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Stereoisomers of a Tetraamine Macrocyclic Ligand Complex of Nickel(II)

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Received June 15, 1983

Five stereoisomers of the complex (5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) have been prepared, characterized, and shown to be derived from variations in the configurations of the two asymmetric carbon centers and the four asymmetric nitrogen centers. The assignments of structures to these isomers have been accomplished by means of thorough stereochemical analysis combined with proton magnetic resonance and infrared spectral data of these species. The relative energies of these species are discussed in terms of the conformational energies of the chelate ring systems and methyl substituent interaction energies.

Introduction

The extreme kinetic inertness and very high thermodynamic stability of tetraamine macrocyclic ligand complexes are significant for inorganic stereochemistry,[1,2] since they greatly enhance the number of potentially isolable isomers of these complexes.[3-5] Previously, Curtis et al. described the synthesis of four isomeric hexamethyl-1,4,8,11-tetraazacyclotetradecanes depicted in Chart I.[6,7] The stereoisomers of the nickel(II) complexes of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *meso*-1,7-CTH or tet a, and *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *rac*-1,7-CTH or tet b, have been reported by Warner and Busch.[8] The present paper concerns the stereoisomers of the nickel(II) complexes of *rac*-5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *rac*-1,4-CTH or tet c, and *meso*-5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *meso*-1,4-CTH or tet d.

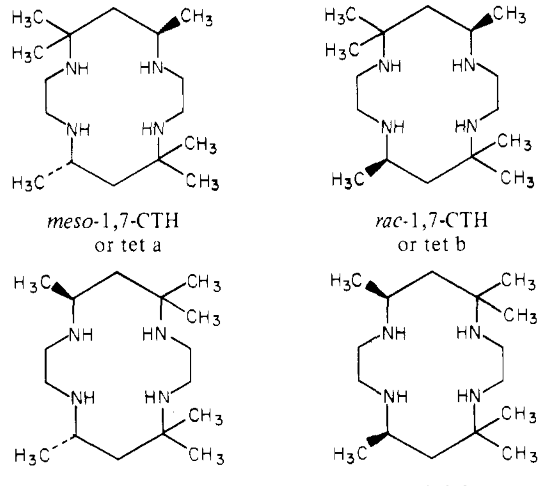
The complex ion $[Ni(1,4\text{-CTH})]^{2+}$ can exist in 20 theoretically possible diastereoisomeric forms, depending on the configurations of the two asymmetric carbon centers and the four asymmetric nitrogen centers. Five of these diastereomers, one $[Ni(\textit{rac}\text{-}1,4\text{-CTH})]^{2+}$ complex and four isomeric $[Ni(\textit{meso}\text{-}1,4\text{-CTH})]^{2+}$ complexes, have been synthesized and characterized. Apart from their intrinsic interest, the conformational properties of these stereoisomers now presented will also provide a foundation for kinetic and thermodynamic investigations of these complexes, which will be reported subsequently.

Experimental Section

Reagents. $Ni(1,4\text{-CT})(ClO_4)_2$. This complex was prepared by following the method of Curtis.[9,10]

$Ni(\beta\text{-}\textit{rac}\text{-}1,4\text{-CTH})(ClO_4)_2$ and $[Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(acac)](ClO_4)$. A 48-g samples of $Ni(1,4\text{-CT})(ClO_4)_2$ was dissolved in 1000 mL of water and heated to 60 °C. To this solution was added slowly 8 g of sodium borohydride, to prevent foaming over. This solution was stirred at 60 °C for 1 h. Then, it was cooled to room temperature. The pH is then adjusted to about 4 with perchloric acid. The solution was heated afterwards with activated carbon and boiled for 10 min. Filter aid was added, and the solution was filtered and set aside, whereupon a large quantity of orange crystals of $Ni(\beta\text{-}\textit{rac}\text{-}1,4\text{-CTH})(ClO_4)_2$ formed. These orange crystals were separated and washed with cold water and then recrystallized twice from water. Anal. Calcd for $Ni(\beta\text{-}\textit{rac}\text{-}1,4\text{-CTH})(ClO_4)_2$: C, 34.93; H, 6.59; N, 11.63. Found: C, 35.05; H, 6.63; N, 11.66. After the crystals of $Ni(\beta\text{-}\textit{rac}\text{-}1,4\text{-CTH})(ClO_4)_2$ were separated the solution was heated to boiling. Acetylacetone was added to the solution, followed by dilute ammonia. The blue-violet solid of $[Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(acac)](ClO_4)$ was filtered from the cold solution and recrystallized from methyl cyanide by the addition of water. Anal. Calcd for $[Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(acac)]ClO_4$: C, 46.47; H, 8.17; N, 10.32. Found: C, 46.51; H, 8.21; N, 10.35.

Chart I



meso-1,7-CTH or tet a

rac-1,7-CTH or tet b

rac-1,4-CTH or tet c

meso-1,4-CTH or tet d

$Ni(\beta\text{-}\textit{rac}\text{-}1,4\text{-CTH})(NCS)_2$. Upon dissolution of 2.6 g of $Ni(\beta\text{-}\textit{rac}\text{-}1,4\text{-CTH})(ClO_4)_2$ and 2.6 g of KNCS in 100 mL of H_2O that had been acidified with 4 drops of 50% HBF_4, a yellow solution and a white precipitate were obtained. When 100 mL of $CHCl_3$ was added and the mixture stirred, the aqueous layer became almost colorless and the chloroform layer became violet. The white precipitate of $KClO_4$ and KBF_4 was filtered and the chloroform layer isolated. The chloroform solution was dried by filtration through a funnel filled with type 5A molecular sieves. It was evaporated under a stream of air and then dried in vacuo. Anal. Calcd for $Ni(\beta\text{-}\textit{rac}\text{-}1,4\text{-CTH})(NCS)_2$: C, 47.06; H, 7.90; N, 18.28. Found: C, 47.01; H, 7.87; N, 18.29.

$Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(ClO_4)_2$. This isomer was prepared by stirring at room temperature 12.3 g of $[Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(acac)](ClO_4)$ in 600 mL of 2 M $HClO_4$. After 1 h, all of the starting material had decomposed and a bright yellow precipitate remained. This yellow product was filtered, washed with 10^{-4} M $HClO_4$ and ether, and then dried in vacuo (yield 10.6 g). Anal. Calcd for $Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(ClO_4)_2$: C, 34.93; H, 6.59; N, 11.63. Found: C, 35.04; H, 6.62; N, 11.66.

$Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(NCS)_2$. Blue crystals of $Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(NCS)_2$ were prepared by stirring 4 g of $Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(ClO_4)_2$ in 100 mL of 10^{-2} N HBF_4 to which 10 g of NaNCS had been added. An insoluble blue material formed immediately. The mixture was stirred for 1 h. The product was isolated by filtration and dried in vacuo. Anal. Calcd for $Ni(\alpha\text{-}\textit{meso}\text{-}1,4\text{-CTH})(NCS)_2$:

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(1) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540.
(2) Liang, B. F.; Chung, C. S. *Inorg. Chem.* **1981**, *20*, 2152.
(3) Liang, B. F.; Margerum, D. W.; Chung, C. S. *Inorg. Chem.* **1979**, *18*, 2001.
(4) Liang, B. F.; Chung, C. S. *Inorg. Chem.* **1980**, *19*, 1867.
(5) Liang, B. F.; Chung, C. S. *J. Chin. Chem. Soc. (Taipei)* **1979**, *26*, 93.
(6) Curtis, N. F. *J. Chem. Soc.* **1964**, 2644.
(7) Curtis, N. F. *J. Chem. Soc. C* **1967**, 1979.
(8) Warner, L. G.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4092.
(9) Curtis, N. F.; Curtis, Y. M.; Powell, H. K. J. *J. Chem. Soc. A* **1966**, 1015.
(10) Liang, B. F. Ph.D. Dissertation, National Tsing Hua University, Taiwan, Republic of China, 1980.

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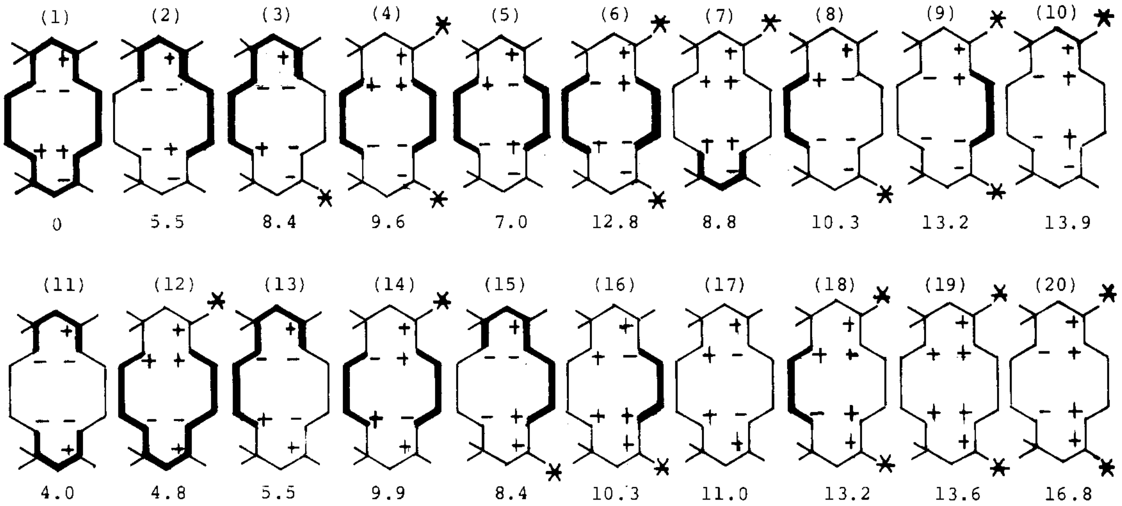

Figure 1. Configurations of [Ni(*rac*-1,4-CTH)]$^{2+}$ (**1–10**) and Ni(*meso*-1,4-CTH)$^{2+}$ (**11–20**). The number below each configurations indicates the total energy of the configuration, relative to the most stable configuration (**1**), in kcal mol^{-1}. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle, and a minus sign, that it is below. Gauche conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines. The axial C(7) methyl group is indicated with an asterisk.

C, 47.06; H, 7.90; N, 18.28. Found: C, 46.97; H, 7.85; N, 18.30.

Ni(*α*-meso-1,4-CTH)Cl$_2$. Blue crystals of Ni(*α*-*meso*-1,4-CTH)Cl$_2$ were prepared by stirring 4 g of Ni(*α*-*meso*-1,4-CTH)(ClO$_4$)$_2$ in 100 mL of 0.1 M HCl to which 10 g of NaCl had been added. An insoluble blue material formed immediately. The mixture was stirred for 1 h and the product isolated by filtration and dried in vacuo. Anal. Calcd for Ni(*α*-*meso*-1,4-CTH)Cl$_2$: C, 46.40; H, 8.76; N, 13.52. Found: C, 46.42; H, 8.79; N, 13.55.

Ni(*β*-meso-1,4-CTH)(ClO$_4$)$_2$. Orange crystals of Ni(*β*-*meso*-1,4-CTH)(ClO$_4$)$_2$ formed when the *α* isomer was boiled in water containing a few drops of ammonia, followed by acidification with perchloric acid and cooling. It was washed with water, ethanol, and ether and then dried in vacuo. Anal. Calcd for Ni(*β*-*meso*-1,4-CTH)(ClO$_4$)$_2$: C, 34.93; H, 6.59; N, 11.63. Found: C, 35.06; H, 6.65; N, 11.65.

