constant to be *ca.* $10^{-4}\ M^{-1}$ on the basis of unpublished polarographic data[14] but the experimental data they cited cannot be used to estimate this constant unless a value for the standard potential of reaction 13 is known. In strongly alkaline solutions of $\mathrm{Co(CN)_5H}^{3-}$

$$\mathrm{Co(CN)_5}^{3-} + \mathrm{e}^- = \mathrm{Co(CN)_5}^{4-} \qquad (13)$$

an anodic polarographic wave[16] commencing at -1.2 V *vs.* sce has been attributed to the reverse of reaction 13 but the thermodynamic reversibility of the wave has not been established. If the known equilibrium constant for

$$2\mathrm{Co(CN)_5}^{3-} + \mathrm{H_2} = 2\mathrm{Co(CN)_5H}^{3-}\ (K = 1.53 \times 10^{5}\ M^{-1\ 11}) \qquad (14)$$

is combined with the ionization constant of water and the calculated value of $K = 10^{-6}\ M^{-1}$ for reaction 5, the standard potential for reaction 13 is calculated to be -1.27 V *vs.* sce. This value is not incompatible with the meager polarographic data presently available.[16]

Combining the value of k_2/k_{-1} obtained from Figure 3 with the pulse radiolysis value[15] of $k_{-1} = 10^5\ \mathrm{sec}^{-1}$ yields $k_2 = 2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, a value reflecting the high reactivity of $\mathrm{Co(CN)_5}^{4-}$ as pointed out by Hanzlik and Vlček.[14] These authors estimated a minimum value for the second-order rate constant for the reaction between $\mathrm{Co(CN)_5}^{4-}$ and *p*-benzoquinone to be *ca.* $10^9\ M^{-1}\ \mathrm{sec}^{-1}$ at 0°. This constant increases to $10^{11}\ M^{-1}$ if the equilibrium constant for reaction 5 obtained from this study ($K = 10^{-6}\ M^{-1}$) is substituted for the estimated value ($K = 10^{-4}\ M^{-1}$) used by Hanzlik and Vlček.[14] This value for the rate constant is uncomfortably large and it seems likely that Hanzlik and Vlček's assumption that reaction 5 proceeded rapidly enough to maintain equilibrium during their measurements caused them to derive an erroneously large rate constant from their data. The value of k_{-1} reported by Venerable, Hart, and Halpern[15] is too low by a factor of 10^2–10^3 to permit the assumption of fast equilibrium for reaction 5 when the $\mathrm{Co(CN)_5}^{4-}$ being generated is exposed to substrates with which it reacts as rapidly as it does with benzoquinone or mercuric cyanide.[17]

Acknowledgment.—We are indebted to Professor H. B. Gray, R. Levenson, and Y. S. Sohn for helpful discussions and assistance in obtaining the low-temperature spectra and magnetic measurements. This work was supported by the National Science Foundation.

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(16) J. Hanzlik and A. A. Vlček, *Chem. Commun.*, 47 (1969).

(17) NOTE ADDED IN PROOF.—There is also a discrepancy between the value reported here for k_1 and the much larger value that would be needed to accommodate the pH dependence reported by Hanzlik and Vlček with the benzoquinone system.[14] The erroneous assumption of preequilibrium for reaction 5 cannot account for this discrepancy. It remains to be explained.

CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORIES,
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Reactions of Coordinated Ligands. XXI. Nitric Acid Oxidation of 1,4,4,10,12,12-Hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-dienenickel(II) Perchlorate

BY E. KENT BAREFIELD AND DARYLE H. BUSCH*

Received June 29, 1970

Oxidative dehydrogenation of the title compound, prepared by the condensation of acetone with $\mathrm{Ni(tm)_2}^{2+}$ (tm = trimethylenediamine), produces two new complexes with three and four imines, respectively. The structures of these new complexes have been established by physical and chemical methods. From the structures of these products the hitherto unknown arrangement of imine donors in the starting material has been determined as trans. Nmr spectral studies indicate these complexes have very stable chelate ring conformations in acidic and nonbasic solvents. In basic solvents there is a base-catalyzed process for ring conformation interconversion.

Introduction

It has been found recently that some Ni(II) complexes of cyclic ligands containing secondary amine donors may be chemically oxidized to forms containing a higher degree of unsaturation in the ligand than was previously present.[1,2] Examples are shown in reactions 1–3. Subsequent to Curtis' report on the preparation of I and II by the condensation of acetone with $\mathrm{Ni(en)_3}^{2+}$,[3] he and his coworkers reported a similar reaction of $\mathrm{Ni(tm)_3}^{2+}$ (tm = trimethylenediamine) with acetone.[4,5] This complex was reported to have limited stability toward acid or base hydrolysis[4] and to be destroyed under oxidative conditions.[5] The stereochemistry of the product from this reaction was not determined.[6] We have succeeded in oxidizing this com-

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* To whom correspondence should be addressed.

