Synthesis and Study of a Nickel(II) Complex Containing a Macrocyclic Ligand Derived from 1,3-Diaminopropane and Methyl Vinyl Ketone[1]

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The macrocyclic complex IV can be synthesized from 1,3-diaminopropane and methyl vinyl ketone in the presence of both Ni(II) and hydrogen ions. Several derivatives of IV are described including two where the macrocyclic ligand must be present in a folded configuration within a hexacoordinate complex. Evidence is presented which indicates that species IIB and IV have a greater tendency to accept fifth and sixth ligands than do complexes IIA and III. The detailed description of the separation and purification of two interconvertible isomers of IV is presented. It is proposed that these isomers are the meso and racemic forms of IV.

Introduction

The potential utility of α,β-unsaturated ketones as precursors in the synthesis of nitrogen-containing ligands was first clearly indicated by Jehn's preparation of I from mesityl oxide and $[Ni(NH_3)_6]^{2+}$.[2] Curtis and Hay demonstrated the value of mesityl oxide as a starting material for the preparation of macrocyclic ligands by using it with ethylenediamine monohydroperchlorate to prepare the dihydroperchlorate salt of the 14-membered ligand shown in IIA.[3] Following Curtis and Hay, Kolinski and Korybut-Daskiewicz investigated the reaction between ethylenediamine monohydroperchlorate and methyl vinyl ketone.[4] They reported the preparation of the dihydroperchlorate salt of the 14-membered ligand shown in IIB. The use of monohydroperchlorate salts in these two successful syntheses, coupled with the findings of Baldwin and Rose concerning the synthesis of yet another imine-containing macrocyclic complex in the presence of hydrogen ions,[5] suggests that hydrogen ions might be influencing the course of the condensation reactions involving ketones such that cyclization is favored. However, in the case of mesityl oxide, a cyclization-inducing role attributed to H^+ cannot be unique because MacDermott and Busch reported the direct synthesis of IIA using only tris(ethylenediamine)nickel(II) chloride and mesityl oxide in methanol.[6]

To our knowledge, reactions using α,β-unsaturated ketones and 1,3-diamines with or without hydrogen ions present have not been employed to prepare 16-membered cyclic ligands or their complexes. The complex III, which does contain a 16-membered ligand formally derived from mesityl oxide, has been prepared but *via a reaction between tris(1,3-diaminopropane)nickel(II) perchlorate and acetone.*[7]

All of the macrocyclic complexes prepared from α,β-unsaturated ketones and diamines containing two or more CH_2 moieties between the primary amine nitrogen atoms can, in principle, be formed in two distinctly geometric forms—one containing the imine functions trans to one another and the other containing the imine functions cis to one another.

I

IIA R = CH₃
IIB R = H

III

IV
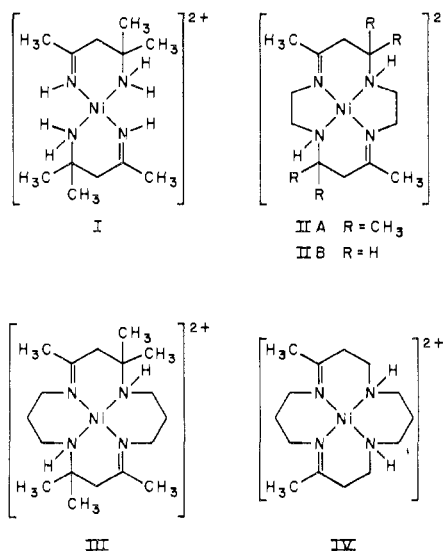
Each of these forms, in turn, can have two interconvertible diastereomers (racemic or meso) depending on the relative placement of the N-H bonds with respect to each other.[8] Finally, each of these diastereomers can fit on the coordination sphere of a metal ion in either (1) a planar or (2) a folded fashion.[9,10]

We report here the preparation of the PF_6^- salt of the 16-membered macrocyclic complex, IV, from methyl vinyl ketone, 1,3-diaminopropane, and Ni(II) in the presence of hydrogen ions. The synthesis of interconvertible isomers of IV, presumably the racemic and meso forms, is described as well as the preparation of the two derivatives of IV in which the macrocyclic ligand is folded. A direct preparation for the PF_6^- salt of IIB from ethylenediamine monohydrohexafluorophosphate, Ni(II), and methyl vinyl ketone is also described.

Experimental Section

Preparation of 1,3-Diaminopropane Dihydrochloride (tmd·2HCl). 1,3-Diaminopropane (henceforth tmd) (71 ml, 0.85 mol) was added to 95% ethanol (750 ml) and cooled below room temperature in an ice bath. Concentrated hydrochloric acid (150 ml, 1.86 mol) was added dropwise at a rate such that the solution temperature remained below 20°. The product was collected, washed with ethanol and then with ether, and dried by passing anhydrous air over the product for 1 hr. This product was used without further purification. *Anal.* Calcd for $C_3H_{12}Cl_2N_2$: N, 19.04. Found: N, 19.28. (Note: the

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fraction which was analyzed was recrystallized from a boiling ethanol-water mixture containing the minimum amount of water necessary to dissolve the sample at the boiling temperature. Upon cooling, the desired compound appeared as long white needles).

Preparation of (6,16-Dimethyl-1,5,9,13-tetraazacyclohexadeca-1,5-diene)nickel(II) Hexafluorophosphate (IV), *cis*-[NiM(16)](PF$_6$)$_2$. tmd (5 ml, 60 mmol) was added to methanol (400 ml) in which tmd·2HCl (8.75 g, 60 mmol) was suspended. The mixture was stirred under N$_2$ and cooled to 5° in an ice bath. Methyl vinyl ketone (12 ml, 146 mmol) was added rapidly to the cooled mixture. Stirring under N$_2$ was continued approximately 10 min and then nickel(II) acetate tetrahydrate (14.8 g, 60 mmol) was added. The solution was tightly stoppered, removed from the ice bath, and set aside at room temperature. After 6 days, the solution was taken to near dryness on a rotatory evaporator and the resulting thick oil was dissolved in water (300 ml) and filtered. While stirring this filtrate vigorously, an aqueous solution (100 ml) containing ammonium hexafluorophosphate (10 g, 61 mmol) was slowly added. The walls of the flask were scratched with a glass rod to initiate crystallization. The resulting yellow solid was collected, washed with water, and air-dried. This solid was recrystallized by dissolving in acetone (100 ml), filtering the subsequent solution, adding absolute ethanol (100 ml), and then adding ether (100–200 ml) slowly until the crystallization processes appeared complete. The following alternate procedure was also employed as the first step in purifying the crude product. The 10 g of crude material was dissolved in 100 ml of acetone and filtered. The resulting solution was eluted with acetone from a column of Merck acid-washed aluminum oxide 71695 (2.2 cm × 20 cm) which had been thoroughly rinsed with acetone. The light yellow band that moved down the column initially was collected in the first 200 ml of yellow eluent. Addition of an equal volume of ether to the yellow solution yielded 5 g of the yellow microcrystalline product (yield of recrystallized product 12%, based on nickel). *Anal.* Calcd for NiC$_{14}$H$_{28}$N$_4$P$_2$F$_{12}$: C, 27.97; H, 4.70; N, 9.32; Ni, 9.77. Found: C, 28.08; H, 4.85; N, 9.34; Ni, 9.78.

