does not involve bond breaking, as this would also lead to racemization. It appears that cis ⇌ trans isomerization occurs via a rapid intramolecular twist which does not go through a symmetrical intermediate.

The rapid cis ⇌ trans isomerization of $Ni(IDA)_2{}^{2-}$ without racemization implies that the intermediate is not symmetrical. One possibility is that cis ⇌ trans isomerization occurs by the unsymmetrical twist mechanism shown in Figure 7 in which only one of the coordinated iminodiacetates undergoes a twist. This mechanism does not racemize the complex and can occur as a low-energy process because only one ligand twists. This mechanism is not available to tris-bidentate ligands in which at least two ligands must be involved and, hence, cis ⇌ trans isomerization of bis-tridentate complexes may be more rapid than racemization of tris-bidentate complexes.

Registry No. Ni(EDTA)(H₂O)²⁻, 56348-48-2; Ni(MED3A)-(H₂O)⁻, 56348-49-3; Ni(EDDA)(H₂O)₂, 21491-91-8; Ni(IDA)₂²⁻, 23314-44-5; Ni(1,3-PDTA)(H₂O)²⁻, 56348-50-6.

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Contribution from the Department of Chemistry,
University of Washington, Seattle, Washington 98195

Studies of Three Nickel(II) Complexes Containing Different Macrocyclic Ligands Derived from Acetylacetone and Triethylenetetramine

WILLIAM H. ELFRING, Jr. and NORMAN J. ROSE*

The synthetic pathways showing the relationship of the complex 12-formyl-11,13-dimethyl-1,4,7,10-tetraazacyclo-trideca-10,12-dienatonickel(II), [Ni(CHOAT)]⁺, to the two other macrocyclic complexes 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II), [Ni(AT)]⁺, and 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienenickel(II), [Ni(ATH)]²⁺, are presented. The electrophilic and hydrolytic reactions involved in these pathways are related to the known chemistry of [Ni(AT)]⁺. A comparative study of the three complexes and another complex containing a linear tetradentate ligand derived from acetylacetone was conducted via infrared, electronic, and PMR spectroscopy. Infrared spectra of samples of the complexes which had been selectively deuterated revealed that those species containing the 1,3-diiminate moiety exhibit the same pattern of bands in the 1600-cm⁻¹ region as do selectively deuterated 1,3-diketonates. It is presumed that the same coupling phenomenon is occurring in the diiminates as has been found in the isoelectronic diketonates. Arguments are presented which account for the trends observed in the electronic spectra of the complexes. The PMR spectra reveal that all the macrocyclic complexes are conformationally fixed (relative to the NMR time scale) and that isomers of two of the three complexes are present in solution.

Introduction

Few classes of coordination compounds have served as the focus of such extensive and continuing research effort as have those prepared from the 1,3-diketones or their nitrogen analogs. For the diketones the most common mode of coordination is that where the ligand is an anionic bidentate donor containing a delocalized π system (I).[1] However, the neutral diketone also can serve as a bidentate ligand (II).[2] When the diketone is bound in this latter fashion the local character of each of the carbonyl bonds is retained. In the case of the nitrogen analogs of the 1,3-diketones two distinct classes can be specified. The members of one class, the 1,4-diazepines, have been known for many years and are readily synthesized from 1,2-diamines and 1,3-diketones.[3] The 1,4-diazepines can exhibit the delocalized (III) and localized (IV) forms seen with the diketones but they cannot serve as chelating agents due to their prohibitively unfavorable geometry. However, the other class of nitrogen analogs is eminently suited for chelation (V–VIII). To our knowledge complexes containing this class have been reported only recently and were first prepared by routes which directly involve 1,3-diketones as starting materials. The initial reports feature chelates with (1) bidentate diiminate ligands (V),[4] (2) linear ligands containing one diiminate group (V where R" = CH₂CH₂NH₂, for instance),[5] (3) macrocyclic ligands containing one diiminate group (VI),[6] (4) macrocyclic ligands containing two diiminate groups (VII),[7] and (5) macrocyclic ligands containing one neutral diimine group (VIII).[8] At least three schemes to obtain chelates containing the diiminate moiety (or ligands of the 1,3-diimine class) are known which do not involve 1,3-diketones as starting materials. In one of these a chelated diiminate group is obtained directly by oxidizing a coordinated 1,3-diamine[9] and in another scheme the ligand is made from an acetylenic aldehyde and a diamine.[10] In the third scheme
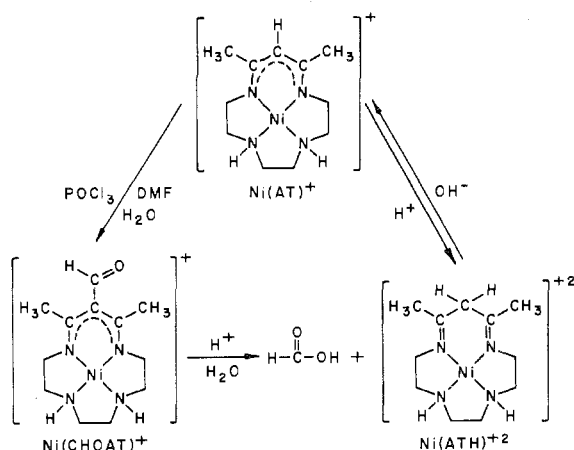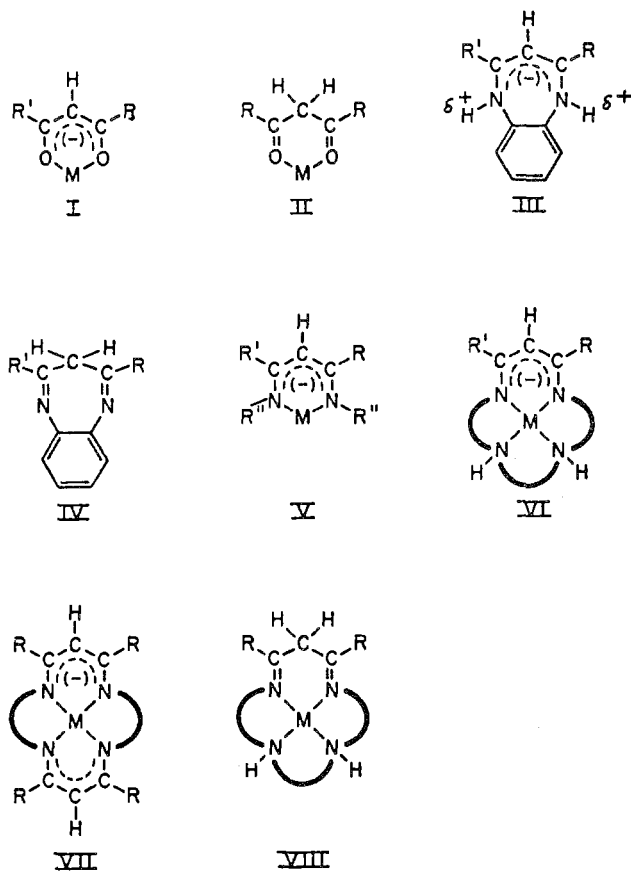
William H. Elfring, Jr., and Norman J. Rose

Figure 1. Chemistry relating [Ni(AT)]+, [Ni(ATH)]2+, and [Ni(CHOAT)]+.

1,2-dithiolium cations serve as starting materials in the syntheses of cyclic diimines.[11]

The initial preparative work on complexes containing either the diiminate (V–VII) or diimine linkages (VIII) has been followed by several synthetic and/or physical studies included among which are (1) the preparation of Ni(II) and Cu(II) complexes containing macrocyclic ligands derived from 1,-3-diketones and various polyamines,[12] (2) synthesis and structure determination of a novel dimer formed by coupling two 1,3-diimine chelates,[13] and (3) investigation of the reaction of Br₂ and other electrophiles with nickel(II) complexes containing ligands of the sort shown in VI.[14]

In this paper we report the details of the syntheses and characterization of [Ni(CHOAT)]+ [8] and [Ni(ATH)]2+ [8] (see Figure 1). The synthetic pathways relating these two complexes to each other and to [Ni(AT)]+ are described (Figure 1). In addition, the infrared, electronic, and proton
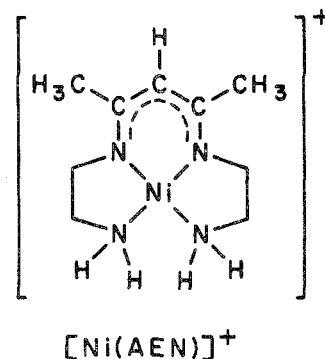
[Ni(AEN)]+

magnetic resonance spectra of these three species as well as those of [Ni(AEN)]+ are compared and discussed.