(1) N. F. Curtis, *Chem. Commun.*, 881 (1966).

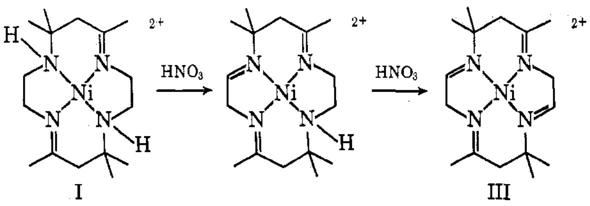
(2) E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, **6**, 2043 (1967).

(3) N. F. Curtis and D. A. House, *Chem. Ind. (London)*, **42**, 1708 (1961); N. F. Curtis and M. M. Blight, *J. Chem. Soc.*, 3016 (1962).

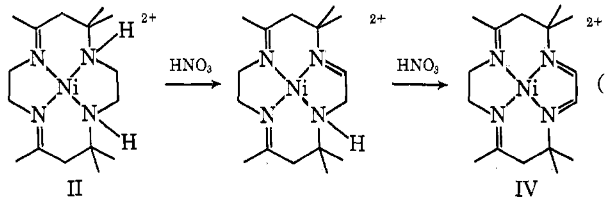
(4) D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, **86**, 223 (1964).

(5) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 1 (1968).

(6) This reaction could also lead to isomers analogous to I and II. At present we have evidence for the existence of only one of these isomers; *vide infra*.



(1)



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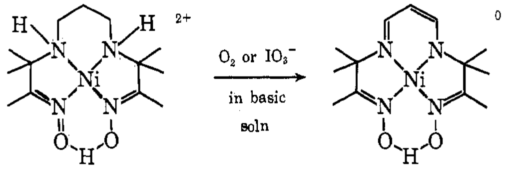


(3)

pound to a mixture of products. These products have been separated and characterized. From their structures the geometrical arrangement of imines in the starting material is inferred. These new products have novel structures and exhibit unusual chelate ring conformational stability. This behavior is discussed and shown to be in contrast to that for compounds III and IV.

Experimental Section

2,4,4,10,12,12-Hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-dienenickel(II) Perchlorate, {Ni(*trans*[16]diene)}$(ClO_4)_2$.—This complex was prepared from $Ni(tm)_3(ClO_4)_2$ and acetone according to the procedure given by Curtis.[4]

Oxidation of {Ni(*trans*[16]diene)}$(ClO_4)_2$.—Ten grams of the diene complex was dissolved in 50 ml of concentrated nitric acid. Dissolution was immediate and a deep orange solution was produced. This solution was heated on a steam bath (75°) for 1.5 hr. A deep green color formed after about 1 hr. Upon cooling, the reaction mixture lightened in color and some pale blue material precipitated. This blue material was removed by filtration and cold acetone was added to the filtrate. A greenish yellow product separated. This material was recrystallized from methanol; yield 6.3 g. *Anal.* Calcd for $NiC_{18}H_{34}N_4Cl_2O_8$: C, 38.31; H, 6.03; N, 9.93. Found: C, 38.32; H, 6.30; N, 9.82. When recrystallized from acetone the complex contained 1 mol of acetone. *Anal.* Calcd for $NiC_{18}H_{34}N_4Cl_2O_8 \cdot C_3H_6O$: C, 40.53; H, 6.43; N, 9.01. Found: C, 40.72; H, 6.34; N, 8.96. The pale blue material which precipitated from the reaction mixture had an infrared spectrum which indicated that water and oxalate were present. *Anal.* Calcd for $NiC_2O_4 \cdot 2.5H_2O$: C, 12.50; H, 2.60; Ni, 30.62. Found: C, 12.03; H, 2.30; Ni, 30.88.

Separation of the Oxidized Products, {Ni(*trans*[16]tetraene)}$(ClO_4)_2$ and {Ni(*trans*[16]triene)}$(ClO_4)_2$.—A 0.6-g sample of the recrystallized greenish yellow product from the oxidation reaction is placed on a 1 × 8 in. column of Dowex 50W-X2 cation-exchange resin on the sodium cycle. Using 0.4 *M* sodium perchlorate solution as the eluting agent (20 ml/hr) produces two well-separated bands which are collected and evaporated to dryness. A small amount of methanol is added to each of the solid fractions followed by a large quantity of nitromethane. The precipitated sodium perchlorate is removed by filtration and the solution is again evaporated to a small volume. Successive filtrations and evaporations lead to approximately 0.2 g of material from the first fraction and about 0.4 g from the second. These were identified as {Ni(*trans*[16]tetraene)}$(ClO_4)_2$ and {Ni(*trans*[16]triene)}$(ClO_4)_2$, respectively (see text).

