$(CO_2C_5H_5)_2$[14]tetraenatoN_4), 20123-03-9; Ni($Me_2(CO_2C_2H_5)_2$-[15]tetraenatoN_4), 38402-72-1; Ni($Me_2(CO_2C_2H_5)_2$[16]tetraenatoN_4), 74466-55-0; Ni(Me_2Nitro_2[15]tetraenatoN_4), 38402-69-6; Ni(Me_2Acyl_2[14]tetraenatoN_4), 20123-01-7; Ni(Me_4Acyl_2[14]tetraenatoN_4), 38402-73-2; Ni(Me_2Nitro_2[14]tetraenatoN_4), 74466-56-1; Ni(Me_4Nitro_2[14]tetraenatoN_4), 38402-74-3; Ni(Me_2Acyl_2[15]-tetraenatoN_4), 38402-68-5; Ni(Me_4Acyl_2[15]tetraenatoN_4), 38402-70-9; Ni(Me_4Nitro_2[15]tetraenatoN_4), 38402-71-0; Ni(Me_2[14]-tetraenatoN_4), 67326-88-9; Ni(Me_2Napcbyl[14]tetraenatoN_4), 74466-57-2; Ni(Me_6Acyl_2[14]tetraenatoN_4), 74466-58-3; Ni(Me_2-[15]tetraenatoN_4), 39018-31-0; Ni(Me_2[16]tetraenatoN_4), 74466-59-4; Ni(Me_2Acyl_2[16]tetraenatoN_4), 68480-82-0; Ni(Me_6Acyl_2[15]-tetraenatoN_4), 53277-09-1; 3-(ethoxymethylidene)-2,4-pentanedione, 33884-41-2; Ni-14-LTD, 53385-23-2; 3,3′-[propylenebis(iminomethylidene)]bis(2,4-pentanedionato)nickel(II), 74466-60-7; HC-$(OEt)_3$, 122-51-0; 2,4-pentanedione, 123-54-6; ethylenediamine, 107-15-3; 1,3-diaminopropane, 109-76-2; 3,3′-[tetramethylethylenebis(iminomethylidene)]bis(2,4-pentanedionato)nickel(II), 74466-61-8; ethyl acrylate, 140-88-5; α-naphthyl isocyanate, 551-06-4; β-(carbomethoxy)propionyl chloride, 1490-25-1; ethyl isocyanate, 542-85-8; p-methylbenzoyl chloride, 874-60-2; benzoyl chloride, 98-88-4; p-nitrobenzoyl chloride, 122-04-3.

Contribution from Evans Chemical Laboratory,
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Synthesis of Superstructure Ligands Using a Novel Methyl Vinyl Ether Functional Group

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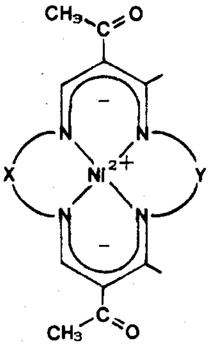
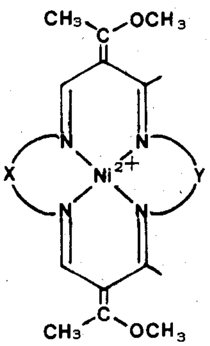
The presence of reactive peripheral functional groups facilitates the synthesis of macrocyclic ligands having superstructure components, designed to mimic the behaviors of biological molecules. The macrocyclic complexes $[Ni[(MeOEthi)_2Me_2[X]tetraeneN_4]]^{2+}$ (X = 14, 15, 16) contain an unusual peripheral conjugated methyl vinyl ether functional group that readily undergoes addition–elimination reactions, especially with amines. This reaction has been used to produce many derivatives whose structures differ either in macrocycle ring size or in the nature of R and R′ on the amine NHRR′. In this way four classes of pendant groups have been produced: (a) those having only small unreactive substituents such as CH_3 or H, (b) large hydrophobic groups such as decyl or naphthyl, (c) additional ligating groups like pyridine, and (d) hydrophilic groups exemplified by an 11-aminoundecanoic acid derivative.

Introduction

In order to develop certain classes of models for biological systems, it is highly useful to have access to functional groups appended to macrocyclic ligands. These functional groups provide points of attachment for superstructures designed to facilitate certain biomimetic properties in the metal complexes of the product ligands.[1,2] One such system of complexes involves those species originally synthesized by Jäger.[3,4] This unique class of structures is shown in structure I.



I

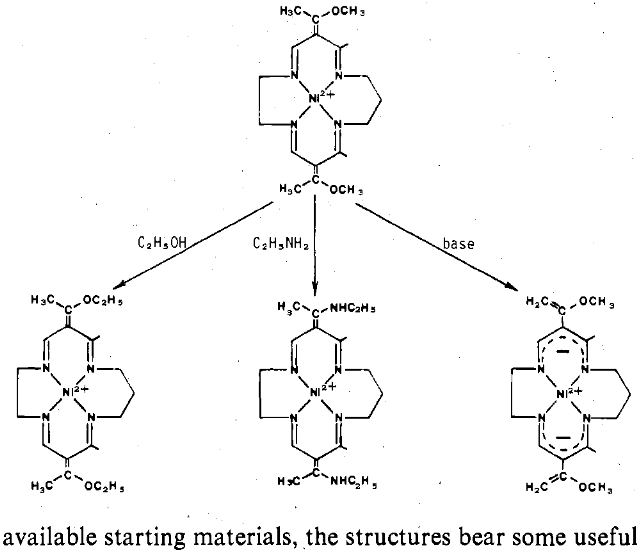


II

X, Y = $(CH_2)_{2,3}$

This species fits the requirements for a suitable starting structure for the synthesis of appropriate ligands since the products can be obtained in reasonable yields from readily available starting materials, the structures bear some useful similarities to porphyrins (four nitrogen donors with substantial unsaturation and delocalization), and they contain functional groups on the ligand periphery. A preliminary communication from these laboratories showed that this species can be alkylated[5] to yield compounds of structure II. Alkylation occurs at the oxygen atoms (formerly of the acetyl groups) as verified by a crystal structure determination.[5] This produces rather novel vinyl ether substituents on the periphery of the unsaturated six-membered chelate rings. These substituents are selectively reactive toward nucleophiles as seen in Scheme I.

Scheme I



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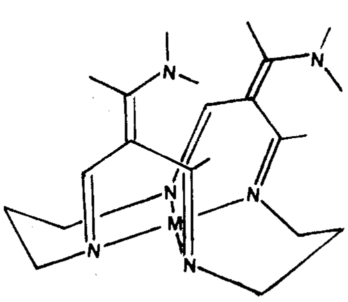
[1] Pillsbury, D. G.; Busch, D. H. J. Am. Chem. Soc. 1976, 98, 7836.
[2] Schammel, W. P.; Mertes, K. S. B.; Christoph, G. G. J. Am. Chem. Soc. 1979, 101, 1622.
[3] Jäger, E. Z. Anorg. Allg. Chem. 1966, 346, 76.
[4] Jäger, E. Z. Chem. 1968, 8 (30), 392.
[5] Hipp, C. J.; Corfield, P. W. R.; Mokren, J. D.; Busch, D. H. J. Am. Chem. Soc. 1973, 95, 4465.

0020-1669/80/1319-3159$01.00/0

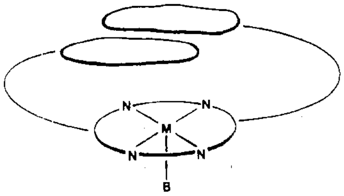
The preliminary work was restricted to the macrocyclic complexes with 15-membered rings, and the reactivity of this methylated species suggested that such substances provided suitable starting materials for the synthesis of varieties of ligands of interest as models for biological systems. Here, the general reactivities of these methylated species and their derivatives are delineated. We have previously reported a series of *dry cave* ligands that are derived from these starting materials.[2] Our present concern is with other products.

The starting material for this synthesis (structure II) has a saddle conformation in which the two unsaturated chelate rings are folded sharply upward on the same side of the NiN_4 plane.[5] Similar conformations are expected[2] for the derivatives reported here (structure III). Thus, the two amino groups (vide infra), that replace the methoxy group, are predicted to project above the complex on the same side of the coordination plane.

