ΔH_C and ΔH_B for the various donors (1.4 kcal mol^{-1}) could be ascertained.

An immediate application of the procedure outlined above is to predict the enthalpy of adduct formation of bis(hexafluoroacetylacetonato)copper(II) with trimethylamine *N*-oxide in carbon tetrachloride. According to Table II, the reported value in *o*-dichlorobenzene should be corrected by

$$\Delta H[\mathrm{Cu(hfac)_2 \cdot base}]_{\mathrm{CCl_4}} = \Delta H[\mathrm{Cu(hfac)_2 \cdot base}]_{o\text{-}\mathrm{Cl_2C_6H_4}} - 1.4 \text{ kcal mol}^{-1} \quad (5)$$

producing a value of -12.8 kcal mol^{-1}.

It is of interest to consider what approach could be taken for a system in which no adduct could be found that is soluble in CCl_4 or C_6H_{12}. Thus, although a solvation-free displacement reaction could be obtained, one could not find a solvation-minimized adduct formation reaction for any donor which could be subtracted to give the result for B′. A reliable spectroscopic method could be developed for estimating enthalpies from frequency shifts of donors (for example, the $-\Delta H$ *vs.* $\Delta\nu_{CO}$ relation[11] for ethyl acetate), and a CCl_4 equivalent enthalpy could be estimated from the frequency shift of the adduct (one would have to show that $\Delta\nu_{CO}$ was independent of the solvent employed). We should consider the eventuality that the enthalpy predicted from a spectroscopic correlation of the above type is in error. This introduces a constant error in all of the enthalpy values for this acid which would lead to incorrect E_A and C_A numbers for the acid. However, all the other base parameters in the correlation could predict enthalpies which are also off by approximately this constant amount. Thus, conclusions regarding trends in the importance of the base properties which influence the interaction would be valid. Clearly, other base displacement reactions in polar solvents could also be correctly predicted.

Acknowledgment.—Generous support of this research by the National Science Foundation through Grant NSF 2554 and through the Paint Research Institute is appreciated.

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[11] D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, **90**, 5706 (1968).

CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Synthesis, Properties, and Electrochemical Studies of a Series of Nickel(II) Complexes with Related Macrocyclic Ligands of Varied Unsaturation

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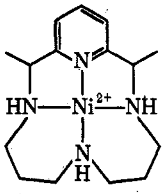
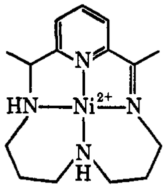
A complete series of nickel(II) complexes has been produced wherein a macrocyclic ligand containing four nitrogen donors varies stepwise from one unsaturated and three saturated donors through four unsaturated donors. The ligands are all derivatives obtained formally by hydrogenation or oxidative dehydrogenation of 2,12-dimethyl-1,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR). Complexes of the parent ligand and the fully reduced ligand (CR + 4H) have been studied earlier. The monoene derivative $Ni(CR + 2H)^{2+}$ was prepared both by reduction of $Ni(CR)^{2+}$ and by aerial oxidation of $Ni(CR + 4H)^{2+}$. $Ni(CR - 2H)^{2+}$ was obtained by chemical oxidation of $Ni(CR)^{2+}$. The electrochemical behavior of the entire series of complexes has been studied using both acetonitrile and methanol as solvents. A spectrum of oxidation states was obtained, ranging (formally) from 3+ to 1+ and zero, depending on the ligand. The effect of ligand unsaturation on the ease of electrochemical reduction and oxidation was most clearly seen in acetonitrile where simple reversible electron-transfer reactions prevailed. In methanol, electrochemical reductions were accompanied by hydrogenation processes. Here, for each complex, the total number of electrons involved in reduction was exactly enough to hydrogenate the imine functions present in the macrocyclic ring structure as well as to produce the same final product containing univalent nickel.