Results and Discussion

To date there is evidence indicating that one or more complexes containing the 1,3-diiminate moiety show both similarities and striking differences in reactions with common electrophiles compared to the isoelectronic 1,3-diketonates.[15] For example, reactions of [Ni(AT)]+ [8] and [Cu(AT)]+ [12] with the simplest electrophile, the proton, yield [Ni(ATH)]2+ and [Cu(ATH)]2+ (see Figure 1 and Experimental Section). These results are not unexpected given the fact that Ni(II) complexes containing the diketone linkage, II, have been isolated in the solid state[2a,b] and also have been shown to exist in solution.[2c] Further, in methanolic or aqueous solutions it has been postulated that a Cu(II) complex like that shown in II (where R = CH₃) is an intermediate in the formation of the classical 1,3-diketonate chelate.[16] The similarity in the 1,3-diiminate and 1,3-diketonate chelates extends to formylation reactions, at least in the case of [Ni(AT)]+ in that this complex is readily formylated in a manner directly analogous to that employed with the tris(1,3-diketonate) complexes.[15a,c,d] The product [Ni(CHOAT)]+ is unstable in acidic solution and hydrolyzes over a period of minutes to [Ni(ATH)]2+ and formic acid (see Figure 1 and Experimental Section). This hydrolysis reaction probably follows a course similar to that observed for an acetylated 1,3-diiminate chelate[14b] and is most likely initiated by electrophilic attack of a proton at the carbon atom bound to the formyl group.[14c]

The similarities between the reactivity of the coordinated 1,3-diiminate and 1,3-diketonate moieties do not necessarily include bromination reactions. Thus, the tris(1,3-diketonates) readily react with bromine to yield products with the H atom of I substituted by Br.[15a] In the case of species like [Ni(AT)]+, however, the reaction with bromine ultimately leads to products featuring unsaturated linkages not present in the starting materials.[14a] We have observed that [Ni(AT)]+ readily reacts with another common electrophilic reagent, CH₃I, under a variety of mild conditions but have not characterized the product or products. The alkylation of [Ni(AT)]+ may lead to several new species in that there are three atoms on the coordinated AT ligand which are undoubtedly susceptible to electrophilic attack, namely, the methine carbon atom and the two nitrogen atoms of the 1,3-diiminate ring.[14b]

Some inferences concerning the electronic character of the six-membered ring in [Ni(AT)]+ or [Ni(ATH)]2+ can be drawn from the results of proton–deuterium exchange experiments monitored via PMR spectroscopy. The methine proton of the 1,3-diiminate ring in [Ni(AT)]+ or [Ni(ATH)]2+ (depending on pH) readily exchanges with deuterium at room temperature in both acidic and basic D₂O whereas the methyl protons do not exchange at all over a period of hours at a pD of ~13.[17] By way of contrast we cite the exchange reactions observed for [Co(en)₂(acac)]2+ [18] and 1,7-[NiCT]2+,[19] Curtis' macrocyclic complex derived from acetone and ethylenediamine. In both of these latter species the methyl protons

Table I. Solid State Magnetic and Solution Molecularity Data

| Compd | Temp, °K | $10^6 \chi_M$(cor), cgsu | μ_{eff}, BM | Conductivity data[a] | | Apparent mol wt | |
				Λ_0, cm² ohm⁻¹ equiv⁻¹	Slope	Calcd	Found
[Ni(AT)]PF₆	296.5	62.7	0.38	188	900	220	219[a]
[Ni(ATH)](PF₆)₂	296.5	34.1	0.28			559	556[b]
[Ni(CHOAT)]PF₆	296.5	31.9	0.27	182	800	220	223[c]
[Ni(AEN)]PF₆	296.5	26.0	0.25	188	900		

[a] Acetone. [b] Determined in H_2O by titration. A dissociation reaction involving a single proton was assumed (see Figure 1). [c] Acetonitrile.

Table II. Predominant Ir Bands for Selected 1,3-Diiminate and 1,3-Diketonate Complexes (1490–3700 cm⁻¹)[a]

Compd	N–H str	N–H def	N–D str	C⸺O str A₁	C⸺N str A₁	C⸺C str B₂
K[Pt(acac)Cl₂]				1563 s[d]		1538 s[d]
K[Pt(acac)Cl₂-d]				1553 s[d]		1500 s[d]
[Ni(AEN)]PF₆	3343 s, 3280 s	1590 m			1558 m	1532 s
[Ni(AEN)-d₅]PF₆			2490 s, 2420 s		1550 m	1498 s
[Ni(AT)]PF₆	3272 s				1563 m	1528 s
[Ni(AT)-d₃]PF₆			2440 s, 2410 s		1555 m	1496 s
[Ni(ATH)](PF₆)₂,[b]	3252 s[c]				1685 s[c]	
[Ni(ATH)-d₄](PF₆)₂			2435 s, 2405 s		1680 s	

[a] Nujol mulls. [b] Spectra of this salt exhibit bands at 3685, 3620, and 1620 cm⁻¹ the intensities of which vary depending upon the drying procedure. These bands are assigned to the modes of "lattice" water moelcules.[23] [c] Closely spaced doublet. [d] See ref 22.

exchange with deuterium under basic conditions. Clearly the methyl protons of [Ni(AT)]⁺, a *monovalent* cation, are less acidic than the corresponding protons of two *divalent* cations, each of which also features the methyl group of interest on a six-membered chelate ring containing some degree of unsaturation. A further distinction between [Ni(AT)]⁺ and [Co(en)₂(acac)]²⁺ [18] is noted in that the methine proton of the latter exchanges only under acidic conditions. The proton–deuterium exchange at the methine carbon atom of [Ni(AT)]⁺ in basic solution is not readily accounted for simply in terms of the electronic structure shown in VI. A more complicated bonding description, perhaps featuring contributions from various valence-bond structures containing localized double bonds,[14a] may be more desirable. The bonding description ultimately used for AT complexes must account for the metal ion dependency of certain properties as well. Thus, some significant metal ion effect[12] clearly causes the striking difference in the K_a's of [Ni(ATH)]²⁺, 10⁻⁶,[8] and [Cu(ATH)]²⁺, 10⁻⁹.[12]

Primarily the PF₆⁻ salts of [Ni(AT)]⁺, [Ni(ATH)]²⁺, [Ni(AEN)]⁺, and [Ni(CHOAT)]⁺ were employed for the infrared, electronic, and PMR spectral investigations reported below. All of these complexes have diamagnetic ground states. That [Ni(CHOAT)]PF₆ is a 1:1 electrolyte in solution is evident from the conductance and apparent molecular weight data collected in Table I. The Onsager plot for [Ni(CHOAT)]PF₆ (as well as for [Ni(AT)]PF₆ and [Ni(AEN)]PF₆) in acetone is a straight line. Both the slope and intercept, Λ_0, of this line compare favorably with those expected for 1:1 electrolytes (Λ_0 = 157–190 ohm⁻¹ equiv⁻¹ cm² and slope = 800–1000).[20]

Infrared Spectra. Predominant absorptions found in the Nujol mull spectra of [Ni(AEN)]PF₆, [Ni(AT)]PF₆, and [Ni(ATH)](PF₆)₂ and their deuterio analogs appear in Table II. Assignments for the nondeuterated species are in agreement with those reported earlier for AT and/or ATH complexes.[6,12] Further, the ratios of N–H to N–D frequencies are as expected from those found for isotopic replacement studies with coordinated amine groups (i.e., 1.32–1.36).[21] Clearly, the most striking feature of the data is the shift occurring in the C–C stretching frequency upon deuteration of the methine carbon atom in the two 1,3-diiminate complexes. A similar shift has been observed in the C–C stretching frequency of the isoelectronic 1,3-diketonate moiety[22] in K[Pt(acac)Cl₂] upon deuteration of the methine carbon atom. A detailed investigation of the infrared spectrum of [Pt-

Table III. Predominant Ir Bands of [Ni(CHOAT)]PF₆ (1500–3500 cm⁻¹)

Assignment	[Ni(CHOAT)]PF₆[a]	[Ni(CHOAT)-d₂]PF₆[a]	[Ni(CHOAT)]PF₆[b]
N–H str	3250 s, 3140 m, br		3200 m
N–D str		2400 m, 2300 m	
C⸺O str	1606 s	1605 s	1625 s
C⸺N, C⸺C str	1555 s, br	1545 s, br	1550 s

[a] Nujol mull. [b] Acetontrile solution.