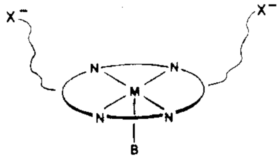


III

With suitable monofunctional nucleophiles, nonbridging hydrophobic groups may be attached to the macrocyclic system to produce ligands which have general structure IV.



IV



V

In addition, one can see possibilities for producing species with ligands, as seen in structure V, with isolated hydrophilic groups. This could be done if one could produce reactions with monofunctional nucleophiles which include hydrophilic groups on the end of long aliphatic chains. Finally, nickel complexes containing appended groups with potentially coordinating heteroatoms could be synthesized in much the same way as was done previously on a very different macrocycle usually abbreviated at TAAB.[6]

Experimental Section

Measurements. Proton NMR spectra were measured at 60 MHz on a Varian A-60-A or EM-360L spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP-80 or HX90 spectrometer operating in the Fourier transform mode using either broad-band or off-resonance proton decoupling.

Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Chemalytics, Inc., Tuscon, Ariz. Many nitrogen analyses were performed in these laboratories with a Coleman Model 29 nitrogen analyzer.

Conductance measurements were obtained with an Industrial Instruments, Inc., Model RC 16B conductivity bridge on solutions about 1×10^{-3} M. Electronic spectra were measured on a Cary Model 14-R recording spectrophotometer using matched 1-cm quartz cells. Infrared spectra were obtained with a Perkin-Elmer 337 or 457 infrared spectrophotometer. Nujol mulls were prepared on a 1:1 sample, and the region from 4000 to 400 cm^{-1} was scanned.

Syntheses. (3,10-Diacetyl-4,9-dimethyl-1,5,8,12-tetraazacyclotetradeca-1,3,8,10-tetraenato)nickel(II) ([Ni(Ac$_2$Me$_2$[14)tetraenatoN$_4$)]), (3,11-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclopentadeca-1,3,9,11-tetraenato)nickel(II) ([Ni(Ac$_2$Me$_2$[15]tetraenatoN$_4$)]), and (3,11-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato)nickel(II) ([Ni(Ac$_2$Me$_2$[16]tetraenatoN$_4$)]). These three complexes were synthesized according to previously published procedures.[3,4,7]

[2,11-Dimethyl-3,10-bis(1-methoxyethylidene)-1,5,8,12-tetraazacyclopentadeca-1,4,8,11-tetraene]nickel(II) Perchlorate ([Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$). This species was synthesized, as reported earlier,[5] by the reaction of excess methyl fluorosulfonate, in dichloromethane, with [Ni(Ac$_2$Me$_2$[15]tetraenatoN$_4$)]. The addition of methanolic lithium perchlorate to the methanol solution of the product resulted in the isolation of the perchlorate salt of this species. *Caution*! Methyl fluorosulfonate is a dangerous reagent.

[2,11-Dimethyl-3,10-bis(1-methoxyethylidene)-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene]nickel(II) Hexafluorophosphate ([Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$). This species was synthesized in a manner similar to that for the corresponding 15-membered ring derivative.

To a solution of 1.0 g (2.77 mmol) of [Ni(Ac$_2$Me$_2$[14]tetraenatoN$_4$)] in about 50 mL of dichloromethane (dried over 4A sieves) was added an excess (1.0 g, 8.8 mmol) of methyl fluorosulfonate. This solution was allowed to stand for 6 h at room temperature. During this period of time, the color of the solution changed from dark red-orange to light amber orange and a precipitate formed. The dichloromethane was removed on a rotary evaporator, and the residue was dissolved in methanol. A methanolic solution of ammonium hexafluorophosphate was added, producing golden crystals, yield 1.5 g (80%). Anal. Calcd for $NiC_{18}H_{28}N_4O_2P_2F_{12}$: C, 31.74; H, 4.14; N, 8.23. Found: C, 31.48; H, 4.20; N, 8.37.

[2,12-Dimethyl-3,11-bis(1-methoxyethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). This species was synthesized in the same manner as was [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$ except that the reaction time was reduced to 2 h and the color change observed was from orange-red to yellow-green; yield 75–80%. Anal. Calcd for $NiC_{20}H_{32}N_4O_2P_2F_{12}$: C, 33.87; H, 4.56; N, 7.90. Found: C, 34.07; H, 4.63; N, 7.77.

[2,11-Dimethyl-3,10-bis[1-(dimethylamino)ethylidene]-1,5,8,12-tetraazacyclopentadeca-1,4,8,11-tetraene]nickel(II) Perchlorate ([Ni[(Me$_2$NEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$). To 0.5 g (0.79 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$ dissolved in about 50 mL of acetonitrile was added an excess of dimethylamine. An orange to red color change was observed immediately upon addition of the amine. The solvent was removed, and the residue was dissolved in about 250 mL of hot methanol. Upon reduction of the solvent volume, an orange crystalline material was isolated; yield 0.4 g (70%). Anal. Calcd for $NiC_{21}H_{36}N_6Cl_2O_8$: C, 39.89; H, 6.07; N, 13.30. Found: C, 40.18; H, 5.52; N, 13.56.

[2,11-Dimethyl-3,10-bis[1-(propylamino)ethylidene]-1,5,8,12-tetraazacyclopentadeca-1,4,8,11-tetraene]nickel(II) Perchlorate ([Ni[(PrNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$). To 0.5 g (0.79 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$ dissolved in about 75 mL of acetonitrile was added an excess of *n*-propylamine. A color change from orange to red was observed upon addition of the amine. In the same manner as for [Ni[(Me$_2$NEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$ an orange crystalline product was isolated; yield 0.5 g (70%). Anal. Calcd for $NiC_{23}H_{40}N_6Cl_2O_8$: C, 41.96; H, 6.14; N, 12.77. Found: C, 41.86; H, 5.86; N, 12.98.

[2,11-Dimethyl-3,10-bis[1-(allylamino)ethylidene]-1,5,8,12-tetraazacyclopentadeca-1,4,8,11-tetraene]nickel(II) Perchlorate ([Ni[(AlyNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$). With the same method as for the preparation of [Ni[(Me$_2$NEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$, 0.5 g (0.79 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$ was treated with excess allylamine to yield the orange crystalline product, yield 0.4 g (70%). Anal. Calcd for $NiC_{23}H_{36}N_6Cl_2O_8$: C, 42.22; H, 5.56; N, 12.85. Found: C, 41.99; H, 5.47; N, 13.07.

[2,11-Dimethyl-3,10-bis[1-[*N*-(1-naphthyl)ethylenediamino]ethylidene]-1,5,8,12-tetraazacyclopentadeca-1,4,8,11-tetraene]nickel(II)

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(6) Katovič, V.; Taylor, L. T.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 2122.

(7) Riley, D. P.; Busch, D. H. *Inorg. Synth.* **1978**, *18*, 36.

Hexafluorophosphate ([Ni[(NapEnEthi)$_2$Me$_2$[15]tetraeneN$_4$]](PF$_6$)$_2$). For preparation of this complex, 4.87 g (7.0 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](PF$_6$)$_2$ was dissolved in 100 mL of acetonitrile. To this solution were added 3.65 g (14.0 mmol) of *N*-(1-naphthyl)ethylenediamine dihydrochloride and 3.0 (30 mmol) of triethylamine, and the mixture was stirred for 1–2 h. The color changed from orange to red after stirring for a few minutes. The solvent was removed on a rotary evaporator, and the residue was dissolved in hot methanol. This solution was filtered through filter aid to remove tarry residues. To the filtrate was added about 1.0 g of ammonium hexafluorophosphate and the orange powder precipitated; yield 0.4 g (6%). No attempt was made to improve the yield. Anal. Calcd for $NiC_{41}H_{48}N_8P_2F_{12}$: C, 51.56; H, 5.24; N, 11.19. Found: C, 51.36; H, 5.32; N, 11.57.