Introduction

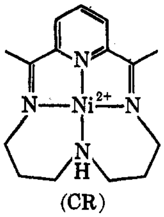
As part of the short-range goals of our broad research program on the metal complexes of the new synthetic macrocyclic ligands, we are particularly concerned with developing and studying systems within which systematic variations in electronic structure can be produced. The complexes derived from condensation of 2,6-diacetylpyridine with γ,γ'-diaminodipropylamine in the presence of nickel(II) have provided a useful early example. Structures I–IV show the variation obtained in the ligands and permit easy establishment of a very simple system of abbreviations. Since its discovery by Curry[1] the complex of structure III has come to be known as $Ni(CR)^{2+}$. It is the parent of the series of complexes and the other three are derivatives produced from it by oxidation or reduction.



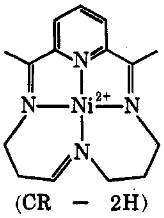
(CR + 4H)
I



(CR + 2H)
II



(CR)
III



(CR − 2H)
IV

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[1] J. D. Curry, Ph.D. Dissertation, The Ohio State University, 1964.

Karn and Busch[2] first produced $Ni(CR + 4H)^{2+}$ by catalytic hydrogenation of $Ni(CR)^{2+}$. The substance exists in isomeric meso and racemic forms as a result of the presence of two asymmetric carbon atoms in the ligand. These were separated and identified and the structural assignments were confirmed by an X-ray crystal structure determination.[3] The meso isomer is much more abundant than the racemate so that our studies have generally been confined to the meso form. An additional isomerism due to the configuration of the symmetrically located secondary amine of $Ni(CR + 4H)^{2+}$ has recently been detected and explained.[4]

We now report synthesis and characterization of the two remaining members of the series $Ni(CR + 2H)^{2+}$, structure II, and $Ni(CR - 2H)^{2+}$, structure IV. Detailed electrochemical studies have been made on the series of complexes.

Results and Discussion

Synthesis and Characterization of the New Complexes.—The reaction of $Ni(CR)(ClO_4)_2$ with concentrated nitric acid produces a red-orange solution from which a dark red compound can be isolated. A portion of the infrared spectrum for this compound is shown in Figure 1a. Comparison of the infrared spectrum of the product with that for $Ni(CR)(ClO_4)_2$, Figure 1b, reveals an obvious difference in the presence of the sharp absorption at 1656 cm^{-1} which is normally associated with an unconjugated imine. In addition there are no absorptions above 3000 cm^{-1} for NH stretching vibrations. This suggests that an additional imine function has been introduced into the complex at the nitrogen atom opposite the pyridine ring (structure IV). Evidence for the presence of the required vinylic CH stretching absorption in the infrared spectrum is obscured by absorptions arising from the pyridine ring hydrogens. However, comparison of the nmr spectrum in the aromatic proton region of $Ni(CR)^{2+}$ with that of the new compound $Ni(CR - 2H)^{2+}$ permits the assignment of a triplet at 8.16 ppm (corresponding to one proton) in the spectrum of $Ni(CR - 2H)^{2+}$ to the vinylic hydrogen and confirms the gross structure of the complex. In addition, the methyl resonance appears as a doublet at 2.62 ppm. This is consistent with the introduction of the new imine since this causes one side of the molecule to be different from the other.

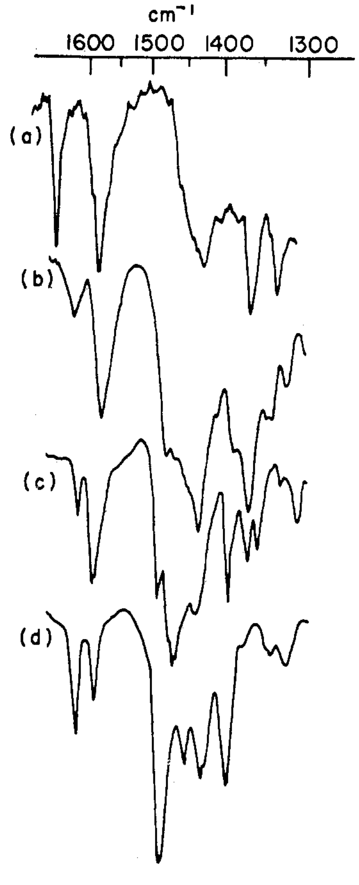

Figure 1.—Infrared spectral bands obtained on Nujol mulls of the perchlorate salts of (a) $Ni(CR - 2H)^{2+}$, (b) $Ni(CR)^{2+}$, (c) $Ni(CR + 2H)^{2+}$, and (d) α-*meso*-$Ni(CR + 4H)^{2+}$.

