The Stereochemistry and Proton Resonance Study of Bis[3-(N-substituted amino)methylenecamphorato]nickel(II) Complexes

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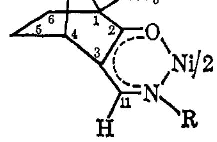
Abstract: A series of bis[3-(N-substituted amino)methylenecamphorato]nickel(II) complexes has been prepared by a nonaqueous method. The stereochemistry of the complexes in solid and solution phases has been investigated in order to evaluate the influence of intramolecular steric interactions on the relative stabilities of the planar and tetrahedral configurations. In the solid phase, depending upon the nature of the amine substituent R, the complexes are either diamagnetic and planar or tetrahedral with magnetic moments >3 BM. In chloroform solution the complex with R = H is planar; complexes having R = aryl or isopropyl are tetrahedral; and those with R = methyl, ethyl, or benzyl are involved in a planar $\rightleftarrows$ tetrahedral equilibrium. The paramagnetic complexes exhibit well-resolved isotropic pmr shifts, and some of the resonance signals may be assigned with certainty. The temperature dependence of pmr shifts of several complexes was measured. *meso* and active diastereomers were detected by pmr for a complex prepared from racemic ligand. Split resonance signals observed for several other complexes are believed to result from restricted rotation of the R group. A brief comparison of these complexes with several other series of complexes involved in the planar $\rightleftarrows$ tetrahedral equilibrium is given.

The stereochemistry of bis-chelate complexes of nickel(II) has been the subject of intensive investigation in recent years, and efforts have been made to determine the factors responsible for stabilizing the planar or the tetrahedral coordination geometry. Often minor variations in the structure of the ligands produce marked changes in stereochemistry, and in a number of instances the configuration of a complex in the crystalline phase differs from that in solutions of a noncoordinating solvents.

The existence of a dynamic equilibrium in solution between the planar and tetrahedral (or pseudotetrahedral) configurations for several series of bisbidentate nickel(II) complexes[2-6] has permitted quantitative measurements of the relative stabilities of the two stereoisomers. The isotropic pmr shifts observed in these complexes provide a convenient and sensitive means of monitoring the planar $\rightleftarrows$ tetrahedral equilibrium over a range of temperatures, and the thermodynamic parameters ΔG, ΔH, and ΔS of the configurational change can be obtained. The over-all conclusion arising from these studies is that nickel(II) prefers the planar stereochemistry, but bulky ligand substituents may introduce large intramolecular nonbonded interactions which are somewhat relieved if the complex assumes a pseudotetrahedral configuration.

Some of the more interesting aspects of these investigations have been proton resonance studies of complexes having asymmetric ligand substituents. When a racemic ligand is used to prepare a bis-chelate complex of one of the above types, twice as many pmr signals may be observed as for the corresponding complex prepared from an optically pure ligand.[3d,g] It has been shown that one set of signals is due to the *meso* complex (+, −); the other set arises from a *d,l* pair (+,+ and −,−). Apparently the separate resonance signals result primarily from unequal ΔG values for the two diastereomers.[3d,g,h] The nickel atom itself is at a center of dissymmetry in the tetrahedral form of these complexes, and additional diastereomers are possible as a result of this third center of dissymmetry. For example, the diastereomers $\Lambda(+,+)$ and $\Delta(+,+)$ would exist for a complex having ligands of (+) chirality. Here Λ and Δ denote left- and right-hand helicity, respectively, about the C_2 axis of the complex.[3g] However, pmr signals attributable to these additional species have not been observed for bis-bidentate complexes.[7] Apparently the $\Delta \rightleftarrows \Lambda$ interconversion is rapid on the nmr time scale, and an averaged spectrum is observed.[3g,h]

Bis[3-(N-substituted amino)methylenecamphorato]nickel(II) complexes (I), hereafter abbreviated [R-amc]$_2$Ni where R is the amine substituent, were expected to have conjugated chelate rings similar to those found



I

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(1) National Science Foundation Predoctoral Trainee, 1965–present.

(2) Bis(aminotroponeimine) complexes: D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(3) Bis(salicylaldimine) complexes: (a) L. Sacconi, P. Paoletti, and M. Ciampolini, *ibid.*, **85**, 411 (1963); (b) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); (c) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **85**, 821 (1963); (d) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964); (e) L. Sacconi, M. Ciampolini, and N. Nardi, *ibid.*, **86**, 819 (1964); (f) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964); (g) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967); (h) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **90**, 5735 (1968).

(4) Bis(*o*-hydroxynaphthaldimine) complexes: A. Chakravorty and R. H. Holm. *Inorg, Chem.*, **3**, 1010 (1964).

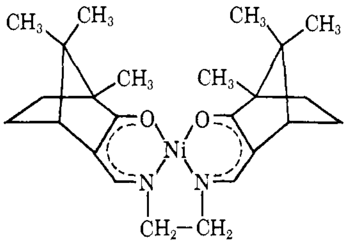
(5) Bis(pyrrole-2-aldimine) complexes: R. H. Holm, A. Chakravorty, and L. J. Theriot, *ibid.*, **5**, 625 (1966).

(6) Bis(β-ketoamine) complexes: (a) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965); (b) G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

(7) Recently it has been shown that in certain tetradentate complexes of the salicylaldimine series, the barrier to $\Delta \rightleftarrows \Lambda$ interconversion is sufficiently high that pmr signals of diastereomeric species differing only in the chirality of the nickel atom may be distinguished: M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 4561 (1968).

in the bis[β-ketoamino]nickel(II) complexes,[6] and it was anticipated that the rapid planar $\rightleftarrows$ tetrahedral equilibrium would occur for some members of this new series of complexes. The bicyclic ring methyls were expected to introduce intramolecular steric interactions not found in any of the systems previously studied;[2–6] and in addition, the ligands possess a built-in asymmetry which could lead to interesting pmr studies of diastereomers. This paper reports the synthesis and stereochemical investigations of this previously unknown series of complexes.

Complexes of the tetradentate ligand "bisformylcamphorethylenediimine" have been known for some time.[8] The solution paramagnetism of the nickel(II) complex II had long been a subject of controversy until Bluck, Odell, and Olliff demonstrated that slow oxidative decomposition of the complex in solution is responsible for the paramagnetism.[9] Our investigations of the analogous bis-complexes I support their conclusions in that the complexes I are also air sensitive and must be prepared and handled in an inert atmosphere. We are currently investigating the oxidized species.



II

Experimental Section

Synthesis of Ligands, R-amc-H. 3-Hydroxymethylenecamphor was prepared from (+)-camphor or (+,−)-camphor by treatment with sodium and isoamyl formate as described by Hauser, *et al.*[10] Ligands having R = phenyl, *m*- or *p*-tolyl, β-naphthyl, or benzyl were made by treating a methanol solution of 3-hydroxymethylenecamphor with a 30% acetic acid solution of the purified amine.[11] The solutions were warmed for about an hour, and the products which precipitated upon cooling the solutions were recrystallized from methanol or from chloroform and petroleum ether. Ligands having R = methyl, ethyl, or isopropyl were prepared by adding excess amine directly to methanol solutions of hydroxymethylenecamphor. The solutions were refluxed for 2 hr and then the excess amine and most of the solvent were removed under vacuum. The crystalline products were recrystallized from chloroform and petroleum ether. H-amc-H precipitated from a solution of 3-hydroxymethylenecamphor in concentrated aqueous ammonia after refluxing for several hours and was recrystallized from methanol. All ligands were identified by pmr.