Ni(*β*-meso-1,4-CTH)(NCS)$_2$. This derivative was prepared from Ni(*β*-*meso*-1,4-CTH)(ClO$_4$)$_2$ by following the same procedure described above for Ni(*rac*-1,4-CTH)(NCS)$_2$. Anal. Calcd for Ni(*β*-*meso*-1,4-CTH)(NCS)$_2$: C, 47.06; H, 7.90; N, 18.28. Found: C, 46.99; H, 7.86; N, 18.30.

Ni(*γ*-meso-1,4-CTH)(ClO$_4$)$_2$. Orange crystals of Ni(*γ*-*meso*-1,4-CTH)(ClO$_4$)$_2$ formed when a solution of Ni(*α*-*meso*-1,4-CTH)(ClO$_4$)$_2$ in dilute aqueous ammonia was allowed to crystallize by slow evaporation. Anal. Calcd for Ni(*γ*-*meso*-1,4-CTH)(ClO$_4$)$_2$: C, 34.93; H, 6.59; N, 11.63. Found: C, 35.05; H, 6.64; N, 11.64.

Ni(*γ*-meso-1,4-CTH)(NCS)$_2$. This derivative was prepared from Ni(*γ*-*meso*-1,4-CTH)(ClO$_4$)$_2$ following the same procedure described above for Ni(*rac*-1,4-CTH)(NCS)$_2$. Anal. Calcd for Ni(*γ*-*meso*-1,4-CTH)(NCS)$_2$: C, 47.06; H, 7.90; N, 18.28. Found: C, 46.98; H, 7.88; N, 18.31.

Ni(*δ*-meso-1,4-CTH)(ClO$_4$)$_2$. A 2.6-g sample of Ni(*α*-*meso*-1,4-CTH)(ClO$_4$)$_2$ was dissolved in 50 mL of H$_2$O at 80 °C that had been acidified with HClO$_4$ and then 10 drops of concentrated aqueous ammonia was added. When the solution was cooled, a yellow product was deposited. This product was filtered and dried in vacuo. Anal. Calcd for Ni(*δ*-*meso*-1,4-CTH)(ClO$_4$)$_2$: C, 34.93; H, 6.59; N, 11.63. Found: C, 35.03; H, 6.63; N, 11.65.

Ni(*δ*-meso-1,4-CTH)(NCS)$_2$. This derivative was prepared from Ni(*δ*-*meso*-1,4-CTH)(ClO$_4$)$_2$ by following the same procedure described above for Ni(*β*-*rac*-1,4-CTH)(NCS)$_2$. Anal. Calcd for Ni(*δ*-*meso*-1,4-CTH)(NCS)$_2$: C, 47.06; H, 7.90; N, 18.28. Found: C, 46.99; H, 7.89; N, 18.31.

Instrumentation. A Cary 17 spectrophotometer with a thermostated cell compartment was used to measure electronic absorption spectra. Proton magnetic resonance data were obtained with use of JEOL FX-100 NMR spectrometers. Infrared spectra were determined from Nujol mulls sandwiched between KBr plates and KBr pellets with use of a Perkin-Elmer 580 spectrophotometer. For pH measurements, a Radiometer PHM 64 equipped with a GK 2401 B combination electrode was used.

Table I. Electronic Absorption Spectra of Isomers of Ni(1,4-CTH)$^{2+}$

isomer	color	medium	ν_{max}, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}
Ni(*β*-*rac*-1,4-CTH)$^{2+}$	orange	H$_2$O	21 800	74
		CH$_3$NO$_2$	21 800	66
		Me$_2$SO	21 800	76
Ni(*α*-*meso*-1,4-CTH)$^{2+}$	yellow	H$_2$O	22 600	63
		CH$_3$NO$_2$	22 600	55
	green	Me$_2$SO	26 500	21
			22 600	25
			16 500	7
			9 740	11
Ni(*β*-*meso*-1,4-CTH)$^{2+}$	orange	H$_2$O	22 200	109
		CH$_3$NO$_2$	22 200	101
		Me$_2$SO	22 200	111
Ni(*γ*-*meso*-1,4-CTH)$^{2+}$	orange	H$_2$O	21 900	104
		CH$_3$NO$_2$	21 900	97
		Me$_2$SO	21 900	106
Ni(*δ*-*meso*-1,4-CTH)$^{2+}$	yellow	H$_2$O	22 500	69
		CH$_3$NO$_2$	22 500	61
	yellow-green	Me$_2$SO	26 200	23
			22 500	28
			16 600	9
			9 710	14

Results and Discussion

Stereochemical Considerations. There are two asymmetric carbons in Ni(1,4-CTH)$^{2+}$. The presence of these two asymmetric centers affords the possibility of two diastereomers, Ni(*meso*-1,4-CTH)$^{2+}$ and Ni(*rac*-1,4-CTH)$^{2+}$. Each of these complex ions can exist in 10 theoretically possible diastereoisomeric forms, depending on the configurations of the four coordinated secondary amines, which are asymmetric.

The configurations of these isomers are represented in Figure 1, together with their relative (chelate ring conformational plus substituent interaction) energies assessed by the method described by Curtis.[11]

Electronic Absorption Spectra. Five diastereomers of [Ni(1,4-CTH)]$^{2+}$ have been prepared as described in the Experimental Section. The electronic absorption spectra of these stereoisomers are given in Table I. Each of these isomers dissolves in water or nitromethane to give a yellow solution, and its electronic absorption spectrum is typical of singlet-state, four-coordinate, square-planar nickel(II) as shown in Table

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(11) Whimp, P. O.; Bailey, M. F.; Curtis, N. F. *J. Chem. Soc. A* **1970**, 1956.