Deuteration of acidic protons was accomplished by dissolving a sample of complex in D_2O by heating. After dissolution was complete NaOD was added to give a pH of about 10. The solution was allowed to stand for 10–15 hr, filtered, and evaporated to a small volume. The crystals which formed were collected, washed with a small amount of D_2O, and dried *in vacuo* over P_4O_{10}.

Physical Measurements.—Infrared spectra were obtained on Nujol mulls and KBr pellets with a Perkin-Elmer 337 spectrophotometer. Nmr spectra were obtained on Varian A-60, A-60A, and HA100 spectrometers. Spectra were obtained on 10–15 wt % DMSO-d_6, trifluoroacetic acid, nitromethane-d_3, and concentrated nitric acid solutions. Chemical shift data are in ppm *vs.* an external TMS standard for the nitric acid solutions and internal TMS for the others. Visible spectra were taken on a Cary 14 spectrophotometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Results and Discussion

Preparation and Characterization of the Oxidized Products.—Oxidation of the orange complex obtained from the reaction of $Ni(tm)_3(ClO_4)_2$ and acetone leads initially to two products, a pale blue-green material and a green-yellow material. Chromatography of the green-yellow material on ion-exchange resin yields two fractions. A greenish yellow material, compound A, is isolated from the first fraction and a yellow material, compound B, from the second.

These complexes are very soluble in strong acids such as concentrated nitric acid and trifluoroacetic acid and in organic solvents such as DMSO and nitromethane. Recrystallizations may be performed with methanol, acetone, or water since the complexes have limited solubilities at room temperature in these solvents. Crystalline complexes containing acetone and nitromethane are easily obtained but the solvent molecules in these adducts may be removed by recrystallization from other solvents.

Compound A is a 2:1 electrolyte in water (10^{-3} *M* solution) and its visible spectrum in aqueous solution consists of one band at 24,390 cm^{-1} (ϵ 112). This suggests a planar configuration for this complex in water. The presence of a band at 3049 cm^{-1} in the infrared spectrum of the new compound, absent in the starting material, indicates the presence of a vinylic hydrogen while the absence of absorptions for N–H stretching modes ($\sim$3200 cm^{-1}) suggests the presence of at least two additional sites of unsaturation. Other features of the infrared spectrum for this compound include a strong absorption at 1647 cm^{-1} for –C=N– and bands for uncoordinated perchlorate at 1100 and 620 cm^{-1}. If the possible cyclized structures for the starting material (structures V and VI) are considered, the above data are consistent with both products VII and VIII. Each of these possible products has two additional imines and no N–H stretch would be expected in the infrared spectrum. This hypothesis ignores, for the present, the additional possibility of olefinic unsaturation. The nmr spectrum of compound A in concentrated nitric acid (Figure 1a) contains three resonances of equal intensity at 1.32, 1.52, and 2.45 ppm (downfield from ex-

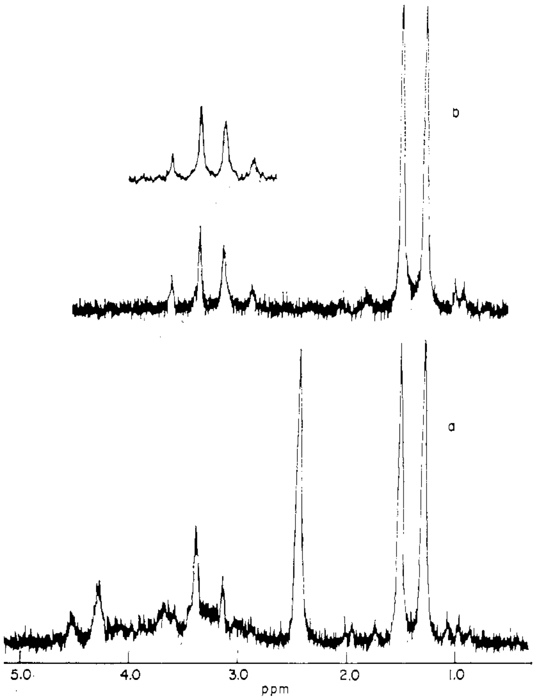
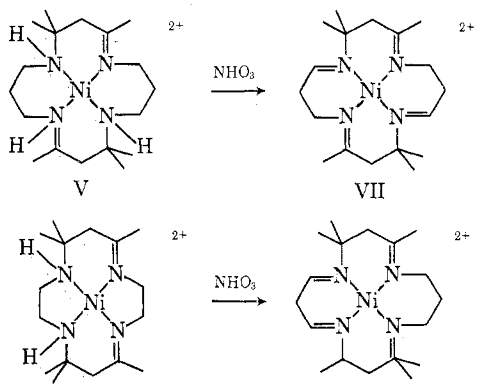


Figure 1.—Nmr spectra in concentrated nitric acid of (a) Ni(*trans*[16]tetraene)$^{2+}$ and (b) deuterated Ni(*trans*[16]tetraene)$^{2+}$.