Preparation of the Complexes. The bis[3-(N-substituted amino)-methylenecamphorato]nickel(II) complexes are sensitive to moisture and oxygen (see Discussion) and must be prepared and handled in a dry, inert atmosphere. The most successful method of preparing the complexes was found to be the nonaqueous method used for β-ketoamine complexes of nickel(II).[12] The inert gas apparatus used in preparing cobalt(II) and vanadium(III) β-ketoamine complexes was employed.[12] The reaction mixtures were stirred at room temperature under nitrogen for 2–3 hr; then the solvent was removed under vacuum, and the residues were extracted with hot *n*-heptane. The complexes crystallized from the *n*-heptane solutions after volume reduction and cooling. They were recrystallized at least two additional times from *n*-heptane.

Magnetic Susceptibility Measurements. Solid-phase magnetic susceptibilities were determined by either the Gouy method or the Faraday method. An Alpha 4-in. water-cooled electromagnet was used for either method. Determinations by the Gouy method involved a Mettler B semimicro balance and tapered magnet pole tips; a Cahn Gram electrobalance and Heyding pole tips were used for the Faraday method. Several measurements were made at each of four field strengths. The magnetic standards used were an aqueous $NiCl_2$ solution[13] and $HgCo(CNS)_4$.[14] Magnetic moments were calculated according to the Curie law.

Solution susceptibilities were determined in chloroform solution by the Gouy method using freshly boiled distilled water as the standard.[13] Chloroform was distilled from P_2O_5 under a nitrogen atmosphere into the Gouy tube containing a known weight of complex. The tube was sealed by means of a small stopcock during the measurements.

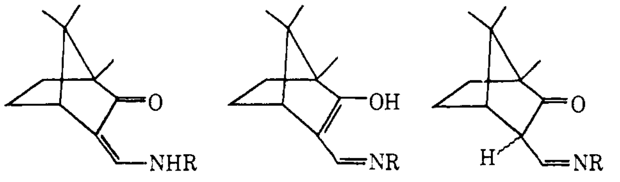
Proton Resonance Spectra. Proton magnetic resonance spectra of ligands and complexes were obtained using Varian Models A-60 and HA-100 spectrometers. Solutions of the complexes were made under nitrogen using degassed deuteriochloroform as the solvent and tetramethylsilane as the internal standard. Sample tubes were sealed *in vacuo*. Solutions prepared in this manner proved to be stable for at least several months. Frequencies were measured by sidebanding when necessary. Spectra over a range of temperatures were obtained on the 100-MHz instrument.

Electronic Absorption Spectra. Absorption spectra in the ligand field region were obtained on a Cary Model 14 spectrophotometer. Solutions of complexes in chloroform were prepared under nitrogen. Mull spectra were obtained on samples ground in mineral oil and pressed between two sample cells.

Molecular Weights. Attempts were made to determine molecular weights of several complexes in solution using a Hewlett-Packard Model 302 vapor pressure osmometer. The results were not reproducible even when measurements were made in an argon atmosphere. It appeared that the complexes were decomposing during the measurements, probably as a result of traces of moisture in the instrument.

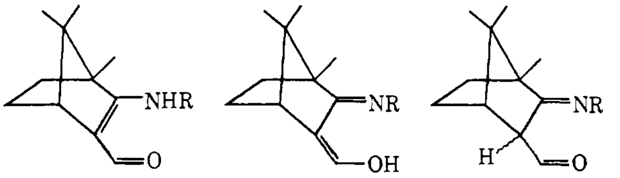
Results and Discussion

Structure of the Ligands. The ligands used in this investigation are readily prepared by condensing the desired primary amine with 3-hydroxymethylenecamphor. One expects the amine to condense at the hydroxymethylene carbon, but the possibility of condensation at the 2-carbon could not *a priori* be excluded. Thus two ligand constitutional isomers are considered (III and IV); each may occur in three tautomeric forms.



a b c

III



a b c

IV

Proton nmr has been used previously to distinguish between these isomers in compounds derived from con-

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(8) For a list of references, see R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966).

(9) R. S. Bluck, A. L. Odell, and R. W. Olliff, *J. Chem. Soc.*, 4660 (1964).

(10) C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, 8, 59 (1954).

(11) A. W. Bishop, L. Claisen, and W. Sinclair, *Ann.*, 281, 314 (1894).

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

(13) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960.

(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

Table I. Results of Elemental Analyses for Bis[3-(N-substituted amino)methylenecamphorato]nickel(II) Complexes

R	Color	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
H	Green	63.64	64.09	7.77	7.68	6.75	6.69
H[a]	Green		63.83		7.96		6.49
CH_3	Green	65.03	64.79	8.19	8.10	6.32	6.24
C_2H_5	Green	66.26	65.98	8.55	8.89	5.94	5.88
$CH_2C_6H_5$	Green	72.61	72.74	7.45	7.50	4.70	4.81
i-C_3H_7	Red	67.34	67.58	8.88	8.97	5.61	5.58
C_6H_5	Red	71.97	72.22	7.11	7.14	4.94	4.86
C_6H_5[a]	Red		71.89		7.40		5.29
p-$C_6H_4CH_3$	Green	72.61	72.48	7.45	7.47	4.70	4.73
m-$C_6H_4CH_3$	Red		72.77		7.41		4.54
β-$C_{10}H_7$	Red	75.57	75.64	6.64	6.79	4.20	4.18

[a] Ligand prepared from racemic camphor.

densation of primary amines with β-diketones.[15] The predominant structure is often easily identified for compounds of this type which have one or more protons on the α-carbon of the amine substituent, R. The 100-MHz pmr spectrum of the ligand derived from methylamine and (+)-hydroxymethylenecamphor is shown in Figure 1. The two signals centered around 293 Hz are assigned to the N-methyl protons.[15b] Comparison of the 60- and 100-MHz spectra of this compound reveals that these signals are components of a doublet resulting from spin–spin coupling (J = 4.8 Hz). The coupling is of the same magnitude as observed in other similar compounds and is attributed to the N proton.[15] Thus all structures with the imine moiety are ruled out (IIIb, c; IVb, c). This information alone is not sufficient to distinguish between structures IIIa and IVa. Attention is directed to the two resonances centered around 630 Hz which are attributed to the proton on the 11-carbon.[15b] This is also a doublet (J = 12.5 Hz) which must arise from spin coupling with N–H. This coupling is consistent only with structure IIIa.

