Table VI. Summary of Results for Reaction of Cr^{2+} and ICH_2Y

Y	$k(25$ °C), s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	% $CrYCH_3$ product
$-CO(NH_2)^a$	0.56	6.7	-37.2	38
$-CO_2H^b$	1.1	5.4	-40.4	81
$-CN^c$	9.2	5.4	-35.8	75
$-CNCo(NH_3)_5{}^c$	45.2	3.8	-38.2	0

^{a} This work. ^{b} Reference 2. ^{c} Reference 7.

Table VII. Summary of Results for Reaction of Hg^{2+} and $CrCH_2Y$

| Y	$k(25$ °C), M^{-1} s^{-1}	% $CrYCH_2Hg$ product	σ_I for Y^a
$-CO(NH_2)^b$	2.5×10^3	50	0.28
$-CO_2H^c$		100	0.30
$-CN^d$	8.7	50	0.57
$-OCH_3{}^e$	91		0.30
$-CH_2CN^e$	81		0.20

^{a} Reference 12. ^{b} This work. ^{c} Reference 2. ^{d} References 3 and 7. ^{e} Reference 1.

for analogous reactions of vitamin B_{12r}. The products of the chromium(II) reaction are also given in Table VI. The amount of $CrYCH_3$ clearly depends on the Y substituent. The basicity of the Y group appears to have a minor influence on the amount of $CrYCH_3$ product since a nitrile function generally is a much poorer base toward metal ions than a carboxamide group, yet the latter gives much less $CrYCH_3$ product. The unpaired electron distribution in the $^{\bullet}CH_2Y$ radical intermediate might affect the product distribution. Unfortunately, the theoretical predictions for the electron distribution are only available for $^{\bullet}CH_2CN$.[10,11] It is noteworthy that the reactions with vitamin B_{12r} do not appear to yield the analogous $CoYCH_3$ products.[9]

The results for some reactions of Hg^{2+} with $CrCH_2Y$ are summarized in Table VII. The reactivity trends of these reactions are consistent with electrophilic attack of Hg^{2+} at the α-carbon.[1] The rate decreases with increasing electron-withdrawing power and steric bulk of the Y group.[1] On the basis of th σ_I values for the substituents (Table VII)[12] the rate constant for Y $\equiv$ –CO-

(NH_2) should be similar to that for Y $\equiv$ –OCH_3. In fact, $CrCH_2CO(NH_2)^{2+}$ is about 25 times more reactive than expected on this basis. This may be due to neighboring-group participation of the carboxamide group in the reaction with Hg^{2+}.

The formation of the $CrYCH_2Hg$ product was originally explained for Y $\equiv$ –CO_2H on the basis of chelation in the reactant.[2] However, the more recent work with Y $\equiv$ –CN[3] indicates that competition between solvent water and –Y for the coordination site on chromium is a more probable explanation, as shown in eq 9.

$$\text{(9)}$$
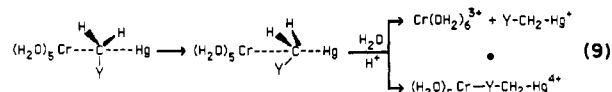
The protonation equilibrium of $CrCH_2CO(NH_2)^{2+}$ was unexpected in view of the normally low basicity of the carboxamide group. The simplest rationalization is that the –$CH_2CO(NH_2)^-$ ligand retains a substantial amount of anion character in the complex, with the result that it is far more basic than a normal carboxamide substituent.

The acidolysis of $CrCH_2CO(NH_2)^{2+}$ is unusual in that substantial amounts of the carboxylate analogue are produced. This reaction can be understood in conjunction with the protonation reaction by the reaction sequence shown in eq 10.

$$\text{(10)}$$
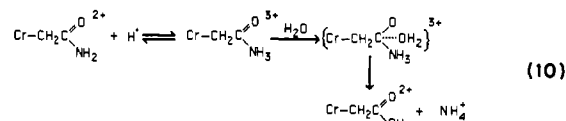
The parallel formation of the O-bonded carboxamide complex in the acidolysis reaction can be explained if the attack of H_2O or H_3O^+ is analogous to that of Hg^{2+}, shown in eq 9, to generate some $Cr(OH_2)_6{}^{3+}$ and some $(H_2O)_5CrO(NH_2)CCH_3$ in this reaction pathway.