Preparation of *cis*-A[NiM(16)]Cl(PF$_6$). A filtered acetone solution (13 ml) saturated with lithium chloride was added to a filtered acetone solution (30 ml) containing *cis*-[NiM(16)](PF$_6$)$_2$ (2.0 g). The solution was cooled (~5°) for several hours. Yellow crystals with a slightly green cast were collected, washed with a few milliliters of acetone, and finally washed with ether. The product was used without further purification. *Anal.* Calcd for NiC$_{14}$H$_{28}$N$_4$ClPF$_6$: C, 34.21; H, 5.74; F, 23.19; Cl, 7.21. Found: C, 34.38; H, 5.84; F, 23.43; Cl, 7.13.

Preparation of *cis*-A[NiM(16)]Cl$_2$. A filtered solution of acetone (50 ml) saturated with lithium chloride was filtered into a beaker containing *cis*-[NiM(16)](PF$_6$)$_2$ (2.0 g). The undissolved salt turned from the characteristic yellow color to a blue solid, and the supernatant acetone became green. The blue solid was filtered under N$_2$ and washed with a small amount of acetone. The product was dried under anhydrous N$_2$ after washing with ether. (The product is very hygroscopic and turns yellow if exposed to the air unless very carefully dried under anhydrous N$_2$.) The blue solid obtained is nearly isomerically pure A when the total metathesis is carried out rapidly (within 15 min or less). Traces of isomer B were removed by carefully washing the product with an 80% hexane–20% dichloromethane mixture.

The isomeric purity of the sample can be estimated as follows. Dissolve a 0.1-g sample in ~5 ml of 0.01 *M* acid. Filter into this yellow solution ~10 ml of 0.01 *M* acid containing ammonium hexafluorophosphate (0.1 g). Collect the resulting solid, wash with ethanol and ether, and then air-dry. Dissolve the product in 1 ml of acetonitrile and obtain the pmr spectrum as quickly as possible. If any peaks are noted in the 0 to +20 ppm region downfield from internal TMS some isomer B was present in the original sample. *Anal.* Calcd for NiC$_{14}$H$_{28}$N$_4$Cl$_2$: C, 44.02; H, 7.39; N, 14.66. Found: C, 44.07; H, 7.03; N, 14.42.

Preparation of *cis*-B[NiM(16)]Cl$_2$. *cis*-A[NiM(16)]Cl$_2$ was dissolved in a slight excess of dichloromethane and filtered. (It is not necessary to use pure *cis*-A[NiM(16)]Cl$_2$ in this synthesis; see previous preparation.) Hexane was added dropwise until a nearly white precipitate just started to form; then the mixture was cooled to 5° and kept at this temperature throughout the subsequent steps. (If a white precipitate formed, the solution was filtered again before refrigeration.) More hexane was added daily to the point of incipient cloudiness until blue crystals volunteered. This procedure usually required 3–6 days. The blue crystals were collected by filtration, washed with hexane, and dried *in vacuo* over P$_4$O$_{10}$ (Note: these crystals can be handled in the air.) *Anal.* Calcd for NiC$_{14}$H$_{28}$N$_4$Cl$_2$: C, 44.02; H, 7.39; Cl, 18.56. Found: C, 43.85; H, 7.24; Cl, 18.52.

Molecular weight: calcd, 282; found, 283 (in dichloromethane).

Preparation of *cis*-BNiM(16)(H$_2$O)Cl$_2$. The same procedure as above was followed except that about $^1/_2$ drop of water/100 ml of solution was introduced after 2 or 3 days of the process had passed. Cooling the solution for a few hours (to ~5°) after addition of the water afforded blue needle crystals. The blue crystals were collected by filtration, washed with acetone, and dried in a stream of N$_2$. Further drying *in vacuo* over P$_4$O$_{10}$ resulted in the loss of the water with subsequent formation of *cis*-B[NiM(16)Cl$_2$]. *Anal.* Calcd for NiC$_{14}$H$_{30}$N$_4$OCl$_2$ (with one H$_2$O molecule) before drying *in vacuo*: C, 42.03; H, 7.56. Found: C, 42.23; H, 7.66. Calcd for NiCl$_{14}$H$_{28}$N$_4$Cl$_2$ after drying *in vacuo*: C, 44.02; H, 7.39; N, 14.66; Cl, 18.56. Found: C, 44.05; H, 7.08; N, 14.44; Cl, 18.59.

Preparation of *cis*-A[NiM(16)](PF$_6$)$_2$. This compound was obtained from *cis*-A[NiM(16)]Cl(PF$_6$) in two ways. In method 1, *cis*-A[NiM(16)]Cl(PF$_6$) (2.0 g) was added to 10 ml of an aqueous HCl solution (0.01 *M*). A yellow solution and a yellow solid resulted. The solid was collected by suction filtration and the filtrate was saved for use in method 2. The yellow solid was washed with absolute ethanol and then washed with ether. In method 2, a solution of 5–10 ml of 0.01 *M* acid containing ammonium hexafluorophosphate (1.0 g) was filtered into the solution retained for use with method 2. The yellow product was collected and dried under anhydrous air after washing with absolute ethanol and ether. *Anal.* Calcd for NiC$_{14}$H$_{28}$N$_4$P$_2$F$_{12}$: C, 27.97; H, 4.70; N, 9.32. Found: C, 28.37; H, 4.58; N, 9.23.

Preparation of *cis*-B[NiM(16)](PF$_6$)$_2$. *cis*-B[NiM(16)Cl$_2$] (2.0 g) was dissolved in 15 ml of an aqueous HCl solution (0.01 *M*) and filtered. A solution obtained by dissolving ammonium hexafluorophosphate (2.0 g) into 10 ml of an aqueous HCl solution (0.01 *M*) was filtered into the solution of *cis*-B[NiM(16)Cl$_2$]. The product that volunteered was collected and dried using the same procedure given in the previous preparation. *Anal.* Calcd for NiC$_{14}$H$_{28}$N$_4$P$_2$F$_{12}$: C, 27.97; H, 4.70; N, 9.32. Found: C, 28.22; H, 4.45; N, 9.07.

The following metatheses were performed using *cis*-[NiM(16)]-(PF$_6$)$_2$ as obtained *via* the alumina column or the acetone–ethanol–ether crystallization.

Preparation of *cis*-NiM(16)(H$_2$O)$_2$(Br)$_2$. A filtered acetone solution (100 ml) of lithium bromide (1.0 g) was added to a filtered acetone solution (30 ml) of *cis*-[NiM(16)](PF$_6$)$_2$ (2.0 g). A small amount of oily, yellow material formed. The supernatant liquid was rapidly decanted into a clean flask and set aside, whereupon a blue product formed. The product was filtered in the absence of moist air and recrystallized by dissolving in dichloroethane and adding hexane to incipient cloudiness. Upon standing, the solution deposited blue crystals. The blue crystals rapidly picked up moisture when exposed to air and turned from blue to green to yellow. The resulting yellow solid was dried *in vacuo* over P$_4$O$_{10}$ at room temperature. Samples, so prepared, were used for the studies reported herein. *Anal.* Calcd for NiC$_{14}$H$_{32}$N$_4$O$_2$Br$_2$: C, 33.30; H, 6.34; N, 11.09; Br, 31.65. Found: C, 33.42; H, 6.33; N, 10.75; Br, 31.77.

Preparation of *cis*-[NiM(16)]I$_2$. A filtered acetone solution (25 ml) of NaI (1.0 g) was added to a filtered acetone solution (30 ml) of *cis*-[NiM(16)](PF$_6$)$_2$ (2.0 g). The yellow product that separated was washed with acetone and then with ether and air-dried (yield 1.85 g, 98%). The product was recrystallized from boiling methanol. *Anal.* Calcd for NiC$_{14}$H$_{28}$N$_4$I$_2$: C, 29.77; H, 4.99; N, 9.92; Ni, 10.39; I, 44.93. Found: C, 29.60; H, 5.15; N, 9.49; Ni, 10.35; I, 44.93. (See ref 11 for a similar metathesis.)