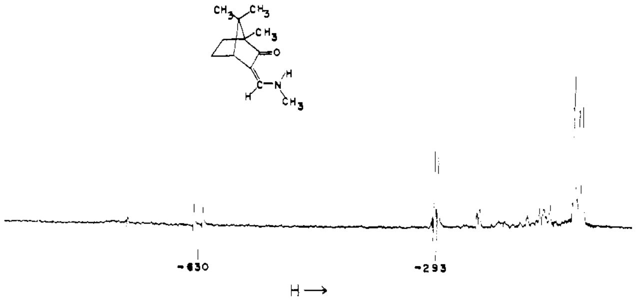

Figure 1. Proton resonance spectrum of CH_3-(+)amc-H in $CDCl_3$ solution. Frequencies shown are chemical shifts at 100 MHz relative to tetramethylsilane.

Unfortunately many of the ligands used in this investigation lack protons on the α-carbon of R, and a similar structural analysis cannot be made. It appears reasonable to assume that constitutional isomer III predominates in all cases, but the relative concentrations of tautomers a, b, and c may vary depending upon R. For simplicity the complexes described herein are referred to as derivatives of 3-(N-substituted amino)methylenecamphor (structure IIIa).

Preparation of the Complexes. The bis[3-(N-substituted amino)methylenecamphorato]nickel(II) complexes are listed in Table I with the results of elemental microanalyses. In general it was found that melting points are not good criteria of purity for these complexes, so elemental analyses were often repeated for subsequent preparations of a given complex and whenever purity was questionable. These complexes are believed to have the general structure I and are therefore analogous to the bis(β-ketoamino)nickel(II) complexes.[6] The nonaqueous synthesis[12] which proved so successful in the latter series of complexes was found to be the most convenient means of synthesizing the complexes I. Most complexes were prepared using ligands derived from (+)-camphor, although in two instances (R = H, C_6H_5) complexes derived from racemic camphor were also prepared.

Initial attempts at preparing complexes of this series under the same conditions employed in preparing the bis(β-ketoamino)nickel(II) complexes,[6,12] *i.e.*, in the presence of air, failed. The products obtained were paramagnetic and insoluble in organic solvents. Colors ranged from red or yellow to blue, depending upon the R group. Elemental analyses were consistently low for carbon, hydrogen, and nitrogen. However, the complexes I can readily be prepared and handled in an inert atmosphere. This apparent sensitivity to atmospheric oxygen is very unusual for complexes of nickel(II) and suggests that the ligands are largely responsible. The complex II is also air sensitive[9] but requires a considerably longer exposure than the corresponding bis complexes. Crystalline complexes I may be handled for short periods in air without detectable change. Qualitative observations indicate that sensitivity to oxygen varies somewhat with the nature of R. In the solid phase, paramagnetic complexes appear to decompose in air more rapidly than those which are diamagnetic. An interesting observation is that $[C_6H_5\text{-}(+,-)\text{amc}]_2\text{Ni}$ is decomposed by air much more rapidly than the isomer prepared from optically pure camphor, $[C_6H_5\text{-}(+)\text{amc}]_2\text{Ni}$.

Stereochemistry of the Complexes. In several well-known series of bis-chelate nickel(II) complexes having N_2O_2 donor sets, the stereochemistry of the coordination sphere depends mainly upon the size of the nitrogen substituent.[2-6] Bulky substituents generally result in paramagnetic, pseudotetrahedral complexes; small substituents lead to diamagnetic complexes which are

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(15) (a) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099, 3914 (1961); **84**, 2691 (1962); (b) G. O. Dudek and G. P. Volpp, *ibid.*, **85**, 2697 (1963); (c) G. O. Dudek and E. P. Dudek, *ibid.*, **86**, 4283 (1964); **88**, 2407 (1966); (d) G. O. Dudek, *ibid.*, **85**, 694 (1963); (e) G. O. Dudek and G. P. Volpp, *J. Org. Chem.*, **30**, 50 (1965).

presumed to be planar or nearly planar; and substituents of intermediate size may allow a dynamic equilibrium in solution between planar and tetrahedral forms. It appears that the planar configuration is preferred in the absence of steric strain introduced by the nitrogen substituent. The electronic structure of the ligand has a definite but at present poorly understood effect on the stereochemistry. Molecular association by means of which nickel becomes five- or six-coordinate has been observed in some instances and may contribute to the paramagnetism.[8,16]

The effective magnetic moments of complexes I in the solid phase and in chloroform solution are given in Table II. In the solid phase the complexes are either diamagnetic or paramagnetic with $\mu_{eff} > 3$ BM, depending upon R. In chloroform solution at room temperature all complexes except [H-amc]$_2$Ni show some paramagnetism. The solution moments of [CH$_3$-(+)amc]$_2$Ni and [C$_6$H$_5$CH$_2$-(+)amc]$_2$Ni were not accurately measured but were estimated from the magnitudes of isotropic pmr shifts (*vide infra*).

Table II. Magnetic Moments in Solid and Solution Phases[a]

R	Solid μ_{eff}, BM[b]	Solution μ_{eff}, BM[b,e]
H[c]	Diamagnetic[f]	Diamagnetic[f]
H	Diamagnetic[f]	Diamagnetic[f]
CH$_3$	Diamagnetic[f]	<1[d]
C$_2$H$_5$	Diamagnetic[f]	1.40
CH$_2$C$_6$H$_5$	Diamagnetic[f]	<1[d]
i-C$_3$H$_7$	3.03	2.82
C$_6$H$_5$[c]	3.26	2.92
C$_6$H$_5$	3.30	3.08
p-C$_6$H$_4$CH$_3$	Diamagnetic[f]	2.98
m-C$_6$H$_4$CH$_3$	3.12	2.85
β-C$_{10}$H$_7$	3.22	3.14

[a] All measurements made at room temperature 20–25°. [b] Calculated according to the Curie law. [c] Ligand prepared from racemic camphor. [d] Moment estimated from magnitude of isotropic pmr shifts. [e] All solution measurements made in chloroform. [f] Accurate susceptibility not determined.

The criterion of diamagnetism for planar four-coordinate nickel(II) complexes is well established experimentally, and although theory indicates the possibility of a triplet ground state, it has not been observed.[16] Thus a planar or nearly planar configuration is assumed in the solid phase for diamagnetic complexes of structure I and for [H-amc]$_2$Ni in chloroform solution. The chloroform solution of [H-amc]$_2$Ni shows an absorption band in the visible region at ~16,300 cm^{-1} (Table III). A similar band at 16,000 cm^{-1} is found for complex II which is constrained to approximate planarity.