ternal TMS). The two bands at 1.32 and 1.52 ppm may be assigned to the *gem*-dimethyl groups while the lower field resonance is assigned to the imine methyl.[7] The remaining downfield portion of the spectrum is second order and rather complicated. In trifluoroacetic acid an additional triplet is observed at 8.11 ppm with an intensity corresponding to two protons. This resonance is obscured when nitric acid is used as solvent. Warner, *et al.*,[7] have shown that the complexes shown as structures I and II readily exchange protons α to the imine carbon atom in the six-membered chelate rings when dissolved in basic D$_2$O while those protons in the ethylenediamine rings (α to either the imine nitrogen or to the amine nitrogen) do not exchange over long periods of time. The nmr spectrum for a sample of compound A recrystallized from basic D$_2$O is shown in Figure 1b. The *gem*-methyl resonances at 1.32 and 1.52 ppm remain, while the absorption assigned to the imine methyl has disappeared, as expected. The complex lower field pattern attributable to the various methylene resonances in the molecule has been replaced by an AB pattern which is centered at 3.22 ppm and corresponds to four protons. In trifluoroacetic acid a singlet corresponding in intensity to two protons is also observed at 8.11 ppm. Such spectra could only result from a complex having structure VII where deuteration of all protons α to an imine carbon atom has occurred. Dreiding stereomodels indicate that a complex of this structure must have distinctly nonplanar chelate rings. Therefore the observation of a doublet for the *gem*-methyl resonances indicates that both of the methyl-substituted chelate rings have the same conformation. One possible set of ring conformations is shown in Figure 2a.



V VII

VI VIII

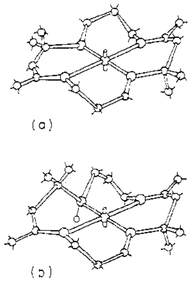


Figure 2.—Stereochemical projection of (a) Ni(*trans*[16]tetraene)$^{2+}$ and (b) Ni(*trans*[16]triene)$^{2+}$.

The AB pattern which is observed arises because of fixed chelate ring conformations which produce axial and equatorial hydrogens on the carbon α to the imine nitrogen in the unsubstituted six-membered rings. The fact that only one AB pattern is observed means that the two unsubstituted chelate rings have identical conformations. The presence of this AB pattern which integrates for four protons and the absence of absorptions for olefinic protons in the 5–7-ppm region eliminates the possibility of olefinic unsaturation. The observation of the *gem*-methyl doublet and the methylene AB pattern indicates that there can only be slow conformational interchange at the temperature of the measurement (37°).

The alternate possibility, complex VIII, should have a first-order spectrum consisting of some combination of a quintet and a triplet with an intensity corresponding to six protons in addition to the *gem*-methyl resonances and the low-field vinylic hydrogen resonance. From the simplicity of the nmr for the deuterated sample it is concluded that compound A has structure VII and that the starting material must have structure V with the trans geometrical arrangement of imines. These complexes should be properly named as 2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-dienenickel(II), Ni(*trans*[16]diene)$^{2+}$, and 2,4,4,10,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,5,9,13-tetraenenickel(II), Ni(*trans*[16]tetraene)$^{2+}$.

Compound B, the second complex obtained from the ion-exchange column, is also a 2:1 electrolyte in water. Its visible spectrum indicates that it too is planar four-coordinate (λ_{max} 23,695 cm^{-1}, ϵ 107). The infrared

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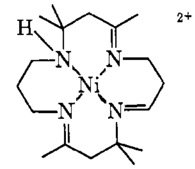
[7] L. G. Warner, Ph.D. Dissertation, The Ohio State University, 1968; L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968).

spectrum contains absorptions both for vinylic C—H (3045 cm^{-1}) and for N—H (3185 cm^{-1}) in addition to absorptions for -C═N- (1645 cm^{-1}) and uncoördinated perchlorate. Structure IX is consistent with these infrared data. This complex, Ni(*trans*[16]triene)$^{2+}$, with one secondary amine and one new imine, would be an expected intermediate in the reaction path leading to the fully oxidized complex, structure VII. Further oxidation of a pure sample of compound B in concentrated nitric acid, in fact, results in partial conversion to the fully oxidized complex. This establishes the structure of the second compound as that shown as structure IX and demonstrates that it is a precursor to compound A in the original oxidation reaction.



IX

The absence of carbon–carbon unsaturation in any of the products from this reaction is somewhat puzzling. The production of a carbon–carbon double bond would conjugate three sites of unsaturation and might be expected to be favored electronically. The absence of such unsaturation must come as a result of the nitric acid oxidant and the mechanism of oxidation. Similar results have been obtained with nitric acid oxidations of coordinated ligands in other systems where conjugation would result through the production of olefinic unsaturation.[8] Only one example of the production of such conjugation by oxidation has come to light.[2] This single example is that shown as reaction 3 (above) where iodate or oxygen was used as the oxidizing agent. In this case oxidation probably occurs at the secondary amine followed by tautomerization. Indeed, the chelate ring has a fully delocalized π-electron system. Certainly additional work in this area should prove fruitful.

