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Detection and Identification of Diastereomers of Bis[3-(N-substituted amino)methylenecamphorato]nickel(II) Complexes by Proton Resonance

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Complexes of the bis[3-(N-R-amino)methylenecamphorato]nickel(II) series, where R is (+)- or (−)-α-phenylethyl or 1-adamantyl and the camphor moiety is (+) or (−), have been prepared in order to investigate stereoisomerism by proton nmr. Six diastereomers are detected in the isotropically shifted pmr spectrum of the complex having R = α-phenylethyl when it is prepared from racemic ligand. The resonance signals in this spectrum are assigned to the individual diastereomers by comparison with the spectra of optically pure complexes and the spectra of mixed-ligand complexes prepared by ligand-exchange reactions. The pmr spectrum of the complex having R = 1-adamantyl shows doubling of many of the resonances, and this is attributed to the occurrence of Δ and Λ tetrahedral diastereomers which interconvert at a rate slow on the nmr time scale. An appreciable degree of stereoselectivity is observed which may be explained by consideration of intramolecular steric interactions. A brief discussion of possible mechanisms of Δ ⇄ Λ isomerization is given.

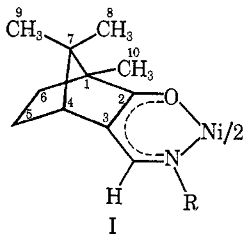
The detection and identification of stereoisomers of paramagnetic transition metal complexes by nuclear magnetic resonance has been a subject of increasing interest in recent years.[2,3] It is now well known that the short electron relaxation times of some paramagnetic metal ions allow well-resolved resonance signals of ligand nuclei. By means of electron–nuclear interactions of either the contact or the dipolar type, chemical shift differences among ligand nuclei are amplified by an order of magnitude or more compared to a diamagnetic complex or the free ligand.[4] This amplification often makes it possible to resolve resonance signals arising from corresponding nuclei on several geometrical and/or optical isomers.

Chemical shift differences among stereoisomers of four-coordinate nickel(II) complexes are largest when the complexes are involved in a rapid planar ⇄ tetrahedral equilibrium. Such systems obey the equation

$$\frac{\Delta f_i}{f} = -a_i \frac{\gamma_e g \beta S(S+1)}{\gamma_H (6SKT)} \left[1 + \exp \frac{\Delta G}{RT} \right]^{-1} \quad (1)$$

where the symbols have their usual meanings.[4,5] It has been shown that slight differences in the free energy, ΔG, of the equilibrium for the various isomers are primarily responsible for the observed pmr signal separations.[2b,d] Inherent differences in the electron–nuclear coupling constants, a_i, at corresponding positions among the isomers could also produce the signal separations, and smaller signal splittings originating from differences in a_i's have been found in complexes not involved in the planar ⇄ tetrahedral equilibrium. Recently, for nickel(II) complexes of certain salicylaldimine ligands having two asymmetric centers per ligand, the six expected diastereomers have been detected by pmr.[2d] These complexes are involved in the planar ⇄ tetrahedral equilibrium. Resonance signals were assigned to specific diastereomers using spectra of optically pure complexes and mixed-ligand species prepared through ligand exchange. Actually, more than six diastereomers are possible as a result of the center of asymmetry at the nickel atom, but in all reported cases the rate of inversion about this center is rapid on the nmr time scale.

We recently described a new series of four-coordinate nickel(II) complexes derived from 3-(N-substituted amino)methylenecamphor, I, where R is H, *n*-alkyl, *sec*-alkyl, or aryl.[2m] Some members of this series are involved in the planar ⇄ tetrahedral equilibrium in solution. The spatial requirements of the bicyclic ring substituents in these complexes suggest that intramolecular nonbonded interactions may be more pronounced in these complexes than in those of the salicylaldimine series which have relatively flat ligands. Such interactions are expected to lead to marked differences in ΔG among isomers involved in the planar ⇄ tetrahedral equilibrium. This would in turn allow ready pmr detection of all diastereomers present in a mixture. The present paper describes the study of complexes I having R = α-phenylethyl and 1-ada-



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[1] NSF Predoctoral Trainee, 1965–1969.

[2] Four-coordinate complexes: (a) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964); (b) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967); (c) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *ibid.*, **90**, 4561 (1968); (d) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **90**, 5735 (1968); (e) J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408 (1968); (f) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 5305 (1968); (g) C. C. McDonald and W. D. Phillips, *ibid.*, **85**, 3736 (1963); (h) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963); (i) S. Y. Shaw and E. P. Dudek, *Inorg. Chem.*, **8**, 1360 (1969); (j) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965); (k) L. H. Pignolet and W. D. Horrocks, Jr., *ibid.*, **91**, 3976 (1969); (l) D. H. Gerlach and R. H. Holm, *ibid.*, **91**, 3457 (1969); (m) C. R. Powers and G. W. Everett, Jr., *ibid.*, **91**, 3468 (1969).

[3] Six-coordinate complexes: (a) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *ibid.*, **89**, 6472 (1967); (b) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315, 1607 (1967); (c) Y. T. Chen and G. W. Everett, Jr., *J. Am. Chem. Soc.*, **90**, 6660 (1968).

[4] D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965).

[5] W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 3779 (1965).

