

The Oxidation and Reduction Behavior of Macrocyclic Complexes of Nickel. Electrochemical and Electron Spin Resonance Studies

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Abstract: Electrochemical and electron spin resonance studies have been carried out on an extensive series of macrocyclic complexes of nickel, which vary in the nature and degree of ligand unsaturation, charge type, and ring size. Oxidation of complexes containing neutral and dianion ligand systems produces stable six-coordinate and square planar nickel(III) species, respectively. The one-electron reduction products of the parent nickel(II) macrocycles exist as either d^9 nickel(I) complexes or as metal stabilized anion radicals, depending upon the nature of the ligand unsaturation. The overall redox behavior of the family of macrocycles is discussed in terms of their chemical reactivity patterns, stereochemistry, and charge type. Comparisons are made to other similarly structured complex types including the tetraphenylporphyrin complexes of nickel.

The significant chemical behavior of transition metal complexes very often depends on their facile redox properties. This is true to a large degree for the natural and synthetic complexes involving macrocyclic ligands. These substances undergo a diverse array of chemical reactions, such as ligand oxidative dehydrogenation,¹⁻⁵ metal alkylation,⁶⁻⁹ ligand substitution,¹⁰⁻¹² and hydrogenation.¹³⁻¹⁵ The success of some of these reactions is intimately linked with the ability of higher and lower oxidation states of these complexes to function as reactive intermediates. The ability of macrocyclic ligands to stabilize a wide range of oxidation states of a coordinated metal ion has been amply demonstrated by the studies of Olson and Vasilevskis.¹⁶ Simultaneous and subsequent work conducted in our laboratories^{1, 17, 18} and by Endicott and coworkers¹⁹ has proven the generality of their observations. It becomes highly significant, therefore, when the availability of an extensive series of macrocyclic complexes permits an opportunity, to provide a sound chemical basis for the evaluation of redox-structure relationships. We present here a

broad family of synthetic macrocyclic complexes of nickel (Figure 1) which are ideally suited to this purpose. The substances studied all involve coordination of tetradentate macrocyclic ligands in a square planar fashion. Electrochemical studies of these complexes have enabled us to systematically establish the electronic and structural features which promote and retard their electron transfer reactions. We have initiated similar studies of macrocyclic complexes of cobalt and iron.^{1, 20} Further, through the use of epr spectroscopy, it has been possible to determine the mutual influence of metal ions and ligands in establishing different electron density distributions and coordination geometries when various oxidation state levels are achieved by the metal complex.

Results

The electrochemical data for the entire series of nickel complexes are presented in Table I, and the corresponding epr spectral parameters are given in Table II. The number of electrons transferred in each electrode process was determined in the majority of cases by direct controlled potential coulometry (Table III). Unless otherwise stated, the calculated n values established that these complexes undergo single electron transfer reactions in acetonitrile solution. With few exceptions, cyclic voltammetric curves showed that each electrode process has peak potential separations of 60 mV and peak current ratios of unity. This, together with the identity of the multiple and single scan cyclic voltammograms, established the simplicity of the electron transfer. Electrochemical reversibility was further established by recording the current-potential curves of a large number of electrolytically oxidized and reduced complexes. In each case, the measured half-wave potential for the product was identical with that of the starting material. Representative current-potential curves for the series of nickel complexes are shown^{21, 22}

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- (2) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
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- (18) F. V. Lovecchio and D. H. Busch, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass, April 1972, INOR 147.
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(21) In some examples, notably with the [14]dienes, published data show¹⁸ that the experimentally obtained curve for the Ni(II) \rightarrow Ni(III) oxidation process is a distorted one. In view of the contrasting behavior for the remainder of our series, we have reexamined the electrochemistry of these compounds. The most simply obtained curve is identical with that reported earlier. However, if the platinum electrode is brought to a reproducibly preconditioned state prior to each run, there is a marked improvement in the character of the current-potential

