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Organometallic Nitrosyl Chemistry. 7.[1] Evidence for the Existence of $(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I$ (R = H, CH_3)

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In a recent paper,[2] Efraty and co-workers report that the complexes $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3) are air stable in the solid state as well as in solution. Furthermore, they state: "This feature is of considerable interest, since it contrasts with the failure to synthesize the related carbonyl derivative $C_5H_5Mn(CO)(NO)I$ by the ... reaction between $[C_5H_5Mn(CO)_2(NO)]^+PF_6^-$ and KI or by the direct iodination of the dimer $[C_5H_5Mn(CO)(NO)]_2$.[3] Evidently, both of the attempted syntheses of the carbonyl analogue ... resulted in the formation of carbonyl- and nitrosyl-free decomposition products of an unknown nature." We take exception to these statements and now present evidence that $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$ and its methylcyclopentadienyl congener can indeed be synthesized by these types of reactions.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions, and all reactants were of reagent grade purity.

Preparation of $(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I$ (R = H or CH_3). Method A. To a stirred solution of $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$[3] (0.36 g, 1.0 mmol) in dichloromethane (50 mL) at room temperature was added solid I_2 (0.26 g, 1.0 mmol). The original red-violet solution rapidly turned green-brown and a dark green solid precipitated. After 3 min the reaction mixture was filtered and the filtrate was taken to dryness in vacuo to obtain ~0.5 g of a green-brown solid. This solid was formulated as slightly impure $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$ by virtue of its IR spectrum in CH_2Cl_2 which exhibited strong absorptions at 2030 and 1776 cm^{-1}, its ^1H NMR spectrum in $CDCl_3$ which showed a strong, sharp peak at δ 5.30, and its ambient temperature mass spectrum which is summarized in Table I. Analytically pure samples of this compound could not be obtained because of its proclivity to decompose both in solution and in the solid state. For instance, a stirred dichloromethane solution (20 mL) containing 0.2 g of $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$ slowly deposited a green solid which was insoluble in all common organic solvents; after 72 h complete decomposition had occurred. As a solid, the complex decomposed similarly but over a longer period of time (~8 days).

The reaction between $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)]_2$[4] and I_2 in dichloromethane afforded impure $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)I$ in an identical manner as evidenced by the IR spectrum of the product in CH_2Cl_2 which showed strong absorptions at 2050 and 1772 cm^{-1}. Furthermore, the elemental composition of this product was confirmed by a molecular weight determination using an A.E.I. MS50 high-resolution mass spectrometer (calcd 318.8902, found 318.8908). Benzene could also be employed as the solvent for both transformations.

Table I. Mass Spectral Data for $(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I$ Complexes[a]

R = H			R = CH_3	
m/e	rel abund	assignment[b]	rel abund	*m/e*
305	57	$(RC_5H_4)Mn(CO)(NO)I^+$	31	319
277	69	$(RC_5H_4)Mn(NO)I^+$	58	291
275	12	$(RC_5H_4)Mn(CO)I^+$	8	289
247	80	$(RC_5H_4)MnI^+$	100	261
186	0	$H(RC_5H_4)_2Mn^+$	33	214
185	0	$(RC_5H_4)_2Mn^+$	29	213
192	45	$RC_5H_4I^+$	29	206
182	60	MnI^+	63	182
130	34	$(RC_5H_4)_2^+$	38	158
120	100	$(RC_5H_4)Mn^+$	71	134
65	(150)	$RC_5H_4^+$	(158)	79
55	29	Mn^+	50	55

[a] Probe temperature ~70 °C. Reference 14. [b] Reference 15.

Method B. Solid KI (2.20 g, 13.3 mmol) was added to a stirred yellow solution of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$[3] (4.50 g, 12.8 mmol) in acetone (100 mL) at room temperature. A reaction occurred immediately as evidenced by a change in color to gray-brown, evolution of a gas, and formation of an off-white precipitate. The reaction mixture was stirred for 5 min during which time gas evolution ceased. The solvent was removed under reduced pressure, the resulting gray residue was extracted with three 25-mL portions of CH_2Cl_2, and the extracts were taken to dryness in vacuo to obtain a green-brown solid which exhibited the spectroscopic characteristics of $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$ (vide supra).

An acetone solution of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(NO)]PF_6$[4] reacted with KI completely analogously.