Table II. Proton Magnetic Resonance Data for Diamagnetic [Ni(1,4-CTH)]$^{2+}$ Isomers in Me$_2$SO Solutions^{a-c}

isomer	Me(I)	Me(II)	Me(III)	$J_{\mathrm{Me(I)}}{}^{d}$
Ni(*β-rac*-1,4-CTH)$^{2+\ d}$	1.09 (3), 1.18 (3)	1.27 (6)	2.16 (6)	5.4
Ni(*β-meso*-1,4-CTH)$^{2+\ d}$	0.94 (3), 1.05 (3)	1.09 (6)	2.10 (6)	6.6
Ni(*γ-meso*-1,4-CTH)$^{2+\ d}$	0.98 (3), 1.09 (3)	1.14 (6)	2.02 (3), 2.16 (3)	6.6

^{a} All chemical shifts in units of ppm from internal Me$_4$Si. ^{b} Estimated relative intensities are given in parentheses. ^{c} At 25 °C. ^{d} Units are Hz.

I. The single absorption band in the characteristic 21 000–23 000-cm^{-1} region is assigned to the ${}^1A_{1g} \rightarrow {}^1E_g$ transition of square-planar nickel complexes.[12] In dimethyl sulfoxide, the spectra of Ni(*β-meso*-1,4-CTH)$^{2+}$, Ni(*γ-meso*-1,4-CTH)$^{2+}$, and Ni(*β-rac*-1,4-CTH)$^{2+}$ show only the characteristic ${}^1A_{1g} \rightarrow {}^1E_g$ band. On the other hand, Ni(*α-meso*-1,4-CTH)$^{2+}$ and Ni(*δ-meso*-1,4-CTH)$^{2+}$ dissolve in dimethyl sulfoxide to give green and yellow-green solutions, respectively, and their electronic absorption spectra show the characteristic absorptions for singlet ground state, square-planar nickel(II) complexes and for triplet ground state, tetragonally distorted pseudooctahedral nickel(II) complexes,[13,14] indicating both singlet and triplet nickel(II) complexes present in solution (eq 1). Here NiL^{2+} is Ni(*α-meso*-1,4-CTH)$^{2+}$ or Ni(*δ-meso*-1,4-CTH)$^{2+}$.

$$\mathrm{NiL^{2+} + 2Me_2SO \rightleftarrows NiL{\cdot}2Me_2SO^{2+}} \tag{1}$$

The apparent $\epsilon_{\max}$ values of the singlet band, ν_s, for Ni(*α-meso*-1,4-CTH)(ClO)$_2$ in Me$_2$SO at 25, 38, and 45 °C are 23.2, 26.9, and 29.5 M^{-1} cm^{-1}, respectively. These results indicate the equilibrium constant of this reaction (eq 1) decreases with increasing temperature. Similar results are found in the case of Ni(*δ-meso*-1,4-CTH)(ClO$_4$)$_2$ in Me$_2$SO. Me$_2$SO is a very good coordinating solvent because of its extremely high polarity. The donor number of this solvent is 29.8, much larger than those of nitromethane and water,[15] which fail to form triplet-state, six-coordinated nickel(II) complexes at room temperature. Steric interactions are also of importance in determining the extent of axial addition. The fact that axial additions are not observed with Ni(*β-rac*-1,4-CTH)$^{2+}$, Ni(*β-meso*-1,4-CTH)$^{2+}$, and Ni(*γ-meso*-1,4-CTH)$^{2+}$ in Me$_2$SO at room temperature suggests the axial methyl groups of these complexes sterically congest the axial sites.

Proton Magnetic Resonance Spectra of Solutions Containing Diamagnetic Complexes. The ^{1}H NMR spectra of these stereoisomers were obtained with Me$_2$SO-d_6 as the solvent. As pointed out previously, the solutions of Ni(*α-meso*-1,4-CTH)$^{2+}$ and Ni(*δ-meso*-1,4-CTH)$^{2+}$ contain both singlet and triplet ground state nickel(II) complexes at room temperature. Therefore, their spectra were not obtained. The ^{1}H NMR spectra for the other three isomers are shown in Figure 2 (supplementary material). The assignments of the resonances based on similar considerations reported by Warner and Busch[8] are given in Table II.

The doublets in the 0.9–1.2 ppm region of the spectra are due to the methyl groups attached to the asymmetric carbons, Me(I). As pointed out by Warner and Busch,[8] protons that lie over the NiN$_4$ plane experience low-field shifts, while those that lie in the plane experience high-field shifts.[16] The results listed in Table II indicate that all the methyl groups attached to the asymmetric carbons of these three stereoisomers are equatorial.

The remaining methyl resonances are due to the geminal methyl groups. The equatorial geminal Me(II) resonances occur in the high-field portion, 1.1–1.3 ppm, and the axial geminal Me(III) resonances occur in the low-field portion, 1.9–2.2 ppm. The magnitude of the deshielding of axial methyl groups is very sensitive to the radial and angular orientations of these protons with respect to the axial site of the metal ion center, and any change in six-membered chelate ring conformations has a significant effect on these methyl proton resonances.[17–19] As shown in Table II, only one resonance pattern of the axial methyl groups Me(III) is observed in the spectra of [Ni(*β-meso*-1,4-CTH)]$^{2+}$ and [Ni(*β-rac*-1,4-CTH)]$^{2+}$, indicating that the six-membered chelate ring conformations for each of these two complexes are pairwise equivalent. On the other hand, [Ni(*γ-meso*-1,4-CTH)]$^{2+}$, which exhibits two axial methyl resonances in its ^{1}H NMR spectrum, must contain six-membered chelate rings of different conformations. As pointed out by Busch,[8] the relative nonbonded chemical environments of the equatorial methyl groups, which lie out away from all other atoms in the complex, change very little with changes in six-membered chelate ring conformations. The resonance patterns for the geminal equatorial methyl groups and the methyl groups attached to the asymmetric carbons given in Table II support this point of view.