The third reaction product, the pale blue-green material previously mentioned, has an absorption in the infrared spectrum at 3388 cm^{-1} for water and strong absorptions at 1640, 1455, and 1310 cm^{-1} which suggest coordinated oxalate. Analytical data for this material correspond quite well to the composition $NiC_2O_4 \cdot 2.5H_2O$. The properties of the solid are essentially identical with those reported for $NiC_2O_4 \cdot 2H_2O$.[9] The isolation of such a complex, although unexpected, is not too surprising. Degradative oxidation would be expected to lead ultimately to CO_2 and H_2O. The presence of oxalate indicates the incomplete oxidation of the alkyl portion of a chelate ring. At least one similar report exists in the nitric acid decomposition of Co(en)$_2$(salicylate)$^+$.[10] Good yields of Co(en)$_2$(oxalate)$^+$ were obtained on prolonged nitric acid oxidation of the above complex. Here the suggested mechanism is somewhat more clear as one carboxylate group is already attached to the metal ion and cleavage of two carbon–carbon bonds of the aromatic ring would permit formation of the second carboxylate donor. In the present case the macrocycle must be decomposed, perhaps hydrolytically. This may be followed by incomplete oxidation and then sequestering of the oxalate ion by the nickel ion. No attempt has been made to detect other incompletely oxidized fragments which may be present.

The possibility of the presence of two isomeric forms of the starting material, *i.e.*, cis and trans diene complexes, cannot be completely discounted. However, only one form has been reported by Curtis,[4,5] and our fractional crystallization of 10 g of the original diene did not indicate the presence of more than one form. Likewise, paper and ion-exchange chromatography indicated that the starting material is homogeneous. The possibility that decomposition of the cis diene resulted in the formation of the nickel oxalate appears unlikely since oxidation of pure triene complex also resulted in some nickel oxalate in a decomposition product. In addition, reduction products obtained from reaction of Ni(*trans*[16]tetraene)$^{2+}$ and Ni(*trans*[16]triene)$^{2+}$ with H_2 over platinum oxide have infrared spectra identical with that for the reduction product of the parent trans diene. On the basis of this evidence it appears that, if any of the cis diene is formed in the original condensation, it is only a small amount and it is probably lost in the work-up of the reaction mixture.

Chelate Ring Conformational Stability.—Nmr studies on these new complexes indicate there are rather high-energy requirements for flexing of the chelate rings in acidic and nonbasic media. The absence of ring conformation changes at 37° for the tetraene complex has already been mentioned. The nmr spectrum in concentrated nitric acid of this complex and for the deuterated form, which are shown in Figure 3, are unchanged

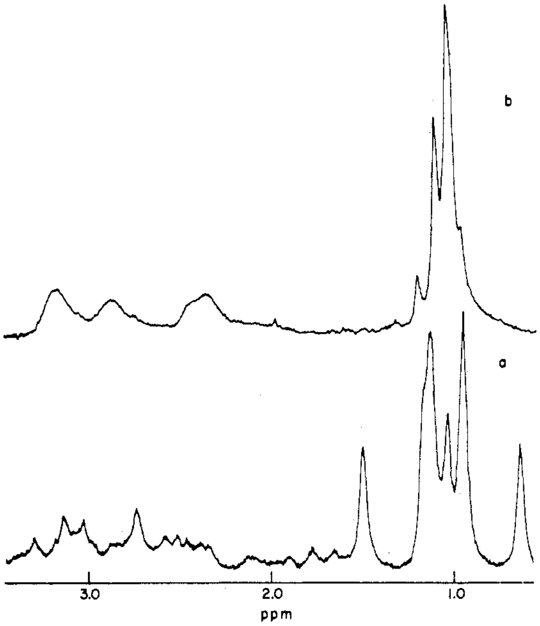


Figure 3.—Nmr spectra in concentrated nitric acid of deuterated Ni(*trans*[16]triene)$^{2+}$ at (a) 37° and (b) 80°.

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[8] Unpublished results.

[9] "Gmelins Handbuch," Vol. 57, Part B, No. 3, 1966.

