were obtained on standing.

(b) Trans Isomer. (i) Refluxing *trans*-[$RuNO(S_2CNMe_2)_2Cl$] (0.09 g) and AgN_3 (0.08 g) in methanol for ~6 h gave a brown suspension. Filtration, followed by evaporation, gave a brown solid (0.05 g). This was dissolved in a minimum amount of CH_2Cl_2 and passed through neutral alumina (12 in. × 1/2 in.). The trans isomer was eluted with CH_2Cl_2 as a yellow band. Methanol was added, and orange needles were obtained on standing; yield 0.022 g (24%). A thin brown band of the hydroxo complex remained at the head of the column. When *trans*-[$RuNO(S_2CNMe_2)_2Cl$] was refluxed with AgN_3 for only 2 h, lower yields of the trans isomer were obtained (4%). The cis isomer was eluted second from the column (20%).

(ii) A more convenient preparation entailed heating solid *cis*-[$RuNO(S_2CNMe_2)_2N_3$] in air to a temperature of approximately 180 °C. At ca. 150 °C, the brown crystals changed to yellow. The sample was left at 170–180 °C for approximately 10 min. The yellow product was washed with diethyl ether.

[$RuNO(S_2CNMe_2)_2SCN$]. (a) Cis Isomer. The method described for the azido complex was followed. The yield of product from 0.06 g of *cis*-[$RuNO(S_2CNMe_2)_2I$] and 0.025 g of AgSCN was 0.045 g, 85%. Dissolution in CH_2Cl_2 and passage through an alumina column showed only traces of trans isomer (pale yellow band) which eluted first. The cis isomer was present as a brown band. Recrystallization from CH_2Cl_2/CH_3OH gave brown crystals.

(b) Trans Isomer. Solid *cis*-[$RuNO(S_2CNMe_2)_2SCN$] was heated in air to approximately 220 °C. At 210–215 °C, a color change from brown to tan occurred. Under the microscope the product appeared as tiny yellow crystals. The sample was left at 220 °C for about 10 min. The product was then washed with ether and recrystallized from CH_2Cl_2/CH_3OH.

Poor yields of the complex were obtained by refluxing *trans*-[$RuNO(S_2CNMe_2)_2Cl$] (0.1 g) with AgSCN (0.09 g) in methanol for 4 h. The brown product (0.09 g) obtained after filtration was treated as for the cis isomer. The trans isomer was eluted first (4%) followed by the cis complex (15%). The trans hydroxo complex remained at the head of the column.

[$RuNO(S_2CNMe_2)_2NCO$]. (a) Cis Isomer. (i) A mixture of *cis*-[$RuNO(S_2CNMe_2)_2I$] (0.1 g) and AgNCO (0.05 g) was refluxed in methanol for 10 min. A color change from brown to yellow occurred. A yellow-brown solid was isolated after filtration. Dissolution in CH_2Cl_2 and passage through neutral alumina gave a light brown band which was readily eluted with CH_2Cl_2. Khaki crystals were obtained; yield 0.015 g, 18%. A second yellow band, not shifted by CH_2Cl_2, was readily eluted with CH_3OH and yielded amber crystals of *trans*-[$RuNO(S_2CNMe_2)_2OH$]·CH_3OH; yield 0.015 g, 18%.

(ii) Heating *cis*-[$RuNO(S_2CNMe_2)_2I$] (0.1 g) in acetonitrile with a slight excess of $AgPF_6$, followed by cooling and filtering, gave a yellow-orange solution. Solid KNCO (0.05 g) was added and a brown solution resulted after boiling the mixture for several minutes. The solid was treated as in (i). The yellow trans isomer was eluted first (5%) followed by the cis isomer (25%).

(b) Trans Isomer. Heating solid *cis*-[$RuNO(S_2CNMe_2)_2NCO$] in air to approximately 175 °C resulted in quantitative conversion to the yellow trans isomers. The product was washed with ether.

Sodium *N*-Methyl-*N*-ethyldithiocarbamate. *N*-Methyl-*N*-ethylamine hydrochloride (1 g) was dissolved in chilled methanol (10 cm^3). Addition of CS_2 (1 cm^3) was followed by an aqueous solution of NaOH (1 g in a minimum volume). Stirring gradually gave a yellow solution which upon slow evaporation yielded white crystals. These were collected, washed with ether and pentane, and recrystallized twice from methanol. The mother liquor yielded several batches of crystals: total yield 1.4 g, 64%; mp 113–115 °C.

Silver Salts. These were prepared by metathesis from silver nitrate and the required sodium salt. The labeled nitrite, $Ag^{15}NO_2$, was prepared from $AgClO_4$ and $Na^{15}NO_2$ (^{15}N 99%); yield 76%.

Acknowledgment. The authors wish to thank the National Science Foundation for support of this research. We also thank Dr. M. Barfield and Dr. D. Gust for their assistance in obtaining ^{15}N and ^{13}C NMR spectra.