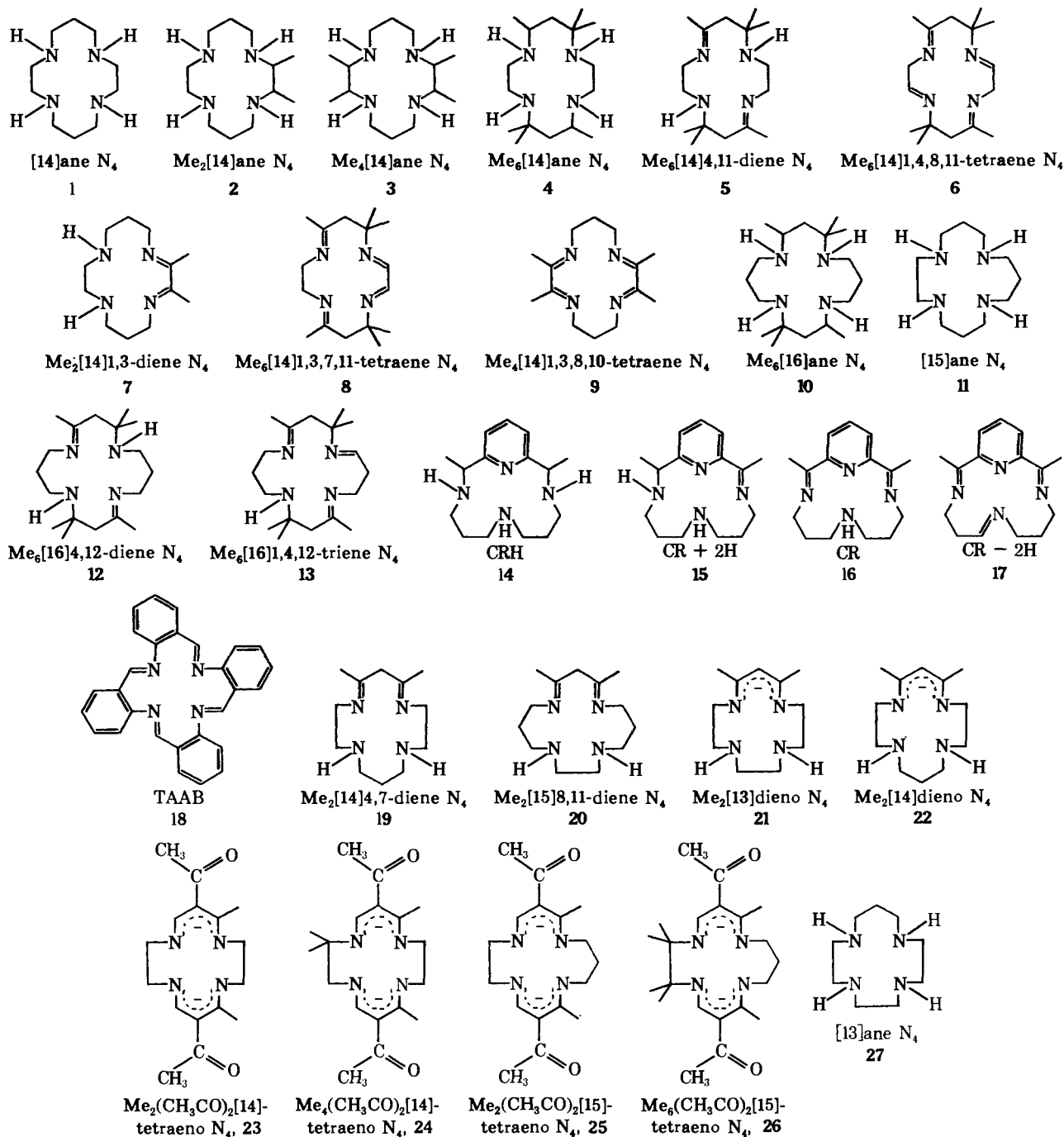


Figure 1. Macrocyclic ligands in complexes of nickel. The sources of the compounds are as follows: 1, E. K. Barefield, *Inorg. Chem.*, **11**, 2273 (1972); 2, 3, and 7, E. S. Gore, E. K. Barefield, and D. H. Busch, unpublished results; 4, A. M. Tait and D. H. Busch, *Inorg. Nucl. Chem. Lett.*, **8**, 491 (1972); 5, N. F. Curtis and R. W. Hay, *Chem. Commun.*, 524 (1966); 6 and 8, N. F. Curtis, *ibid.*, 881 (1966); 9, D. A. Baldwin and N. J. Rose, Abstracts of the 157th Meeting of the American Chemical Society, Minneapolis, Minn., 1969; 10, E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 1216 (1971); 11 and 27, L. Martin, L. Zompa, and D. H. Busch, unpublished results; 12 and 13, ref 3; 14, 15, 16, and 17, ref 14; 18, G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 4830 (1964); 19, 20, 21, and 22, S. Cummings and R. E. Seivers, *ibid.*, **92**, 215 (1970); ref 32; 23, 24, 25, and 26, E. G. Jager, *Z. Anorg. Allg. Chem.*, **364**, 178 (1969), also previous papers in that series and unpublished extensions by C. J. Hipp and D. H. Busch.

in Figure 2. In Figure 3 are shown typical esr spectra obtained for these complexes.

Electrochemical Behavior of Complexes with Neutral

curve. In order to obtain reversible behavior it was necessary to maintain a small positive potential at the platinum working electrode for a few minutes prior to the recording of the current-potential curve. Several variations, including different methods of solvent purification and various electrode pretreatments as well as different electrodes and changes in supporting electrolyte (from ClO_4^- to BF_4^-), did not alter these results. We agree with the remainder of the observations of Olson and Vasilevskis on the electrochemistry of these complexes.

Ligands. Considering first the macrocyclic complexes containing neutral ligands, we see that whether or not unsaturation is present in the ligand system each com-

While we have no mechanistic explanation for the anomalous results it is well known that surface effects on solid electrodes can produce drastic alterations in recorded current-potential curves.²² In the present case, the $E_{1/2}$'s in Table I have been calculated from the more reversible waves obtained since this is more consistent with the values observed for the entire family of nickel complexes.

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Table I. Electrochemical Behavior of Macrocyclic Complexes of Nickel^a

Neutral ligand	Oxidation potential (V)	Reduction potential (V)	
	Ni(L) ²⁺ → Ni(L) ³⁺	Ni(L) ²⁺ → Ni(L) ⁺	Ni(L) ⁺ → Ni(L) ⁰
[13]aneN ₄	+0.7 → +0.9 ^e	-1.70	
[14]aneN ₄	+0.67	-1.70	
Me ₂ [14]aneN ₄	+0.68	-1.73	
Me ₄ [14]aneN ₄	+0.71	-1.66	
Me ₆ [14]aneN ₄	+0.87	-1.57	
Me ₈ [14]4,11-dieneN ₄	+0.98	-1.57	
Me ₆ [14]1,4,8,11-tetraeneN ₄	+1.05	-1.35	-2.0 (i) ^b
[15]aneN ₄	+0.90	-1.5 (i) ^b	
Me ₆ [16]aneN ₄	~+1.3 ^e	-1.40	
Me ₈ [16]4,12-dieneN ₄	+1.3	-1.37	
Me ₆ [16]1,4,12-trieneN ₄	+1.3	-1.30	
Me ₂ [14]1,3-dieneN ₄	+0.86	-1.16	
CR + 4H ^c	+0.89	-1.53	
CR + 2H ^c	+0.93	-1.25	-1.88 (i)
CR ^c	+1.03	-0.96	-1.55
CR - 2H ^c	+1.05	-0.84	-1.45
Me ₆ [14]1,3,7,11-tetraeneN ₄	+1.05	-0.76	-1.62
Me ₄ [14]1,3,8,10-tetraeneN ₄	+1.00	-0.82	-1.15
Me ₂ [14]4,7-dieneN ₄	+0.72	~-1.5 (i)	
Me ₂ [15]8,11-dieneN ₄	+0.94	~-1.5 (i)	
Monoanionic ligand	Ni(L) ⁺ → Ni(L) ²⁺	Ni(L) ⁺ → Ni(L) ⁰	
(Me ₂ [13]dienoN ₄) ⁻	+0.27 (i) ^d	-2.30	
(Me ₂ [14]dienoN ₄) ⁻	+0.23 (i) ^d	-2.34	
Complexed dianionic ligand	Ni(L) ⁺ → Ni(L) ²⁺	Ni(L) ⁰ → Ni(L) ⁺	
(Me ₂ (CH ₃ CO) ₂ [14]tetraenoN ₄) ²⁻	+0.97 (i)	+0.25	
(Me ₄ (CH ₃ CO) ₂ [14]tetraenoN ₄) ²⁻	+0.98 (i)	+0.26	
(Me ₂ (CH ₃ CO) ₂ [15]tetraenoN ₄) ²⁻	+0.92 (i)	+0.27	
(Me ₄ (CH ₃ CO) ₂ [15]tetraenoN ₄) ²⁻	+0.96 (i)	+0.28	

^a In acetonitrile solution, 0.1 M (*n*-Bu)₄NBF₄, volts vs. Ag|Ag⁺ (0.1 M) reference electrode. ^b i = irreversible. ^c These complexes display additional quasireversible waves at approximately +1.0 V. ^d The electrochemical behavior of the series of Ni(CR)²⁺ complexes is reported in detail in ref 14. ^e Oxidation waves very distorted and drawn out. Therefore only an approximate potential range for oxidation is given.

Table II. ESR Data for Nickel Complexes with Macrocyclic Ligands in Frozen Acetonitrile (77K °) Containing 0.1 M (*n*-Bu)₄NBF₄

Macrocycle	1 e ⁻ reduction product		Oxidation state characterization	1 e ⁻ oxidation product				Oxidation state characterization
	<i>g</i>	<i>g</i> _⊥		<i>g</i>	<i>g</i> _⊥	<i>A</i> ^e	<i>A</i> _⊥ ^e	
Me ₂ [14]aneN ₄ (2)	2.261	2.060	Ni(I)	2.020	2.205	21.3	16.5	Ni(III)
Me ₆ [14]aneN ₄ (4)	2.266	2.055	Ni(I)	2.029	2.215	21.3		Ni(III)
Me ₈ [14]4,11-dieneN ₄ (5)	2.226	2.055	Ni(I)	2.024	2.199	22.5		Ni(III)
Me ₆ [14]1,4,8,11-tetraeneN ₄ (6)	2.195	2.053	Ni(I)	2.018	2.186	24.2	17	Ni(III)
Me ₂ [14]1,3-dieneN ₄ (7)	2.004 ^{b,d} (40) ^c		Ligand radical	2.023	2.197	23.1	16	Ni(III)
Me ₈ [14]1,3,7,11-tetraeneN ₄ (8)	2.003 ^b (24) ^c		Ligand radical	2.016	2.180	24.0	21	Ni(III)
	2.003 ^{a,b} (20) ^c							
Me ₄ [14]1,3,8,10-tetraeneN ₄ (9)	1.999 ^b (25) ^c		Ligand radical	2.023	2.172	25.4	19	Ni(III)
	1.999 ^{a,b} (24) ^c							
CRH (14)	2.250	2.066	Ni(I)	2.023	2.198	22.2		Ni(III)
CR + 2H (15)	2.005 ^{b,d} (31) ^c		Ligand radical					
CR (16)	2.003 ^{b,d} (34) ^c		Ligand radical	2.023	2.175	23.9	19	Ni(III)
Me ₂ [14](CH ₃ CO) ₂ [14]tetraeneN ₄ (23)				2.138	2.016			Ni(III)
				2.144 ^f	2.012 ^f			