This method of preparing the $(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I$ complexes could also be effected in tetrahydrofuran as both conversions went to completion within 10 min. However, IR monitoring of the final reaction mixtures indicated that both of the desired products decomposed more rapidly in this solvent. This decomposition was complete after 6 h.

Preparation of $(\eta^5\text{-}C_5H_5)Mn(NO)[P(C_6H_5)_3]I$. A solution of $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$ was prepared by method B using 1.05 g (3.00 mmol) of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$ and 0.50 g (3.3 mmol) of NaI in acetone. The reaction mixture was filtered to remove the $NaPF_6$ byproduct, and the stirred green-brown filtrate was treated with 0.80 g (3.0 mmol) of solid $P(C_6H_5)_3$. Vigorous gas evolution occurred immediately and the solution developed a brown coloration. After 5 min a brown, crystalline solid began to precipitate, and crystallization was complete after 15 min. The solid was collected, washed with acetone (2 × 10 mL), and dried in vacuo to obtain 0.93 g (58% yield) of pure $(\eta^5\text{-}C_5H_5)Mn(NO)[P(C_6H_5)_3]I$.

Anal. Calcd for $C_{23}H_{20}$ MnNOPI: C, 51.23; H, 3.74; N, 2.60. Found:[5] C, 51.33; H, 3.50; N, 2.65. ν_{NO}[6] (CH_2Cl_2) 1720 cm^{-1}. ^1H NMR[7] ($CDCl_3$) δ 7.38 (15 H, m), 4.72 (5 H, s). Mp[8] (under N_2) 156 °C dec.

Preparation of $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)[P(C_6H_5)_3]I$. A stirred CH_2Cl_2 solution (50 mL) of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)I$ prepared by method A from 0.77 g (2.0 mmol) of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)]_2$ and 0.51 g (2.0 mmol) of I_2 was treated with 0.90 g (3.5 mmol) of solid $P(C_6H_5)_3$ at room temperature. The solution became brown and vigorous gas evolution occurred. After 15 min, hexanes (20 mL) were added, and the final reaction mixture was filtered. Slow concentration of the filtrate under reduced pressure afforded 1.64 g (74% yield) of $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)[P(C_6H_5)_3]I$ as a brown, microcrystalline solid.

Anal. Calcd for $C_{24}H_{22}$MnNOPI: C, 52.10; H, 4.01; N, 2.53. Found:[5] C, 51.77; H, 3.81; N, 2.63. ν_{NO}[6] (CH_2Cl_2) 1720 cm^{-1}. ^1H NMR[7] ($CDCl_3$) δ 7.33 (15 H, m), 4.93 (2 H, b), 4.40 (1 H, b), 3.84 (1 H, b), 1.90 (3 H, s). Mp[8] (under N_2) 132–133 °C.

Isolation of $(\eta^5\text{-}RC_5H_4)_2Mn_2(NO)_3I$ (R = H or CH_3). If benzene was used as the solvent for method A or if the impure gray solid from method B was extracted with benzene, a second nitrosyl-containing product remained in the solid residue. Extraction of either residue with dichloromethane produced a red-black solution. The addition

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Table II. Mass Spectral Data for $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{NO})_3\text{I}$[a]

m/e	rel abund	assignment[b]
485	17	$(\text{C}_6\text{H}_7)_2\text{Mn}_2(\text{NO})_3\text{I}^+$
455	43	$(\text{C}_6\text{H}_7)_2\text{Mn}_2(\text{NO})_2\text{I}^+$
425	14	$(\text{C}_6\text{H}_7)_2\text{Mn}_2(\text{NO})\text{I}^+$
395	71	$(\text{C}_6\text{H}_7)_2\text{Mn}_2\text{I}^+$
261	7	$(\text{C}_6\text{H}_7)\text{MnI}^+$
237	9	Mn_2I^+
213	25	$(\text{C}_6\text{H}_7)_2\text{Mn}^+$
194	69	$(\text{C}_6\text{H}_7)\text{Mn}(\text{NO})_2^+$
182	12	MnI^+
164	22	$(\text{C}_6\text{H}_7)\text{Mn}(\text{NO})^+$
134	100	$(\text{C}_6\text{H}_7)\text{Mn}^+$
79	57	C_6H_7^+
55	50	Mn^+

[a] Probe temperature ~140 °C. Reference 14. [b] Reference 15.

of hexanes and concentration of the solution under reduced pressure resulted in the crystallization of $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2(\text{NO})_3\text{I}$ as a red-black solid.