Registry No. *trans*-[$RuNO(S_2CNMe_2)_2Cl$], 72075-88-8; *trans*-[$RuNO(S_2CNEt_2)_2Cl$], 72075-89-9; *trans*-[$RuNO(S_2CNMePh)_2Cl$], 72075-90-2; *trans*-[$RuNO(S_2CNMeEt)_2Cl$], 72075-91-3; *trans*-[$RuNO(S_2CNMe_2)_2N_3$], 72075-92-4; *trans*-[$RuNO(S_2CNMe_2)_2NCO$], 72075-93-5; *trans*-[$RuNO(S_2CNMe_2)_2SCN$], 72075-94-6; *trans*-[$RuNO(S_2CNMe_2)_2OH$], 72075-95-7; *trans*-[$RuNO(S_2CNMe_2)_2H_2O$]BF_4, 72075-97-9; *trans*-[$RuNO(S_2CNMe_2)_2CH_3OH$]PF_6, 72075-99-1; *cis*-[$RuNO(S_2CNMe_2)_3$], 51139-59-4; *cis*-[$RuNO(S_2CNMe_2)_2F$], 72076-00-7; *cis*-[$RuNO(S_2CNMe_2)_2Br$], 72076-01-8; *cis*-[$RuNO(S_2CNMe_2)_2I$], 72076-02-9; *cis*-[$RuNO(S_2CNEt_2)_2Br$], 72076-03-0; *cis*-[$RuNO(S_2CNEt_2)_2I$], 72076-04-1; *cis*-[$RuNO(S_2CNMeEt)_2Br$], 72076-05-2; *cis*-[$RuNO(S_2CNMeEt)_2I$], 72076-06-3; *cis*-[$RuNO(S_2CNMe_2)_2NO_2$], 72076-07-4; *cis*-[$RuNO(S_2CNMe_2)_2N_3$], 72120-76-4; *cis*-[$RuNO(S_2CNMe_2)_2SCN$], 72120-77-5; *cis*-[$RuNO(S_2CNMe_2)_2NCO$], 72120-78-6; $RuNOCl_3$, 18902-42-6.

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Novel Transition-Metal Complexes of Camphorquinone Dioxime Ligands

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Received June 25, 1979

Camphorquinone dioxime, H_2CQD, is known to exist in four isomeric forms (α, β, γ, and δ) which differ by the orientations of the OH groups on their oxime nitrogen atoms. The deprotonated β-$HCQD^-$ coordinates via the two N atoms to form the square-planar complexes Pd(β-HCQD)$_2$, Pt(β-HCQD)$_2$, and Cu(β-HCQD)$_2$·H_2O·$^1/_2$dioxane. However, δ- and α-$HCQD^-$ coordinate via one N and one O atom to yield square-planar complexes of the type Pd(δ-HCQD)$_2$, Ni(δ-HCQD)$_2$, and Ni(α-HCQD)$_2$. The neutral β-H_2CQD ligand forms Pd(β-H_2CQD)Cl_2, Pt(β-H_2CQD)Cl_2, and Cu(β-H_2CQD)Cl_2 complexes in which the ligand coordinates through both N atoms. Spectroscopic evidence indicates that α-, γ-, and δ-H_2CQD are monodentate ligands, coordinating via only one N atom, in Pd(α-H_2CQD)$_2Cl_2$, Pd(α-H_2CQD)$_2Cl_2$, and Pd(γ-H_2CQD)$_2Cl_2$. Finally, structures for two complexes of the unusual composition Ni(δ-HCQD)$_2$(δ-H_2CQD)$_2$ and [Pt(γ-HCQD)(γ-H_2CQD)Cl]$_2$ have been suggested. Ultraviolet–visible, infrared, ESR, and ^1H NMR spectroscopy were employed to characterize these new types of α-dioxime complexes.

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 camphorquinone dioxime ligands, H_2CQD, until last year when work in this laboratory[6] and in Osaka University[7–9] was reported.

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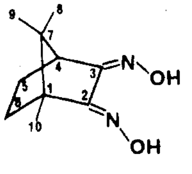
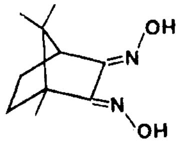
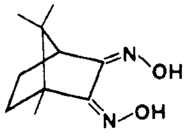
Our interest in this area evolved from previous studies of optically active ligands[10,11] and a desire to prepare complexes with optically active α-dioxime ligands. Unlike dimethylglyoxime, H_2DMG, or cyclohexanedione dioxime, H_2CHD, camphorquinone dioxime has been isolated in four isomeric forms which, henceforth, are referred to as α-, β-, γ-, and δ-H_2CQD as shown below. 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.



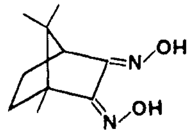
α



β



γ



δ

Experimental Section

Spectral Data. ^1H NMR spectra were obtained on a Varian HA-100 spectrometer using Me_4Si as internal reference. IR spectra (4000–200 cm^{-1}) were obtained with KBr pellets by 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(γ-$H_2CQD)_2Cl_2$ in MeOH was measured to be 33.25 $cm^2\ \Omega^{-1}\ M^{-1}$ using an Industrial Instruments Model RC16-B2 conductivity bridge. The cell constant was 0.3712, and the concentration of Pd(γ-$H_2CQD)_2Cl_2$ was 1.79×10^{-3} M.

Starting Materials. $Pd(PhCN)_2Cl_2$[12] and $Pt(PhCN)_2Cl_2$[13] were prepared according to published procedures. The optically active isomeric camphorquinone dioxime ligands were prepared from (+)-camphor by the procedures of Forster.[14] Deuterium-exchange reactions of the camphorquinone dioxime ligands and Ni(δ-$HCQD)_2$ were carried out by refluxing the compounds for 10 h in CH_3OD and then reisolating them by subsequent removal of the solvent under vacuum.

Preparation of Ni(δ-HCQD)$_2$. Single crystals of Ni(δ-$HCQD)_2$ were prepared by dissolving 0.64 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 10 mL of MeOH at 50 °C. Then 1.24 mmol of γ-H_2CQD was added. While the mixture was being stirred, 1.24 mmol of NaOMe in 10 mL of MeOH was added. The resulting green solution was refluxed for 2–3 h. 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(δ-$HCQD)_2$, 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(α-HCQD)$_2$. This compound was prepared by dissolving 0.32 mmol of α-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 needle-like crystals of Ni(α-$HCQD)_2$ 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(δ-HCQD)$_2$(δ-H$_2$CQD)$_2$. This complex was prepared by dissolving 0.96 mmol of γ-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 1 h 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 h 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 needle-like 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(β-HCQD)$_2$·H$_2$O·$^1/_2$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 γ-H_2CQD. The dark brown solution was refluxed for 2–3 h. 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 needle-like 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 $Cu(C_{10}H_{15}N_2O_2)_2 \cdot H_2O \cdot {}^1/_2C_4H_8O_2$: C, 51.19; H, 7.04; N, 10.86. Found: C, 51.02; H, 6.99; N, 10.54.