Mull spectra of those complexes which are paramagnetic in the solid phase reveal a broad absorption in the near-infrared centered around 6250 cm^{-1} and a weak shoulder at 10,500 cm^{-1} (Figure 2 and Table III). The position and contour of this band are essentially identical with those found for paramagnetic, pseudotetrahedral bis(β-ketoamino)nickel(II) complexes which have chelate rings similar to those of complexes I.[6a] The mull spectra are also quite similar to that of bis(N-isopropylsalicylaldiminato)nickel(II) which has been shown to be pseudotetrahedral by X-ray studies.[17] Since the magnetic moments of complexes I in the solid phase are close to those observed for bis(N-isopropylsalicylaldiminato)nickel(II)[3a,b] and other related nickel(II) complexes having similar absorption spectra,[3,4,6] it must be concluded that the paramagnetic nickel(II) aminomethylenecamphorates are (pseudo)tetrahedral.[18]

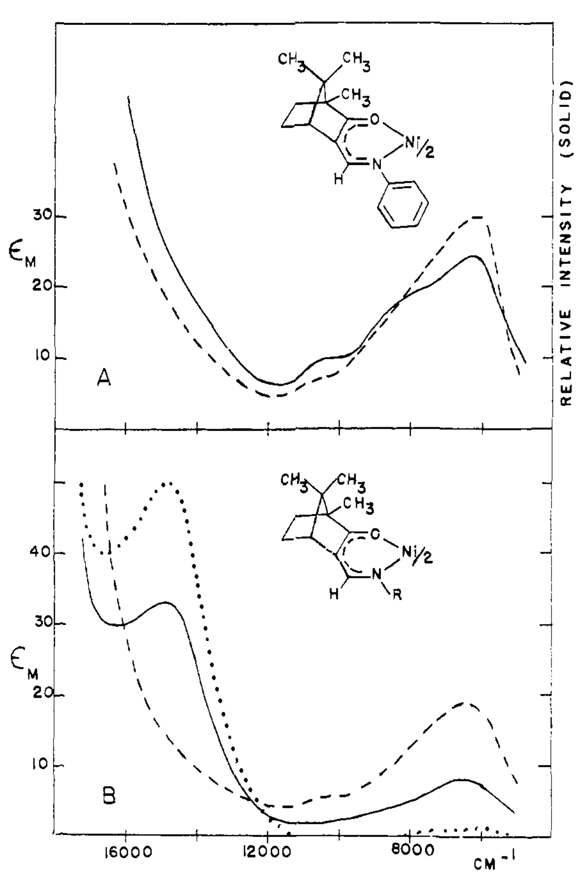

Figure 2. Electronic absorption spectra: (A) [C$_6$H$_5$-(+)amc]$_2$Ni: -----, mull; ———, chloroform solution. (B) ....., [C$_6$H$_5$CH$_2$-(+)amc]$_2$Ni in chloroform solution; -----, [*i*-C$_3$H$_7$-(+)amc]$_2$Ni in chloroform solution; ———, [C$_2$H$_5$-(+)amc]$_2$Ni in chloroform solution.

Electronic absorption spectra of the complexes in chloroform solution, with the exception of [H-amc]$_2$Ni and [CH$_3$-(+)amc]$_2$Ni, reveal the broad near-infrared absorption characteristic of the tetrahedral NiN$_2$O$_2$ chromophore (Figure 2 and Table III). The intensity of the absorption roughly parallels the observed magnetic moments in solution. In addition to this absorption, a band in the visible region, ~14,900 cm^{-1}, appears for complexes having intermediate solution moments (those having R = CH$_3$, C$_2$H$_5$, C$_6$H$_5$CH$_2$). The intensity of this latter band varies inversely with the observed moments, demonstrating that the absorption originates in the planar form of the complexes. These observations are clearly consistent with the presence of both planar and tetrahedral species in solutions of [C$_2$H$_5$-(+)-amc]$_2$Ni and [C$_6$H$_5$CH$_2$-(+)amc]$_2$Ni. Apparently the fraction of tetrahedral molecules in solutions of [CH$_3$-(+)amc]$_2$Ni is small, and the near-infrared absorption

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(16) For a concise summary, see L. Sacconi, *Transition Metal Chem.*, 4, 199 (1968).

(17) M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *Acta Cryst.*, 17, 1159 (1964).

(18) The observed moments of [*i*-C$_3$H$_7$-(+)amc]$_2$Ni and [*m*-C$_6$H$_4$-CH$_3$-(+)amc]$_2$Ni in the solid phase are somewhat lower than expected and may indicate that a fraction of the molecules are planar. This phenomenon has been observed previously.[3g,6]

Table III. Ligand Field Spectral Data[a]

R	Medium[b]	λ_{max}, cm^{-1} (ϵ_M)[c]			
H	$CHCl_3$				16,300 (84)
CH_3	$CHCl_3$				14,900 (51)
C_2H_5	$CHCl_3$	6350 (8.4)			14,900 (34)
$CH_2C_6H_5$	$CHCl_3$	6000–7000 (1.2)			14,900 (50)
i-C_3H_7	$CHCl_3$	6250 (20.1)	10,500 (sh)		
C_6H_5	$CHCl_3$	6270 (24.6)	10,500 (sh)		
	Mull	6170	10,600 (sh)		
C_6H_5[d]	$CHCl_3$	6270 (20.3)	10,500 (sh)		
p-$C_6H_4CH_3$	$CHCl_3$	6300 (25.1)	10,500 (sh)		
β-$C_{10}H_7$	$CHCl_3$	6100 (24.9)	10,400 (sh)		
	Mull	5960			

[a] All measurements made at room temperature. [b] Mull spectra taken in mineral oil. [c] sh = shoulder. [d] Ligand prepared from racemic camphor.

Table IV. Isotropic Proton Resonance Shifts for Bis[3-(N-substituted amino)methylenecamphorato]nickel(II) Complexes[a]

R	Substituent[b]	Δf_i, Hz (at 100 MHz)[c]
C_6H_5	(8,9,10)-CH_3[d]	+653, +165, −190
	o-H, m-H, p-H	+1015, −1808, +1627
	a (4-H)	−1425
	d	+643
	e	+1106
C_6H_5[e]	(8,9,10)-CH_3[d]	+677 +164, −185 +662,
	o-H, m-H, p-H	+1025, −1818, +1635
	a (4-H)	−1426
	d	+583 +655
	e	+1100
m-$C_6H_4CH_3$	(8,9,10)-CH_3[d]	+652, +163, −191
	m-CH_3	+418
	o-H, m-H, p-H	+1000, −1693, +1597
	a (4-H)	−1380
	d	+620
	e	+1139
p-$C_6H_4CH_3$	(8,9,10)-CH_3[d]	+640, +157, −188
	p-CH_3	−2250
	o-H, m-H	+1004, −1823
	a (4-H)	−1443
	d	+672
	e	+1128
β-$C_{10}H_7$	(8,9,10)-CH_3[d]	+687 +169, −191 +707,
	4-, 5-, 7-naph-H[f]	−1890, −585, −760
	a (4-H)	−1480
	d	+596 +663
	e	+1135 +1168
i-C_3H_7	(8,9,10)-CH_3[d]	+581, +161, −240
	Isopropyl-CH_3	−1110 −1202
	a (4-H)	−1530
	d	+798
	e	+1262
C_2H_5	(8,9,10)-CH_3[d]	+103, +26, −49
	Ethyl-CH_3	−111
	Ethyl-CH_2	−4780 −4490
	C_{11}-H	−10,850
	a (4-H)	−309

[a] All measurements made at ~30°. [b] Assignment of signals labeled a, d, and e are not unequivocally established (see Discussion). [c] $\Delta f_i = f_i(\text{complex}) - f_i(\text{ligand})$. [d] Detailed assignments for these signals are not known. [e] Ligand prepared from racemic camphor. [f] Assigned on basis of direction and magnitude of shifts and observed spin–spin splittings.

band is not detectable. The spectrum of $[H\text{-amc}]_2Ni$ shows no measurable amount of tetrahedral complex, and the strongly paramagnetic complexes appear to exist largely in the tetrahedral form.

