

with $\pi \approx 16,400 \text{ cm}^{-1}$. Estimates⁵² for the spin-equilibrium complex $\text{Fe}(o\text{-phen})_2(\text{NCS})_2$ resulted in values of $Dq(\text{low spin}) \approx 16,300 \text{ cm}^{-1}$ and $Dq(\text{high spin}) \approx 11,900 \text{ cm}^{-1}$. The results of the earlier studies are in good agreement with those obtained from

(52) E. König and K. Madeja, *Inorg. Chem.*, **6**, 48 (1967).

the spectral data of the $[\text{14}] \text{aneN}_4\text{-Fe}$ complexes.

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Synthesis of Metal Complexes with Macrocyclic Ligands Having Prescribed Patterns of Unsaturation. Oxidative Dehydrogenation of Fused-Ring Systems Involving Charged, Delocalized Six-Membered Chelate Rings

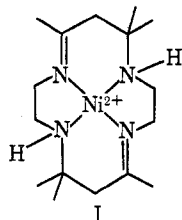
BY CHRISTIAN J. HIPPI, LEONARD F. LINDOY, AND DARYLE H. BUSCH*

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Metal ion promoted oxidative dehydrogenation shares with coordination template effects the distinction of being a new synthetic technique uniquely suited to the preparation of ligands that are difficult to produce by other means. Oxidation of the chelate rings that are formed by deprotonation of β -diimines produces a pattern of unsaturation that has not previously been achieved by this general class of reaction. This pattern both places a localized $\text{C}=\text{C}$ group in the six-membered ring and extends the unsaturation into the adjacent chelate ring. This reaction has been effected by bromine oxidation of the macrocyclic nickel(II) complexes 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate and 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienatonickel(II) perchlorate (or hexafluorophosphate). The structures of the products were established through conductivity and magnetic susceptibility measurements and visible, infrared, and nmr spectroscopy.

Introduction

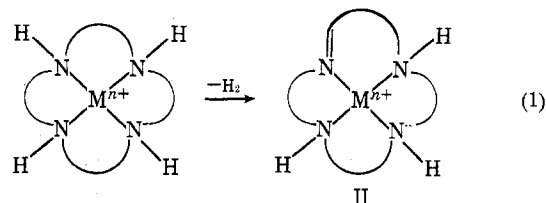
The discovery that the complex having structure I



is formed by the reaction between ethylenediamine and acetone in the presence of nickel(II) salts^{1,2} represented the initial example of the new synthetic macrocyclic ligands containing four nitrogen donors. Many such substances are known now³ and they form an important new class of coordination compounds that have aroused much interest because of the fundamental structural relationship they bear to such critical natural products as heme proteins, chlorophyll, and vitamin B₁₂.⁴

Two novel chemical reactions have figured in the synthesis of many of these new complexes—coordination template reactions³⁻⁵ and oxidative dehydrogenation reactions.^{3,6,7} The latter reactions have uniformly involved the conversion of secondary amine

groups into azomethine linkages through the abstraction of 1 mol of hydrogen (eq 1). Such linkages have



been introduced into five-⁸ and six-membered chelate rings.⁷ Goedken⁸ has shown that simple bidentate ligands, e.g., ethylenediamine and *o*-phenylenediamine, in $\text{Fe}^{\text{II}}(\text{diamine})(\text{CN})_4^{2-}$ can be oxidatively dehydrogenated to α -diimines while remaining coordinated. Also, the early work of Vassian and Murmann⁹ showed that, when two α -diimine linkages are produced in one chelate ring, ionization of a proton may occur producing a β -diketonate-like chelate structure.

The converse process, hydrogenation of coordinated imine groups, is well documented among complexes containing macrocyclic ligands.^{6,10,11} Such processes have been observed both chemically^{6,10,12} and electrochemically.^{11,13}

The mechanism of the oxidative dehydrogenation

(1) N. F. Curtis, *J. Chem. Soc.*, 4409 (1960).

(2) N. F. Curtis and D. A. House, *Chem. Ind. (London)*, 1708 (1961).

(3) L. F. Lindoy and D. H. Busch, "Preparative Inorganic Reactions," Vol. 6, W. L. Jolly, Ed., Interscience, New York, N. Y., 1971.

(4) D. H. Busch, K. Farmery, V. Goedken, V. Katović, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, **No. 100**, 44 (1971).

(5) D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius Alfred Werner*, 174 (1967).

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

(7) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 108 (1971).

(8) V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 207 (1972).

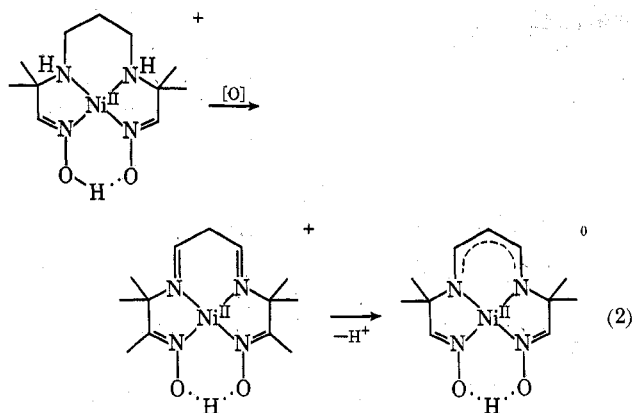
(9) E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, **6**, 2043 (1967).

(10) J. L. Karn and D. H. Busch, *ibid.*, **8**, 1149 (1969).

(11) E. K. Barefield, F. V. Lovecchio, N. E. Tokel, E. Ochaj, and D. H. Busch, *ibid.*, **11**, 283 (1972).

