Summary. It has been shown that the tripodlike amine tricarboxylate ligands, nta and β-alada, coordinate as quadridentate chelating agents to Cr(III), not as terdentate ligands with the amine free as previously reported. Absorption spectral changes which had been ascribed to ter-/quadridentate changes in coordination are, in fact, associated with dimer formation instead, where cis-coordinated waters in the monomers are replaced by bridging hydroxides in the dimers. The conclusions reached in this study are consistent with previously reported studies of the corresponding Co(III)–nta complex. Deuteron NMR spectroscopy was instrumental to the study of the mode of ligand coordination and the dimerization process.

Acknowledgment. The authors thank D. Appel for his continuing help in obtaining NMR data. Acknowledgment is made to W. D. Wheeler and C. A. Green for helpful discussions. This study was partially supported by the USDA (Grant No. 82-CRCR-1-1005) and NIH (Grant No. GM 23081). The Nicolet NT-200WB was acquired with the assistance of the Boeing Corp.

Registry No. K$_2$[Cr(nta)(OH)]$_2$, 38122-55-3; Li$_2$[Cr(nta)(OH)]$_2$, 102539-13-9; K[Cr(nta)(acac)], 102628-85-3; K$_2$[Cr(nta)(mal)], 102539-14-0; K$_2$[Cr(nta)(ox)], 102629-49-2; *unsym*-[Cr(β-alada)(H$_2$O)$_2$], 26268-77-9; *unsym*-K[Cr(β-alada)(acac)], 102539-15-1; *sym*-K[Cr(β-alada)(acac)], 102628-86-4; *unsym*-K$_2$[Cr(β-alada)(mal)], 102539-16-2; *sym*-K$_2$[Cr(β-alada)(mal)], 102628-87-5; *unsym*-K$_2$[Cr(β-alada)(ox)], 102575-54-2; Cr(nta)(H$_2$O), 18042-08-5; H$_3$nta-d_6, 102539-17-3; *trans*-(*N*)-K[Co(gly)(nta)], 23242-64-0; β-H$_3$alada-d_4, 102539-18-4; *unsym,trans*(*N*)-NH$_4$[Co(β-alada)(gly)], 102628-88-6; D$_2$, 7782-39-0.

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Conformational Characterization of the Stereoisomers of a Nickel(II) Macrocyclic Tetraamine Complex

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Six stereoisomers of the complex (5,5,7,12,12,14-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

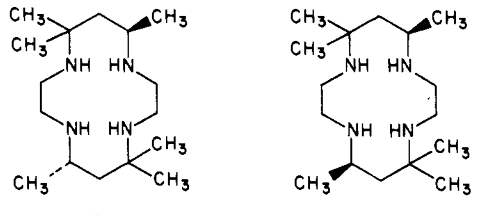
In a previous paper[1] we reported the stereochemistry of the diastereoisomers of the complex (5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), [Ni(1,4-CTH)]$^{2+}$. This paper concerns the diastereoisomers of the nickel(II) complexes of *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *meso*-1,7-CTH or tet a, and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *rac*-1,7-CTH or tet b (Chart I). The complex ion [Ni(1,7-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. Four of these diastereoisomers, Ni(β-*meso*-1,7-CTH)(ClO$_4$)$_2$, Ni(α-*rac*-1,7-CTH)(ClO$_4$)$_2$, Ni(β-*rac*-1,7-CTH)(ClO$_4$)$_2$, and Ni(γ-*rac*-1,7-CTH)(ClO$_4$)$_2$, have been prepared, and their X-ray crystal structures have been reported by Curtis et al.[2-4] In this work, two new stereoisomers of this complex, the δ and the ϵ diastereoisomers, were prepared. The electronic, infrared, and proton magnetic resonance spectra, as well as the stereochemistry of these six isomers in solution, were investigated.

Experimental Section

Reagents. Ni(β-*meso*-1,7-CTH)(ClO$_4$)$_2$, Ni(α-*rac*-1,7-CTH)(ClO$_4$)$_2$, Ni(β-*rac*-1,7-CTH)(ClO$_4$)$_2$, and Ni(γ-*rac*-1,7-CTH)(ClO$_4$)$_2$. These complexes were prepared by using the reported procedures.[3-6]

Ni(δ-*rac*-1,7-CTH)(ClO$_4$)$_2$. A 0.5-g sample of Ni(α-*rac*-1,7-CTH)(ClO$_4$)$_2$ was dissolved in 100 mL of water at 80 °C that had been acidified with a few drops of 70% HClO$_4$, and then 4 drops of diluted aqueous ammonia was added. This solution was still acidic. After the solution was cooled, a yellow product crystallized. This product was filtered and dried in vacuo. Anal. Calcd for C$_{16}$H$_{36}$N$_4$NiCl$_2$O$_8$: C, 35.45; H, 6.69; N, 10.34. Found: 35.50; H, 6.63; N, 10.26.

Chart I



I
tet a or *meso*-1,7-CTH

II
tet b or *rac*-1,7-CTH

Ni(ϵ-*rac*-1,7-CTH)(ClO$_4$)$_2$. The isomer was prepared by stirring at room temperature 0.5 g of Ni(α-*rac*-1,7-CTH)(ClO$_4$)$_2$ in 100 mL of diluted aqueous ammonia. An excess of sodium perchlorate was added; the orange product precipitated. This product was filtered, washed with water, ethanol, and ether, and then dried in vacuo. Anal. Calcd for C$_{16}$H$_{36}$N$_4$NiCl$_2$O$_8$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.42; H, 6.51; N, 10.28.

