

Formation of the Schiff base probably occurs at the C_3 rather than the C_2 carbonyl group. This is suggested by the work of Forster[9] in which he noted that CQ reacted with aniline to form a Schiff base only at the C_3 position, probably because this is the sterically least hindered site.

The electronic absorption spectrum (Table III) of the complex exhibits broad bands at 587 nm(ϵ = 26 $cm^{-1}M^{-1}$) and 975 nm(ϵ = 9.8 $cm^{-1}M^{-1}$). Although the low ϵ values (less than 100)[19] suggest an octahedral geometry for the complex, the magnetic moment (3.5 B.M.) is more consistent with a tetrahedral geometry (Figure 4). It is possible

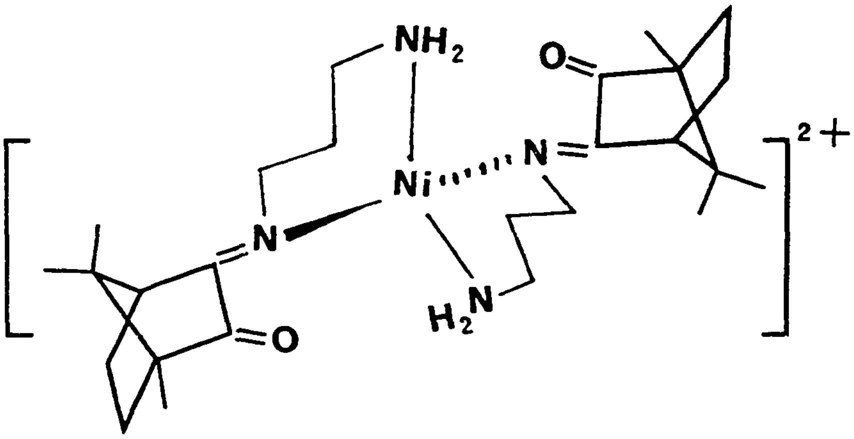


Figure 4. The $Ni(CQdpNH_2)_2^{2+}$ ion.

that weak coordination of the carbonyl groups gives rise to these somewhat contradictory results.

$\underline{Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2 \cdot CH_3CN}$ This bright yellow Zn complex was prepared in the same way as the analogous Ni(II) complex described above. Its infrared spectrum (Table II) is very similar to that of the corresponding Ni(II) complex and suggests that these complexes have similar coordination around the metal ions. The tendency of Zn(II) to form tetrahedral complexes suggests such a structure (Figure 4) for this complex. The KBr spectrum also exhibits $\nu(C\equiv N)$ absorptions at 2250 and 2290 cm^{-1} for the uncoordinated CH_3CN.

The proton NMR spectrum of the complex in d_3-CH_3CN gives 3 methyl-proton signals as sharp singlets at δ values of 0.71, 0.91, and 1.04 ppm. The phenyl proton signals of the $B(C_6H_5)_4^-$ anion appear between 6.7 and 7.4 ppm. The protons of the propyl chain are observed as multiplets at 3.8 and 3.0 ppm, while the broad signal of the amino protons coincides with the multiplets at 3.8 ppm. The sharp singlet at 1.9 ppm corresponds to free CH_3CN. Most important of all is the C_4 proton which occurs at 2.5 ppm in CQ but shifts to 3.15 ppm in the Zn complex. Such a shift is expected when this proton is adjacent to an N-atom coordinated to a metal ion, as observed in our previous ^1H NMR studies of camphorquinonedioxime metal complexes.[2,4] This result confirms our earlier assumption for the Ni complex that Schiff base formation occurs at the least hindered C_3 carbonyl.

$[Ni(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$ This brown nickel(II) complex may be prepared by the reaction of Ni(II), H_2NdpNH_2, and isonitrosoepicamphor. Based on elemental analytical

$$Ni^{2+} + 2\ HCQE + H_2NdpNH_2 + 2\ CH_3CN \longrightarrow Ni(HCQEdpCQE)(CH_3CN)_2^{+} + H^{+} + 2\ H_2O \qquad (3)$$

results, octahedral structures such as those shown in Figures 5, 6, and 7 may be suggested for the complex. The infrared spectrum of the complex shows absorptions at 2250, 2280 and 2310 cm^{-1} in the region characteristic

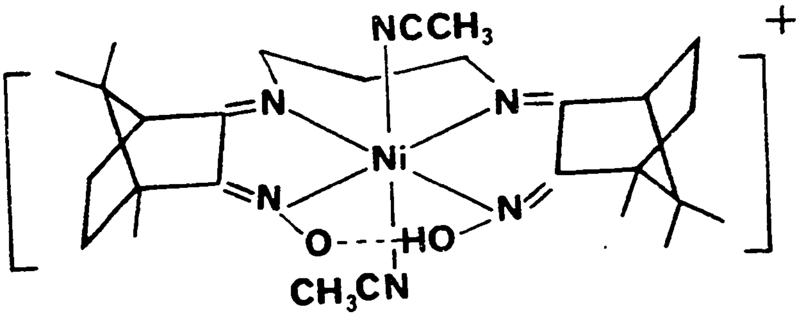


Figure 5. The $[\mathrm{Ni(HCQEdpCQE)(CH_3CN)_2}]^+$ ion with two 5-membered chelate rings.