Preparation of *cis*-[NiM(16)(NCS)$_2$]. A filtered acetone solution (25 ml) saturated with sodium thiocyanate was added to a filtered acetone solution (30 ml) of *cis*-[NiM(16)](PF$_6$)$_2$ (2.0 g). The solution rapidly changed colors and deposited a mauve precipitate. Recrystallization of the precipitate from dichloroethane–hexane yielded mauve crystals of the anhydrous bis(thiocyanate) salt (yield 0.8 g, 56%). *Anal.* Calcd for NiC$_{16}$H$_{28}$N$_6$S$_2$: C, 44.98; H, 6.60; Ni, 13.74. Found: C, 44.94; H, 6.71; Ni, 13.55. Molecular weight: calcd, 427; found, 412 (in dichloromethane).

Preparation of *cis*-[(NiM(16))$_2$ox](PF$_6$)$_2$. Potassium oxalate (1.0 g) was added to water (30 ml) in which *cis*-[NiM(16)](PF$_6$)$_2$ (2.0 g) was suspended. The solution was stirred approximately 30 min while a mauve solid formed replacing the yellow one. The solution was filtered and the resulting precipitate washed with two 5-ml portions of ethanol–ether (1:1), washed with ether, and finally air-dried. The product was recrystallized by dissolving it in acetonitrile (15 ml) and adding ethanol (20 ml) and then ether, slowly, to incipient cloudiness. The solution was set aside until crystallization was

(11) N. J. Rose, M. S. Elder, and D. H. Busch, *Inorg. Chem.*, 6, 1924 (1967).

complete and the product was collected (yield 1.22 g, 75%). *Anal.* Calcd for $Ni_2C_{30}H_{56}N_8O_4P_2F_{12}$: C, 36.02; H, 5.64; N, 11.21; F, 22.79. Found: C, 36.21; H, 5.79; N, 11.60; F, 23.10.

Preparation of *cis*-[NiM(16)acac]PF$_6$. The same procedure was used here as with the oxalate derivative except sodium acetylacetonate (0.5 g, 4.1 mmol) was used in place of the potassium oxalate. The solution was stirred for 2 hr and filtered. The violet precipitate was recrystallized from acetonitrile and ether (yield 1.60 g, 87%). *Anal.* Calcd for $NiC_{19}H_{35}N_4O_2PF_6$: C, 41.10; H, 6.35; N, 10.09; F, 20.53. Found: C, 41.28; H, 6.47; N, 9.98; F, 20.77.

Preparation of Ethylenediamine Monohydrohexafluorophosphate (en·HPF$_6$). A 65% hexafluorophosphoric acid solution (46 ml, 325 mmol) was added to absolute ethanol (200 ml) and *cooled below room temperature* in an ice bath. Ethylenediamine (20 ml, 325 mmol) was added slowly and great care was taken to *keep the solution below* 10°. The solution was cooled to 5° before the product was collected by filtration. The white solid was washed with absolute ethanol and with ether and then air-dried. (Note: if the solution temperature was allowed to rise above 10°, a very copious white precipitate formed which looked the same as the correct material but was almost totally insoluble in methanol in the proportions used in the following preparations.) *Caution!* Solutions of HPF$_6$ should be used with the same precautions applied to solutions of HF! *Anal.* Calcd for $C_2H_9N_2PF_6$: N, 13.59. Found: N, 13.63.

Preparation of 5,12-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) Hexafluorophosphate (IIB), [NiM(14)](PF$_6$)$_2$. Ethylenediamine (4 ml, 64 mmol) was added to en·HPF$_6$ (19.8 g, 96 mmol) suspended in methanol (200 ml). The mixture was filtered and cooled to 5° under N$_2$. Methyl vinyl ketone (10 ml, 122 mmol) was added rapidly. About 10 min after addition of the methyl vinyl ketone, nickel(II) acetate tetrahydrate (12.0 g, 48 mmol) was added. The solution was stoppered and allowed to return to room temperature while being stirred. The color changed from purple to orange during the warming period. The solution was set aside at room temperature. After 3 days, the solution was filtered. (A small number of orange crystals often appeared on the second day. When present, they were collected in the filtration step and combined with the bulk of the product.) Approximately 50 ml of benzene (enough to cause cloudiness in the solution) was added, and the solution was allowed to stand open to the air several hours. The orange crystals which formed were filtered, washed with absolute ethanol and then with ether, and air-dried (yield 7 g, 26%). The orange crystals were recrystallized by dissolving them in a minimum volume of acetone and adding an equal volume of absolute ethanol and then ether to incipient cloudiness. The resulting microcrystalline product appeared light yellow. *Anal.* Calcd for $NiC_{12}H_{24}N_4P_2F_{12}$: C, 25.15; H, 4.22; N, 9.78; F, 39.79; Ni, 10.25. Found: C, 25.21; H, 4.15; N, 9.85; F, 40.00; Ni, 10.43.

Physical Measurements. Infrared data were obtained on a Beckman IR 10 spectrometer (Nujol mulls). Electronic spectra were recorded using a Cary Model 14 or a Cary Model 14H spectrophotometer. Magnetic measurements were made by the Faraday method using HgCo(NCS)$_4$ as a calibrant. Molecular weights were determined at 37° with a Mechrolab Model 301-A vapor pressure osmometer. Proton magnetic resonance spectra were obtained on either a Varian A-60, T-60, or HR/HA-60 spectrometer, using TMS as an internal standard. Conductivity measurements were obtained using acetone as the solvent on a Beckman RC-18A conductivity bridge at 25.0 ± 0.1°.

Elemental analyses were performed by Chemalytics, Inc., or Alfred Bernhardt Microanalytical Laboratory except for some of the nitrogen analyses which were performed by the authors using a Coleman Model 29 nitrogen analyzer.

High-resolution mass spectra were obtained on an AEI MS-9 double-focusing spectrometer (70 eV at approximately 300°). Peaks were assigned by two methods: (1) perfluorotributylamine was used as the standard and the unknown peaks were "scope matched"; (2) perfluorokerosene was used as the standard and the current signal was collected on a DEC PDP-12 computer. Programs to collect the data and process it were obtained from Professor A. L. Crittenden, University of Washington.

Results and Discussion

Complex IIA was first synthesized from the direct reaction of [Ni(en)$_3$](ClO$_4$)$_2$ with acetone[7] and later *via* other routes as already noted.[3] In contrast to IIA, complex IIB has only been prepared up to this time by first making the macrocyclic ligand in a separate synthesis involving en, methyl vinyl ketone, and hydrogen ions and by then combining this ligand

Table I. Methods Used to Attempt the Synthesis of *cis*-[NiM(16)](PF$_6$)$_2$

Scheme	Mol of Ni(OAc)$_2$·4H$_2$O initially present	Mol of TMD·2HCl	Mol of TMD	Mol of MVK[a]	Yield, %
A[b]	1	1	1	2	13
B	0[c]	1	1	2	0
C	1	0	2	2	0
D	1	0	3	2	0

[a] MVK = methyl vinyl ketone. [b] The yields using scheme A are the same whether the nickel(II) salt is added before or shortly after the addition of methyl vinyl ketone. Scheme A also works if 2 mol of tmd and 1 mol of trifluoroacetic acid are substituted for the tmd·2HCl and tmd. [c] Appropriate amount of Ni(OAc)$_2$·4H$_2$O, 1 mol, added just before work-up procedure at the end of 6 days.