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{Mn}_2\text{N}_3\text{O}_3\text{I}$: C, 26.29; H, 2.21; N, 9.19. Found:[5] C, 26.46; H, 2.47; N, 9.23. ν_{NO}[6] (CH_2Cl_2) 1748, 1526 cm^{-1}. Mp[8] (under N_2) 182 °C dec.

Calcd for $\text{C}_{12}\text{H}_{14}\text{Mn}_2\text{N}_3\text{O}_3\text{I}$: C, 29.72; H, 2.91; N, 8.66. Found:[5] C, 30.31; H, 3.33; N, 8.44. ν_{NO}[6] (CH_2Cl_2) 1734, 1520 cm^{-1}. Mp[8] (under N_2) 146–147 °C.

The yields of the $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2(\text{NO})_3\text{I}$ complexes from either method were ~10%.

Results and Discussion

Contrary to the claims of other investigators,[2,3] we find that the previously unknown complex $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})(\text{NO})\text{I}$ and its methylcyclopentadienyl analogue can be easily prepared by either of the reactions

$$[(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})]_2 + \text{I}_2 \xrightarrow[\text{C}_6\text{H}_6]{\text{CH}_2\text{Cl}_2\text{ or}} 2(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})\text{I} \quad (1)$$

$$[(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{NO})]\text{PF}_6 + \text{I}^- \xrightarrow[\text{acetone}]{\text{THF or}} (\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})\text{I} + \text{CO} + \text{PF}_6^- \quad (2)$$

$$\text{R} = \text{H or CH}_3$$

both of which proceed rapidly to completion at room temperature. Minor nitrosyl-containing products of both reactions 1 and 2 are the novel bimetallic compounds $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2(\text{NO})_3\text{I}$, which can be isolated in ~10% yields. They are red-black, relatively air-stable solids that are soluble in polar organic solvents, sparingly soluble in benzene, and insoluble in hexanes. Their solutions display IR absorptions at ~1740 and ~1520 cm^{-1} attributable to terminal and bridging nitrosyl ligands, respectively. The mass spectrum of the methylcyclopentadienyl complex (Table II) exhibits peaks due to the parent ion, P^+, and the ions $[\text{P} - \text{NO}]^+$, $[\text{P} - 2\text{NO}]^+$, and $[\text{P} - 3\text{NO}]^+$, as well as those arising from cleavage of the bimetallic species, e.g., $(\text{C}_6\text{H}_7)\text{Mn}(\text{NO})_2^+$ and $(\text{C}_6\text{H}_7)\text{MnI}^+$. Hence, these complexes apparently belong to the general class of compounds $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2(\text{NO})_3\text{X}$ of which the members with R = H and X = $\eta^1\text{-C}_5\text{H}_5$,[9] $-\text{NO}_2$,[10] and $-\text{C}_6\text{H}_5$[11] have been well characterized. Consistent with this view is the fact that the ^{1}H NMR spectrum of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{NO})_3\text{I}$ in CDCl_3 consists of one pair of resonances of equal intensity at δ 5.53 and 5.34 and a second pair of resonances of different, yet equal, intensity at δ 5.30 and 5.20. These two pairs of signals are probably due to the cis and trans isomers, respectively.[11]

In contrast, the $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})\text{I}$ complexes (the principal products of reactions 1 and 2) are air-sensitive, green-brown solids that dissolve freely in common organic solvents except paraffin hydrocarbons. They decompose slowly both in solution and in the solid state even when maintained in an atmosphere of prepurified nitrogen.[12] Their IR spectra (vide supra) exhibit the customary absorptions indicative of terminal carbonyl and nitrosyl ligands, and their proton NMR spectra display resonances characteristic of a $\eta^5\text{-RC}_5\text{H}_4$ ligand. The fragmentation patterns evident in their mass spectra (Table I) are also consistent with these formulations.