Preparation of Cu(β-H$_2$CQD)Cl$_2$. This complex was prepared by mixing 0.32 mmol of $CuCl_2 \cdot 2H_2O$ with 0.32 mmol of γ-H_2CQD in 10 mL of absolute EtOH. After stirring of the mixture overnight, the green solution was evaporated to dryness. The solid was dissolved in 15 mL of CH_3CN from which green needle-like 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(β-HCQD)$_2$. This Pd(II) complex was prepared by suspending 0.32 mmol of β-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 the resulting yellow solution was warmed at 70 °C in a hot H_2O bath for about 15 min, it was filtered into a flask containing 5 mL of H_2O. The filtrate totaling about 40 mL was left standing for a period of several days after which a crop of yellow needle-like crystals of Pd(β-$HCQD)_2$ were 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(δ-HCQD)$_2$. Yellow $Pd(PhCN)_2Cl_2$ (0.32 mmol) was added to 10 mL of MeOH containing 0.64 mmol of δ-H_2CQD and an equivalent amount of Et_3N. After stirring of the mixture at 50 °C for 2 h, the yellow solution was filtered, and the filtrate was cooled to −25 °C. Yellow crystals of Pd(δ-$HCQD)_2$ crystallized out after 24 h 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 of $CHCl_3$ solutions of γ-H_2CQD (0.32 mmol) and $Pd(PhCN)_2Cl_2$ (0.16 mmol) at room temperature, yellow crystals of Pd(γ-$H_2CQD)_2Cl_2$ almost immediately started to crystallize out of the solution. The reaction was complete within 15–30 min in 80% yield. Anal. Calcd for $Pd(C_{10}H_{16}N_2O_2)_2Cl_2$: 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-$H_2CQD)_2Cl_2$; yield 80%. Anal. Calcd for $Pd(C_{10}H_{16}N_2O_2)_2Cl_2$: 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-$H_2CQD)_2Cl_2$; yield 80%. Anal. Calcd for $Pd(C_{10}H_{16}H_2O_2)_2Cl_2$: 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_2CQD (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.

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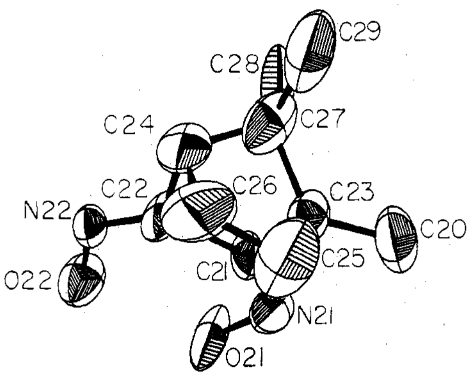


Figure 1. Computer-generated perspective view of γ-H_2CQD.

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 1278 g/mol while the calculated value for dimeric Pt(γ-HCQD)(γ-H_2CQD)Cl is 1250.2 g/mol.

Preparation of Pt(HCQD)$_2$·H_2O. When 2 equiv of NaOMe was added to [Pt(γ-HCQD)(γ-H_2CQD)Cl]$_2$ in methanol, an orange solution was obtained. After being stirred for 15 min, 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 $Pt(C_{10}H_{15}N_2O_2)_2{\cdot}H_2O$: 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 from equimolar Pd(γ-H_2CQD)$_2Cl_2$ and Et_3N in acetone solvent, in a manner similar to that used for the preparation of Pt(HCQD)$_2$·H_2O. After being stirred for 15 min, 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 $Pd(C_{10}H_{15}N_2O_2)_2{\cdot}H_2O$: C, 46.64; H, 6.28; N, 10.88. Found: C, 46.88; H, 6.36; N, 10.83.

Results and Discussions

Camphorquinone Dioxime 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 1 in which the oxime O atoms are directed toward 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 N–OH.[17] Therefore, we assign the band at 1600 cm^{-1} to a C=N stretching vibration.

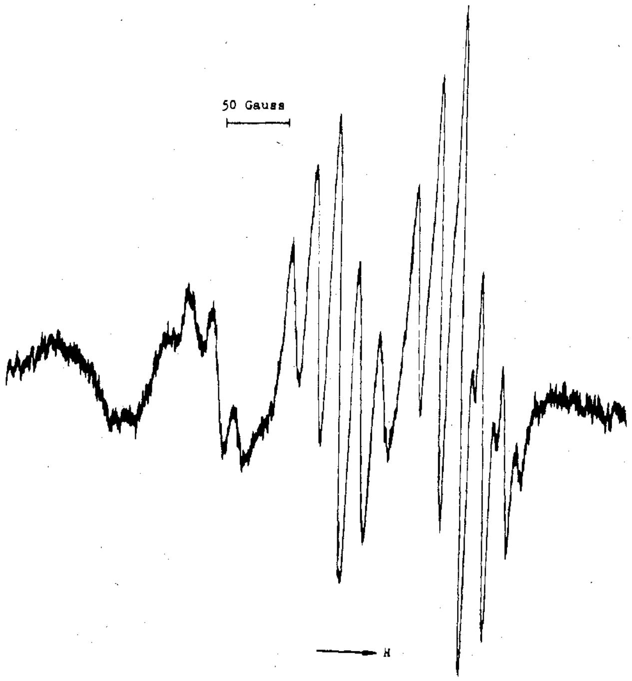
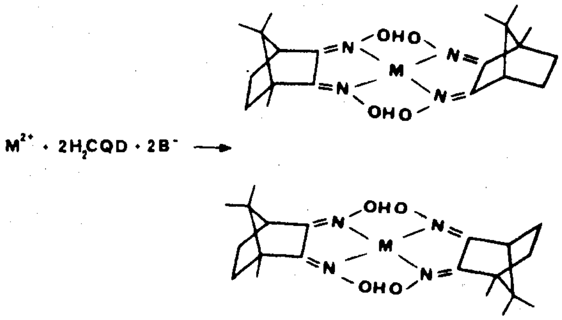


Figure 2. ESR spectrum of Cu(β-HCQD)$_2$ in $CHCl_3$ at room temperature recorded on a Varian E-3 ESR spectrometer. $g = 2.08$ measured by comparison with perylene radical cation.

