

Figure 2. EPR spectra of copper(II) 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrinate (3) in 1:1 toluene/ CH_2Cl_2 : (A) at 77 K; (B) at 300 K.

Despite the steric bulk of the four pivoyl groups on each face of the porphyrin, the metallation of **2** by anhydrous $\text{Cu}(\text{ClO}_4)_2$ in DMF occurs at a rate greater than $7.6 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 60 °C. This rate is significantly more rapid than the rate of $8.4 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ associated with H_2TTP under identical reaction conditions.¹³ Clearly, the assumption that the pivoyl groups prevent the incorporation of copper ion into the porphyrin must be revised. The rapid rate of metallation of the bis-picket-fence porphyrin suggests that either the porphyrin ring can assume a conformation which is very favorable for metal ion complexation or a new pathway for metalation is available.¹⁴

- (13) Longo, F. R.; Brown, E. M.; Quimby, D. J.; Adler, A. D.; Meot-Ner, M. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 420. Rate quoted at 60 °C was calculated from data presented therein.
- (14) An alternative pathway for metalation could involve the participation of the carbonyl oxygen lone pairs found on the pivoyl group(s). In the case of the picket-fence porphyrin the conformation of the porphyrin plane might make this pathway less favorable.

The formation of copper(II) 5,10,15,20-tetrakis(2,6-dipivalamidophenyl)porphyrinate (**3**) is demonstrated by its visible (Table I) and EPR spectra. It is interesting to note that the Soret band of **3** also exhibits a blue-shift relative to copper(II) picket-fence porphyrinate¹¹ and Cu^{II} -TPP. The EPR spectrum of **3** (Figure 2) indicates that both the g values [$g(\text{iso}) = 2.193$, $g(z) = 2.075$, $g(x,y) = 2.122$] and A values ($\times 10^4 \text{ cm}^{-1}$) [$A(\text{iso})\text{Cu} = 88$, $A(z)\text{Cu} = 183$, $A(x,y)\text{Cu} = 38$, $A(\text{iso})\text{N} = 15$, $A(z)\text{N} = 13$, $A(x,y)\text{N} = 16$]¹⁵ are similar to those of copper(II) porphyrinates.¹⁶ The degree of resolution of the nitrogen superhyperfine structure in the EPR spectrum of copper(II) porphyrinates is indicative of the extent of porphyrin aggregation.¹⁶ The 17-line hyperfine splitting pattern observed in the $g(x,y)$ region of the EPR spectrum at 77 K indicates that **3** does not aggregate in solution. Previous investigators have shown that the coordination of a Lewis base such as pyridine to the copper(II) ion is reflected by a marked increase in the g factor and a decrease in the nitrogen superhyperfine coupling constant.¹⁶ Since the g factor and A -values remain virtually unchanged in 1:1 toluene/ CH_2Cl_2 and pyridine solvent, it is clear that the pivoyl groups prevent the coordination of pyridine by the copper(II) ion. Collman reports the formation of $\text{Fe}^{\text{II}}\alpha,\alpha,\alpha,\alpha\text{-T}(o\text{-}((\text{CH}_3)_3\text{CONH})\text{PP(L)}_2$ ($L = 1$ -methylimidazole), although this species is disfavored compared to the 1:1 base/metal adduct.¹⁴ In solution, the steric interaction of the pivoyl substituents on the sterically congested face of picket-fence porphyrin can be diminished by the deformation of the porphyrin plane. In this configuration, the deformed metalloporphyrin can bind two molecules of solvent at the metal center. In the case of the cofacially substituted sterically hindered bis-picket-fence metalloporphyrin **3**, preferential distortion of the porphyrin plane to relieve the steric interaction of the pivoyl groups on one porphyrin face will increase steric interaction on the opposite face. For this reason, it is not surprising that **3** is unable to coordinate a base such as pyridine to the copper ion even at 77 K.

Note Added in Proof. An alternative synthesis of tetrakis(2,6-dinitrophenyl)porphyrin has been reported: Quintana, C. A.; Assink, R. A.; Shelnut, J. A. *Inorg. Chem.* **1989**, *28*, 3421.

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- (15) $[\text{Cu}(\text{por})] = 1 \times 10^{-4} \text{ M}$ in 1:1 toluene/ CH_2Cl_2 or pyridine. Isotropic X-band EPR measurements were at 298 K; anisotropic measurements were at 77 K. Modulation amplitude is 5 G.
- (16) (a) MacCragh, A.; Storm, C. B.; Koski, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 1470. (b) Lin, W. C. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, Chapter 7.