Proton Magnetic Resonance Spectra of Paramagnetic Hexacoordinate Complexes NiLX$_2$. The proton magnetic resonance spectra of these five stereoisomers of general formula NiLX$_2$ (L = tetraamine macrocyclic ligand; X = Cl or NCS) are shown in Figure 3 (supplementary material). The spectral data and the assignments of the resonances following the considerations reported by Dei[20] are given in Table III. These results indicate both the resonance position and the line width are strictly related to the conformational character of each resonating proton. The signals are spread over a very large spectral range, and the resonances of the protons are very sensitive to the conformations of the chelate rings.[21,22] Thus, a larger number of resonance signals is expected for the complex containing nonequivalent chelate rings. In contrast, a smaller number of resonance signals is expected for the complex whose chelate rings are pairwise equivalent. The results obtained on the basis of the number of resonance signals are given in Table IV.

The five-membered chelate ring may adopt a stable gauche conformation or an unstable conformation, depending on the configurations of the consecutive pair of the asymmetric nitrogens. The two asymmetric nitrogens within a stable gauche five-membered chelate ring are of the same *R* or *S* configuration, while the two asymmetric nitrogens within an unstable five-membered chelate ring are of opposite configurations, *R* and *S*.

As pointed out by Dei,[20] the axial and equatorial geminal proton signals are well split; in particular the difference of ca. −180 and ca. −20 ppm for the equatorial and axial ethylenic protons, respectively, indicates the existence of a quite regular gauche conformation of the five-membered chelate rings. The resonance signals for the protons of the ethylenic chains given in Table III indicate that [Ni(*β-rac*-1,4-CTH)(NCS)$_2$],

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Table III. Isotropic Shift Data (ppm)[a] and Spectral Assignments for Paramagnetic [Ni(1,4-CTH)X$_2$] Isomers in CDCl$_3$ Solution at 34 °C

	5-membered chelate rings[b,c]		6-membered chelate rings[b,c]					
isomer	CH$_{ax}$(f)	CH$_{eq}$(e)	α-CH$_{ax}$(c)	β-CH$_{ax}$(b)	β-CH$_{eq}$(a)	Me(III)	Me(II)	Me(I)
[Ni(*β-rac*-1,4-CTH)(NCS)$_2$]	−21	−181 −185	−53	+4.9	+16.4	−20.3	+4.2	−14.8
[Ni(*α-meso*-1,4-CTH)Cl$_2$]	−21	−180 −176	−45	+7.3	+16.9 +17.3	−23.6	+5.6 +7.2	−22.9 −1.3
[Ni(*β-meso*-1,4-CTH)(NCS)$_2$]	−34	−136.8 −80.9	−51	+6.3	+16.2	−23.1	+5.7	−17.7
[Ni(*γ-meso*-1,4-CTH)(NCS)$_2$]	−21.1 −33	−79.8, −178 −171, −131	−50	+6.6	+15.2 +16.1	−22.3	+5.2 +4.7	−17.1
[Ni(*δ-meso*-1,4-CTH)(NCS)$_2$]	−22	−191 −165	−50	+6.4	+16.0 +14.2	−22.8	+5.7 +5.3	−17.8 −1.7

[a] The isotropic shifts are determined relative to the shifts of the free ligands or diamagnetic nickel(II) complexes: α-CH, −2.8 ppm (average); β-CH, −1.7 ppm (average); Me$_{eq}$, −1.1 ppm; Me$_{ax}$, −2.0 ppm. [b] Key: ax = axial; eq = equatorial. [c] See Figure 3.

Table IV. Conformations of the Diastereoisomers of [Ni(1,4-CTH)X$_2$]

diastereoisomers	5-membered chelate ring conformations	6-membered chelate ring conformations	Me on asymmetric C
[Ni(*β-rac*-1,4-CTH)(NCS)$_2$]	equiv, two stable gauche rings	equiv	two equatorial groups
[Ni(*α-meso*-1,4-CTH)Cl$_2$]	equiv, two stable gauche rings	nonequiv	one equatorial group and one distorted axial group
[Ni(*β-meso*-1,4-CTH)(NCS)$_2$]	equiv, two unstable distorted rings	equiv	two equatorial groups
[Ni(*γ-meso*-1,4-CTH)(NCS)$_2$]	nonequiv, one stable gauche ring and one unstable distorted ring	nonequiv	two equatorial groups
[Ni(*δ-meso*-1,4-CTH)(NCS)$_2$]	equiv, two stable gauche rings	nonequiv	one equatorial group and one distorted axial group

[Ni(*α-meso*-1,4-CTH)(NCS)$_2$], and [Ni(*β-meso*-1,4-CTH)(NCS)$_2$] all contain two stable gauche five-membered chelate rings; [Ni(*γ-meso*-1,4-CTH)(NCS)$_2$] contains one stable gauche five-membered chelate ring and one unstable five-membered chelate ring while [Ni(*β-meso*-1,4-CTH)(NCS)$_2$] contains two unstable five-membered chelate rings.

The conformation of the unstable five-membered chelate ring is of interest. If the unstable five-membered chelate ring were of the exactly eclipsed conformation, the resonances of the protons of the ethylenic chain would occur together in the −80 to −90 ppm region.[23,24] This has not been observed. The isotropic shift data for the two unstable five-membered chelate rings of [Ni(*β-meso*-1,4-CTH)(NCS)$_2$] and one unstable five-membered chelate ring of [Ni(*γ-meso*-1,4-CTH)(NCS)$_2$] listed in Table III are very similar to the reported data of [Ni(*β-rac*-1,7-CTH)NCS)$_2$],[20] indicating the unstable five-membered chelate rings of [Ni(*β-meso*-1,4-CTH)(NCS)$_2$] and [Ni(*γ-meso*-1,4-CTH)Cl$_2$] adopt conformations similar to that of [Ni(*β-rac*-1,7-CTH)(NCS)$_2$], a strongly distorted guache conformation in which the methylenic protons of the ethylenic chains are intermediate between the axial–equatorial limiting positions.[17]

The six-membered ring conformations have been discussed by Warner and Busch.[8,9] The six-membered chelate ring may adopt a stable chair conformation or an unstable twist conformation, depending on the configurations of the consecutive pair of the asymmetric nitrogens and the asymmetric carbon as shown in Figure 1.