(acac)Cl₂]⁻ and three of its deuterio analogs resulted in the assignments which are recorded for that C_{2v} complex in Table II.[22] The lowering of the C–C stretching mode by 38 cm⁻¹ upon deuteration of the methine carbon atom is ascribed to reduction of coupling of that mode with the C–D in-plane bend vis-a-vis the C–H in-plane bend.[22] Despite the lower molecular symmetry, C_2, of [Ni(AEN)]⁺ and [Ni(AT)]⁺ with respect to [Pt(acac)Cl₂]⁻, the 1,3–diiminate chelate ring can be presumed to have "local" C_{2v} symmetry. Given this assumption we treat the 1,3-diiminate spectra in a manner analogous to that of [Pt(acac)Cl₂]⁻. The resulting assignments are recorded in Table II.

The predominant bands in the infrared spectrum of [Ni(CHOAT)]PF₆ along with proposed assignments are listed in Table III. The broad band at 1606 cm⁻¹ (Nujol spectrum) which is assigned to the C=O stretching vibration of the formyl C=O bond occurs at a lower frequency than the analogous bands in the monoformylated [Co(acac)₃] (1670 cm⁻¹)[15c,d] or Jager's acetylated Ni(II) complexes (1645 cm⁻¹).[7a] Both the plain and deuterated complexes of [Ni(CHOAT)]PF₆ show two absorptions confidently assigned to NH (or ND) stretching modes. The broader lower energy bond of the two (3140 cm⁻¹) may indicate that one of the N–H groups is participating in hydrogen bonding,[23,24] presumably with the formyl oxygen atom. Such interaction of the formyl oxygen atom with the secondary amine proton would tend to stabilize charge delocalization from the 1,3-diiminate chelate ring out to the C=O bond and thus account in part for the particularly low value for ν(C=O). Evidence for such hydrogen bonding is found in the solution infrared spectrum of [Ni(CHOAT)]PF₆ which shows an increase in the C=O stretching frequency to 1625 cm⁻¹ (compared to 1606 cm⁻¹ found in the Nujol spectrum) and a single –NH stretching
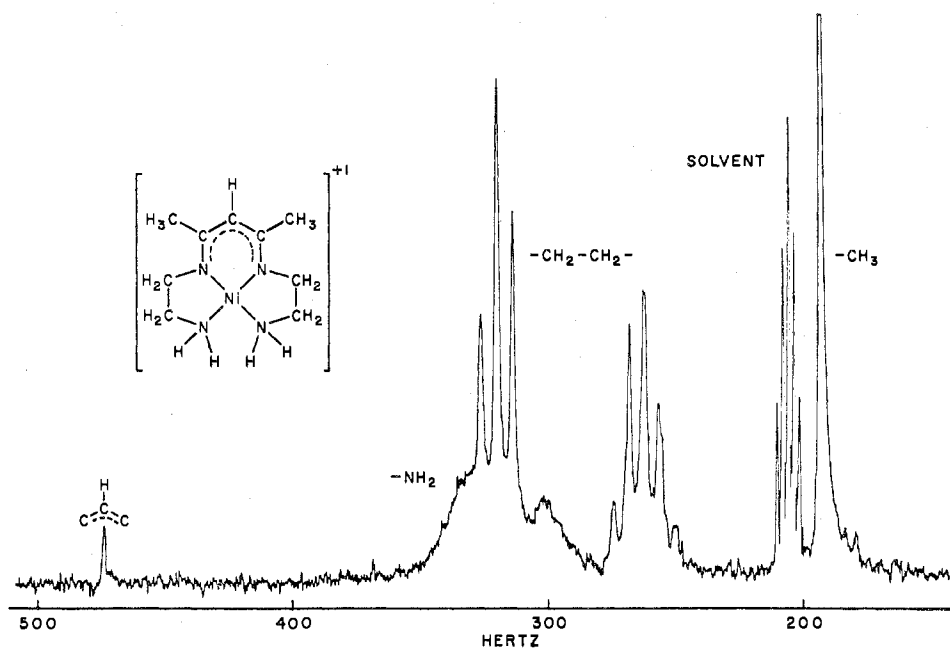
Figure 2. Complete 100-MHz PMR spectrum (at 500-Hz sweep width) of [Ni(AEN)]PF$_6$ in acetone-d_6. Resonance positions are shown in hertz downfield from internal TMS (Table IV). The peak at ~300 Hz is due to water in the sample. The multiplet at 270 Hz is caused by additional coupling with the amine protons. This coupling is reduced on deuteration of the amine groups (see Figure 3).
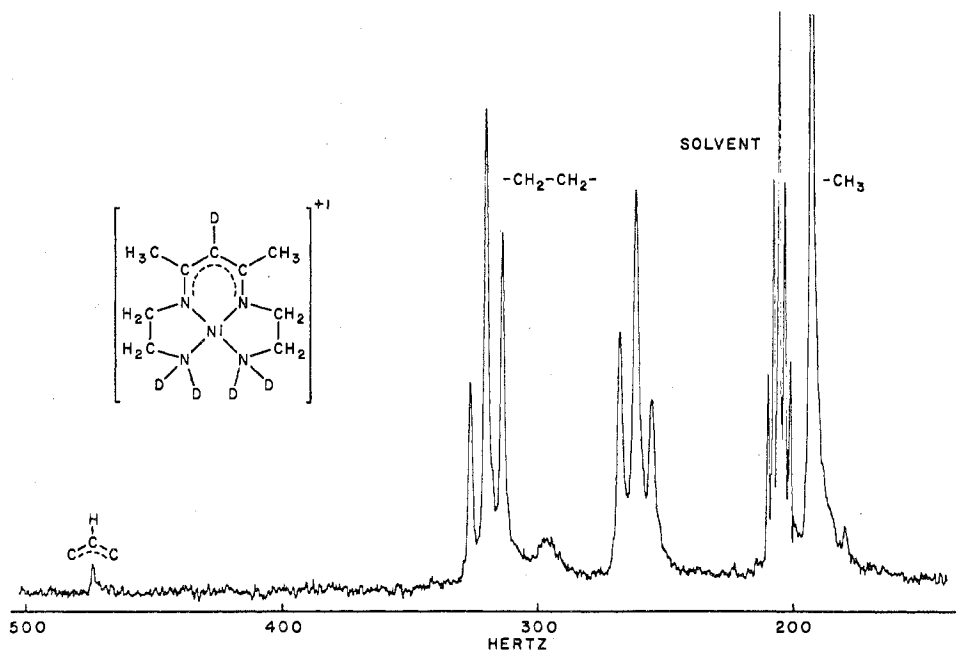

Figure 3. Complete 100-MHz PMR spectrum (at 500-Hz sweep width) of [Ni(AEN)-d_5]PF$_6$ in acetone-d_6. Resonance positions are shown in hertz downfield from internal TMS (Table IV). The peak at ~300 Hz is due to water in the sample.

frequency at 3200 cm^{-1} with no broad lower frequency component. Thus, a diminished intermolecular hydrogen bonding between the amine protons and the formyl oxygen atom upon going from the solid to solution states is consistent with both the observed increase in the C=O stretching frequency and the "simpler, sharper" resonances observed in the N–H stretching region. However, it must be noted that a conformational change could also affect the C=O stretching frequency. If, in solution, the plane described by the three atoms of the formyl group were not as favorably positioned for charge delocalization with the β-diiminate moiety as in the solid state, then an increase in the stretching frequency would also result.