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Synthesis and Reactivity of a Nickel(II) Complex with a Macrocyclic Containing a Peripheral Hydroxyl Group

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The neutral nickel(II) complex of an anionic macrocyclic ligand, (6,14-diacetyl-10-hydroxy-7,13-dimethyl-1,4,8,11-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ($[\text{Ni}(\text{Ac}_2\text{Me}_2(\text{OH})[15]\text{tetraenato-}k^4\text{M})]$), is formed by a template reaction involving the closure of [3,3'-(ethylenebis(iminomethylidene))bis(2,4-pentanedionato)]nickel(II) with 1,3-diamino-2-propanol. The uncoordinated hydroxyl group on the macrocyclic ligand reacts smoothly with acylating agents. Previous reports have indicated that hydroxyl groups on the carbon framework of transition-metal complexes exhibit low reactivity toward electrophilic reagents. The differences in behavior are discussed.

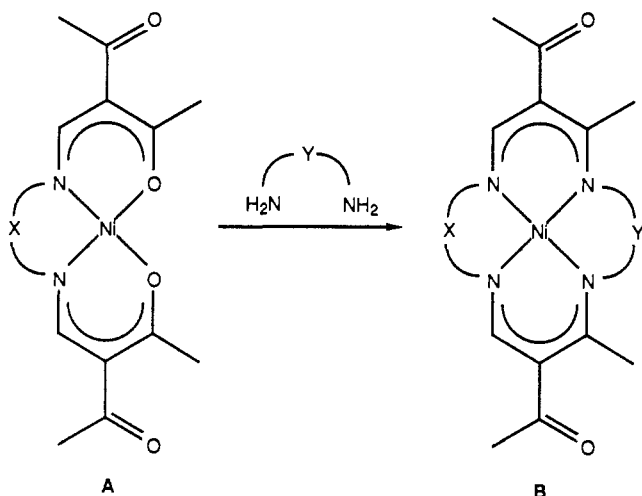
Introduction

With the continued expansion of chelate chemistry and organometallic chemistry into such areas as inclusion chemistry and bioinorganic chemistry it has become increasingly routine to

conduct organic chemical reactions on both coordinated and free functional moieties within the metal complexes. This focuses attention on the relative reactivities of functional groups in the presence and absence of the metal ion of the chelate. An abnormal absence of reactivity toward electrophiles has been reported for uncoordinated alcoholic OH groups in a number of chelate complexes. We report here the synthesis and characterization of a nickel(II) complex of a macrocyclic ligand having an appended

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Scheme I



initial orange band was eluted with chloroform, isolated, and identified as the starting material by using infrared and ^{13}C NMR spectroscopy. A pink band was eluted by using a mixture of chloroform and methanol (95:5). This band was collected and concentrated to give the macrocyclic nickel(II) complex, **1**, yield 2.3 g (40%). Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_4\text{NiO}_2\cdot\text{H}_2\text{O}$: C, 49.91; H, 6.40; N, 13.69; Ni, 14.35. Found: C, 50.20; H, 6.78; N, 13.69; Ni, 14.48. IR (Nujol mull): ν_{max} 3300 (broad), 1575 cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$): δ 192.32 (s, C=O), 166.76 (s, C=C), 156.67 (d, CH=C), 111.63 (s, C=C), 67.37 (d, CH—OH), 58.23 (t, CH_2N), 52.55 (t, CH_2N), 27.95 (q, CH_3), 17.86 (q, CH_3).