with Ni(II) salts.[4] Synthetic efforts to prepare complexes from 4-hydroxy-2-butanone (the hydrated form of methyl vinyl ketone) and [Ni(en)$_3$]$^{2+}$ have not afforded macrocyclic complexes but have resulted in the isolation of complexes containing a linear tetradentate ligand.[6] Such complexes of linear tetradentate ligands are readily synthesized. Thus, under much the same conditions as those used in the [Ni(en)$_3$]$^{2+}$–4-hydroxy-2-butanone reaction,[6] we combined [Ni(en)$_3$]Cl$_2$ and methyl vinyl ketone and also obtained a complex containing a linear tetradentate species.[12] However, with just [Ni(en)$_3$]$^{2+}$ and methyl vinyl ketone as reactants, we observed no evidence indicating that a macrocyclic complex had formed. But, when nickel acetate was added to a methanolic solution containing ethylenediamine monohydrohexafluorophosphate and methyl vinyl ketone, the macrocyclic complex did form (see Experimental Section). We presume that the macrocyclic ligand forms under the influence of the protons present and then the Ni(II) ions merely sequester the ligand *via* complexation. Such a conjecture is consistent with the work of Kolinski, *et al.*, since our preparation differs from theirs only in two ways: (1) the use of the hydrohexafluorophosphate salt of en instead of the hydroperchlorate salt and (2) the isolation (or lack of it) of the free ligand.[4]

Less work has been done on the synthesis of complexes from 1,3-diaminopropane (than from ethylenediamine) using simple ketones, β-hydroxy ketones, or α,β-unsaturated ketones. Thus, to our knowledge, complex III has been prepared only from [Ni(tmd)$_3$]$^{2+}$ salts and acetone.[7] Reactions between diacetone alcohol (the hydrated form of mesityl oxide) and Ni(II)-tmd complexes have not led to isolatable amounts of III or other macrocyclic species.[6] Similarly, our attempts at the synthesis of IV from methyl vinyl ketone and Ni(II)-tmd complexes have been unsuccessful. However, in the presence of both nickel(II) ions and hydrogen ions, complex IV is formed in a low but reasonable yield. The mechanism for this reaction is undoubtedly rather complex and no attempt is made here to elucidate it. However, the importance of the presence of *both* hydrogen and Ni(II) ions can be deduced from variations of the successful reaction (scheme A in Table I) which were tried. In Table I, scheme A is meant to represent the synthesis reported in the Experimental Section. Schemes B, C, and D are variations involving only reagents shown in the table. Notably, no macrocyclic complex could be isolated from the reaction mixtures when the Ni(II) salt was added after 6 days (scheme B) instead of initially or when hydrogen ions were omitted (schemes C and D).

A single-crystal X-ray diffraction study on one of the

(12) J. F. Myers, Thesis, University of Washington, 1972.

Table II. Characteristic Bands in the Infrared and Electronic Spectra of $[NiM(14)]^{2+}$ and $[NiM(16)]^{2+}$ Derivatives

Complex	N–H str, cm^{-1}	C=N str, cm^{-1}	Anion modes, cm^{-1}	λ_{max}, cm^{-1} (ϵ)	Solvent
$[NiM14](PF_6)_2$	3235	1640	830	22,500 (90)	Acetone
			550		
cis-A$[NiM(16)](PF_6)_2$	3265	1645	830	22,860 (104)[a,b]	Acetone
	3290		550		
				22,250[c]	Nujol
				22,940 (52)[a]	1:1 acetone–water
				22,940 (30)[d]	1:1 acetone–water
				22,860 (75)[a]	Acetonitrile
				22,860 (20)[e]	Acetonitrile
cis-B$[NiM(16)](PF_6)_2$	3278	1645	830	23,070 (101)[b]	Acetone
			550		
				22,470[c]	Nujol
				22,940 (26)[a]	1:1 acetone–water
				22,940 (30)[d]	1:1 acetone–water
				22,860 (18)[a]	Acetonitrile
				22,860 (20)[e]	Acetonitrile
cis-A$[NiM(16)]Cl(PF_6)$	3280[f,g]	1645	840	23,392[c]	Nujol
			555		
				26,140 (59.2)	Acetone
				23,000 sh	Acetone
				16,500 (19.9)	Acetone
				8,000 (5.8)	Acetone
cis-A$[NiM(16)Cl_2]$	3260	1660			
cis-B$[NiM(16)Cl_2]$	3240	1660		23,150 (64)	H$_2$O
	3275			7,700 (3.5)	CH$_2$Cl$_2$
				12,600 sh	CH$_2$Cl$_2$
				16,650 (10.3)	CH$_2$Cl$_2$
				26,200 (21.6)	CH$_2$Cl$_2$
cis-$[NiM(16)]I_2$	3450	1645		23,040 (76)	H$_2$O
				23,202[c]	Nujol
cis-NiM(16)(H$_2$O)$_2$Br$_2$	3400 b	1650		23,000 (76)	H$_2$O
				23,148[c]	Nujol
cis-$[(NiM(16))_2$ox$](PF_6)_2$	3300	1650	830	11,000 (8.5)	Acetone
	3250		550	18,100 (22.5)	Acetone
			1640 (ox)[h]		
cis-$[NiM(16)$acac$]PF_6$	3300	1660	830	10,900 (9.5)	Acetone
			555	18,000 (11.7)	Acetone
			1595 (acac)		
			1510 (acac)		
cis-$[NiM(16)(NCS)_2]$	3290	1665	2080	10,400 (10.9)	CH$_2$Cl$_2$
	3220	1650		17,800 (11.7)	CH$_2$Cl$_2$

[a] Fresh solution. [b] The extinction coefficient is very sensitive to small amounts of water in the acetone. Values up to 112 have been obtained using freshly distilled acetone. The numbers given in the table were taken using freshly opened reagent grade acetone. [c] Spectra taken *via* diffuse transmittance. [d] Sample 4 hr old. [e] Sample 2 days old. [f] Very weak. [g] There is another weak peak adjacent to the 3280-cm^{-1} band and centered at ~3400 cm^{-1}. No assignment is made for this extremely broad band at 3400 cm^{-1}. [h] See text for further mention of oxalate bands.

derivatives of IV has definitively established that the cis imine positional isomer is the one we have isolated.[13] The significance of finding the cis isomer cannot be assessed at this time even though the predominant products of the other macrocyclic species obtained from en or tmd and mesityl oxide or methyl vinyl ketone are known to be or are postulated to be the trans isomers IIA, IIB, and III.[7,8,14,15] In our synthesis, the cis-$[NiM(16)](PF_6)_2$ which is isolated represents only 13% of the nickel(II) present. We know from exploratory experiments using column chromatography that the reaction mixture contains several different nickel(II) complexes and thus the trans complex may also be present.

The relative ease with which dimethylglyoxime (in H$_2$O–EtOH–NH$_3$ solutions) removes the Ni(II) ion from IIB and IV follows that reported by Curtis for IIA and III.[7] Apparently, ring size is the determining factor. Thus, dimethylglyoxime removes the Ni(II) ion from III and IV immediately whereas IIA and IIB are essentially untouched by this reagent.

(13) J. F. Myers and C. H. L. Kennard, *J. Chem. Soc., Chem. Commun.*, 77 (1972).

(14) E. Sledziewska and D. J. Vonderschmitt, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 20, 117 (1972).

(15) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, 10, 108 (1971).

The relative sensitivity of IIB and IV to acid parallels the relative ease with which the Ni(II) ion is removed by dimethylglyoxime. Thus, IIB is not affected by 0.01 *M* acid whereas solutions of IV change from the characteristic yellow color to a very pale green in hours (0.01 *M* acid) or minutes (0.1 *M* acid) as the complex decomposes.