[2,11-Dimethyl-3,10-bis[1-(dimethylamino)ethylidene]-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene]nickel(II) Hexafluorophosphate ([Ni[(Me$_2$NEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$). This complex was formed by dissolving 1.04 g (1.5 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$ in 100 mL of acetonitrile followed by the addition of an excess of dimethylamine to this solution. The orange to red color change was observed immediately upon mixing. The acetonitrile was removed, and the residue was dissolved in ~200 mL of hot methanol. Upon reduction of solvent volume, an orange crystalline material precipitated; yield 0.94 g (87%). Anal. Calcd for $NiC_{20}H_{34}N_6P_2F_{12}$: C, 33.96; H, 4.86; N, 11.89. Found: C, 33.79; H, 4.90; N, 11.81.

[2,11-Dimethyl-3,10-bis[1-(allylamino)ethylidene]-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene]nickel(II) Hexafluorophosphate ([Ni[(AlyNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$. This complex was formed by dissolving 0.56 g (0.8 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$ in 100 mL of acetonitrile followed by the addition of an excess of allylamine to the solution. An orange to red color change was observed immediately upon mixing. The acetonitrile was removed, and hot methanol (200 mL) was added to produce a red-orange solution. Reduction of the solvent volume resulted in the isolation of an orange crystalline product, yield 0.49 g (82%). Anal. Calcd for $NiC_{22}H_{34}N_6P_2F_{12}$: C, 36.13; H, 4.70; N, 11.50. Found: C, 35.91; H, 4.57; N, 11.50.

[2,11-Dimethyl-3,10-bis[1-(ethylamino)ethylidene]-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene]nickel(II) Hexafluorophosphate ([Ni[(EtNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$). This complex was prepared by dissolving 0.98 g (1.4 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$ in 100 mL of acetonitrile and by adding an excess of ethylamine to this solution. An orange to red color change was observed immediately upon mixing. The acetonitrile was removed on a rotary evaporator, and to the residue was added about 200 mL of hot methanol. This methanol solution was reduced in volume to yield an orange crystalline precipitate, yield 0.75 g (74%). Anal. Calcd for $NiC_{20}H_{34}N_6P_2F_{12}$: C, 33.96; H, 4.86; N, 11.89. Found: C, 34.04; H, 4.85; N, 11.92.

[2,12-Dimethyl-3,11-bis[1-(ethylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(EtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 3.0 g (4.2 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 300 mL of methanol was added dropwise an excess of ethylamine. After a few minutes of stirring, a yellow powder precipitated; yield 2.1 g (68%). Anal. Calcd for $NiC_{22}H_{38}N_6P_2F_{12}$: C, 35.93; H, 5.22; N, 11.43. Found: C, 35.75; H, 5.15; N, 11.28.

[2,12-Dimethyl-3,11-bis[1-(methylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(MeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 1.72 g (2.4 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in acetonitrile (about 50 mL) was added an excess of methylamine hydrochloride along with an excess of triethylamine. Immediately upon the addition of the triethylamine, the color changed from yellow-green to orange-red. This solution was filtered, and the solvent was evaporated. Then 100 mL of methanol was added to the residue, and upon reduction of the solvent volume, a yellow crystalline product precipitated; yield 1.36 g (79%). Anal. Calcd for $NiC_{20}H_{34}N_6P_2F_{12}$: C, 33.96; H, 4.86; N, 11.89. Found: C, 33.63; H, 4.88; N, 12.22.

[2,12-Dimethyl-3,11-bis(1-aminoethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(NH$_2$Ethi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). Ammonia gas was bubbled through an acetonitrile solution of 3.2 g (4.5 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$. The color immediately changed from yellow-green to orange. The solvent was removed on a rotary evaporator, and the residue was dissolved in about 100 mL of methanol. The yellow crystalline product was isolated upon reduction of solvent volume; yield 2.3 g (70%). Anal. Calcd for $NiC_{18}H_{36}N_6P_2F_{12}$: C, 31.55; H, 5.31; N, 12.27. Found: C, 31.64; H, 5.17; N, 12.18.

[2,12-Dimethyl-3,11-bis[1-(decylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(DecNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 2.0 g (2.8 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in about 50 mL of acetonitrile was added 0.88 g (5.7 mmol) of decylamine. The color changed immediately from yellow-green to orange. The acetonitrile was removed, and about 100 mL of methanol was added to dissolve the residue. Reduction of the solvent volume resulted in the isolation of the yellow powdery product, yield 2.0 g (70%). Anal. Calcd for $NiC_{38}H_{70}N_6P_2F_{12}$: C, 47.55; H, 7.37; N, 8.76. Found: C, 47.74; H, 7.34; N, 8.47.

[2,12-Dimethyl-3,11-bis[1-(dimethylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(Me$_2$NEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). An excess of dimethylamine was added to 0.68 g (0.96 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 100 mL of acetonitrile. The color changed immediately from yellow-green to orange-red. The solvent was removed on a rotary evaporator, and 200 mL of methanol was added to the residue. This solution was filtered and reduced in volume to produce a yellow crystalline solid, yield 0.58 g (79%). Anal. Calcd for $NiC_{22}H_{38}N_6P_2F_{12}$: C, 35.93; H, 5.22; N, 11.43. Found: C, 35.70; H, 5.05; N, 11.19.

[2,12-Dimethyl-3,11-bis[1-[*N*-(1-naphthyl)ethylenediamino]ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(NapEnNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 5.33 g (7.5 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 75 mL of acetonitrile was added 3.9 g (15.0 mmol) of *N*-(1-naphthyl)ethylenediamine hydrochloride, followed by the addition of 3.9 g (39.0 mmol) of triethylamine. The resulting solution was stirred for about 15 min, and an orange precipitate separated from the solution. Upon isolation of the orange solid (found to be the chloride salt of the product species), the volume of the filtrate was reduced to a point where large amounts of a white crystalline substance precipitated. This white species was found to be triethylamine hydrochloride from the NMR spectrum. Ethanol was added to the remaining solution, and the solvent volume was reduced to produce an orange solid, yield ~3.0 g (~40%). Anal. Calcd for $NiC_{42}H_{50}N_8P_2F_{12}$: C, 49.66; H, 4.97; N, 11.03. Found: C, 49.72; H, 5.09; N, 11.15.

[2,12-Dimethyl-3,11-bis[1-[*d*-*α*-(1-naphthyl)ethylamino]ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(NapEtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 6.42 g (9.1 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 75 mL of acetonitrile was added 3.10 g (18.2 mmol) of *d*-*α*-(1-naphthyl)ethylamine dropwise with stirring. The color changed from yellow-green to red-orange immediately upon addition of the amine. The acetonitrile was removed on a rotary evaporator, and to the solid residue was added methanol. Filtering this solution and reducing the solvent volume resulted in the isolation of the yellow powdery product, yield 3.20 g (36%). Anal. Calcd for $NiC_{42}H_{53}N_6P_2F_{12}$: C, 51.07; H, 5.11; N, 8.51. Found: C, 51.05; H, 5.07; N, 8.28.

[2,12-Dimethyl-3,11-bis[1-(1-naphthylmethylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(NapMeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 6.05 g (8.5 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 100 mL of acetonitrile was added dropwise 2.68 g (17.0 mmol) of 1-naphthylmethylamine, and after 5 min of stirring, the yellow solid precipitated. This was removed by filtration, and more solid was isolated from the filtrate by the evaporation of the acetonitrile and addition of methanol; yield 7.26 g (89%). Anal. Calcd for $NiC_{40}H_{46}N_6P_2F_{12}$: C, 50.06; H, 4.84; N, 8.76. Found: C, 50.34; H, 4.80; N, 8.46.

[2,11-Dimethyl-3,10-bis[1-[2-(2-pyridineethylamino)ethylidene]-1,5,8,12-tetraazacyclopentadeca-1,4,8,11-tetraene]nickel(II) Hexafluorophosphate ([Ni[(2-pyEtNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](PF$_6$)$_2$). To 1.0 g (1.4 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 50 mL of methanol was added 0.36 g (2.8 mmol) of 2-(2-aminoethyl)pyridine. An orange to red color change was evident upon mixing. This solution was then reduced in volume to about 10 mL and let stand overnight (~12 h). Large red crystals were then isolated; yield 0.4 g (32%). Anal. Calcd for $NiC_{31}H_{42}N_8P_2F_{12}$: C, 42.53; H, 4.85; N, 12.80. Found: C, 42.29; H, 4.63; N, 12.97.