Experimental Section

The preparation and handling of standard reagents and general experimental procedures and equipment have been described previously.[2,7] The iodoacetamide (Aldrich Chemical Co.) was used as supplied.

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Notes

Contribution from the Department of Chemistry,
National Tsing Hua University,
Hsinchu, Taiwan 30043, Republic of China

A Proton Magnetic Resonance Study of the Conformational Characterization of Nickel(II)–Tetraaza Macrocyclic Complexes

Jy-Wann Chen, Chi-Chang Chang, and Chung-Sun Chung*

The coordination chemistry of metal-ion complexes of macrocyclic tetraamine ligands has attracted great interest because they provide stimulating examples for studying the conformational properties of the molecules, owing to the possible stable arrangements that the ligand can adopt around the metal ion.[1]

Proton magnetic resonance spectroscopy is perhaps the most powerful tool available to inorganic chemists for obtaining conformational information about metal complexes in solution.[2] Previously, Ito and Busch reported the detailed stereochemistry of $[1SR,2SR,4RS,7RS,8SR,9SR,11RS,14RS)$-2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) chloride.[3] In order to investigate the effects of methyl substituents on the conformational characterization of nickel(II)–tetraaza macrocyclic complexes, the detailed stereochemistry in solution of three closely related complexes that have the same trans-I or $1SR,4RS,8SR,11RS$ configuration arising from the four chiral nitrogen centers,[4,5] as shown in Figure 1, has been accomplished

(1) Lee, C.-S.; Wu, S.-Y.; Chung, C.-S. *Inorg. Chem.* **1984,** *23,* 1298–1303.

(2) Hawkins, C. J.; Palmer, J. A. L. *Coord. Chem. Rev.* **1982,** *44,* 1.
(3) Ito, T.; Busch, D. H. *J. Am. Chem. Soc.* **1973,** *95,* 7528–7530.
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(5) Herron, N.; Moore, P. *Inorg. Chim. Acta* **1979,** *36,* 89–96.
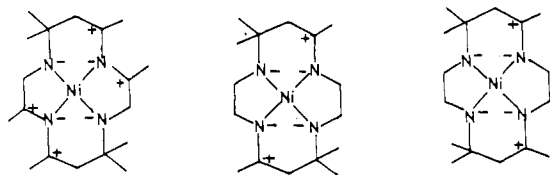
I. [Ni(α-Me₈cyclam B)]²⁺   II.[Ni(β-rac-1,7-CTH)]²⁺   III.[Ni(β-meso-1,4-CTH)]²⁺

Figure 1. Configurations of (I) [Ni(α-Me$_8$cyclam B)]$^{2+}$, (II) [Ni(β-rac-1,7-CTH)]$^{2+}$, and (III) [Ni(β-meso-1,4-CTH)]$^{2+}$. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle, and a minus sign, that it is below.

Table I. ^{1}H NMR 400-MHz Data for [Ni(α-Me$_8$cyclam B)]$^{2+}$ in D$_2$O Solution

proton	chem shift^{a,b} (coupling const, Hz)	rel area
Me(I)$_{eq}$	1.07, d	6
	($J_{Me(I)_{eq}-H_g}$ = 6.2)	
Me(II)$_{eq}$	1.11, s	6
Me(III)$_{ax}$	2.36, s	6
Me(IV)$_{ax}$	1.65, d	6
	($J_{Me(I)_{eq}-H_g}$ = 6.2)	
H$_a$	2.20, d	2
	(J_{ab} = 12, J_{ac} < 0.5)	
H$_b$	2.75, q	2
	(J_{ab} = 12, J_{bc} = 5)	
H$_c$	2.99, quin	2
	(J_{bc} = 5, J_{ca} < 0.5, $J_{Me(IV)-H_c}$ = 6.2)	
H$_e$	1.35, q	2
	(J_{ef} = 15, J_{eg} = 11)	
H$_f$	1.80, q	2
	(J_{fe} = 15, J_{fg} = 3)	
H$_g$	3.28, m	2
	($J_{Me(I)-H_g}$ = 6.2, J_{ge} = 11, J_{gf} = 3)	

^{a}All chemical shifts in units of ppm downfield from internal DDS. ^{b}s = singlet; d = doublet; q = quartet; quin = quintet; m = multiplet.

by means of proton magnetic resonance spectroscopy, and detailed comparisons of the structures of these complexes in solution are reported here.

