The Stereoisomers of a Macrocyclic Nickel(II) Complex Containing Six Asymmetric Centers. Factors Determining the Stabilities of Configurations and Conformations

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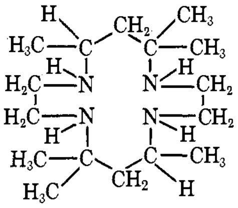
Abstract: The complex ion $Ni(1,7\text{-}CTH)^{2+}$ (structure I) can exist in 20 theoretically possible isomeric forms, depending on the configurations of the two asymmetric carbon centers and the four asymmetric nitrogen centers. Three isomers have been characterized. Thorough stereochemical analysis combined with pmr and infrared spectral data permit assignments of structures to these species. From the structures that exist and the analysis presented, it may be inferred that (a) the stabilities of the definable conformations for six-membered chelate rings vary in the sequence chair > twist > boat; (b) when either of two linked five-membered and six-membered chelate rings must exist in an unfavorable conformation in order for the other to exist in a favorable conformation, the six-membered ring will have the stable form; and (c) the selection of the equatorial over the axial site for such bulky groups as CH_3 is at least as large for six-membered chelate rings as for five-membered chelate rings.

Since the proper analysis of the conformations of five-membered diamine chelate rings by Corey and Bailar,[1] use of their results has led to significant advances in the stereochemistries of many kinds of complexes. The intricate isomer patterns possible for such ligands as 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (structure I, abbreviated 1,7-CTH)[2] now permit us to assess certain parallel relationships for the very common six-membered diamine chelate rings.

Stereochemical Considerations

Bosnich, Tobe, *et al.*,[3] have discussed the stereochemistry of the corresponding unsubstituted macrocycle (cyclam). They point out the possible existence of five basic structural forms, as determined by the distribution of nitrogen atom configurations with respect to five- and six-membered chelate rings. These are of fundamental importance to the discussion to follow.



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Each secondary amine proton is approximately axial and either resides above or below the plane containing the nickel and four nitrogen atoms. Three of these forms are nonenantiomeric (a, b, and c; see Figure 1) and two are enantiomers (d and e, Figure 1). The numerals 3 and 2, respectively, represent the 3 and 2 carbon chains which span adjacent coordinated secondary amines. The + and − notation represents secondary amine protons above and below the nickel(II)–four nitrogen plane, respectively.

Assuming the chelate ring conformers which are analogous to those predicted[3] to be the most strain free for $Co(cyclam)X_2^{3+}$, there are 4 *meso* and 16 racemic diastereoisomers for the $Ni(1,7\text{-}CTH)^{2+}$ system. These diastereoisomers arise not only from the asymmetry of the four nitrogen donor atoms and their various combinations, but also from the asymmetry of two carbon atoms present in the macrocyclic ligand. These asymmetric carbons occur at positions 7 and 14 in the ligand 1,7-CTH. The ligand positional isomer 1,7-CTH has two diastereomeric forms, C-*meso* and C-racemic. The two asymmetric carbons of the C-*meso* form are of opposite configurations, *R* and *S*, while the two asymmetric carbons within each enantiomeric form of the racemate are of the same *R* or *S* configuration.[4]

The occurrence of a center of symmetry (i), a reflection plane (σ), or an even improper rotation axis (S_n) in the point group describing a given $Ni(CTH)^{2+}$ isomer identified the structure as a *meso* diastereoisomer. The absence of these elements of symmetry affords the possibility of racemic forms. The *meso* diastereoisomers of $Ni(1,7\text{-}CTH)^{2+}$ belong to the C_i point group which has, in addition to identity, E, a center of inversion (i) as its symmetry element. The racemic forms belong either to the C_2 point group, whose only element of symmetry, besides E, is a twofold axis of rotation, or to the point group C_1 which has only the identity element E.[5]

As shown in Tables I and II there are ten diastereoisomeric forms each for $Ni(\textit{meso}\text{-}1,7\text{-}CTH)^{2+}$ and for $Ni(\textit{dl}\text{-}1,7\text{-}CTH)^{2+}$. These forms differ from each other in one or more of the following: basic form (NH orientations, as in Figure 1), point group, orientation of the methyl groups on the asymmetric carbon atoms, conformations of the chelate rings, or position of the

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[1] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[2] We have adopted the notation 1,7-CTH for this ligand in order to relate by label to its parent, the corresponding 1,7-diene, which is the famous macrocycle of Curtis: N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

[3] B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1100 (1965); B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

[4] The *R–S* nomenclature for absolute configurations is that of Cahn and Ingold as described by E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 92.

[5] F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963.

Table I. The Possible Stereoisomers of Ni(*meso*-1,7-CTH)$^{2+}$

Isomer no.	Point group	Basic form (Figure 1)	Chelate ring conformations[a]	Methyl on asym carbon[b]
1	C_i	b	CC; gRgS	ee
2	C_i	b	CC; gRgS	aa
3	C_i	c	TRTS; pp	ee
4	C_i	c	TRTS; pp	aa
5	C_1	a	CC; pp	ae
6	C_1	d	CT; gg′	ea[c]
7	C_1	d	CT; gg′	ae[c]
8	C_1	d	CT; gg′	aa′[d]
9	C_1	d	CT; gg′	ee′[d]
10	C_1	e	TRTR; gRgR	ae

[a] The conformations of six-membered rings are indicated first by either C (for chair) or T (for twist), followed by the five-membered rings which are either g (gauche) of p (eclipsed). R and S indicate the antipodal configurations of the dissymmetric rings. Nonequivalent rings are indicated by the prime. [b] Axial (a) and equatorial (e) orientations are indicated. Nonequivalent positions are indicated by the prime. [c] Asymmetric carbon is opposite the unique nitrogen. [d] Asymmetric carbon is adjacent to the unique nitrogen.

Table II. The Possible Stereoisomers of Ni(*rac*-1,7-CTH)$^{2+}$

Isomer no.	Point group	Basic form (Figure 1)	Chelate ring conformations[a]	Methyl on asym carbon[b]
1	C_2	a	CC; pp	ee
2	C_2	a	CC; pp	aa
3	C_1	b	CC; gRgS	ae
4	C_1	c	TRTS; pp	ae
5	C_1	d	TC; gg′	aa[c]
6	C_1	d	TC; gg′	ee[c]
7	C_1	d	TC; gg′	ae[d]
8	C_1	d	TC; gg′	ea[d]
9	C_2	e	TRTR; gRgR	aa
10	C_2	e	TRTR; gRgR	ee

[a] The conformations of six-membered rings are indicated first by either C (for chair) or T (for twist), followed by the five-membered rings which are either g (gauche) or p (eclipsed). R and S indicate the antipodal configurations of the dissymmetric rings. Nonequivalent rings are indicated by the prime. [b] Axial (a) and equatorial (e) orientations are indicated. Nonequivalent positions are indicated by the prime. [c] Asymmetric carbon is opposite the unique nitrogen. [d] Asymmetric carbon is adjacent to the unique nitrogen.

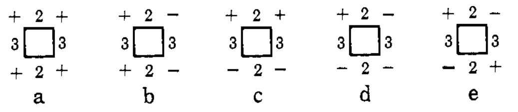
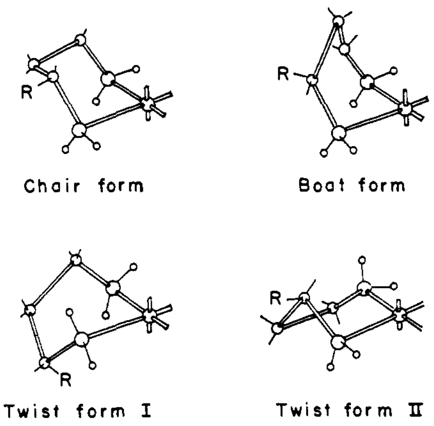


Figure 1. Schematic representations of the basic forms of M(cyclam)$^{2+}$ and M(CTH)$^{2+}$.

methyl of the asymmetric carbon with respect to a unique nitrogen atom.