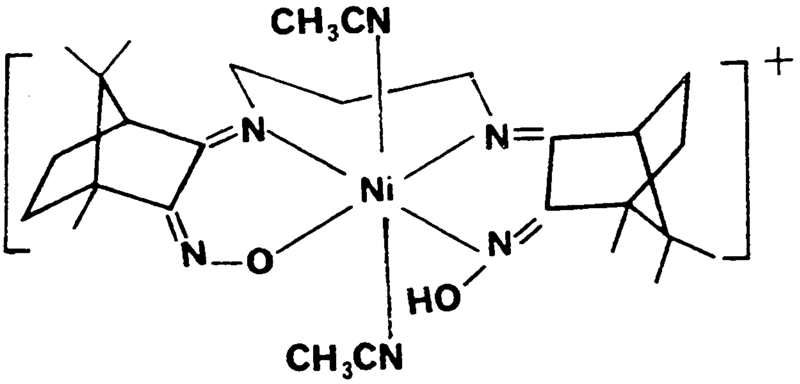


Figure 6. The $[\mathrm{Ni(HCQEdpCQE)(CH_3CN)_2}]^+$ ion with one 5-membered and one 6-membered chelate ring.

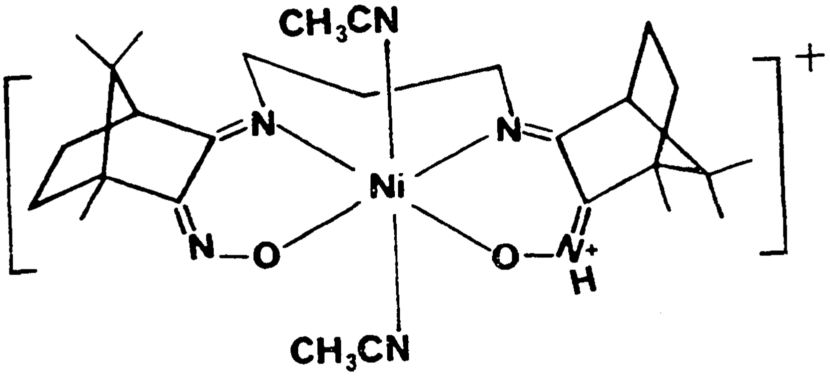


Figure 7. The $[Ni(HCQEdpCQE)(CH_3CN)_2]^+$ ion with two 6-membered chelate rings.

of coordinated CH_3CN ligands.[20] The IR spectrum also shows bands at 1620 and 1650 cm^{-1}, which may be attributed to the ν(C=N) modes of the oxime and imine groups, although a specific assignment is not possible. The magnetic moment (3.27 B.M.) and electronic spectrum (Table III) are also consistent with octahedral coordination for the Ni(II).

Whether the complex has the structure shown in Figure 5, 6, or 7 cannot be established on the basis of the available data. However, it might be noted that the formation of 6-membered chelate rings such as those shown in Figures 6 and 7 is not unreasonable in view of the known[1] structure of bis(δ-camphorquinonedioximato)nickel(II) in which the ligands form 6-membered rings by coordinating *via* N and O atoms.

$(HCQM)_2(H_2NdpNH_2)$ Following the procedure used by Uhlig[13] for the condensation of 1,3-diaminopropane with diacetylmonoxime to give bis-(diacetylmonoxime-imine)-1,3-propane, HCQM failed to react with H_2NdpNH_2 to give the desirable monoxime-imine ligand. Instead a product of the composition $(HCQM)_2(H_2NdpNH_2)$, in which HCQM and H_2NdpNH_2 co-crystallized, was obtained.

The IR spectrum of this pale yellow crystalline solid in $CHCl_3$ or in a KBr pellet shows both $\nu(C{=}O)$ and $\nu(C{=}N)$ absorptions at 1751 and 1653 cm^{-1}, respectively, which are identical to those of unreacted HCQM[3]. The $\nu(N\text{-}H)$ absorptions of the H_2NdpNH_2 are found at 3280 and 3350 cm^{-1}. The ^1H NMR spectrum taken in $CDCl_3$ shows proton signals which are merely a combination of those of the reactants since no changes in chemical shifts from those of HCQM[3] and H_2NdpNH_2 are observed. It is uncertain what causes this unusual co-crystallization of the two organic compounds. However intermolecular H-bonding between the amino groups of H_2NdpNH_2 and the carbonyl or the oxime group of HCQM probably plays a role.