The $CHCl_3$ solution IR spectra of α- and δ-H_2CQD give ν(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 ν(C=N) absorptions of β-H_2CQD are not readily observed due to extensive H bonding which broadens the region between 1600 and 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 and 1100 cm^{-1} [18] as intense bands.

Bis(β-camphorquinone dioximato)copper(II)–Water–Hemikis(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 eq 1. Two isomeric products are possible.



(1)

When $Cu(OAc)_2{\cdot}H_2O$ was reacted with γ-H_2CQD in MeOH, only a dark brown product, Cu(β-HCQD)$_2$·H_2O·$^1/_2$dioxane, was obtained. The IR spectrum of the complex exhibits ν-

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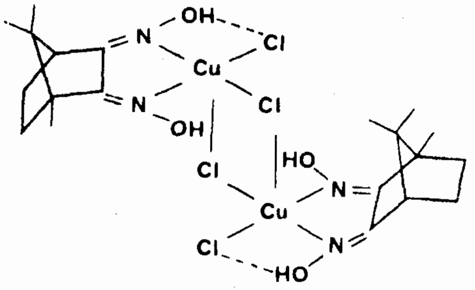

Figure 3. Cu(β-H_2CQD)Cl_2 dimer.

(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 2. By analogy with results reported by Wiersema and Windle[22] for Cu$(HDMG)_2$, Cu(β-HCQD)$_2$ should have four lines due to copper (^{63}Cu, ^{65}Cu, $I = {}^3/_2$) nuclear hyperfine interaction plus extra lines due to nitrogen (^{14}N, $I = 1$) hyperfine interactions which can be accounted for as 9 nitrogen hyperfine lines per 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 2) of Cu(β-HCQD)$_2$ is nearly identical with 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(β-HCQD)$_2$·H_2O·$^1/_2$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 (ϵ 7.9 × 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]

(β-Camphorquinone dioxime)copper(II) Chloride, 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 3. 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} (Table V), 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-camphorquinone dioximato)nickel(II), Ni(δ-HCQD)$_2$. This brown complex was prepared by addition of NaOMe to a methanol solution of $Ni(NO_3)_2$·$6H_2O$ and γ-H_2CQD. Our earlier single-crystal X-ray structural study[6] established that the ligand forms a six-membered chelate ring by coordinating to the Ni through the N and O atoms in a trans manner as shown in Figure 4.

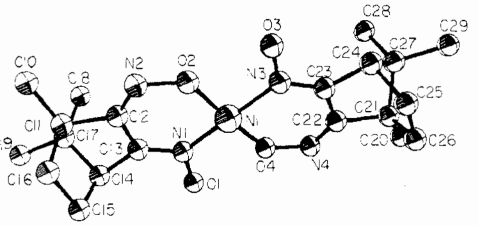

Figure 4. Computer-generated perspective view of Ni(δ-HCQD)$_2$.

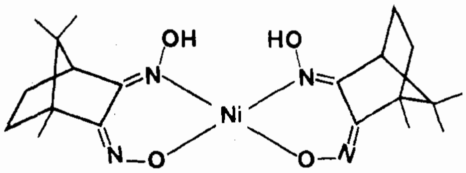

Figure 5. Cis isomer of Ni(δ-HCQD)$_2$.

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(δ-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 ν(C═N) absorption occurs at 1560 cm^{-1}.

Bis(α-camphorquinone dioximato)nickel(II), Ni(α-HCQD)$_2$. This green complex was prepared by adding α-H_2CQD to a methanol solution of $Ni(OAc)_2$·$4H_2O$. It also probably has trans N,O coordination around the Ni as in the case of Ni(δ-HCQD)$_2$. This assumption is supported by the presence of two different ν(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(δ-HCQD)$_2$ and Ni(α-HCQD)$_2$ were in good agreement with theirs.

Although the coordination around Ni is very similar in both Ni(α-HCQD)$_2$ and Ni(δ-HCQD)$_2$ complexes, Ni(α-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 5) around Ni been detected. Such an arrangement of ligands with two oxime protons placed on the same side of the complex would presumably be less stable due to the lack of hydrogen bonding which is present in the other Ni complex.

^{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 6) are almost identical; their absorption maxima and ϵ values are summarized in Table II.

Bis(δ-camphorquinone dioximato)bis(δ-camphorquinone dioxime)nickel(II), Ni(δ-HCQD)$_2$(δ-H_2CQD)$_2$. This unstable complex was prepared using a 3:1 ratio of γ-H_2CQD to $Ni(NO_3)_2$·$6H_2O$ and crystallized from anhydrous CH_3CN at −25 °C. Once the complex crystallized out, further attempts to

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Table I. ^{1}H NMR Spectra of the M(HCQD)$_2$ Complexes

		NMR spectra, ppm		
complex	solvent	O-H	C(4)-H	methyl-H
Ni(α-HCQD)$_2$	*a*	11.10[d]	2.62	0.88, 0.90, 1.39[c]
	b	*f*	2.62	0.88, 0.94, 1.39
Ni(δ-HCQD)$_2$	*a*	10.94[d]	3.20	0.82, 0.96, 1.12[c]
	b	*f*	3.20	0.82, 1.00, 1.12
Ni(δ-HCQD)$_2$-(δ-H$_2$CQD)$_2$	*b*	*f*	3.25	0.82, 0.86, 0.96 1.01, 1.09, 1.12
δ-H$_2$CQD	*b*	*f*	3.10	0.86, 1.01, 1.09[c]
Pd(β-HCQD)$_2$	*a*	12.35[e]	2.90	0.82, 1.00, 1.38[c]
Pd(δ-HCQD)$_2$	Me$_2$SO-*d*$_6$	*f*	3.24	0.80, 0.95, 1.12[c]
Pt(β-HCQD)$_2$	*a*	12.56[e]	3.0	0.82, 0.98, 1.42[c]

[a] CHCl$_3$-*d*. [b] Acetone-*d*$_6$. [c] C10-methyl. [d] Sharp singlet. [e] Broad and asymmetrical. [f] Not observed.