Although a more complete analysis appears elsewhere,[6] brief attention must be given to the six-membered ring conformations. Figure 2 shows the familar *chair* and *boat* forms adapted to chelate rings and the asymmetric *twist* forms that are of importance only in fused-ring systems. In order to incorporate the latter conformation into a fused-ring system, the equatorial bonds to hydrogens are replaced by bonds between the nitrogen and further ring members. This so constrains the structure that interchange between twist and chair (or boat) forms requires the prior rupture of a bond. In contrast, the chair and boat conformers are interchangeable without bond cleavage. The boat form would place the two geminal methyl's both in equatorial sites. All the basic forms (Figure 1) except d have pairs of chelate rings of the same conformational type. In form d, one six-membered ring has the chair and the other the twist conformation. Tables I and II also summarize the conformations.



Chair form

Boat form

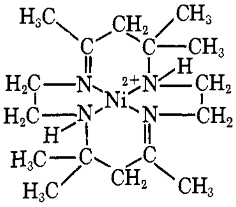
Twist form I

Twist form II

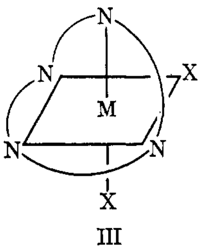
Figure 2. Conformations of saturated six-membered diamine chelate rings.

Isomers of Ni(1,7-CTH)$^{2+}$

Ni(1,7-CTH)$^{2+}$ is prepared by reduction of the two imine functions of Ni(1,7-CT)$^{2+}$ (structure II).[2,7,8] This hydrogenation produces two asymmetric carbon centers and two new nitrogen asymmetric centers. The presence of the asymmetric carbons results in the existence of noninterconvertible diastereoisomers for both the free ligand 1,7-CTH and its metal complexes. Thus, the hydrogenation of the two imine groups generates the two basic diastereoisomers Ni(*meso*-1,7-CTH)$^{2+}$ and Ni(*rac*-1,7-CTH)$^{2+}$. Based on symmetry and steric arguments, Curtis[2,7,8] assumed that the *meso* ligand can coordinate only with its four donor atoms arrayed in a single plane, while the racemic ligand may coordinate in either this planar fashion or in a folded form (structure III). On this basis, the isomers called *tet a* and *tet b* by Curtis are equated to the *meso* and racemic forms of 1,7-CTH, respectively. This has



II



III

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(6) L. G. Warner and D. H. Busch, "Coordination Chemistry—Papers Presented in Honor of Professor John C. Bailar, Jr.," Plenum Press, New York, N. Y., 1969.

(7) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

(8) N. F. Curtis, *ibid.*, *C*, 1979 (1967).

Table III. Infrared Data for the Ni(1,7-CTH)(ClO$_4$)$_2$ Isomers[a,b]

Isomer	ν(NH)	ν(CO)	ν_3(ClO)$_4$	ν_4(ClO$_4$)
Ni(*meso*-1,7-CTH)$^{2+}$	3185 s, sp	...	1095 s, br	623 s, sp
$\{$[Ni(*rac*-1,7-CTH)]$_2$C$_2$O$_4\}^{2+}$	3257 s, sp	1645 s, br	1099 s, sp	625 s, sp
α-Ni(*rac*-1,7-CTH)$^{2+}$	3215 sh	...	1110 s, br	625 s, sp
	3195 s, sp			
	3175 sh			
β-Ni(*rac*-1,7-CTH)$^{2+}$	3195 s, sp	...	1110 s, br	625 s, sp

[a] All units in cm^{-1}. [b] sp = sharp, sh = shoulder, br = broad, s = strong.

Table IV. Electronic Absorption Spectra for the Ni(1,7-CTH)(ClO$_4$)$_2$ Isomers[a]

			$\nu_{\max}$ ($\epsilon_{\max}$)	
Isomer	Color	Medium	30 min	17 hr
Ni(*meso*-1,7-CTH)$^{2+}$	Yellow-orange	H$_2$O	21,600 (80)	21,600 (80)
		H$_2$O[b]	21,700 (79)	...
[Ni(*rac*-1,7-CTH)]$_2$C$_2$O$_4$$^{2+}$	Blue	Nujol	10,100 m, br	...
			17,000 m	...
			27,100	...
		Reflectance[b]	10,100	...
			17,200	...
			28,600	...
α-Ni(*rac*-1,7-CTH)$^{2+}$	Yellow	Nujol	22,700	...
		10^{-2} *N* HClO$_4$	22,400 (68)	22,400 (68)
		H$_2$O	22,400 (68)	22,100 (105)
		H$_2$O[b]	22,570 (70)	...
β-Ni(*rac*-1,7-CTH)$^{2+}$	Orange	10^{-2} *N* HClO$_4$	22,100 (105)	22,100 (105)
		H$_2$O	22,100 (105)	22,100 (105)
		Nujol	22,100	...

[a] All units in cm^{-1}. [b] Data from ref 2 and 7.

been confirmed by X-ray crystallographic analyses.[2,7,9] Curtis[7,8] has also reported that Ni(*rac*-1,7-CTH)$^{2+}$ exists in α and β isomeric forms, which was first ascribed to "conformational isomerism" but has more recently been ascribed to differences in configurations of the asymmetric nitrogens. Very little information has previously been published concerning the synthesis, characterization, and diastereoisomeric relationships of these isomers. The present study leads to clarification of these matters.

Following the general procedures described by Curtis[7] for the reduction of the imine functions of the complex Ni(1,7-CT)(ClO$_4$)$_2$ yields two species. The first is yellow-orange Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$. It precipitates from the reduction mixture upon acidification with perchloric acid and cooling and is purified by recrystallization. The second is the blue oxalate-bridged dimer $\{$[Ni(*rac*-1,7-CTH)]$_2$C$_2$O$_4\}$(ClO$_4$)$_2$. This oxalate-bridged dimer is only sparingly soluble in water so it is easily washed free of contaminating traces of the first isomer.

The infrared spectrum of Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$ shows ν(NH), but no ν(CN of imine) (Table III), thus indicating complete reduction. Incomplete reduction of the imine functions of Ni(1,7-CT)(ClO$_4$)$_2$ gives a macrocyclic monene nickel(II) complex[10] which is reported to contaminate Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$.[8] No such contamination was observed in this study. The characteristic ionic perchlorate bands, ν_3 and ν_4,[11,12] occur at 1095 and 623 cm^1, respectively (Table III). The electronic absorption spectrum shows only one band at 21,600 cm^{-1}, which is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition of square-planar nickel(II) complexes (Table IV). This spectrum agrees well with that reported by Curtis.[7]

The oxalate-bridged dimer exhibits an electronic spectrum which is typical of triplet-state, six-coordinated nickel(II). The three bands which occur at about 10,000, 17,000, and 27,000 cm^{-1} (Table IV) are assigned, respectively, to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The infrared spectrum shows the characteristic ν(NH), ν_3(ClO$_4^-$), and ν_4(ClO$_4^-$) bands (Table III). Only one ν(CO) band occurs for the C$_2$O$_4$$^{2-}$ anion, thus indicating the equivalence of both the carboxylate functions.[13,14] This dimeric complex contains Ni(II) in a *cis*-N$_2$O$_2$ coordination environment, and the macrocyclic tetramine ligand is folded into its *cis* conformation (structure III). The oxalate is coordinated as a bidentate ligand and forms five-membered chelate rings.[13,14]

Decomposition of the oxalate-bridged dimer by stirring at room temperature in 40% aqueous perchloric acid yields a yellow powder which is the α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$ isomer. It is sparingly soluble in 10^{-2} *N* HClO$_4$, but can be recrystallized from this medium by dissolving at room temperature and cooling in a refrigerator for 12 hr. Decomposition of the oxalate-bridged dimer in basic aqueous media in the presence of CaCl$_2$ yields the orange β-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$ isomer upon reacidification of the solution after removal of the CaC$_2$O$_4$. This isomer is easily recrystallized from acidic or neutral aqueous solution. Both these isomers are square-planar nickel(II) complexes as is evident from their electronic absorption spectra, which show only the characteristic $^1A_{1g} \rightarrow {}^1E_g$ band in the 21,000–23,000-cm^{-1} region (Table IV).