There is no electronic spectral evidence of molecular association occurring for any of the complexes. However, the temperature dependence of isotropic pmr shifts indicates there may be some association at lower temperatures for two of the complexes (*vide infra*).

Proton Resonance Studies. The paramagnetic bis[3-(N-substituted amino)methylenecamphorato]nickel(II) complexes show well-resolved isotropic pmr shifts as has been observed for several other series of tetrahedral bis-bidentate nickel(II) complexes.[2–6,19,20] The shifts relative to the corresponding free ligand resonances are given in Table IV. The magnitude of the pmr shifts for a given complex is proportional to the mole fraction of tetrahedral form present in the solution and is in agreement with solution magnetic moments (Table II) and the intensities of the near-infrared absorption band (Table III). Typical 100-MHz spectra in deuteriochloroform solution at 30° are presented in Figures 3–5.

(a) **Signal Assignments and Spin Delocalization.** Detailed assignment of all proton resonances in the bis[3-(N-substituted amino)methylenecamphorato]nickel(II) complexes is not possible at present. However, most of the signals may be identified as to the number and type of protons from which they arise, and in some instances ligand substitutions enable unequivocal assignments to be made. Attention is directed to the spectrum of $[C_6H_5\text{-}(+)\text{amc}]_2Ni$ (Figure 3A). The three strong signals at −287, +68, and +556 Hz each have an area of 3.0 and are assigned to the camphor methyls. Specific assignments of these resonances to the C_8, C_9, and C_{10} methyls are not possible at this time. The multiple signal at +930 Hz has an area of 2. Methyl substitution at the p-phenyl position reduces the area of this signal to 1 and gives rise to a new resonance of area 3 at −2480 Hz (Figure 3B). Thus a component of the resonance at +930 Hz is due to the *para* proton. Methyl substitution at one of the m-phenyl positions reduces the area of the resonance at −2505 Hz from 2 to 1 and produces a new signal of area 3 at +188 Hz, thereby demonstrating that the −2505-Hz resonance arises from the *meta* protons. The broad signal at +318 Hz occurs only for complexes having an aromatic amine substituent. This signal has an area of about 2 and is assigned to the *ortho* protons.

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(19) J. E. Parks and R. H. Holm, *Inorg. Chem.*, 7, 1408 (1968).

(20) D. R. Eaton and E. A. LaLancette, *J. Chem. Phys.*, 41, 3534 (1964).

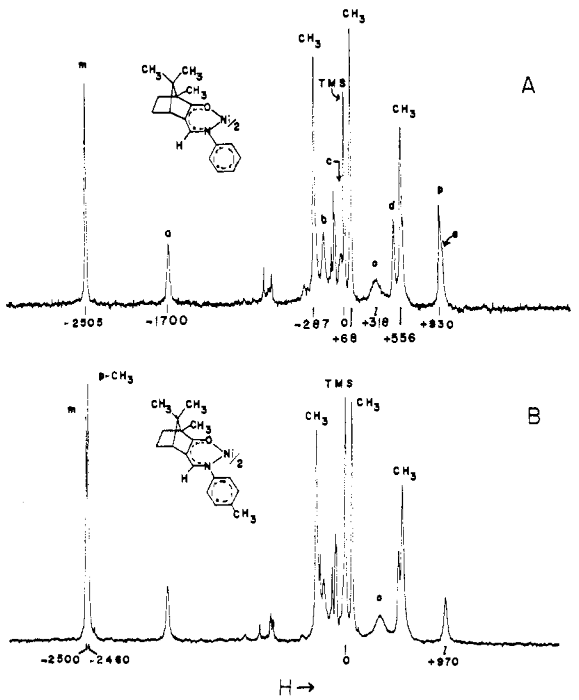

Figure 3. 100-MHz proton resonance spectra in $CDCl_3$ solution at ~30°: (A) $[C_6H_5\text{-}(+)amc]_2Ni$; (B) $[p\text{-}C_6H_4CH_3\text{-}(+)amc]_2Ni$. Frequencies shown are chemical shifts relative to tetramethylsilane.

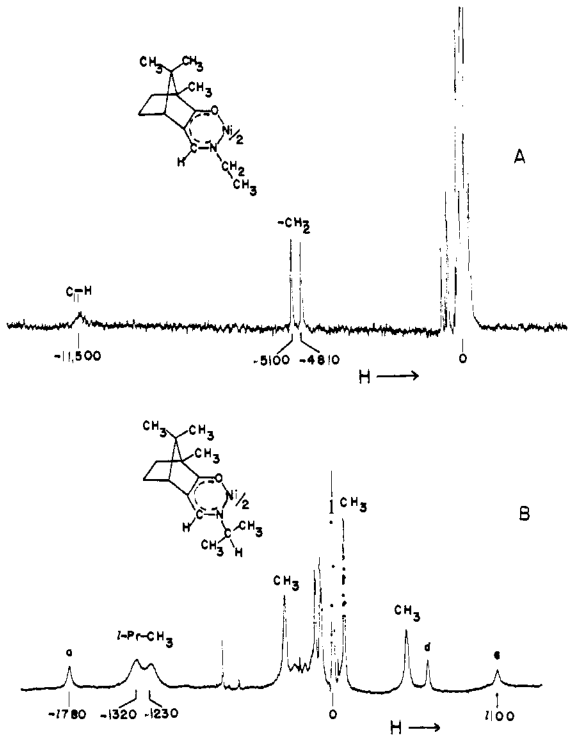

Figure 5. 100-MHz proton resonance spectra in $CDCl_3$ solution at ~30°: (A) $[C_2H_5\text{-}(+)amc]_2Ni$; (B) $[i\text{-}C_3H_7\text{-}(+)amc]_2Ni$. Frequencies shown are chemical shifts relative to tetramethylsilane.

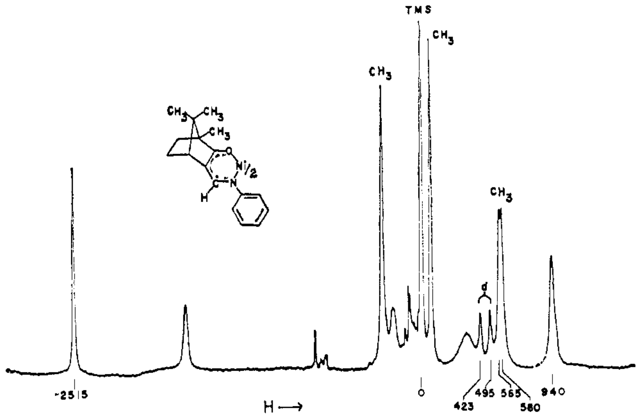

Figure 4. 100-MHz proton resonance spectrum of $[C_6H_5\text{-}(+, -)\text{-}amc]_2Ni$ in $CDCl_3$ solution at ~30°. Frequencies given are chemical shifts relative to tetramethylsilane.