Table II. UV-Visible Spectra of Ni Complexes

complex	λ_{max}, nm	ε, cm^{-1} M^{-1}
Ni(δ-HCQD)$_2$[a]	576	3.5×10
	413 sh[b]	1.6×10^3
	360 sh	3.3×10^3
	308	1.8×10^4
Ni(α-HCQD)$_2$[a]	576	3.3×10
	405 sh	8.8×10^2
	359 sh	1.6×10^3
	306	1.3×10^4
Ni(δ-H$_2$CQD)$_2$(δ-HCQD)$_2$[c]	413	
	359	
	304	

[a] In CHCl$_3$. [b] Shoulder. [c] As KBr pellet.

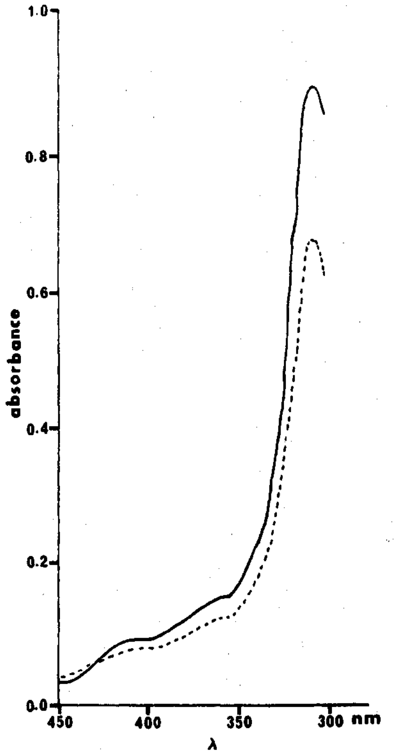

Figure 6. UV-visible spectra of Ni(δ-HCQD)$_2$ (—) and Ni(α-HCQD)$_2$ (- - -) in CHCl$_3$.

recrystallize it led only to Ni(δ-HCQD)$_2$.

Proton NMR studies established that all four ligands in Ni(δ-HCQD)$_2$(δ-H$_2$CQD)$_2$ have the δ structure. In acetone-*d*$_6$, six methyl proton signals of equal intensity are observed (Table I). The signals at 0.86, 1.01, and 1.09 ppm can be assigned to the free δ-H$_2$CQD ligand while those at 0.82, 0.96, and 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 acetone-*d*$_6$. 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)$_2$.

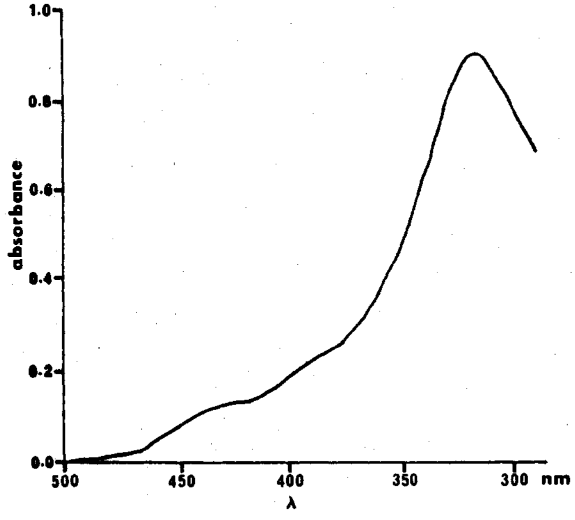

Figure 7. UV-visible spectrum of Ni(δ-H$_2$CQD)$_2$(δ-HCQD)$_2$ as KBr pellet.

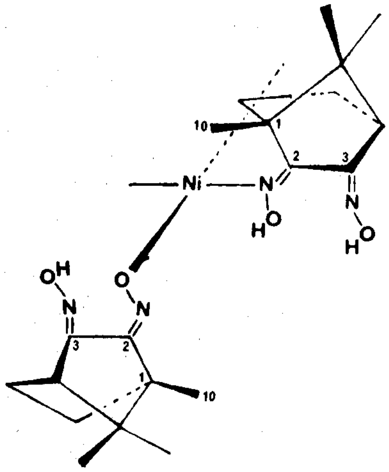

Figure 8. Ni(δ-H$_2$CQD)$_2$(δ-HCQD)$_2$ square-planar coordination with trans N$_2$O$_2$. Two other ligands are omitted for clarity.

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 and 3100 cm^{-1} [26] in the solid-state IR spectrum.

The UV-vis absorption spectrum (Figure 7) of the solid complex pressed into a KBr pellet is very similar to solution spectra of Ni(δ-HDCQD)$_2$ 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

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of these donors around the Ni as shown in Figure 8. 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-camphorquinone dioximato)palladium(II), Pd(β-HCQD)$_2$. The yellow complex Pd(β-$HCQD)_2$ was prepared in $H_2O/MeOH/CHCl_3$ (1:3:1) from $Pd(PhCN)_2Cl_2$, β-H_2CQD, and NaOMe. This is a different method from the one reported by Nakamura et al.,[9] and the product is probably a mixture of two isomers with structures shown in eq 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 (ε 2.0×10^3 cm^{-1} M^{-1}) and a charge-transfer band at 274 nm (ε 1.4×10^4 cm^{-1} M^{-1}).