^a Reduced with Zn/Hg. ^b Isotropic signal. ^c Peak to peak width in gauss. ^d Reduced with Na/Hg. ^e In gauss; if no entry, A not resolved. ^f In ethylene chloride.

plex undergoes at least one reversible or nearly reversible oxidation and a similar reduction process, producing species formally containing Ni(III) and Ni(I), respectively. This is characteristic of the remarkable ability of the cyclic ligand structure to stabilize unusual oxidation states of the coordinated metal ion. This characteristic behavior was first reported by Olson and Vasilevskis in their pioneering redox study¹⁶ of the nickel complexes of Me₆[14]aneN₄ and Me₈[14]4,11-dieneN₄. The occurrence of these reversible reactions undoubtedly stems from the general resistance of these complexes toward dissociation under a variety of solu-

tion conditions. The surprisingly mild potential (+0.68 V) under which NiMe₂[14]aneN₄²⁺ is oxidized to NiMe₂[14]aneN₄³⁺ has led to the synthesis and characterization of an entire series of trivalent nickel complexes containing this ligand.^{23,24}

A pronounced shift in oxidation state stability occurs when there is a change in macrocyclic ring size. An increase in ring size promotes the ease of formation of Ni(I), while rendering the oxidation to Ni(III) more difficult. The difference between the [14]aneN₄ and

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

(24) E. Gore and D. H. Busch, *Inorg. Chem.*, 12, 1 (1973).

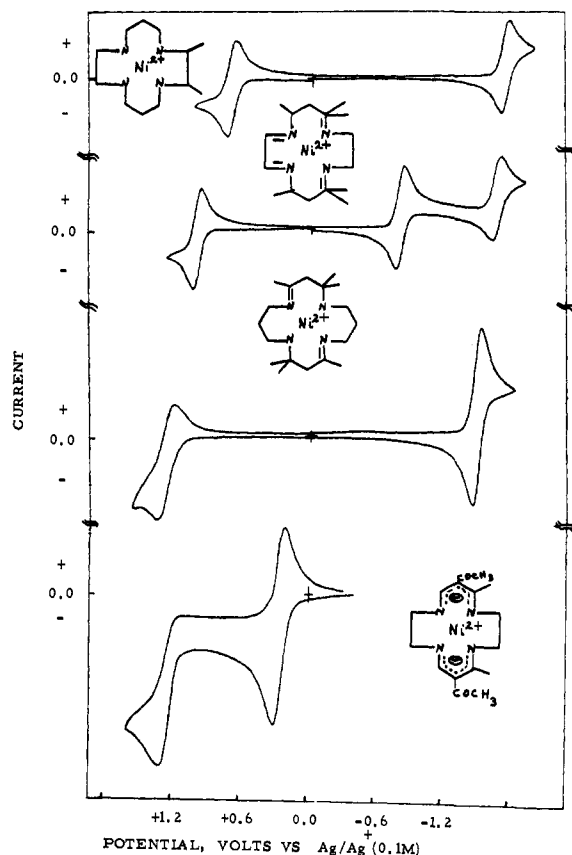


Figure 2. Current-potential curves for some complexes of nickel with macrocyclic ligands.

Table III. Coulometric n Values for the Nickel Complexes with Macrocyclic Ligands

Complex	Electrochemical process	Coulometric n value
$\text{Ni}^{\text{II}}\text{Me}_2[14]\text{janeN}_4$	Oxidation	1.00
$\text{Ni}^{\text{II}}\text{Me}_6[14]\text{janeN}_4$	Oxidation	0.82
$\text{Ni}^{\text{II}}\text{Me}_6[14]\text{janeN}_4$	Reduction	1.01
$\text{Ni}^{\text{II}}\text{Me}_6[14]1,4,8,11\text{-teteneN}_4$	Reduction	0.94
$\text{Ni}^{\text{II}}\text{CRH}$	Oxidation	1.04
$\text{Ni}^{\text{II}}\text{Me}_2[14]1,3\text{-dieneN}_4$	Oxidation	1.09
$\text{Ni}^{\text{II}}\text{Me}_2[14]1,3\text{-dieneN}_4$	Reduction	1.12
$\text{Ni}^{\text{II}}\text{Me}_6[14]1,3,7,11\text{-teteneN}_4$	Reduction	1.01
$\text{Ni}^{\text{II}}\text{Me}_2[15]4,6,12,14\text{-tetenatoN}_4$	Oxidation	0.99
$\text{Ni}^{\text{II}}\text{Me}_6[16]4,12\text{-dieneN}_4$	Reduction	1.3
$\text{Ni}^{\text{II}}\text{TAAB}$	Oxidation	1.19
$\text{Ni}^{\text{II}}\text{TAAB}$	Reduction	0.98

[16]janeN₄ complexes amounts to 0.3 V. We suggest that this difference is primarily due to deviations from the ideal metal-donor atom distances accompanying the redox changes $\text{Ni}(\text{III}) \rightleftharpoons \text{Ni}(\text{II}) \rightleftharpoons \text{Ni}(\text{I})$. This concept of optimum fit between the coordinated metal ion and the "hole size" provided by the macrocyclic ligand is also in accord with theoretical conclusions and electronic spectral studies carried out in our laboratories (*vide supra*).

The more common effect of ligand unsaturation also favors the formation of the lower valent states of the complexes and causes the $\text{Ni}(\text{II}) \rightleftharpoons \text{Ni}(\text{III})$ process to occur at higher energy. The presence of an α -diimine stabilizes Ni(II) to a larger degree than do isolated imines.

The effect of the α -diimine function on the reduction

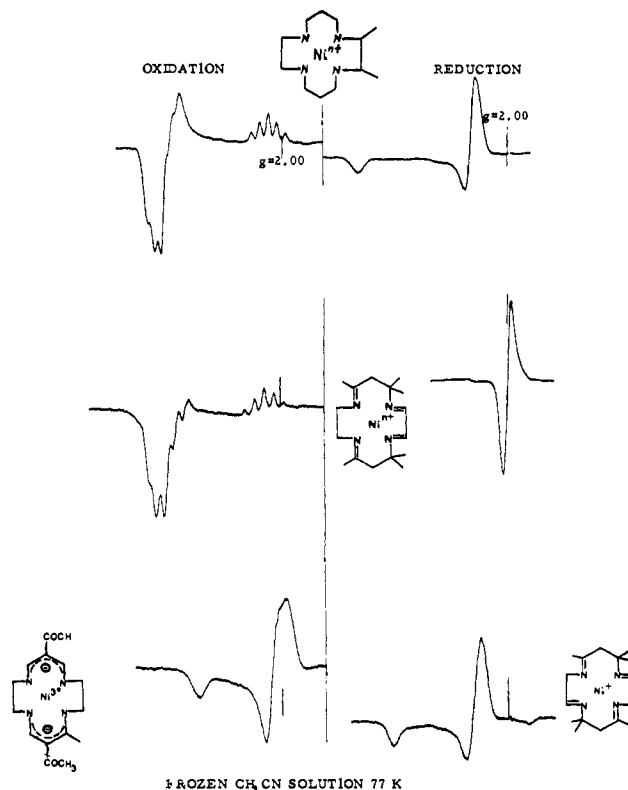


Figure 3. ESR spectra for redox products of some complexes of nickel with macrocyclic ligands.

reactions of the nickel macrocycles is very pronounced and structures containing this moiety form stable complexes in lower valence states under the influence of relatively mild potentials. An illustrative example is $\text{Ni}^{\text{II}}(\text{Me}_4[14]1,3,8,10\text{-tetraeneN}_4)^{2+}$ which undergoes two electrochemically reversible one-electron reductions at -0.82 and -1.15 V producing (formally) Ni(I) and Ni(0), respectively. This contrasts with the behavior of the structure containing only isolated imines, $\text{Ni}^{\text{II}}([14]1,4,8,11\text{-tetraeneN}_4)^{2+}$, which is reduced in acetonitrile solution only with much greater difficulty (-1.35 and *ca.* -2.0 V).