PMR Spectra. The PMR spectra of PF$_6$⁻ salts of [Ni-(AEN)]⁺, [Ni(AT)]⁺, [Ni(ATH)]²⁺, and [Ni(CHOAT)]⁺

in acetone-d_6 provide complementary evidence to that obtained from the infrared spectra for the general characterization of the complexes and, in particular, for the specific sites of isotopic substitution in the deuterated samples (Table IV). From the PMR spectra the strongest line of evidence emerges in support of the presence, in solution, of the possible racemic and meso isomers of the macrocyclic complexes.[19]

The PMR spectra of the complexes are shown in Figures 2–6 and the chemical shift data are gathered in Table IV. The PMR spectrum of [Ni(AEN)]⁺ (Figure 2) shows a single sharp absorption of the methine proton at 475 Hz with a relative peak area of 0.9, a broad absorption of the amine protons at 330 Hz, a complex multiplet of the ethylenic protons centered at 291 Hz, and a single methyl absorption at 193 Hz with a relative peak area of 6.0. These assignments are

Table IV. 100-MHz PMR Spectra of PF$_6^-$ Salts in Acetone-$d_6{}^a$

Compd	–CHO	–NH–^{b}	–CH=	–CH$_2$–	–CH$_2$CH$_2$–	–CH$_3$
[Ni(AEN)]$^+$		330	475		291^c	193
[Ni(AT)]$^{+\,d}$		478	475 (465)^d		370–276^e	189 (187)^d
[Ni(ATH)]$^{2+}$		515		434	414–270^e	216^f
[Ni(CHOAT)]$^{+\,d}$	993 (987)^d	510 (465)^d			397–280^e	240

^{a} Values in Hz downfield from internal TMS. ^{b} Broad signal. ^{c} Approximate center of AA'BB' pattern. ^{d} Parentheses indicate position assigned to peaks of the minor isomer. ^{e} Limits of broad multiplets. ^{f} Multiplet.
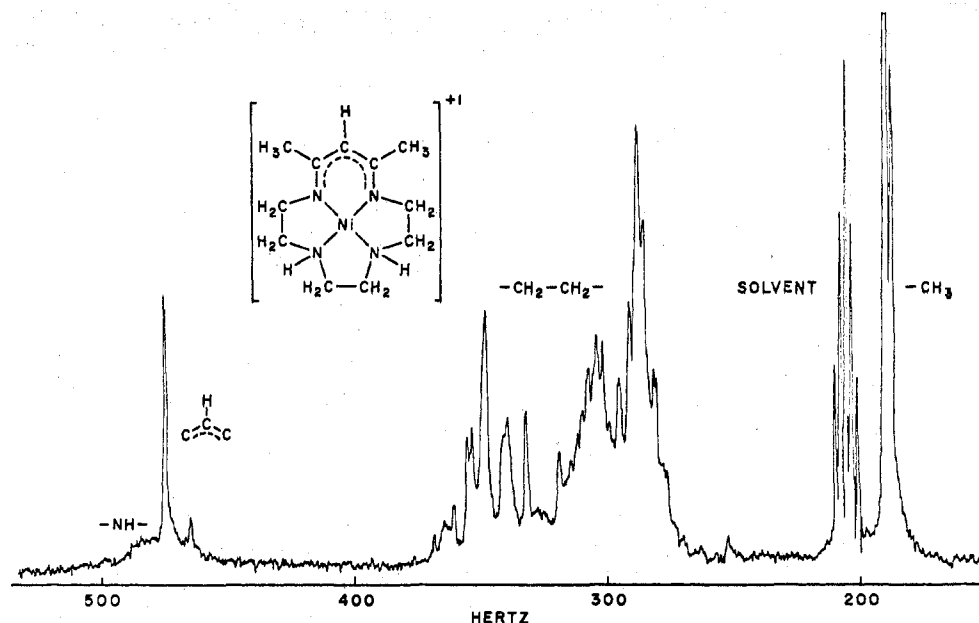

Figure 4. Complete 100-MHz PMR spectrum (at 500-Hz sweep width) of [Ni(AT)]PF$_6$ in acetone-d_6. Resonance positions are shown in hertz downfield from internal TMS (Table IV). Small peaks appearing at 465 and 187 Hz are presumably due to the methine proton and methyl proton resonances of the less stable isomer (see text).
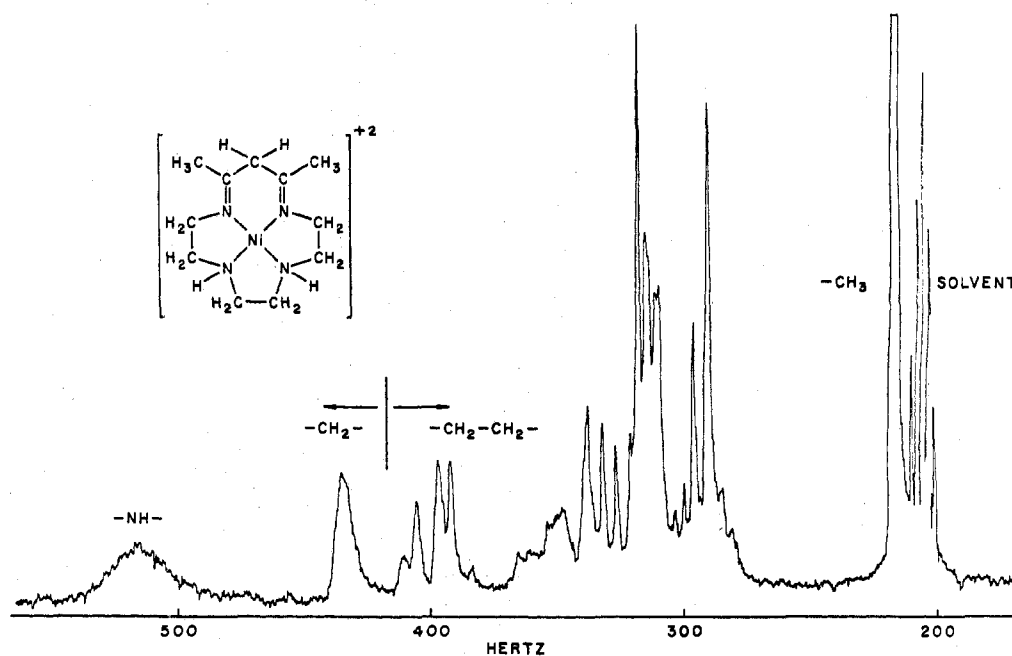

Figure 5. Complete 100-MHz PMR spectrum (at 500-Hz sweep width) of [Ni(ATH)](PF$_6$)$_2$ in acetone-d_6. Resonance positions are shown in hertz downfield from internal TMS (Table IV). The intense peak at ~290 Hz is due to water in the sample.

consistent with the changes seen in the spectrum of the deuterated sample (Figure 3) where there is an absence of the broad absorption at 330 Hz and a diminished intensity in the 475-Hz peak. The ethylenic portion of this spectrum, the two unsymmetrical triplets, has a relative area of 8.2 (calcd 8). The upfield part of the ethylenic resonances "simplifies" upon deuteration due to the loss in coupling of two of the ethylenic

protons with the amine protons.[19] Thus, the upfield triplet (262 Hz) is confidently assigned to the CH$_2$ group adjacent to the amine nitrogen atom and therefore the triplet centered at 321 Hz must be assigned to the other CH$_2$ group. The upfield triplet is somewhat broader than the other one because of H–D coupling.
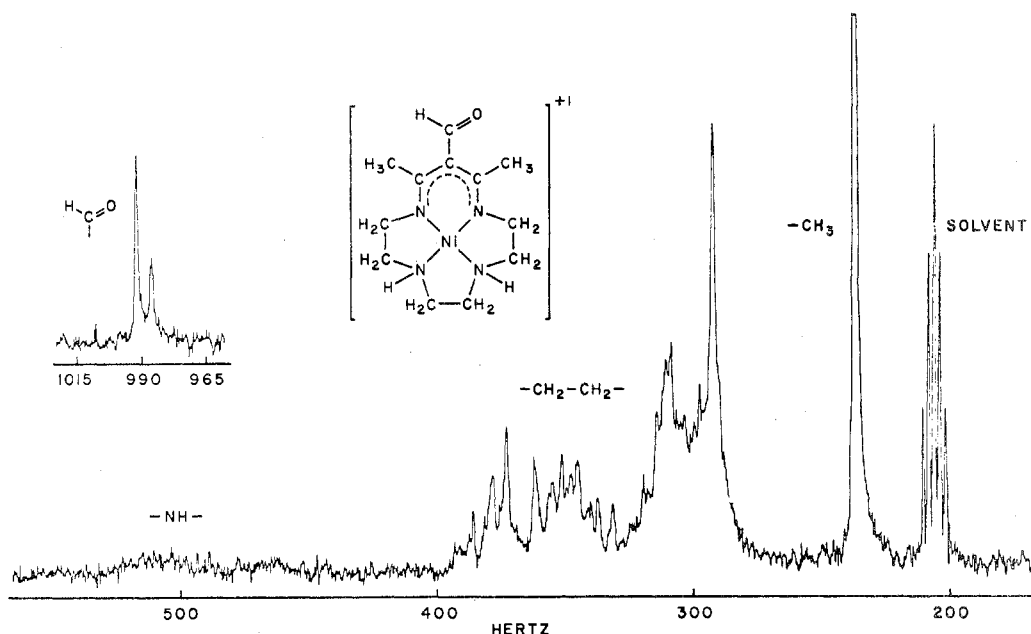
There is support for this notion in that spectra of [Ni-

Figure 6. Complete 100-MHz PMR spectrum (at 500-Hz sweep width) of [Ni(CHOAT)]PF$_6$ in acetone-d_6. Resonance positions are shown in hertz downfield from internal TMS (Table IV).