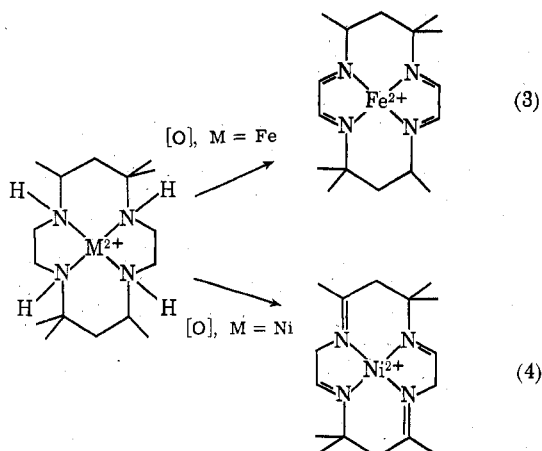
(12) V. Katović, L. T. Taylor, F. L. Urbach, W. H. White, and D. H. Busch, *ibid.*, **11**, 479 (1972).

(13) N. E. Tokel, V. Katović, K. Farmery, L. B. Anderson, and D. H. Busch, *J. Amer. Chem. Soc.*, **92**, 400 (1970).



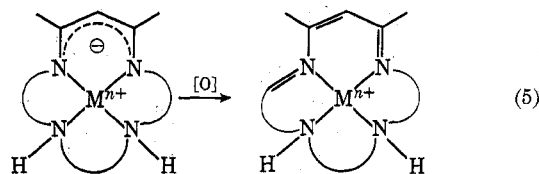
reaction is not thoroughly understood; however, higher oxidation states of the metal seem almost certain to be involved.¹⁴⁻¹⁶ The role of the metal ion is emphasized by the transition element specificity of the reaction. Iron promotes the reaction with mild oxidizing agents,¹⁵ while nickel and copper require progressively stronger oxidizing agents^{6-8,16a} and cobalt does not appear to work at all. Trivalent iron^{15,16b} and nickel¹⁴ appear to be active oxidizing agents in the reaction. For example, under appropriate conditions, solutions of the pure Fe(III) complex will produce new azomethine linkages *via* oxidative dehydrogenation in the absence of other oxidizing agents.^{16b}

The metal ion specificity extends to the locations of the sites of unsaturation in the dehydrogenated ligands. For iron, the imine functions are produced in conjugated pairs (α -diimine groups)¹⁵ while the imines are produced in electronically isolated locations¹⁷ in the case of nickel (eq 3 and 4).

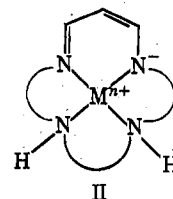


We are concerned with solution of the general problem of generating any degree of saturation whatsoever in the structure of macrocyclic complexes. Prior to this report there have been no instances in which carbon-carbon saturation has been produced in the macrocycle by metal ion promoted oxidative dehydrogenation. We wish to report a new reaction in which the ring segment oxidized is the coordinated anion of a

β -amino keto imine. The reaction produces both a C=C linkage and unsaturation in the adjacent fused chelate ring. This is shown schematically in eq 5.

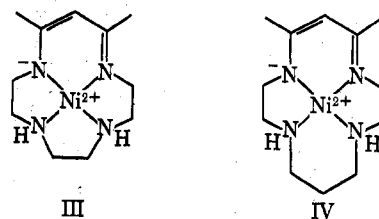


Perhaps the structural relationships are more apparent if one thinks of the oxidation as involving the negatively charged nitrogen in one resonance form of the starting material (structure II). Clearly this new re-



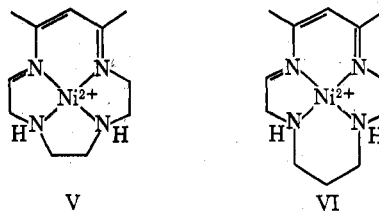
action constitutes a major contribution toward the ultimate goal of learning how to synthesize any macrocyclic ligand having any desired degree of unsaturation.

Ideal reactants for the characterization of this new reaction have recently become available.^{18,19} These substances have structures III and IV.²⁰



Results

The complexes Ni([13]dienoN₄)⁺¹⁸ (III) and Ni([14]-dienoN₄)⁺¹⁹ (IV) which contain uninegative macrocyclic Schiff base ligands with 13 and 14 ring members, respectively, are readily oxidized with bromine to produce, in each case, two isomeric substances (Scheme I). The structures of the resultant products have been deduced from analytical data, conductance and magnetic susceptibility measurements, and infrared, visible,



(18) S. C. Cummings and R. E. Sievers, *J. Amer. Chem. Soc.*, **92**, 215 (1970); *Inorg. Chem.*, **9**, 1131 (1970).

(19) S. C. Cummings, Abstracts, 3rd Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, 1970; also, private communication.

(20) Structure III—the name of the ligand is 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienato, abbreviated 11,13-Me₂[13]-10,12-dienoN₄, or more simply just [13]dienoN₄. Structure IV—the name of the ligand is 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienato, abbreviated 12,14-Me₂[14]-11,13-dienoN₄, or more simply [14]dienoN₄. For a summary of the system of abbreviations, see V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, in press.