Ni(β-*meso*-1,7-CTH)Cl$_2$, Ni(β-*meso*-1,7-CTH)(NCS)$_2$, Ni(α-*rac*-1,7-CTH)(NCS)$_2$, Ni(β-*rac*-1,7-CTH)(NCS)$_2$, and Ni(γ-*rac*-1,7-CTH)(NCS)$_2$. These complexes were prepared by using the methods described by Ito and Toriumi,[7] Warner and Busch,[6] and Dei.[8]

Ni(α-*rac*-1,7-CTH)Cl$_2$. This derivative was prepared by stirring 4 g of Ni(α-*rac*-1,7-CTH)(ClO$_4$)$_2$ in 100 mL of 0.1 N 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 was isolated by filtration and dried in vacuo. Anal. Calcd for C$_{16}$H$_{36}$N$_4$NiCl$_2$: C, 46.41; H, 8.76; N, 13.53. Found: C, 46.42; H, 8.79; N, 13.55.

Ni(δ-*rac*-1,7-CTH)Cl$_2$. This derivative was prepared from Ni(δ-*rac*-1,7-CTH)(ClO$_4$)$_2$ by following the same procedure described above for

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Ni(α-*rac*-1,7-CTH)Cl$_2$. Anal. Calcd for $C_{16}H_{36}N_4NiCl_2$: C, 46.41; H, 8.76; N, 13.53. Found: C, 46.45; H, 8.75; N, 13.56.

Ni(δ-*rac*-1,7-CTH)(NCS)$_2$. This derivative was prepared by stirring 2 g of Ni(δ-*rac*-1,7-CTH)(ClO$_4$)$_2$ in 50 mL of 10^{-2} N HBF$_4$ to which 5 g of NaNCS had been added. An insoluble blue material formed immediately. The mixture was stirred for 2 h and the product isolated by filtration. It was washed with water, ethanol, and ether and then dried in vacuo. Anal. Calcd for $C_{18}H_{36}N_6NiS_2$: C, 47.06; H, 7.90; N, 18.30. Found: C, 47.07; H, 7.87; N, 18.26.

Ni(ε-*rac*-1,7-CTH)(NCS)$_2$. Upon dissolution of 1.3 g of Ni(ε-*rac*-1,7-CTH)(ClO$_4$)$_2$ and 1.3 g of KNCS in 50 mL of H$_2$O that had been acidified with 2 drops of 50% HBF$_4$, a yellow solution and a white precipitate were obtained. When 50 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 off and the chloroform layer isolated. The chloroform solution was dried by filtration through a Büchner funnel filled with Type 5A molecular sieves. It was evaporated to dryness under a stream of air and dried in vacuo. Anal. Calcd for $C_{18}H_{36}N_6NiS_2$: C, 47.06; H, 7.90; N, 18.30. Found: C, 46.99; H, 7.85; N, 18.45.

Instrumentation. Cary 17 and Perkin-Elmer Lambda-5 UV-vis spectrophotometers with a thermostated cell compartment were used to measure electronic absorption spectra. Proton magnetic resonance spectra were determined on a JEOL FX-100 spectrometer and a Bruker AM-400 NMR spectrometer. Shifts were calibrated from internal tetramethylsilane. Infrared spectra were determined from Nujol mulls sandwiched between KRS-5 plates and from KBr pellets with use of a JASCO A-3 infrared spectrophotometer and a Perkin-Elmer 580 spectrophotometer.

Results and Discussion

Stereochemical Considerations. There are two asymmetric carbons in Ni(1,7-CTH)$^{2+}$. The presence of these two asymmetric centers affords the possibility of two diastereoisomers, Ni(*meso*-1,7-CTH)$^{2+}$ and Ni(*rac*-1,7-CTH)$^{2+}$. Each of these complex ions can exist in 10 theoretically possible diastereoisomeric forms, depending on the configuraitons of the four asymmetric coordinated secondary amines. The configurations of these isomers are represented in Figure 1, together with their relative (chelate ring conformational plus substituent interaction) energies assessed by Curtis.[9]

The six-membered chelate ring may adopt a stable chair conformation or unstable twist conformations, depending on the configurations of the consecutive pair of the asymmetric nitrogens and the asymmetric carbon.[10,11] As shown in Figure 1, a stable chair six-membered chelate ring has the (4*S*, 7*S*, 8*R*) or (4*R*, 7*R*, 8*S*) configurations of the chiral (4-nitrogen, 7-carbon, 8-nitrogen) centers. The three asymmetric centers of the most unstable six-membered chelate ring are of the same *R* or *S* configuration. The relative energies of the six-membered chelate rings are given in eq 1 in terms of the configurations of the three asymmetric centers.

$$(4SR,\ 7SR,\ 8RS) < (4RS,\ 7SR,\ 8RS) < (4RS,\ 7SR,\ 8SR) < (4RS,\ 7RS,\ 8RS) \quad (1)$$

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 configuration, *R* and *S*.[1]

Electronic Absorption Spectra. The electronic spectral data for the six diastereoisomers of Ni(1,7-CTH)$^{2+}$ in solutions measured in this work and reported previously[6] are given in Table I. The complexes Ni(β-*meso*-1,7-CTH)(ClO$_4$)$_2$, Ni(β-*rac*-1,7-CTH)(ClO$_4$)$_2$, Ni(γ-*rac*-1,7-CTH)(ClO$_4$)$_2$, and Ni(ε-*rac*-1,7-CTH)(ClO$_4$)$_2$ dissolve in each of these solvents, CH$_3$CN, Me$_2$SO, acetone, and H$_2$O, to give yellow or yellow-orange solutions. The electronic absorption spectrum of each of these complexes in solution is typical of singlet-state, four-coordinate, square-planar nickel(II) (Table I). The characteristic single absorption band in the 21 000–23 000-cm^{-1} region is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition of square-planar tetraamine macrocyclic ligand complexes of nickel(II).[6,12]