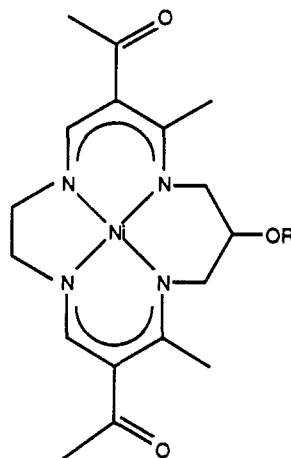
(3,11-Diacetyl-4,10-dimethyl-7-acetoxy-1,5,9,13-tetraazacyclopentadeca-1,3,9,11-tetraenato- $\kappa^4\text{N}$)nickel(II), $[\text{Ni}(\text{Ac}_2\text{Me}_2(\text{OAc})[15]\text{tetraenato-}\kappa^4\text{N})]$. $[\text{Ni}(\text{Ac}_2\text{Me}_2(\text{OH})[15]\text{tetraenato-}\kappa^4\text{N})]$ (1.90 g, 4.9 mmol), acetic anhydride (0.5 mL, 5.3 mmol), and triethylamine (0.75 mL, 5.4 mmol), in dry dichloromethane (250 mL) containing a trace of 4-(dimethylamino)pyridine, were stirred at room temperature for 18 h. The resulting red solution was concentrated under reduced pressure and purified by using column chromatography over neutral alumina. The acetylated complex was obtained; yield 1.61 g (76%). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{N}_4\text{O}_4\text{Ni}$: C, 52.69; H, 6.05; N, 12.94; Ni, 13.55. Found: C, 52.45; H, 6.15; N, 12.81; Ni, 13.48. IR (KBr pellet): 1735, 1625 (weak), 1585 cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 193.67, 169.97, 168.34, 156.21, 112.54, 70.82, 59.03, 49.19, 27.92, 20.61, 18.37 ppm. ^1H NMR (CDCl_3): 1.94 (s, 3 H, CH_3), 2.16 (s, 6 H, CH_3), 2.30 (s, 6 H, CH_3), 3.05 (s, 4 H, CH_2N), 3.58, 3.76 (AB quartet of doublets, 4 H, $J = 13.6$ Hz, CH_2N), 4.81 (quin, 1 H, $J = 5.6$ Hz, CH—O), 7.46 (s, 2 H, CH=). MS: m/z 434, 432 (M^{++}).

(3,11-Diacetyl-4,10-dimethyl-7-(benzoyloxy)-1,5,9,13-tetraazacyclopentadeca-1,3,9,11-tetraenato- $\kappa^4\text{N}$)nickel(II), $[\text{Ni}(\text{Ac}_2\text{Me}_2(\text{OCOPh})[15]\text{tetraenato-}\kappa^4\text{N})]$. Benzoyl chloride (0.14 g, 1.0 mmol) and 4-(dimethylamino)pyridine (1.22 g, 1.0 mmol) were added to a stirred suspension of $[\text{Ni}(\text{Ac}_2\text{Me}_2(\text{OH})[15]\text{tetraenato-}\kappa^4\text{N})]$ (1; 0.4 g, 1.0 mmol) in chloroform (100 mL) under dry conditions. A red solution was obtained after 24 h at room temperature. The solution was concentrated, and the crude material was purified by chromatography over neutral alumina. The red band that moved rapidly with chloroform elution was collected and concentrated to give the benzoate ester **2**, yield 0.19 g (38%). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_4\text{Ni}$: C, 58.21; H, 5.70; N, 11.31; Ni, 11.86. Found: C, 58.10; H, 5.83; N, 11.28; Ni, 11.92. IR (KBr pellet): 1715, 1630, 1580 cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 194.00 (s), 168.84 (s), 165.90 (s), 165.51 (d), 133.45 (d), 129.68 (d), 128.60 (d), 112.95 (s), 71.68 (d), 59.29 (t), 49.71 (t), 28.18 (q), 18.85 (q). MS: m/z 494, 496 (M^{++}).

Results and Discussion

The template ring closure of linear tetradentate ligands of general structure A (Scheme I), with use of their N_2O_2 -chelated nickel(II) complexes, occurs under vigorous conditions to give a nickel(II) macrocyclic complex of general structure B (Scheme I).^{9,10} The complex $\{3,3'-(\text{ethylenebis(iminomethylidene)bis(2,4-pentanedionato)})\text{nickel(II)}$ reacted with excess 1,3-diamino-2-propanol at 150 °C for 1 h to give the macrocyclic ligand derivative (6,14-diacetyl-7,13-dimethyl-10-hydroxy-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato- $\kappa^4\text{N}$)nickel(II) (**1**). If the reaction is continued until the starting nickel(II) chelate is completely consumed, the separation of the product mixture is

very difficult. It is more convenient to perform the macrocyclization reaction with excess 1,3-diamino-2-propanol at 160 °C for 1 h. Under these conditions significant quantities of the starting material remain and isolation of the nickel(II) complex of the hydroxyl-containing macrocycle **1** was achieved by using



- (1) R = H
- (2) R = COPh
- (3) R = COCH₃

column chromatography over neutral alumina. Due to the unfavorable solubility properties of the crude product it was not possible to load the sample as a solution in the solvent chosen for initial elution. Crude product was deposited on neutral alumina by concentrating a solution in dichloromethane containing 5% methanol. The supported sample was loaded as a thin layer on the top of a neutral alumina column. Initial elution with dioxane gave an orange component, which was identified as the starting material by using ^{13}C NMR and IR spectroscopy.