In its ^1H NMR spectrum (Table I) taken in $CHCl_3$-*d*, the oxime proton with a chemical shift of 12.35 ppm downfield from Me_4Si is observed as a broad asymmetric peak. Although Marov et al.,[27] who studied the H bonding of Ni(II) α-dioximates by ^1H NMR, suggested that an asymmetric peak indicates the presence of isomers, there is no 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-camphorquinone dioximato)palladium(II), Pd(δ-HCQD)$_2$. Yellow crystals of Pd(δ-$HCQD)_2$ could be obtained by reacting $Pd(PhCN)_2Cl_2$ with δ-H_2CQD in MeOH in the presence of Et_3N. This procedure is different from the one reported by Nakamura et al.[9] and gave crystals of Pd(δ-$H_2CQD)_2$ so that elemental analyses and an ^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 Me_2SO-d_6 is almost identical with that of Ni(δ-$HCQD)_2$. Its IR absorptions at 1560 and 1620 cm^{-1} may be assigned to the N-coordinated and O-coordinated oxime ν(C=N) frequencies, respectively. The ν(OH) absorptions are observed at 3400 and 2600 cm^{-1}.

Bis(β-camphorquinone dioximato)platinum(II), Pt(β-HCQD)$_2$. This complex was prepared by reacting $Pt(PhCN)_2Cl_2$ with NaOMe and β-H_2CQD in a 1:3:1 $CHCl_3/MeOH/H_2O$ solution. The brown crystalline product has the structures shown in eq 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 1.3×10^3 cm^{-1} M^{-1}) and 340 nm (ε 4.0×10^3 cm^{-1} M^{-1}). Absorptions at 305 nm (ε 1.09×10^4 cm^{-1} M^{-1}) and 273 nm (1.14×10^4 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 ^1H 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-camphorquinone dioxime)platinum(II) Chloride, *trans*-Pd(γ-H$_2$CQD)$_2$Cl$_2$.** A $CHCl_3$ solution of $Pd(PhCN)_2Cl_2$ in the presence of γ-H_2CQD gives large yellow needle-like crystals of Pd(γ-$H_2CQD)_2Cl_2$. Spectra and a conductivity measurement on this complex suggest that the γ-H_2CQD 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 comparison of 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 IV). The ^1H NMR spectrum of Pd(γ-$H_2CQD)_2Cl_2$ is summarized in Table III. The presence of other isomers is not observed. The downfield shift of the C4–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 C3 oxime is more favorable. Although coordination at the C2–N (Figure 9) is possible, this position is less favorable because of the steric interaction of the remainder of the metal complex with the C10 methyl group. Attempts to make Pd(β-$HCQD)_2$ out of Pd(γ-$H_2CQD)_2Cl_2$ 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 insoluble in common organic solvents such as $CHCl_3$, methanol, or H_2O.

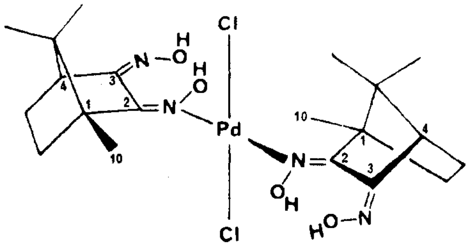

Figure 9. *trans*-Pd(γ-$H_2CQD)_2Cl_2$.

Table III. ^1H NMR of Metal Camphorquinone Dioxime (H_2CQD) Dichloride Complexes

complex	solvent	NMR of methyl-H, ppm
Pd(γ-$H_2CQD)_2Cl_2$	acetone-d_6	0.92, 1.1, 1.12
	Me_2SO-d_6	0.76, 0.91, 1.02
γ-H_2CQD	Me_2SO-d_6	0.76, 0.91, 1.02
Pd(α-$H_2CQD)_2Cl_2$	MeOH-*d*/acetone-d_6	0.92, 0.95, 1.02, 1.41
	Me_2SO-d_6	0.84, 1.33
α-H_2CQD	Me_2SO-d_6	0.84, 1.33
Pd(δ-$H_2CQD)_2Cl_2$	MeOH-*d*/acetone-d_6	0.84, 0.87, 0.98, 1.06
	Me_2SO-d_6	0.74, 0.88, 0.98
δ-H_2CQD	Me_2SO-d_6	0.74, 0.88, 0.98
Pd(β-$H_2CQD)Cl_2$	CH_3CN-d_3	0.98, 1.04, 1.34
	Me_2SO-d_6	0.84, 0.90, 0.94, 1.30, 1.34
β-H_2CQD	Me_2SO-d_6	0.83, 1.31
[Pt(γ-HCQD)-(γ-$H_2CQD)Cl]_2$	acetone-d_6	0.90, 1.00, 1.07, 1.10, 1.12
	Me_2SO-d_6	0.74, 0.90, 0.98, 1.04

Table IV. IR[a] Absorption Frequencies (cm^{-1}) of Metal H_2CQD Dichloride Complexes

complex	ν(C=N→M)[b]	ν(C=N)[c]	ν(M–Cl)
Pd(γ-$H_2CQD)_2Cl_2$	1535	1615	345
Pd(δ-$H_2CQD)_2Cl_2$	1555	1680	300–350[d]
Pd(α-$H_2CQD)_2Cl_2$	1560	1680	300–350[d]
[Pt(γ-H_2CQD)-(γ-HCQD)Cl]$_2$	1560	1610	330

[a] As KBr pellet. [b] Coordinated ν(C=N). [c] Uncoordinated ν(C=N). [d] Several ν(M–Cl) are observed in this region.

When a strongly coordinating solvent such as Me_2SO is added to a MeOH solution of the complex, Me_2SO displaces the γ-H_2CQD ligands which were identified by their characteristic ^1H NMR spectrum (Table III).