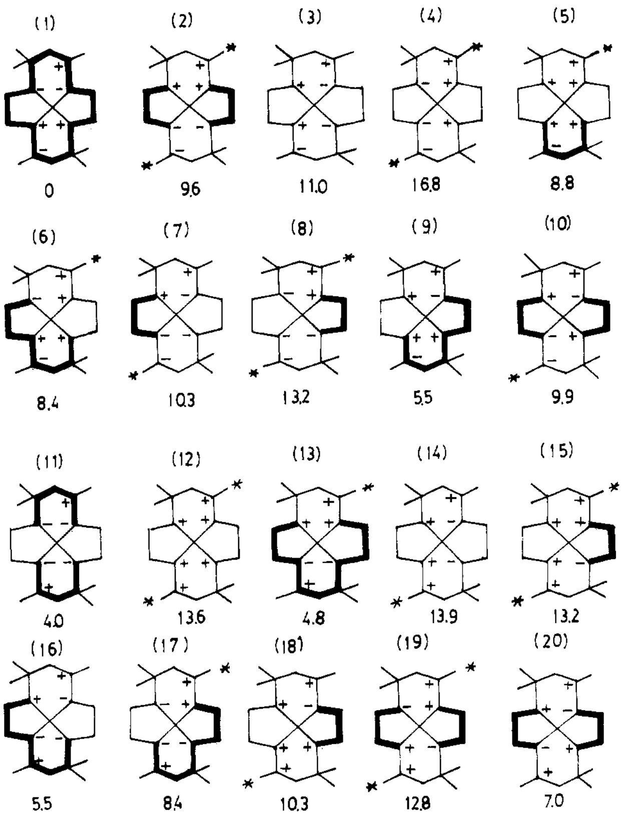

Figure 1. Configurational isomers of Ni(*meso*-1,7-CTH)$^{2+}$ (1–10) and Ni(*rac*-1,7-CTH)$^{2+}$ (11–20). The number below each configuration indicates the total energy of the configuration, relative to the most stable configuration (1), in kcal mol^{-1}. A plus sign at an asymmetric center indicates 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 five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by heavier lines. The axial C5 and C12 methyl groups are indicated with an asterisk.

Ni(α-*rac*-1,7-CTH)(ClO$_4$)$_2$ and Ni(δ-*rac*-1,7-CTH)(ClO$_4$)$_2$ dissolve in acetone and water to give yellow diamagnetic square-planar nickel(II) species. However, in acetonitrile and dimethyl sulfoxide, they give violet and green solutions, respectively. The visible spectral data show a mixture of diamagnetic square-planar and paramagnetic solvated species present in these solutions (eq 2). Here S is a solvent molecule. From the apparent

$$[NiL]^{2+} + 2S \rightleftarrows [NiLS_2]^{2+} \quad (2)$$

extinction coefficients of the singlet band, ν_s, for these two complexes, it can be seen that the rodlike acetonitrile is coordinated more strongly than dimethyl sulfoxide. The donor abilities of the solvents used in this work vary in the order[13,14] MeCN (14.1) < acetone (17.0) < H$_2$O (18.0) < Me$_2$SO (29.8). However, the tendency of axial coordination varies in the order acetone, H$_2$O < Me$_2$SO < MeCN. It is interesting to note that the weakest donor molecule, MeCN, is most strongly bound. This result indicates that steric interactions are of importance in determining the extent of axial addition.[15] Axial additions are not observed

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Table I. Electronic Absorption Spectral Data for the Isomers of Ni(1,7-CTH)(ClO_4)$_2$