Experimental Section

Reagents. The complexes Ni(β-rac-1,7-CTH)(ClO$_4$)$_2$ and Ni(β-meso-1,4-CTH)(ClO$_4$)$_2$ used in this work are the same as those reported previously.[1,6-9] Ni(α-Me$_8$cyclam B)(ClO$_4$)$_2$ was prepared according to the methods described in the literature.[3,10] All the complexes were satisfactorily analyzed for C, H, and N. Anal. Calcd for Ni(β-rac-1,7-CTH)(ClO$_4$)$_2$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.38; H, 6.60; N, 10.45. Calcd for Ni(β-meso-1,4-CTH)(ClO$_4$)$_2$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.05; H, 6.63; N, 10.66. Calcd for Ni(α-Me$_8$cyclam B)(ClO$_4$)$_2$: C, 37.92; H, 7.07; N, 9.83. Found: C, 38.02; H, 7.00; N, 9.74.

Instrumentation. Proton magnetic resonance data were obtained by using a Bruker AM-400 NMR spectrometer. The chemical shifts were calibrated from internal DSS. Concentrations of samples were 10–20% by weight, and spectra were obtained at 25 °C.

Results and Discussion

The proton magnetic resonance spectra of [Ni(α-Me$_8$cyclam B)]$^{2+}$, [Ni(β-rac-1,7-CTH)]$^{2+}$, and [Ni(β-meso-1,4-CTH)]$^{2+}$ are shown in Figures 2, 3, and 4, respectively. The assignments of the resonances, as reported in Tables I–III, are based on (i) the intensity ratios, (ii) stereospecific deuteriation according to Scheme I, (iii) spin-decoupling experiments, (iv) inductive effects of the amine groups, and (v) the deshielding effect for protons situated above the plane of square-planar nickel(II) complexes.[9,11] The

(6) Curtis, N. F.; Swann, D. A.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1973**, 1963–1974.
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(8) Curtis, N. F. *J. Chem. Soc.* **1964**, 2644–2650.
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Table II. ^{1}H NMR 400-MHz Data for [Ni(β-rac-1,7-CTH)]$^{2+}$ in D$_2$O Solution

| proton	chem shift^{a,b} (coupling const, Hz)	rel area
Me(I)$_{eq}$	1.00, d	6
	($J_{Me(I)_{eq}-H_g}$ = 6.2)	
Me(II)$_{eq}$	1.10, s	6
Me(III)$_{ax}$	2.15, s	6
H$_a$	2.39, m	2
	(J_{ab} = 12, J_{ac} = 12, J_{ad} = 5.4)	
H$_c$	2.45, m	2
	(J_{cd} = 12, J_{ca} = 12, J_{cb} = 5.4)	
H$_b$	2.53, q	2
	(J_{ba} = 12, J_{bc} = 5.4, J_{bd} < 0.5)	
H$_d$	2.62, q	2
	(J_{dc} = 12, J_{da} = 5.4, J_{db} < 0.5)	
H$_e$	1.15, q	2
	(J_{ef} = 15.7, J_{eg} = 12)	
H$_f$	1.76, q	2
	(J_{fe} = 15.7, J_{fg} = 3)	
H$_g$	3.42, m	2
	($J_{Me(I)_{eq}-H_g}$ = 6.2, J_{ge} = 12, J_{gf} = 3)	

^{a}All chemical shifts in units of ppm downfield from internal DDS. ^{b}s = singlet; d = doublet; q = quartet; m = multiplet.