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(9) M. Bailey, private communication.

(10) N. F. Curtis, *Chem. Commun.*, 88 (1966).

(11) B. J. Hathaway, D. G. Holah, and M. Hudson, *J. Chem. Soc.*, 4586 (1963).

(12) B. J. Hathaway and A. E. Underhill, *ibid.*, 309 (1961).

(13) N. F. Curtis, *ibid.*, 4109 (1963).

(14) N. F. Curtis, *ibid.*, *A*, 1584 (1968).

Isomerism in the Ni(CTH)$^{2+}$ system is expected to be due primarily to the configurations about the two asymmetric carbons and four asymmetric coordinated secondary amine nitrogens for these complexes. The latter asymmetric centers are capable of configurational inversion after deprotonation, and this property was used in attempts to generate isomeric forms of Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$. The initially prepared isomer was recrystallized from neutral and acidic aqueous media and by dissolving in hot aqueous sodium hydroxide and then precipitating by dumping into an ice–60% HClO$_4$ mixture. No evidence for any species other than the starting material was detected *via* fractionation from 10^{-2} *N* HClO$_4$ and examination *via* absorption, infrared, and pmr spectroscopy. These observations coupled with the fact that the singlet–singlet transition at 21,600 cm^{-1} remains constant in both its band position and extinction coefficient over 17 hr (Table IV) suggest the presence of only one stable diastereoisomer due to the asymmetry of the four coordinated secondary amine nitrogens. The occurrence of a rapidly established equilibrium between diastereoisomers of Ni(*meso*-1,7-CTH)$^{2+}$ which have very similar physical properties is not ruled out. However, the resolution and simplicity of the pmr spectra of each sample of this complex (see later section) lead to the conclusion that there is only one thermodynamically stable diastereoisomer for this complex.

It is obvious that α- and β-Ni(*rac*-1,7-CTH)$^{2+}$ are diastereoisomers related through configurational differences among the coordinated asymmetric secondary amine nitrogens. The α isomer, being square planar and formed in a strong acid medium by elimination of the bidentate oxalate in the oxalate-bridged dimer, must contain the same ligand isomer as the parent, with respect to the set of four asymmetric nitrogen configurations. Ligand isomerization from the parent complex to the α isomer must only involve a macrocyclic ligand conformational change from the folded *cis* form to the planar *trans* form. In 10^{-2} *N* HClO$_4$ the absorption band position and extinction coefficient for the spectrum of the α isomer remains constant (Table IV). However, in neutral aqueous media the band position and extinction coefficient change to eventually correspond to those of the β isomer. In contrast, the absorption band position and extinction coefficient of the spectrum of the β isomer remain constant as a function of time in neutral or basic aqueous media (Table IV). These observations indicate that the α isomer readily isomerizes to the β isomer under conditions where there can be significant amine proton exchange. The presence of the α isomer in neutral aqueous solutions of the β isomer had been demonstrated by the formation of the highly insoluble α-Ni(*rac*-1,7-CTH)(NCS)$_2$ derivative from concentrated solutions of the β-diperchlorate by addition of NaNCS. Therefore, in neutral aqueous solutions there must exist the equilibrium

$$\alpha\text{-Ni}(rac\text{-1,7-CTH})^{2+} \rightleftharpoons \beta\text{-Ni}(rac\text{-1,7-CTH})^{2+}$$

It is strongly shifted toward the β isomer. The β isomer must, therefore, contain the set of four asymmetric nitrogen configurations which gives rise to the thermodynamically most stable square-planar complex containing the *rac*-1,7-CTH ligand. The α isomer contains that set of nitrogen configurations which yields the most stable isomer containing the ligand coordinated in the *cis* or folded conformation, a conformation that can only be stablized by the incorporation of a bidentate chelate in the nickel(II) coordination sphere. In the absence of a bidentate ligand α-*rac*-1,7-CTH readily isomerizes to assume an unstable *trans* or planar conformation which can only be preserved by inhibiting proton exchange, thereby preventing changes in the configurations of the coordinated secondary amine nitrogens.

Both the Ni(*meso*-1,7-CTH)$^{2+}$ and β-Ni(*rac*-1,7-CTH)$^{2+}$ isomers dissolve in H$_2$O, acetone, dimethyl sulfoxide (DMSO), and acetonitrile to give yellow solutions which show the single electronic absorption band that is characteristic of four-coordinate, square-planar nickel(II) complexes (Table V). However, while α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$ dissolves in water and acetone to give yellow, square-planar species, it readily dissolves in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile to give blue, green, and violet solutions, respectively. These solutions show the presence of both triplet and singlet ground-state nickel(II) complexes. The electronic absorption spectra of these solutions show the characteristic absorption for square-planar nickel(II), ν_s, and for tetragonally distorted, pseudo-octahedral, triplet nickel(II).

Table V. Electronic Absorption Spectra for Ni(1,7-CTH)(ClO$_4$)$_2$ Isomers in Nonaqueous Media

Isomer	Solvent	Color	ν	$\nu_{\max}{}^{a}$ ($\epsilon_{\max}$)
Ni(*meso*-1,7-CTH)$^{2+}$	CH$_3$CN	Yellow	ν_s	21,300 (63)
β-Ni(*rac*-1,7-CTH)$^{2+}$	CH$_3$CN	Yellow	ν_s	21,700 (101)
α-Ni(*rac*-1,7-CTH)$^{2+}$	Acetone	Yellow	ν_s	22,030 (71)
	DMSO^{b}	Green	ν_1	9,680 (15)
			ν_2	. . .
			ν_3	. . .
			ν_4	16,360 (11)
			ν_s	22,500 (27)
			ν_5	26,240 (25)
	DMF^{b}	Blue	ν_1	10,150 (23)
			ν_2	12,580 (sh)
			ν_3	. . .
			ν_4	18,050 (14)
			ν_s	22,080 (4)
			ν_5	26,810 (31)
	CH$_3$CN^{b}	Violet	ν_1	10,810 (12)
			ν_2	12,270 (9)
			ν_3	. . .
			ν_4	17,980 (16)
			ν_s	22,470 (8)
			ν_5	27,860 (24)

[a] All units in cm^{-1}. [b] Solutions contain equilibrium mixtures of singlet and triplet states; ν_s = singlet band, ν_1 to ν_5 = triplet bands.

As seen in Table VI the intensity of the ν_s ($^1A_{1g} \rightarrow {}^1E_g$) band increases while the intensities of the ν_1 ($^3B_{1g} \rightarrow {}^3E_g$) and ν_4 ($^3B_{1g} \rightarrow {}^3E_g$, $^3A_{2g}$(F)) bands decrease as the temperature of the α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$–

Table VI. Temperature Dependence of the Absorption Spectra for α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$ in DMSO

Spectral band, cm^{-1}	Absorbance			
	17°	32°	47°	64°
ν_1 (9680)	0.438	0.409	0.367	0.326
ν_4 (16,370)	0.253	0.251	0.241	0.237
ν_5 (26,100)	0.719	0.629	0.636	0.660
ν_s (22,500)	0.825	0.853	0.998	1.183

DMSO solution increases. The temperature dependence of the changes in absorption for the triplet and singlet state species is reversible and indicates the occurrence of the following equilibrium for this α isomer in DMSO, DMF, and acetonitrile (s = a solvent molecule).

$$\underset{\text{planar, singlet}}{\alpha\text{-Ni}(rac\text{-}1,7\text{-CTH})^{2+}} + 2\text{s} \rightleftharpoons \underset{\text{tetragonal, triplet}}{[\alpha\text{-Ni}(rac\text{-}1,7\text{-CTH})\cdot 2\text{s}]^{2+}}$$

As the temperature increases the equilibrium is shifted in favor of the planar, singlet nickel(II) species.

The singlet band, ν_s, overlaps the triplet bands, ν_4 and ν_5, but not ν_1. The large amount of overlap between ν_s and ν_5 is believed to account for the erratic variation in the intensity of the latter as a function of temperature. This overlap and the fact that the extinction coefficients of the singlet and triplet state bands are not known make quantitative analysis of the equilibrium data impossible without additional data.