isomer	solvent	color	ν_{max}, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	transition[b]
Ni(*β-meso*-1,7-CTH)$^{2+}$	CH_3CN[a]	yellow	21 300	63.0	$^1A_{1g} \rightarrow {}^1E_g$
	Me_2SO	yellow	21 500	86.3	$^1A_{1g} \rightarrow {}^1E_g$
	acetone	yellow	21 280	77.5	$^1A_{1g} \rightarrow {}^1E_g$
	H_2O[a]	yellow-orange	21 600	80.0	$^1A_{1g} \rightarrow {}^1E_g$
Ni(*α-rac*-1,7-CTH)$^{2+}$	CH_3CN[a]	violet	10 810	12.0	$^3B_{1g} \rightarrow {}^3E_g{}^a$
			12 270	9.0	$^3B_{1g} \rightarrow {}^3B_{2g}$
					$^3B_{1g} \rightarrow {}^3A_{2g}(F)$
			17 980	16.0	$^3B_{1g} \rightarrow {}^3E_g{}^b$
			22 470	8.0	$^1A_{1g} \rightarrow {}^1E_g$
			27 864	24.0	$^3B_{1g} \rightarrow {}^3A_{2g}(P), {}^3E_g(P)$
	Me_2SO[a]	green	9 680	15.0	$^3B_{1g} \rightarrow {}^3E_g{}^a$
					$^3B_{1g} \rightarrow {}^3B_{2g}$
					$^3B_{1g} \rightarrow {}^3A_{2g}(F)$
			16 360	11.0	$^3B_{1g} \rightarrow {}^3E_g{}^b$
			22 500	27.0	$^1A_{1g} \rightarrow {}^1E_g$
			26 240	25.0	$^3B_{1g} \rightarrow {}^3A_{2g}(P), {}^3E_g(P)$
	acetone[a]	yellow	22 030	71.0	$^1A_{1g} \rightarrow {}^1E_g$
	H_2O[a]	yellow	22 400	68.0	$^1A_{1g} \rightarrow {}^1E_g$
Ni(*β-rac*-1,7-CTH)$^{2+}$	CH_3CN[a]	yellow	21 700	101.0	$^1A_{1g} \rightarrow {}^1E_g$
	Me_2SO	yellow	22 170	111.3	$^1A_{1g} \rightarrow {}^1E_g$
	acetone	yellow	21 800	99.0	$^1A_{1g} \rightarrow {}^1E_g$
	H_2O[a]	yellow	22 026	105.0	$^1A_{1g} \rightarrow {}^1E_g$
Ni(*γ-rac*-1,7-CTH)$^{2+}$	CH_3CN	yellow-orange	21 367	112.0	$^1A_{1g} \rightarrow {}^1E_g$
	Me_2SO	orange	21 480	125.0	$^1A_{1g} \rightarrow {}^1E_g$
	acetone	orange	21 191	105.0	$^1A_{1g} \rightarrow {}^1E_g$
	H_2O	yellow	21 767	109.0	$^1A_{1g} \rightarrow {}^1E_g$
Ni(*δ-rac*-1,7-CTH)$^{2+}$	CH_3CN	violet	11 037	15.0	$^3B_{1g} \rightarrow {}^3E_g{}^a$
			12 315	8.0 sh	$^3B_{1g} \rightarrow {}^3B_{2g}$
					$^3B_{1g} \rightarrow {}^3A_{2g}(F)$
			17 953	15.0	$^3B_{1g} \rightarrow {}^3E_g{}^b$
			21 882	7.0	$^1A_{1g} \rightarrow {}^1E_g$
			27 778	23.0	$^3B_{1g} \rightarrow {}^3A_{2g}(P), {}^3E_g(P)$
	Me_2SO	yellow-green	<11 000	?	$^3B_{1g} \rightarrow {}^3E_g{}^a$
					$^3B_{1g} \rightarrow {}^3B_{2g}$
					$^3B_{1g} \rightarrow {}^3A_{2g}(F)$
			16 340	11.0	$^3B_{1g} \rightarrow {}^3E_g{}^b$
			22 371	28.0	$^1A_{1g} \rightarrow {}^1E_g$
			26 247	27.7	$^3B_{1g} \rightarrow {}^3A_{2g}(P), {}^3E_g(P)$
	acetone	yellow	22 051	75.0	$^1A_{1g} \rightarrow {}^1E_g$
	H_2O	yellow	22 168	72.0	$^1A_{1g} \rightarrow {}^1E_g$
Ni(*ε-rac*-1,7-CTH)$^{2+}$	CH_3CN	orange	21 600	103.0	$^1A_{1g} \rightarrow {}^1E_g$
	Me_2SO	yellow-orange	22 012	114.0	$^1A_{1g} \rightarrow {}^1E_g$
	acetone	orange	21 748	103.5	$^1A_{1g} \rightarrow {}^1E_g$
	H_2O	yellow	21 940	107.6	$^1A_{1g} \rightarrow {}^1E_g$

[a] Data from ref 6. [b] References 6, 12, 25.

Table II. Isotropic Shift Data (ppm)[a,b] and Spectral Assignments for Paramagnetic Ni(1,7-CTH)X_2 Isomers in $CDCl_3$ Solution at 34 °C

	5-membered chelate rings		6-membered chelate rings					
isomer	CH_{ax}	CH_{eq}	α-CH_{ax}	β-CH_{ax}	β-CH_{eq}	Me(II)$_{eq}$	Me(III)$_{ax}$	Me(I)
Ni(*β-meso*-1,7-CTH)Cl_2[c]	−30	−189	−55	+5	+13.8	−20.1	+4.2	−13.7
	−20	−180						
Ni(*α-rac*-1,7-CTH)Cl_2[d]	−33	−180	−51	+6	+18.0	−20.1	+4.1	−17.2
	−25	−175						
Ni(*β-rac*-1,7-CTH)$(NCS)_2$[c]	−33	−76	−49	+6	+15.5	−22.7	+4.7	−17.3
		−125						
Ni(*γ-rac*-1,7-CTH)$(NCS)_2$[c]		−194	−47	+7	+15.4	−19.8	+4.0	+0.7
	−23	−163			+17.4			−14.9
Ni(*δ-rac*-1,7-CTH)Cl_2[d]	−33.7	−78, −170	−52	+6	+16.9	−20.0	+4.0	−17.1
	−20.0	−130, −177			+18.0			
Ni(*ε-rac*-1,7-CTH)$(NCS)_2$[d]	−34.3	−78, −195	−50	+6.8	+15.8	−22.4	+5.1	+0.4
	−18.5	−127, −169			+23.0			−17.1

[a] The isotropic shifts are determined relative to the shifts of the diamagnetic nickel(II) complexes: (a) β-CH_{eq}, −1.8 ppm; (b) β-CH_{ax}, −1.2 ppm; (c) α-CH_{ax}, −3.4 ppm; (d) CH_{eq}, −2.6 ppm; (e) CH_{ax}, −2.4 ppm; Me(I), −1.0 ppm; Me(II)$_{eq}$, −1.1 ppm; Me(III)$_{ax}$, −2.2 ppm. [b] Key: ax = axial; eq = equatorial. [c] Reference 8. [d] This work.

with Ni(*β-meso*-1,7-CTH)$^{2+}$, Ni(*β-rac*-1,7-CTH)$^{2+}$, Ni(*γ-rac*-1,7-CTH)$^{2+}$, and Ni(*ε-rac*-1,7-CTH)$^{2+}$ since the axial methyl groups sterically congest the axial sites.