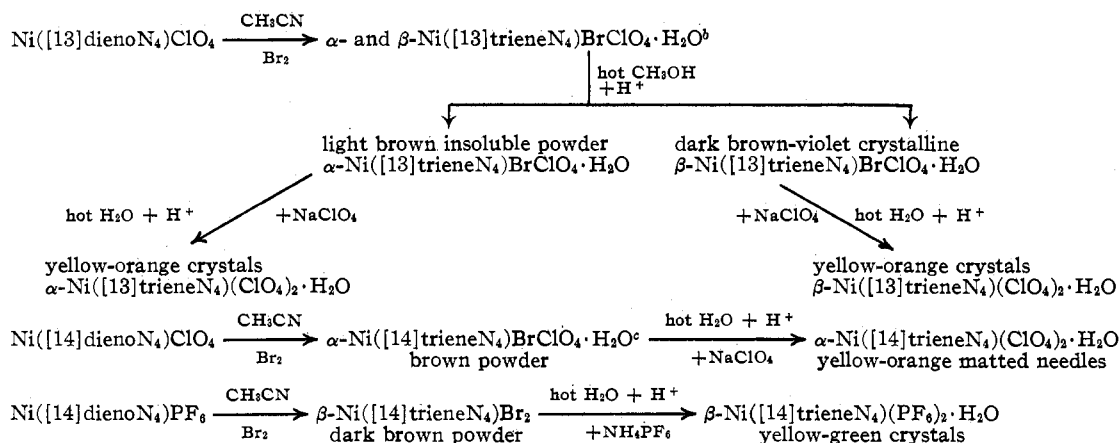
(14) N. F. Curtis and D. F. Cook, *Chem. Commun.*, 962 (1967).

(15) J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, Abstracts, 162nd Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR 140; *J. Amer. Chem. Soc.*, in press; V. L. Goedken, P. H. Merrell, and D. H. Busch, *ibid.*, in press.

(16) (a) V. L. Goedken and D. H. Busch, *Inorg. Chem.*, **10**, 2679 (1971); (b) V. L. Goedken and D. H. Busch, *J. Amer. Chem. Soc.*, in press.

(17) E. S. Gore and D. H. Busch, unpublished results.

SCHEME I^a
OXIDATION REACTIONS OF Ni([13]dienoN₄)ClO₄ AND Ni([14]dienoN₄)X (X⁻ = ClO₄⁻, PF₆⁻)
WITH BROMINE IN ACETONITRILE



^a The designations α and β refer to different isomers produced from the oxidation reactions. ^b The ligand has structure V and is named 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-1,10,12-triene, abbreviated 11,13-Me₂[13]-1,10,12-triene-1,4,7,10-N₄ or [13]trieneN₄. ^c This ligand has structure IV and is named 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,11,13-triene, abbreviated 12,14-Me₂[14]-1,11,13-triene-1,4,8,11-N₄ or [14]trieneN₄.

and nmr spectra. The products of these reactions are assigned structures V and VI.

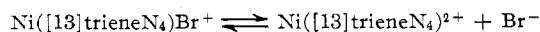
13-Membered Ring Derivatives.—The oxidation products derived from Ni([13]dienoN₄)ClO₄ are salts of the dipositive cations $\alpha\text{-Ni}([13]\text{trieneN}_4)^{2+}$ and $\beta\text{-Ni}([13]\text{trieneN}_4)^{2+}$ (Scheme I). Their electrolyte types have been established by conductance studies as shown in Table I. The bromoperchlorates have con-

TABLE I^a
CONDUCTANCE DATA FOR THE COMPLEXES OF THE
13-MEMBERED MACROCYCLIC LIGANDS

Complex	Δm^b (solvent)
Ni([13]dienoN ₄)ClO ₄	155 (CH ₃ CN)
$\alpha\text{-Ni}([13]\text{trieneN}_4)\text{BrClO}_4 \cdot \text{H}_2\text{O}$	117 (CH ₃ NO ₂)
$\beta\text{-Ni}([13]\text{trieneN}_4)\text{BrClO}_4 \cdot \text{H}_2\text{O}$	68 (CH ₃ NO ₂)
$\alpha\text{-Ni}([13]\text{trieneN}_4)(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	176 (CH ₃ NO ₂); 279 (CH ₃ CN)
$\beta\text{-Ni}([13]\text{trieneN}_4)(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	166 (CH ₃ NO ₂); 281 (CH ₃ CN)

^a Values reported for 1:1 and 2:1 electrolytes in nitromethane are 80–95 and 160–190, respectively: T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **8**, 146 (1969); values reported for 1:1 and 2:1 electrolytes in acetonitrile are 135–155 and 250–310, respectively: M. Ciampolini and P. Paoletti, *ibid.*, **6**, 1261 (1967). See also W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971). ^b Approximately $(1-5) \times 10^{-4}$ M solutions; in cm²/(ohm mol).

ductance values in nitromethane solutions which are consistent with a five-coordinate species (β isomer) and the equilibrium between four- and five-coordinate species (α isomer)



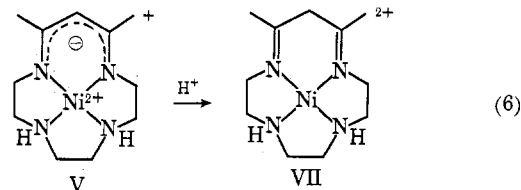
Such an equilibrium behavior has also recently been reported for other Ni(II) macrocyclic complexes with halide anions.^{21,22} The values given for the diperchlorate derivatives in acetonitrile and nitromethane are consistent with their formulation as 2:1 electrolytes as is required if oxidation of the Ni([13]dienoN₄)ClO₄ complex to Ni([13]trieneN₄)²⁺ has occurred.

This facile oxidizability was anticipated to some extent in view of preliminary reports on the electrochem-

ical behavior of these and related substances.^{23,24} It has been shown that Ni(III) can be formed by oxidation of the complexes of structures III and IV at exceptionally low potentials.²⁴ As indicated above, the intermediacy of Ni(III) in closely related ligand oxidation processes seems to be established and the ease of attaining this intermediate may signal the ease of oxidative dehydrogenation.

Since stable Ni(III) complexes have been isolated,^{25,26} the site of the oxidation required specific consideration. Ni(III) is a d⁷ system and would ordinarily be expected to exhibit at least one spin ($S = 1/2$ for low-spin form).^{25,26} The oxidation products are uniformly diamagnetic, supporting the assumption that the central metal ion is Ni(II) and that the ligand, not the metal, remains oxidized in these final products.