The complexes IIA, IIB, III and IV can be divided up into another set of two classes based on their interactions with simple Lewis bases. In acetone and in the solid state, the PF$_6^-$ salts of IIB and IV exhibit electronic spectra typical of square-planar Ni(II) species (Table II). However, in solvents with a more basic character (in the Lewis sense), there is clear evidence that Ni(II) ions are present in both the singlet (tetracoordinate square planar) and triplet (hexacoordinate) states. We first had an indication of the presence of the triplet species with the observation that the apparent extinction coefficient of the 23,000-cm^{-1} band of IV diminishes markedly as the mole ratio of water to acetone changes from 0 to 1. Subsequent investigations in equimolar acetone-water solutions revealed that (1) the electronic spectrum of IV contained four bands that may be attributed to a tetragonally distorted six-coordinate species (9070, 12,050, 17,300, 27,250 cm^{-1})[16] in addition to the absorption at 23,000 cm^{-1} and (2) the apparent magnetic moment of Ni(II)

Table III. Selected Peaks Mass Matched from [NiM(14)](PF$_6$)$_2$ and cis-[NiM(16)(NCS)$_2$][a]

Major fragment	Mass calcd	Mass found[b]	Mass found[c]
[^{58}NiM(14) − 8H]$^+$	274.073	274.064	
cis-[^{60}NiM(16)(NCS)]$^+$	370.140	370.140	370.136
cis-[^{58}NiM(16)(NCS)]$^+$	368.142	368.150	368.143
cis-[^{60}NiM(16) − H]$^+$	311.157	311.159	311.154
cis-[^{58}NiM(16)]$^+$	310.167	310.153	310.160
cis-[^{58}NiM(16) − H]$^+$	309.159	309.166	309.152
cis-[^{58}NiM(16) − 6H]$^+$	304.120		304.119
cis-[^{58}NiM(16) − 8H]$^+$	302.104		302.103
cis-[^{58}NiM(16) − 9H]$^+$	301.097		301.095
cis-[^{60}NiM(16) − CH$_9$]$^+$	291.094	291.088	291.097
cis-[^{58}NiM(16) − CH$_9$]$^+$	289.096	289.087	289.099
cis-[^{58}NiM(16) − CH$_{11}$]$^+$	287.081	287.073	287.065
[M(16)]$^+$ [d]	252.231	252.225	252.229

[a] Probe temperature ~300°. [b] Matching done with perfluorotributylamine by hand. [c] Matching done with perfluorokerosene using computer. [d] [M(16)] = C$_{14}$N$_4$H$_{28}$.

present in the equimolar acetone–water mixture is 2.4 BM (by the Evans method).[17] An equilibrium involving the coordination of two molecules of a Lewis base (in this case water) accounts for our experimental observations (eq 1).

$$2B + [NiN_4]^{2+} \rightleftarrows [NiN_4B_2]^{2+} \qquad (1)$$
$$\quad\text{singlet} \qquad\quad \text{triplet}$$

In the equation the four N's represent a ligand with four donor atoms which are always bound to Ni(II) whereas the two B's represent the two molecules of a Lewis base which may or may not be bound. The presence of similar equilibria has been proposed and/or observed in other systems where B is H$_2$O or other Lewis bases.[18-20]

A convenient way to detect the presence of the equilibria represented in eq 1 utilizes a pmr spectrometer. Because the two reactions of eq 1 are rapid on the nmr time scale, the observed chemical shifts of protons in the system (those of N$_4$ and of B) will have values determined by the fraction of diamagnetic and paramagnetic species present and by the chemical shift of the protons in the diamagnetic and in the paramagnetic species. For diamagnetic macrocyclic species of the sort considered here, the chemical shifts of all the macrocyclic ligand protons occur in a range of −2 to −5 ppm relative to TMS. For paramagnetic species such as cis-B-[NiM(16)Cl$_2$], the resonances are observed in the range of +40 to −200 ppm (in CDCl$_3$).[21] Thus, it is expected that only a fraction of the Ni(II) ions need to be present in the triplet state for detection by the pmr technique. We confirmed the qualitative use of the technique by observing the spectrum of PF$_6^-$ salts of IV in acetone as a function of the addition of small amounts of water. Upon dropwise addition of water to the acetone samples, the resonances became noticeably broadened and moved dramatically.

By using this pmr technique or by simply observing the range over which the resonances occur, it has been determined that IIB and IV (as PF$_6^-$ salts) exhibit the singlet–triplet equilibria in the following solvents: H$_2$O, CH$_3$CN, acetone–water, acetone–pyridine, CH$_3$CN–H$_2$O.[21] In these same solvents, we have determined that the resonances of all the protons of IIA and III (as PF$_6^-$ salts) are found in the region typical of the singlet species. Further, others have shown that the

(16) G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, 5, 2114 (1966).
(17) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(18) D. H. Busch, *Advan. Chem. Ser.*, No. 62, 616 (1967).
(19) W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, 3, 463 (1964).
(20) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 3, 468 (1964).
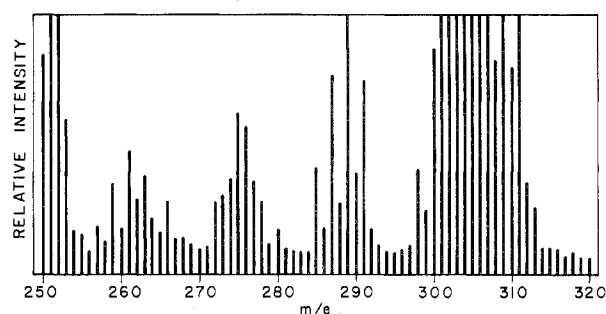(21) J. F. Myers and I. Bertini, unpublished results.

Figure 1. A portion of the mass spectrum obtained from the complex cis-[NiM(16)(NCS)$_2$].
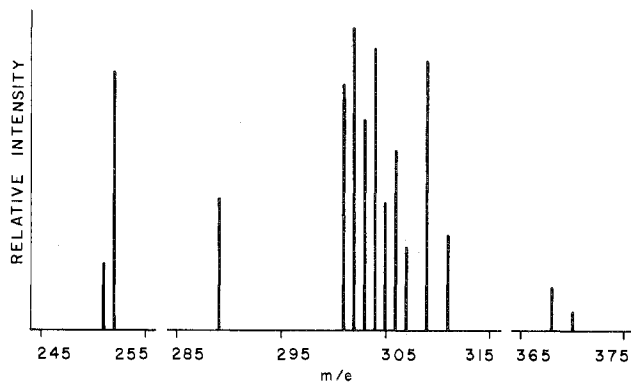

Figure 2. High-intensity peaks of the mass spectrum shown in Figure 1. Two of the less intense peaks of the high-mass region (where peaks are assigned to the fragments [NiM(16)(NCS)]$^+$ at mass 368 and 370 (^{58}Ni and ^{60}Ni)), are also included.

peaks in the pmr spectra of several derivatives of IIA in a variety of solvents, including D$_2$O, show no evidence of shifting from typical diamagnetic positions or of broadening.[8,22] Likewise, it is reported that the spectrum of III "is essentially the same in all solvents tried regardless of their acidity or basicity."[15] Significantly, we conclude that whereas the tendency to remove the Ni(II) ion from the macrocyclic species IIA, IIB, III, and IV is determined by ring size (14 vs. 16), the tendency to accept fifth and sixth ligands is determined by the presence or absence of the geminal methyl groups. When the geminal methyl groups are present, the tendency is markedly reduced, a finding consistent with the known stereochemistry of IIA.[8]

Mass spectra were obtained from [NiM(14)](PF$_6$)$_2$, cis-[NiM(16)](PF$_6$)$_2$, and cis-[NiM(16)(NCS)$_2$] by heating a probe (on which solutions of the compounds had been previously evaporated) in the mass spectrometer. Although the very low volatility of the PF$_6^-$ salts limited their utility for mass spectral work, at least one reasonably intense peak representing a substantial portion of the macrocyclic complex was identified for each sample: the m/e ratios of these peaks correspond to [NiM(14) − 8H]$^+$ and [NiM(16) − 4H]$^+$. The most interesting results from the mass spectral data were obtained on the more volatile species cis-[NiM(16)(NCS)$_2$] (see Table III). The second column of the table shows the calculated mass and the last two columns show the masses obtained experimentally. Figures 1 and 2 are included to illustrate graphically the spectra obtained from cis-[NiM(16)-(NCS)$_2$] in the high mass region.