Water is a good donor solvent and exhibits as great a ligand field strength as DMSO and DMF, yet only singlet-state, square-planar species are observed when α-Ni(*rac*-1,7-CTH)$(ClO_4)_2$ is dissolved in aqueous media. Macrocyclic complexes of the type represented by Ni(CTH)$^{2+}$ have been described[15] as "irregular doughnut-shaped masses of hydrophobic material with positively charged Lewis acids occupying the hole." It is suggested that the hydrophobic nature of these complexes imposes restrictions upon the ability of water to be separated from the bulk of the solvent and to coordinate by inducing bulk solvent structuring. A second restriction would be the possible tendency of water to hydrogen bond to the secondary amine protons which lie approximately parallel to the axial coordination positions of Ni(CTH)$^{2+}$ complexes. In either case the availability of water and axial sites of the Ni(II) complex for coordination would be significantly reduced.

Not only does water fail to coordinate with the isomer, it seems to induce conversion from the triplet to singlet state. Attempts were made to isolate the solid derivatives, [α-Ni(*rac*-1,7-CTH)·2s]$(ClO_4)_2$, by evaporation of DMSO, DMF, and acetonitrile solutions of the isomer to dryness or by the addition of ether. Violet solids were obtained, but they very rapidly turned yellow upon contact with a moist atmosphere. These yellow solids were found to be the anhydrous parent, α-Ni(*rac*-1,7-CTH)$(ClO_4)_2$. The violet solvated adducts were not further characterized. This solid-state reaction from triplet to singlet state nickel(II) with loss of monodentate ligands from the coordination sphere is very similar to that observed for the high-spin coordination-number isomer of *meso*-Ni(1,7-CT)$(NCS)_2$.[16]

Isomers of Ni(1,7-CTH)(NCS)$_2$. Addition of NaNCS to an acidic aqueous solution of α-Ni(rac-1,7-CTH)$(ClO_4)_2$ causes an immediate precipitation of the very insoluble, light blue dithiocyanato derivative of this isomer. Similar additions to acidic aqueous solutions of Ni(*meso*-1,7-CTH)$(ClO_4)_2$ and β-Ni(*rac*-1,7-CTH)$(ClO_4)_2$ causes no precipitation or color change. However, the corresponding dithiocyanato derivatives were isolated by extraction of these mixed perchlorate–thiocyanate solutions with chloroform. The resulting violet chloroform solutions yield violet solids upon evaporation almost to dryness.

These dithiocyanato derivatives of Ni(*meso*-1,7-CTH)$^{2+}$ and α- and β-Ni(*rac*-1,7-CTH)$^{2+}$ exhibit magnetic moments of 3.15, 3.17, and 3.16 BM, respectively, and are typical of six-coordinated nickel(II). Their electronic absorption spectra, both in the solid state and in chloroform solutions, are typical of tetragonally distorted, pseudo-octahedral nickel(II).[17,18] Therefore, these three isomeric complexes must contain two thiocyanate anions axially coordinated with the macrocyclic ligand being coordinated in a planar conformation. All three isomers show ν(CN or NCS$^-$) bands in the 2000–2100-cm^{-1} region of their infrared spectra (Table VII). Only one band is observed for Ni(*meso*-1,7-CTH)$(NCS)_2$ and α-Ni(*rac*-1,7-CTH)$(NCS)_2$ in both the solid and solution states. The β-Ni(*rac*-1,7-CTH)$(NCS)_2$ isomer, however, shows two bands split by 55 cm^{-1} in the solid state and 34 cm^{-1} in chloroform solution. This indicates that the axial sites are very similar, if not identical for the former two isomers, while in the latter isomer the two axial sites are quite different. The ν(CS) region of the infrared spectrum 620–860 cm^{-1}, which is used to determine the nature of thiocyanate coordination,[19] is obscured by macrocyclic ligand bands in each of these isomers. However, it is assumed that the thiocyanate is nitrogen bonded, since this is the normal mode for coordination in nickel(II) systems.

Table VII. Infrared Data for Ni(1,7-CTH)$(NCS)_2$ Isomers

Isomer	Medium	ν(CN of NCS), cm^{-1}
Ni(*meso*-1,7-CTH)$^{2+}$	Nujol	2058
	CHCl$_3$	2058
α-Ni(*rac*-1,7-CTH)$^{2+}$	Nujol	2079
β-Ni(*rac*-1,7-CTH)$^{2+}$	Nujol	2083, 2028
	CHCl$_3$	2083, 2049

Only the β-Ni(*rac*-1,7-CTH)$(NCS)_2$ isomer is soluble in nitromethane. It gives a yellow-orange solution whose molar conductance is 50 ohm^{-1} at a concentration of 5×10^{-3} *M*. The electronic absorption spectrum exhibits bands at 10,400, 21,700, and 27,400 cm^{-1} whose extinction coefficients are 5, 49, and $\sim$20, respectively. The 10,400- and 27,400-cm^{-1} bands have been tentatively assigned to the six-coordinated, tetragonal nickel(II) transitions ν_1 ($^3B_{1g} \rightarrow {}^3E_g$) and ν_5 ($^3B_{1g} \rightarrow {}^3E_g$, $^3A_{2g}(P)$), respectively. The 21,700-cm^{-1} band is assigned to the singlet-state, square-planar nickel(II) transition ν_s ($^1A_{1g} \rightarrow {}^1E_g$). The data indicate partial dissociation of thiocyanate anions and the presence of the equilibrium

$$\underset{\text{tetragonal, triplet}}{\beta\text{-Ni}(rac\text{-}1,7\text{-CTH})(\text{NCS})_2} \rightleftharpoons \underset{\text{planar, singlet}}{\beta\text{-Ni}(rac\text{-}1,7\text{-CTH})^{2+}} + 2\text{NCS}^-$$

Structural Assignments for the Diastereoisomers. Structural assignments for the diastereomers of the Ni(1,7-CTH)$^{2+}$ rest heavily upon pmr spectra of the dia-

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(15) D. H. Busch, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966.

(16) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Am. Chem. Soc.*, **90**, 6938 (1968).

(17) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 7, 1795 (1968).

(18) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).

(19) V. Gutman, *ibid.*, **2**, 239 (1967).

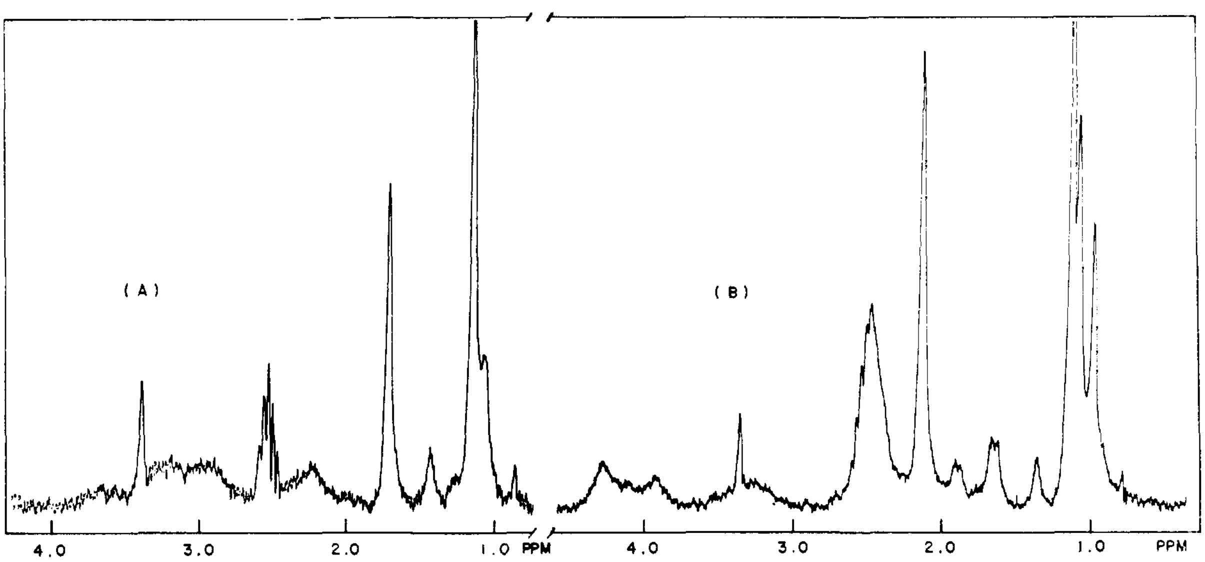

Figure 3. (A) Proton magnetic resonance spectrum of Ni(*meso*-1,7-CTH)$^{2+}$; (B) proton magnetic resonance spectrum of β-Ni(*rac*-1,7-CTH)$^{2+}$.

magnetic diperchlorate derivatives. The assignments of methyl proton resonances for these derivatives are given in Table VIII, and typical spectra are shown in Figure 3. Analyses of these pmr spectra have permitted conclusions to be made which relate not only to the gross structures of these isomers, but also to chelate ring conformations and orientations of peripheral methyl substituents.