The most significant feature of these spectra is the resonance signals for the methyl groups attached to the asymmetric carbons. The results listed in Table III indicate two types of methyl groups attached to the asymmetric carbons.[24] The equatorial methyl substituents resonate in the range −15 to −23 ppm, while the distorted axial methyl substituents resonate in the range −1 to −2 ppm. The conformation information obtained is summarized in Table IV.

Structural Assignments for the Diastereoisomers. The complex ion [Ni(*rac*-1,4-CTH)]$^{2+}$ can exist in 10 theoretically possible diastereoisomeric forms as shown in Figure 1. There are only two possible structures, **1** and **5** in Figure 1, that are consistent with the conformational information for [Ni(*β-rac*-1,4-CTH)(NCS)$_2$] listed in Table IV.

Isomerization reactions of this type of complexes are base catalyzed due to the required inversion of nitrogen atoms in the complexes. [Ni(*rac*-1,4-CTH)]$^{2+}$ is stable in hot basic solution, no other isomer being formed after significant time has elapsed. The fact that only [Ni(*β-rac*-1,4-CTH)]$^{2+}$ exists in hot basic solution indicates [Ni(*β-rac*-1,4-CTH)]$^{2+}$ is the most stable diastereoisomer, much more stable than any other diastereoisomer of [Ni(1,4-CTH)]$^{2+}$.

Structure **1** shown in Figure 1 has the two secondary amine protons across the mouth of the six-membered chelate rings on the same side of the NiN$_4$ plane, thus giving rise to chair conformations for these rings. On the other hand, structure **5** in Figure 1 has the two secondary amine protons across the mouth of the six-membered chelate rings on the opposite sides of the NiN$_4$ plane, thus giving rise to twist conformations for these rings, which are less stable than the chair form. On the basis of the relative stabilities of these two isomers, structure **1** in Figure 1 is assigned to [Ni(*rac*-1,4-CTH)]$^{2+}$. The final energy values in Figure 1 indicate that all the other isomers of [Ni(*rac*-1,4-CTH)]$^{2+}$, structures **2**–**10**, are much more unstable than [Ni(*β-rac*-1,4-CTH)]$^{2+}$, in agreement with the result of the isomerization reaction. The structure of [Ni(*β-rac*-1,4-CTH)]$^{2+}$ is shown in Figure 4.

The 10 theoretically possible diastereoisomeric forms for [Ni(*meso*-1,4-CTH)]$^{2+}$ are shown as structures **11**–**20** in Figure 1. There is only one possible structure, **14** in Figure 1, that is consistent with the conformational information for [Ni(*α-meso*-1,4-CTH)]$^{2+}$ listed in Table IV. In addition, this is the only isomeric form that readily forms a derivative with the macrocyclic folded as shown in Figure 5, in agreement with the folded complex [Ni(*α-meso*-1,4-CTH)(acac)](ClO$_4$) described in the Experimental Section. Therefore, this structure, **14** in Figure 1, is assigned to [Ni(*α-meso*-1,4-CTH)]$^{2+}$, and the structure is shown in Figure 4.

There are two possible structures, **11** and **17** in Figure 1, that are consistent with the conformational information for [Ni(*β-meso*-1,4-CTH)(NCS)$_2$] listed in Table IV. The fact

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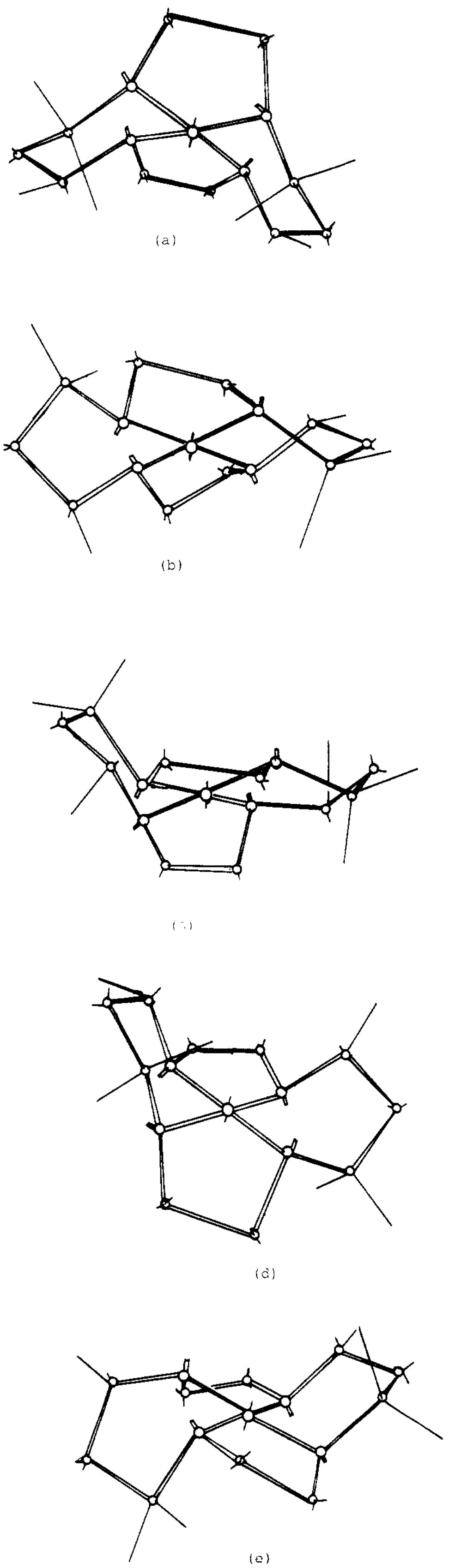

Figure 4. Idealized structures of [Ni(1,4-CTH)]$^{2+}$ isomers: (a) [Ni(β-*rac*-1,4-CTH)]$^{2+}$; (b) [Ni(α-*meso*-1,4-CTH)]$^{2+}$; (c) [Ni(β-*meso*-1,4-CTH)]$^{2+}$; (d) [Ni(γ-*meso*-1,4-CTH)]$^{2+}$; (e) [Ni(δ-*meso*-1,4-CTH)]$^{2+}$.