The peaks with the largest m/e ratio which could be identified, mass 368 and 370, are assigned to the fragments [^{58}NiM(16)(NCS]$^+$ and [^{60}NiM(16)(NCS)]$^+$, respectively. The next series of major peaks occur below mass 312,

(22) W. H. Elfring, Jr., Thesis, University of Washington, 1972.

Table IV. Magnetic Susceptibilities of $[NiM(14)]^{2+}$ and $[NiM(16)]^{2+}$ Derivatives

Complex	T, °K	χ^a	$\chi_m{}^a$	Diamag cor^a	μ_{eff}, BM
$[NiM(14)](PF_6)_2$	298	−0.403	−231	256	
cis-$[NiM(16)](PF_6)_2$	296	−0.472	−283	280	
cis-$[NiM(16)]I_2$	296	−0.601	−339	272	
cis-A$[NiM(16)]Cl(PF_6)$	296	−0.502	−247	248	
cis-$[NiM(16)(NCS)_2]$	296	8.937	3816	232	3.10
cis-B$[NiM(16)Cl_2]$	296	10.164	3883	216	3.11
cis-$[NiM(16)_2ox](PF_6)_2$	298	7.149	3575	238	3.01
cis-$[NiM(16)acac]PF_6$	298	6.925	3797	280	3.12
cis-$NiM(16)(H_2O)_2Br_2$	298	0.307	145	240	0.95

^{a} In cgs units $\times 10^6$.

Table V. Conductivity Data for Acetone Solutions of $[NiM(16)]^{2+}$ Derivatives

Complex	Concn range, equiv $\times 10^{-3}$	Λ_0, cm^2 ohm^{-1} equiv^{-1}	Slope
cis-$NiM(16)](PF_6)_2$	0.033–1.3	214	3180
cis-A$[NiM(16)]Cl(PF_6)$	0.058–0.58	190	1810
cis-$[(NiM(16))_2ox](PF_6)_2$	0.067–0.56	195	2240
cis-$[NiM(16)acac]PF_6$	0.47–1.58	174	689^a

^{a} Calculated slope 646.

suggesting that all the species giving rise to these peaks have lost the last SCN⁻ moiety (SCN⁻ = ~58 mass units). From the appearance of the spectra in this region, (*i.e.*, below 312) it is proposed that a stepwise dissociation of hydrogen atoms from the ligand is occurring. This observation may not be surprising when one considers how easily complex III loses four hydrogen atoms to form the tetraene complex.[15] The peak at mass 252 corresponds to $C_{14}N_4H_{28}$, the empirical formula of the cyclic ligand complete with all 28 protons. However, it is interesting to note that peaks corresponding to the stepwise dissociation of hydrogen atoms are not observed in the region immediately below 252. This observation along with the one made above concerning the region of the spectrum below 312 may illustrate the importance of bound metal ions in oxidative dehydrogenation of ligands.[23,24]

The derivative chemistry of IV in terms of the preparation of square-planar or pseudooctahedral species (with the cyclic ligand in either the planar or folded configuration) is similar to other macrocyclic nickel complexes whereas the derivative chemistry of IV in terms of interconvertible racemic–meso isomers (*vide infra*) is more nearly unique because the ratio of isomers present must depend on relatively small differences in the interaction of each species with the solvent and/or the anion present. In the discussions of derivative chemistry to follow, it is important to know that it was always the PF_6^- salt of IV, cis-$[NiM(16)](PF_6)_2$, that was isolated from the reaction mixture and that the pmr spectra of the cis-$[NiM(16)](PF_6)_2$ samples are essentially identical in CH_3CN whether the initial purification of the species was done *via* crystallization from mixtures of acetone, ethanol, and ether or *via* column chromatography on alumina. Since *all* of the derivatives reported herein were made from the PF_6^- salt, we assume, as previously stated, *all* have a cis arrangement of the imine linkage because the single-crystal X-ray diffraction study showed that one derivative has this arrangement.[13] Below we discuss first the general derivative chemistry and then the more narrow chemistry of the interconvertible isomers.

(23) B. C. Lane, J. E. Lester, and F. Basolo, *Chem. Commun.*, 1618 (1971).

(24) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, 6, 1 (1971).
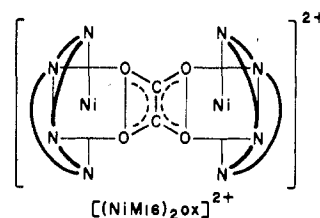
Figure 3. A schematic representation of the proposed structure for $[(NiM(16))_2ox]^{2+}$ showing the macrocyclic ligand in a folded configuration.

General Derivative Chemistry. In water or acetone, a variety of derivatives including square-planar and pseudo-octahedral or tetragonally distorted hexacoordinate ones can be prepared from cis-$[NiM(16)](PF_6)_2$ using the appropriate alkali metal salts. (See Experimental Section.) The derivatives prepared, along with their properties, are collected in Tables II, IV, and V. The $[NiM(16)]^{2+}$ moiety in the iodide salt has the properties of a square-planar species whereas all the other derivatives besides the hydrated bromide salt have characteristics typical of pseudooctahedral or tetragonally distorted hexacoordinate species. The value for the moment of the hydrated bromide salt suggests that it, like Ni(TAAB)·Br_2·H_2O (a macrocyclic complex derived from *o*-amino-benzaldehyde), may contain both singlet and triplet Ni(II) complexes (Table IV).[25]

For the bis(thiocyanato) complex, as well as for the complexes $[NiM(16)acac]^+$ and $[(NiM(16))_2ox]^{2+}$, only two of the three bands in the electronic spectra generally associated with pseudooctahedral Ni(II) species are observed. Presumably the third is "hidden" in the shoulders of the intense bands which are present in the ultraviolet portions of the spectra. For $[NiM(16)(NCS)_2]$, the band in the infrared spectrum (Nujol mull) assigned to the $C{\equiv}N$ stretching vibration of NCS⁻ occurs at 2080 cm⁻¹, the same position found for $\nu_{C{\equiv}N}$ in the spectrum of the high-spin, bis(thiocyanato) complex of IIA.[8] At liquid nitrogen temperatures, the 2080-cm⁻¹ band splits into a doublet, 2081 and 2091 cm⁻¹, a fact which may indicate a cis rather than a trans arrangement of the NCS⁻ ions although other factors could also account for the multiplicity observed.