Structures of the Products of the Electrode Reaction—Neutral Ligand Cases. Electron paramagnetic resonance studies have provided detailed information on the electron density distribution and coordination geometry displayed by these oxidation and reduction products (Table II). For the oxidized products the anisotropic epr spectra at liquid N₂ temperature show axial symmetry, with $g_{\perp} > g_{\parallel}$ and a value of g_{\perp} considerably greater than 2. In all cases g_{\parallel} is split into five lines with intensity ratios of 1:2:3:2:1. In some cases, this splitting is also resolved for g_{\perp} . These observations are consistent in each case with the existence of a low spin, d⁷, six-coordinate Ni^{III} complex, in which two solvent molecules (CH₃CN) are axially and equivalently coordinated. These conclusions are consistent with the theoretically anticipated epr spectrum for such a system. Assuming D_{4h} symmetry, the most reasonable electronic configuration for the metal complex is $(e_g)^4(b_{2g})^2(a_{1g})^1$, *i.e.*, with the unpaired electron in the d_{z^2} orbital. Then, according to the method outlined by Maki, *et al.*,²⁵ the g factors are given $g_{\perp} = 2 - (6\lambda/\Delta)$, and

(25) A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

$g_{\parallel} = 2$, where $\lambda =$ the spin-orbit coupling constant and $\Delta = E[(e_g)^3(b_{2g})^2(a_{1g})^2] - E[(e_g)^4(b_{2g})^2(a_{1g})^1]$. Since the λ is negative, $g_{\perp} > g_{\parallel}$, consistent with our observed results.

Other workers have reported²⁶⁻³⁰ the preparation of Ni(III) complexes with a variety of ligands. In most cases the authenticity of the Ni(III) state was based solely on stoichiometry and magnetic moment measurements. However, magnetic moment measurements, although useful for determining the number of unpaired electrons in a complex, do not permit the determination of the distribution of the electron density.

One cannot distinguish between an authentic d⁷ Ni(III) species and a Ni(II) stabilized cation radical on the basis of magnetic moment measurements alone. An advantage of epr studies is that one can in fact distinguish between the two possibilities. Indeed in some cases, reexamination³¹ of supposedly authentic Ni(III) complexes using epr has revealed that the structure would be more properly described as a Ni(II) stabilized cation radical.

The complexes studied in this report are unique in that for the first time the d⁷ Ni(III) state has been established unambiguously in a lengthy series of complexes. The anisotropic g values are consistent with a d⁷ Ni(III) formulation, and unlike other purported Ni(III) complexes the appearance of superhyperfine coupling with axial ligands establishes the location of the unpaired electron as being the d_{z^2} orbital. Furthermore the axial symmetry of the g values and superhyperfine splitting patterns enable us to establish the geometry of the complexes as pseudo- D_{4h} . The superhyperfine splitting confirms the coordination of CH₃CN solvent molecules in the two axial sites.

The epr spectra obtained for the one-electron reduction products can be divided into two categories (Table II). In all the structures containing saturated or isolated imine ligand systems, axially symmetric spectra are observed with $g_{\perp} < g_{\parallel}$. This suggests a d⁹, Ni(I) configuration, i.e., $(e_g)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1$. For this situation, $g_{\perp} = 2 - (2\lambda/\alpha_{\perp})$, and $g_{\parallel} = 2 - (8\lambda/\alpha_{\parallel})$, where $\alpha_{\perp} = E[(e_g)^3(a_{1g})^2(b_{2g})^2(b_{1g})^2] - E[(e_g)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1]$ and $\alpha_{\parallel} = E[(e_g)^4(a_{1g})^2(b_{2g})^1(b_{1g})^2] - E[(e_g)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1]$. From this, $g_{\perp} < g_{\parallel}$, again consistent with our observations. For the one-electron reduction products of complexes containing α -diimine bonding functions, an isotropic epr spectrum with no hyperfine splitting is observed, with a g value very nearly equal to the free electron value (2.0023). Here, the unpaired electron is clearly delocalized onto the ligand system, and these complexes should be formulated as Ni(II)-stabilized ligand anion radicals.

Electrochemical Behavior of Complexes with Anionic Ligands. The redox pattern for the nickel complexes containing dianionic ligands shows two one-electron oxidations, only the first of which is electrochemically reversible (Figure 2). The same behavior was observed in methylene chloride solution. No reductions were noted for these complexes in the observable range of

potentials in acetonitrile (up to -2.8 V). The anisotropic epr spectrum of the stable one-electron oxidation product shows no resolvable fine structure and has $g_{\perp} < g_{\parallel}$, with the value of g_{\parallel} considerably greater than 2. Entirely equivalent results were obtained from electrolytically generated species in methylene chloride. These data lead us to formulate the oxidized species as a low spin, square planar nickel(III) complex. The electronic configuration is given by $(e_g)^4(a_{1g})^2(b_{2g})^1$, and the g values are $g_{\perp} = 2 - (2\lambda/\delta_{\perp})$ and $g_{\parallel} = 2 - (8\lambda/\delta_{\parallel})$. Here, $\delta_{\perp} = E[(e_g)^3(a_{1g})^2(b_{2g})^2] - E[(e_g)^4(a_{1g})^2(b_{2g})^1]$ and $\delta_{\parallel} = E[(e_g)^4(a_{1g})^2(b_{1g})^1] - E[(e_g)^4(a_{1g})^2(b_{2g})^1]$. Note here that $g_{\perp} < g_{\parallel}$, consistent with our observed order of g values. The absence of axially coordinated ligands is further substantiated by the observed solvent independence of the oxidation process. Since methylene chloride and acetonitrile represent very weak and moderately strong ligands, respectively, the similarity of both the electrochemistry and epr spectra in these solvents would imply their noncoordination in these oxidized complexes. In the absence of further information, such as nickel hyperfine coupling constants, it is not possible to determine the amount, if any, of delocalization of the unpaired electron onto the macrocyclic ligand.

The synthesis of macrocyclic complexes containing uninegative ligands has recently been accomplished,³² and their preliminary electrochemistry has been reported.¹⁸ We have repeated the electrochemical measurements, and these results are included in Table I. The oxidation patterns for these complexes consist of totally irreversible waves, followed by "quasi"-reversible electrode processes and suggest relatively complicated behavior. We are at present engaged in a systematic redox study of a series of macrocyclic complexes containing charge delocalized ligand systems of these types, and these results will be reported in a future communication.