In early observations,[5] we found that recrystallization of *meso*-$Ni(CR + 4H)(ClO_4)_2$ from hot water produced an impure product which contained a new intense band in the absorption spectrum at 365 mμ. Subsequently it was established that heating an aqueous solution of α-*meso*-$Ni(CR + 4H)^{2+}$ for a number of hours while bubbling air through the solution results in a 6–8% conversion to a new complex. The reaction of $Ni(CR)(ClO_4)_2$ with 0.25 mol of BH_4^- results in a 30–35% yield of a complex having infrared, visible, and nmr spectra identical with those observed for the complex obtained by the aerial oxidation of $Ni(CR + 4H)^{2+}$. A portion of the infrared spectrum for this complex, $[Ni(CR + 2H)](ClO_4)_2$, is shown in Figure 1c.

Although the differences in infrared spectra for $Ni(CR)(ClO_4)_2$, $Ni(CR + 2H)(ClO_4)_2$, and α-*meso*-$Ni(CR + 4H)(ClO_4)_2$ are rather subtle, the relative intensities of the bands at 1610 and 1570 cm^{-1} indicate the presence of increasing unsaturation in that order if the 1570-cm^{-1} band contains the C=N stretching absorption.[2] That is, the intensity of the 1570-cm^{-1} absorption decreases in the order $Ni(CR)^{2+} > Ni(CR + 2H)^{2+} >$ α-*meso*-$Ni(CR + 4H)^{2+}$, suggesting the presence in those complexes of two, one, and zero imine functions, respectively.

The nmr spectrum of $Ni(CR + 2H)^{2+}$ is quite conclusive. Two methyl resonances are present in 1:1 ratio in the spectrum of this monoimine derivative. One of these is a doublet centered at 1.74 ppm and the other a singlet at 2.07 ppm. The nmr spectrum for $Ni(CR)^{2+}$ contains a singlet at 2.07 ppm while the fully saturated complexes ($Ni(CR + 4H)^{2+}$) have doublets at about 1.7 ppm. Additionally, the three pyridine protons appear as an ABC pattern because of the unsymmetrical substitution on the aromatic ring, *i.e.*, one electron-withdrawing and one electron-donating group. This confirms the presence of both types of methyl groups in the new complex and establishes the structure of $Ni(CR + 2H)^{2+}$ as that shown in II.

Oxidative dehydrogenations of the type described here are still unusual although they will no doubt become more common as a means of introducing un-

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[2] (a) J. L. Karn, Ph.D. Dissertation, The Ohio State University, 1966; (b) J. L. Karn and D. H. Busch, *Inorg. Chem.*, **8**, 1149 (1969).

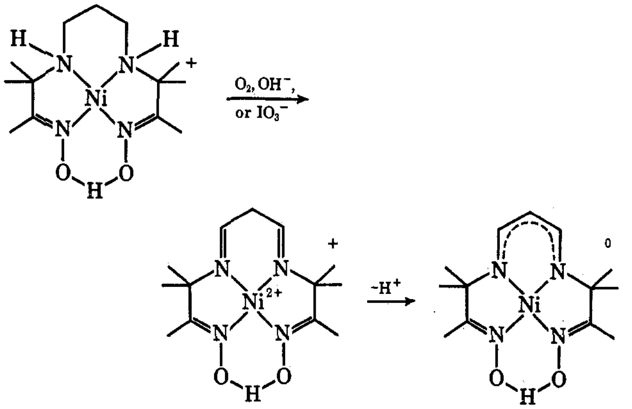
[3] E. B. Fleischer and R. Dewar, *Nature (London)*, **222**, 372 (1969).

