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Camphorquinone Oxime and Imine Complexes of Nickel(II) and Zinc(II)

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The nickel complexes $[Ni(CQM)(py)_3(H_2O)]PF_6{\cdot}H_2O$ and $[Ni(CQE)(py)_3(H_2O)]PF_6{\cdot}{}^1/_2H_2O$ of isonitrosocamphor (HCQM) and isonitrosoepicamphor (HCQE), as well as the complex $[Ni(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$ formed by the Schiff-base reaction between HCQE and 1,3-diaminopropane (H_2NdpNH_2) in the presence of Ni(II), were prepared and characterized by their IR, visible, and near-IR spectra, magnetic moments, and conductivities. Also prepared were the $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$ and $Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2$ complexes of the Schiff-base ligand formed by the reaction of camphorquinone (CQ) with H_2NdpNH_2. The proton NMR spectrum of the $Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2$ complex indicated that formation of the Schiff base occurred only at the least hindered carbonyl of CQ. Possible structures of all complexes are discussed.

Introduction

Recently we reported[1,2] the preparation of a series of transition-metal complexes of camphorquinone dioxime. Unlike other dioxime ligands, this one was found to bond to transition metals via N and O atoms, as well as by the normal N,N-mode of coordination. In addition, camphorquinone dioxime formed complexes in which the ligand was monodentate coordinating via only one N atom. These unusual modes of coordination were attributed to the larger angles in the chelate ring resulting from the strained nature of the bicyclic ligand.

In the present study, we undertook the preparation of complexes of the monooximes of camphorquinone (CQ). These monooximes occur in two isomeric forms known as isonitrosocamphor (HCQM) and isonitrosoepicamphor (HCQE) (see Figure 1). Each is capable of existing in two isomeric forms[3] with the OH group either syn or anti to the carbonyl oxygen. Unlike the case of reactions of isomers of camphorquinone dioxime,[1,2,4] the products of Ni(II) reactions with HCQM and HCQE do not depend upon the syn or anti form of the reacting ligand. Schiff-base complexes formed by the condensation of HCQE or camphorquinone (CQ) with 1,3-diaminopropane with Ni(II) and Zn(II) have also been prepared, and the limitations of such condensation reactions in this system are discussed.

Experimental Section

Spectral Data. Proton NMR spectra were obtained on Perkin-Elmer R-20B and A-60 spectrometers using Me_4Si as an internal reference and $CHCl_3$-*d* or CH_3CN-d_3 as solvents. Infrared spectra (4000–200 cm^{-1}) were obtained on KBr pellets by 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 by employing an Industrial Instruments conductivity bridge Model RC16-B2. The solution concentrations were approximately 2×10^{-3} M on the basis of the formula weights of the analyzed complexes.

Magnetic Moments. The values of μ_{eff} (μ_B) for individual complexes were obtained in CH_3CN by 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 by using the procedure of Evans et al.[10] 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 h 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 absolute EtOH for 6 h. 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 $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$ by 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

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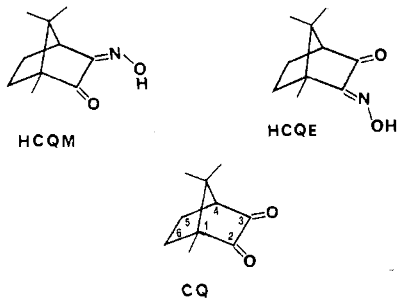

Figure 1. Camphorquinone and its monooxime derivatives.

Table I. Physical Properties of the Complexes

compd	color	molar conductance[a]	μ, μ_B
$[Ni(CQM)(py)_3(H_2O)]PF_6\cdot H_2O$	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	[f]
$[Ni(HCQEdpCQE)(CH_3CN)_2]$-$B(C_6H_5)_4$[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 $cm^2\ ohm^{-1}\ M^{-1}$ in CH_3CN solvent. [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 mole of Ni. [f] Diamagnetic.

$NiBC_{47}H_{55}N_4O_2\cdot 2CH_3CN$: 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

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

could 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 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 comparison of 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}. On the basis of 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.