[10] K. Garbett and R. D. Gillard, *J. Chem. Soc.*, 979 (1968).

at 80°. This indicates that the *gem*-methyl groups, as well as the A and B methylene protons, are still distinctly nonequivalent at the higher temperature and that they interchange only slowly under these conditions. Figure 2a shows a stereochemical projection which indicates one possible set of ring conformations which would lead to such nonequivalence. A 100-Mc nmr spectrum at 37° of a deuterated sample of Ni(*trans*[16]triene)$^{2+}$ in concentrated nitric acid is shown in Figure 3a. Deuteration has removed the downfield resonance for the imine methyl groups. The upfield methyl region is very complex consisting of six absorptions. The resonances at 1.28 and 1.85 ppm integrate for about 1.5 protons each. The large number of methyl resonances and the nonintegral results from integrations could indicate there are two different compounds in this fraction. However, all attempts to detect more than one complex failed. An alternative explanation is that in strong acid there are ring conformations which would allow the possibility of diastereoisomers because of the asymmetric nitrogen (there would be no proton exchange in acid media) and the dissymmetry of the ligand itself. This dissymmetry is present if there are flexed chelate rings of fixed conformation. One possible set of ring conformations is shown by the stereochemical projection given in Figure 2b. Such isomers would have different nmr patterns since differences in chemical shifts for the methyl groups are due not only to ring position relative to a site of unsaturation but also to the proximity of the methyl groups to the unoccupied axial coordination sites. It has been proposed that the downfield chemical shifts for the axial methyls of the gem pair in compounds of structures I and II are due to partial deshielding of the methyl group in close proximity to the nickel ion.[7] At 80° the nmr spectrum of deuterated Ni(*trans*[16]triene)$^{2+}$ is that shown in Figure 3b. The six-line methyl pattern has collapsed to a much simpler one. This indicates that the methyl groups are interchanging positions and are equivalent on the nmr time scale. This must come as a result of an increased rate of ring flexing which in the limit would give the spectrum of the enantiomeric pair, these being nondistinguishable. These observations indicate that although a substantial stereochemical rigidity exists in the triene complex in acid solution at room temperature, at elevated temperatures nmr patterns collapse consistent with chelate ring conformational changes. Examination of stereomodels indicates that introduction of the additional imine for the tetraene complex markedly increases the rigidity of the cyclic ligand over that of the triene complex.

Nmr spectra of Ni(*trans*[16]tetraene)$^{2+}$ and Ni(*trans*[16]triene)$^{2+}$ at 37° in pure DMSO are shown in Figures 4 and 5. The spectrum for the fully oxidized complex has a broad resonance at 1.18 ppm for the *gem*-methyl groups and an absorption at 2.25 ppm for the imine methyl. The remainder of the spectrum consists of two broad resonances at 3.13 and 4.22 ppm, which are due to the various methylenes in the complex, and a poorly resolved triplet at 8.17 ppm ($J \approx 4$ cps) for the imine protons.

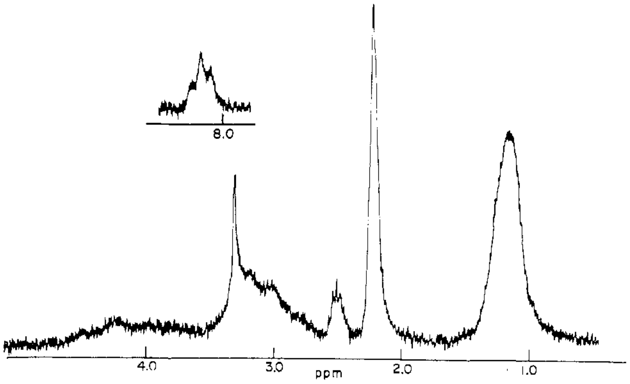

Figure 4.—Nmr spectrum in DMSO-d_6 of Ni(*trans*[16]tetraene)$^{2+}$. Sharp resonance at ~3.3 ppm is due to water. Absorptions attributed to the complex are the same in well-dried solvent.

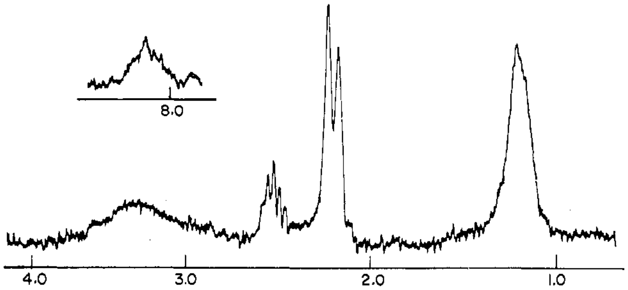

Figure 5.—Nmr spectrum in DMSO-d_6 at 37° of Ni(*trans*-[16]triene)$^{2+}$.

The spectrum of the triene complex also has a broad resonance for the *gem*-methyl groups at 1.20 ppm and doublet at 2.18 and 2.23 ppm for the imine methyls which have different chemical shifts in this medium. A small shoulder at 1.16 ppm may be due to the center methylene of the unsubstituted chelate ring. This resonance is apparently shifted and obscured in all other spectra by the complicated methyl resonances. The remaining portions of the spectrum are very poorly resolved although a triplet is present at 8.12 ppm for the proton on the imine carbon.