[4] E. Ochiai and D. H. Busch, *Inorg. Chem.*, **8**, 1798 (1969).

[5] E. Ochiai and D. H. Busch, unpublished results.

saturation in a variety of complexes containing secondary amine donor atoms. The known examples have recently been summarized.[6] In no case has carbon–carbon unsaturation been produced directly. In one example oxidation followed by ionization effectively produces C–C unsaturation (Scheme I).[7] In other cases[6,8,9] chemical oxidations have invariably produced unsaturation at secondary amine sites. Attempts to produce unsaturation in the ligands studied here beyond that of structure IV produced total destruction of the complex.

SCHEME I



The new complex $Ni(CR + 2H)^{2+}$ has two predominant bands in the visible region of its spectrum. These occur at 450 mμ (ε 320) and 365 mμ (ε 2240). The band at 450 mμ is probably some combination of the three transitions theoretically expected for planar species with some borrowing in intensity from the higher energy absorption. The 365-mμ absorption must be due to a charge-transfer process or perhaps to a low-energy ligand transition as the extinction coefficient of >2000 rules out a predominantly d–d transition. Karn[2] and Ochiai[5] both observed an equilibrium between four- and six-coordinate species for *α-meso*-$Ni(CR + 4H)^{2+}$ in aqueous solution. Ochiai found[5] that the percentage of triplet species varied with the solvent (acetonitrile > water > methanol > acetone). However, no solid-state solvates have been obtained. On the other hand, $Ni(CR)^{2+}$ is fully six-coordinate in water and other coordinating solvents and a six-coordinate diaquo species can be isolated. Although $Ni(CR + 2H)^{2+}$ appeared to be planar in water, more concentrated solutions were examined to try to determine whether a low-energy triplet transition could be observed in aqueous solution. A new transition at about 710 mμ was observed for more concentrated solutions. Although singlet–triplet transitions are possible for d^8 planar complexes, they are rarely observed for nickel(II). To establish that this transition was, in fact, due to the presence of a triplet species, a spectrum was obtained in DMSO. In this solvent the intensity of an absorption at 725 mμ was found to be quite large and a new transition appeared at about 520 mμ with an intensity near that of the previously mentioned singlet–singlet transition at 450 mμ. This indicates a solvent dependence for the transition at about 700 mμ which is best explained by an increase in the amount of triplet species at the expense of the four-coordinate form. The observation of this low-energy triplet band, which varies in intensity with solvent, appears to place this complex in a systematic position in the series indicating the relative tendency to coordinate solvent: $Ni(CR + 4H)^{2+} < Ni(CR + 2H)^{2+} < Ni(CR)^{2+}$.

The electronic spectrum for $Ni(CR - 2H)^{2+}$ appears to be largely charge transfer in nature. In aqueous solution it consists of a shoulder at 415 mμ (ε 1110), a band at 390 mμ (ε 1450), and a shoulder at 310 mμ (ε 3380). The solid-state spectrum is essentially the same. No low-energy absorptions have been observed in spectra obtained on aqueous solutions of this complex. This indicates that the amount of triplet species present is small, if indeed any is present. This complex also does not coordinate other solvents, such as methanol, acetonitrile, and dimethylfornamide.

Electrochemical Results.—The different degrees of ligand unsaturation provided by the complexes $Ni(CR + 4H)^{2+}$, $Ni(CR + 2H)^{2+}$, $Ni(CR)^{2+}$, and $Ni(CR - 2H)^{2+}$ present an opportunity to examine systematically the redox behavior as a function of extent and arrangement of π-electron delocalization. Electrochemical measurements have been carried out on these complexes in acetonitrile and methanol at the rotating and stationary platinum wire and dropping mercury electrodes, respectively. For each polarographic wave an assignment of *n*, the number of electrons transferred in the electrode process, was made by comparing the observed diffusion current heights with those obtained from standard compounds whose *n* values have been determined coulometrically.[10] The electrode reaction was further characterized by values of peak potential separations, and anodic to cathodic peak current ratios measured from cyclic voltammetric curves. Representative current–potential curves are shown in Figures 2–4 and a summary of the results obtained is given in Table I.