The epr studies reported here were carried out on solutions which were 0.1 M in tetra-*n*-butylammonium tetrafluoroborate. The electrolyte strongly influences the resolution of any superhyperfine structure. Spectra run on samples of $[\text{Ni}^{II}(\text{Me}_2[14]\text{janeN}_4)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_3$ without added electrolyte failed to show resolution of superhyperfine structure. Experiments showed that until the solutions were made at least 0.05 M in electrolyte, no fine structure could be resolved. In addition the resolution did not depend on the anion present in the electrolyte (both ClO_4^- and PF_6^- gave the same splitting as BF_4^-), but the resolution did depend on the cation. Tetramethylammonium salts produced no fine structure, tetraethylammonium salts produced very poorly resolved spectra, and tetra-*n*-propylammonium salts produced well-resolved fine structure when the concentration was at least 0.1 M . This phenomenon whereby added salts improve the resolution has been noted by other authors.³³

Discussion

Variation of Redox Properties with Structural Parameters. The overall oxidation-reduction behavior of the macrocyclic nickel complexes is a composite function of

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degree and type of ligand unsaturation and macrocyclic ring size, as well as the number and position of ring substituents, charge type, and coordination number. With a broad family of complexes such as those described here, the observed pattern of behavior can be meaningfully related to other physical and chemical properties of these complexes. For example, one is able to evaluate the important effect of macrocyclic ring size. We noted earlier in the text that, in a progression to larger macrocyclic rings, the Ni(II) \rightarrow Ni(I) process is seen to occur with greater ease while the Ni(II) \rightarrow Ni(III) electrode reaction requires more energy. This we feel is an interesting consequence of the increased "hole size" provided for the coordinated ion by the large ligand system. As a result, this ligand can more easily accommodate the larger Ni(I) ion, while experiencing more difficulty encompassing the smaller Ni(III) ion. Consequently, the Ni(II)/Ni(I) and Ni(II)/Ni(III) redox potentials for the complexes involving the 16-membered rings are both shifted to more positive values (Table I). The oxidation waves for the Ni[16]N₄ series are also accordingly somewhat less than electrochemically reversible despite exhaustive electrode surface pretreatment procedures. The result of strain energy calculations carried out in our laboratories confirm these conclusions.³⁴ The techniques involved have been reported earlier.³⁵ For planar or near planar chelation by the macrocyclic ligand and using a metal-ligand distance of 2.00 Å, our results have shown that the strain energy experienced by a 16-membered macrocyclic ring upon coordination is 8.79 kcal, compared to 2.40 kcal for a 14-membered ring. Other experimental observations support these conclusions. For example, the 14-membered ring exerts a considerably stronger ligand field toward a coordinated metal ion than does the corresponding 16-membered ring.³⁶ Also, complexes of [16]N₄ are much less resistant to solution decomposition³⁷ than the analogous [14]N₄ complexes.

A different origin of steric strain can be seen if one notes the difference (\sim 4.6 kcal) between the ease of oxidation of the Ni([14]aneN₄)²⁺ derivatives. In each case, the Ni(III) complex contains two axially coordinated solvent molecules, as shown by our epr results, while the Ni(II) complex is four-coordinate. Furthermore the macrocyclic ligand is coordinated to the nickel ion in a square planar fashion. Conformational analysis studies carried out in our laboratories have shown^{34,35} that this situation can lead to appreciable nonbonding interactions between these extraplanar ligands (solvent) and the axially oriented methyl groups on the six-membered chelate rings of the Me₆[14]aneN₄ complexes. This effect becomes exaggerated in the Ni(III) complexes since the increased oxidation state of the central metal ion causes a contraction in the equilibrium metal-ligand distances. The less highly substituted derivatives of the series, such as Me₂[14]aneN₄ and [14]aneN₄, do not have to overcome this extra "strain" energy, and their electrochemical oxidations therefore occur with greater ease. It is interesting to notice that complexes

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with these different ligands display comparable variations in ligand field strengths³⁶ and aquation rates (Co(III) complexes)³⁸ which have been attributed to the same types of steric interactions. If one stays within the same chelated ligand framework and ring size, a smaller but noticeable effect on the oxidation potential of the Ni(II) \rightarrow Ni(III) process can be seen from the presence of variable amounts of ligand unsaturation. For example, E_{I-III} for Ni^{II}(Me₆[14]aneN₄)²⁺, Ni^{II}(Me₆[14]-4,11-dieneN₄)²⁺, and Ni^{II}(Me₆[14]1,4,8,11-tetraeneN₄)²⁺ are +0.87, +0.98 and +1.05 V, respectively. The corresponding values for Ni^{II}(Me₂[14]aneN₄)²⁺, Ni^{II}(Me₂[14]1,3-dieneN₄)²⁺ and Ni^{II}(Me₂[14]1,3,8,10-tetraeneN₄)²⁺ are +0.68, +0.86, and +1.00 V, respectively. These series of values probably reflect the increasing degree of polarizability of the metal-ligand bond in the more unsaturated derivatives. This increases the stability of the Ni^{II} complex relative to Ni(III). Paralleling this, we have shown^{36,39} from electronic spectral studies that increasing the amount of ligand unsaturation results in a stronger ligand field toward the coordinated Ni(II) ion.

The type of ligand unsaturation present in these complexes has a profound influence on the electron distribution found in their lower valent states. For example, the chemical reactivity and relative ligand field strengths of the lower valent nickel complexes can be readily understood in terms of their corresponding electrochemical and epr behavior. All of the nickel(II) complexes containing only isolated imines, including the highly unsaturated structure Ni^{II}([14]1,4,8,11-tetraeneN₄)²⁺, have very negative half-wave potentials, signifying that the added electron is entering a relatively high energy orbital. An examination of the epr spectra of these complexes established this orbital as being the highest unfilled metal d orbital in D_{4h} symmetry, $d_{x^2-y^2}$. The combined effect of the relative ligand field strength produced by the macrocyclic ligands and the spin-orbit interactions in the complexes can be ascertained if we recall that for these complexes the value of g_{\parallel} should vary linearly with $(\lambda/\alpha_{\parallel})$, where λ is the spin-orbit coupling constant and α_{\parallel} is the value of $10Dq_{xy}$ for a d⁹ system. The trend of g_{\parallel} values observed for the series of Ni(I) complexes is given in Table IV. Also tabulated

Table IV. Ni(I) g_{\parallel} Values and Co(III) and Ni(II) Dq Values

Complex	g_{\parallel}	Co(III) $10Dq_{xy}$ (cm ⁻¹)	Ni(II) $10Dq_{xy}$ (cm ⁻¹)
Ni ^I (Me ₆ [14]aneN ₄) ²⁺	2.266	2600	1398
Ni ^I (Me ₂ [14]aneN ₄) ²⁺	2.261	2710	1414
Ni ^I (Me ₆ [14]4,11-dieneN ₄) ²⁺	2.226	2780	1569
Ni ^I (Me ₆ [14]1,4,8,11-tetraeneN ₄) ²⁺	2.195	2944	

are the known values of $10Dq_{xy}$ for the corresponding ligands based on spectral data obtained from a series of Co(III) and Ni(II) macrocyclic complexes.³⁶ It is likely for this series of complexes that λ becomes smaller as the degree of ligand unsaturation increases. The quantity (λ/Dq) will therefore decrease and the observed g_{\parallel} value will be closer to 2 for the more unsaturated

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derivatives. The experimentally obtained g_{\parallel} values tabulated above reflect this trend.

In contrast to the above, we noted earlier in the text that the presence of an α -diimine function greatly reduces the energy requirements for electron addition. In these complexes, the epr spectrum for the one-electron reduction product is isotropic with an observed g tensor near the free electron value. The presence of conjugated diimines therefore delocalizes added electron density to a large degree and, as mentioned previously, the added electron has predominantly ligand character. It is significant that only complexes containing this bonding moiety show free radical type epr spectra and that only one α -diimine is necessary to produce this situation, as evidenced by the spectral parameters obtained for $\text{Ni}([\text{14}]\text{1,3-dieneN}_4)^+$. It is concluded that an antibonding ligand π^* orbital lies lower than the predominantly metal ($d_{x^2-y^2}$) σ^* orbital in these complexes.