Table I

Characterization of the Complexes

	% C		% H		% N		μ_{eff}, BM	
	Calcd	Found	Calcd	Found	Calcd	Found	Solid	Soln[d]
Ni(AA)[a]	73.20	73.87	7.76	7.90	4.49	4.53	e	e
Ni(BB)[a]		73.65		7.84		4.72	e	e
Ni(CC)[a]		73.43		7.71		4.23	3.31	3.14
Ni(DD)[a]		73.30		7.80		4.23	Diamagnetic	3.01
Racemic mixture[b]		72.84		7.72		4.82		
$\mathrm{Ni(C_{10}H_{15}\text{-}(+)\text{-}amc)_2}$[c]	73.79	73.95	8.85	8.83	4.10	4.10	3.28	3.17
$\mathrm{Ni(C_{10}H_{15}\text{-}(+,-)\text{-}amc)_2}$[c]		74.13		9.07		4.38		

[a] See text for nomenclature. [b] Sample prepared from racemic ligand mixture. [c] Complex having R = 1-adamantyl. [d] Chloroform solution at 25°. [e] Moments not measured since these complexes are enantiomers of Ni(CC) and Ni(DD).

mantyl. Where R is α-phenylethyl, the chirality of R and of the camphor moiety may be varied, leading to all the isomers expected for complexes with four effective asymmetric ligand centers. The complex having R = 1-adamantyl was prepared in an effort to provide a high barrier to $\Delta \rightleftarrows \Lambda$ interconversion in the tetrahedral complex in hopes of allowing nmr detection of diastereomers differing only in the chirality about the Ni atom. Δ and Λ signify right- and left-hand helicity, respectively, about the C_2 axis of the complex.

Experimental Section

Syntheses.—Racemic, (+)-, and (−)-hydroxymethylenecamphor were prepared as described previously.[2m] The 3-(α-phenylethylamino)methylene camphor ligands were synthesized by treating methanol solutions of hydroxymethylenecamphor with racemic α-phenylethylamine in 30% acetic acid solution. Products from this reaction were dissolved in hot methanol. When (+)-hydroxymethylenecamphor was used, cooling the methanol solution resulted in precipitation of 3-{(+) α-phenylethylamino}-methylene-(+)-camphor (mp 145°). The other diastereomer, 3-{(−)-α-phenylethylamino}methylene-(+)-camphor (mp 110–115°), was obtained by adding water to the methanol filtrate.[6] Similarly, using (−)-hydroxymethylenecamphor, 3-{(−)-α-phenylethylamino}methylene-(−)-camphor crystallizes upon cooling the methanol solution; 3-{(+)-α-phenylethylamino}-methylene-(−)-camphor precipitates when water is added to the filtrate. The racemic mixture of ligands is obtained from the reaction of (+,−)-α-phenylethylamine with (+,−)-hydroxymethylenecamphor. Water is added to the warm methanol solution to prevent fractional crystallization of the components. 3-(1-Adamantylamino)methylenecamphor was prepared in a similar fashion using (+)- and (+,−)-hydroxymethylenecamphor. The ligands were characterized by their pmr spectra.

All nickel(II) complexes were prepared by the nonaqueous method previously described.[2m,7] Preparations were carried out *in vacuo* or under an inert atmosphere on account of the sensitivity of these complexes to oxygen.[2m] The mixture of complexes prepared from 3-[(+,−)-α-phenylethylamino]methylene-(+,−)-camphor precipitated as a gummy substance. Better samples were obtained by treating an *n*-heptane solution of the gummy product with pyridine, forming crystalline bis-pyridine adducts.[2d] The pyridine was removed from the crystalline samples at 65° *in vacuo*. The results of elemental analyses are presented in Table I.

Physical Measurements.—Magnetic susceptibility measurements on complexes in solution and solid phases were made by the Gouy and Faraday methods, respectively, using techniques described previously.[2m] Results are given in Table I. Pmr spectra of nickel(II) complexes in chloroform solution were recorded on a Varian Model HA-100 instrument operating in HR mode. All samples were sealed *in vacuo* and contained tetramethylsilane as the reference.

Results and Discussion

Complexes with R = α-Phenylethyl. Detection and Identification of Diastereomers.—When racemic α-phenylethylamine condenses with racemic hydroxymethylenecamphor, four 3-(α-phenylethylamino)-methylenecamphor ligands may be formed, each comprising 25% of the total. These four ligands, designated A, B, C, and D, are defined in terms of the chiralities of the amine and camphor portions: A, (+-camphor, (+)-amine; B, (+)-camphor, (−)-amine; C, (−)-camphor, (+)-amine; D, (−)-camphor, (−)-amine. Ligands A and D are enantiomers as are ligands B and C. Treatment of this ligand mixture with tetraethylammonium tetrabromonickelate(II) according to the nonaqueous procedure previously described[2m,7] leads to nickel(II) complexes containing two of the above ligands in all combinations. Thus Ni(AB) is a complex containing one A ligand and one B ligand. The ten complexes possible and their stereochemical relationships are shown in Table II. It may be seen that there are four enantiomeric pairs and two optically inactive *meso* species, giving a total of six diastereomers. The assumption is made that the rate of inversion about the center of asymmetry located at Ni is rapid on the nmr time scale in these complexes as is found for other tetrahedral bis-chelate Ni(II) complexes.[2] The six diastereomers should, in principle, be distinguishable by nmr. In addition, for two of the diastereomers (2 and 3) the ligands bound to a given nickel atom are diastereomeric, and the resonances of all signals from these species could show addi-