All the complexes studied gave very well defined polarographic waves. In most instances a very small prewave was observed for the reduction cycle. This was attributed to an adsorption process. In fact, as the concentration of the complex was increased to about 10 m*M*, the ratio of the prewave height to the limiting current of the main reduction wave became insignificant, in accord with expectations for an adsorption process.[11]

The oxidation processes in acetonitrile are all reversible, or nearly so, and correspond in each case to the formation of a Ni(III) species. A typical current–potential curve for this process is shown in Figure 3. Trivalent nickel, although generally uncommon, is not unusual with macrocyclic ligands.[12-14] The ease of oxidation for this family of complexes is seen to decrease in a continuous fashion as the extent of ligand unsaturation increases. It was not possible to offer electrochemical–structure relationships in the earlier

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

(7) E. G. Vassian and R. K. Murmann, *ibid.*, **6**, 2043 (1967).

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

(9) J. Dabrowiak, V. L. Goedken, and D. H. Busch, unpublished results. We have extensive results on the oxidative dehydrogenation of iron complexes of macrocyclic ligands.

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

(11) J. Heyrovsky, "Principles of Polarography," Academic Press, New York, N. Y., 1966, p 289.

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

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

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

TABLE I

ELECTROCHEMICAL DATA FOR THE NICKEL(II) COMPLEXES[a]

Complex	Solvent[b]	Reduction $E_{1/2}$ (1)	$E_{1/2}$ (2)	$E_{1/2}$ (3)	Σn[c]	Oxidation $E_{1/2}$
$Ni(CR + 4H)^{2+}$	CH_3CN		−1.53 (1)		1	+0·89 (1)
$Ni(CR + 2H)^{2+}$	CH_3CN	−1.25 (1)	−1.88 (1)		2	+0·93 (1)
$Ni(CR)^{2+}$	CH_3CN	−0.96 (1)	−1.55 (1)		2	+1·03 (1)
$Ni(CR - 2H)^{2+}$	CH_3CN	−0.84 (1)	−1.45 (1)		2	+1·05 (1)
$Ni(CR + 4H)^{2+}$	CH_3OH			−1.15 (1)	1	. . .
$Ni(CR + 2H)^{2+}$	CH_3OH		−0.88 (2)	−1.16 (1)	3	. . .
$Ni(CR)^{2+}$	CH_3OH	−0.65 (1)	∼−0.92 (3)	−1.17 (1)	5	. . .
$Ni(CR - 2H)^{2+}$	CH_3OH	−0.52 (1)	∼−0.92 (?)[d]	−1.09 (?)[d]	7	. . .

[a] The ClO_4^- salts of the complexes were investigated; numbers in parentheses indicate the Δn value for the particular reduction process; [complex] = 5×10^{-4} *M* in methanol and at concentrations ranging from 1 to 3×10^{-3} *M* in acetonitrile; $E_{1/2}$ values in methanol reported *vs.* sce, in acetonitrile *vs.* the Ag–Ag$^+$ (0.1 *M*) reference electrode. [b] For both solvents, the electrolyte is 0.05 *M* Et_4NClO_4. [c] The total number of electrons was determined from the height of the diffusion current. [d] Maximum prevented exact wave analysis.