Bis(δ-camphorquinone dioxime)palladium(II) Chloride, Pd(δ-H$_2$CQD)$_2$Cl$_2$. 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 and 350 cm^{-1} in its IR spectrum (Table IV). A possible structure of Pd(δ-$H_2CQD)_2Cl_2$ is shown in Figure 10. The coordinated and uncoordinated oxime C=N absorption bands

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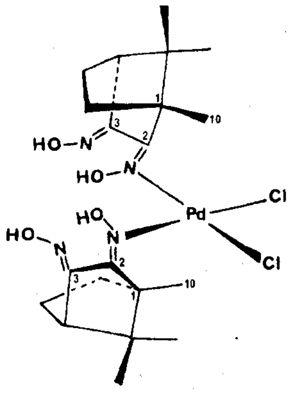

Figure 10. *cis*-$Pd(\delta\text{-}H_2CQD)_2Cl_2$.

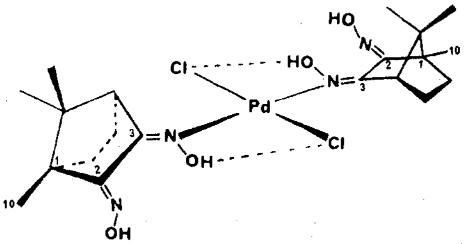

Figure 11. *trans*-$Pd(\alpha\text{-}H_2CQD)_2Cl_2$.

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 III) consistent with the assumption that more than one isomer is present. When excess Me_2SO is added to a solution of the complex, the free δ-H_2CQD is regenerated.

Bis(α-camphorquinone dioxime)palladium(II) Chloride, $Pd(\alpha\text{-}H_2CQD)_2Cl_2$. $Pd(\alpha\text{-}H_2CQD)_2Cl_2$ can be prepared in a manner similar to that of $Pd(\delta\text{-}H_2CQD)_2Cl_2$ and probably exists as cis and trans isomers. Its possible structure is shown in Figure 11. Its ^1H NMR and IR spectra are summarized in Tables III and IV. Four methyl proton signals appear at 0.92, 0.95, 1.02, and 1.41 ppm. Coordinated and uncoordinated $\nu(C{=}N)$ 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 11).

Bis(β-camphorquinone dioxime)palladium(II) Chloride, $Pd(\beta\text{-}H_2CQD)Cl_2$. When a CH_3CN solution of $Pd(\gamma\text{-}H_2CQD)_2Cl_2$ was allowed to stand for a period of 1–2 weeks at room temperature, $Pd(\beta\text{-}H_2CQD)Cl_2$ began to crystallize out. In this reaction, the γ-H_2CQD ligand is transformed into the β-isomer. A nearly quantitative yield of the $Pd(\beta\text{-}H_2CQD)Cl_2$ complex can be obtained by direct reaction between the ligand and $Pd(PhCN)_2Cl_2$.

As in the case of $Cu(\beta\text{-}H_2CQD)Cl_2$, an intense, sharp band at 1430 cm^{-1} may be assigned to the $\nu(C{=}N)$ 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 $Pd(\beta\text{-}H_2CQD)Cl_2$ and $Cu(\beta\text{-}H_2CQD)Cl_2$ have similar square-planar structures (Figure 3) with possible intermolecular bridging.

The β-H_2CQD ligand is not displaced when the complex is dissolved in Me_2SO, but formation of other Pd complexes occurs as indicated by the appearance of new signals in the ^1H NMR spectrum (Table III).

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.

Table V. IR[a] Absorption Frequencies (cm^{-1}) of $M(dioxime)Cl_2$ Complexes

complex	$\nu(C{=}N)$	$\nu(OH)$	$\nu(M{-}Cl)$
$Cu(H_2DMG)Cl_2$	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.

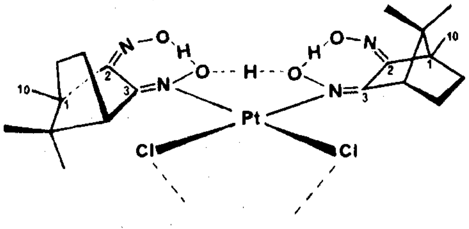

Figure 12. $[Pt(\gamma\text{-}H_2CQD)(\gamma\text{-}HCQD)Cl]_2$.

Bis[(γ-camphorquinone dioxime)(γ-camphorquinone dioximato)platinum(II) chloride], $[Pt(\gamma\text{-}HCQD)(\gamma\text{-}H_2CQD)Cl]_2$. This dimeric complex was prepared by the reaction of K_2PtCl_4 and γ-H_2CQD. A possible structure is shown in Figure 12. 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 $\nu(C{=}N)$ vibrations of the coordinated and uncoordinated oxime groups. The broad $\nu(OH)$ absorptions at 3100 and 2800 cm^{-1} resemble those of γ-H_2CQD, suggesting that γ-H_2CQD and γ-$HCQD^-$ are present in the complex. As in the case of $Pd(\gamma\text{-}H_2CQD)_2Cl_2$, addition of base to a methanol solution of $[Pt(\gamma\text{-}HCQD)(\gamma\text{-}H_2CQD)Cl]_2$ yielded the highly insoluble complex $Pt(HCQD)_2{\cdot}H_2O$ of unknown structure. Attempts to isolate pure $Pt(\alpha\text{-}H_2CQD)_2Cl_2$ and $Pt(\delta\text{-}H_2CQD)_2Cl_2$ were unsuccessful.

Conclusion

Camphorquinone dioxime has been shown to be capable of being either a bidentate or monodentate ligand. As a bidentate ligand in the complexes $Ni(\alpha\text{-}HCQD)_2$, $Ni(\delta\text{-}HCQD)_2$, and $Pd(\delta\text{-}HCQD)_2$, 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 $\nu(C{=}N)$ absorptions in the IR spectrum.