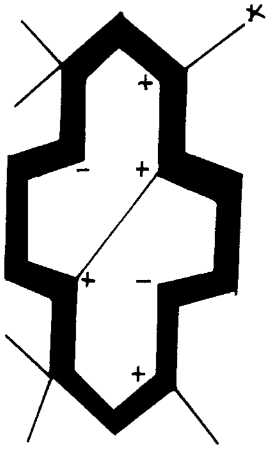

Figure 5. Configuration of the folded [Ni(α-*meso*-1,4-CTH)]$^{2+}$. For details see caption to Figure 1.

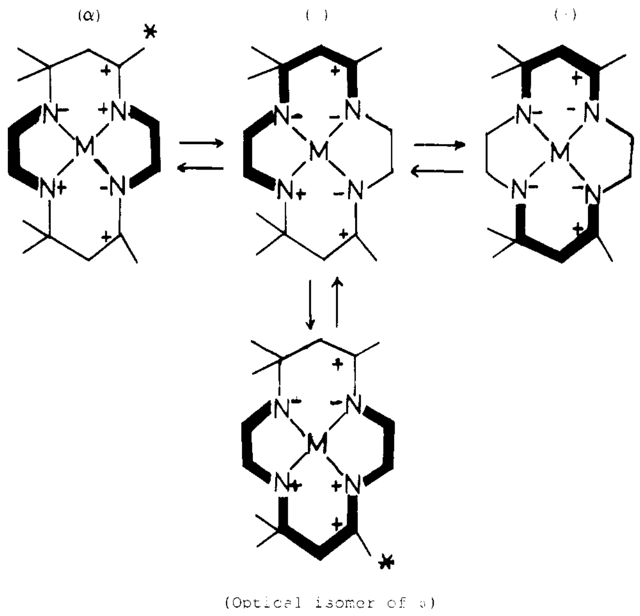

Figure 6. Reaction scheme for the configurational conversions of [Ni(*meso*-1,4-CTH)]$^{2+}$ isomers. For details see caption to Figure 1.

Table V. Infrared Data[a] for the [Ni(1,4-CTH)(NCS)$_2$] Isomers

isomer	ν(CN of NCS), cm^{-1}	Δν(CN of NCS), cm^{-1}
Ni(β-*rac*-1,4-CTH)(NCS)$_2$	2015	0
Ni(α-*meso*-1,4-CTH)(NCS)$_2$	2029, 2042	13
Ni(β-*meso*-1,4-CTH)(NCS)$_2$	2013, 2065	52
Ni(γ-*meso*-1,4-CTH)(NCS)$_2$	2010, 2057	47
Ni(δ-*meso*-1,4-CTH)(NCS)$_2$	2035, 2065	30

[a] All spectra obtained by using a pellet made from a mixture of the sample with KBr.

that [Ni(β-*meso*-1,4-CTH)]$^{2+}$ is the predominant form in basic solution of [Ni(*meso*-1,4-CTH)]$^{2+}$ indicates that [Ni(β-*meso*-1,4-CTH)]$^{2+}$ is the most stable isomer of [Ni(*meso*-1,4-CTH)]$^{2+}$. On this basis, structure **17** in Figure 1, which is highly unstable, can be ruled out, and structure **11** shown in Figure 1 is assigned to the [Ni(β-*meso*-1,4-CTH)]$^{2+}$ isomer. This structure is shown in Figure 4.

There is only one possible structure, **13** in Figure 1, that is consistent with the conformational information for [Ni(γ-*meso*-1,4-CTH)(NCS)$_2$] listed in Table IV. The only possible structure that is consistent with the conformational information for [Ni(δ-*meso*-1,4-CTH)(NCS)$_2$] is **12** in Figure 1. The idealized structures for these isomers are shown in Figure 4.

It is interesting to note that the four stable forms of these 10 theoretically possible isomers of [Ni(*meso*-1,4-CTH)]$^{2+}$, **11**, **12**, **13**, and **14** in Figure 1, are the structures assigned to the β, δ, γ, and α diastereoisomers, respectively. All the other forms are relatively unstable. A scheme for the isomerization reactions of these diastereoisomers is shown in Figure 6. The thermodynamics and kinetics of these reactions are the subject of a continuing study.

Infrared Spectral Studies of Ni(1,4-CTH)(NCS)$_2$ Isomers. The infrared data for the bis(thiocyanato) derivatives of these five stereoisomers are tabulated in Table V. All five isomers show ν(CN of NCS) bands in the 2010–2065-cm^{-1} region. Only one ν(CN of NCS) band is observed for [Ni(β-*rac*-1,4-CTH)(NCS)$_2$]. All the other stereoisomers show two ν(CN of NCS) bands. These results indicate that the axial sites are identical or very similar for [Ni(β-*rac*-1,4-CTH)(NCS)$_2$], while in the other isomers the two axial sites are different,[25] in agreement with the structures of these isomers given in Figure 4. The splitting of the two ν(CN of NCS) bands for [Ni(1,4-CTH)(NCS)$_2$] can be taken as measure of the degree of the difference of the axial sites of the complex. As shown in Figure 4, in [Ni(β-*meso*-1,4-CTH)(NCS)$_2$] all of the four amine protons are above the nickel(II)–four-nitrogen plane. In [Ni(γ-*meso*-1,4-CTH)(NCS)$_2$] three amine protons are above the nickel(II)–four-nitrogen plane; only one amine proton is below this plane. In [Ni(δ-*meso*-1,4-CTH)(NCS)$_2$] or [Ni(α-*meso*-1,4-CTH)(NCS)$_2$], two amine protons are above and the other two amine protons are below the nickel(II)–four-nitrogen plane. Thus we may expect the degree of the difference on the axial sites varies in the order [Ni(β-*meso*-1,4-CTH)(NCS)$_2$] > [Ni(γ-*meso*-1,4-CTH)(NCS)$_2$] > [Ni(δ-*meso*-1,4-CTH)(NCS)$_2$], [Ni(α-*meso*-1,4-CTH)(NCS)$_2$] > [Ni(β-*rac*-1,4-CTH)(NCS)$_2$]. The values of the splittings of the ν(CN of NCS) bandsof these isomers listed in Table V substantiate this expectation.