Table VIII. Proton Magnetic Resonance Data for Ni(CTH)$^{2+}$ Isomers in DMSO Solutions[a,b]

Isomer	Me(I)		Me(II)	Me(III)	Δ(II-III)	$J_{\mathrm{Me(I)}}$[c]
Ni(*meso*-1,7-CTH)$^{2+}$	1.08 (3)	1.15 (3)	1.15 (6)	1.72 (6)	0.57	4.3
β-Ni(*rac*-1,7-CTH)$^{2+}$	0.97 (3)	1.07 (3)	1.11 (6)	2.12 (6)	1.01	6.0

[a] All chemical shifts in units of ppm downfield from internal TMS. [b] Estimated relative intensities are given in parentheses. [c] Units are cps.

The pmr spectra were obtained using DMSO as the solvent. Solutions of α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$ are paramagnetic; therefore, its spectrum was not obtained. No isomerizations or pmr spectral changes were observed over 24 hr, thus indicating the small tendency for secondary amine proton dissociation and amine nitrogen configurational inversion in d_6-DMSO. The weak broad resonances which appear in the 3.0–4.5-ppm region of each spectrum are believed to be due to these undissociated secondary amine protons. The multiplet at ~2.5 ppm and the singlet at ~3.4 ppm are solvent resonances and are due to partially protonated d_6-DMSO and water, respectively. The resonances of weak to medium intensity which occur in the 1.3–1.6-ppm region of the spectra are probably due to the protons on the methylene groups at the center of the six-membered chelate rings. The resonances of weak to medium intensity which occur in the low-field portion of the spectra between 2.0 and 3.0 ppm are assigned to those protons on the dimethylene chains of the five-membered chelate rings and to the protons attached to the asymmetric carbons. This latter assignment is based upon proximity of these groups to the deshielding coordinated secondary amine nitrogens. More detailed analysis of the resonances in these regions is not possible due to the low limits of resolution.

The most prominent features of these pmr spectra are the three to five sharp, intense resonances which appear between 0.95 and 2.20 ppm (Figure 3 and Table VIII). These resonances are due to the six methyl groups within each isomer. The orientation of the geminal carbon atom in a six-membered chelate ring in the twist or chair conformation produces an axial and equatorial distinction between the two geminal methyl groups (see, for example, Figure 4). Similarly, the asymmetric carbon of the six-membered chelate rings provides axial and equatorial distinctions for the group attached to it (Figure 4). Thus, the methyl group attached to this carbon can be either axial or equatorial. An axial group lies over the NiN$_4$ plane and its bond axis is approximately parallel with the axial coordination linkage of the metal ion. In contrast, an equatorial group lies out away from the metal ion center and its bond axis is parallel to the NiN$_4$ plane. Changing the conformation of a six-membered chelate ring to the boat form results in the loss of the axial and equatorial distinctions for the methyl groups. Such a conformation causes all the methyl group to be oriented out away from the metal ion center so that none of these groups reside over the NiN$_4$ plane.

The resonances due to the methyl groups attached to the asymmetric carbons (Me(I)) must be doublets, for they are coupled with the single proton attached to this carbon. This coupling should be associated with a constant of the order J = 2–9 cps.[20] A single dou-

(20) L. M. Jackman, "Applications of Nuclear Magnetic Resonance

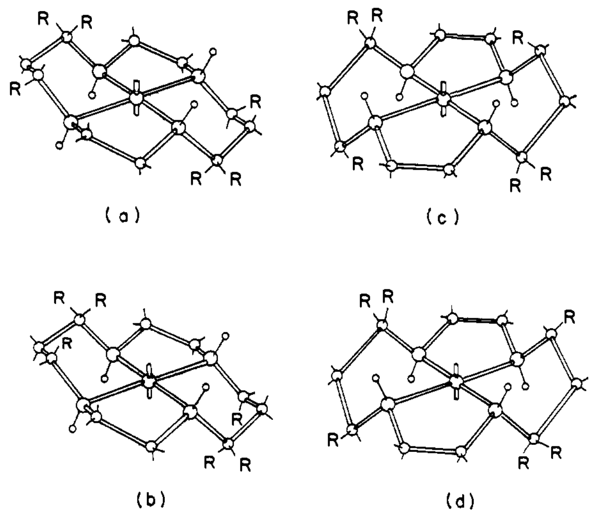

Figure 4. Idealized structures for Ni(*meso*-1,7-CTH)$^{2+}$.

blet, exhibiting a coupling constant of 3.7–6.1 cps, appears in the high-field portion of the pmr spectrum of each isomer. In the case of Ni(*meso*-1,7-CTH)$^{2+}$ the low-field component of this doublet overlaps completely with the resonance due to Me(II) (Figure 3, Table VIII).

The remaining methyl resonances are due to the axial and equatorial geminal methyl groups Me(III) and Me(II), respectively. The relatively large chemical shift differences (Δ(II–III)) observed here indicate that a relatively large nonbonding effect is occurring. This effect is identical with that observed for the geminal methyl group of the Ni(CT)$^{2+}$ system and is explained on the same basis.[21] Square-planar d_8 systems exhibit magnetic anisotropy with respect to the plane of the metal ion and four donor atoms. Protons which lie over this plane experience low-field shifts, while those which lie in the plane experience high-field shifts.[22] Therefore the equatorial methyl groups, Me(II), are assigned to the singlet in the high-field portion of the pmr spectra, and the axial methyl groups, Me(III), are assigned to the singlets which occur in the low-field portion of the spectra. The equatorial groups, Me(II), lie out away from the metal and out of the NiN_4 plane; therefore, they should give rise to resonances in the region normally expected for methyl groups attached to a saturated carbon. The axial groups Me(III) lie over the NiN_4 plane and in toward the metal ion center and experience deshielding by the anisotropy of the Ni(II) complex.

One consequence of these assignments, as shown in Table VIII, is that both methyl groups attached to the asymmetric carbons (Me(I)) must be equatorial in all of the Ni(1,7-CTH)$^{2+}$ isomers studied. Its resonance always occurs in the same region as the equatorial geminal methyl group (Me(II)). No doublets have been observed in the same low-field portion of the spectra where the axial geminal methyl resonances ((MeIII)) occur.

A second general conclusion is also readily drawn. In those cases where only one Me(III) resonance occurs in the low-field portion of these spectra, the two six-membered chelate rings within a given structure must have the same conformation. When two Me(III) resonances appear in the low-field portion of the spectra, the two six-membered chelate rings within that isomer must be of different conformations. The magnitude of the deshielding of protons over the plane of square-planar d^8 complexes is a function of the radial and angular orientation of the protons with respect to the axial site of the metal ion center. Therefore as the six-membered chelate ring conformations change, the axial methyl group orientation changes with respect to the NiN_4 plane. Any change in this orientation causes changes in the nonbonded chemical environment experienced by these methyl groups and gives rise to altered chemical shifts. On the other hand, methyl groups in equatorial positions lie out away from all other atoms in the complex. Therefore their relative nonbonded chemical environments change very little with changes in six-membered chelate ring conformations, and only one resonance pattern is observed for such groups.