Table II

Diastereomers of Bis[3-(α-phenylethylamino)-methylenecamphorato]nickel(II)

Diastereomer	Complexes[a]	Relationship	Chem shift[b]
1	Ni(AA), Ni(DD)	Enantiomers	+62
2	Ni(AB), Ni(CD)	Enantiomers	+90
3	Ni(AC), Ni(BD)	Enantiomers	+67, +102
4	Ni(BB), Ni(CC)	Enantiomers	+97
5	Ni(AD)	*meso*	+89
6	Ni(BC)	*meso*	+105

[a] See text for nomenclature. [b] Chemical shift of a methyl resonance in hertz at 100 MHz relative to tetramethylsilane. All measurements at 30°.

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(6) W. J. Pope and J. Read, *J. Chem. Soc.*, 171 (1909).

(7) R. H. Holm, F. Röhrscheid, and G. W. Everett, Jr., *Inorg. Syn.*, **11**, 72 (1968).

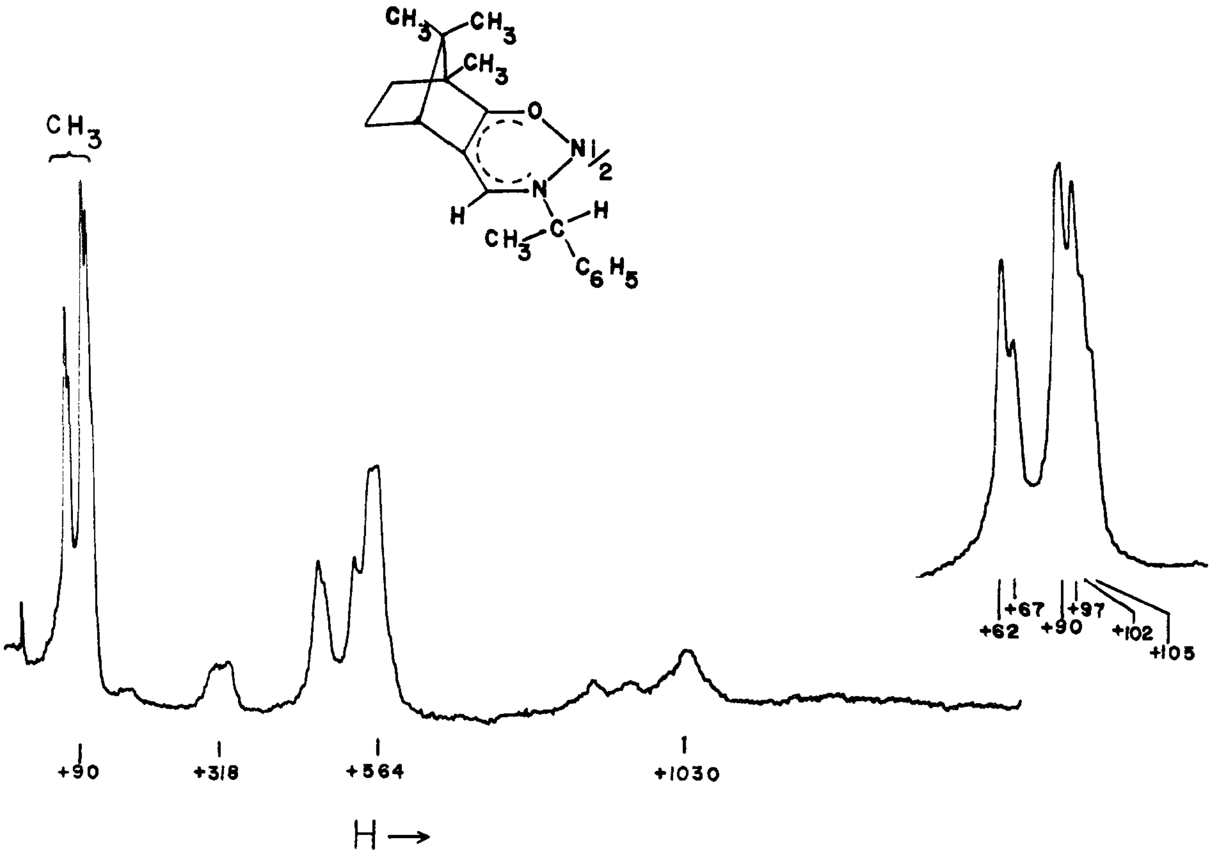

Figure 1.—Upfield region of the proton resonance spectrum of the complex prepared from racemic ligand. The insert is an expansion of the methyl resonances. Frequencies given are chemical shifts at 100 MHz relative to tetramethylsilane.

tional splitting. This has been observed previously.[2d] Thus up to eight nmr signals could be observed for each ligand proton in the fully racemic mixture of complexes.

The upfield portion of the pmr spectrum of the mixture of complexes prepared from the racemic ligand 3-[(+,−)-α-phenylethylamino]methylene-(+,−)-camphor is shown in Figure 1. Assignment of groups of resonances is made using arguments presented previously;[2m] thus signals around +90 and +560 Hz arise from two of the camphor methyls, and those around +320, +475, and +1000 Hz are due to two of the camphor methylenes. The insert is an expansion of the group of methyl resonances centered around +90 Hz. Six methyl resonances are clearly evident from this expansion. Resonance signals from other protons show several components, but the resolution is generally poorer than that of this methyl signal.