Proton Magnetic Resonance Spectra of the Paramagnetic Hexacoordinate Complexes NiLX_2. The isotropic shift data for the bis(isothiocyanato) and dichloro derivatives of these stereoisomers reported by Dei[8] and measured in this work are tabulated in Table II. The proton magnetic resonance spectra measured in this work are deposited as supplemental material. Both the resonance position and the line width are strictly related to the conformational character of each resonating proton.[16–19] The

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Table III. Conformations of the Diastereoisomers of Ni(1,7-CTH)X_2

diastereoisomer	5-membered chelate ring conformations	6-membered chelate ring conformations	Me on asymmetric C
Ni(β-*meso*-1,7-CTH)Cl_2	equiv, two stable gauche rings	equiv	two equatorial groups
Ni(α-*rac*-1,7-CTH)Cl_2	equiv, two stable gauche rings	equiv	two equatorial groups
Ni(β-*rac*-1,7-CTH)$(NCS)_2$	equiv, two unstable distorted rings	equiv	two equatorial groups
Ni(γ-*rac*-1,7-CTH)$(NCS)_2$	equiv, two stable gauche rings	nonequiv	one equatorial group and one distorted axial group
Ni(δ-*rac*-1,7-CTH)Cl_2	nonequiv, one stable gauche ring and one unstable distorted ring	nonequiv	two equatorial groups
Ni(ϵ-*rac*-1,7-CTH)$(NCS)_2$	nonequiv, one stable gauche ring and one unstable distorted ring	nonequiv	one equatorial group and one distorted axial group

number of resonance signals is useful in the structural assignments for these diastereoisomers: a large number of resonance signals is expected for the diastereoisomer containing nonequivalent chelate rings; a smaller number of resonance signals is expected for the diastereoisomer whose chelate rings are pairwise equivalent. The results obtained on the basis of the number of resonance signals are given in Table II.

The five-membered chelate ring may adopt a stable gauche conformation or an unstable conformation (Figure 1). The isotropic shifts of the axial protons of the ethylene chain occurs in the range −18 to −35 ppm, and these signals are not sensitive to the conformations of the chelete rings. In contrast, the signals of the equatorial protons of the ethylene chain are very sensitive to the conformations of the five-membered chelate rings. The isotropic shifts of the equatorial protons of the ethylene chain in a stable gauche five-membered ring appear between −160 and −200 ppm. On the other hand, the isotropic shifts of these protons in an unstable five-membered ring appear between −70 and −130 ppm. Two resonance signals of these equatorial protons indicate the two five-membered chelate rings are pairwise equivalent; four resonance signals are expected for the complex containing nonequivalent five-membered chelate rings. The isotropic shift data given in Table II indicate that Ni(β-*meso*-1,7-CTH)Cl_2, Ni(α-*rac*-1,7-CTH)Cl_2, and Ni(γ-*rac*-1,7-CTH)$(NCS)_2$ contain two equivalent stable gauche five-membered chelate rings each; Ni(β-*rac*-1,7-CTH)$(NCS)_2$ contains two equivalent unstable five-membered chelate rings; Ni(δ-*rac*-1,7-CTH)Cl_2 and Ni(ϵ-*rac*-1,7-CTH)$(NCS)_2$ contain one stable gauche five-membered chelate ring and one unstable five-membered chelate ring each.

If the unstable five-membered chelate ring were of the exactly eclipsed conformation, the isotropic shift signals of the protons of the ethylenic chain would occur together in the −80 to −90 ppm region.[17,19] This has not been observed. The isotropic shift data for the unstable five-membered chelate rings of Ni(β-*rac*-1,7-CTH)$(NCS)_2$, Ni(δ-*rac*-1,7-CTH)Cl_2, and Ni(ϵ-*rac*-1,7-CTH)$(NCS)_2$ listed in Table II are very similar and indicate these unstable chelate rings adopt a very strongly distorted gauche conformation in which the methylene protons of the ethylenic chain are intermediate between the axial–equatorial limiting positions.

The isotropic shift signals that appear between the −47 and −55 ppm region of the spectra are assigned to the protons attached to the asymmetric carbons in the six-membered chelate rings. The isotropic shifts of the axial protons attached on the methylene carbons at the center of the six-membered chelate rings appear in the 5–7-ppm region. The signals of the equatorial protons on the methylene carbons at the center of the six-membered rings that appear between 14 and 23 ppm are very sensitive to the conformations of the six-membered chelate rings. One resonance signal of these protons indicates the two six-membered chelate rings are pairwise equivalent; two resonance signals are expected for the complex containing nonequivalent six-membered chelate rings. The isotropic shift data of these protons given in Table II indicate that Ni(β-*meso*-1,7-CTH)Cl_2, Ni(α-*rac*-1,7-CTH)Cl_2, and Ni(β-*rac*-1,7-CTH)$(NCS)_2$ contain two equivalent six-membered chelate rings; Ni(γ-*rac*-1,7-CTH)$(NCS)_2$, Ni(δ-*rac*-1,7-CTH)Cl_2, and Ni(ϵ-*rac*-1,7-CTH)$(NCS)_2$ contain two nonequivalent six-membered chelate rings.

(A) 1.0 (B) 2.8

Figure 2. Configurations of stable coordinated *rac*-1,7-CTH with the macrocycle folded along the line shown; key as in Figure 1.

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.[6,8] Similarly, the asymmetric carbon of the six-membered ring provides axial and equatorial distinctions for the groups attached to it. Thus, the methyl group attached to this carbon can be either axial or equatorial. The isotropic shift signals of the equatorial geminal methyl groups, which oriented out away from the metal ion center, appear in the −20 to −23 ppm region; the isotropic shift signals of the axial geminal methyl groups, which reside over the NiN_4 plane, appear in the 4.0–5.1-ppm region. The signals of the equatorial methyl groups attached to the asymmetric carbons appear in the −13.7 to −17.3 ppm region; the signals of the axial methyl groups attached to the asymmetric carbons appear in the 0.4–0.7-ppm region. The results given in Table II indicate that Ni(β-*meso*-1,7-CTH)Cl_2, Ni(α-*rac*-1,7-CTH)Cl_2, Ni(β-*rac*-1,7-CTH)$(NCS)_2$, and Ni(δ-*rac*-1,7-CTH)Cl_2 contain two equatorial methyl groups attached to the asymmetric carbons; Ni(γ-*rac*-1,7-CTH)$(NCS)_2$ and Ni(ϵ-*rac*-1,7-CTH)$(NCS)_2$ contain one equatorial methyl group and one axial methyl group attached to the asymmetric carbons.