(AEN)-d_5] taken in D$_2$O at pD ~12 (where deuterium exchange between -ND$_2$ and bulk D$_2$O is expected to be rapid) show the two triplets to be virtual mirror images of each other. This AA'BB' spectrum[25] indicates that the flexing of the ethylenic ring is quite fast on the NMR time scale and that [Ni(AEN)]$^+$ is different from the three other macrocyclic species (Figures 4–6) for which detailed analysis of the PMR spectra[26] shows that the five-membered chelate rings are conformationally fixed as in the Curtis macrocyclic complex.[19] Such differences in conformational lability between five-membered chelate rings within tetradentate linear and macrocyclic ligands is to be expected.

The data collected in Table IV for [Ni(AT)]$^+$ are consistent with the assignments made previously for this species.[6,8] The assignments have been substantiated, where possible, by deuteration studies explicitly similar to those just described for [Ni(AEN)]$^+$.

The PMR spectrum of [Ni(ATH)]$^{2+}$ (Figure 5, in the downfield portion) shows two broad absorption peaks. The one at 515 Hz is assigned to the amine protons and the other at 434 Hz is assigned to the protons of the unique methylene carbon atom. These two assignments are supported by relative intensity data and studies of the deuterated samples as noted below. Relative to the spectrum of [Ni(ATH)]$^{2+}$ the intensity of the peak at 434 Hz is significantly diminished in a spectrum of [Ni(ATH)-d_x]$^{2+}$ prepared by dissolving [Ni(AT)]$^+$ in acidic D$_2$O. Furthermore in the spectrum of [Ni(ATH)-d_4]$^{2+}$ (see Experimental Section) there is an absence of absorptions at 515 Hz and only a slight absorption at 434 Hz. There is little question concerning the assignment of the methyl and ethylene protons. Thus, in D$_2$O (pD ~2) the relative intensity of the proposed ethylenic proton resonances of [Ni(ATH)-d_4]$^{2+}$ to that of the methyl protons is 11.9:6.0 (calcd 12:6). The ethylenic portion of the spectrum consists of a series of overlapping multiplets that extends from 414 to 270 Hz.

The PMR spectrum of [Ni(CHOAT)]$^+$ (Figure 6) consists of a single sharp peak at 993 Hz which is in the region expected for a formyl proton (1000–970 Hz) in organic molecules[27] and for the formyl proton in the monoformylated tris(acetylacetonate)cobalt(III) complex.[15c,d] This peak is accompanied by a minor peak, at 987 Hz, that is presumably caused by the formyl proton associated with the lesser favored of the two possible diastereomers, racemic and meso. Con-

sistent with this assignment, the shift of the minor peak relative to the major peak is proportional to the main magnetic field strength, thus eliminating the possibility that these peaks arise from coupling. The broad peak at 510 Hz has been assigned to the amine protons. There is also a barely detectable resonance at 465 Hz tentatively assigned to the amine protons of the minor isomer. The methyl peak at 240 Hz appears to be a singlet. The shift to lower field of the methyl resonance relative to that of [Ni(AT)]$^+$ is presumably caused by (1) the diamagnetic shielding of the carbonyl group and (2) the deshielding occurring through the σ-bonding network due to the replacement of a hydrogen atom by a more electronegative substituent. This same effect is observed in substituents ortho to carbonyls in aromatic systems.[27] In the PMR spectrum of [Ni(CHOAT)-d_2]$^+$ only the peaks due to the amine protons are absent. The relative peak areas for this spectrum are as follows: formyl proton, 1.1; ethylenic protons, 12.8; methyl protons, 6.0.

Racemic and Meso Isomers of the Macrocyclic Complexes. The major evidence for the presence of isomers of [Ni(AT)]$^+$ is to be found in the PMR spectra in acetone-d_6, in acetonitrile-d_3, and in water. In all these solvents there is a minor peak upfield from the primary methyl peak and in acetone or acetonitrile there is also a minor peak upfield from the primary methine proton resonance (see Figures 4 and 7 and note that a resonance attributed to the methine proton is not observable in water). In acetone and acetonitrile these minor peaks appear in a matter of hours (relative to a freshly prepared sample) and do not change further beyond about 12 hr. These primary and minor peaks are believed to be absorptions due to the methine and methyl protons of the two possible isomers, the racemic and meso ones. Relative intensity data of the methyl resonances of [Ni(AT)]$^+$ in D$_2$O (pD ~12) at 42° indicate an isomer ratio of approximately 4:1. This value is to be compared with 6:1, the racemic to meso isomer ratio of 1,-7-[Ni(CT)]$^{2+}$ in D$_2$O (pD ~7) at 35°.[19] Presumably, in the [Ni(AT)]$^+$ case the minor peak is attributable to the meso isomer. This inference is drawn from the X-ray crystallographic evidence assuming that the isomer found in the solid state for the ClO$_4^-$ salt[28] is also the predominant one in solution.

An examination of the PMR spectra of [Ni(ATH)]$^{2+}$ salts dissolved in various solvents reveals that no simple "doubling"
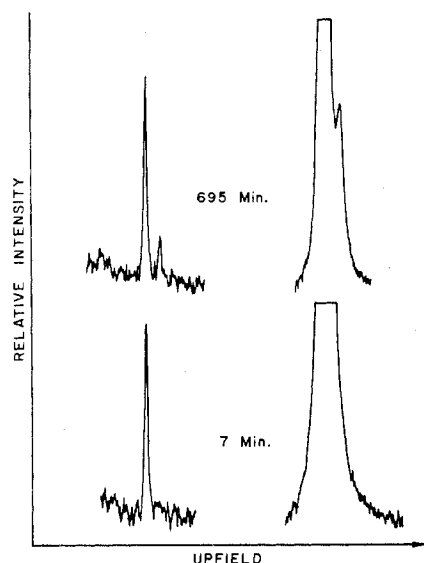
Figure 7. The 60-MHz spectra of [Ni(AT)]PF$_6$ in acetonitrile-d_3 showing the resonances of the methine proton (left, at 500-Hz sweep width) and methyl protons (right, at 100-Hz sweep width). The smaller adjacent peaks that appear with time are assigned to the less stable isomer of [Ni(AT)]PF$_6$ (see text).
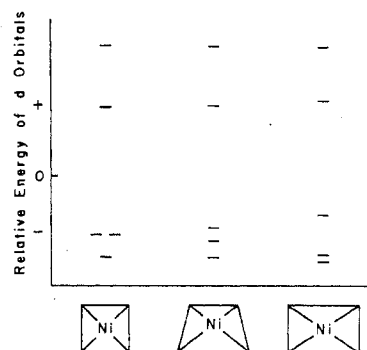

Figure 8. Crystal field diagrams for planar tetracoordinate Ni(II) complexes with square, trapezoidal, and rectangular shapes. A charge of 1− was used to simulate the ligating atoms. See ref 32 and the text for further details.

Table V. Electronic Spectra of PF$_6^-$ Salts in Acetone

Compd	ν_{max}, cm^{-1} (ϵ)	Compd	ν_{max}, cm^{-1} (ϵ)
[Ni(AEN)]$^+$	19,000 (105)	[Ni(CHOAT)]$^+$	21,700 (288)
[Ni(AT)]$^+$	20,200 (136)	[Ni(ATH)]$^{2+}$	24,700 (103)

of peaks is to be found unlike the situation with [Ni(AT)]$^+$ and [Ni(CHOAT)]$^+$ where multiplicity is observed respectively for the methyl and methine proton resonances and for the formyl proton resonance. In fact, with one possible exception the character of the spectra of [Ni(ATH)]$^{2+}$ is dependent only on the solvent and not on the history of the samples (including whether or not they have been recrystallized). That possible exception is the spectrum of [Ni(ATH)]$^{2+}$ prepared in situ by acidifying a D$_2$O solution of [Ni(AT)]$^+$ in which both isomers were known to be present prior to acidification to a pD of about 2. The comparison of this spectrum to that of a sample prepared by dissolving a [Ni(ATH)]$^{2+}$ salt in acidic D$_2$O reveals a partially resolved doublet for one of the peaks in the ethylenic region instead of a singlet and a slight broadening of the methyl proton resonances. Since these differences are quite small and might well be instrumental in source, it is reasonable to conclude that one isomer of [Ni(ATH)]$^{2+}$ is especially favored, a situation much like that found for racemic 1,4-[Ni(CT)]$^{2+}$.[19]

In hopes of definitively establishing the stereochemistry of one of the macrocyclic species in solution, column chromatography was employed.