The pseudooctahedral species containing either the acetylacetonate or the oxalate moiety forms when the relatively insoluble cis-$[NiM(16)](PF_6)_2$ is suspended in an aqueous solution of an alkali metal salt of acetylacetone or oxalic acid. These six-coordinate complexes, like the known oxalate derivatives of other macrocyclic complexes,[9,10] must contain the M(16) ligand in a folded configuration on the coordination sphere (Figure 3). The portion of the infrared spectrum readily assigned to oxalate bands (namely, peaks at 1640 and 1305 cm⁻¹ and a shoulder at 1350 cm⁻¹) is similar to that reported by Karn and Busch[10] for their oxalate derivative.

The complex cis-$[NiM(16)acac]PF_6$ has an infrared spectrum characteristic of the cyclic complexes in that a sharp single band is observed at 3300 cm⁻¹ (assigned to the N–H stretch) as well as a sharp singlet at 1660 cm⁻¹ (assigned to the C=N stretch) (see Table II). Two new bands are found in the infrared spectrum that are not present in the parent complex, cis-$[NiM(16)](PF_6)_2$. These new bands are found at 1595 and 1510 cm⁻¹ and are presumed to arise from the C=O and C=C stretches of the coordinated acetylacetonate. A comparison of the spectrum of Ni(acac)$_2$·2H_2O supports

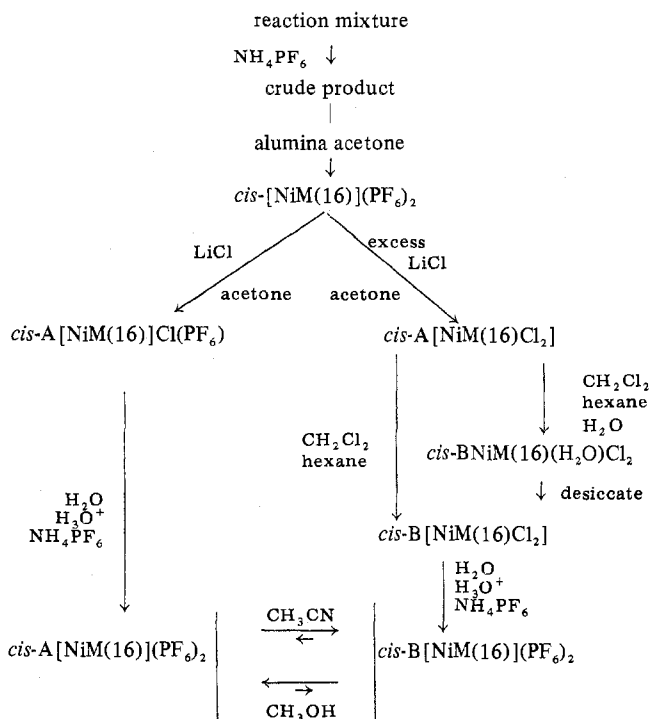(25) G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, 86, 4830 (1964).

reaction mixture

NH_4PF_6 ↓

crude product

|

alumina acetone

↓

cis-[NiM(16)](PF$_6$)$_2$

LiCl ⟋ ⟍ excess LiCl

acetone acetone

cis-A[NiM(16)]Cl(PF$_6$)   *cis*-A[NiM(16)Cl$_2$]

CH$_2$Cl$_2$
hexane
↓ H$_2$O

CH$_2$Cl$_2$
hexane   *cis*-BNiM(16)(H$_2$O)Cl$_2$

↓ desiccate

H$_2$O
H$_3$O$^+$
NH$_4$PF$_6$ *cis*-B[NiM(16)Cl$_2$]

H$_2$O
H$_3$O$^+$
NH$_4$PF$_6$

CH$_3$CN
⇄

cis-A[NiM(16)](PF$_6$)$_2$ *cis*-B[NiM(16)](PF$_6$)$_2$

⟶
CH$_3$OH

Figure 4. Schematic representation of the separation and purification of the interconvertible isomers of *cis*-[NiM(16)]$^{2+}$.

this assignment, since bands are found at 1600 and 1515 cm^{-1} in the complex Ni(acac)$_2 \cdot$2H$_2$O.[26] Support for the proposed formulation is also obtained from conductivity measurements in acetone. A slope of 689 (in a plot of Λ_e *vs.* equivalent concentration) is found (Table V) and is in close agreement with the theoretical slope of 646 calculated for a 1:1 electrolyte with a Λ_0 of 174 cm^2 ohm^{-1} equiv^{-1}.[27]

Interconvertible Isomers. The interconvertible isomers of *cis*-[NiM(16)]$^{2+}$ can be separated and purified by the experimental scheme outlined in Figure 4 and described in detail in the Experimental Section. Table II contains data concerning the electronic and the infrared spectra of these isomers. As noted in the table the infrared spectra of the pairs of isomers, the two PF$_6^-$ salts, and the two dichloro complexes are to be distinguished by multiplicity changes in the N–H stretching bands. An examination of the spectra themselves also reveals that there are intensity differences in the fingerprint regions. Both of the dichloro species are blue and presumably best described as tetragonally distorted hexacoordinate species although definitive electronic spectral data (Table II) and molecular weight data (Experimental Section) are available only on *cis*-B[NiM(16)Cl$_2$] due to the fact that *cis*-A[NiM(16)Cl$_2$] is hygroscopic and therefore more difficult to handle than are the crystals of *cis*-B[NiM(16)Cl$_2$].[28]

The *cis*-A[NiM(16)]Cl(PF$_6$), a greenish yellow species, volunteers from acetone solutions of *cis*-[NiM(16)](PF$_6$)$_2$ containing limited quantities of LiCl. This species is interesting for two reasons. First, it volunteers as isomer A even though the *cis*-[NiM(16)](PF$_6$)$_2$ from which it is derived is known to be about a 4:1 mixture of isomers A and B,

(26) The spectrum of Ni(acac)$_2 \cdot$2H$_2$O was obtained as a Nujol mull. The complex was prepared according to R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

(27) S. Glasstone, "Introduction to Electrochemistry," Van Nostrand, Princeton, N. J., 1942.

(28) *cis*-B[NiM(16)Cl$_2$] can be handled in the atmosphere without change whereas *cis*-A[NiM(16)Cl$_2$] turns yellow upon exposure to air.
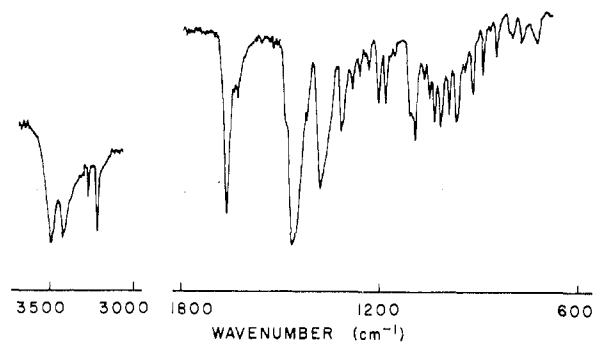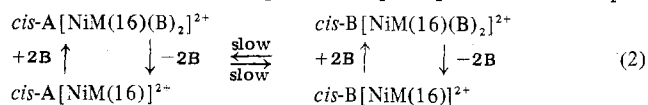

Figure 5. A portion of the infrared spectrum of *cis*-BNiM(16)-(H$_2$O)Cl$_2$ taken as a Nujol mull.

respectively (*vide infra*). Second, in the solid state *cis*-A[NiM(16)] Cl(PF$_6$) contains Ni(II) principally as a singlet species (Table IV) whereas, in acetone solution, there is clear evidence from the electronic spectrum that both singlet and triplet species are present (Table II).