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 groups to be oriented out away from the metal ion center so that none of these groups reside over the NiN_4 plane.[4,6] As a result, no methyl group isotropic shift signals would appear in the 4–5-ppm region or in the 0–1-ppm region. All these signals would occur together in the −19.8 to −22.7 ppm region and in the −13.7 to −17.3 ppm region. This is not observed in this study. The results given in Table II indicate the six-membered chelate ring may adopt a stable chair conformation or an unstable twist conformation, not a boat conformation.

Structural Assignments for the Diastereoisomers. There are four asymmetric nitrogens in Ni(*meso*-1,7-CTH)$^{2+}$. The presence of these four asymmetric centers affords the possibility of 10 diastereoisomers, (1)–(10) in Figure 1. The only possible structure that is consistent with the conformational information for Ni(β-*meso*-1,7-CTH)$^{2+}$ listed in Table III is structure 1 in Figure 1, the most stable isomeric form of Ni(*meso*-1,7-CTH)$^{2+}$. This structure is assigned to Ni(β-*meso*-1,7-CTH)$^{2+}$, in agreement with the result established by X-ray crystallography.[4]

The 10 theoretically possible diastereoisomeric forms for Ni(*rac*-1,7-CTH)$^{2+}$ are shown as structures 11–20 in Figure 1. There is only one possible structure, (20) in Figure 1, that is consistent with the conformational information for Ni(α-*rac*-1,7-CTH)$^{2+}$ listed in Table III. In addition, this is the most stable isomeric form that readily forms a derivative with the macrocycle in folded

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Table IV. Configurations of the Stereoisomers of Ni(1,7-CTH)$^{2+}$

stereoisomer	configurations of the six asymmetric centers	configuration in Figure 1
Ni(β-*meso*-1,7-CTH)$^{2+}$	N1*RS*, N4*RS*, C7*RS*, N8*SR*, N11*SR*, C14*SR*	1
Ni(α-*rac*-1,7-CTH)$^{2+}$	N1*RS*, N4*RS*, C7*SR*, N8*RS*, N11*RS*, C14*SR*	20
Ni(β-*rac*-1,7-CTH)$^{2+}$	N1*RS*, N4*SR*, C7*SR*, N8*RS*, N11*SR*, C14*SR*	11
Ni(γ-*rac*-1,7-CTH)$^{2+}$	N1*RS*, N4*RS*, C7*SR*, N8*SR*, N11*SR*, C14*SR*	13
Ni(δ-*rac*-1,7-CTH)$^{2+}$	N1*RS*, N4*RS*, C7*SR*, N8*RS*, N11*SR*, C14*SR*	16
Ni(ϵ-*rac*-1,7-CTH)$^{2+}$	N1*RS*, N4*SR*, C7*SR*, N8*SR*, N11*SR*, C14*SR*	17

coordination (structure A in Figure 2), in agreement with the folded complex [Ni(α-*rac*-1,7-CTH)(acac)](ClO$_4$) reported by Curtis et al.,[20] whose structure has been established by X-ray crystallography. Therefore, the structure (20) in Figure 1 is assigned to Ni(α-*rac*-1,7-CTH)$^{2+}$. A molecular model of this isomer indicates that the two axial sites are quite open and accessible to small unidentate ligands, as the methyl groups attached to the asymmetric carbons are all equatorial.

The theoretically possible configurations of coordinated *rac*-1,7-CTH have been described and discussed by Curtis et al.[9] The two preferred folded forms of coordinated *rac*-1,7-CTH are shown in Figure 2, together with their relative energies assessed by Curtis et al.[9] It is interesting to note that folded structure A is observed for [Ni(α-*rac*-1,7-CTH)(CH$_3$COO)](ClO$_4$),[9,21] and that folded structure B is observed for [Cu(*rac*-1,7-CTH)(H$_2$O)](ClO$_4$)$_2$ (blue) or [Cu(*rac*-1,7-CTH)(NO$_3$)](ClO$_4$) (blue).[22,23]

There is only one possible structure, (11) in Figure 1, that is consistent with the conformational information for Ni(β-*rac*-1,7-CTH)$^{2+}$ listed in Table III. This is the most stable isomeric form of Ni(*rac*-1,7-CTH)$^{2+}$ and is assigned to the Ni(β-*rac*-1,7-CTH)$^{2+}$ isomer, in agreement with the structure established by X-ray crystallography.[4]

There is only one possible structure, (13) in Figure 1, that is consistent with the conformational information for Ni(γ-*rac*-1,7-CTH)$^{2+}$ listed in Table III. One of the two methyl groups attached to the asymmetric carbons of this isomer is axial. This methyl group and the geminal methyl groups sterically congest the axial sites. Thus, Ni(γ-*rac*-1,7-CTH)$^{2+}$ does not undergo axial additions with the solvents listed in Table I.

The only possible structure that is consistent with the conformational information for Ni(δ-*rac*-1,7-CTH)$^{2+}$ is (16) in Figure 1. A molecular model of this isomer indicates that the two axial sites are quite open and accessible to small unidentate ligands, as the methyl groups attached to the asymmetric carbons are all equatorial. The only possible structure that is consistent with the results listed in Table III for Ni(ϵ-*rac*-1,7-CTH)$^{2+}$ is (17) in Figure 1. Like the γ diastereoisomer, one of the two methyl groups attached to the asymmetric carbon of Ni(ϵ-*rac*-1,7-CTH)$^{2+}$ is axial and this isomer does not undergo axial additions with the solvents listed in Table I.