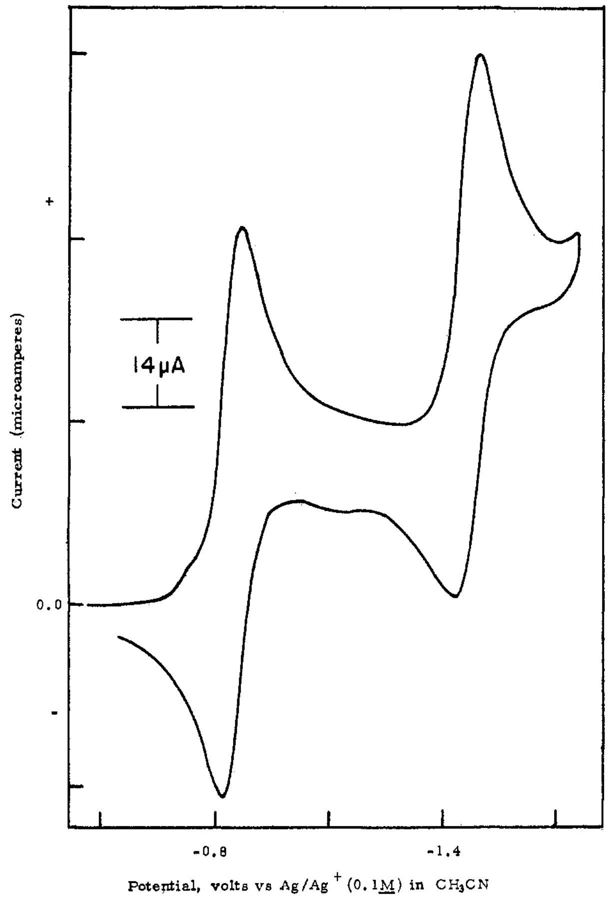


Figure 2.—Cyclic voltammetric reduction waves of 2.49×10^{-3} *M* $Ni(CR - 2H)^{2+}$ in acetonitrile solution at 25°, at a platinum wire electrode.

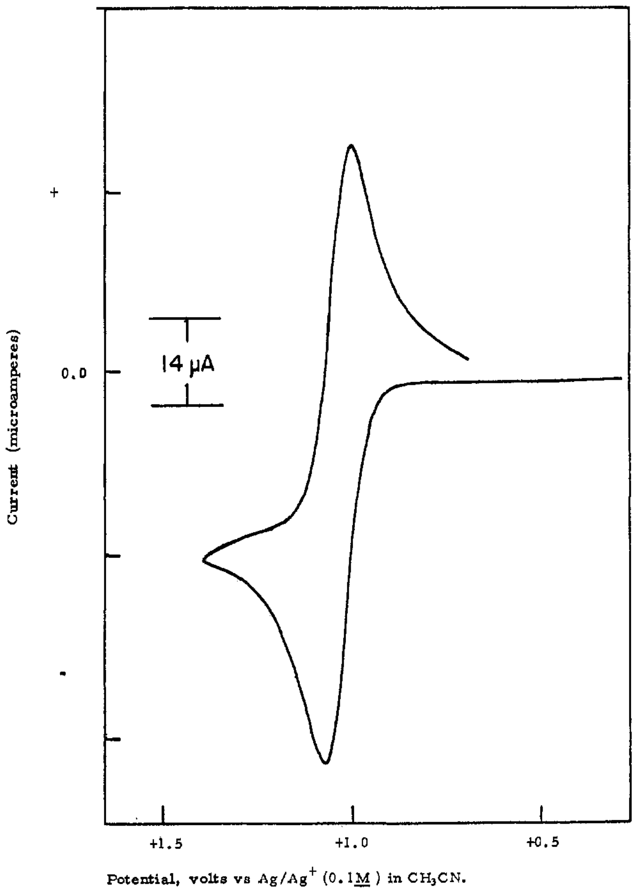
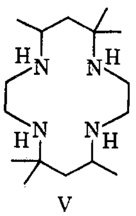
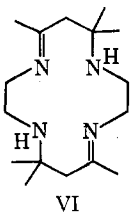


Figure 3.—Cyclic voltammetric oxidation wave of 2.73×10^{-3} *M* $Ni(CR)^{2+}$ in acetonitrile solution at 25°, at a platinum wire electrode.

work of Olson and Vasilevskis[13] on the NiL^{2+}–NiL^{3+} couple (where L equals the fully reduced and the trans-diene Curtis ligands, 1,7-CTH (V) and 1,7-CT (VI), respectively) because of the reported irreversible nature of the $Ni(CT)^{2+}$ oxidation. Further work involving these and ligands having variable modes and greater degrees of unsaturation is being carried out in this laboratory in an effort to clarify further the influence of such effects on the observed redox behavior of complexes.