In the complexes $Pd(\beta\text{-}HCQD)_2$, $Pt(\beta\text{-}HCQD)_2$, and $Cu(\beta\text{-}HCQD)_2{\cdot}H_2O{\cdot}{}^1/_2$dioxane, β-$HCQD^-$ coordinates to the metal ion by N,N chelation. In this case, only N-coordinated $\nu(C{=}N)$ absorptions are observed in their IR spectra. The failure to obtain $Ni(\beta\text{-}HCQD)_2$, even from the reaction of Ni^{2+} with β-H_2CQD and base, is believed to be due to the bicyclic nature of the ligand which increases the C–C–N angles so that formation of five-membered chelate rings around Ni(II) becomes less favorable. This is supported by our earlier crystal structure determination of $Ni(\delta\text{-}HCQD)_2$.[6] The isolation of $Cu(\beta\text{-}HCQD)_2{\cdot}H_2O{\cdot}{}^1/_2$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 con-

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sidering 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 five-membered rings of the $Cu(\beta\text{-}HCQD)_2\cdot H_2O\cdot {}^1/_2$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 and 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 bonds 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 8 and 12.

Acknowledgment. We appreciate the support of this research by the National Institute of General Medical Sciences (Grant No. GM12626).

Registry No. $Ni(\delta\text{-}HCQD)_2$, 52139-64-7; $Ni(\alpha\text{-}HCQD)_2$, 52231-70-6; $Ni(\delta\text{-}HCQD)_2(\delta\text{-}H_2CQD)_2$, 72100-32-4; $Cu(\beta\text{-}HCQD)_2$, 72100-33-5; $Cu(\beta\text{-}H_2CQD)Cl_2$, 72100-34-6; $Pd(\beta\text{-}HCQD)_2$, 71212-51-6; $Pd(\delta\text{-}HCQD)_2$, 72100-35-7; $Pt(\beta\text{-}HCQD)_2$, 72100-36-8; $Pd(\gamma\text{-}H_2CQD)_2Cl_2$, 72100-37-9; $Pd(\delta\text{-}H_2CQD)_2Cl_2$, 72121-18-7; $Pd(\alpha\text{-}H_2CQD)_2Cl_2$, 72150-72-2; $Pd(\beta\text{-}H_2CQD)Cl_2$, 72100-38-0; $Pt(\beta\text{-}H_2CQD)Cl_2$, 72100-39-1; $Pd(H_2CHD)Cl_2$, 72100-40-4; $Pd(H_2DMG)Cl_2$, 30184-40-8; $[Pt(\gamma\text{-}HCQD)(\gamma\text{-}H_2CQD)Cl]_2$, 72121-19-8.

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Coordinately Unsaturated Metal Clusters. A Neutron Diffraction Study of the Crystal and Molecular Structure of the Trimeric Rhodium Complex $\{HRh[P(OCH_3)_3]_2\}_3$[1]

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Received July 26, 1979

The molecular structure of $\{HRh[P(OCH_3)_3]_2\}_3$ has been determined by using neutron diffraction techniques [T = 110 K]. The trimeric rhodium complex is monoclinic, space group $P2_1$ [C_2^2, No. 4], with a = 10.792 (6) Å, b = 13.438 (8) Å, c = 13.438 (8) Å, β = 91.64 (4)°, V_c = 1948.02 Å^3, and d_{calcd} = 1.801 g cm^{-3} for Z = 2. The neutral molecule consists of a triangular array of Rh atoms each bonded in an approximately square-planar fashion to two terminal $P(OCH_3)_3$ groups and two bridging hydride ligands. The Rh–Rh separations involving single hydrogen bridges are 2.803 (7), 2.780 (6), and 2.856 (8) Å and the average Rh–H_b distance is 1.76 (3) Å. The bridging Rh–H_b separations reported here are the first interactions to be characterized structurally with neutron crystallographic techniques (T = 110 K). A discussion of the origin of the structural distortion from planarity of the $\{HRhP_2\}_3$ cluster core is presented.

Introduction

The di- and trimeric rhodium clusters $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ (**1**) and $\{HRh[P(OCH_3)_3]_2\}_3$ (**2**) have recently been shown to be exceedingly active catalysts toward the hydrogenation of olefins.[3,4] These two clusters, the smallest oligomers for a potentially large set of hydrides of the form $\{HRh[P(OR)_3]_2\}_x$, have been shown to reversibly and rapidly add 1 molecule of hydrogen/molecule of cluster without detectable fragmentation of the cluster. The fact that the clusters themselves, rather than mononuclear $H_3Rh[P(OR)_3]_2$ fragments, are the principal intermediates in the catalytic hydrogenation of olefins suggests that these clusters, their hydrogen adducts, and the hydrogen adduct–olefin complexes[4] may be viewed as tentative models of intermediates in olefin hydrogenation on metal surfaces.[6-13] Accordingly, the precise structural and stereochemical features of these polynuclear rhodium species are of considerable interest especially since the detailed structural characterization, at the molecular level, of hydrocarbon substrates chemisorbed on metal surfaces is an exceedingly difficult task.[12] The isolation of large single crystals of complexes **1** and **2** has allowed structural characterization of these potential catalytic surface–substrate models.[4,12,13] We report here the complete neutron diffraction structural characterization of **2**. Although the nonhydrogen atom framework was previously determined by X-ray diffraction,[3] the complete structural characterization of the $\{HRhP_2\}_3$ core required neutron diffraction analysis. A preliminary account of this work has been previously reported.[4]

Experimental Section

The trimeric rhodium complex, **2**, is monoclinic space group $P2_1$ [C_2^2, No. 4] with a = 10.792 (6) Å, b = 13.438 (8) Å, c = 13.438

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(1) This work was performed under the auspices of the Office of Basic Energy Sciences of the United States Department of Energy. We also wish to acknowledge the partial support of this collaborative research by the National Science Foundation (Grant No. CHE-78-20698) through a grant to J.M.W. and E.L.M.

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