It is interesting to note that the five stable forms of these ten theoretically possible diastereoisomers of Ni(*rac*-1,7-CTH)$^{2+}$, (20), (11), (13), (16), and (17) in Figure 1, are the structures assigned to the α, β, γ, δ, and ϵ diastereoisomers, respectively. All the other forms are relatively unstable. A scheme for the isomerization reactions of these five diastereoisomers is shown in Figure 3. The thermodynamics and kinetics of these reactions are subject of a continuing study. The configurations of these six stereoisomers are listed in Table IV.

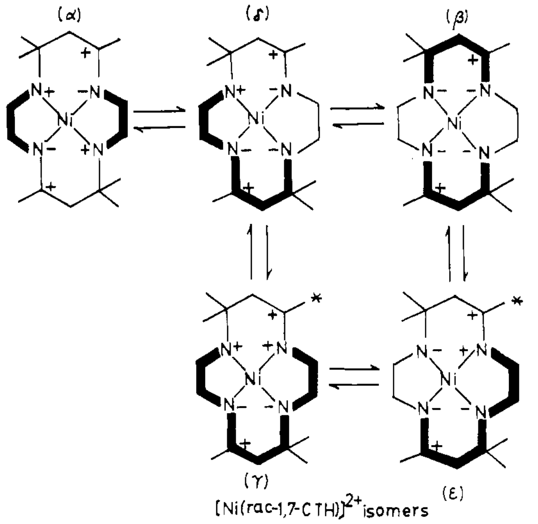

Figure 3. Reaction scheme for the configurational isomerizations of Ni(*rac*-1,7-CTH)$^{2+}$ isomers; key as in Figure 1.

Table V. Infrared Spectral Data[a] for Ni(1,7-CTH)(NCS)$_2$ Isomers

isomer	ν(CN of NCS),[b] cm^{-1}	$\Delta\nu$(CN), cm^{-1}
Ni(β-*meso*-1,7-CTH)(NCS)$_2$	2058 s sp	0
Ni(α-*rac*-1,7-CTH)(NCS)$_2$	2079 s sp 2039 w	40
Ni(β-*rac*-1,7-CTH)(NCS)$_2$	2083 s sp 2028 s sp	55
Ni(γ-*rac*-1,7-CTH)(NCS)$_2$	2076 s sp 2047 sh	29
Ni(δ-*rac*-1,7-CTH)(NCS)$_2$	2081 s sp 2037 w	44
Ni(ϵ-*rac*-1,7-CTH)(NCS)$_2$	2082 s sp 2032 s sp	50

[a] All spectra were obtained by using a pellet made from a mixture of the sample with KBr or Nujol mulls sandwiched between KRS-5 plates. [b] s = strong; sp = sharp; w = weak; sh = shoulder.

Infrared Spectral Studies of Ni(1,7-CTH)(NCS)$_2$ Isomers. The infrared spectral data for the bis(isothiocyanato) derivatives of these six stereoisomers are tabulated in Table V. All these isomers show ν(CN of NCS) bands in the 2020–2085-cm^{-1} region. Only one ν(CN of NCS) band is observed for Ni(β-*meso*-1,7-CTH)(NCS)$_2$. All the other stereoisomers show two ν(CN of NCS) bands. These results indicate that the two axial sites are identical or very similar for Ni(β-*meso*-1,7-CTH)(NCS)$_2$, while in the other five isomers the two axial sites are different,[24] in agreement with the structures of these isomers. Ni(β-*meso*-1,7-CTH)(NCS)$_2$ has a center of inversion as its symmetry element, and the two axial sites are identical. The racemic forms belong to either the C_2 or the C_1 point group; therefore, the two axial sites are different. The splitting of the two ν(CN of NCS) bands for Ni(1,7-CTH)(NCS)$_2$ can be taken as measure of the degree of the difference of the complex. As shown in Figure 3, in Ni(β-*rac*-1,7-CTH)(NCS)$_2$ all of the four amine protons are above the NiN$_4$ plane. In Ni(ϵ-*rac*-1,7-CTH)(NCS)$_2$ and Ni(δ-*rac*-1,7-CTH)(NCS)$_2$, three amine protons are above the NiN$_4$ plane; only one amine proton is below this plane. In Ni(α-*rac*-1,7-CTH)(NCS)$_2$ and Ni(γ-*rac*-1,7-CTH)(NCS)$_2$, two amine protons are above and the other two amine protons are below the NiN$_4$ plane. Thus, we may expect that the degree of the difference on the axial sites varies in the other Ni(β-*rac*-1,7-CTH)(NCS)$_2$ > Ni(ϵ-*rac*-1,7-CTH)(NCS)$_2$ > Ni(δ-*rac*-1,7-CTH)(NCS)$_2$ >

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Ni(α-*rac*-1,7-CTH)$(NCS)_2$ > Ni(γ-*rac*-1,7-CTH)$(NCS)_2$ > Ni(β-*meso*-1,7-CTH)$(NCS)_2$. The values of the splitting of the ν(CN of NCS) bands of these isomers listed in Table V substantiate this expectation.

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Registry No. Ni(δ-*rac*-1,7-CTH)$(ClO_4)_2$, 102629-52-7; Ni(α-*rac*-1,7-CTH)$(ClO_4)_2$, 51372-01-1; Ni(ϵ-*rac*-1,7-CTH)$(ClO_4)_2$, 102629-54-9; Ni(α-*rac*-1,7-CTH)Cl_2, 102629-55-0; Ni(δ-*rac*-1,7-CTH)Cl_2, 102629-56-1; Ni(δ-*rac*-1,7-CTH)$(NCS)_2$, 102629-57-2; Ni(ϵ-*rac*-1,7-CTH)$(NCS)_2$, 102629-58-3; Ni(β-*meso*-1,7-CTH)$(NCS)_2$, 14409-17-7; Ni(α-*rac*-1,7-CTH)$(NCS)_2$, 26029-89-0; Ni(β-*rac*-1,7-CTH)$(NCS)_2$, 26029-90-3; Ni(γ-*rac*-1,7-CTH)$(NCS)_2$, 15557-17-2.