[2,12-Dimethyl-3,11-bis[1-(*n*-butylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 3.0 g (4.2 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 50 mL of acetonitrile was added 0.65 g (8.9 mmol) of *n*-butylamine. After 1 h of stirring, the volume was reduced to 15 mL, and 100 mL of methanol was added. Further volume reduction resulted in formation of the yellow crystalline product, yield 3.1 g (93%). Anal. Calcd for $NiC_{26}H_{46}N_6P_2F_{12}$: C, 39.46; H, 5.86; N, 10.62. Found: C, 39.61; H, 5.88; N, 10.68.

[2,12-Dimethyl-3,11-bis[1-(*tert*-butylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(*t*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). This complex was prepared in the same way as [Ni[(*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ using 3.0 g (4.2 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ and 0.65 g (8.9 mmol) of *tert*-butylamine; yield 1.7 g (51%). Anal. Calcd for $NiC_{26}H_{46}N_6P_2F_{12}$: C, 39.46; H, 5.46; N, 10.62. Found: C, 38.79; H, 5.77; N, 10.28.

[2,12-Dimethyl-3,11-bis[1-(benzylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(BzNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To 3.0 g (4.2 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ dissolved in 250 mL of acetonitrile was added dropwise 1.0 g (9.3 mmol) of benzylamine. After 1 h of stirring, the volume was reduced to 50 mL, and 100 mL of ethanol was added. Further volume reduction caused precipitation of the yellow powder, yield 2.8 g (77%). Anal. Calcd for $NiC_{32}N_{42}N_6P_2F_{12}$: C, 44.73; H, 4.93; N, 9.78. Found: C, 45.07; H, 5.09; N, 9.96.

[2,12-Dimethyl-3,11-bis[1-(10-carboxylatodecylamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraenato]nickel(II)-Bis(sodium hexafluorophosphate) ([Ni[(CO$_2$DecNHEthi)$_2$Me$_2$[16]tetraenatoN$_4$]](NaPF$_6$)$_2$). To 1.14 g (2.8 mmol) of 11-aminoundecanoic acid in about 50 mL of methanol was added 0.23 g (5.8 mmol) of sodium hydroxide. The clear solution was then filtered and was added to a solution containing 2.0 g (2.82 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ in 50 mL of acetonitrile. Upon addition of the amino acid solution, the color changed from yellow-green to orange, and upon reduction of solvent volume and addition of ethanol, the yellow powder precipitated; yield 0.5 g (17%). Anal. Calcd for $NiC_{40}H_{65}N_6O_4Na_2P_2F_{12}$: C, 44.00; H, 6.29; N, 7.70; Na, 4.21. Found: C, 43.86; H, 6.38; N, 7.64; Na, 4.01.

[2,12-Dimethyl-3,11-bis(1-methoxyethylene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraenato]nickel(II) ([Ni[(MeOVinyl)$_2$Me$_2$[16]tetraenatoN$_4$]]). In 50 mL of acetonitrile was dissolved 0.47 g (0.7 mmol) of [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$. An ethanol solution containing an excess (more than 1.4 mmol) of sodium ethoxide was added to this solution. The color changed from yellow-green to deep red-purple immediately upon the addition of the base. The resulting solution was evaporated to dryness, and 50 mL of dichloromethane was added. The solution was then passed through filter aid, and the dichloromethane was removed. The residue was dissolved in hot acetonitrile (~100 mL). Upon reduction of the solvent volume and cooling, the purple crystalline product was isolated; yield 0.15 g (60%). Anal. Calcd for $NiC_{20}H_{30}N_6$: C, 57.57; H, 7.26; N, 13.43. Found: C, 57.01; H, 7.53; N, 13.33.

[2,12-Dimethyl-3,11-bis[1-(ethylmethylamine)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(MeEtNEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To a solution of 1.5 g (2.1 mmol) of [Ni[(EtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ was added an ethanol solution containing an excess of sodium ethoxide. The color changed immediately from yellow to red upon addition of the base. This solution was evaporated to dryness, and the residue was dissolved in dichloromethane and filtered. To this solution was added 1.5 g (13 mmol) of methyl fluorosulfonate. The color changed from red to orange. The solvent was removed, the residue was dissolved in 100 mL of methanol, and 1.5 g (9.0 mmol) of ammonium hexafluorophosphate was added. Upon reduction of solvent volume, the orange crystalline product precipitated; yield 1.0 g (65%). Anal. Calcd for $NiC_{24}H_{42}N_6P_2F_{12}$: C, 37.76; H, 5.56; N, 11.01. Found: C, 37.64; H, 5.45; N, 10.51.

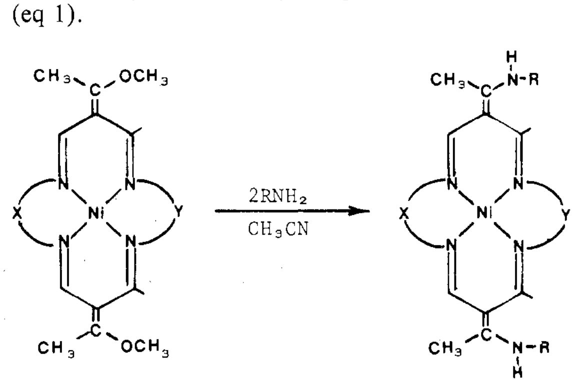
[2,12-Dimethyl-3,11-bis[1-(dimethylamino)-2-deuterioethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene]nickel(II) Hexafluorophosphate ([Ni[(Me$_2$NDEthi)$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$). To a solution of 1.1 g (1.5 mmol) of [Ni[(Me$_2$NEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ in 50 mL of acetonitrile was added an ethanol solution containing an excess of sodium ethoxide. The color changed from orange to red upon addition of the base. The solvent was removed, dichloromethane was added to dissolve the residue, and this solution was filtered. A 0.50-g amount (4.4 mmol) of trifluorodeuterioacetic acid was added to the solution, yielding an orange solution. The solvent was evaporated, and 1.2 g (7.4 mmol) of ammonium hexafluorophosphate dissolved in 50 mL of methanol was added to the residue. The orange crystalline product precipitated; yield 0.75 g (70%). The proton NMR and the infrared spectra support the proposed structure.

[Ni[(EtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ from [Ni[(NH$_2$Ethi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$. To a solution of 1.38 g (2.0 mmol) of [Ni[(NH$_2$Ethi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ in acetonitrile was added an ethanol solution which contained sodium ethoxide produced by adding 0.095 g (4.1 mmol) of sodium metal. The color changed from yellow to red upon the addition of base. With the same procedures as followed in the above [Ni[(MeEtNEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ synthesis, an excess of ethyl iodide was used to produce the orange crystalline product, yield 1.0 g (70%). The infrared spectrum confirms the proposed structure of the product.

Results and Discussion

The work described here involves the synthesis of a series of substituted derivatives of nickel(II) complexes with macrocyclic ligands, by performing nucleophilic substitutions on reactive sites on the ligand periphery. The reactions at these peripheral sites are designed to append structural units to the ring in order to confer certain specific properties on the ligand and its complexes. In particular, through the use of a variety of amines as nucleophiles, a large collection of macrocyclic nickel(II) complexes were synthesized with a variety of amine substituents. Most of the amine derivatives were characterized by elemental analysis, molar conductivity, and electronic and infrared spectroscopy. Also, in several cases, proton NMR and ^{13}C NMR spectra were employed for further characterization. These species can be deprotonated with strong bases to yield neutral complexes which can be characterized by mass spectrometry and osmometry in addition to the above methods.

Macrocyclic Nickel(II) Complexes Derived from Monoamines. As has already been discussed, compound I ([Ni(Ac$_2$Me$_2$[*Z*]tetraenatoN$_4$)], *Z* = 14, 15, 16) readily methylates to yield compound II ([Ni[(MeOEthi)$_2$Me$_2$[*Z*]tetraeneN$_4$]]$^{2+}$, *Z* = 14, 15, 16). In the case of the 15-membered macrocycle, this methylated species had previously been synthesized, and preliminary results[5] on its reactive properties are summarized in Scheme I. The generality of these reactions is explored here. Primary aliphatic amines were found to react with all three of the methylated macrocyclic species, regardless of ring size (eq 1).