Using the ∼90-Hz group of methyl signals, the six diastereomers may be matched with their respective resonances in the following manner. Ni(AA) was prepared; its pmr spectrum (Figure 2) shows a single methyl resonance at +62 Hz in the region of interest. Similarly Ni(BB) shows a single resonance at +97 Hz (Figure 3). A 1:1 mixture of these complexes in chloroform solution shows the resonances at +62 and +97 Hz and in addition a new resonance appears at +90 Hz (Figure 4). The latter signal is assigned to Ni(AB), formed from a ligand-exchange reaction. Ligand exchange appears to be complete in the time required to prepare the sample and record the spectrum (about 30 min). Thus signals arising from diastereomers **1**, **2**, and **4** are assigned. Preparation of Ni(CC) and Ni(DD) was necessary in order that Ni(BC) and Ni(BD) could be obtained through ligand exchange with Ni(BB). The pmr spectrum of a 1:1 mixture of Ni(BB) and Ni(CC) showed a resonance due to the enantiomers Ni(BB) and Ni(CC) at +97 Hz and a new resonance due to Ni(BC) at +105 Hz (diastereomer **6**). Pmr of a mixture of Ni(BB) and Ni(DD) revealed the expected signals at +97 and +62 Hz and *two* new signals attributable to Ni(BD) at +67 and +102 Hz. This doubling of resonances is expected for diastereomer **3**, since ligands B and D are diastereomers. The observed signal separation for Ni(BD) is considerably larger than that reported for nickel(II)-salicylaldimine complexes.[2d] A similar doubling was expected but not observed for diastereomer **2**. The signal arising from the remaining diastereomer, Ni(AD), must lie under the envelope of the other signals. The enantiomers Ni(AA) and Ni(DD) were mixed to form Ni(AD). In addition to the resonance at +62 Hz arising from the enantiomeric pair, a signal at +89 Hz appeared. The latter is close to the +90-Hz resonance assigned to diastereomer **2**, and a slight splitting of this signal may be seen upon close examination of Figure 1. The above assignments are summarized in Table II.

Other pmr signals in Figure 1 are not as well resolved as those of the +90-Hz methyl signal, and

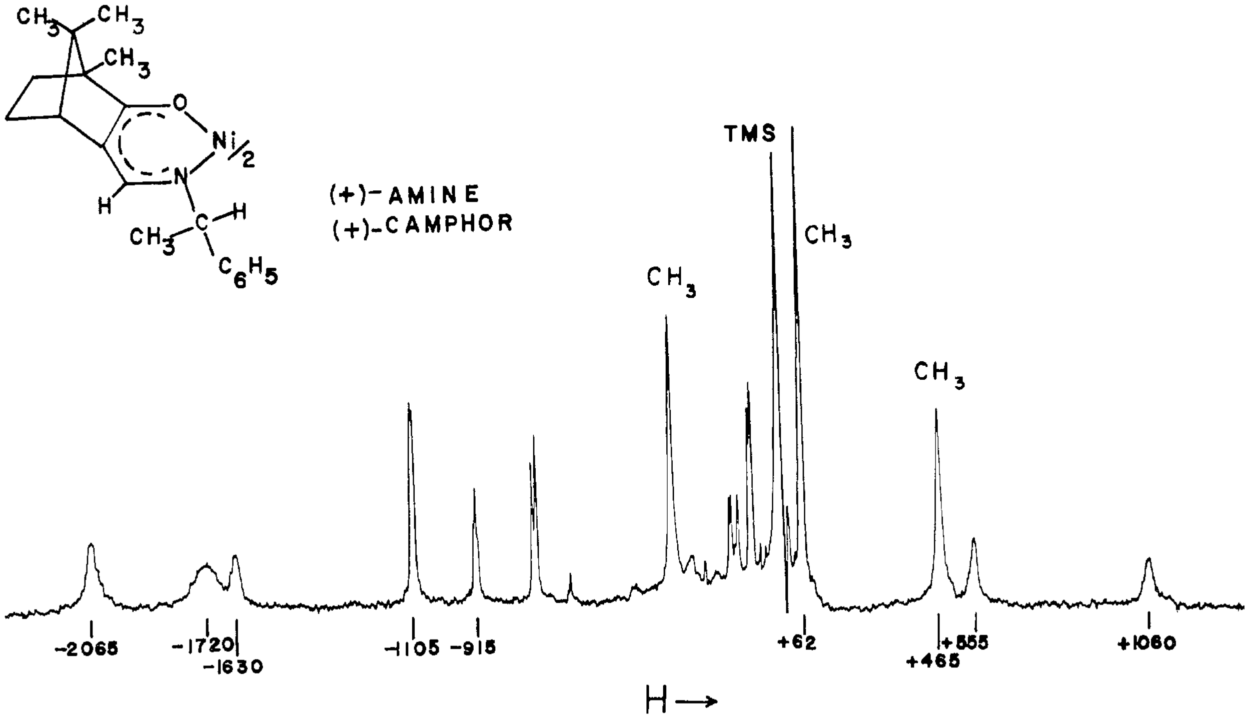

Figure 2.—Proton resonance spectrum at 100 MHz of Ni(AA). Frequencies shown are chemical shifts relative to tetramethylsilane.