$[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4\cdot MeOH\cdot H_2O$ This green solid was obtained by adding $(HCQM)_2(H_2NdpNH_2)$ to a MeOH solution containing $NiCl_2\cdot 6H_2O$ and $NaB(C_6H_5)_4$. Conductivity data (Table I) indicate that the compound is a 1:1 electrolyte which suggests that the oxime ligands are deprotonated. The magnetic moment after correction for the diamagnetic contributions of the ligands is 2.28 B.M., smaller than the normal value (2.8-3.4 B.M.)[19] for octahedral Ni(II) complexes. The electronic absorption spectrum (Table III) exhibits maxima at 585 nm(ϵ = 45.5 $cm^{-1}M^{-1}$) and 1020 nm(ϵ = 10 $cm^{-1}M^{-1}$).

Its IR spectrum taken on a KBr pellet is very similar to that of $[Ni(CQM)(Py)_3(H_2O)]PF_6 \cdot H_2O$ with intense absorptions at 1540 and 1670 cm^{-1}. These may be assigned to the ν(C=N) and ν(C=O) modes, respectively, of the coordinated CQM^- ligand. The ν(N-H) absorptions are observed as medium intense bands at 3290 and 3350 cm^{-1}, as in the case of $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$.

In an attempt to confirm the presence of the various ligands in this nickel complex, it was dissolved in d-$CHCl_3$ containing a few drops of d_4-MeOH and KCN. After filtering off the cyano nickel complex which formed, the ^1H NMR spectrum of the resulting solution indicated the presence of CQM^-, H_2NdpNH_2 as well as $B(C_6H_5)_4^-$ and free MeOH. This spectrum suggested that both CQM^- and H_2NdpNH_2 are present as ligands in the complex. The presence of OH^- in the complex was deduced from the analytical results and the overall charge required by the conductivity data.

A possible structure for the complex would be one in which the two Ni atoms are bridged by an OH^- group and possibly by another ligand or donor group.

Although it was expected that HCQM might react with H_2NdpNH_2 to yield a Schiff base complex of the type, $[Ni(HCQEdpCQE)(CH_3CN)_2]^+$, formed in the analogous reaction with HCQE, Schiff base condensation with HCQM does not occur. This is presumably prevented for steric reasons by the methyl group at the C-1 carbon atom. This is probably the same reason why only the C-3 carbonyl group of CQ condensed with H_2NdpNH_2 to give $Ni(CQdpNH_2)_2{}^{2+}$ and $Zn(CQdpNH_2)_2{}^{2+}$ rather than forming the macrocyclic complex shown in Figure 3.

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SUMMARY

The present study has shown that camphorquinonedioxime has interesting properties as a ligand. It is not only capable of being a bidentate ligand but a monodentate ligand as well. In the complexes $Pd(\delta\text{-HCQD})_2$, $Ni(\delta\text{-HCQD})_2$ and $Ni(\alpha\text{-HCQD})_2$, the anionic $\delta\text{-HCQD}^-$ and $\alpha\text{-HCQD}^-$ forms behave as bidentate ligands coordinating to the metal ion via their N and O atoms. An X-ray structural study of $Ni(\delta\text{-HCQD})_2$ suggests that this type of coordination is due to the bicyclic nature of the ligand which causes the C-C-N angles in the chelate ring to become larger so that formation of a 6-membered rather than a 5-membered chelate ring becomes more favorable than it would be in an unstrained system. This mode of coordination is characterized by the presence of both the N-coordinated and O-coordinated $\nu(C=N)$ absorptions in the IR spectra of these complexes. The $\beta\text{-HCQD}^-$ ligand, however, coordinates through both N atoms to yield square planar complexes of the type $Pd(\beta\text{-HCQD})_2$, $Pt(\beta\text{-HCQD})_2$ and $Cu(\beta\text{-HCQD})_2\cdot H_2O\cdot 1/2$dioxane. This mode of coordination is characterized by the presence of only N-coordinated $\nu(C=N)$ absorptions in the IR spectrum. It is interesting that Cu(II) forms only the N,N-coordinated complex, whereas