(1)

(a) X, Y = $(CH_2)_2$
(b) X = $(CH_2)_2$, Y = $(CH_2)_3$
(c) X, Y = $(CH_2)_3$

Four monoamine derivatives of the 15-membered macrocyclic complex were prepared. These products are derived from *n*-propylamine ([Ni[(PrNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$), allylamine ([Ni[(AlyNHEthi)Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$), and dimethylamine ([Ni-

Table I. Conductance[a] and Electronic Spectra Data[b] for Simple Monoamine Derivatives

compd	Λ, Ω^{-1} mol^{-1} cm^2	ν_{max}, cm^{-1} × 10^3	ε, M^{-1} cm^{-1}
[Ni[(PrNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$	287	20.7	1019
		26.3	4.7 × 10^4
		35.3	1.4 × 10^4
[Ni[(AlyNHEthi)$_2$Me$_2$[15]tetraneneN$_4$]](ClO$_4$)$_2$	284	20.6	1058
		26.5	4.4 × 10^4
		35.2	1.3 × 10^4
[Ni[(Me$_2$NEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$	290	20.7	918
		25.7	3.6 × 10^4
		34.7	9.8 × 10^4
[Ni[(EtNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$	318	20.7	1271
		25.1	4.3 × 10^4
		36.4	1.5 × 10^4
[Ni[AlyNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$	313	20.8	~1450
		25.0	4.5 × 10^4
		36.0	1.6 × 10^4
[Ni[(Me$_2$NEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$	297	20.4	sh[c]
		24.3	3.0 × 10^4
		35.8	1.05 × 10^4
[Ni[(MeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	255	21.7	sh
		27.4	2.3 × 10^4
		29.9	3.4 × 10^4
[Ni[(EtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	289	22.2	sh
		27.5	2.8 × 10^4
		29.9	4.3 × 10^4
[Ni[(NH$_2$Ethi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	285	23.2	~280
		27.1	2.2 × 10^4
		31.0	2.9 × 10^4
[Ni[(DecNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	257	22.2	sh
		27.4	3.0 × 10^4
		29.9	4.3 × 10^4
[Ni[(Me$_2$NEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	261	20.8	sh
		26.7	2.0 × 10^4
		28.1	3.4 × 10^4
[Ni[(NapEnNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	250	22.2	sh
		27.1	3.4 × 10^4
		29.9	5.2 × 10^4
[Ni[(NapEtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$		22.2	sh
		26.9	3.4 × 10^4
		29.5	5.2 × 10^4
[Ni[(NapMeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	273	22.0	sh
		27.1	2.2 × 10^4
		29.7	4.1 × 10^4
[Ni[(*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	234		
[Ni[(BzNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	275		
[Ni[(*t*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$	258		

[a] On ~1 × 10^{-3} M acetonitrile solutions at 25 °C. [b] Spectra run at 5 × 10^{-3} to 5 × 10^{-5} M in 1-cm quartz cells. [c] Shoulder.

[(Me$_2$NEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$). Formation of this last species demonstrated that a secondary amine can also displace the methoxy groups and form an amine derivative. In addition the product from the reaction of *N*-(1-naphthyl)ethylenediamine (NapEnNH$_2$) with the methylated starting material was isolated. The 14-membered analogue, [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, was found to undergo the same reaction (eq 1a). The ethylamine derivative, [Ni[(EtNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, the allylamine derivative, [Ni[(AlyNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, and the dimethylamine derivative, [Ni[(Me$_2$NEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, were synthesized and identified by elemental analysis and infrared spectroscopy.

The methoxy 16-membered macrocyclic derivative [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ undergoes reactions with amines as shown in eq 1c. Eight simple monoamine derivatives were formed and studied. They are derived from ethylamine (EtNH$_2$), methylamine (MeNH$_2$), ammonia (NH$_3$), decylamine (DecNH$_2$), dimethylamine (Me$_2$NH), *N*-(1-naphthyl)ethylenediamine (NapEnNH$_2$), *d*-*α*-(1-naphthyl)ethylamine (NapEtNH$_2$), and 1-naphthylmethylamine (NapMeNH$_2$). All of the macrocyclic derivatives of these amines have elemental analyses consistent with their proposed structures. In addition, their infrared spectra are very similar to those of the amine derivatives of the other ring sizes. They all show N–H stretches (except for dimethylamine derivatives) at about 3400 cm^{-1}, and all show a double-bond region rich in bands. In the solid state, the ammonia compound exhibits three separate N–H stretching frequencies, but in acetonitrile solution, only two stretching frequencies are observed at 3250 and 3360 cm^{-1}, as expected. When present, hexafluorophosphate exhibits stretching bands at 850 and 555 cm^{-1}.

Molar conductance data for these complexes fall in the range for 2:1 electrolytes in acetonitrile[8] (260–315 Ω^{-1} mol^{-1} cm^2; Table I). This of course supports the analytical data which provide evidence for the presence of two anions per complex cation. The conductance data for [Ni[(NapEnNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ were not obtained because of its limited solubility.

The electronic spectral data listed in Table I are typical of those observed for square-planar nickel(II) complexes. The

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(8) DuBois, T. D.; Meek, D. W. *Inorg. Chem.* **1969**, *8*, 146.
(9) Urbach, F. L.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 408.
(10) Chang, C. K.; Traylor, T. G. *J. Am. Chem. Soc.* **1973**, *95*, 5810, 8475, 8477.
(11) Westland, A. D. *J. Chem. Soc.* **1965**, 3060.

Table II. Proton NMR Spectra Data[a] for Nickel(II) Complexes of Macrocyclic Ligands Derived from Monoamines

compd	methyl	methylene	aromatic	NH
$[Ni[(MeOEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	2.33, 2.50, 4.18	3.23, 3.63[g]	7.90	
$[Ni[(MeNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	2.22, 2.44, 3.17	2.2,[b] 3.4[b]	7.60	7.0[b]
$[Ni[(EtNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$[c]	1.25,[f] 2.12, 2.32	3.04, 3.3[b]	7.48	6.9[b]
$[Ni[(NH_2Ethi)_2Me_2[16]tetraeneN_4]](PF_6)_2$[c]	2.21, 2.32	3.1, 3.4[b]	7.58	6.7[b]
$[Ni[(NapEnNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	2.13[b]	3.0, 3.4,[b] 3.75	7.4,[b] 8.2[b]	6.7[b]
$[Ni[(NapEtNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	1.88,[e] 2.24	3.10, 3.34	7.7[b]	not seen
$[Ni[(NapMeNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$[d]	2.04, 2.40	2.7,[b] 3.03, 3.4,[b] 4.8[b]	7.8[b]	6.8[b]
$[Ni[(2\text{-}pyEtNHEthi)_2Me_2[15]tetraeneN_4]](PF_6)_2$	2.30[b]	3.35, 3.8[b]	7.3,[b] 7.7[b]	8.5[b]
$[Ni[(NMe_2Ethi)_2Me_2[16]tetraeneN_4]](PF_6)_2$[c]	1.85, 2.33, 3.20	3.02, 3.35[g]	7.40	
$[Ni[(n\text{-}BuNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$[c]	0.93, 2.12, 2.30	1.03, 1.55,[b] 3.04, 3.38[g]	7.48	6.73[b]
$[Ni[(BzNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$[c]	2.08, 2.32	1.97, 3.03, 3.38,[g] 4.58	7.35, 7.52	7.02[b]
$[Ni[(t\text{-}BuNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$[c]	1.67, 2.13, 2.47	3.07, 3.38[g]	7.53	6.63[b]

[a] Chemical shifts given in δ (ppm from Me_4Si), run on concentrated solution in CD_3NO_2 unless otherwise noted. [b] Broad. [c] Run in CD_3CN solution. [d] Run in $Me_2SO\text{-}d_6$ solution. [e] Doublet. [f] Triplet. [g] Multiplet.