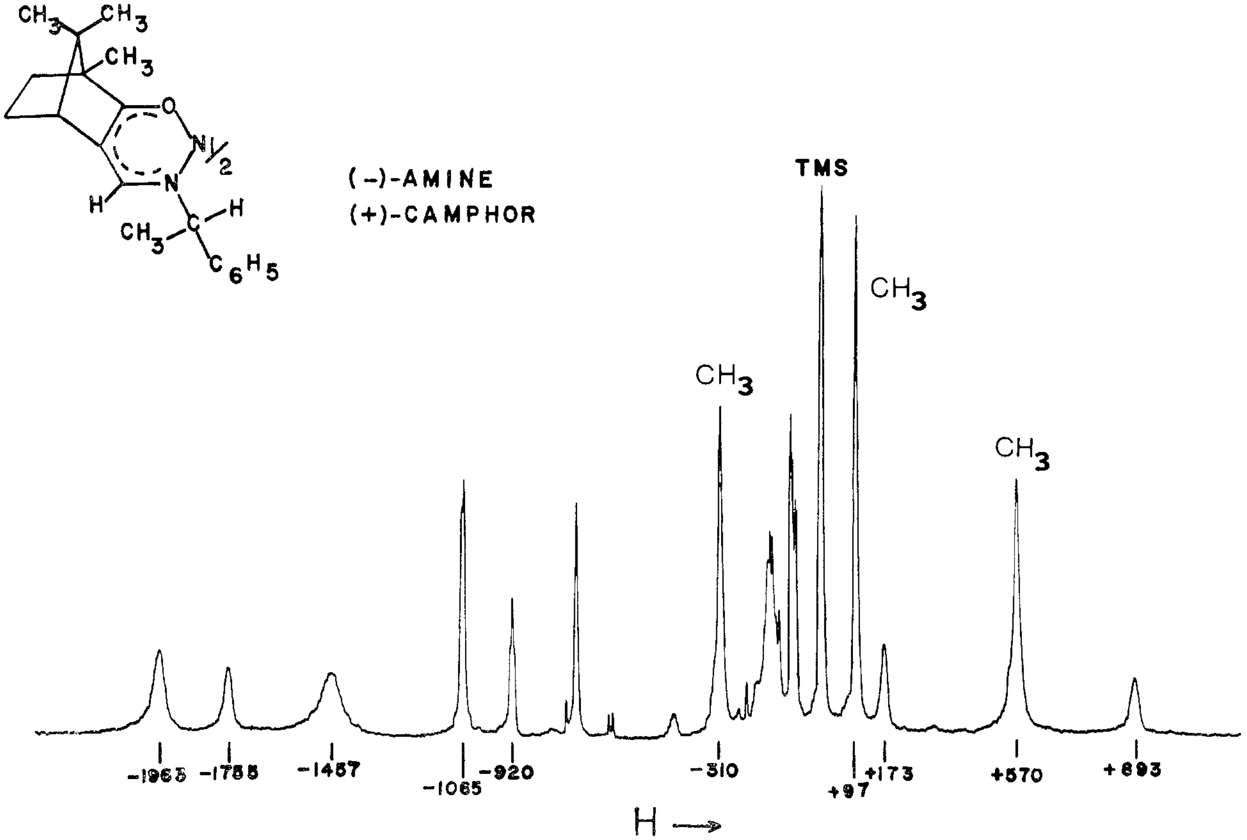

Figure 3.—Proton resonance spectrum of Ni(BB) at 100 MHz. Frequencies shown are chemical shifts relative to tetramethylsilane.

unequivocal assignments could not be made. However the signals in Figure 4 can be assigned by comparison with Figures 2 and 3. Thus the camphor methylene signals at +893, +1030, and +1060 Hz are assigned to Ni(BB), Ni(AB), and Ni(AA), respectively. Resonances of the other upfield camphor methylene signals at +173, +323, and +555 Hz are assigned to Ni (BB), Ni(AB), and Ni(AA), respectively. The other upfield camphor methyl resonances occur at +465 Hz for Ni(AA) and +570 Hz for Ni(BB); the