The simplest interpretation that could be applied to account for the change in charge of the macrocyclic complex from 1+ to 2+ would not involve oxidation. These and most related structures are readily protonated (eq 6).^{19,27} The structure of the resultant



complex contains two equivalent imine groups separated by a methylene group (eq 6). This can be distinguished from structure V very readily; *i.e.*, the former contains a symmetry plane and equivalent methyl groups. Nmr has been used for this purpose (see below). The results conclusively show that ligand oxidation, not protonation, has occurred.

Changes in the infrared spectra also support the

(23) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969).

(24) D. P. Rillima, J. F. Endicott, and E. Papaconstantinou, *ibid.*, **10**, 1739 (1971).

(25) E. K. Barefield and D. H. Busch, *Chem. Commun.*, 522 (1970).

(26) E. S. Gore and D. H. Busch, *Inorg. Chem.*, in press.

(27) C. J. Hipp and D. H. Busch, unpublished results.

(21) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 1216 (1971).

(22) W. Rosen and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4694 (1969).

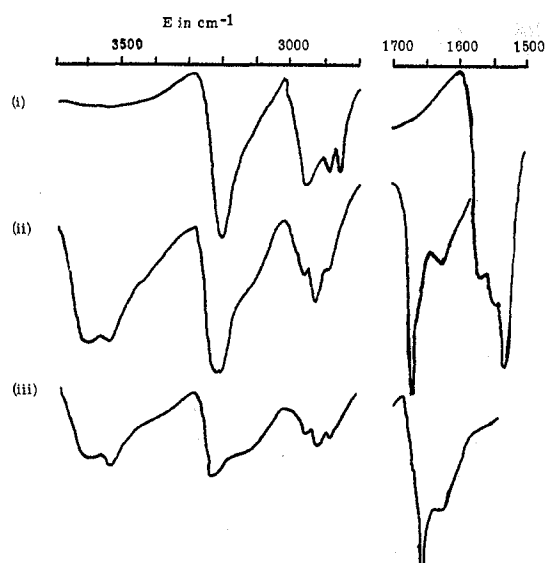


Figure 1.—Infrared spectra of the 13-membered ring derivatives: (i) Ni([13]dienoN₄)ClO₄; (ii) α -Ni([13]trieneN₄)(ClO₄)₂·H₂O; (iii) β -Ni([13]trieneN₄)(ClO₄)₂·H₂O. Samples prepared in halo oil mulls.

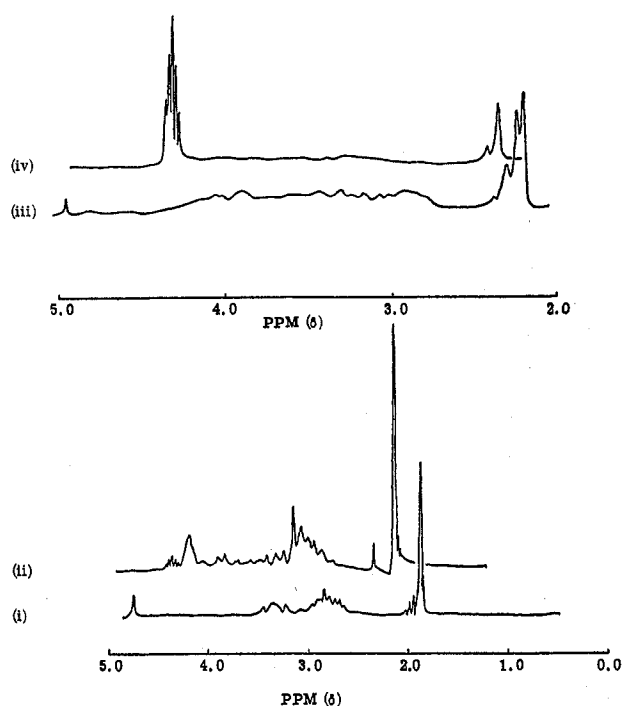


Figure 2.—Nmr spectra of the 13-membered ring derivatives: (i) Ni([13]dienoN₄)ClO₄ (CD₃CN); (ii) Ni([13]dieneN₄)(PF₆)₂·H₂O (CD₃CN); (iii) α -Ni([13]trieneN₄)(PF₆)₂·H₂O (CD₃CN); (iv) β -Ni([13]trieneN₄)(PF₆)₂·H₂O (CD₃NO₂). Tetramethylsilane, internal standard; solvent given in parentheses; 60-MHz spectra in i and ii and 100-MHz spectra in iii and iv. The ligand in ii has structure VII and is named 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene,¹⁹ abbreviated 11,13-Me₂[13]-10,13-dieneN₄ or [13]dieneN₄.

interpretation given here (Figure 1). The conjugated C=N and C=C bands that are found in the 1500–1600-cm⁻¹ region for Ni([13]dienoN₄)⁺ do not appear in the infrared spectra of the oxidation product. These characteristic modes are replaced by a sharp imine stretch at 1670 cm⁻¹ (α isomer) or 1650 cm⁻¹ (β isomer). These changes clearly support the suggestion

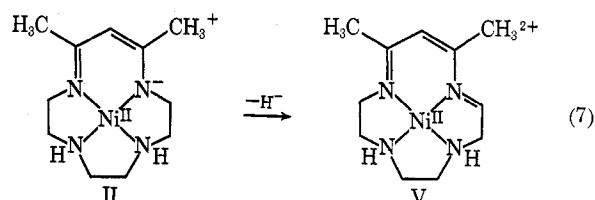
that the delocalized anionic ring has been oxidized. The distinction between the C=N modes for the α and β isomers is useful in monitoring the isomeric purity of samples.