If the six-membered chelate rings were of the boat conformation neither geminal methyl groups would be axial. As a result no methyl proton resonances would appear in the low-field portion of the spectrum; all these resonances would occur together in the 1.0–1.3-ppm region. This has not been observed.

The following summarizes the conclusions that can be made on the basis of the methyl proton resonance assignments and the observations made with respect to methyl group orientations and chelate ring conformations as a function of the point group for each of the possible diastereoisomeric structures (Tables I and II). (a) Those isomers which exhibit only one singlet (Me(III)) in the low-field portion of their pmr spectra must be *meso*-diastereoisomers of C_i symmetry or racemic diastereoisomers of C_2 symmetry. (b) All three isomers contain exclusively six-membered chelate rings of the twist and chair conformations. (c) The methyl groups attached to the asymmetric carbons are always equatorial.

The pmr spectrum of the Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$ isomer shows that the Me(I) doublet overlaps with the Me(II) singlet in the high-field portion of the spectrum. Only one Me(III) singlet occurs in the low-field portion of the spectrum (Table VIII, Figure 3). Consequently, according to observation a, it must be of symmetry C_i and be a *meso* diastereoisomer (Table I). This coincides with the preliminary X-ray data[2] on the Cu(*meso*-1,7-CTH)I$_2$ complex. It shows that the complex contains an inversion center. There are four possible structures (Figure 4) which are consistent with these data. Structures shown in Figures 4b and 4c can be eliminated because of the axial orientation of the methyl groups (Me(I)) which are bonded to the asymmetric carbons.

The structure of Figure 4a has the two secondary amine protons across the "mouth" of the six-membered chelate rings on the same side of the NiN_4, thus giving rise to chair conformations for these rings and staggered conformations for the five-membered chelate rings. Structure 4d has the two secondary amine protons

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Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 85.

[21] It has been shown in earlier studies (ref 16) that locating a CH$_3$ above the plane in such structures causes a large downfield shift.

[22] D. A. Buckingham and J. P. Stevens, *J. Chem. Soc.*, 4583 (1964).

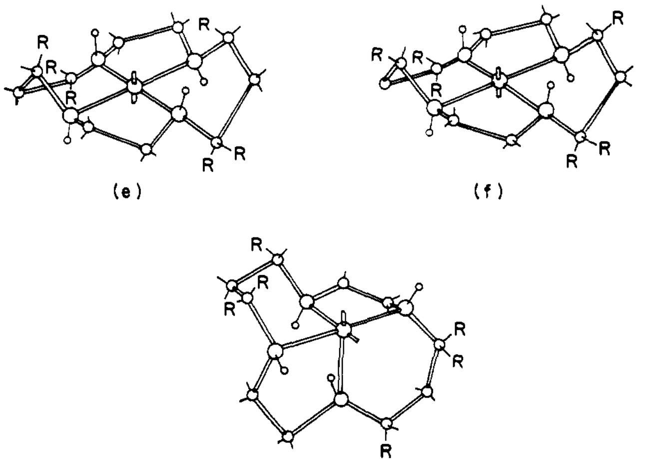

Figure 5. Idealized structures for α-Ni(*rac*-1,7-CTH)$^{2+}$.

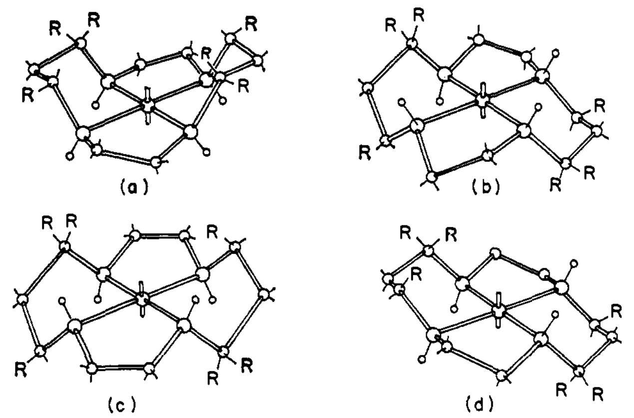

Figure 6. Idealized structures for β-Ni(*rac*-1,7-CTH)$^{2+}$.

across the mouth of the six-membered chelate rings on opposite sides of the NiN_4 plane. This causes the six-membered chelate rings to occur in the twist conformation and the five-membered chelate rings to be in the eclipsed conformation. This latter five-membered chelate ring conformation is not common in metal chelates.[1,23] The directly analogous Ni(cyclam)Cl_2 complex has the structure 4a (or 4b) (minus the methyl groups),[3] and no evidence for specific analogous to 4c or 4d has been found. Similarly there are three possible sets of secondary amine configurations in *trans*-[Co(trien)X_2]$^{n+}$, where the secondary amines are across the mouth of the five-membered chelate ring. The enantiomeric forms have staggered five-membered chelate rings while the *meso* diastereoisomer has an eclipsed five-membered chelate ring spanning the two secondary amine nitrogens. Only the racemic diastereoisomer has been observed.[24] On this basis the structure shown in Figure 4a is assigned to the Ni(*meso*-1,7-CTH)$^{2+}$ isomer (isomer 1, Table I).

The α-Ni(*rac*-1,7-CTH)(ClO_4)$_2$ isomer is paramagnetic in DMSO and is only slightly soluble in other solvents suitable for obtaining pmr spectra; thus no pmr spectrum was obtained. The structure of this isomer is easily inferred, however, because X-ray analysis of the [Ni(*rac*-1,7-CTH)(CH_3CO_2)]ClO_4 complex has been completed.[25] The structure of this acetato perchlorate derivative is shown in Figure 5. The macrocyclic ligand is coordinated in its folded or *cis* conformation and the acetate functions as a bidentate ligand which occupies *cis* coordination sites. The structure predicted by Bosnich, *et al.*,[3] for [*cis*-Co(cyclam)X_2]$^{n+}$ closely approximates the structure shown in Figure 5. The basic form for the set of four nitrogen configurations is e (Figure 1). It is easily concluded that the ligand form in the bridged oxalate dimer, {[α-Ni(*rac*-1,7-CTH)]$_2C_2O_4$}(ClO_4)$_2$, is identical with that of [Ni(*rac*-1,7-CTH)(CH_3CO_2)]ClO_4. Thus, α-Ni(*rac*-1,7-CTH)(ClO_4)$_2$ must also contain the same ligand form with respect to the nitrogen configurations, because it was obtained from the oxalate-bridged dimer under conditions known to give rise to retention of nitrogen configurations. Therefore, it contains either of the structures given in Figure 5e and 5f. When a model of the complex is built and the ligand is folded into its planar conformation, it is seen that α-Ni(*rac*-1,7-CTH)(ClO_4)$_2$ has the structure of Figure 5f (isomer 10, Table II). This isomer is therefore a racemate of C_2 symmetry.

A Dreiding stereomodel of this isomer strongly suggests that significant strain exists throughout the entire system, in structures requiring the macrocyclic ligand to be planar. Only when this ligand diastereoisomer folds along the line which includes the nitrogens adjacent to the geminal carbons and the metal ions, and in a direction which causes the protons attached to the nitrogen atoms adjacent to the asymmetric carbons to point toward each other, is this strain released. This would explain why this particular isomer is most readily formed under those conditions where the ligand must fold in order to accommodate a bidentate ligand. It also explains why in solution under conditions which allow secondary amine proton dissociation (neutral or basic aqueous media) this isomer readily isomerizes to give an equilibrium mixture of α-Ni(*rac*-1,7-CTH)$^{2+}$ and β-Ni(*rac*-1,7-CTH)$^{2+}$, which is composed almost entirely of the β isomer.