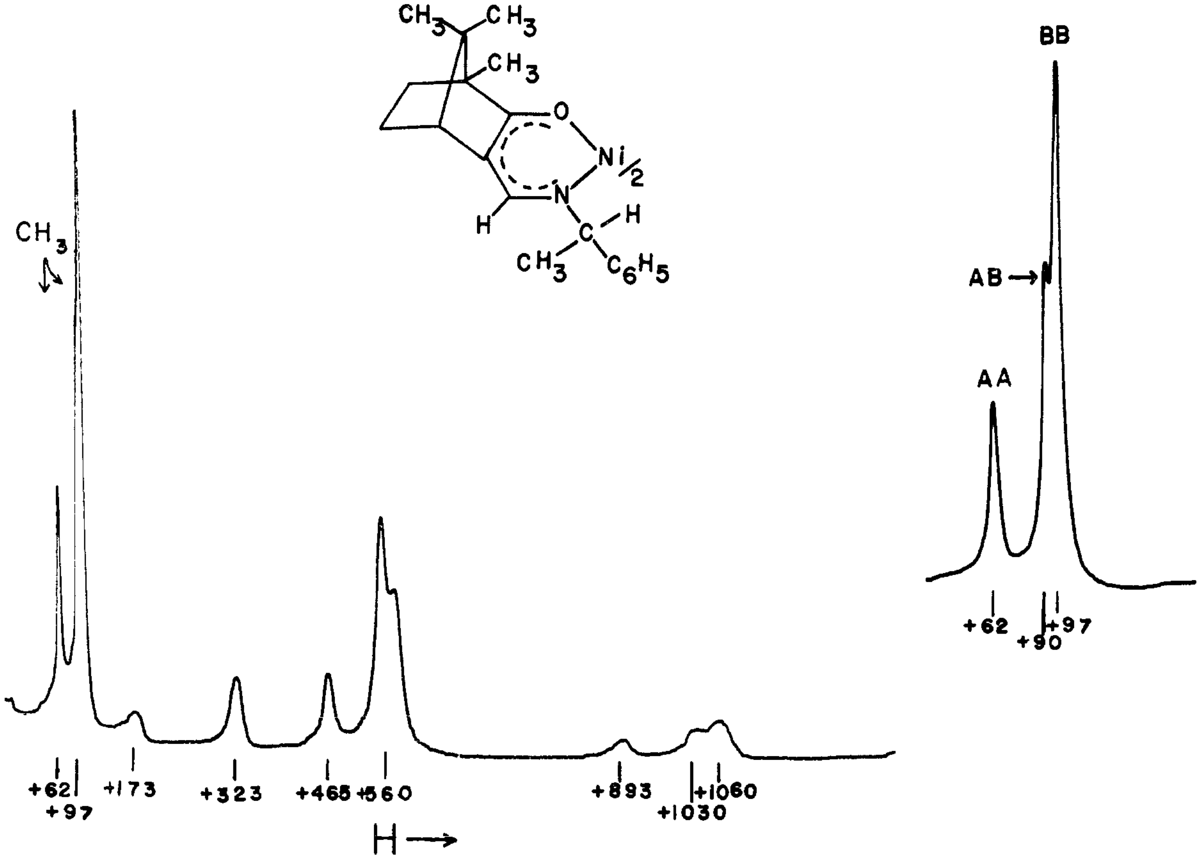

Figure 4.—Proton resonance spectrum of a 1:1 mixture of Ni(AA) and Ni(BB). The insert is an expansion of the methyl resonances Frequencies given are chemical shifts at 100 MHz relative to tetramethylsilane.

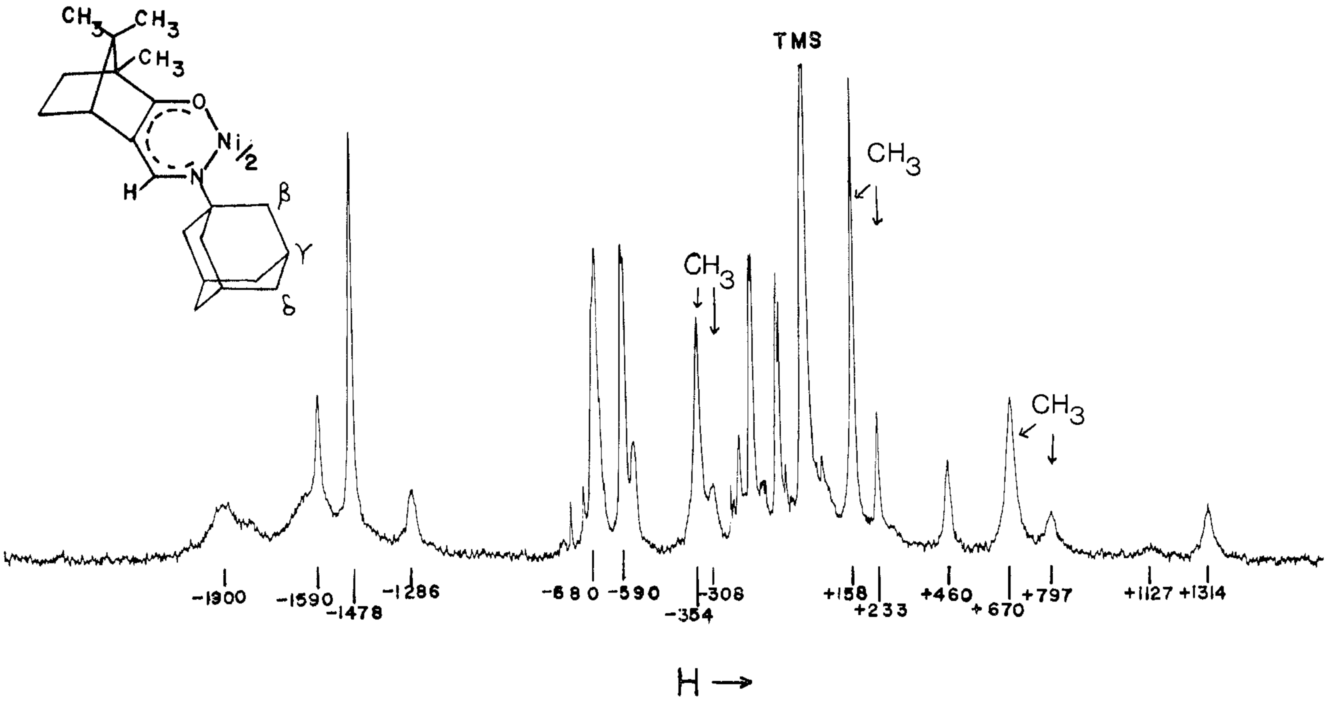

Figure 5.—The 100-MHz proton resonance spectrum of bis[3-(1-adamantylamino)methylene-(+)-camphorato]nickel(II). Frequencies shown are chemical shifts relative to tetramethylsilane.

signal arising from Ni(AB) is under the envelope centered around +560 Hz. The similarity of the amplitudes of the methylene and methyl resonances at +323 and +465 Hz is a result of the 2:1 statistical abundance of Ni(AB) over Ni(AA).