It is apparent that a phenyl proton on $[C_6H_5\text{-}(+)\text{-}amc]_2Ni$ experiences a pmr shift of opposite sign than that of a methyl group at the same position. This is good evidence that electron spin exists predominantly in the π system of the ligand. The direction of pmr shifts implies positive spin density in the p–π orbitals of the *ortho* and *para* carbons and negative spin density in the p–π orbital of the *meta* carbon, and indicates a positive spin density in p–π of nitrogen. This pattern of spin densities is the same as observed in similar series of tetrahedral nickel(II) complexes such as the β-ketoamines.

The distribution of spin in β-ketoamine complexes is consistent only with a spin delocalization mechanism involving fractional transfer of β spin from the highest filled ligand molecular orbital, HFMO, to the d orbitals of nickel which contain unpaired electrons of α spin.[6a] This same mechanism is assumed for the aminomethylenecamphorate complexes and is expected to result in positive π spin density at C_3 and negative spin densities at C_2 and C_{11}. The above assumption is supported by the occurrence of the resonance signal due to the proton on C_{11} at very low fields. Although this signal is extremely broad and difficult to observe for the strongly paramagnetic complexes of series I, it may easily be seen in the spectra of others such as $[C_2H_5\text{-}(+)amc]_2Ni$ (Figure 5A).

Five proton resonances in addition to those assigned above are expected for the complex $[C_6H_5\text{-}(+)amc]_2Ni$. These should arise from the five inequivalent bicyclic ring protons, 4-H, 5-*exo*-H, 5-*endo*-H, 6-*exo*-H, and 6-*endo*-H. Careful examination of the spectrum (Figure 3A) reveals a total of five unassigned signals, a–e, having the characteristic broadness of resonances from a paramagnetic molecule. The areas of signals a, d, and e can be measured; each has an area ~1. Most of these signals may also be found in spectra of other complexes (Figures 3B, 4, 5). The sharper signals around −100 and −750 Hz are due to traces of free ligand and chloroform. Unequivocal assignments of signals a–e cannot be made, but it seems entirely reasonable to assign signal a to 4-H since 4-H is analogous to the proton of a methyl group bound to an aromatic site having positive π spin density, and its pmr signal should be shifted downfield.

Implicit in the above discussion of spin delocalization is the assumption that dipolar (or pseudocontact) interactions make a relatively small contribution to the observed shifts. There is no means of justifying this assumption except to point out that dipolar shifts appear to be unimportant in analogous bis-chelate nickel(II) complexes.[2–6] The shifts observed for the camphor methyls in complexes I may have appreciable dipolar contributions. Attempts at a rough calculation of the *relative* dipolar shifts expected for the 8-, 9-, and 10-methyls by comparing their geometrical factors[21] gave inconclusive results.

(b) Detection of Diastereomers. Previous pmr studies of bis-chelate nickel(II) complexes involved in the planar $\rightleftarrows$ tetrahedral equilibrium have demonstrated that *meso* (+,−) and active (+,+ and −,−) diastereomers often have measurably different pmr spectra (see introductory section). In order to investigate the occurrence of this phenomenon for the aminomethylenecamphor complexes, $[C_6H_5\text{-}(+,-)amc]_2Ni$ was prepared using ligand derived from racemic camphor. It is likely that *meso* and active diastereomers are formed in approximately the statistical 1:1 ratio. The solution magnetic moment of this diastereomeric mixture is somewhat lower than that of the (+,+) diastereomer (Table II), indicating that the configurational equilibrium for the *meso* complex is displaced more toward the planar form. A comparison of the intensities of the 6270-cm^{-1} absorption bands (Table III) for $[C_6H_5\text{-}(+)amc]_2Ni$ and $[C_6H_5\text{-}(+,-)amc]_2Ni$ lends support to this conclusion. The pmr spectrum of $[C_6H_5\text{-}(+,-)amc]_2Ni$ (Figure 4) shows distinct splitting for only two resonance signals: the most upfield camphor methyl signal and one of the camphor methylene signals, d. The high-field component of the methylene signal is clearly due to the active diastereomer since its resonance frequency is within error of that observed for $[C_6H_5\text{-}(+)amc]_2Ni$. Occurrence of the *meso* component at lower field indicates a smaller fraction of tetrahedral molecules for this diastereomer and is in qualitative agreement with the spectral and magnetic data. The components of the methyl resonance cannot be assigned with certainty since the splitting is small. It would appear that the upfield component is due to the *meso* complex. A slight difference in the hyperfine coupling constants between *meso* and active species at this methyl group could be responsible for this apparent shift reversal.

Space-filling molecular models serve to explain why the *meso* complex has a smaller preference for the tetrahedral configuration. In *either* the Δ or Λ tetrahedral configuration for the *meso* complex, the R group of one ligand is in close proximity to the $8\text{-}CH_3$ of the second ligand; the R group of the second ligand faces the *endo* side of the bicyclic ring of the first ligand and should experience little steric interaction. In the case of the (+,+) complex in the Δ configuration both R groups face the *endo* sides of the opposite ligands, but in the Λ configuration both R's are in position to interact sterically with the $8\text{-}CH_3$'s of the opposite ligands.[22] Thus the active diastereomer can select the tetrahedral configuration which minimizes intramolecular steric interactions (Δ for the (+,+) diastereomer), whereas the steric interactions are identical in both configurations for the *meso* diastereomer. If this stereoselectivity occurs to some extent for the active diastereomer it would result in a more negative ΔG for the active than for the *meso* diastereomer, leading to a smaller mole portion of tetrahedral species for the latter.

Split pmr signals are observed for three of the active complexes. The spectra of $[i\text{-}C_3H_7\text{-}(+)amc]_2Ni$ and $[C_2H_5\text{-}(+)amc]_2Ni$ are shown in Figure 5. In these cases the split signals may be assigned to protons on the R group, CH_3 for R = isopropyl and CH_2 for R = ethyl. There are two mechanisms which could cause signal splitting in active complexes. (1) If the barrier to $\Delta \rightleftarrows \Lambda$ interconversion were sufficiently large that the lifetime of each configuration is long on the pmr time scale, the Δ and Λ molecules could have different spectra because they are diastereomeric. This mechanism is deemed unlikely for the above two complexes in view of the facts that splitting is not observed for protons other than those on the amine substituent and is not found for most other active complexes of structure I. Furthermore in all previous pmr studies of bis-chelate nickel(II) complexes with asymmetric ligand centers, the rate of $\Delta \rightleftarrows \Lambda$ interconversion was found to be very rapid, and the resonances of Δ and Λ diastereomers are averaged (see introductory section).