The broad absorptions observed for the *gem*-methyl protons indicate a fast interconversion of these methyl groups at room temperature. This must occur as a result of a flexing motion for the chelate rings to which they are attached. The apparent instability of the chelate ring conformations for these complexes in DMSO stands in contrast to their behavior in nitric or trifluoroacetic acid. This is surprising, particularly for the fully oxidized complex which has no secondary nitrogen atoms that might invert, thereby providing a pathway for conformation interchange. As previously stated, stereomodels of the fully oxidized product indicate the chelate rings to have very restricted movement and that flexing of a chelate ring from one form to another should be a high-energy process. However, if the carbon atom α to the imine carbon is deprotonated, this would allow a facile conversion of that ring conformation to another since reprotonation could occur on either side of the tricovalent carbon. One mechanism of this kind is depicted in Figure 6. If there is considerable bond angle strain at the center carbon of the chelate rings, the acidity of either proton might be expected to increase since planarity of the carbon would be permitted upon deprotonation. The inductive effects of the adjacent imine and the metal atom are, of course, of much importance in promoting exchange of the protons on the carbon α to the imine carbon in the several systems studied up to this time.

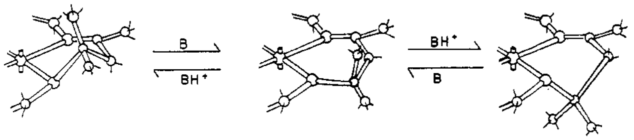

Figure 6.—Possible mechanism for interconversion of chelate ring conformations in Ni(*trans*[16]tetraene)$^{2+}$.

Two types of experiments were designed to test the hypothesis that the presence of a base is necessary for interconversion of chelate rings. The first of these was addition of a strong acid such as trifluoroacetic to DMSO solutions of the complex in an effort to neutralize the basicity of the solvent. The results of these experiments are shown in Figures 7 and 8 for the tetraene and triene complexes, respectively. Figure 7 shows the nmr for the methyl group region of Ni(*trans*-[16]tetraene)$^{2+}$ in pure DMSO and in 1:1 and 2:1 trifluoroacetic acid–DMSO mixtures. Little effect is seen in the nmr spectra upon addition of small amounts of acid, but as the ratio of acid to DMSO approaches 1:1, the broad absorption for the *gem*-methyl groups has begun to separate into two separate signals. At a ratio of acid to DMSO of 2:1, the nmr spectrum approaches that for solutions in the pure acid. Similar spectra in identical solvent mixtures are shown in Figure 8 for the triene complex.

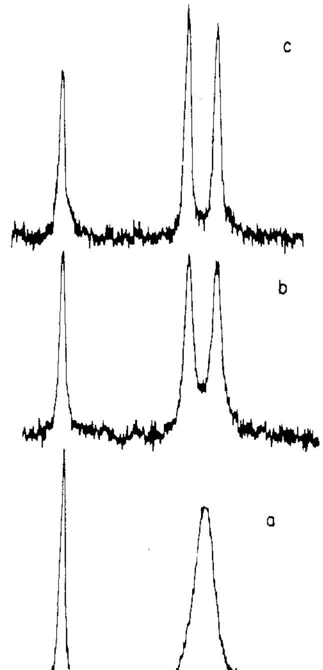

Figure 7.—Nmr spectra of Ni(*trans*[16]tetraene)$^{2+}$ in (a) pure DMSO, (b) 2:1 DMSO–CF_3CO_2H, and (c) 1:2 DMSO–CF_3CO_2H.

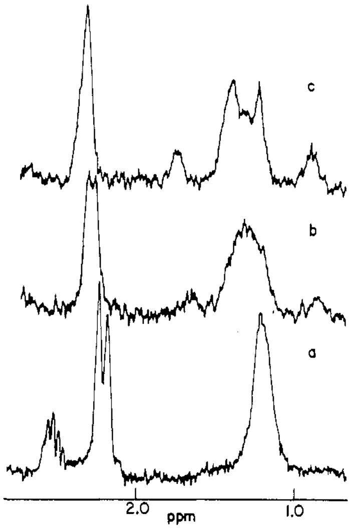

Figure 8.—Nmr spectra of Ni(*trans*[16]triene)$^{2+}$ in (a) pure DMSO, (b) 2:1 DMSO–CF_3CO_2H, and (c) 1:2 DMSO–CF_3CO_2H.

The presence of the downfield triplet for the imine vinylic proton, although poorly resolved, shows that the rate of exchange of the methylene protons on the carbon α to the imine carbon in the unsubstituted chelate ring is not fast enough to lose completely the spin–spin coupling between the imine and α protons. Exchange in this ring must be occurring, however, since the spectrum of a deuterated sample of Ni(*trans*[16]tetraene)$^{2+}$ in DMSO contains only a broad unresolved signal for the nondeuterated methylene instead of the AB pattern obtained in acidic media. This indicates that the unsubstituted rings are flexing fast enough so that the axial–equatorial distinction is reduced for the methylene protons.