The solution magnetic moments of Ni(CC) and Ni(DD), which are enantiomers of Ni(BB) and Ni(AA), are in the range observed previously for tetrahedral complexes of series I. Isotropic shifts of the ligand protons are comparable to those of other complexes of series I which are known to be fully tetrahedral by their adherence to the Curie law.[2m] Thus it appears that the planar ⇄ tetrahedral equilibrium for the six bis[3-(α-phenylethylamino)methylenecamphorato]-nickel(II) diastereomers is displaced far to the right. Small inequivalences in ΔG among the diastereomers could arise from differences in intramolecular steric interactions, presumably in the tetrahedral configuration.[2b] This would result in slight differences in the mole fractions of tetrahedral molecules, N_t. The ratios of isotropic shifts of corresponding protons among the diastereomers are directly proportional to ratios of N_t according to eq 1 if it is assumed that a_i and g are

$$N_t = \left[1 + \exp\frac{\Delta G}{RT}\right]^{-1} = \frac{\mu_{\text{obsd}}^2}{\mu_{\text{tet}}^2} \qquad (2)$$

constant. The quantities μ_{obsd} and μ_{tet} are magnetic moments of a complex involved in the equilibrium and in the fully tetrahedral form, respectively. The methyl resonances of Ni(DD) and Ni(CC) occur at +62 and +97 Hz, respectively, corresponding to isotropic shifts of 159 and 194 Hz. The ratio of these shifts (0.82) is within experimental error of the ratio (0.92 ± 0.1) of the squares of the solution magnetic moments of these complexes. If it may be assumed that μ_{tet} is essentially the same for the two complexes, the signal separations could result from free energy differences alone. On the other hand, comparison of the spectra of Ni(AA) and Ni(BB) (Figures 2 and 3) reveals distinctly different *patterns* of shifts, especially in the upfield region. These differences must arise from differences in a_i's. It appears that differences in both ΔG and a_i values are responsible for the observed signal separations among diastereomers in these complexes. This is further supported by the apparent lack of any simple correlation of the observed order of pmr shifts with the relative stabilities of diastereomers predicted from consideration of the intramolecular steric interactions. A correlation of this type was found for certain nickel(II)–salicylaldimine complexes for which free energy differences are believed to be primarily responsible for the observed pmr signal separations.[2d]

Slow $\Delta \rightleftarrows \Lambda$ Interconversion. Detection of Tetrahedral Diastereomers.—For all the tetrahedral bis-chelate nickel(II) complexes of optically active ligands studied thus far, the rate of interconversion between Δ and Λ configurations is rapid on the nmr time scale, and distinct resonance signals arising from Δ and Λ tetrahedral diastereomers have not been observed. Recently, it has been shown that the rate of planar ⇄ tetrahedral interconversion of dibromobis(methylphenyl-*p*-anisylphosphine)nickel(II) is sufficiently slow at low temperatures that separate resonance signals of planar and tetrahedral molecules may be observed.[2k] However the nickel atom in the tetrahedral form of this complex is not at a center of dissymmetry, and Δ and Λ diastereomers analogous to those of bis-bidentate complexes of chiral ligands are nonexistent. In bis-chelate complexes the $\Delta \rightleftarrows \Lambda$ interconversion may be accomplished by ligand exchange or by an intramolecular mechanism such as rotation of the chelate ring planes through a square-planar intermediate. This intramolecular mechanism should be affected by a very large R group in complexes of structure I, since the planar intermediate would be sterically difficult to attain. Complex I, R = 1-adamantyl, was prepared in order to investigate the effect of a large, rigid substituent on the stability of Δ and Λ diastereomers.

The solution magnetic moment of bis[3-(1-adamantylamino)methylene-(+)-camphorato]nickel(II) is the highest found for any complex of series I. The complex must be very nearly or completely in the tetrahedral form at ambient temperatures. The pmr spectrum in chloroform solution at 30° is shown in Figure 5. Comparison of this spectrum with those of other complexes of series I reveals a number of signals at low field which must arise from the adamantyl protons. Resonances of aliphatic amine substituents are generally found at low field in complexes of series I and related series. The group of signals centered around −640 Hz has an area of 6 relative to the group farther downfield of area 10. One of the smaller signals in the latter group (either at −1590 or −1286 Hz) arises from the bridgehead proton of the camphor ring.[2m] The very broad signals at −1900 and −1600 Hz have the same general appearance as the isopropyl methyl resonances in the complex having R = isopropyl.[2m] These are assigned to the six β protons of the adamantyl group which are related to the methyl protons of an isopropyl group. The broadening is a result of the proximity of these protons to the nickel atom.[8] Two equally intense β resonances occur since the adamantyl substituent is bound to an asymmetric group (the remainder of the complex). The six protons may be divided into two sets of three equivalent protons, and the two sets are diastereotopic.[9] The other two sharper signals in this region are assigned to the three equivalent γ protons of the adamantyl group. The reason for the occurrence of two signals is discussed below. Resonances centered around −640 Hz are assigned to the six δ adamantyl protons. These are split into two groups of equal area as a result of the inequivalence of axial and equatorial positions. The above assignments are not unequivocal and are based on the experimental observation that isotropic shifts of protons on aliphatic hydrocarbon substituents generally decrease with the number of bonds from the spin-containing π system. It is possible that the mechanism of spin delocalization in the rigid, cagelike adamantyl substituent is different from that occurring in open-chain groups, and some of the assignments should be reversed.[10] For example, one of the reso-