To inhibit isomerization and racemization of these species during the course of such chromatographic experiments, it is necessary to "block" inversions of the coordinated secondary amine nitrogen atoms. This has been most commonly and effectively done by performing the chromatographic separations in acidic media.[19,29] However, given the chemical characteristics of the species being considered here, the use of acidic solutions essentially limited the study to one complex, namely, [Ni(ATH)]$^{2+}$ (see Figure 1 and recall the synthesis of [Ni(ATH)]$^{2+}$). In two successive experiments fractions of the eluted solution were observed to rotate polarized light with a difference of 0.015° found between the fraction with the largest positive and largest negative rotations. Unfortunately, it cannot be concluded with certainty that the *racemic* form of [Ni(ATH)]$^{2+}$ is present in these solutions. The reason for this relates to a change occurring during the course of the experiment. The entire sample was eluted from the column (in about 6 hr) and each fraction's absorbance was measured at 400 nm. Because the original amount of [Ni(ATH)]$^{2+}$ placed on the column was known, it was discovered that the extinction coefficient of the sample had undergone an apparent

increase of approximately 30%. A similar increase occurs in 6 hr in a solution of the complex in 0.01 M HCl although there is no observable change in the PMR spectrum during this same time period. Clearly, some new species must be forming in the solution. If this new species contains asymmetric sites, such as would be the case if Cunningham and Sievers' dimer formed[13] or if carbinolamines[30] formed from water and the imine atoms of [Ni(ATH)]$^{2+}$, then the observed partial resolution could be attributed to the new species and not to the presence of *racemic* [Ni(ATH)]$^{2+}$. Thus, it seems quite likely that resolution attempts will be fraught with great difficulty and that a single-crystal X-ray determination may be ultimately required to establish the stereochemistry of the predominant isomer of any sample of [Ni(ATH)]$^{2+}$.

Electronic Spectra. Even though all the species discussed above are diamagnetic, some reservation needs to be employed before routinely cataloging them among square-planar Ni(II) complexes. Thus, crystal field calculations performed in the manner of Companion et al.[31] using the trapezoidal shape of the [Ni(AT)]$^+$ coordination polygon[28,32] reveal the following. Within the limitations of the crystal field formalism, it is reasonable to compare the lowest energy d–d transitions of complexes like [Ni(AT)]$^+$ with those of square-planar or rectangularly distorted Ni(II) complexes (Figure 8). Any more extensive comparisons employing this formalism are clearly not warranted in view of the obvious differences in the diagrams. Accordingly, the discussion below is restricted to gross comparison of the lowest energy d–d transition among tetracoordinate diamagnetic Ni(II) species.

In "square-planar" Ni(II) macrocyclic complexes containing both imine and amine nitrogen donor atoms, the energy of the lowest energy d–d transition ranges from approximately 20,000 cm^{-1} to values beyond 24,000 cm^{-1}.[35,36] Significantly, the transition energy for [Ni(ATH)]$^{2+}$ is one of the highest yet found (Table V). Another 13-membered-ring macrocyclic complex, that derived from acetone and trien,[37] also exhibits a transition well up in the range of values (23,800 cm^{-1}). It is tempting to suggest that the energy of the d–d transition should increase for any 13-membered-ring complex compared to the larger ringed species because the Ni(II) ion experiences a stronger field in the smaller ring due to relatively shorter Ni–N bonds. Even though the available single-crystal X-ray data[28] suggest that this relative shortening does occur, there must be several other significant factors to be considered. Thus, [Ni(AT)]$^+$ exhibits values well down in the range whereas [Ni(CHOAT)]$^+$ is intermediate (Table V). The

observed trend in the $[Ni(AT)]^+$–$[Ni(CHOAT)]^+$–$[Ni(ATH)]^{2+}$ spectra may result from the same factors thought to be operating in the case of $[Ni(acac)_3]^-$ and $[Ni(acHac)_3]^{2+}$, the latter of which has chelate rings like that shown in II.[2c] acHac has a Dq of 976 cm^{-1} and that of acac$^-$ is 903 cm^{-1}.[2c] This result is accounted for in part by the fact that the methine carbon atom of acac$^-$ has a much higher negative charge than acHac, thus making the dipole moment of acac$^-$ much less than acHac.[2c] Similar arguments can be directly applied to the complexes considered here. Relative to $(AT)^-$, $(CHOAT)^-$ would be expected to have a less negatively charged methine carbon atom because of the electron-withdrawing effects of the formyl group; and ATH being protonated at the methine carbon atom is expected to have a still smaller negative charge at that atom.

Experimental Section

Physical Measurements. Infrared measurements were made with a Beckman Model IR10 spectrophotometer. Solid samples were prepared as Nujol or Fluorolube mulls suspended between polished KBr plates. The electronic spectra were all obtained in solution with a Cary Model 14 recording spectrophotometer. Molecular weight measurements were made at 37° with a Model 301A vapor pressure osmometer manufactured by Mechrolab, Inc. Benzil was employed as a calibrant and only fresh reagent grade solvents were used in the determinations. The pH measurements were made either with a Model 7 Corning pH meter equipped with standard calomel and hydrogen electrodes or with pHydrion paper. Conductivity measurements were made at 25.00 ± 0.05° with a Model RC-18A Beckman conductivity bridge. The conductivity cell was equipped with platinized platinum electrodes separated by about 1 cm. Fresh reagent grade solvents were used for all conductivity measurements. Magnetic susceptibility measurements were made by the Faraday technique.

Proton magnetic resonance spectra were recorded with Varian Associates HA/HR-60, HA/HR-100, and HA/HR-220 instruments. Either HOD (2–5% of H_2O v/v) or *tert*-butyl alcohol (TBA) was used as an internal lock in D_2O. Chemical shifts in D_2O were measured relative to 3-(trimethylsilyl)propanesulfonic acid sodium salt (DSS). In nonaqueous solvents tetramethylsilane (TMS) was used both as a standard and as an internal lock. All samples were prepared at a concentration of 0.1–0.2 g/ml of solvent. The best method found for obtaining $[Ni(ATH)\text{-}d_4]^{2+}$ in solution for PMR measurements was to prepare it directly from $[Ni(AT)\text{-}d_3]PF_6$. This was accomplished by adding 0.2 g of $[Ni(AT)\text{-}d_3]PF_6$ to approximately 1 ml of D_2O and then by adding 2–4 drops of 12 N DCl (or 12 N HCl) to the mixture. After swirling of the solution for several minutes, it was filtered directly into the NMR tube through a glass wool pad packed inside a disposable pipet. The efficacy of this in situ preparation was demonstrated in that identical spectra were obtained with $[Ni(ATH)\text{-}d_4](PF_6)_2$ in D_2O at pD ∼2. All spectra were obtained with freshly prepared samples.

Preparations. The starting materials were obtained commercially and used without further purification. All solvents were reagent grade. Deuterated solvents were obtained from Stohler Isotope Chemicals. Elemental analyses were performed by the Alfred Bernhardt Microanalytisches Laboratorium, Engelskirchen, West Germany, or by Chemalytics, Inc., Tempe, Ariz. All nitrogen analyses were carried out on a departmental Model 29 Coleman nitrogen analyzer. All reactions were carried out at room temperature unless otherwise indicated. The products were dried at room temperature for 18 hr over P_4O_{10} at ∼1 Torr.