Table III. ^{1}H NMR 400-MHz Data for [Ni(β-meso-1,4-CTH)]$^{2+}$ in D$_2$O Solution

proton	chem shift^{a,b} (coupling const, Hz)	rel area
Me(I)$_{eq}$	1.03, d	6
	($J_{Me(I)_{eq}-H_g}$ = 6.2)	
Me(II)$_{eq}$	1.13, s	6
Me(III)$_{ax}$	2.17, s	6
H$_a$, H$_{a'}$	2.47, q	4
H$_c$, H$_{c'}$	(J_{ab} = $J_{a'b'}$ = J_{cd} = $J_{c'd'}$ = 12, $J_{ab'}$ = $J_{a'b}$ = $J_{cd'}$ = $J_{c'd}$ = 4.5)	
H$_d$, H$_{d'}$	2.58, q	2
H$_b$, H$_{b'}$	2.64, q	2
H$_e$	1.22, q	2
	(J_{ef} = 15.5, J_{eg} = 12.2)	
H$_f$	1.78, q	2
	(J_{fe} = 15.5, J_{fg} = 3)	
H$_g$	3.44, m	2
	($J_{Me(I)_{eq}-H_g}$ = 6.2, J_{ge} = 12.2, J_{gf} = 3)	

^{a}All chemical shifts in units of ppm downfield from internal DDS. ^{b}s = singlet; d = doublet; q = quartet; m = multiplet.

Scheme I
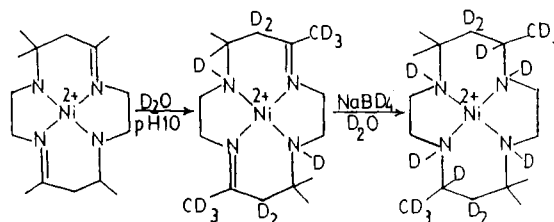
100-MHz ^{1}H NMR spectrum of [Ni(α-Me$_8$cyclam B)]$^{2+}$ has been reported by Ito and Busch.[3]

The number of resonance signals indicates that the two six-membered chelate rings for each of these three complexes are pairwise equivalent. The coupling constants associated with the six-membered rings of these three complexes indicate that all the six-membered chelate rings adopt a stable chair conformation. As shown in Tables I–III, J_{gf} (=3 Hz) falls near the usual range for gauche hydrogen ($\theta \simeq 60°$; 3.8–4.4 Hz),[12-14] while J_{eg}(=11–12 Hz) is consistent with trans hydrogen ($\theta \simeq 180°$; 10.0–12.4 Hz).[11-14] The values of the chemical shifts of the methyl groups

(12) Ito, T.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1970**, *32*, 155–164.
(13) Yano, S.; Ito, H.; Koike, Y.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3184–3189.
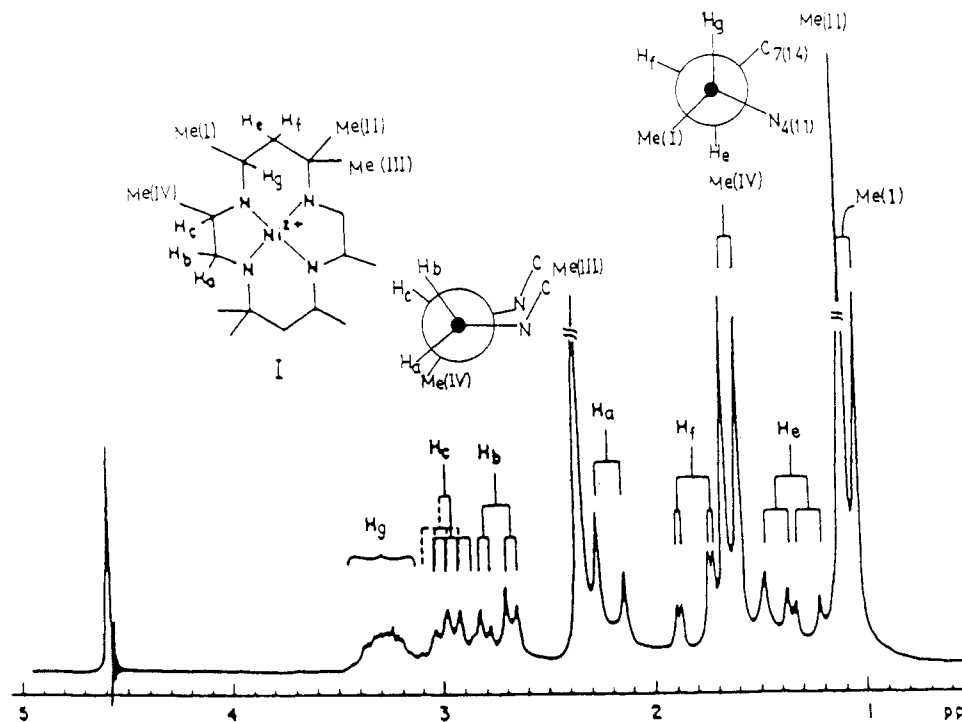(14) Ito, T.; Saito, H.; Ito, H. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 607–610.