The pmr spectrum of the β-Ni(*rac*-1,7-CTH)(ClO_4)$_2$ isomer (Figure 3) shows a well-resolved Me(I) doublet which partially overlaps the Me(II) singlet in the high-field portion. Only one singlet appears in the low-field portion of the spectrum, and it is assigned to the Me(III) resonance due to the axial geminal methyl groups (Table VIII). It can therefore be concluded that only the structures given in Figures 6a and 5f are possible for this isomer. These two structures are racemic diastereoisomers of C_2 symmetry (Table II). Within each structure the six-membered chelate rings have identical conformations, and both the methyl groups (Me(I)) attached to the symmetric carbons are equatorial. Since it is already known that structure 5f (isomer 10, Table II) represents α-Ni(*rac*-1,7-CTH)$^{2+}$ isomer, the structure given in Figure 6a (isomer 1, Table II) must represent the β-Ni(*rac*-1,7-CTH)$^{2+}$ isomer. This isomer is a racemate, and several unsuccessful attempts were made to resolve it into it enantiomers by chromatographic methods. The low solubility of the available salts may be a contributing factor in these negative results.

It is interesting to note that the five-membered chelate rings within this structure are in the eclipsed con-

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(23) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

(24) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).

(25) M. Bailey, private communication, 1968.

formation which is presumably less stable than the staggered conformations. In spite of this fact, it appears that this structure, Figure 6a, is the thermodynamically most stable structure of all those possible for the Ni(*rac*-1,7-CTH)$^{2+}$ planar isomers. This suggests that the relative stabilities of the six-membered chelate rings are more important than those of the five-membered rings and that the chair conformation of six-membered chelate rings is more stable than the twist or boat conformations. These results also suggest, as do the Drieding models for these structures, that six-membered chelate rings in chair conformations, which have axially oriented methyl groups attached to asymmetric carbons, are not stable, because of steric interactions between these axial groups and the axial geminal methyl groups. These probable steric interactions between methyl groups could be relieved by a change of the chelate ring into the boat conformation, but there is no evidence that this occurs.

Isomerization from α to β or from the structure of Figure 5f to that of Figure 6a involves the dissociation of the secondary amine protons from and configurational inversions of two nitrogens (adjacent to the geminal carbons), in a presumably stepwise process. If this dissociation and configurational inversion is stepwise, the structure given in Figure 6b (isomer 6, Table II) is a necessary intermediate. There is no evidence that this intermediate ever builds up to significant concentrations in solution.

The Ni(*meso*-1,7-CTH)$^{2+}$ and α-Ni(*rac*-1,7-CTH]$^{2+}$ isomers (Figures 4a and 5f) are symmetrical with respect to the NiN_4 plane; that is, the chemical environments above and below this plane are identical within each isomeric structure. The β-Ni(*rac*-1,7-CTH)$^{2+}$ isomer (Figure 6a), on the other hand, is unsymmetrical with respect to this plane; one axial site is "cupped" by the two six-membered chelate rings, while the other is relatively free and is surrounded by the four secondary amine protons. The symmetrical environments about the axial positions of the first two isomers is reflected in the fact that the dithiocyanato derivatives of these two isomers exhibit only one antisymmetric thiocyanate stretching frequency ($\nu_{(CN)}$) in the 2050–2100-cm^{-1} region of the infrared (Table VII). Two $\nu_{(CN)}$ bands are observed for the dithiocyanato derivative of β-Ni(*rac*-1,7-CTH)$^{2+}$ in both the solid and solution states, thus reflecting the presence of thiocyanates in two different environments.[26]

The chemical shift difference between the axial geminal methyl, Me(III), and equatorial geminal methyl protons, Me(II), is greater for β-Ni(*rac*-1,7-CTH)$^{2+}$ than for Ni(*meso*-1,7-CTH)$^{2+}$. This indicates that the axial geminal methyl groups lie more over the NiN_4 plane and closer to the metal ion center when there are two six-membered chelate rings of the chair conformation on the same side of the NiN_4 plane than when one of these chair-form rings is on each side of NiN_4 plane. This conclusion is supported by the fact that the Dq^z (NCS) for these tetragonal dithiocyanato derivatives increases in the order:[27] α-Ni(*rac*-1,7-CTH)$^{2+}$ < β-Ni(*rac*-1,7-CTH)$^{2+}$ < Ni(*meso*-1,7-CTH)$^{2+}$. As the axial sites of the Ni(1,7-CTH)$^{2+}$ complexes become more and more hindered, the increased repulsive interaction existing between methyl groups of the macrocyclic ligand and the axially coordinated ligand weakens the ligand field of that monodentate group.

Experimental Section

Physical Measurements. Infrared spectra of dry solids were determined from Nujol mulls sandwiched between KBr plates and potassium bromide pellets using a Perkin-Elmer 337 spectrophotometer. Infrared spectra of solutions were taken using CaF_2 plates and lead spacers.

Electronic absorption spectra were determined using a Cary Model 14 recording spectrophotometer. Spectra of solid samples were determined *via* diffuse transmittance through Nujol mulls impregnated upon Whatman No. 1 filter paper or through Dow Corning 200 fluid (a dimethylpolysiloxane) mulls sandwiched between microscope slides. This latter technique was used when it was desirable to protect the sample from the atmosphere or when low-temperature solid-state spectra were desired. Solution spectra were taken using 1-cm matched quartz cells. When temperature variation was required jacketed cells were used and thermostatically controlled solutions were pumped through them using a Haake Type-F thermostatic control unit, purchased from RHO Scientific, Inc. Temperatures were measured directly using a 0–100° thermometer.

Proton magnetic resonance data were obtained using Varian Model A-60, A-60A, or HA-100 nmr spectrometers. The chemical shift data were determined using the side-banding technique. Concentrations of samples were 10–20% by weight, and spectra were obtained at 37°. The pD of D_2O solutions was adjusted by addition of concentrated mineral acids or saturated NaOH–D_2O solutions.

Electrical resistances of water and nitromethane solutions were measured using an Industrial Instrument RC-16-B conductivity bridge and conductance cells with platinum electrodes and cell constants of 2.120 and 2.116. The resistances, R, were determined at 25° and 1000 cps for approximately 10^{-3} M solutions. Molar conductances, λ_m, were calculated using the relationship $\lambda_m = K \times 10^3/R\ M$, where K is the cell constant and M is the molar concentration.

Magnetic susceptibilities, χ_g, were determined using both the Gouy and Faraday methods. The Gouy measurements were determined using a Consolidated Engineering Corp. electromagnet and power supply operating at 8 A. The force developed on the sample was determined using a Sauter Monopan Model 200/0.01 balance. Pyrex Gouy tubes made from 15-cm long 0.5-mm o.d. tubing were fitted with 10/30 ground-glass joints. These tubes were calibrated with $HgCo(NCS)_4$ following the method of Figgis and Nyholm.[28] The tube constant, K, was determined from the following relationship, $K = [4981 \times 10^{-6}/(T + 10°)°K][w/\Delta w']$, where °K is the temperature, w is the weight of the calibrant, and $\Delta w'$ is the force produced by the magnetic field corrected for the diamagnetism of the tube. Molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.[29,30] The molar susceptibility of 1,7-CTH was experimentally determined to be -246×10^{-6}.

Where insufficient sample for a Gouy determination was available, the Faraday method was used. A Faraday magnetic susceptibility balance equipped with a Cahn Gram electrobalance and a Varian 4-in. electromagnet, fitted with specially shaped pole pieces, was used through the courtesy of Professor D. W. Meek and with the help of Mr. Bill Cook, Mr. Bob Sperati, and Dr. L. Lindoy.

Gas–liquid chromatograms were obtained using an F & M Scientific 700 laboratory chromatograph equipped with a Sargent Model SR recorder. Commercially packed Hewlett-Packard, F & M Scientific Division, columns were used. These columns were 6 ft in length. The liquid phase was 10% Apiezon L and 10% KOH on a support of 60–80 WAW 700 packing.

Elemental analyses for carbon, hydrogen, and nitrogen were performed by Mr. Peter Kovi of this research group, using an F & M Model 185 CHN analyzer, and by Galbraith Laboratories, Inc. Analysis of all other elements were performed by Galbraith Laboratories, Inc.

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(27) L. G. Warner, Ph.D. Thesis, The Ohio State University, 1968.