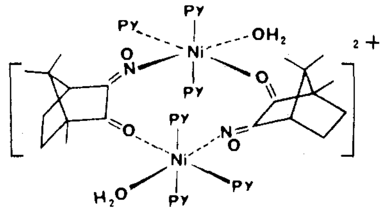

Figure 2. The dimeric structure of $[Ni(CQM)(py)_3(H_2O)]PF_6\cdot H_2O$.

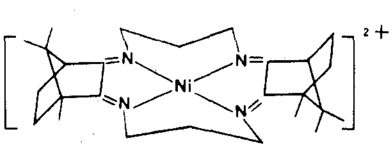

Figure 3. [*N*,*N*″:*N*′,*N*‴-Di(1,3-propane)bis(camphorquinone diimine)]nickel(II) ion.

The anion PF_6^- gives a characteristic broad, intense absorption between 820 and 860 cm^{-1}. The coordination of pyridine to Ni(II) is evidenced by the vibrational frequencies of pyridine at 626 and 426 cm^{-1} and also by 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 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 monooximes of *o*-benzoquinones. In the case that the complex is monomeric, both the carbonyl O and the oxime N atoms of the CQM^- ligand would probably coordinate to the same Ni atom. The magnetic moment (Table I) and electronic spectrum (Table III) of the complex are consistent[19] with those of 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 the preparation of the nickel complex of CQM^- and probably has the same type of structure because its electronic absorption spectrum (Table III) and magnetic moment (Table I) 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 $\nu(C{=}O)$ and $\nu(C{=}N)$ absorptions at 1675 and 1520 cm^{-1}, respectively, in its infrared spectrum.

Although carbonyl–oxime compounds are known[5] to be poorly coordinating ligands for Ni(II), the monooxime of *o*-benzoquinone forms Ni(II) complexes, which are perhaps stabilized by delocalization through the highly conjugated ligand system. In the present studies of isonitrosocamphor and

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Table II. IR[a] Absorption Spectra (cm^{-1}) of the Complexes

compd	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.

Table III. Visible and Near-IR Absorption Bands in CH_3CN Solvent

compd	max abs,[a] nm
$[Ni(CQM)(py)_3\cdot H_2O]PF_6\cdot H_2O$	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 mole of Ni.

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.

$[Ni(CQdpNH_2)_2][B(C_6H_5)_4]_2$. In an attempt to prepare the complex [*N,N″:N′,N‴*-di(1,3-propane)bis(camphorquinone diimine)]nickel(II) (Figure 3), a green compound was isolated when a mixture of $Ni(NO_3)_2\cdot 6H_2O$, CQ, and H_2NdpNH_2 in absolute 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 eq 2.

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

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 C(3) 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[12] 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 μ_B) is more consistent with a tetrahedral geometry (Figure 4). It is possible that weak coordination of the carbonyl groups gives rise to these somewhat contradictory results.

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

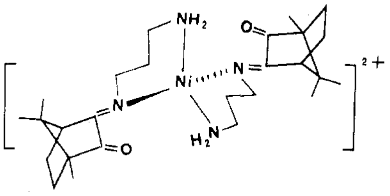

Figure 4. The $Ni(CQdpNH_2)_2^{2+}$ ion.

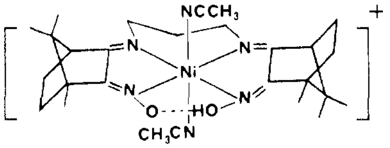

Figure 5. The $[Ni(HCQEdpCQE)(CH_3CN)_2]^+$ ion with two five-membered chelate rings.

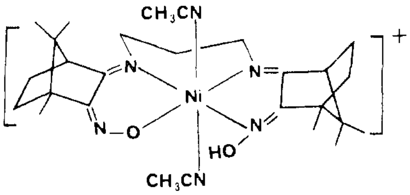

Figure 6. The $[Ni(HCQEdpCQE)(CH_3CN)_2]^+$ ion with one five-membered and one six-membered chelate ring.