(2) If the structural interconversion is rapid, but the R groups are not free to rotate through 360° about the C–N bond axis, splitting is expected only for those resonance signals arising from protons on R. This is precisely what is observed. Models indicate that for these two complexes in the Λ configuration, steric interactions between the isopropyl and ethyl methyls and the $8\text{-}CH_3$'s of the opposite ligands could occur. This would prevent complete rotation of R, resulting in inequivalency of the isopropyl methyls and the two methylene protons of ethyl. In the Δ configuration the R groups probably have unrestricted rotation. Rapid $\Delta \rightleftarrows \Lambda$ interconversion would average the restricted and unrestricted environments of each type of proton but would not make them equivalent. On the basis of these arguments we conclude that mechanism 2 is responsible for the split resonance signals found for $[i\text{-}C_3H_7\text{-}(+)amc]_2Ni$ and $[C_2H_5\text{-}(+)amc]_2Ni$. Splitting also is observed for one of the camphor methyl resonances and signals d and e of $[\beta\text{-}C_{10}H_7\text{-}(+)amc]_2Ni$ (see Table IV). The origin of this splitting is not completely understood. The β-naphthyl groups may have restricted rotation in this complex, thus generating diastereomers similar to those found for bis(N,N′-di-α-naphthylaminotroponeiminato)nickel(II).[2] Although only one diastereomer was found for the β-naphthyl analog of the complex, the occurrence of isomerism for the aminomethylenecamphorate complex could be attributed to the greater degree of intramolecular steric interactions.

(c) Temperature Dependence of Pmr Shifts. The most accurate means of studying the planar $\rightleftarrows$ tetrahedral configurational equilibrium in nickel(II) complexes is to follow the temperature variation of the isotropic shift of one of the proton resonance signals. Equation 1 relates the observed shift, Δf_i, of a resonance signal to the free energy of the planar → tetrahedral structural change. The other symbols in (1) have their

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

usual meanings.[23] Proton magnetic resonance spectra of four of the aminomethylenecamphor complexes were recorded at intervals of a few degrees in the temperature

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[21] W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem., Soc.*, **86**, 3031 (1964).

[22] These relationships are based on the known absolute configuration of (+)-camphor: F. H. Allen and D. Rogers, *Chem. Commun.*, 837 (1966). The opposite relationships hold for the (−,−) complex.

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

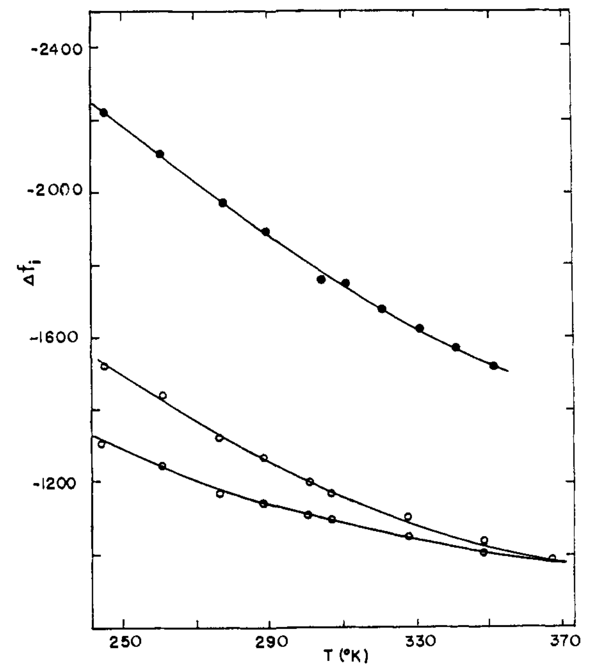

Figure 6. Temperature dependence of isotropic pmr shifts: ●, *m*-phenyl proton of [C$_6$H$_5$-(+)amc]$_2$Ni; ○, isopropyl methyls of [*i*-C$_3$H$_7$-(+)amc]$_2$Ni. Values of Δf_i are in Hz measured at 100 MHz.

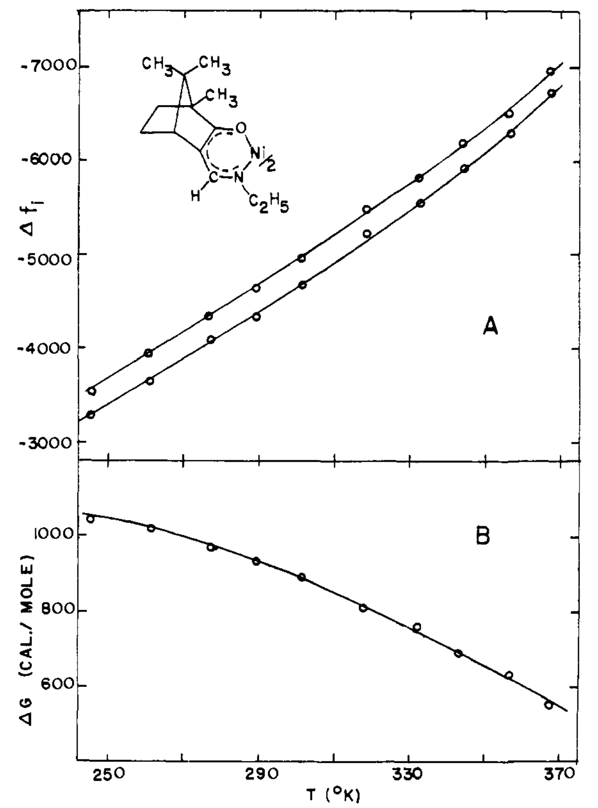

Figure 7. (A) Temperature dependence of isotropic pmr shifts of the ethyl-CH$_2$ protons of [C$_2$H$_5$-(+)amc]$_2$Ni. (B) Temperature dependence of the free-energy change for the planar → tetrahedral conversion of [C$_2$H$_4$-(+)amc]$_2$Ni.

range −30 to +100°. Plots of contact shifts as a function of temperature are shown in Figures 6 and 7A.