Table III. Mass Spectral Data for $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{I}$ Complexes[a]

R = H			R = CH$_3$	
m/e	rel abund	assignment[b]	rel abund	*m/e*
277	3	$(\text{RC}_5\text{H}_4)\text{Mn}(\text{NO})\text{I}^+$	9	291
262	100	$\text{P}(\text{C}_6\text{H}_5)_3^+$	100	262
247	8	$(\text{RC}_5\text{H}_4)\text{MnI}^+$	0	261
185	22	$(\text{RC}_5\text{H}_4)_2\text{Mn}^+$	14	213
185		$\text{P}(\text{C}_6\text{H}_5)_2^+$	5	185
182	6	MnI^+	9	182
120	26	$(\text{RC}_5\text{H}_4)\text{Mn}^+$	14	134
108	30	$\text{HP}(\text{C}_6\text{H}_5)^+$	29	108
107	20	$\text{P}(\text{C}_6\text{H}_5)^+$	18	107
65	8	RC_5H_4^+	9	79
55	10	Mn^+	9	55

[a] Probe temperature ~130 °C. Reference 14. [b] Reference 15.

Furthermore, regardless of the method by which solutions of $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})\text{I}$ are prepared, they readily evolve carbon monoxide when treated with triphenylphosphine, i.e.

$$(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})\text{I} + \text{P}(\text{C}_6\text{H}_5)_3 \rightarrow (\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{I} + \text{CO} \quad (3)$$

and the new crystalline complexes $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{I}$ (R = H or CH_3) can be isolated from the final reaction mixture in good yields (>58% based on the original reactants in eq 1 or 2). These latter compounds are brown, air-stable solids which are soluble in dichloromethane and chloroform but which are only sparingly soluble in benzene, tetrahydrofuran or acetone. Their IR spectra in CH_2Cl_2 display nitrosyl-stretching absorptions at 1720 cm^{-1} which are ~50 cm^{-1} lower than those exhibited by the $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})\text{I}$ complexes in CH_2Cl_2. This fact is consistent with the replacement of a carbonyl ligand by the better electron-donating group $\text{P}(\text{C}_6\text{H}_5)_3$. The ^{1}H NMR spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{I}$ in CDCl_3 consists of a multiplet centered at δ 7.38 and a singlet at δ 4.72 of relative intensity 3:1, and hence these resonances can be assigned to the phenyl and cyclopentadienyl protons, respectively. The mass spectra of the two triphenylphosphine complexes (Table III) reveal fragmentation patterns attributable to $(\text{RC}_5\text{H}_4)\text{Mn}(\text{NO})\text{I}^+$ and $\text{P}(\text{C}_6\text{H}_5)_3^+$. Parent ion peaks are not detectable even at ionization potentials of 20 eV.

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Registry No. $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})(\text{NO})\text{I}$, 69120-55-4; $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})\text{I}$, 69120-56-5; $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{I}$, 69120-57-6; $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{I}$, 69120-58-7; *cis*-$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{NO})_3\text{I}$, 69222-30-6; *trans*-$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{NO})_3\text{I}$, 69155-17-5; $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})(\text{NO})$, 69120-59-8; $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})(\text{NO})$, 69155-23-3; $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{NO})]\text{PF}_6$, 31921-90-1; $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{NO})]\text{PF}_6$, 52202-14-9; $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{NO})_3\text{I}$, 69120-60-1.

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(15) The assignments involve the most abundant naturally occurring isotopes in each fragment.

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Conformational Characterization of Nickel(II)-Tetraaza Macrocyclic Complexes through Isotropic Shift Studies

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Macrocyclic complexes provide stimulating examples for studying the conformational properties of the molecules, owing to the possible stable arrangements which the ligand can adopt around the metal ion.

The detection and the investigation of the different conformers for a given macrocyclic complex have been usually accomplished by means of X-ray diffractometric analysis[1-4] and/or proton magnetic resonance spectroscopy of solutions containing diamagnetic complexes.[4-7] The use of the latter technique, however, is limited by strong *J-J* coupling effects, which make difficult the interpretation and the assignment of the resonance signals of nonequivalent proton sets. If the complexes, however, are paramagnetic, the resulting large isotropic shifts can provide a powerful tool for the detection of the isomers and for obtaining conformational information. Indeed it has been shown that the contact shift contribution drastically depends on the conformational character, i.e., axial or equatorial, of the resonating proton.[8-10]

The results of an ^{1}H NMR investigation on some hexacoordinate selected complexes of general formula $NiLX_2$ (L = tetraamine macrocyclic ligand; X = Cl or NCS) are here reported and neatly show the conformational characterization of the nickel(II) macrocyclic moieties.