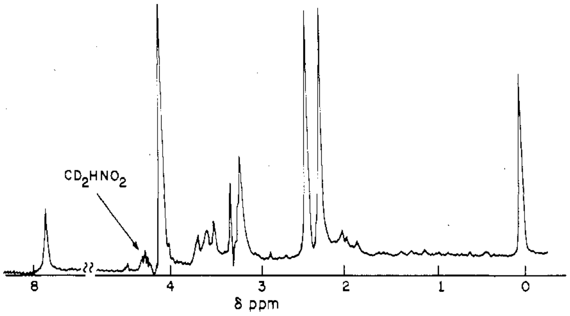


Figure 1. Proton NMR spectrum of $[Ni[(MeOEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$.

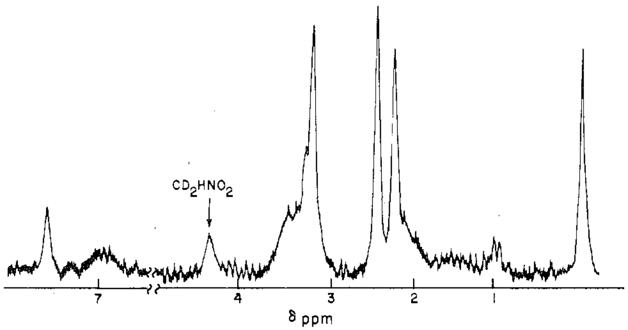


Figure 2. Proton NMR spectrum of $[Ni[(MeNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$.

spectra generally display a band at about 20.7 × 10^3 cm^{-1} with an extinction coefficient of about 1000. In the higher energy portions of the spectra, intense bands appear. In a related square-planar nickel(II) species, a visible band occurs at about (20–21) × 10^3 cm^{-1} but with much lower intensities. The large molar absorbance in these complexes could be the result of "intensity stealing" from the very strong ultraviolet absorption bands. In light of the fact that the parent methoxy species is known to contain square-planar nickel(II),[5] it seems most reasonable to assign the metal to a square-planar environment, and the electronic spectral results are consistent with this assignment.

From the results summarized here it is clear that the nucleophilic substitution reaction of the methoxy compounds $[Ni[(MeOEthi)_2Me_2[Z]tetraeneN_4]]^{2+}$ with amines is quite general and that a broad family of compounds of the general structure in eq 1 can be prepared. The formation of secondary amine derivatives from dimethylamine further extends the generality. It should be noted, however, that while the secondary amine diethylamine reacts with the methoxy compound, attempts to isolate a product from this reaction failed. The extra steric interactions caused by the larger ethyl groups may impede the nucleophilic substitution. Also, the aromatic amine aniline failed to react with the parent methoxy species; this is most likely due to the poor nucleophilic character of aromatic amines.

Proton magnetic resonance data for several of these simple amine complexes, along with the parent methoxy derivative, are listed in Table II. In addition, the ^1H NMR spectra for $[Ni[(MeOEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$ and $[Ni[(MeNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$ are shown in Figures 1 and 2, respectively.

Structure VI represents the skeletal macrocyclic structure common to all of the 16-membered derivatives. The different protons are labeled in this structure for reference purposes. In the methoxy starting material (for which the structure had been proven earlier), one would expect three methyl resonances, two close together (a and b) and one further downfield due to the methyl groups of the methoxy group; this is observed. In addition, a complex methylene pattern is observed for protons at c, c′, d, and d′ as well as a single peak at low field for the vinyl protons (e) on the unsaturated six-membered chelate ring. For a demonstration of how the spectra are consistent with the proposed structures, the spectrum of the methylamine derivative is considered. In this spectrum, three methyl resonances are seen near other peaks and the sharp peak at low field attributed to the vinyl protons (e) is observed. In addition, a broad absorption at about 7.0 ppm from Me_4Si is indicative of an NH band.

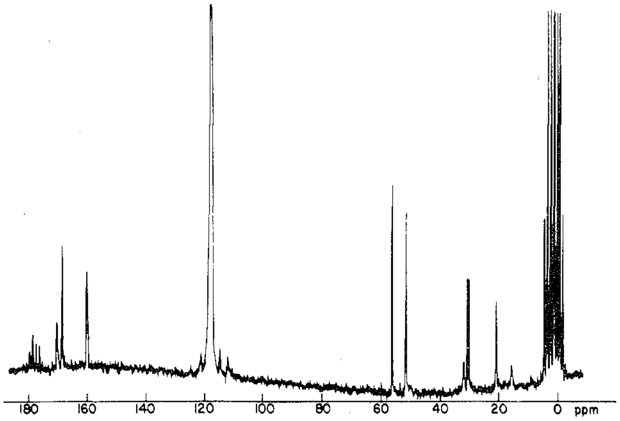
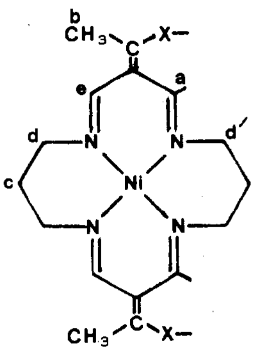


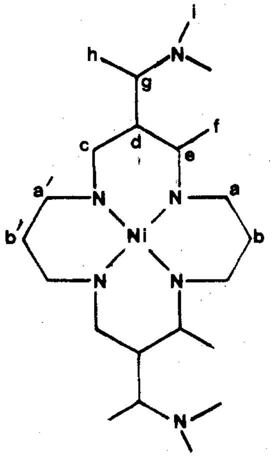
Figure 3. ^{13}C NMR spectrum of $[Ni[(MeNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$.

^{13}C NMR data for six of these complexes are summarized in Table III, and an example is shown in Figure 3. The resonances have been assigned, according to structure VII, through the use of the off-resonance decoupling technique. An X-ray structure determination has shown that the nitrogen atom of the substituent group has a planar array of groups.

There are several features of the basic macrocycle which are common to all of the complexes. Two methyl resonances



VI

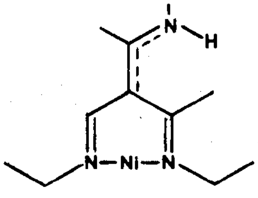


VII

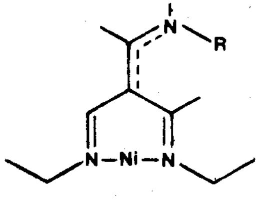
are observed between 15 and 21 ppm from Me_4Si due to carbons f and h. Methylene resonances observed between 29 and 31 ppm are assigned to carbons b and b′; those between 51 and 56 ppm are due to a and a′, the methylenes bonded to nitrogen. A single resonance near 110 ppm is due to the quaternary carbon d. The resonance near 160 ppm splits into a doublet in the off-resonance spectrum and is therefore assigned to carbon c. Two resonances between 165 and 175 ppm are due to carbons e and g. The resonances due to the amine substituents are found in the expected regions.

As shown in Figure 4, the spectrum of $[Ni[(Me_2NEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$ at 300 K exhibits only a single resonance due to the amine methyl groups at 44.4 ppm. At 238 K however, two distinct resonances appear at 46.4 and 42.2 ppm with coalescence occurring near 278 K. In contrast to the above example, the spectra of the methylamine, *n*-butylamine, and benzylamine complexes show broadening of the resonances due to carbons d, g, i, and h or f as shown by the example in Figure 3. When the substituent on the nitrogen is the bulky *tert*-butyl group, all resonances are sharp.

The above data indicate that there is rotation about the C–N bond and that the barrier to rotation is dependent upon the nature of the nitrogen substituents. This suggests that there is a favored orientation of a single nitrogen substituent relative to the macrocycle. Referring back to structure III, one may direct one's view of the structure toward the edge of the NiN_4 plane so that an unsaturated chelate ring appears above that plane. This produces the useful projections used in structures VIII and IX. As shown in those structures, the R group can be oriented in a direction approximately perpendicular to the macrocycle plane (VIII) or roughly parallel to the plane (IX). When the nitrogen substituents are identical, neither of these orientations is preferred. When only one substituent is present, structure VIII would be favored since the interaction between the macrocycle and the small hydrogen atom would be less than the interaction between the macrocycle and the nonhydrogen R group. When R is very bulky as in the *tert*-butyl case, structure VIII is highly favored and only that single conformer is present in significant amounts at ambient temperatures.