Acknowledgment. The authors are grateful to the Chemistry Research Center, National Science Council of the Republic of China, for financial support. We are grateful to Dr. Chi-Chao Wan and Yuan-Chung Hsieh for performing elemental analyses and for providing laboratory facilities.

Registry No. Ni(β-*rac*-1,4-CTH)(ClO$_4$)$_2$, 57427-11-9; Ni(β-*rac*-1,4-CTH)(NCS)$_2$, 89361-31-9; [Ni(α-*meso*-1,4-CTH)(acac)](ClO$_4$), 89278-58-0; Ni(α-*meso*-1,4-CTH)(ClO$_4$)$_2$, 89361-33-1; Ni(α-*meso*-1,4-CTH)(NCS)$_2$, 89394-78-5; Ni(α-*meso*-1,4-CTH)Cl$_2$, 89394-79-6; Ni(β-*meso*-1,4-CTH)(ClO$_4$)$_2$, 89361-35-3; Ni(β-*meso*-1,4-CTH)(NCS)$_2$, 89394-80-9; Ni(γ-*meso*-1,4-CTH)(ClO$_4$)$_2$, 89361-37-5; Ni(γ-*meso*-1,4-CTH)(NCS)$_2$, 89394-81-0; Ni(δ-*meso*-1,4-CTH)(ClO$_4$)$_2$, 87302-44-1; Ni(δ-*meso*-1,4-CTH)(NCS)$_2$, 89361-38-6; Ni(1,4-CT)(ClO$_4$)$_2$, 14875-35-5.

Supplementary Material Available: Figures 2 and 3 (^{1}H NMR spectra) (2 pages). Ordering information is given on any current masthead page.

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Notes

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Preparation and Characterization of Low-Spin Iron(II) Porphyrin Complexes with Bis(phosphine) or Bis(phosphite) Axial Ligands

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Received July 5, 1983

Axial ligation in iron porphyrin complexes has been the subject of extensive investigations, in connection with its biological significance. Several reports have attempted to correlate Mössbauer data of hexacoordinate low-spin Fe(II) porphyrin complexes with the electronic properties of the fifth and sixth axial ligands.[1,2] In most cases, it is tacitly assumed that the nature of iron–porphyrin bonds is unaffected by changes in axial ligands, whereas the bonding situation is rather complicated in some cases. For example, Sams et al.[2] explained the apparent anomaly in Mössbauer parameters for carbonyl hemochromes by considering a cis effect or an "electron sink" capability of macrocyclic planar ligands.

We have prepared and characterized several new low-spin Fe(II) complexes, Fe(p)L$_2$, where p = the dianion of meso-tetraphenylporphine (TPP) or phthalocyanine (Pc) and L = trialkylphosphine (PR$_3$) or trialkyl phosphite (P(OR)$_3$). With these complexes having axial ligands of distinct σ- and π-bonding characteristics, a comparative Mössbauer investigation was carried out to verify such an "electron sink" capability of macrocycles. This study also offers the characterization of the electronic spectra of Fe(p)L$_2$.

Experimental Section

^{57}Fe(TPP)Cl was synthesized and purified following published methods.[3-5] ^{57}Fe(TPP)(PR$_3$)$_2$ (R = Et, *n*-Bu) was prepared by refluxing a solution of ^{57}Fe(TPP)Cl (70 mg) in PR$_3$ (1 mL) and dichloromethane (70 mL) under nitrogen for 1 h, reducing to a small volume by vacuum evaporation, and adding methanol. The black-purple crystals that resulted were collected and washed with methanol. ^{57}Fe(TPP)[P(OR)$_3$]$_2$ (R = Me, Et, *n*-Bu) was prepared similarly. Anal. Calcd for Fe(TPP)(PBu$_3$)$_2$: C, 76.1; H, 7.70; N, 5.22. Found: C, 76.2; H, 7.58; N, 5.23. Other ^{57}Fe(TPP)L$_2$ complexes also gave correct analyses.

FePc was purchased from Eastman Kodak. FePc(PEt$_3$)$_2$ was prepared by combining FePc (420 mg) and an excess of PEt$_3$ in benzene (170 mL) and stirring the suspension for 10 h. The filtered solution was then evaporated to a small volume and diethyl ether–ethanol (1:1) was added. On partial evaporation dark crystals precipitated. Recrystallization from toluene–pentane yielded dark green crystals. FePc[P(*n*-Bu)$_3$]$_2$ and FePc[P(OEt)$_3$]$_2$ were prepared as described.[6,7] Anal. Calcd for FePc(PEt$_3$)$_2$: C, 65.7; H, 5.76; N, 13.93. Found: C, 65.4; H, 5.65; N, 13.99. Other FePcL$_2$ complexes also gave correct analyses.

Electronic spectra were measured as dichloromethane solutions with small amounts of axial ligand to prevent dissociation and autoxidation with a Hitachi 200-10 spectrophotometer.

Mössbauer spectra were measured with an Elscint AME-30A equipped with a ^{57}Co(Rh) source. Powder samples were loaded under nitrogen into acrylic cells that were then sealed with resin. The Doppler velocity scale was calibrated with a metallic ^{57}Fe foil, the isomer shift δ is quoted relative to the centroid of the iron-foil spectrum. Estimated

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