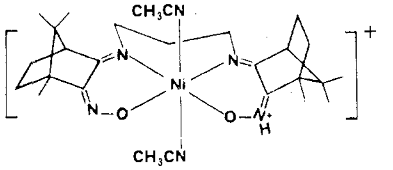

Figure 7. The $[Ni(HCQEdpCQE)(CH_3CN)_2]^+$ ion with two six-membered chelate rings.

The proton NMR spectrum of the complex in CH_3CN-d_3 gives three methyl proton signals as sharp singlets at δ 0.71, 0.91, and 1.04. 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 a broad signal for the amino protons coincides with the multiplet 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 (camphorquinone dioxime) 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 (eq 3). On the basis

$$\mathrm{Ni^{2+} + 2HCQE + H_2NdpNH_2 + 2CH_3CN \rightarrow Ni(HCQEdpCQE)(CH_3CN)_2^+ + H^+ + 2H_2O} \quad (3)$$

of elemental analytical results, octahedral structures such as those shown in Figures 5–7 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 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 (Table I) 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 six-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-camphorquinone dioximato)nickel(II) in which the ligands form six-membered rings by coordinating via N and O atoms.

$(HCQM)_2(H_2NdpNH_2)$. When the procedure used by Uhlig[13] for the condensation of 1,3-diaminopropane with diacetyl monooxime to give *N,N′*-(1,3-propane)(diacetyl oxime imine) was followed, HCQM failed to react with H_2NdpNH_2 to give the desirable monooxime imine ligand. Instead, a product of the composition $(HCQM)_2(H_2NdpNH_2)$, in which HCQM and H_2NdpNH_2 cocrystallized, was obtained.

The IR spectrum of this pale yellow crystalline solid in $CHCl_3$ or in a KBr pellet shows both ν(C=O) and ν(C=N) absorptions at 1751 and 1653 cm^{-1}, respectively, which are identical with those of unreacted HCQM.[3] The ν(N—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 cocrystallization 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 μ_B, smaller than the normal value (2.8–3.4 μ_B[19]) for octahedral Ni(II) complexes.

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-intensity 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 $CHCl_3$-*d* containing a few drops of MeOH-d_4 and KCN. After the cyano nickel complex ($K_2Ni(CN)_4$) which formed was filtered off, the ^1H NMR spectrum of the resulting solution indicated the presence of CQM^- and 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) 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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Registry No. $[Ni(CQM)(py)_3(H_2O)]PF_6$, 72581-91-0; $[Ni(CQE)(py)_3(H_2O)]PF_6$, 72581-93-2; $Ni(CQdpNH_2)_2[B(C_6H_5)_4]_2$, 72581-95-4; $Zn(CQdpNH_2)_2[B(C_6H_5)_4]_2$, 72599-25-8; $[Ni(HCQEdpCQE)(CH_3CN)_2]B(C_6H_5)_4$, 72708-87-3; $[Ni_2(CQM)_2(OH)(H_2NdpNH_2)]B(C_6H_5)_4$, 72708-85-1; $(HCQM)_2(H_2NdpNH_2)$, 72581-88-5; CQ, 465-29-2; HCQE, 72581-89-6; HCQM, 663-17-2; 1,3-diaminopropane, 109-76-2.

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Synthesis and Characterization of Copper(II) Squarate Complexes

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A number of new copper(II) complexes containing an oxocarbon dianion (squarate, croconate, or rhodizonate ion) and nitrogenous counterligands have been prepared. Both monomeric and dimeric mixed-ligand complexes were isolated when the oxocarbon dianion used was the squarate ion. In these dimeric complexes the squarate ion functions as a bis-monodentate bridging ligand when the counterligand is 2,2′-bipyridine or 1,10-phenanthroline and as a bis-bidentate bridging ligand when the counterligand is 1,1,7,7-tetraethyldiethylenetriamine. In addition to normal spectral characterization, a temperature-dependent study of the magnetic susceptibility of several of the squarate dimers, indicating weak antiferromagnetic exchange interaction, is reported.

Although the chemistry of cyclic oxocarbon systems has been studied for over 100 years,[3,4] it was not until the synthesis of 1,2-dihydroxycyclobutenedione,[5] $H_2C_4O_4$, commonly referred to as squaric acid, that the coordination chemistry of