This type of electron distribution becomes important in directing the course of the reactions of coordinated ligands in these low valent complexes. For example, we reported earlier on the electrochemical behavior of a complete series of nickel macrocycles derived from chemical oxidation and reduction of the parent species, $\text{Ni}(\text{CR})^{2+}$. It was found¹⁴ that although the more unsaturated derivatives of the series underwent simple one-electron transfer in acetonitrile, the use of the protic solvent methanol led to electrochemical reduction accompanied by hydrogenation of the imine function of the macrocyclic ring. We indicated that the hydrogenation process occurs readily since the added electron density resides mainly on the ligands of these complexes. These inferences are now substantiated by the free radical epr spectrum obtained for electrolytically produced $\text{Ni}(\text{CR})^+$ (Tables I and II). This spectrum clearly requires extensive delocalization onto the ligand system. This contrasts with the anisotropic spectrum observed for the complex with the most saturated ligand system, $\text{Ni}(\text{CR}+4\text{H})^+$, which is indicative of a d^9 metal complex. Thus, the reported facile hydrogenation of $\text{Ni}(\text{CR})^+$ in protic media is readily understood.

The redox patterns of structures containing anionic ligands convincingly demonstrate the influence of negative charge in determining the course of electron transfer reactions of macrocyclic complexes. This feature promotes the occurrence of higher oxidation states of the complex, while rendering its reductions more difficult (Table I). Also apparent is the tendency toward reduced coordination number in these complexes, as evidenced by the square planar nature of their one-electron oxidation products (above). The "Ni(III) ion" in these oxidized complexes presumably possesses an effective charge which is low enough to prevent solvent coordination in acetonitrile solution.

Additivity of Ligand Structural Effects on Electrode Potentials. It is apparent from the above discussion that when a metal ion is encompassed by a planar macrocyclic ligand, its redox sequences are affected by several different factors. Furthermore, without the benefit of a systematically related series of structures, the influence of some of these factors, while considerable in extent, may not be obvious. We have therefore made an attempt to calculate the relative magnitudes of these effects. The discussion to follow will refer

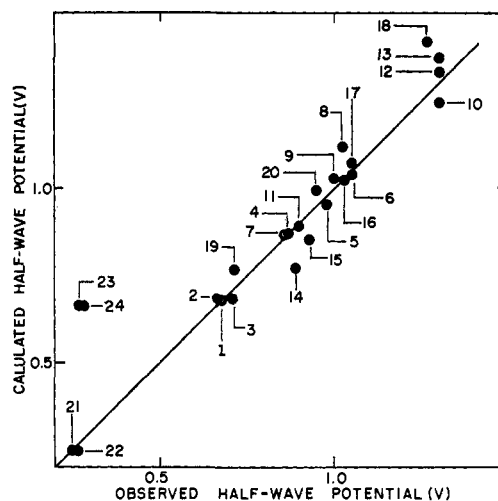
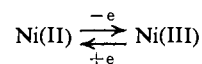


Figure 4. Relationship between calculated and observed reversible half-wave potentials for the $\text{Ni}(\text{II}) \rightleftharpoons \text{Ni}(\text{III})$ redox process of macrocyclic complexes. Numbers are identified in Figure 1.

mainly to the



process for each complex because our epr results show that each complex uniformly produces Ni(III) species. This uniformity gives a valid structural basis for comparison. Since the oxidation potential for the complex $\text{Ni}(\text{Me}_6[14]\text{janeN}_4)^{2+}$ has been reported in the literature most often, it will be used as a reference point. Examination of Table I shows that three factors cause an increase (more positive value) in $E_{1/2}$: the presence of a larger macrocyclic ring; the presence of axial methyl groups in the six-membered chelate rings; the presence of ligand unsaturation. The absence of these three factors, in addition to the presence of delocalized charge, causes a decrease in $E_{1/2}$. It is expected that these results are general and will apply to other metal ions and other kinds of cyclic ligand systems. From examination of appropriate pairs of complexes, it becomes possible to quantitatively correlate a structural feature with a change in $E_{1/2}$. For example, the potential difference between the oxidation process of $\text{Ni}^{\text{II}}(\text{Me}_6[14]4,11\text{-dieneN}_4)^{2+}$ and $\text{Ni}^{\text{II}}(\text{Me}_6[16]4,12\text{-dieneN}_4)^{2+}$ represents the effect of a change in ring size. Similarly, the potential difference between the oxidation processes of $\text{Ni}^{\text{II}}(\text{Me}_6[14]\text{janeN}_4)^{2+}$ and $\text{Ni}^{\text{II}}(\text{Me}_6[14]\text{janeN}_4)^{2+}$ represents the effect of axial methyl groups in the six-membered chelate rings. Continuing in this fashion, we estimate the following contributions to the reversible half-wave potential: (1) [14] \rightarrow [15](ring size effect), $\Delta E_{1/2} = +225$ mV; (2) [14] \rightarrow [16](ring size effect), $+375$; (3) two axial methyl groups in six-membered chelate rings, $+183$; (4) delocalized charge, -430 ; (5) isolated imine, $+43$; (6) α -diimine, $+170$. The extent to which an observed $E_{1/2}$ reflects the sum of these contributions is shown in Figure 4. The best straight line through the data set has a calculated slope of 0.92 ± 0.037 , an intercept of $+0.06 \pm 0.036$, and a correlation coefficient of 0.984 ± 0.036 . For the series of macrocyclic complexes containing charge delocalized chelate rings, an increase in ring size does not affect the redox potential. This causes a sharp discontinuity from the linear relationship of Figure 4. This clearly

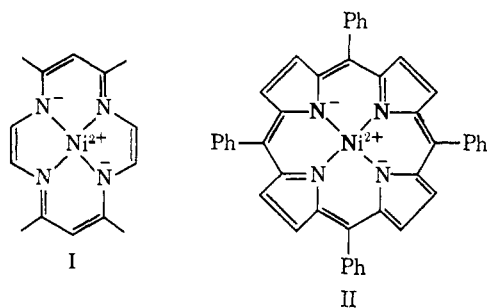
indicates the common structural feature which governs the redox behavior for this family of complexes, namely the metal ion in combination with the two six-membered, charged chelate rings. Apparently the nature and size of the remaining chelate rings are of far less importance.

Experimentally obtained redox data are able to be interpreted more clearly in view of the additive potential concept. For example, the $\text{Ni}^{\text{II}}(\text{Me}_6[14]\text{janeN}_4)^{2+}$ oxidation potential occurs at +0.87 V, virtually identical with the value of +0.86 V obtained for $\text{Ni}^{\text{II}}(\text{Me}_2[14]1,3\text{-dieneN}_4)^{2+}$. One might conclude from this that the presence of an α -diimine has no additional effect on the ease of formation of Ni(III). However, if the effect of the axial methyl groups in the six-membered chelate rings of $\text{Me}_6[14]\text{janeN}_4^{24}$ is quantitatively considered through the use of the above data, the "adjusted" half-wave potential for this complex becomes +0.69 V and the influence of the α -diimine bond is clearly seen. Similar arguments apply to the complexes of $\text{Me}_4[14]1,3,8,10\text{-tetraeneN}_4$ and $\text{Me}_6[14]1,4,8,11\text{-tetraeneN}_4$, which have oxidation potentials of +1.00 and +1.05 V, respectively. Thus, by the use of the data above, one is able to standardize observed potential values, enabling more meaningful comparisons to be made.