the most stable form of the N(II) complex is N,O-bonded. The smaller ionic radius of Cu(II) would presumably favor N,O-coordination which would give the larger 6-membered ring. The preference of Cu(II) for N,N-coordination might be related to the higher M-N bond strength for Cu(II) as compared to Ni(II). The higher Cu-N bond strength apparently more than compensates for the strain in the 5-membered rings of $Cu(\beta\text{-}HCQD)_2 \cdot H_2O \cdot 1/2$dioxane. Neutral $\beta\text{-}H_2CQD$ behaves as a bidentate ligand in the complexes $Pd(\beta\text{-}H_2CQD)Cl_2$, $Pt(\beta\text{-}H_2CQD)Cl_2$ and $Cu(\beta\text{-}H_2CQD)Cl_2$ in which $\beta\text{-}H_2CQD$ coordinates to the metal ion by N,N chelation. This type of coordination is characterized by a strong IR absorption for $\nu(C{=}N)$ between 1450 and 1400 cm^{-1}.

Evidence from the infrared and proton NMR spectra indicates that α, δ and $\gamma\text{-}H_2CQD$ act as monodentate ligands, coordinating <u>via</u> only one N atom in $Pd(\alpha\text{-}H_2CQD)_2Cl_2$, $Pd(\delta\text{-}H_2CQD)_2Cl_2$ and $Pd(\gamma\text{-}H_2CQD)_2Cl_2$. This type of complex is probably stabilized to some extent by inter- or intramolecular H-bonding, which presumably is also a stabilizing force in the two complexes $[Pt(\gamma\text{-}HCQD)(\gamma\text{-}H_2CQD)Cl]_2$ and $Ni(\delta\text{-}HCQD)_2(\delta\text{-}H_2CQD)_2$.

In the reaction of $Ni(\delta\text{-}HCQD)_2$ or $Pd(\delta\text{-}HCQD)_2$ with aqueous $AgNO_3$ in $H_2O/MeOH/CHCl_3$, the two complexes

$[Ni(\delta\text{-HCQD})_2Ag]_3\cdot 1/2H_2O\cdot 1.3CHCl_3$ and $[Pd(\delta\text{-HCQD})_2Ag]_3\cdot 1.1CHCl_3$, respectively, were obtained. In each case X-ray structural studies indicate that the square planar $M(\delta\text{-HCQD})_2^-$ anion complex behaves as a multidentate ligand coordinating to a linear chain of three silver atoms via its O and N atoms. The coordination at the metal ion is that of cis N_2O_2 rather than trans N_2O_2 as observed in $Ni(\delta\text{-HCQD})_2$. In these Ni_3Ag_3 and Pd_3Ag_3 hexanuclear clusters, the short Ag-Ag distances, averaging 3.05 and 3.17 Å, respectively, suggest substantial Ag-Ag interactions. Since the reactions of $Ni(\alpha\text{-HCQD})_2$ and $Pd(\alpha\text{-HCQD})_2$ with aqueous $AgNO_3$ proceeded in a manner similar to that of $Ni(\delta\text{-HCQD})_2$ and gave the complexes $[Ni(\alpha\text{-HCQD})Ag]\cdot 1/2AgNO_3$ and $[Pd(\alpha\text{-HCQD})_2Ag]\cdot 1/2AgNO_3$, respectively, hexanuclear metal clusters may also be found in these complexes. This type of cluster compound is characterized by the presence of two $\nu(C{=}N)$ absorptions at 1610 and 1560 cm^{-1} in their IR spectra. Similar $\nu(C{=}N)$ absorptions are also observed in the IR spectrum of the pyridine adduct $[Ni(\delta\text{-HCQD})_2(Py)_2]\cdot CHCl_3$, suggesting that the $\delta\text{-HCQD}^-$ ligand probably coordinates to Ni(II) through cis N,O chelation.

Nickel(II) complexes of the camphorquinone mono-oxime, (HCQM) and (HCQE) have been prepared and shown to have the composition $[Ni(CQM)(Py)_3(H_2O)]\cdot H_2O$ and $[Ni(CQE)(Py)_3(H_2O)]\cdot 1/2H_2O$. Their IR spectra indicate that both the carbonyl O and the oxime N atoms are coordinated to the Ni(II). The Schiff base complex $[Ni(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$ formed by the reaction between 1,3-diaminopropane and HCQE in the presence of Ni(II) could have 5-membered or 6-membered chelate rings. However a similar Schiff base Ni(II) complex is not obtained when HCQM is substituted for HCQE. A possible explanation for this is the steric interaction between the C_1 methyl of HCQM and 1,3-diaminopropane which probably prevents the formation of the Schiff base ligand $(HCQMdpCQM)^-$. This view is supported by the isolation of the two complexes $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$ and $Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2\cdot CH_3CN$ in which the ligand $CQdpNH_2$ is obtained by the formation of a Schiff base at the least hindered carbonyl of camphorquinone with 1,3-diaminopropane.

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