Preparation of 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) Hexafluorophosphate, $[Ni(AT)]PF_6$. The ligand solution was prepared by dissolving triethylenetetramine (29.2 g, 0.2 mol) and 2,4-pentanedione (20.0 g, 0.2 mol) in 800 ml of 20% acetic acid contained in a 2-l. beaker. After 18 hr a solution of $NiCl_2\cdot6H_2O$ (47.6 g, 0.2 mol) in 200 ml of water was added to the resulting straw yellow ligand solution and then, with rigorous stirring, 175 g of sodium hydroxide was steadily added. After 24 hr of stirring the dark red-orange solution was filtered until clear. A filtered solution of $NaPF_6$ (15 g, 100 ml of H_2O, and NaOH (to neutrality)) was slowly added and the resulting orange solid was collected, rinsed well with water, and dried; yield 19.0 g, 23%. Crystallization was effected by dissolving 19.0 g of the crude product in 190 ml of acetone, filtering, adding water until crystals formed, and then cooling to about 5° for

about 18 hr. The small orange needle crystals were collected, rinsed with water, and dried; yield 11.3 g, 14%. Anal. Calcd for $NiC_{11}H_{21}N_4PF_6$: C, 31.99; H, 5.09; N, 13.57; Ni, 14.23; F, 27.63. Found: C, 32.16; H, 5.27; N, 13.64; Ni, 14.38; F, 27.78.

Preparation of 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienenickel(II) Tetrachlorozincate, $[Ni(ATH)]ZnCl_4$. To 75 ml of methanol saturated with HCl(g) was added $[Ni(AT)]PF_6$ (4.73 g, 11.5 mmol). After filtering, 8 ml of methanol saturated with $ZnCl_2$ was added slowly to the stirring solution. The resulting microcrystalline yellow precipitate was collected, rinsed well with acetone, and dried; yield 4.1 g, 75%. The product was recrystallized from boiling methanol. Anal. Calcd for $NiC_{11}H_{22}N_4ZnCl_4$: C, 27.74; H, 4.67; N, 11.76; Ni, 12.33; Cl, 29.78. Found: C, 27.88; H, 4.76; N, 11.43; Ni, 12.50; Cl, 29.64.

Preparation of $[Ni(ATH)](PF_6)_2$.[38] To 20 ml of a filtered solution of $[Ni(ATH)]ZnCl_4$ (5.1 g, 10.7 mmol) was slowly added a filtered solution of $NaPF_6$ (3.6 g, 21.4 mmol) in 25 ml of water. (Note: for best results the pH of the $NaPF_6$ solution must be adjusted to 5.5 with NaOH prior to addition.) After cooling of the mixture for about 6 hr at 5°, the yellow crystals were collected and dried; yield 2.1 g, 35%. The product was recrystallized by dissolving 2.1 g in 40 ml of methanol, adding ether until cloudy, and then cooling at 5° for about 6 hr. The resulting yellow crystals were collected, washed with ether, and dried for 48 hr. Subsequent fractions were collected by adding ether to the filtrate and cooling again. Drying of this salt at room temperature for 48 hr or longer over P_4O_{10} at ∼1 Torr removes most of the lattice water. However, a sample containing no water of crystallization, as evidenced by the infrared and PMR spectra, was never obtained. Anal. Calcd for $NiC_{11}H_{22}N_4P_2F_{12}$: C, 23.63; H, 3.97; N, 10.02; Ni, 10.50; F, 40.79. Found: C, 23.67; H, 4.08; N, 10.10; Ni, 10.90; F, 40.56. ($[Ni(ATH)](PF_6)_2$ may also be prepared directly from $[Ni(AT)]PF_6$ by using the $[Ni(ATH)\text{-}d_4](PF_6)_2$ preparation described below.)

Preparation of $[Ni(AT)]Cl\cdot xH_2O$. To a filtered, stirring solution of $[Ni(AT)]PF_6$ (2.0 g, 4.85 mmol) in 80 ml of acetone was added slowly about 120 ml of acetone saturated with LiCl. Immediately a microcrystalline orange precipitate formed which was collected, rinsed with acetone, and dried; yield 1.6 g, 98%. Since this product visibly decomposes in the presence of moisture and air, it was used immediately to form $[Ni(AT)\text{-}d_3]PF_6$ as described below.

Preparation of $[Ni(AT)\text{-}d_3]PF_6$. A filtered solution of $[Ni(AT)]Cl\cdot xH_2O$ dissolved in 25 ml of D_2O containing a few drops of 40% NaOD was stirred for 10 min. Then a filtered solution of 1.05 g of $NaPF_6$ dissolved in 7 ml of D_2O was slowly added. (Note: pD was adjusted to approximately 11 with 40% NaOD prior to addition.) The resulting microcrystalline orange precipitate was collected with a minimum exposure to moist air and dried; yield 1.1 g, 70%. Deuteration at the methine and secondary amine positions was determined to be almost 100% complete by infrared and pmr measurements.

Preparation of $[Ni(ATH)\text{-}d_4](PF_6)_2$ and $[Ni(ATH)\text{-}d_2](PF_6)_2$. A slurry was formed by adding 3.15 g of $[Ni(AT)\text{-}d_3]PF_6$ to a filtered solution of 1.7 g of $NaPF_6$ in 25 ml of D_2O. Then about 0.25 ml of $POCl_3$ was slowly added to the rapidly stirring slurry until a yellow, slightly cloudy solution formed. The yellow solution was rapidly filtered and then cooled in an ice bath for about 6 hr. The yellow crystals were collected and dried; yield 3.15 g, 74%. The preparation of $[Ni(ATH)\text{-}d_x](PF_6)_2$ where $1 < x < 2$ was identical except for the substitution of $[Ni(AT)]PF_6$ for $[Ni(AT)\text{-}d_3]PF_6$. Deuteration at the methylene position varied from 60 to 80% complete as determined by PMR measurements.

Preparation of 12-Formyl-11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) Hexafluorophosphate, $[Ni(CHOAT)]PF_6$.[39] This procedure was adopted from that of Collman.[15c] $POCl_3$ (2.76 ml, 30 mmol) was slowly added dropwise with stirring to a cooled solution of $[Ni(AT)]PF_6$ (6.2 g, 15 mmol) in 80 ml of DMF. The temperature during addition was maintained at less than 5°. After addition the solution was stirred at 0° for $1/2$ hr and then at room temperature for $1/2$ hr. The resulting red solution was then poured into 750 ml of a stirring 1:1 water–ice mixture containing 7 g of sodium carbonate monohydrate and 3.6 g of sodium hydroxide. After the ice had melted, the resulting yellow solution was maintained at a temperature of 5° overnight. After filtering, the yellow solution was reduced in volume on a rotary evaporator until a white oil began to separate. At this point 500 ml of acetone was slowly added to the stirring mixture with the result that a white solid formed. Stirring

was continued for $^1/_2$ hr and then the solid was removed by filtration. The remaining filtrate was reduced again in volume until white crystals began to form and then was cooled in an ice bath for $^1/_2$ hr. The white crystals were removed by filtration and then acetone was slowly added to the filtrate until it turned cloudy. After cooling of the mixture several hours in an ice bath a crystalline yellow product formed. It was collected and rinsed with acetone. Several fractions were collected after further additions of acetone. The combined yield was 2.2 g. The PF$_6^-$ salt was prepared by dissolving the crude product (2.2 g) in 50 ml of water containing 5 drops of 30% sodium hydroxide and then slowly adding a filtered solution of 1.1 g of NaPF$_6$ in 10 ml of water. (Note: the pH of the NaPF$_6$ solution was adjusted to 10 with 30% sodium hydroxide prior to addition.) The first yellow crystalline fraction was collected immediately and a second fraction was collected after cooling the solution at 5° overnight. The product was dried and recrystallized by dissolving 1.1 g in 30 ml of warm water containing 5 drops of 30% sodium hydroxide, filtering, and then cooling the solution at 5° overnight. [Ni(CHOAT)-d_2]PF$_6$ was prepared by following this same recrystallization only substituting D$_2$O and NaOD. The small yellow needle crystals were collected and dried for 48 hr; yield 0.6 g, 10%. Anal. Calcd for NiC$_{12}$H$_{22}$N$_4$OPF$_6$: C, 32.68; H, 4.81; N, 12.71; F, 25.86. Found: C, 32.74; H, 4.58; N, 12.74; F, 26.09.