VIII



IX

Table III. ^{13}C NMR Data for Simple Monoamine Derivatives

compound[a]	chem shifts[b]
$[Ni[(NH_2Ethi)_2Me_2[16]tetraeneN_4]]^{2+}$	169.4, 167.5, 161.3, 111.5, 56.2, 51.3, 30.4, 29.9, 20.5, 19.8
$[Ni[(MeNHEthi)_2Me_2[16]tetraeneN_4]]^{2+}$	170.0,[c] 168.3, 159.9, 112.4,[c] 56.2, 51.5, 31.8,[c] 30.6, 30.2, 20.9, 15.5[c]
$[Ni[(Me_2NEthi)_2Me_2[16]tetraeneN_4]]^{2+}$	173.7, 168.0, 159.5, 111.4, 56.2, 51.1, 44.4, 30.6, 30.5, 20.8, 19.4
$[Ni[(n\text{-}BuNHEthi)_2Me_2[16]tetraeneN_4]]^{2+}$	168.7,[c] 168.1, 159.9, 112.3,[c] 56.2, 51.3, 45.8,[c] 31.7, 30.5, 30.1, 20.6, 15.3,[c] 13.8
$[Ni[(BzNHEthi)_2Me_2[16]tetraeneN_4]]^{2+}$	168.6, 168.2, 160.3, 137.2, 129.9, 129.1, 112.4,[c] 56.2, 51.3, 49.6,[c] 30.4, 30.0, 21.0, 16.3[c]
$[Ni[(t\text{-}BuNHEthi)_2Me_2[16]tetraeneN_4]]^{2+}$	167.9, 167.4, 159.6, 112.7, 56.5, 55.9, 50.9, 30.1, 29.7, 20.3, 16.2

[a] As PF_6^- salts. [b] CD_3CN solution; ppm relative to Me_4Si. [c] Broad.

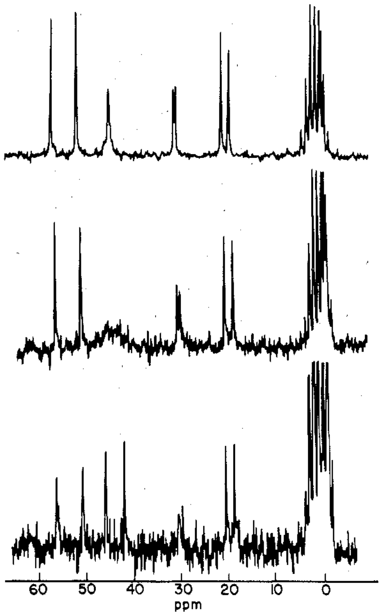


Figure 4. Variation of ^{13}C NMR spectra with temperature for $[Ni[(Me_2NEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$.

Variable-temperature ^{13}C NMR spectra also show that at low temperatures the rate of boat–chair interconversion of the saturated side chains of the macrocycle decreases, causing the resonances of methylene carbons to broaden.

Several of the complexes were subjected to electrochemical studies. There are two well-defined oxidation waves of equal height; the first has been assigned to the Ni(II)/Ni(III) couple and the second has been assigned to a ligand oxidation.[12] Electrochemical parameters (Table IV) were obtained from rotating-electrode voltammetry and cyclic voltammetry, using

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(12) Busch, D. H.; Pillsbury, D. G.; Lovecchio, F. V.; Tait, A. M.; Hung, Y.; Jackels, S. C.; Rakowski, M. C.; Schammel, W. P.; Martin, L. Y. *ACS Symp. Ser.* **1977**, *No. 38*, 32.

Table IV. Electrochemical Data[a] for the Simple Monoamine Derivatives

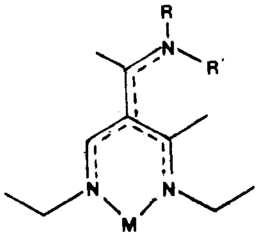
complex	$E_{1/2}$,[b] V	$\lvert E_{3/4} - E_{1/4} \rvert$,[b] mV	E_p,[c] V
$[Ni[(Me_2NEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	+0.745 +1.080	70 70	+0.775 +1.085
$[Ni[(MeNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	+0.800	80	+0.835 +1.260
$[Ni[(n\text{-}BuNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	+0.810	75	+0.835 +1.240
$[Ni[(BzNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	+0.830	85	+0.835 +1.305
$[Ni[(t\text{-}BuNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	+0.845	75	+0.870 +1.190 +1.400
$[Ni[(NH_2Ethi)_2Me_2[16]tetraeneN_4]](PF_6)_2$	+0.870	80	+0.900 +1.420

[a] CH_3CN solution with 0.1 M $n\text{-}Bu_4NBF_4$ supporting electrolyte; Ag/Ag^+ (0.1 N) reference electrode. [b] Obtained from rotating platinum electrode voltammetry. [c] Obtained from cyclic voltammetry; scan rate 50 mV/s.

a platinum disk electrode. From the values of $E_{1/2}$ for the first oxidation it is apparent that the electron-donating ability and other properties of the nitrogen substituent directly influence the oxidation potential at the metal center. Although the differences are small, $E_{1/2}$ appears to change in the uncommon sequence

$$CH_3 < n\text{-}Bu < Bz < t\text{-}Bu < H$$

Crystal structure data from related complexes[2,13] indicate that the nitrogen substituent exerts its inductive effect through a delocalized π system which extends all the way back to the metal as shown in structure X.



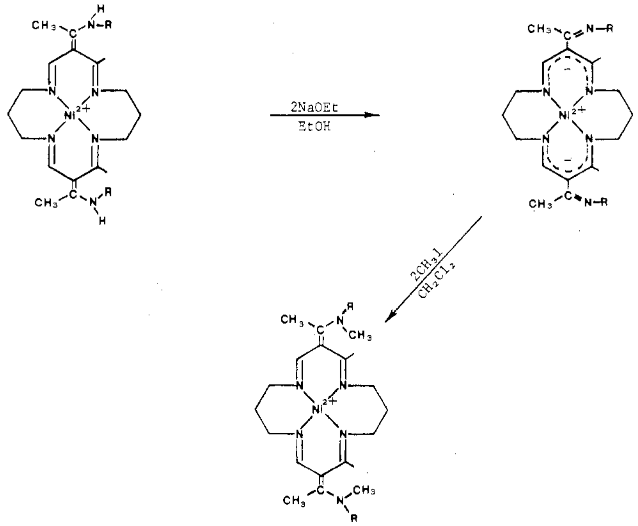
X

In summary, it has been demonstrated that these reactive methoxy compounds ($[Ni[(MeOEthi)_2Me_2[Z]tetraeneN_4]]^{2+}$, Z = 14, 15, 16) all undergo nucleophilic substitution reactions with a variety of aliphatic amines. This produces derivatives with the general structure given in eq 1 and provides a route for the attachment of desirable groups to this macrocyclic ligand system. The three derivatives containing naphthyl groups exemplify structures having large hydrophobic groups.

Neutral Macrocyclic Nickel(II) Complexes and Their Reactions. Deprotonation reactions were conducted on several of the salt complexes described in the preceding paragraphs. This resulted in the formation of neutral species with dianionic ligands as shown in Scheme II. This deprotonation is accomplished through the addition of an excess of strong base, and the neutral complexes are formed by removal of protons from their extracyclic N–H groups. Weaker bases such as triethylamine do not serve to deprotonate these species.

More extensive efforts were dedicated to the investigation of the nature and properties of the neutral amine derivatives. Therefore, strong base was added to the ethylamine derivative, thus forming in solution the corresponding neutral complex which was then allowed to react with the electrophilic species methyl iodide. From this reaction, a product was isolated and shown to be the methylated species $[Ni[(MeEtNEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$. Evidence points toward the fact that the methylations took place on the amine nitrogen; hence the deprotonation must have occurred there as well. This is shown in Scheme II.