It is of some significance to assess the generality of additive half-wave potentials for other metal ions and different ligand systems. In a related series of iron complexes of macrocycles recently reported,¹ if the reversible half-wave potential for the $\text{Fe}(\text{II}) \rightleftharpoons \text{Fe}(\text{III})$ process is evaluated in the same fashion as the nickel complexes discussed here, the average values of structural contributions can be estimated. In addition,

	$\Delta E_{1/2}$, mV	
	Fe(II)/ Fe(III)	Ni(II)/ Ni(III)
Axial methyl groups	+110	+183
Isolated imine	+49	+43
α -Diimine	+304	+170

comparison of the ligands $\text{Me}_6[14]\text{janeN}_4$ and $\text{Me}_2[14]\text{aneN}_4$ for the $\text{Co}(\text{II}) \rightleftharpoons \text{Co}(\text{III})$ and $\text{Cu}(\text{II}) \rightleftharpoons \text{Cu}(\text{III})$ redox processes yields $\Delta E_{1/2}$'s of 170 and 160 mV, respectively.⁴⁰ Thus for the limited data available, the general idea of additive structural contributions to account for observed redox potentials appears to be valid. The presence of an α -diimine appears to stabilize Fe(II) to a larger degree than Ni(II). This is consistent with the synthetic observations for the two different metal ions with similar ligands. For example, $\text{Fe}^{\text{II}}(\text{Me}_6[14]\text{janeN}_4)$ and $\text{Fe}^{\text{II}}(\text{Me}_6[14]4,11\text{-dieneN}_4)$ react in solution with molecular oxygen to yield structures which ultimately contain α -diimine groups.¹ Similar reactions with nickel derivatives produce complexes containing only isolated imines.² The few other instances where comparison is possible, namely, for the tetraphenyl porphyrin complexes of Ni(II) (structure II) and for $[\text{Ni}^{\text{II}}(\text{Me}_4[14]2,4,6,9,11,13\text{-hexeneN}_4)]^0$ (structure I), show that^{41,42} redox reactions of these complexes do not produce stable changes in the oxidation state of the coordinated metal ion. Consider, for example, the first oxidation process for the complex of structure I. By our empirical calculations we estimate



its potential to be +0.24 V, which is not very close to the observed value of -0.20 V. However, it is significant in this case, that the initial oxidation product is not an authentic Ni(III) complex but is a Ni^{II} stabilized cation radical. Clearly, this radical is stabilized by the presence of an extensive π -electron system and this probably accounts for the more cathodic potential experimentally observed. The redox reactions of nickel complexes containing porphyrin ligands proceed in much the same fashion. $(\text{Ni}^{\text{II}}\text{TPP}^{2-})^0$, for example, is ultimately oxidized to a π -cation radical. In our attempts to rationalize the redox behavior of this complex, we would therefore expect to overestimate the value of its first oxidation potential. Surprisingly then, our calculated value for $E_{1/2}$ (+0.76 V) is rather close to the observed value of +0.70 V. In addition to this $\text{Ni}^{\text{II}}(\text{TPP}^{2-})$ readily displays reversible electrochemical reductions in direct contrast to structure I and the compounds numbered 23 through 26 in Figure 1. We feel that these factors can be attributed to the aromatic π -electron system of the porphyrin ligand. Such aromaticity should impart an increased stability toward oxidation. Similar electrochemical results have been obtained^{43,44} for the metal complexes of the aromatic ligand system, TAAB^{2-} , as well as for the aromatic organic dianions of substituted azocines.⁴⁵ The reduction behavior of $\text{Ni}^{\text{II}}(\text{TPP}^{2-})$ can be understood in terms of the theoretical calculations of Zerner and Gouterman.⁴⁶ According to these authors, the energy of the unoccupied ligand, e_g (π) orbital of $\text{Ni}(\text{TPP}^{2-})$, is lower than that of the metal ion $d_{x^2-y^2}$ level and would be a ready receptacle for added electron density. This is substantiated by the free radical epr spectrum obtained⁴¹ for the one-electron reduction product of $\text{Ni}^{\text{II}}(\text{TPP}^{2-})$, implying a ligand based orbital for the odd electron. For the similarly charged macrocycles, $\text{Ni}^{\text{II}}(\text{tetraeno}^{2-})$, which do not contain such an aromatic π -bonding network, the π -antibonding ligand orbital is not so low in energy, and, consequently, no reductions are observed in acetonitrile solutions of these complexes. Since the nickel complex of structure I is reported to contain an aromatic ligand, its redox reactions should be similar to those of $\text{Ni}^{\text{II}}(\text{TPP}^{2-})$. Indeed it does undergo reduction very easily in acetonitrile. Surprisingly, however, it does not oxidize further, despite a considerable amount of available anodic potential range.

Electrochemical Data and the Control of Chemical Reactions. With a knowledge of the factors which con-

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tol chemical properties, such as redox potentials, one could envision that through the use of proper synthetic design a chemical environment could be provided for a complex which would enable it to possess the proper reactivity for the performance of a desired chemical function. Consider, for example, the well-known process of reversible oxygenation exhibited by hemoglobin,⁴⁷ vitamin B_{12r},⁴⁸ and a number of synthetic chelate complexes.⁴⁹ In all of the oxygen adducts of these complexes, it is necessary for the metal ion to coordinate to the oxygen molecule without being irreversibly oxidized by it. The way in which this requirement is met is discussed by Wang, Nakahara, and Fleischer in the case of hemoglobin⁴⁷ and by Vogt, Faigenbaum, and Weiberly for the synthetic chelates.⁴⁹ According to Wang, the hydrophobic groups of the protein in hemoglobin provide a medium of low dielectric in the vicinity of the heme iron-oxygen bond. This immeasurably retards the process of charge separation which would be required for oxidation of the heme iron. For the structurally simpler synthetic chelates, this should not be the major consideration for oxidative stability. As Vogt, *et al.*, point out,⁴⁹ the oxidation potentials of the metal ions in these complexes must have a certain value to prevent their irreversible oxidation by molecular oxygen. He further suggests that these oxidation potentials can be "adjusted by chelation with the proper ligands." The synthetic macrocycles may eventually provide a thorough test for these hypotheses.

In a broader chemical sense, it is useful to summarize how the nature of the redox products described here can serve as guidelines for establishing general criteria of chemical reactivity. For example, in ligand oxidative dehydrogenation reactions of macrocyclic complexes, it is generally recognized that reactive intermediates involve higher oxidation states of the coordinated metal ion.^{2,3,5} The Ni(III) complexes reported here represent intermediates of this class. For complexes involving neutral ligands, the coordination of solvent to Ni(III) has been shown by esr measurements. For charge-delocalized ligands, the Ni(III) complexes are square planar. This suggests that oxidative dehydrogenations of neutral coordinated ligands may require the use of at least moderately coordinating solvents, whereas the corresponding reactions for charge delocalized ligands may proceed smoothly in their absence. The different possible reaction pathways for the lower valent complexes may also provide a basis for general chemical classification. For the metal ion promoted ligand hydrogenation reactions mentioned earlier, an organic electrochemistry parallel can be found in the reduction behavior of a large number of Schiff bases reported by Lund⁵⁰ and Scott and Jira.⁵¹ These authors found that simple one electron reductions to radical anions occurred in dimethylformamide whereas in an alcohol-water medium the parent molecules were hydrogenated to the corresponding amines. Although this type of electrochemistry is