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[8] (a) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961); (b) G. N. La Mar and G. R. Van Hecke, *J. Am. Chem. Soc.*, **91**, 3442 (1969).

[9] K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, New York, N. Y., 1967.

[10] The isotropic shift pattern of adamantyl protons found in a γ-substituted aminotroponeimine complex of nickel(II) is distinctly different from that shown in Figure 5. Only three resonances were found, and both upfield and downfield shifts were observed. The pattern of shifts was interpreted as evidence for spin polarization through the σ bonds: D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Am. Chem. Soc.*, **89**, 4040 (1967).

nances around −640 Hz of area 3 could arise from the γ protons. It is clear, however, that in the present system all the adamantyl resonances are shifted downfield.

The upfield region of the spectrum shown in Figure 5 contains nearly twice the expected number of signals. Generally two camphor methyl and two camphor methylene resonances are found in this region when R is an aliphatic substituent.[2m] Resonances at +158 and +670 and at +460 and +1314 Hz are in the range expected for the methyls and methylenes, respectively, but smaller satellite resonances are found for three of these signals. In addition, the methyl resonance at −354 Hz and the adamantyl resonances at −1478 and −590 Hz also have satellites. Careful integration carried out on an expanded spectrum revealed that in each case the area of the smaller resonance must be added to that of the larger in order to obtain relative areas consistent with signal assignments. For example, the combined areas of resonances at +158 and +233 Hz and also of resonances at +670 and +797 Hz and at −354 and −308 Hz are each equal to 3 relative to the areas of the adamantyl resonances as discussed above. These six signals are assigned to the three camphor methyls. The combined areas of the two most upfield signals (+1127 and +1314 Hz) have a relative area of 1; the resonance at +460 Hz has an area less than 1 but equal to the area of the +1314-Hz resonance. The satellite of the +460-Hz signal is probably the broad shoulder just upfield of the +233-Hz signal. In each case the ratio of areas of small to large signals is the same and equals 0.25.

We attribute the observed signal doubling to the occurrence of Δ and Λ tetrahedral diastereomers having long lifetimes ($>10^{-2}$ sec) on the nmr time scale. This is the first known example of this phenomenon for bis-chelate nickel(II) complexes. In an attempt to increase the rate of $\Delta \rightleftarrows \Lambda$ interconversion and possibly effect coalescence of the split resonances, an nmr spectrum was recorded at 80°. Isotropic shifts were smaller, as required from eq 1 and 2 where $N_t \cong 1$, but no significant change in the overall pattern of signals was observed. The apparent stereoselectivity may be explained by intramolecular steric interactions which are more severe in the Λ diastereomer when (+)-camphor is used as starting material. Models show that in the Λ configuration the adamantyl group on each ligand is very close to the 8-CH_3 of the other ligand, whereas in the Δ configuration both adamantyl groups face the *endo* sides of the adjacent ligands and experience little steric interaction. Thus the larger pmr signals are believed to arise from the Δ isomers. Evidence for a stereoselective effect of this sort has been presented previously.[2m]

If racemic ligand is used to prepare the complex, three resonances are expected for each proton. These arise from the three *dl* pairs: $\Delta(++)$, $\Lambda(--)$; $\Delta(--)$, $\Lambda(++)$; $\Delta(+-)$, $\Lambda(+-)$. Consistent with this is the observed splitting of signals at −1478, −1286, −590, −354, and +158 Hz in the spectrum of the complex prepared from racemic ligand.

The above results imply that an *intra*molecular mechanism for the $\Delta \rightleftarrows \Lambda$ isomerization is more important than ligand exchange for bis-chelate nickel(II) complexes. The fact that ligand exchange does occur in complexes I is evident from the pmr investigation of complexes having R = α-phenylethyl. However, the rate of ligand exchange must be slow on the nmr time scale, since separate resonances are observed for species such as $\Delta(++)$ and $\Delta(+-)$. Possible intramolecular mechanisms include those where metal–ligand bonds are broken, forming two- or three-coordinate intermediates, and the one in which the chelate rings rotate relative to one another through a planar intermediate. The latter is deemed most likely in view of the fact that in several complexes of series I and other series the planar and tetrahedral configurations are involved in the rapid equilibrium: Δ-tetrahedral $\rightleftarrows$ planar $\rightleftarrows$ Λ-tetrahedral. The rate of isomerization by this mechanism is expected to be altered significantly by introduction of a very large, rigid N substituent. This is precisely what is found for the complex having R = 1-adamantyl.

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