Scheme II



Strongest evidence for the assigned site of methylation is found in the infrared spectrum. While analytical data confirm that methyl groups were added to the species, the infrared spectrum of the final product demonstrates the removal of the proton from the nitrogen atom since the N–H stretching mode is absent. The remainder of the spectrum is typical of the salt complexes.

A related result follows from the reactions of the neutral ammonia derivative. This species was formed through deprotonation of the ammonia salt complex $[Ni[(NH_2Ethi)_2Me_2[16]tetraeneN_4]](PF_6)_2$. The deprotonation product was not isolated but was treated with ethyl iodide to yield a crystalline product whose analysis and infrared spectrum are essentially identical with those of the previously discussed ethylamine derivative $[Ni[(EtNHEthi)_2Me_2[16]tetraeneN_4]](PF_6)_2$. This confirms the reaction given in Scheme II (where R = H).

In addition to the deprotonation of amine derivatives, the parent 16-membered ring methoxy species were deprotonated, and the new compounds were isolated and characterized. This species gave an infrared spectrum with two weak absorptions in the double-bond stretching region (1630 and 1540 cm^{-1}). Analytical data confirm that the species are neutral since no evidence for a counterion exists. Electronic spectral bands occur at 18.5×10^3 cm^{-1} (207), 27.0×10^3 cm^{-1} (1.1×10^4), and 29.9×10^3 cm^{-1} (5.2×10^4); these values are comparable to those of other neutral nickel(II) species. It is not known

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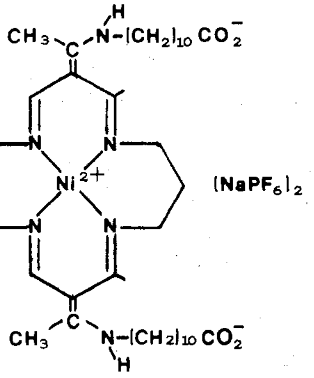
(13) Unpublished results show that the atoms bonded to the nitrogen atom are coplanar with it. Further, the bond between the nitrogen and the vinyl carbon is considerably shorter than a single bond (Stevens, J. C. Thesis, The Ohio State University, Columbus, Ohio, 1979).

exactly where this species has deprotonated but evidence from previous work[5] shows that it probably occurs at the vinyl methyl group to yield [Ni[(MeOVinyl)$_2$Me$_2$[16]tetraenatoN$_4$]] (Scheme I).

Macrocyclic Nickel(II) Complexes Derived from Amines Containing Additional Functional Groups. One possible exploitation of the nucleophilic action of amines on the reactive macrocyclic species under study here concerns the use of amines which contain potentially useful functional group(s). As was discussed in the Introduction, it is desirable to synthesize ligands containing hydrophilic groups isolated at the ends of long carbon chains (structure V). Another promising class of compounds involves the attachment of either freely rotating or rigidly fixed groups containing donor atoms capable of bonding to the metal. This type of ligand could promote the formation of pentacoordinate complexes on iron(II) analogous to the porphyrin derivatives studied by Traylor.[10]

Synthesis of a Macrocyclic Nickel(II) Complex with Attached Hydrophilic Moieties. It was found that by reaction of the methoxy species [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$ with the sodium salt of 11-aminoundecanoic acid, it is possible to obtain a yellow powdery product which analyzes very well for the corresponding derivative (structure XI). We assume this compound to be a "lattice compound" composed of the neutral zwitterion complex and containing 2 equiv of sodium hexafluorophosphate. The substance is quite soluble in water despite the presence of the PF$_6^-$ anion, which tends to inhibit water solubility. Other than this enhanced water solubility, the complex resembles, in appearance and behavior, other simpler amine derivatives. For example, its infrared spectrum contains the typical N–H absorption at 3390 cm^{-1} and a rich double-bond region (probably including absorption due to the CO$_2^-$ stretching vibrations). In addition, the molar conductance of 172 Ω^{-1} mol^{-1} cm^2 in methanol corresponds to a 2:1 electrolyte (the range for a 2:1 electrolyte in methanol is 150–190 Ω^{-1} mol^{-1} cm^2). The result confirms the presence in solution of a conducting species. Presumably, this conducting species is the sodium hexafluorophosphate of the "lattice compound".



XI

Synthesis of Nickel(II) Complexes with 15-Membered Macrocyclic Ligands Derived from Amines Containing Additional Donor Atoms. An example of these species is derived from 2-(2-aminoethyl)pyridine (2-pyEtNH$_2$) and essentially contains two potential coordinating pyridine groups able to freely rotate into or around the vicinity of the metal ion. The composition is confirmed by elemental analysis, and the infrared spectrum is typical of these amine derivatives. Also, the molar conductance for this species in acetonitrile is 289 Ω^{-1} mol^{-1} cm^2 which is well within the range for a 2:1 electrolyte. The solution electronic spectrum (ν (ϵ): 20.6 × 10^3 cm^{-1} (1075), 26.6 × 10^3 cm^{-1} (4.4 × 10^4), 36.4 × 10^3 cm^{-1} (1.5 × 10^4)) is very similar to those of simple, amine derivatives, and this suggests the retention of a square-planar, four-coordinate geometry in the nickel(II) complex. The proton NMR spectrum was also obtained for this species, and the data are reported in Table II. This spectrum is also fairly typical except for its NH resonance which is shifted with respect to values obtained by using other compounds. The pyridine moieties give rise to a complex resonance pattern in the aromatic region.

Acknowledgment. This work has been supported by a grant from the U.S. National Science Foundation.

Registry No. [Ni[(MeOEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, 74465-80-8; [Ni[(MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 70021-28-2; [Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$, 50928-64-8; [Ni[(NapEnNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](PF$_6$)$_2$, 74465-82-0; [Ni[(MeOEthi)$_2$Me$_2$[15]tetraeneN$_4$]](PF$_6$)$_2$, 74465-83-1; [Ni[(CO$_2$DecNHEthi)$_2$Me$_2$[16]tetraenatoN$_4$]](NaPF$_6$)$_2$, 74465-86-4; Ni[(MeOVinyl)$_2$Me$_2$[16]tetraenatoN$_4$], 74482-29-4; [Ni[(MeEtNEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74465-88-6; [Ni[(Me$_2$NDEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74482-31-8; [Ni[(PrNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$, 74465-90-0; [Ni[(AlyNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$, 74465-92-2; [Ni[(Me$_2$NEthi)$_2$Me$_2$[15]tetraeneN$_4$]](ClO$_4$)$_2$, 74465-94-4; [Ni[(EtNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, 74465-96-6; [Ni[(AlyNHEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, 74465-98-8; [Ni[(Me$_2$NEthi)$_2$Me$_2$[14]tetraeneN$_4$]](PF$_6$)$_2$, 74466-00-5; [Ni[(MeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-02-7; [Ni[(EtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74482-33-0; [Ni[(NH$_2$Ethi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-04-9; [Ni[(DecNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-06-1; [Ni[(Me$_2$NEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-08-3; [Ni[(NapEnNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-10-7; [Ni[(NapEtNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-12-9; [Ni[(NapMeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-14-1; [Ni[(*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-16-3; [Ni[(BzNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-18-5; [Ni[(*t*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$]](PF$_6$)$_2$, 74466-20-9; Ni(Ac$_2$Me$_2$[14]tetraenatoN$_4$), 20123-01-7; dimethylamine, 124-40-3; [Ni[(2-pyEtNHEthi)$_2$Me$_2$[15]tetraeneN$_4$]](PF$_6$)$_2$, 74482-35-2; *n*-propylamine, 107-10-8; allylamine, 107-11-9; *N*-(1-naphthyl)ethylenediamine dihydrochloride, 1465-25-4; ethylamine, 75-04-7; methylamine hydrochloride, 593-51-1; decylamine, 2016-57-1; *d*-α-(1-naphthyl)ethylamine, 3886-70-2; (1-naphthyl)methylamine, 118-31-0; 2-(2-aminoethyl)pyridine, 2706-56-1; *n*-butylamine, 109-73-9; *tert*-butylamine, 75-64-9; benzylamine, 100-46-9; 11-aminoundecanoic acid, 2432-99-7.