The nmr spectra of α - and β -Ni([13]trieneN₄)(PF₆)₂·H₂O are given in Figure 2. The limited solubility of these materials in appropriate solvents, along with the complexity observed for the methylene resonances, precluded a detailed analysis of these pmr spectra. The most notable features are the methyl singlets at 2.20 and 2.25 ppm (α isomer) and the broadened methyl singlet at 2.36 (β isomer) and a singlet, in both cases, at ~5 ppm which is assigned to the vinyl proton in the six-membered ring (structure V). Observation of two methyl resonances for the α isomer eliminates the possibility of ring protonation, while the β isomer clearly is not the protonation product (VII) whose spectrum is also shown in Figure 2. A consequence of this inequivalence of the methyl groups in the oxidation products is that either the two five-membered chelate rings adjacent to the acetylacetonate residue are nonequivalent or the remote five-membered ring is unsymmetrical.

The likelihood of an isolated imine linkage being generated by oxidative dehydrogenation in this system is remote. The ir and nmr characteristics of such an azomethine proton in a five-membered chelate ring of a nickel(II) complex with a macrocyclic ligand are known. The C-H stretch for this type of proton has been assigned to the region ~3070 cm⁻¹,²⁸ while the nmr resonance expected for such a proton is found at ~8 ppm.²⁹

The additional unsaturation must then be located directly adjacent to one of the nitrogens comprising the formerly charged chelate ring as shown in structure V. This is consistent with the absence of a C-H stretching band at ~3070 cm⁻¹ in the ir spectra of the oxidation products and the absence of nmr signals below ~5 ppm for these complexes.

The oxidation reaction can then be viewed as the formal result of hydride abstraction from Ni([13]dienoN₄)ClO₄ to produce the observed complexes (eq 7).



The visible absorption spectra of the two isomers (Table II) indicate that both are stable in deoxygenated acetonitrile in the presence of water and that, when the water has been removed (by recrystallization from acetonitrile), the β fraction remains unaffected in solution while the spectrum of the α isomer changes with time.

With both isomers, the region below 16,000 cm⁻¹ is transparent and they do not display distinct d-d transitions although they both have low-energy shoulders on the charge-transfer bands whose intensities are in the range expected for d-d transitions.

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

(29) V. L. Goedken and D. H. Busch, *Inorg. Chem.*, in press.

TABLE II
SPECTRAL DATA IN DEOXYGENATED ACETONITRILE
FOR Ni([13]trieneN₄)X₂

Complex	ν_{\max}^a (cm ⁻¹)	Elapsed time, ^b hr
α -Ni([13]trieneN ₄)(ClO ₄) ₂ ·H ₂ O	27,400 (1790)	0
	27,300 (1780)	12
	27,300 (1790)	23
	27,000 (1760)	105
β -Ni([13]trieneN ₄)(ClO ₄) ₂ ·H ₂ O	27,500 (1880)	0
	27,400 (1840)	12
	27,500 (1870)	23
	27,400 (1860)	105
α -Ni([13]trieneN ₄)(PF ₆) ₂ ·CH ₃ CN	27,300 (1870)	0
	27,400 (1970)	1.5
	27,400 (1990)	12
	27,400 (2030)	24
	27,500 (2070)	36
β -Ni([13]trieneN ₄)(PF ₆) ₂ ·CH ₃ CN	27,400 (2150)	0
	27,500 (2190)	12
	27,500 (2170)	40

^a ν_{\max} in cm⁻¹; ϵ in parentheses in l./mol cm. ^b The initial measurement necessarily entailed a ~20-minute delay following sample preparation.

The first charge-transfer band, present in both isomers at 27,400 cm⁻¹ ($\epsilon \sim 2150$, β isomer; $\epsilon < 1900$, α isomer, as Ni([13]trieneN₄)(PF₆)₂·CH₃CN), increased in intensity in the solution containing the α isomer with a limiting value near that of the β isomer (Table II). This is interpreted as evidence for a change in the isomeric composition of the solution.³⁰

The apparent greater thermodynamic stability of the β isomer is also suggested by the variation in the relative abundance of the isomers as the rate of oxidation is changed. The addition of stoichiometric quantities of bromine to Ni([13]dienoN₄)ClO₄ solutions in acetonitrile produced proportionately less α isomer when the rate of oxidation was retarded by dilution of the Br₂ with acetonitrile.

The isomers reported here probably differ in the orientations of their two secondary-amine protons with respect to the plane containing the metal atom and the four nitrogens. The more stable isomer should have an NH proton on each side of the plane, an arrangement that allows all five-membered chelate rings to adopt the favorable gauche forms. The less stable isomer may have both NH protons on the same side of the plane and an essentially eclipsed five-membered chelate ring. Such isomerism is well known among macrocyclic complexes.³¹ It should also be pointed out that both isomers should exist as racemates.

14-Membered Ring Systems.—The oxidation of Ni([14]dienoN₄)X with bromine in acetonitrile yields isomerically different complexes, depending upon the anion present in the starting material (Scheme I). The conductance values for the Ni([14]dienoN₄)X complexes and their oxidation products are given in Table III. Again, the oxidation products display values characteristic of 2:1 electrolytes while the ([14]dienoN₄) complexes are clearly 1:1 electrolytes. Magnetic susceptibility measurements indicate that both the

TABLE III
CONDUCTANCE DATA FOR 14-MEMBERED RING
DERIVATIVES IN ACETONITRILE

Complex	ΛM^a
Ni([14]dienoN ₄)ClO ₄	162
Ni([14]dienoN ₄)PF ₆	142
α -Ni([14]trieneN ₄)(ClO ₄) ₂ ·H ₂ O	266
β -Ni([14]trieneN ₄)(PF ₆) ₂ ·H ₂ O	318

^a Approximately (1–5) × 10⁻⁴ M solutions; in units of cm²/ohm mol.