Figure 2. 400-MHz ¹H NMR spectrum of [Ni(α-Me₈cyclam B)]²⁺ (chloride salt) in D₂O. Chemical shifts are expressed downfield from the internal standard sodium 4,4-dimethyl-4-silapentane-1-sulfonate.
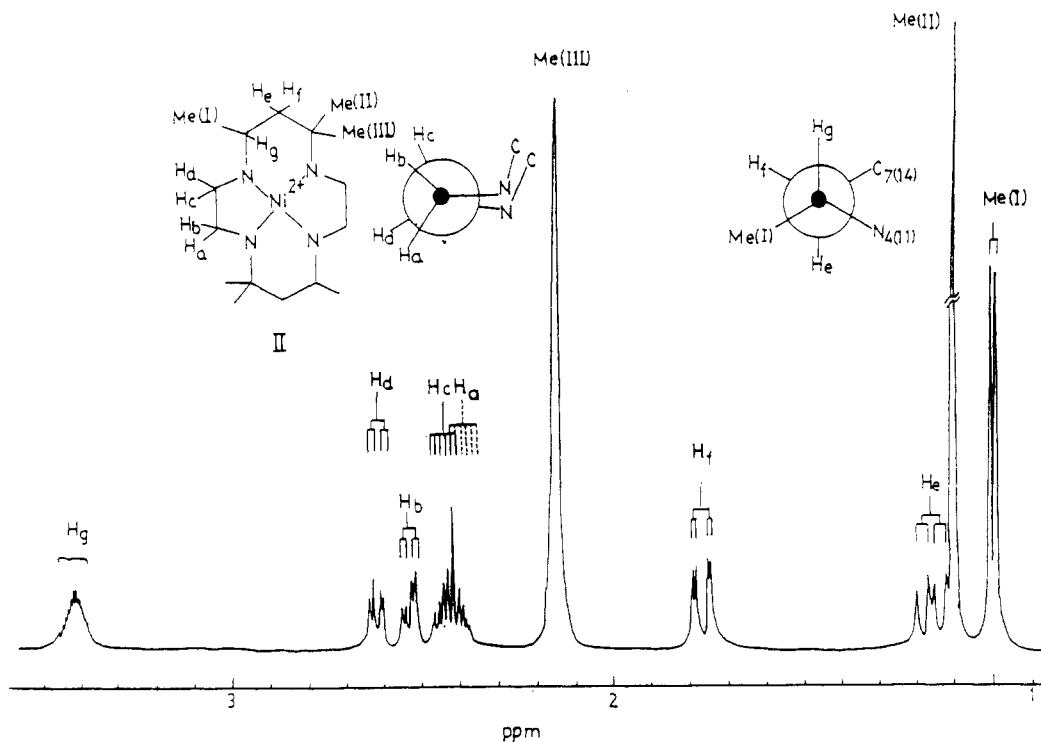

Figure 3. 400-MHz ¹H NMR spectrum of the [Ni(β-rac-1,7-CTH)]²⁺ (perchlorate salt) in D₂O. Chemical shifts are expressed downfield from the internal standard sodium 4,4-dimethyl-4-silapentane-1-sulfonate.

attached to the asymmetric carbons for these three complexes indicate these methyl groups are equatorial. From the values of both the resonance positions and the coupling constants listed in Tables I–III, it is concluded that the six-membered chelate rings of these three complexes adopt the most stable chair form and are virtually unaffected by the methyl substituents.