The pmr shifts of [C$_6$H$_5$-(+)amc]$_2$Ni and [*i*-C$_3$H$_7$-(+)amc]$_2$Ni were found to decrease with increasing temperature, following the Curie law in the temperature range studied. Thus it is apparent that they are fully tetrahedral at these temperatures.[24] Solution magnetic moments of these two complexes at room temperature (Table II) are somewhat lower than the ~3.3 BM found for fully tetrahedral nickel(II) β-ketoamine complexes but are close to the ~3.05 BM found for the nickel(II) β-iminoamines which demonstrate Curie law behavior.[19] It is concluded that either the solution moments of the fully tetrahedral complexes are close to those given in Table II or the presence of tetramethylsilane in the pmr samples displaces the planar ⇄ tetrahedral equilibrium toward the right as has been found for certain cobalt(II) β-ketoamine complexes.[25]

The pmr shifts of [CH$_3$-(+)amc]$_2$Ni and [C$_2$H$_5$-(+)amc]$_2$Ni increase with increasing temperature (Figure 7), demonstrating that a larger fraction of the molecules becomes paramagnetic at higher temperatures. Such behavior is expected where the planar → tetrahedral configurational change is endothermic. If the hyperfine coupling constant a_i is known for a particular proton, ΔG at various temperatures may be obtained from eq 1 using measured Δf_i values for that proton. The coupling constants for the R-methylene protons of [C$_2$H$_5$-(+)amc]$_2$Ni were calculated by methods previously outlined,[6] making use of the solution magnetic moment measured by the Gouy method (Table II). [CH$_3$-(+)amc]$_2$Ni is not sufficiently paramagnetic at normal temperatures for an accurate susceptibility measurement by the Gouy method, so coupling constants cannot be calculated directly as they were for the complex where R = ethyl. It was assumed that the value of a_i for the C$_{11}$ proton of [C$_2$H$_5$-(+)amc]$_2$Ni could be used for the C$_{11}$ proton of [CH$_3$-(+)amc]$_2$Ni, since a_i's are usually not significantly dependent on the nature of R in a homologous series of complexes.[2,3g,6,19] Using the a_i's so obtained for these two complexes and the corresponding Δf_i's at a number of temperatures, values of ΔG at these temperatures were obtained from eq 1. In each case g was taken to be 2.33; *i.e.*, 3.3 BM was assumed for fully tetrahedral complexes.

A plot of ΔG *vs.* temperature for [C$_2$H$_5$-(+)amc]$_2$Ni is shown in Figure 7B; the corresponding plot for [CH$_3$-(+)amc]$_2$Ni is of similar shape and slope but is displaced ~1400 cal to more positive ΔG values. The plots were expected to be linear from the relation, $\Delta G = \Delta H - T\Delta S$, but for both complexes the plots approach linearity only at high temperatures. This behavior has previously been attributed to the occurrence of molecular association,[3d,6] which is favored at lower temperatures. The electronic absorption spectra of these complexes show no bands due to associated species; however, the concentrations of the solutions used in pmr experiments are generally an order of magnitude greater than those used for magnetic and electronic spectral measurements. In an effort to verify the presence of associated species, electronic absorption spectra of [C$_2$H$_5$-(+)amc]$_2$Ni were recorded at room temperature over a range of concentrations (0.01–0.25 *M*) which included those of the magnetic and pmr mea-

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[24] Slight deviations from Curie law behavior were observed for [C$_6$H$_5$-(+)amc]$_2$Ni at the lowest temperatures investigated, indicating the presence of a small amount of planar complex.

[25] G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966).

surements. Within experimental error no deviation from Beer's law was found. Apparently the extent of association is small and can be detected only by the sensitive pmr technique. Attempts to detect association by molecular weight measurements were inconclusive (see Experimental Section).

A qualitative comparison may be made of the relative tendencies of the aminomethylenecamphorates (amcs), salicylaldiminates (sals), β-ketoamineates (ketos), aminotroponeimineates (atis), and pyrrole-2-aldimineates (pyrs) to adopt the tetrahedral stereochemistry in solution at normal temperatures. When the R group is H, complexes of all five series are completely planar. For aromatic R groups the amcs are nearly 100% in the tetrahedral form; the atis vary from 25 to 75% tetrahedral; the ketos are ~10% tetrahedral and show evidence of molecular association; the pyrs are planar; and the sals are strongly associated. Where R is isopropyl the amcs, atis, and the ketos are fully tetrahedral, whereas the sals and pyrs are ~50 and ~10% tetrahedral, respectively. Finally, for R = *n*-alkyl, only the atis are fully tetrahedral. The amc complex having R = ethyl is ~20% tetrahedral (neglecting association) and is comparable to the R = ethyl keto complex which is ~30% tetrahedral. The pyrs are completely planar, and the sals are appreciably associated.

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Volatile Lanthanide Chelates. II. Vapor Pressures, Heats of Vaporization, and Heats of Sublimation[1a]

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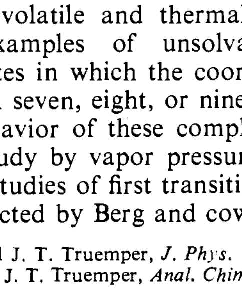
Abstract: Thermodynamic measurements were undertaken on a series of remarkably volatile and thermally stable lanthanide chelates of 2,2,6,6-tetramethyl-3,5-heptanedione. The complexes are unusual examples of unsolvated monomeric lanthanide chelates in which the coordination number is six. Large differences were found in the vapor pressures, heats of vaporization, and heats of sublimation of the tetramethylheptanedionato complexes. The findings corroborate the trend detected by gas chromatography; complexes of the lanthanides with higher atomic number are considerably more volatile than those of the lighter, larger members of the lanthanide series. For example, at 200° vapor pressures range from *ca.* 5 mm for the ytterbium(III) complex down to 0.2 mm for the lanthanum(III) complex. A plot of the heat of vaporization of the chelates *vs.* the atomic number of the metal in general reflects the effects of the lanthanide contraction, but there is an irregularity at gadolinium.

Although it has been known for many years that β-diketonates of metals in the first transition series are volatile, efforts to find similar volatile complexes of the lanthanides were always unsuccessful until very recently.[2-4] Previously known chelates of the lanthanides were invariably either nonvolatile or thermally unstable.

Indeed virtually all other reported lanthanide compounds are either nonvolatile or have very low volatility at temperatures below 700°. In part I[3] we recently described the synthesis and gas chromatographic behavior of the lanthanide complexes of 2,2,6,6-tetramethyl-3,5-heptanedione [H(thd)]. These compounds, Ln(thd)$_3$



are remarkably volatile and thermally stable. They are unusual examples of unsolvated monomeric lanthanide chelates in which the coordination number is six rather than seven, eight, or nine. The gas chromatographic behavior of these complexes suggested a more detailed study by vapor pressure measurements. Vapor pressure studies of first transition series chelates have been conducted by Berg and coworkers[5-7] and by

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(1) (a) Presented in part at the 10th International Conference on Coordination Chemistry, Nikko, Japan, Sept 1967. (b) Ohio State University Research Foundation Visiting Research Associate. (c) Deceased. Dr. Dubois was the victim of a tragic airliner crash on March 9, 1967. (d) Direct correspondence to this author at the Aerospace Research Laboratories, ARC, Wright-Patterson Air Force Base, Ohio 45433.

(2) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, 1965, p 36, and references cited therein.

(3) K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.*, **87**, 5254 (1965).

(4) C. S. Springer, Jr., D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

(5) E. W. Berg and J. T. Truemper, *J. Phys. Chem.*, **64**, 487 (1960).

(6) E. W. Berg and J. T. Truemper, *Anal. Chim. Acta*, **32**, 245 (1965).

(7) E. W. Berg and F. R. Hartlage, Jr., *ibid.*, **33**, 173 (1965); **34**, 46 (1966).