The second test of this hypothesis was to obtain the spectrum in a solvent which has very limited acidic or basic properties. If deprotonation by a base is a necessary part of the methyl interchange, then the spectrum in such a solvent should be the same as that in acidic media. The nmr of Ni(*trans*[16]tetraene)$^{2+}$ and Ni(*trans*[16]triene)$^{2+}$ were obtained in nitromethane-d_3. The overall spectra are identical with those obtained in trifluoroacetic or nitric acid. The methyl group regions of the nmr spectra after addition of a very small amount of pyridine were essentially identical with those obtained in pure DMSO. After addition of a larger amount of pyridine the spectrum for Ni(*trans*[16]tetraene)$^{2+}$ in the *gem*-methyl region consists of one sharp resonance at 1.32 ppm downfield from TMS. The spectrum for Ni(*trans*[16]triene)$^{2+}$ under identical conditions closely resembles the spectrum obtained at

80° in nitric acid where rapid interchange is taking place. The effect observed upon the addition of pyridine, a strong base compared to DMSO, is that expected for the proposed model—a rapid interconversion of the methyl groups and of the methylene protons and, as a result, magnetic equivalence in the nmr.

The mechanism proposed involves base catalysis for interconversion of chelate ring conformations. The data available are not sufficient to determine whether the deprotonation at the methylene carbon by the base (Figure 6) is the rate-determining step or whether there is a preequilibrium involving the base followed by some rate-determining step.

The stereochemical behavior of Ni(*trans*[16]-tetraene)$^{2+}$ is in considerable contrast to that for both Ni(*trans*[14]tetraene)$^{2+}$ and Ni(*cis*[14]tetraene)$^{2+}$ (III and IV), respectively. The *gem*-methyl groups in these complexes are magnetically equivalent in all solvents studied even at room temperature. This is illustrated by the spectra shown in Figure 9 which were obtained on trifluoroacetic acid solutions at 37°. The high-field *gem*-methyl resonances are sharp singlets for both isomers and suggest environmental equivalence for these substituents. An X-ray structure for the *cis*[14]-tetraene shows that the saturated ethylenediamine ring has an eclipsed conformation so that all atoms in the macrocyclic ring are approximately in the same plane except for the carbon atom to which the *gem*-methyls are attached.[11] This atom, however, lies out of the plane by only a few degrees. A simple flexing movement would interconvert the environmental positions of the methyl groups. Models indicate a similar structure for the trans analog. The nmr indicates that this must be a facile process and it is concluded that the energy barrier is much less than that for the more rigid Ni(*trans*-[16]tetraene)$^{2+}$. This reflects the considerable increase in the barrier to ring conformation changes introduced by an additional carbon in the unsubstituted rings for the [16]tetraene. The addition of this carbon produces a greater nonplanarity of the six-membered chelate rings and due to the constraining cyclic nature of the ligand a higher barrier to ring flexing. Interchange of ring conformations and magnetic equivalence of methyl groups in this case is obtained only under basic conditions.

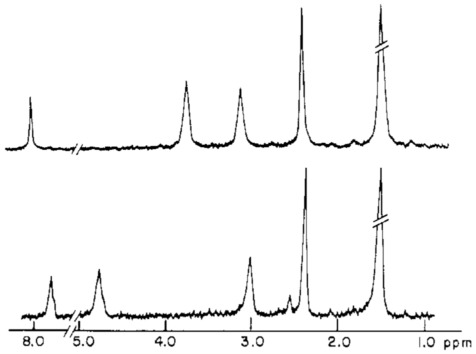

Figure 9.—Nmr spectra in trifluoroacetic acid at 37° of (a) Ni-(*trans*[14]tetraene)$^{2+}$ and (b) Ni(*cis*[14]tetraene)$^{2+}$.

Nothing has been said to this point about the nmr and conformational stabilities of the parent Ni(*trans*-[16]diene)$^{2+}$. The nmr spectrum of this complex is essentially the same in all solvents tried regardless of their acidity or basicity. In trifluoroacetic acid, for example, the essential features are two predominant resonances at 1.40 and 2.38 ppm. These resonances are assigned to the *gem*-methyls and imine methyls, respectively. The broadened singlet at 1.40 ppm indicates that all the *gem*-methyls are essentially equivalent under the conditions of the measurements. Since the solvent is very acidic, no exchange of the protons on nitrogen or carbon is expected. This means the freedom of motion of the chelate rings is great enough in this complex, which has four six-membered chelate rings with only two imines in trans positions, to allow the *gem*-methyl groups to occupy environments that are almost identical. In other words there is no stabilization of a particular conformer which would give an axial–equatorial distinction to the *gem*-methyl groups. In the case of the [14]diene systems studied by Warner, *et al.*,[7] an axial–equatorial distinction was present for the *gem*-methyl groups. Interconversion was accomplished only in basic solution where secondary nitrogen inversion provided the path for this stereochemical change. This demonstrates the very great difference in stereochemical rigidity of the 14- and 16-membered macrocyclic diene systems.

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[11] I. E. Maxwell and M. F. Bailey, *Chem. Commun.*, 883 (1966).