The definitive evidence for the interconvertibility of isomers A and B comes from electronic and pmr spectral studies. In either freshly prepared solutions of acetonitrile or of equimolar acetone-water mixtures, the apparent extinction coefficient of the absorption band at 23,000 cm^{-1} is significantly smaller for B than for A (as the PF$_6^-$ salts) (Table II). Within 4 hr (for the acetone-water solution) and within 2 days (for the acetonitrile solution), the apparent extinction coefficients for the bands are identical, indicating that the equilibrium state between the two isomers has been reached. As was mentioned earlier, solutions containing *cis*-[NiM(16)]$^{2+}$ and Lewis bases such as water or acetonitrile also exhibit an equilibrium between singlet and triplet species. Thus, eq 2

$$\begin{array}{ccc} cis\text{-A}[\text{NiM}(16)(\text{B})_2]^{2+} & & cis\text{-B}[\text{NiM}(16)(\text{B})_2]^{2+} \\ +2\text{B} \uparrow \quad \downarrow -2\text{B} \underset{\text{slow}}{\overset{\text{slow}}{\rightleftarrows}} +2\text{B} \uparrow \quad \downarrow -2\text{B} \\ cis\text{-A}[\text{NiM}(16)]^{2+} & & cis\text{-B}[\text{NiM}(16)]^{2+} \end{array} \quad (2)$$

is proposed as an appropriate representation of the *cis*-[NiM(16)]$^{2+}$ complexes in solution in the presence of the very weakly coordinating anion, PF$_6^-$. In the equation, B represents water, acetonitrile, etc. The validity of eq 2 is strongly substantiated by the pmr spectra of *cis*-A[NiM(16)]-(PF$_6$)$_2$ and *cis*-B[NiM(16)](PF$_6$)$_2$ in acetonitrile. Spectra of fresh solutions of *cis*-A[NiM(16)](PF$_6$)$_2$ in CD$_3$C≡N exhibit nine peaks, all of which are contained in the region of 0 to −40 ppm from internal TMS. Upon standing, eight of these nine peaks diminish greatly in intensity (nearly disappearing) and seven new peaks appear in the region of +30 to −90 ppm. The ninth peak of the original sample increases slightly with time and is thus also associated with the change on standing. Fresh solutions of *cis*-B[NiM(16)](PF$_6$)$_2$ exhibit essentially the same pattern as does the sample of *cis*-A[NiM(16)](PF$_6$)$_2$ upon standing. With time, samples of *cis*-B[NiM(16)](PF$_6$)$_2$ change very little in that only the most intense of the eight peaks definitively characteristic of A become barely detectable. There are two key features of this pmr study which are especially significant to the equilibrium arguments presented herein: (1) samples exhibit resonances which are broad and shifted from positions typical of diamagnetic species; (2) upon standing, the spectra of the two samples become identical. We conclude that the A and B isomers are the racemic and meso isomers of *cis*-[NiM(16)]$^{2+}$. This proposition is consistent with the observed rates of isomerization between racemic and meso forms for similar macrocyclic complexes.[8,22] In the other complexes the rate of isomerization is slow relative to the nmr time scale and thus both

forms, the racemic and meso, should be observed in the pmr spectra of $[NiM(16)]^{2+}$ if they are present.

Before going on to a discussion concerning the racemic-meso isomers, it is appropriate to mention briefly other features of the chemistry related to the isomeric nature of *cis*-$[NiM(16)]^{2+}$. As previously noted the *cis*-$[NiM(16)]$-$(PF_6)_2$ (obtained from the alumina column or from the acetone-ethanol-ether mixture) is approximately a 4:1 mixture of A and B, respectively. So also is the solid obtained from recrystallizing *cis*-B$[NiM(16)](PF_6)_2$ from boiling methanol. The oxalate, acetylacetonate, thiocyanate, bromide, and iodide derivatives were all made from *cis*-$[NiM(16)](PF_6)_2$ but because of the variable solubility properties of the A and B isomers and of the ease with which they may convert it cannot be concluded that the derivatives all exhibit the 4:1 ratio. Of these derivatives, we know only the isomeric makeup for the iodide. A sample of the di-iodide recrystallized from methanol was converted to the $(PF_6^-)_2$ salt in the manner illustrated in Figure 4. The PF_6^- salt resulting from the metathesis does exhibit the same 4:1 isomeric mixture noted above. Unfortunately, the SCN^- derivative as well as the derivatives containing acac and oxalate are essentially insoluble in H_2O so these complexes cannot be treated analogously to the I^- species with a view to determining their isomeric content.

Isomer A: the Racemic or Meso Isomer? The single-crystal X-ray diffraction study by Myers and Kennard[13] was performed on one of two types of crystals that volunteered upon the evaporation of an acetonitrile solution of *cis*-B$[NiM(16)Cl_2]$ exposed to the atmosphere. The single crystal studied contains *cis-meso*-$[NiM(16)(H_2O)Cl]Cl$ and belongs to the space group $P2_1/c$ while the other crystal type observed in the same batch belongs to the group $P2_1$ or $P2_1/m$.[29] We wished to obtain a batch of crystals of the chloroaquo complex containing only the $P2_1/c$ crystals in hopes of definitively associating the meso structure which was found with a specific sample of *cis*-$[NiM(16)]^{2+}$. However, attempts at obtaining crystals from acetonitrile have led either to the anhydrous dichloro species (when *cis*-B$[NiM(16)Cl_2]$-acetonitrile solutions are evaporated in a desiccator over $CaSO_4$) or to yellow solids (when solutions are evaporated in the air). These investigations of the acetonitrile system have led us to the conclusion that the partial pressure of H_2O in the system must be carefully controlled within some as yet unknown region if the species of interest is to be obtained. Extensive efforts have been made to prepare the chloroaquo species from other solvents. Thus, CH_2Cl_2-hexane solutions of *cis*-A$[NiM(16)Cl_2]$ to which very small amounts of water are added deposit blue crystals which we formulate as *cis*-BNiM$(16)(H_2O)Cl_2$. These crystals are very difficult to obtain in a pure state because they are usually contaminated with crystals of *cis*-B$[NiM(16)Cl_2]$. Nevertheless, we are able to formulate the hydrated species as a B iso-

mer with some confidence because, upon desiccation over P_4O_{10}, *cis*-BNiM$(16)(H_2O)Cl_2$ quantitatively converts to *cis*-B$[NiM(16)Cl_2]$. To date, we have succeeded in obtaining only enough pure crystals of *cis*-BNiM$(16)(H_2O)Cl_2$ sufficient for C and H elemental analyses, an infrared spectra (Figure 5), and a preliminary X-ray study. Although the crystals are found to have the same space group as Myers and Kennard's single crystal, $P2_1/c$, they do not have the same unit cell dimensions (*e.g.*, b in one is 7.668 Å and in the other is 10.2 Å).[13] Our efforts have been extended to yet another solvent mixture, $C_2H_4Cl_2$-hexane-H_2O. From this solvent mixture an anhydrous dichloro complex volunteers as crystals belonging to an orthorhombic system. We have terminated our search for a homogeneous batch of crystals of *cis-meso*-$[NiM(16)(H_2O)Cl]Cl$ and, thus, cannot use the available structural data of Myers and Kennard to identify definitively either A or B as the meso species.

Unfortunately, attempts at resolving either A or B *via* column chromatography are also not feasible because the complexes, as noted earlier, are not resistant to the necessary acid which must be present to block inversion of the amine nitrogen atoms.[8] The hours of exposure to the acid in a column experiment make this technique unacceptable. However, for the short periods of time the complexes are exposed to acid in the metatheses illustrated in Figure 4, no appreciable decomposition occurs.

(29) J. F. Myers and C. H. L. Kennard, unpublished results.