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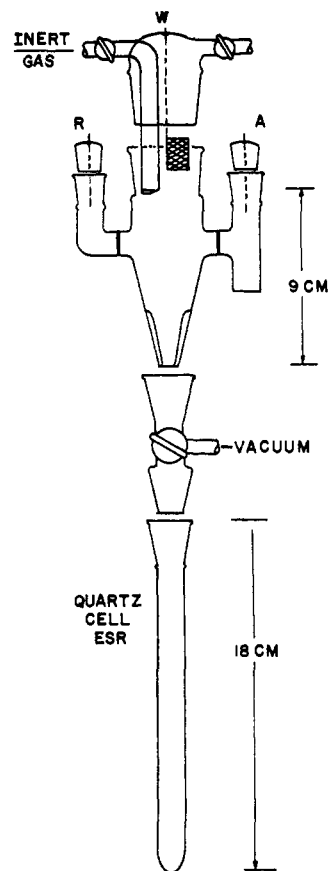


Figure 5. Electrolysis cell for combined coulometry-esr studies: A = auxiliary electrode; W = working electrode; R = reference electrode.

well documented for organic molecules, it is comparatively rare for transition metal complexes. Further, the metal complex has an added dimension of chemical reactivity, since the unpaired electron in the reduced complex can be localized in an orbital of the coordinated metal ion. In this case the substitution lability of the metal center may be altered. An important example of the latter is the formation of metal-alkyl bonds in macrocyclic complexes of cobalt.⁶⁻⁹ The reaction preferences of these lower valent complexes may become clearer when a greater number of metal ions are considered. For example, the first reduction process of Ni^{II}(Me₄[14]1,3,8,10-tetraeneN₄)²⁺ and Fe^{II}(Me₆[14]1,3,8,10-tetraeneN₄)²⁺ occurs at approximately the same potential (*ca.* -0.8 V) in acetonitrile solution.^{1,18} ESR evidence presented earlier shows that the correct formulation for Ni(Me₄[14]1,3,8,10-tetraeneN₄)⁺ is Ni^{II}-(Me₄[14]1,3,8,10-tetraeneN₄)⁻. Similar esr evidence shows⁵² that Fe(Me₆[14]1,3,8,10-tetraeneN₄)⁺ should be formulated as Fe^I(Me₆[14]1,3,8,10-tetraeneN₄)⁺. It would be predicted on this basis that the tetraene ligand should hydrogenate more easily when it is coordinated to nickel.

Experimental Section

The apparatus used for the electrochemical measurements was identical with that previously described.¹⁴ Pretreatment of the platinum electrode began with oxidation of the platinum surface for 15-16 sec. Either K₂Cr₂O₇-H₂SO₄ cleaning solution or hot concentrated HNO₃ was used for this purpose. The electrode was

(52) M. C. Rakowski and D. H. Busch, unpublished results.

then chemically reduced by immersion in a concentrated solution of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. This was followed by rinsings with distilled water and acetonitrile. The electrode was then immediately transferred to the drybox and ready for use. Current-potential curves on electrodes which were treated in this manner showed very low background current from +2.5 to -3.0 V.

A three-compartment cell was designed so that controlled potential electrolysis could be carried out on a sample in approximately 5 min. The central compartment contained a perforated platinum-foil working electrode, the auxiliary compartment a coiled platinum wire. The reference electrode used was a chloride-coated silver wire. This electrode was found to have a potential of +0.30 V vs. $\text{Ag}|\text{Ag}^+$ (0.1 M). Although this electrode showed no sensible deviation from this value over typical time periods of weeks, the precise potential needed for electrolyzing a particular complex was determined by recording its CV each time, immediately prior to electrolysis.

Coulometric n values were determined by electronically integrating the current-time curves obtained during a controlled potential electrolysis.

Spectroquality acetonitrile, obtained from Eastman Kodak, was purified by passing the degassed liquid through freshly activated alumina as previously described¹⁴ and in some cases by distillation over P_2O_5 and CaH_2 . No difference in electrochemical behavior was found in solvents prepared by the two different methods. In each case, further removal of oxygen was accomplished by repeated vacuum line pumping on solidified solvent. Tetra-*n*-butylammonium tetrafluoroborate and tetraethylammonium perchlorate, obtained from Southwestern Analytical, were used as supporting electrolytes. Removal of water from tetraethylammonium perchlorate was accomplished as previously described. The tetra-*n*-butylammonium tetrafluoroborate salt was heated *in vacuo* at 80° for 48 hr prior to use. Again, no difference in electrochemical behavior for the complexes was observed with the two different supporting electrolytes.

Procedure for Combined Controlled Potential Coulometry-Esr Measurements. A precise quantity of complex was weighed out and diluted to volume in a 10-ml volumetric flask. Five milliliters of this solution was transferred to the central compartment of the coulometric cell (Figure 5) and a cyclic voltammogram of the starting material was recorded under N_2 . Highly prepurified nitrogen was then purged into the central compartment and served as a stirring mechanism during the electrolysis. Alternatively, the entire electrolysis could be carried out in a Vacuum Atmospheres Dri-Lab. Both of these procedures were used. Some of the Ni(I) species were also conveniently generated by reduction of the corresponding Ni(II) complexes with sodium amalgam. After the electrolysis of a particular complex was complete, a portion of the coulometrically analyzed sample was transferred in the absence of oxygen to an esr cell. The contents of the esr cell were immediately solidified at liquid nitrogen temperature, and the esr spectrum was recorded.

The esr spectra were recorded on a Varian V-4500 spectrometer operating at 9500 MHz and equipped with a dual cavity. A small sample of DPPH was placed in the reference cavity. Two spectra were recorded for each sample, the field being swept in opposite directions and the average of the g values taken. The g values were calculated by the approximate method of Kneubühl.⁵³ The g_{\parallel} values are accurate to ± 0.005 and the g_{\perp} values to ± 0.01 . The sample tube was placed in a small dewar flask filled with liquid N_2 and designed so that it would fit in the sample cavity of the esr spectrometer.

Acknowledgment. These investigations were supported in part by U. S. Public Health Service Grant GM 10040 from the National Institute of General Medical Sciences and by the National Science Foundation.

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Lanthanide Nitrate Complexes of Some Macrocyclic Polyethers¹

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Abstract: The macrocyclic polyether benzo-15-crown-5 reacts with the hydrated lanthanide(III) nitrates in acetone solution to form complexes of the type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ ($\text{Ln} = \text{La, Ce, Pr, Nd, and Sm}$) with the lighter (*i.e.*, larger) lanthanides and of the type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ ($\text{Ln} = \text{Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu}$) with the heavier (*i.e.*, smaller) lanthanides. The macrocyclic polyether dibenzo-18-crown-6 forms similar complexes of the type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$ ($\text{Ln} = \text{La, Ce, Pr, and Nd}$) in acetonitrile solution with the lighter lanthanides but fails to form stoichiometric complexes under these conditions with the heavier lanthanides. The following three principles seem to determine the lanthanide(III) nitrate coordination chemistry of these macrocyclic polyethers: (a) dibenzo-18-crown-6 forms less stable lanthanide(III) nitrate complexes than benzo-15-crown-5; (b) the thermal stabilities of the unsolvated macrocyclic polyether complexes of the lanthanide(III) nitrates decrease upon increasing atomic number of the lanthanide; (c) the tendencies of the metal ions in the macrocyclic polyether complexes of the lanthanide(III) nitrates to complex with other ligands such as water and acetone increase upon increasing atomic number of the lanthanide. The isotropic nmr shifts of the coordinated macrocyclic polyether and water protons arising from the lanthanides in the complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ ($\text{Ln} = \text{Sm, Eu, Tm, and Yb}$) correlate well with previous observations on tris(dipivaloylmethanato) lanthanide paramagnetic shift reagents. Partial separation of erbium and praseodymium by chromatography of the mixed nitrates on a column of dibenzo-18-crown-6 has been demonstrated.

The use of macrocyclic polyethers as a class of complexing agents has been investigated extensively during the past several years.^{3,4} This class of com-

plexing agents has exhibited potential significance not only in coordination chemistry but also in biological

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