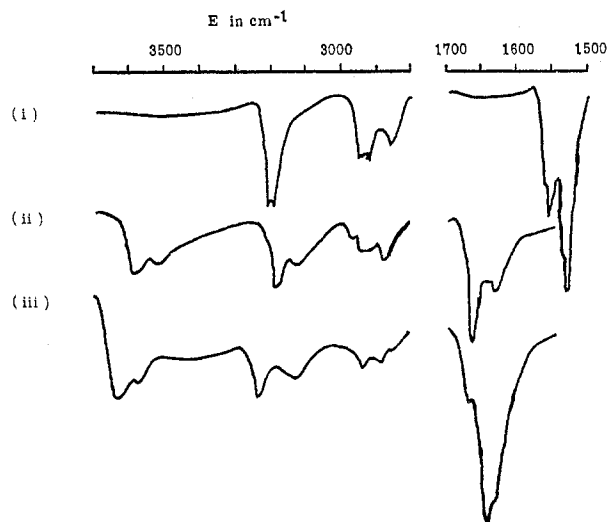
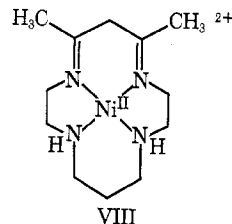


Figure 3.—Infrared spectra of the 14-membered ring derivatives: (i) Ni([14]dienoN₄)ClO₄; (ii) α -Ni([14]trieneN₄)(ClO₄)₂·H₂O; (iii) β -Ni([14]trieneN₄)(PF₆)₂·H₂O. Samples prepared in halo mulls.

starting materials and their oxidation products are diamagnetic in the solid state, requiring oxidation or protonation of the ligand structure in order to rationalize the conductivity data. Also changes occur in the infrared spectra that follow the pattern described earlier for the corresponding 13-membered ring derivatives (Figure 3). Again, the ir spectra of the starting materials exhibit several sharp bands in the 1500–1600-cm⁻¹ region which disappear in the oxidation products. Both isomeric oxidation products show sharp imine stretches at ~1670 cm⁻¹ (α isomer as the diperchlorate; ~1650 cm⁻¹ as the bromoperchlorate) and ~1645 cm⁻¹ (β isomer as the bis(hexafluorophosphate); ~1655 cm⁻¹ as the dibromide).

In this system, the nmr spectra of the two isomers provide a clearly definitive structure proof (Figure 4). They exhibit two distinct methyl singlets (2.32 and 2.46 ppm for the β isomer in deuterionitromethane; 1.67 and 1.76 ppm for the α isomer in deuteriodimethyl sulfoxide). Also, the protonated form of the reactant complex Ni([14]dienoN₄)⁺ has been isolated¹⁹ and, in accord with the symmetry of the molecule (structure VIII), the methyl protons occur as a singlet, as do the



(30) Experimental difficulties, together with uncertainty as to the precise isomeric purity of the original samples, preclude a more detailed analysis of the equilibrium mixture.

(31) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969); L. G. Warner, N. J. Rose, and D. H. Busch, *ibid.*, **90**, 6938 (1968).

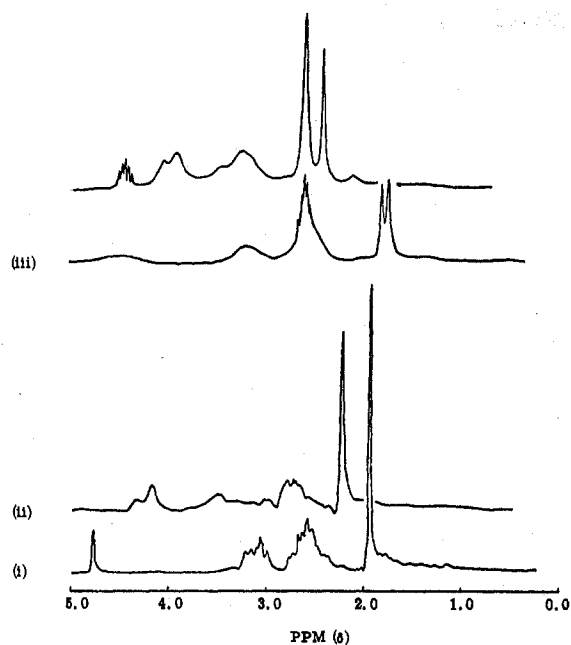


Figure 4.—Nmr spectra of the 14-membered ring derivatives: (i) $\text{Ni}([\text{14}] \text{dienoN}_4)\text{ClO}_4$ (CD_3CN); (ii) $\text{Ni}([\text{14}] \text{dieneN}_4)(\text{PF}_6)_2$ (CD_3NO_2); (iii) $\alpha\text{-Ni}([\text{14}] \text{trieneN}_4)(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (CD_3SOCD_3); (iv) $\beta\text{-Ni}([\text{14}] \text{trieneN}_4)(\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ (CD_3NO_2). Tetramethylsilane, internal standard; solvent given in parentheses; 60-MHz spectra. The ligand in ii has structure VIII and is named 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-11,14-diene,¹⁹ abbreviated 12,14-Me₂[14]-11,14-dieneN₄ or [14]dieneN₄. 3-(Trimethylsilyl)propanesulfonic acid sodium salt used as an internal standard in iii.

corresponding protons in $\text{Ni}([\text{14}] \text{dienoN}_4)^+$ (Figure 4). It is also significant that there is no resonance below ~ 5 ppm in the nmr spectra of the oxidation products. The ir spectra of these isomers also lack a band above 3000 cm^{-1} which might have been attributable to a vinyl C-H stretch, suggesting that the oxidation products α - and β - $\text{Ni}([\text{14}] \text{trieneN}_4)^{2+}$ are analogous in structure to the previously discussed 13-membered ring derivatives.

The indicated structure (VI) then accounts for the observed isomerism in that the NH protons in the six-membered ring would be able to adopt two orientations with respect to the plane of coordination. With both NH protons oriented in the same direction, the six-membered chelate ring can adopt the favored chair conformation. If the NH's are on opposite sides of the coordination plane, the six-membered ring must adopt a "twist" conformation. Both complexes should exist as racemates.