The number of resonance signals indicates that the two five-membered chelate rings for each of these three complexes are pairwise equivalent. In contrast with the six-membered chelate rings, the five-membered rings of these three complexes adopt unstable, distorted conformations and are strongly affected by the methyl substituents. The coupling constants associated with the

five-membered rings are significantly different among these three complexes. The values of the vicinal coupling constants given in Tables I–III indicate that the five-membered chelate rings for [Ni(β-meso-1,4-CTH)]²⁺ are very nearly eclipsed. On the other hand, those for [Ni(β-rac-1,7-CTH)]²⁺ and [Ni(α-Me₈cyclam B)]²⁺ adopt distorted gauche conformations.

It is interesting to note that the value of J_{ac} for [Ni(a-Me₈-cyclam B)]²⁺ (<0.5 Hz) is much smaller than that for [Ni(β-rac-1,7-CTH)]²⁺ (J_{ac} = 12 Hz). From these values, the dihedral angle θ_{ac} for [Ni(β-Me₈cyclam B)]²⁺ is about 90°, while that for [Ni(β-rac-1,7-CTH)]²⁺ is about 165°; so the conformation of the five-membered rings of [Ni(α-Me₈cyclam B)]²⁺ is significantly
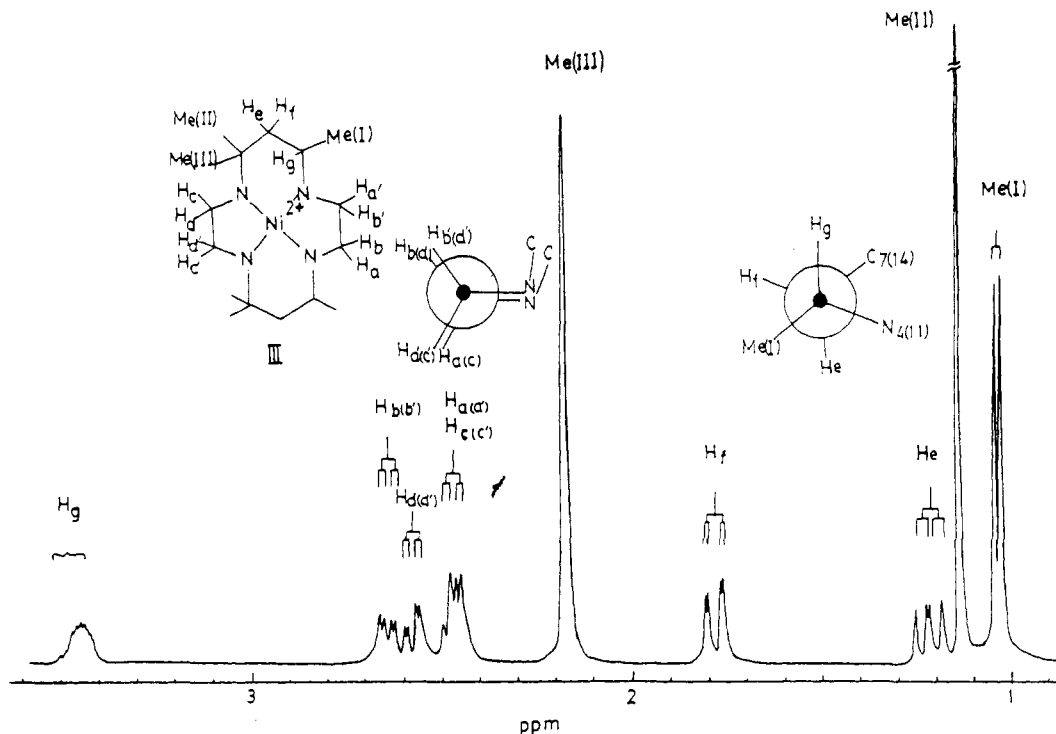
Figure 4. 400-MHz ^{1}H NMR spectrum of the [Ni(β-meso-1,4-CTH)]$^{2+}$ (perchlorate salt) in D_2O. Chemical shifts are expressed downfield from the internal standard sodium 4,4-dimethyl-4-silapentane-1-sulfonate.
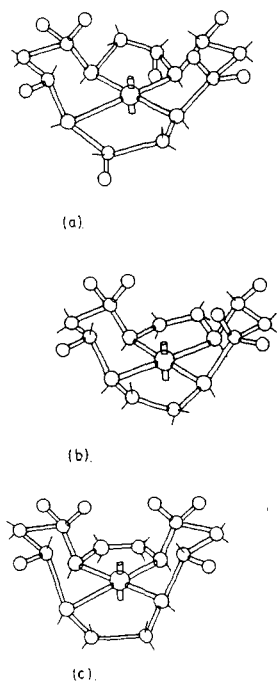