Experimental Section

The ligands 1,4,8,11-tetraazacyclotetradecane ([14]aneN_4) and *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (Me_2[14]aneN_4) were prepared according to published methods.[11,12] Their paramagnetic derivatives Ni([14]aneN_4)Cl_2 and Ni(Me_2[14]aneN_4)Cl_2 were prepared by reaction of equimolar quantities of nickel(II) chloride and of the appropriate ligand in a minimum amount of methanol.

The diperchlorate derivatives of the isomers β-*meso*-, β-*rac*-, and γ-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) (Ni(Me_6[14]aneN_4)) were prepared by reduction of the parent 4,11-diene compound with $NaBH_4$ in basic solution and separated as described.[4,6] Isomers selectively deuterated on the 5,5,14,14-methyl groups were similarly obtained by using a parent 4,11-diene compound obtained by the reaction between the tris(ethylenediamine)nickel(II) ion and hexadeuterioacetone. The dithiocyanato derivatives of the three isomers were prepared by reaction between the appropriate diperchlorate derivative and sodium thiocyanate in dilute acidic solution, according to Warner and Busch.[6] The dichloro analogues of β-meso and γ-rac derivatives were prepared in a similar way by using acetonitrile as solvent and tetraethylammonium chloride. All the complexes were satisfactorily analyzed for C, H, and N.

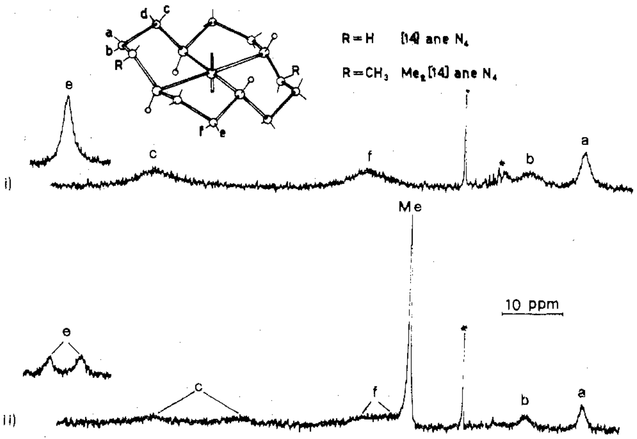

Figure 1. Proton magnetic resonance spectra at 34 °C of $CDCl_3$ solutions of (i) Ni([14]aneN_4)Cl_2 and (ii) Ni(Me_2[14]aneN_4)Cl_2. The resonance signals of protons labeled as d in the scheme are not shown. Signals labeled with * are due to solvent impurities.

^{1}H NMR Measurements. Proton magnetic resonance spectra were recorded on a Varian DA-60 IL spectrometer at 60 MHz and on a Varian EM 390 spectrometer at 90 MHz. Shifts were calibrated from internal tetramethylsilane (Me_4Si). The spectra were recorded both in HR mode (side-band technique used for calibration) and in HA mode in internal lock. Deuteriochloroform (Merck 99.8%) was used as solvent.

Results and Discussion

The ^{1}H NMR spectrum of the paramagnetic Ni([14]aneN_4)Cl_2 is reported in Figure 1 together with a scheme of the molecular structure of the complex.[1] The spectral data are reported in Table I. The conformation of the ligand in this compound is such that the six- and five-membered chelate rings are in a chair and gauche conformation, respectively, so that in the idealized C_{2h} symmetry there are six sets of nonequivalent protons, as labeled in Figure 1. Four of the six sets contain twice as many protons as compared to the remaining two sets. Accordingly, the ^{1}H NMR spectrum of this compound consists of six resonances, four located downfield and two upfield with respect to Me_4Si. The downfield resonances are two times stronger than those upfield. The correspondence between the observed signals and the sets of nonequivalent protons indicates that the conformation is fully retained in solution and no evidence exists of other species (either fast or slow on the ^{1}H NMR time scale) with the conformer shown in Figure 1. The resonance line pattern is completely different from those observed for complexes formed by simple symmetrical diamine ligands. As an example, ^{1}H NMR spectra of solutions containing 1:1 nickel(II) ethylenediamine[9] and nickel(II) 1,3-propanediamine[10] complexes show a single line at −93 ppm and two lines at −175 and +14 ppm, respectively, as a result of the averaging of axial and equatorial methylenic proton resonances by fast conformational interconversion. In contrast with this behavior, the high barrier of interconversion of the chelate ring system in the Ni([14]aneN_4) moiety (as well as in all the 14-membered macrocyclic systems here investigated) allows the observation of "frozen" resonance signals for axial and equatorial protons.