Supplementary Material Available: Figure 4, showing proton magnetic resonance spectra for (A) Ni(α-*rac*-1,7-CTH)Cl_2, (B) Ni(δ-*rac*-1,7-CTH)Cl_2, and (C) Ni(ϵ-*rac*-1,7-CTH)$(NCS)_2$ in $CDCl_3$ solution at 34 °C (signals labeled with an asterisk due to impurities) (1 page). Ordering information is given on any current masthead page.

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Vibrational Spectroscopic Studies of μ-Hydrido-Bridged Metal Clusters. 1. $H_3Mn_3(CO)_{12}$

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Infrared and Raman spectra of $H_3Mn_3(CO)_{12}$ and its partially and fully deuterated analogues are reported and assignments made to the bands associated with ν_{CO}, ν_{MnMn}, and hydrogenic $\nu^{as}{}_{MnH/MnD}$, $\nu^{s}{}_{MnH/MnD}$, and $\gamma_{MnH/MnD}$ vibrations. Multiple bands observed in the regions of metal–hydrogen stretching modes are in part attributed to unequal MnHMn interbond angles in $H_3Mn_3(CO)_{12}$.

Introduction

Identification of the vibrations of μ_2- and μ_3-bridging hydrogen atom ligands in transition-metal hydrides is complicated by the low intensities and broad nature of the bands in infrared and Raman spectra.[1] However, recording spectra at liquid-nitrogen temperature markedly sharpens up these bands and provides a diagnostic aid to their assignments.[2-4] We present here a vibrational spectroscopic study of the μ-hydrido triangulo metal cluster $H_3Mn_3(CO)_{12}$ and of its deuterium-substituted derivatives. An X-ray diffraction study by Kirtley, Olsen, and Bau[5] shows the $H_3Mn_3(CO)_{12}$ compound to crystallize in the triclinic system, space group $P\bar{1}$, with two molecules per unit cell. The hydrogen atoms were located by using Fourier difference techniques and were found to be within the plane of the Mn_3 triangle giving an approximate molecular symmetry of D_{3h}. In more detail it was found that one of the μ-bridging hydrogen atoms has a considerably larger MHM angle (ca. 149°) than the other two (ca. 126 and ca. 119°), giving a more detailed point group of C_1, with C_{2v} worth considering as an approximation.

Experimental Section

$H_3Mn_3(CO)_{12}$ and its deuterium-substituted analogues were prepared from literature methods.[6] Infrared spectra, in the range 4000–200 cm^{-1}, were recorded on Perkin-Elmer 325, Perkin-Elmer 577, and Digilab FTS-14 spectrophotometers; a Beckman RIIC 1R720M interferometer was used in the range 400–10 cm^{-1}. Raman spectra were recorded on a Spex Raman spectrophotometer Model 1401 equipped with a Spectra Physics Model 165 mixed-gas laser. A rotating laser beam device, similar in construction to that reported by Zimmer and Kiefer,[7] was used to obtain the Raman spectra of $H_3Mn_3(CO)_{12}$, which was found to be highly sensitive to laser radiation.

Results and Discussion

To a first approximation it is convenient to divide the molecular vibrations into three main groups: the CO stretching modes, ν_{CO}; the metal–metal stretches, ν_{MM}; and the metal–hydrogen vibrations, $\nu^{as}{}_{MH}$, $\nu^{s}{}_{MH}$, and γ_{MHM}, where the first two MH modes involve MH bond stretching and the latter hydrogen deformation out of the MHM plane (as and s denote asymmetric and symmetric with respect to planes that approximately bisect the MHM angles). The metal–carbon stretching and the metal–carbon–oxygen bending vibrations will not be considered in great detail due to the complexity of the spectrum in the 650–350-cm^{-1} region, where these vibrations are typically observed. A description of ν_{CO} and ν_{MM} vibrations is listed in Table I, based on the approximate molecular symmetry of D_{3h}.

Table I. Symmetry Classifications of the ν_{CO} and ν_{MnMn} Modes in $H_3Mn_3(CO)_{12}$ or $D_3Mn_3(CO)_{12}$, Assuming D_{3h} Skeletal Symmetry[a-c]

description[c]	symmetry	activity
$\nu_{CO(ax)}$	a$'_1$	Ra only
$\nu_{CO(eq)}$		
ν_{MnMn}		
$\nu_{CO(eq)}$	a$'_2$	inactive
$\nu_{CO(ax)}$	e$'$	IR and Ra
$\nu_{CO(eq)}$		
$\nu_{CO(eq)}$		
ν_{MnMn}		
$\nu_{CO(ax)}$	a$''_2$	IR only
$\nu_{CO(ax)}$	e$''$	Ra only

[a] For reasons cited in the text the hydrogenic modes are not suitably described by D_{3h} symmetry. [b] IR = infrared; Ra = Raman. [c] (ax) and (eq) refer to modes involving axial and equatorial carbonyl ligands, respectively.

The CO Stretching Vibrations, ν_{CO}. Assuming a molecular symmetry of D_{3h} for the solution state (vide infra), four infrared-active fundamentals (a$_2''$ + 3e$'$) are predicted and observed (Figure 1). $H_3Mn_3(CO)_{12}$ shows bands at 2078 (m), 2032 (ms), 2008 (m), and 1982 (m) cm^{-1} in hexane solution. The following

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