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Isomers and Derivatives of 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II). Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$. This complex is prepared using a modification of the method described by Curtis.[7] A 30-g sample of Ni(1,7-CT)(ClO$_4$)$_2$ is dissolved in 800 ml of H_2O at 60°. To this solution is added 10 g of NaOH and 13 g of Ni–Al alloy (50% Ni). Small portions of NaOH area dded followed by small portions of the alloy over a period of 0.5 hr. The reaction mixture is stirred constantly and the temperature maintained at 60° for 1 hr after complete addition of the base and alloy. The pH is then adjusted to about 8 with 60% $HClO_4$ and filter aid (Super-Cel) and 300 ml of acetone are added. The mixture is filtered while hot. The filtrate is reduced in volume to about 700 ml. Upon cooling, 10–15 g of a yellow-orange product is deposited. This product is recrystallized (10 g/100 ml) from hot water acidified with several drops of 60% perchloric acid. After the recrystallized product is isolated by filtration, the pH of a 20-ml portion of the filtrate is adjusted to 8 or 9 with NaOH and 0.5 g of $Na_2C_2O_4$ is added. This solution is boiled for 10 min, then cooled. The absence of the blue hemioxalate–perchlorate {[Ni(*rac*-1,7-CTH)]$_2$C$_2$O$_4$}(ClO$_4$)$_2$ attests to the isomeric purity of the desired product. This product is recrystallized and the filtrates are examined as described above until no blue precipitate is observed. After all the blue hemioxalate–perchlorate is isolated from all of the filtrates obtained above, the resulting solution is reduced in volume to 300–400 ml and the pH is adjusted to 8 or 9. The solution is then brought to boiling and 15 g of $CaCl_2$ is added. The resulting precipitate of CaC_2O_4 is filtered off while the solution is hot and 20 g of $NaClO_4$ is added. The pH of this solution is adjusted to 2 or 3 with 60% $HClO_4$ and the solution is cooled to 5°. Eight to ten additional grams of the yellow-orange Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$ is obtained and recrystallized once from hot, dilute $HClO_4$. The combined yields amount to 18–20 g (60–65%). *Anal.* Calcd for $C_{16}H_{36}N_4NiCl_2O_8$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.8; H, 6.49; N, 10.40. An alternate route to this product has been reported by Curtis. A 30-g sample of Ni(1,7-CT)(ClO$_4$)$_2$ is dissolved in 800 ml of H_2O at 70°, and 3.8 g of $NaBH_4$ and 1 g of Borax are added slowly in small portions over a period of 45 min. The solution is vigorously stirred throughout this addition. After all the $NaBH_4$ has been added, the reaction mixture is heated at 80° and stirred for 1 hr. The pH is adjusted to 2 or 3 with 60% $HClO_4$, and 300 ml of acetone is added. The solution is filtered while still hot and the volume of the filtrate is reduced to 600 ml. Upon cooling, 8–12 g of product precipitates. This material is recrystallized and purified as described above. A second crop of product (2–4 g) is obtained from the filtrates after removal of the racemic isomer as the hemioxalate–perchlorate. The total yield is 11–14 g (35–40%). *Anal.* Calcd for $C_{16}H_{36}N_4NiCl_2O_8$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.8; H, 6.60; N, 10.45.

This isomer, Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$, is recrystallized from dilute $HClO_4$ from hot water, and from hot basic solutions dumped into cold acid solutions. All of the recrystallized products gave identical infrared spectra.

The Hemioxalate–Perchlorate, {[Ni(*rac*-1,7-CTH)]$_2$C$_2$O$_4$}(ClO$_4$)$_2$. This material is prepared following the method of Curtis.[7] The original filtrate is combined with all the filtrates from the recrystallization of the Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$. The pH is adjusted to 9 or 10 with NaOH, and 10 g of $Na_2C_2O_4$ is added. The solution is then boiled for 0.5 hr. After cooling the blue product is filtered and washed with cold water, ethanol, and ether and dried *in vacuo.* Yields of 30–35 and 10–15% based upon the parent Ni(1,7-CTH)(ClO$_4$)$_2$ are obtained from the reduction with $NaBH_4$ and Ni–Al alloy, respectively. *Anal.* Calcd from $C_{36}H_{12}N_8Ni_2Cl_2O_{12}$: C, 42.0; H, 7.46; N, 11.51. Found: C, 42.2; H, 7.19; N, 11.7.

Ni(*meso*-1,7-CTH)(NCS)$_2$. Upon dissolution of 1.3 g of Ni(*meso*-1,7-CTH)(ClO$_4$)$_2$ and 1.3 g of KNCS in 50 ml of H_2O that has been acidified with two drops of 50% HBF_4, a yellow solution and a white precipitate are obtained. When 50 ml of $CHCl_3$ is added and the mixture stirred the aqueous layer becomes almost colorless and the chloroform layer becomes violet. The white precipitate of $KClO_4$ and KBF_4 is filtered and the chloroform layer isolated. The chloroform solution is dried by filtration through a Büchner funnel filled with Type 5A molecular sieves. It is evaporated to dryness under a stream of air. A yield of 0.9 g of the pale pink product is obtained. *Anal.* Calcd for $C_{18}H_{36}N_6S_2Ni$: C, 47.06; H, 7.90. N, 18.30. Found: C, 47.1; H, 7.95; N, 18.20.

Isomers and Derivatives of Ni(*rac*-1,7-CTH)$^{2+}$. β-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$. This isomer is prepared by reaction between 9.7 g of the hemioxalate–perchlorate, {[Ni(*rac*-1,7-CTH)]$_2$C$_2$O$_4$}(ClO$_4$)$_2$, and 4.4 g of $CaCl_2$ in 700 ml of water. The pH is adjusted to 11 with NaOH and the mixture is stirred and heated nearly to boiling for 1 hr. After cooling to 5° the CaC_2O_4 is filtered and 10 g of $NaClO_4 \cdot H_2O$ is added. The volume of the solution is reduced to about 100 ml. The resulting orange product is recrystallized from 10^{-2} *N* $HClO_4$ (yield 8.5 g). *Anal.* Calcd for $C_{16}H_{36}N_4NiCl_2O_8$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.45; H, 6.48; N, 10.25.

β-Ni(*rac*-1,7-CTH)(NCS)$_2$. This derivative is prepared from α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$ following the procedure above for Ni(*meso*-1,7-CTH)(NCS)$_2$. *Anal.* Calcd for $C_{18}H_{36}N_6MiS_2$: C, 47.06; H, 7.09; N, 18.30. Found: C, 46.9; H, 7.85; N, 18.5.

α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$. This isomer is prepared by stirring at room temperature 9.7 g of {[α-Ni(*rac*-1,7-CTH)]$_2$C$_2$O$_4$}(ClO$_4$)$_2$ in 300 ml of 60% $HClO_4$ and 150 ml of H_2O. After 4 hr all of the starting material has decomposed and a bright yellow precipitate remains. This yellow product is filtered, washed with water, ethanol, and ether, and then dried *in vacuo* (yield 9.7 g). *Anal.* Calcd for $C_{16}H_{36}N_4NiCl_2O_8$: C, 35.45; H, 6.69, N, 10.34. Found: C, 35.4; H, 6.85; N, 10.6.

α-Ni(*rac*-1,7-CTH)(NCS)$_2$. This derivative is prepared by stirring 2 g of the perchlorate derivative in 50 ml of 10^{-2} *N* HBF_4 to which 5 g of NaNCS has been added. An insoluble blue material forms immediately. The mixture is stirred for 2 hr and the product isolated by filtration. It is washed with water, ethanol, and ether and dried *in vacuo.* The yield is 100%. *Anal.* Calcd for $C_{18}H_{36}N_4S_2Ni$: C, 47.05; H, 7.90; N, 18.30. Found: C, 47.07; H, 7.86; N, 18.25.

When α-Ni(*rac*-1,7-CTH)(ClO$_4$)$_2$ is stirred with 2 equiv of NaNCS in a 1:1:1 ethanol–H_2O–chloroform mixture, a 5–10% yield of blue α-Ni(*rac*-1,7-CTH)(NCS)$_2$ is obtained. Also, slow evaporation at room temperature of neutral aqueous solutions of the perchlorate salt of the β isomer to which has been added to a large excess of NaNCS yields large crystals of the thiocyanate derivative of the α isomer.

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