Preparation of 2,4-Dimethyl-1-(3-azapropyl)-1,5,8-triazaocta-2,4-dienatonickel(II) Chloride, [Ni(AEN)]Cl. The ligand solution was prepared by dissolving ethylenediamine (24.0 g, 0.4 mol) and 2,-4-pentanedione (20.0 g, 0.2 mol) in 800 ml of 20% acetic acid contained in a 2-l. beaker. After 18 hr a solution of NiCl$_2$·6H$_2$O (47.6 g, 0.2 mol) in 200 ml of water was added to the straw yellow ligand solution and then while stirring vigorously 175 g of sodium hydroxide was steadily added. In approximately 1 hr red crystals began to form. Stirring was continued overnight and then the solution was heated to redissolve the product, filtered hot until clear, and then cooled approximately 8 hr at 5°. The red crystals were collected and dried; yield 14 g, 32%. The product was recrystallized from boiling ethanol. Anal. Calcd for NiC$_9$H$_{19}$N$_4$Cl: C, 38.96; H, 6.92; N, 20.20; Cl, 12.79. Found: C, 39.07; H, 6.74; N, 20.05; Cl, 12.81.

Preparation of [Ni(AEN)]PF$_6$. To a filtered solution of [Ni-(AEN)]Cl (5 g, 18 mmol) in 70 ml of water was added a filtered solution of NH$_4$PF$_6$ (2.9 g, 18 mmol) in 10 ml of water. The resultant precipitate was collected and then rinsed first with water followed by ethanol and then ether; yield 5.4 g, 73%. Recrystallization was accomplished by dissolving 5.4 g of the product in 95 ml of acetone and then slowly adding water until the solution became cloudy. After cooling of the mixture on ice for a few hours the red crystals were collected and rinsed with ethanol and then ether; yield 4.3 g, 62%. Anal. Calcd for NiC$_9$H$_{19}$N$_4$PF$_6$: C, 27.93; H, 4.91; F, 29.46; Ni, 15.18. Found: C, 28.08; H, 5.10; F, 29.64; Ni, 15.35.

Preparation of [Ni(AEN)-d_5]Cl. A saturated solution of [Ni-(AEN)]Cl was prepared in warm D$_2$O where the pD of the solution had been adjusted to 13 with 40% NaOD prior to recrystallization. After about 10 min of stirring the solution was filtered and then cooled in an ice bath. The crystals were collected and dried. Deuteration at the primary amine positions was determined to be better than 90% complete by infrared measurements. The methine position was assumed to be better than 90% deuterated based on PMR measurements in acetone-d_6 of [Ni(AEN)-d_5]PF$_6$ which was essentially prepared by the same manner as [Ni(AEN)-d_5]Cl (see below).

Preparation of [Ni(AEN)-d_5]PF$_6$. [Ni(AEN)]Cl (1.4 g) was dissolved in 25 ml of D$_2$O where the pD of the solution had been adjusted to 13 with 40% NaOD prior to addition. The solution was allowed to stir for approximately 10 min. Then a filtered solution of 1.05 g of NaPF$_6$ dissolved in 7 ml of D$_2$O was slowly added. (Note: pD was adjusted to approximately 11 with 40% NaOD prior to addition.) The microcrystalline red precipitate was collected and dried. Deuteration at the methine and secondary amine positions was determined to be better than 90% complete by infrared and PMR measurements.

Attempted Partial Resolution of [Ni(ATH)](PF$_6$)$_2$. A column (120 × 2.2 cm) of Avicel microcrystalline cellulose was washed for 8 hr with 0.01 M HCl. The eluent flow was about 26 ml/hr. The sample, [Ni(ATH)](PF$_6$)$_2$ (0.35 g), was dissolved in a minimum of 0.01 M HCl and loaded onto the column. Thirteen successive fractions were collected and diluted to 10 ml with the eluent, 0.01 M HCl. The first five fractions all showed positive rotations of 0.005–0.002°. The sixth and seventh fractions showed no rotations and the eighth to the

thirteenth fraction showed negative rotations of 0.002–0.010°. The rotations were measured at 546 nm in 10-dm cells with a Perkin-Elmer 141 polarimeter.

Registry No. 2,4-Pentanedione, 123-54-6; triethylenetetramine, 112-24-3; ethylenediamine, 107-15-3; [Ni(AT)]PF$_6$, 55701-26-3; [Ni(ATH)]ZnCl$_4$, 55701-28-5; [Ni(ATH)](PF$_6$)$_2$, 55701-29-6; [Ni(AT)]Cl, 55701-30-9; [Ni(CHOAT)]PF$_6$, 55701-32-1; [Ni-(AEN)]Cl, 55701-33-2; [Ni(AEN)]PF$_6$, 55701-35-4.

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Conformational Dissymmetry. Axial–Equatorial Isomer Distributions of N-Methyl Substituted Aliphatic Five-Membered Chelate Rings

B. BOSNICH* and E. A. SULLIVAN

A number of (S)-N-methylpropylenediamine complexes of Pt(II) and Pt(IV) have been prepared and the equilibrium constants for the axial–equatorial distributions of the N–CH₃ group have been determined. It was found that, generally, there is very little free energy difference between the two internal diastereomers but that apparently very small changes in the chelate ring and/or the other groups coordinated to the platinum atom can cause sharp changes in the isomer distribution. The d–d circular dichroism spectra of the Pt(II) complexes show that the chelate ring and the asymmetrically coordinated N–CH₃ group contribute additively to the spectra and, consequently, provide a method for determining the diastereomer distribution.

That five-membered chelate rings formed by ethylenediamine exist in stable (chiral) conformations was first suggested by Mathieu[1] and the various nonbonding interactions associated with the ring puckering were subsequently amplified by Corey and Bailar.[2] One of the important conclusions of the quantitative analysis was that an ethylenediamine chelate ring with substituents bonded to the carbon atoms would strongly prefer the substituent groups in equatorial dispositions. A large body of data has essentially sustained[3] this prediction, although in certain systems, notably the C-substituted-ethylenediamine Schiff base complexes, axially oriented substituents are sometimes preferred. This was first suggested by circular dichroism data[4] and subsequently confirmed by single-crystal X-ray structures.[5] Despite these exceptions, where the determining factor appears to be the presence of azomethine linkages,[5] all other investigated systems have consistently confirmed the original predictions.

Were only the data derived from octahedral complexes considered, a similar conclusion might be drawn for the N-substituted ethylenediamine chelate ring, namely, that the substituent prefers an equatorial disposition.[6,7] For square-coplanar complexes, however, the experimental results indicate that a significant proportion of the axial isomer may exist at equilibrium.[8,9] Moreover, a recent conformational analysis suggests that the free energy distinction between the axial and equatorial orientations of N-substituted ethylenediamine chelates may not be large even in octahedral systems.[10]

We became concerned with this problem through an interest in designing ligands suitable for metal-assisted asymmetric synthesis where the orientation of the donor atom substituents can play a major role in the diastereotopic discrimination of the substrate. This paper describes a study of the Me-S-pn (CH₃NHCH₂CH(CH₃)NH₂) ligand coordinated to platinum

in both the stable square-coplanar Pt(II) and octahedral Pt(IV) oxidation states. We will show that in all cases the C-methyl group appears to prefer an equatorial orientation but that, in general, the N-methyl substituent displays an erratic preference for its two possible orientations in both the square coplanar and octahedral complexes.

1. Stereochemistry

Figure 1 shows the probable conformations of Me-S-pn coordinated to a square-coplanar complex. Structure I has both methyl groups equatorial and a δ conformation of the chelate ring; the same applies to structure II except that the N-methyl group is orientated axially. Whether the ring conformations are correct or not, the two are chemically distinct species in that they represent two internal diastereomers, namely, R-[Pt(Me-S-pn)Cl₂] (I) and S-[Pt(Me-S-pn)Cl₂] (II).

When K₂[PtCl₄] is treated with Me-S-pn, the water-insoluble yellow compound [Pt(Me-S-pn)Cl₂] is produced. It exists in two distinct crystalline modifications, blocks and needles, which have similar solubilities in water solution. These two forms are easily separated mechanically and, when pure, have almost enantiomorphic circular dichroism although their linear absorption spectra are nearly identical (vide infra). The two forms are quite stable in acidic media but, in neutral or basic solutions, they interconvert to a roughly equal mixture of each other. An X-ray crystal structure[11] of the blocks shows them to be the isomer S-[Pt(Me-S-pn)Cl₂] having the δ chelate ring conformation and an axial N-methyl group as shown in II (Figure 1). Hence we conclude that the needles are R-[Pt(Me-S-pn)Cl₂] with the structure I (Figure 1).

The two isomers could not be characterized by NMR because of their insolubility, but both were converted, in acid solution, to the very soluble diaquo complexes by the action