The visible spectra of the two complexes are entirely unremarkable, resembling those of the corresponding 13-membered ring derivatives. They are comprised of charge-transfer bands along with low-energy shoulders that may be related to d-d transitions.

A reaction which lends substance to the view of these oxidations as the result of formal hydride extraction (eq 7) is that of equimolar quantities of trityl (triphenylmethyl) tetrafluoroborate³² and $\text{Ni}([\text{14}] \text{dienoN}_4)\text{ClO}_4$ in dry acetonitrile under a nitrogen atmosphere. This carbonium ion, which had previously been observed to introduce conjugation into a variety

of unsaturated hydrocarbons *via* hydride extraction and subsequent proton elimination,³³ produces both α - and β - $\text{Ni}([\text{14}] \text{trieneN}_4)\text{BF}_4\text{ClO}_4 \cdot \text{H}_2\text{O}$ from the starting material. The products, isolated by fractional crystallization from acetone and converted to the diperchlorate salts, appear indistinguishable from those generated by bromine oxidation of the same complex.

Experimental Section

Materials.—All solvents and chemicals were reagent grade and were used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were all determined by commercial analytical laboratories.

Physical Measurements.—Visible, near-infrared, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer modified with a special high-intensity lamp (visible and infrared regions). Spectra were obtained on solid samples with Halocarbon grease mulls impregnated on filter paper. Perkin-Elmer Models 337 and 457 recording spectrophotometers were used to obtain the infrared spectra. The spectra were measured in Nujol and halo oil mulls.

Electrical resistances of solutions of the compounds were measured using an Industrial Instruments RC 16B conductivity bridge and a conductivity cell with a constant of 2.20 cm^{-1} . Conductances were determined at room temperature at 1000 cps on solutions that were approximately $(1-5) \times 10^{-4} \text{ M}$.

The magnetic susceptibilities of solid samples were obtained by the Faraday method using a system equipped with a Cahn Electrobalance.³⁴ The nmr spectra were obtained on Varian A-60 A and HA-100 instruments.

Caution! The perchlorate complexes described in this communication were found to be uniformly stable to thermal or shock detonation. Nevertheless, experience with similar species has indicated that perchlorate complexes are potential safety hazards due to their thermal and shock sensitivity, and recognition of this potential for explosive decomposition should be incorporated into the manipulations of these materials.

$\text{Ni}([\text{13}] \text{dieneN}_4)$.—This complex was prepared by the *in situ* method of Cummings^{18,19} followed by addition of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ in excess to the solution after filtration and before adjustment of the pH to 10. The resulting precipitate was washed with water and dried *in vacuo*. Recrystallization of the orange-pink powder from acetonitrile resulted in orange crystals which were dried *in vacuo*. *Anal.* Calcd for $\text{NiC}_{11}\text{H}_{21}\text{N}_4\text{ClO}_4$: C, 35.92; H, 5.71; N, 15.24. Found: C, 35.59; H, 5.61; N, 15.11.

$\text{Ni}([\text{14}] \text{dieneN}_4)\text{ClO}_4$.—A modification of the *in situ* reaction used for the above preparation was employed.^{18,19} Filtration of the reaction solution into concentrated aqueous NaClO_4 , followed by adjustment of the pH to 10, produced the desired compound. The red-brown precipitate was filtered, washed with water, and dried *in vacuo*. Recrystallization of the powder from water yielded red crystals which were dried *in vacuo*. *Anal.* Calcd for $\text{NiC}_{12}\text{H}_{23}\text{N}_4\text{ClO}_4$: C, 37.75; H, 6.03; N, 14.68. Found: C, 38.08; H, 6.05; N, 13.90.

$\text{Ni}([\text{14}] \text{dieneN}_4)\text{PF}_6$.—Metathesis was carried out using the perchlorate compound and a hot aqueous solution of NH_4PF_6 . On cooling, the product separated as red crystals which were dried *in vacuo*. *Anal.* Calcd for $\text{NiC}_{12}\text{H}_{23}\text{N}_4\text{PF}_6$: C, 33.72; H, 5.39; N, 13.11. Found: C, 34.32; H, 5.31; N, 13.07.

α - and β - $\text{Ni}([\text{13}] \text{trieneN}_4)\text{Br}(\text{ClO}_4) \cdot \text{H}_2\text{O}$.— $\text{Ni}([\text{13}] \text{dieneN}_4)\text{ClO}_4$ (6.0 g) was dissolved in 200 ml of acetonitrile at room temperature. Bromine (2.6 g) was added slowly (10 min) to this stirred solution and stirring was continued for several hours. The brown precipitate which formed upon addition of the bromine was filtered, washed with acetonitrile and ether, and dried; yield 6.0 g.

α - $\text{Ni}([\text{13}] \text{trieneN}_4)\text{BrClO}_4 \cdot \text{H}_2\text{O}$.—The product obtained as described in the preceding paragraph was treated with 600 ml of hot acidic methanol for several minutes. The solution was then filtered hot and the insoluble orange-brown powder, which was α - $\text{Ni}([\text{13}] \text{trieneN}_4)\text{BrClO}_4 \cdot \text{H}_2\text{O}$, was washed with methanol and ether and then dried *in vacuo*; yield 1.6 g. *Anal.* Calcd for $\text{NiC}_{11}\text{H}_{21}\text{N}_4\text{BrClO}_4$: C, 28.45; H, 4.78; N, 12.07. Found: C, 28.83; H, 5.00; N, 12.28.

(33) W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).

(34) V. Katović, L. F. Lindoy, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).