Figure 5. Idealized structures for (a) [Ni(α-Me$_8$cyclam B)]$^{2+}$, (b) [Ni(β-rac-1,7-CTH)]$^{2+}$, and (c) [Ni(β-meso-1,4-CTH)]$^{2+}$.

different from that of [Ni(β-rac-1,7-CTH)]$^{2+}$, as shown in Figures 2 and 3. For [Ni(β-rac-1,7-CTH)]$^{2+}$, H$_b$ and H$_d$ are equatorial, while H$_a$ and H$_c$ are axial. For [Ni(β-Me$_8$cyclam B)]$^{2+}$, H$_a$ and H$_c$ are equatorial, while H$_b$ and Me(IV) are axial.

The chemical shifts of the protons on the five-membered rings drastically depend on the conformational character (i.e., axial or equatorial) of the resonance protons.[1,2,15] As shown in Tables I and II, the resonance of the axial H$_c$ for [Ni(β-rac-1,7-CTH)]$^{2+}$ appears in the high-field portion of the spectrum at 2.45 ppm; that of the equatorial H$_c$ for [Ni(α-Me$_8$cyclam B)]$^{2+}$ appears in the low-field portion of the spectrum at 2.99 ppm. In contrast,

(15) Dei, A. *Inorg. Chem.* **1979**, *18*, 891–894.

the resonance of the axial H$_b$ for [Ni(α-Me$_8$cyclam B)]$^{2+}$ appears in the low-field portion of the spectrum at 2.75 ppm; that of the equatorial H$_b$ for [Ni(β-rac-1,7-CTH)]$^{2+}$ appears in the high-field portion of the spectrum at 2.53 ppm.

The configurations of the asymmetric carbon and nitrogen centers of these three complexes have previously been reported.[1-3,9,10] The structures of these three complexes derived from their proton magnetic resonance spectra are shown in Figure 5. The six-membered chelate rings for these three complexes adopt the most stable chair conformation; the five-membered rings adopt unstable, distorted conformations because of the opposite configuration of the consecutive pair of asymmetric nitrogens across the mouth of each of these five-membered rings. It is most interesting to note that the conformations of the five-membered rings for these three complexes are significantly different from each other, as shown in Figure 5. The Drieding models for these structures indicate that the relative stabilities of the conformations of five-membered rings for these three complexes vary in the sequence [Ni(β-rac-1,7-CTH)]$^{2+}$ > [Ni(α-Me$_8$cyclam B)]$^{2+}$ > [Ni(β-meso-1,4-CTH)]$^{2+}$. If the five-membered rings of [Ni(α-Me$_8$cyclam B)]$^{2+}$ adopted the same conformation as that of [Ni(β-rac-1,7-CTH)]$^{2+}$, Me(IV) would be equatorial and a very large steric interaction between this equatorial Me(IV) and Me(I) would result. In order to avoid this large steric interaction, the five-membered rings of [Ni(α-Me$_8$cyclam B)]$^{2+}$ adopt a very distorted gauche conformation in which Me(IV) is in an axial orientation, as shown in Figure 5. If the five-membered rings of [Ni(β-meso-1,4-CTH)]$^{2+}$ adopted a distorted gauche conformation such as that of [Ni(β-rac-1,7-CTH)]$^{2+}$ or that of [Ni(α-Me$_8$-cyclam B)]$^{2+}$, a very large steric interaction between the two axial methyl groups [Me(III) and Me'(III)] on the six-membered rings would result. In order to increase the distance between these two axial methyl groups, the five-membered rings of [Ni(β-meso-1,4-CTH)]$^{2+}$ adopt an unstable conformation that is very nearly eclipsed.