The more polar component was isolated by elution with a 1:1 mixture of dioxane and methanol, followed by removal of the solvent under reduced pressure. The broad-band decoupled ^{13}C NMR spectrum of the second component is consistent with structure **1**, the number of signals reflecting the presence of a mirror plane. The assignment of each resonance was accomplished by using off-resonance decoupling and by comparison with ^{13}C NMR spectra of related complexes. An infrared spectrum after rigorous drying showed a strong absorption at 3300 cm^{-1} attributed to a hydroxyl stretching vibration and is consistent with structure **1**. The results of elemental analysis support the proposed structure and indicate the presence of 1 equiv of water.

Acylation of **1** were performed under a variety of conditions. 4-(Dimethylamino)pyridine has been used as an acylation catalyst for many organic systems;¹¹ for example, the rate of acylation of propan-2-ol by acetic anhydride is increased by a factor of 2×10^4 when pyridine is replaced by 4-(dimethylamino)pyridine.¹² A suspension of the nickel(II) complex **1** reacts with benzoyl chloride and 4-(dimethylamino)pyridine in chloroform at room temperature to give a homogeneous solution. Column chromatography over neutral alumina with chloroform elution gave a rapidly moving band. The infrared spectrum of the material obtained from that band exhibited a strong absorption in the carbonyl region at 1715 cm^{-1} , which was not present in the infrared spectrum of the starting material. The hydroxyl OH stretching frequency was also absent from the infrared spectrum of the product.

A broad-band decoupled ^{13}C NMR spectrum of the product of the acylation reaction showed only 13 carbon environments rather than the expected 14. The missing carbon was identified as C_1 of the phenyl group on the basis of off-resonance decoupling measurements and by comparison of the spectrum with those of related complexes. We attribute the absence of this signal to an unusually slow rate of nuclear spin relaxation. The number of resonances attributed to the macrocycle is consistent with substitution on the mirror plane of the complex. The yield of the

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- (12) Conners, K. A.; Albert, K. S. *J. Pharm. Sci.* **1973**, *62*, 845.

benzoyl ester **2** with use of this procedure was 38%.

A number of alternative procedures were investigated. The reaction of the nickel(II) macrocycle **1** with benzoyl chloride in dry chloroform and with triethylamine and catalytic 4-(dimethylamino)pyridine gave only a 13% yield of the benzoyl ester **2**. Use of benzene as the reaction solvent failed to give improved yields, although the procedure served to dry the nickel(II) complex. However, alternative procedures showed that a stoichiometric amount of 4-(dimethylamino)pyridine does indeed give results superior to those obtained with comparable amounts of triethylamine or those with catalytic amounts of 4-(dimethylamino)pyridine. In the optimized procedures, acetylations were performed in either dry chloroform or dry dichloromethane under a nitrogen atmosphere with a suspension of the macrocyclic nickel(II) complex **1**.

An infrared spectrum of the acetylation product showed a carbonyl band at 1735 cm^{-1} , which was not present in the infrared spectrum of the starting material. The spectrum also showed complete loss of the hydroxyl OH stretching frequency. The ^{13}C NMR spectrum of the product dissolved in deuteriochloroform indicated 11 carbon environments and is fully consistent with structure **3**. The proton NMR spectrum was also examined at an operating frequency of 200 MHz. The protons of the saturated six-membered chelate ring are of particular interest. Those in

the pair of methylene groups give rise to an AB quartet of doublets centered at 3.66 ppm. The AB quartet corresponds to a geminal coupling of $^2J_{\text{HH}} = 13.6\text{ Hz}$ between protons resonating at 3.76 and 3.58 ppm. The further coupling of these protons is due to the proton on the mirror plane of the complex with $^3J_{\text{HH}} = 5.7\text{ Hz}$. This proton itself appears as a quintet at 4.82 ppm. All other resonances in the ^1H NMR spectrum appear as singlets.

The acetylation of the macrocyclic nickel(II) complex **1** was also attempted in dry dichloromethane with use of acetic acid and the coupling reagent *N,N'*-dicyclohexylcarbodiimide. No evidence of acetylation was found with infrared spectroscopy, and most of the starting material was recovered.