β -Ni([13]trieneN₄)BrClO₄·H₂O.—The methanol solution from the above separation was evaporated slowly on a steam bath to a final volume of 150 ml. The solution was left at 0° for several hours, and the resultant brown precipitate was filtered; yield 1.3 g. The infrared spectrum indicated this to be a mixture of isomers. The solid was dissolved in 500 ml of hot acidic methanol and 200 ml of ether was added. On standing at 0°, brown-violet crystals of β -Ni([13]trieneN₄)BrClO₄·H₂O formed. This product was filtered, washed with ether, and dried *in vacuo*; yield 0.4 g. *Anal.* Calcd for NiC₁₁H₂₂N₄BrClO₅: C, 28.45; H, 4.78; N, 12.07. Found: C, 28.36; H, 4.32; N, 11.82.

α - and β -Ni([13]trieneN₄)(ClO₄)₂·H₂O.—The appropriate isomer as the bromoperchlorate was dissolved in a minimum amount of warm, acidic water. Excess NaClO₄ dissolved in water was added slowly. Yellow-orange crystals formed as the solution cooled. The product was washed with acetone and ether and then dried *in vacuo*. For α -Ni([13]trieneN₄)(ClO₄)₂·H₂O the yield was 0.5 g (from 0.7 g of bromoperchlorate). *Anal.* Calcd for NiC₁₁H₂₂N₄Cl₂O₉: C, 27.27; H, 4.55; N, 11.57. Found: C, 27.95; H, 4.22; N, 11.24. For β -Ni([13]trieneN₄)(ClO₄)₂·H₂O the yield was 0.3 g (from 0.4 g of the bromoperchlorate). *Anal.* Calcd for NiC₁₁H₂₂Cl₂O₉: C, 27.27; H, 4.55; N, 11.57. Found: C, 27.61; H, 4.26; N, 11.66.

α - and β -Ni([13]trieneN₄)(PF₆)₂·H₂O.—These preparations were attempted by metathesis in warm water from the corresponding bromoperchlorate complexes. The resultant products were isomerically pure but contained traces of perchlorate as indicated by their ir spectra. This precluded accurate analytical data; however, these yellow crystalline materials were employed in the following reaction.

α - and β -Ni([13]trieneN₄)(PF₆)₂·CH₃CN.—The crystalline products from the above metathesis were recrystallized from acetonitrile, resulting in acetonitrile adducts (ir and nmr results) in which lattice water was absent. These products were in turn used to obtain visible spectra of these isomers in neutral dry acetonitrile.

α -Ni([14]trieneN₄)(ClO₄)₂·H₂O.—Ni([14]dienoN₄)ClO₄ (5.0 g) was dissolved in 100 ml of acetonitrile to which was added, dropwise, with stirring, 2.10 g of bromine (1:1 mole ratio) in 10 ml of acetonitrile. After stirring for 1 hr, the brown precipitate was filtered and treated with 1000 ml of hot acidic methanol, and the insoluble brown fraction was filtered and dried; yield 4.32 g. This material was dissolved in 100 ml of hot acidic water and an aqueous solution of NaClO₄ was added. On cooling, a yellow crystalline product formed. This was filtered and recrystallized from 400 ml of acidic hot water. The matted yellow needles,

which formed upon cooling, were washed with acetone and dried *in vacuo*. *Anal.* Calcd for NiC₁₂H₂₄N₄Cl₂O₉: C, 28.92; H, 4.82; N, 11.24. Found: C, 29.10; H, 4.72; N, 10.98.

β -Ni([14]trieneN₄)(PF₆)₂·H₂O.—Ni([14]dienoN₄)PF₆ (2.0 g) was dissolved in 100 ml of acetonitrile. Bromine (0.77 g) (1:1 mole ratio) in 100 ml of acetonitrile was added dropwise with stirring and the solution was stirred for 1 hr. The dark brown precipitate was filtered and dried; yield 1.6 g. This product was suspended in 200 ml of hot acidic methanol, and the insoluble, dark brown fraction was filtered and dried. One gram of this substance was dissolved in 100 ml of acidic hot water and 2 g of NH₄PF₆ in 10 ml of water was slowly added. Yellow-green crystals formed upon cooling. This product was recrystallized from 50 ml of hot water, yielding yellow-green crystals which were dried *in vacuo*. *Anal.* Calcd for NiC₁₂H₂₄N₄P₂F₁₂O: C, 24.45; H, 4.07; N, 9.51. Found: C, 23.98; H, 3.53; N, 9.45.

α - and β -Ni([14]trieneN₄)BF₄ClO₄·H₂O.—Ni([14]dienoN₄)ClO₄ (0.8 g) was dissolved in 25 ml of dry acetonitrile under an N₂ atmosphere. To this stirred solution was added dropwise 0.7 g (1:1 mole ratio) of trityl tetrafluoroborate³⁹ dissolved in 10 ml of dry acetonitrile. The reaction was refluxed under N₂ for several hours and the resultant amber solution was taken to a minimum volume on a rotary evaporator. Addition of 100 ml of acetone followed by slow evaporation of this solvent produced first α -Ni([14]trieneN₄)BF₄ClO₄·H₂O and then β -Ni([14]trieneN₄)BF₄ClO₄·H₂O as yellow crystals. The isomers were converted to the diperchlorates in hot acidic water and their ir spectra were compared with authentic samples of the respective complexes produced by bromine oxidation. Analytical data were obtained for the more abundant α isomer.

α -Ni([14]trieneN₄)(ClO₄)₂·H₂O.— α -Ni([14]trieneN₄)BF₄ClO₄·H₂O (0.1 g) was dissolved in 10 ml of hot water made acidic with perchloric acid. A concentrated solution of sodium perchlorate in water was then slowly added with stirring. On cooling, yellow-orange matted crystals separated from the solution and were collected by filtration, washed with water and then ether, and dried *in vacuo*. *Anal.* Calcd for C₁₂H₂₄N₄NiCl₂O₉: C, 28.92; H, 4.82; N, 11.24. Found: C, 29.01; H, 4.93; N, 10.88.

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