Conclusions

The acylation of noncoordinated hydroxyl groups in transition-metal complexes can be achieved under mild conditions. We believe that earlier reports concerning the low reactivity of hydroxyl groups in transition-metal complexes was due to ill-defined coordination environments, inappropriate reaction conditions, or the charged nature of the complexes.

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Charge Distribution in Transition-Metal Complexes of a Schiff Base Biquinone Ligand. Structural and Electrochemical Properties of the $\text{M}^{\text{II}}(\text{Cat-N-BQ})_2$, $\text{M}^{\text{III}}(\text{Cat-N-BQ})(\text{Cat-N-SQ})$, $\text{M}^{\text{IV}}(\text{Cat-N-SQ})_2$ Tautomeric Series

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Reactions carried out between 3,5-di-*tert*-butylsemiquinone and ammonia in the presence of a divalent metal ion yield bis complexes of the resulting Schiff base biquinone ligand. The free ligand may chelate with metal ions in forms ranging in charge from 0 to -3, related by successive reduction steps of the two quinone units of the ligand. Three common electronic forms have been found to exist for complexes of these ligands, with the forms related by intramolecular transfer of charge between localized ligand and metal electronic levels. If the metal ion used in the synthetic procedure is redox inactive, the $\text{M}^{\text{II}}(\text{Cat-N-BQ})_2$ form of the complex is obtained. With divalent metal ions that are subject to oxidation the $\text{M}^{\text{III}}(\text{Cat-N-BQ})(\text{Cat-N-SQ})$ or $\text{M}^{\text{IV}}(\text{Cat-N-SQ})_2$ form may result. In this report characterization of the bis(biquinonato)iron complex is presented, which indicates that the metal is high-spin ferric iron and that the complex exists in the mixed-charge ligand form $\text{Fe}^{\text{III}}(\text{Cat-N-BQ})(\text{Cat-N-SQ})$. The complex has an $S = 2$ magnetic ground state, normally associated with high-spin ferrous complexes, due to spin coupling between the radical $\text{Cat-N-SQ}^{\cdot-}$ ligand and the metal. This complex and the nickel complex $\text{Ni}^{\text{II}}(\text{Cat-N-BQ})_2$, which differs in charge distribution, have been characterized structurally. Both crystallize in the triclinic space group $P\bar{1}$, with $Z = 2$, in unit cells of the following dimensions: $\text{Fe}(\text{C}_{28}\text{H}_{40}\text{NO}_2)_2$, $a = 11.753(3)\text{ \AA}$, $b = 12.286(3)\text{ \AA}$, $c = 20.811(6)\text{ \AA}$, $\alpha = 83.26(2)^\circ$, $\beta = 73.62(2)^\circ$, $\gamma = 75.54(2)^\circ$; $\text{Ni}(\text{C}_{28}\text{H}_{40}\text{NO}_2)_2$, $a = 11.703(2)\text{ \AA}$, $b = 12.377(3)\text{ \AA}$, $c = 20.703(4)\text{ \AA}$, $\alpha = 89.05(2)^\circ$, $\beta = 73.78(2)^\circ$, $\gamma = 75.48(2)^\circ$. Structural features of the ligands, with results obtained earlier on the Co and Mn complexes, have been used to show how a consistent pattern of C-O, C-N, and ring C-C bond lengths provides information on ligand charge and on charge distribution within the complex. Examples of complexes in the three charge distribution forms have been studied by using cyclic voltammetry to identify characteristic differences in electrochemistry. Surprisingly, all three types undergo similar electrochemical processes. They show two reversible or quasireversible oxidations, two reversible or quasireversible reductions, and, in some cases, a third irreversible reduction. Charge assignments for the products of the redox processes demonstrate coordination of the biquinone ligand in forms ranging in charge from the neutral radical SQ-N-BQ to the Cat-N-Cat^{3-} trianion.

Introduction

Questions concerning charge distribution between ligand and metal have contributed to the interest in complexes of the semiquinone and catecholate ligands.¹ This results from a similarity in energy between metal and quinone electronic levels, and similar questions exist for the complexes of polyquinone ligands. Complexes of a Schiff base biquinone ligand prepared by condensation of 3,5-di-*tert*-butyl-1,2-semiquinone with ammonia have been

investigated.^{2,3} The ligand (**1**) may coordinate with metal ions in forms ranging in charge from 0 to -3. A +1 diimine form may also exist, but its interaction with metals may differ from the neutral and anionic forms. In the absence of a metal ion with readily available coordination sites, cyclization occurs to give the phenoxazinylate radical anion (**2**).⁴ Studies carried out on

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