V



VI

The electrochemical reductions of the complexes of structures I–IV show a marked and chemically interesting solvent dependence as well as a number of meaningful variations in behavior with structure. The results obtained on acetonitrile solutions will be considered first (Table I). The simplest redox pattern is shown by $Ni(CR + 4H)^{2+}$, which undergoes only a single, nearly reversible, one-electron transfer ($\Delta E = E_p - E_a = 80$ mV) at $E_{1/2} = -1.53$ V in CH_3CN. It is not certain here whether the added electron is local-

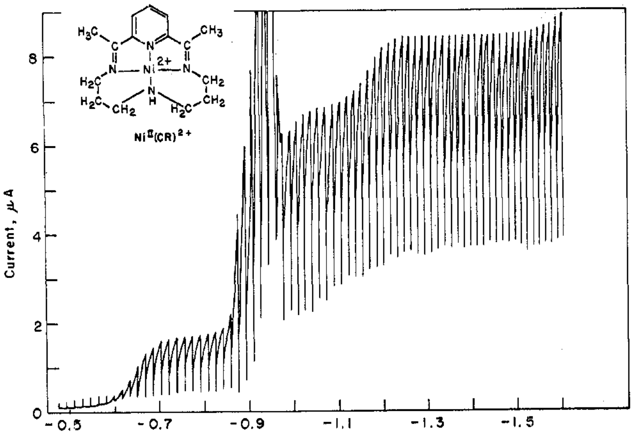


Figure 4.—The polarogram of 5 × 10^{-4} *M* $Ni(CR)^{2+}$ in methanol solution at 25°, at the dme.

ized on the metal or is delocalized mainly, or partly, on the ligand. The observed half-wave potential, however, is similar to that of the $Ni(CTH)^{2+} \rightarrow Ni(CTH)^+$ reduction.[13]

The more unsaturated derivatives of the series each display two one-electron reductions in acetonitrile producing as a final product a formally zerovalent nickel complex (*e.g.*, Figure 2). The first electron addition to $Ni(CR + 2H)^{2+}$ and both addition steps for $Ni(CR)^{2+}$ and $Ni(CR - 2H)^{2+}$ are electrochemically reversible. Multiple-sweep cyclic voltammograms, over moderate scan rates, were identical with those curves obtained from the first-sweep cycle, verifying the simplicity and overall chemical reversibility of the electrode processes involved. The second electron-transfer step for $Ni(CR + 2H)^{2+}$ appears irreversible by cyclic voltammetry. Though we make no claims for the vigor of the assignments, it is helpful to think of the first electron addition as occurring mainly on the delocalized ligand system while the second is more nearly a metal ion reduction.

The polarographic results obtained in methanol are grouped in Table I according to the type of process that has been assigned to the waves. These polarographic results indicate that the first reduction, $E_{1/2}(1)$ for $Ni(CR + 4H)^{2+}$, $Ni(CR)^{2+}$, and $Ni(CR - 2H)^{2+}$, is a one-electron process, while $Ni(CR + 2H)^{2+}$ intially undergoes a two-electron reduction at the dropping mercury electrode ($E_{1/2}(2)$). Cyclic voltammetry at the hanging mercury drop electrode shows that the (one-electron) reduction for the complexes $Ni(CR + 4H)^{2+}$, $Ni(CR)^{2+}$, and $Ni(CR - 2H)^{2+}$ is almost totally nernstian with peak potential separations of 75, 70, and 60 mV, respectively. Complete analysis of the reduction wave for the $Ni(CR + 2H)^{2+}$ complex at the dme has not been possible, due to the presence of a persistent maximum in the rising portions of the polarographic wave. This also results in ill-defined shapes for the stationary-electrode curves.

Upon further cathodic polarization, the complexes show richer electrochemical activities than those observed in acetonitrile (Table I). The most highly unsaturated derivatives display multiple-electron additions ($E_{1/2}(2)$, Table I), followed by simpler one-electron transfers ($E_{1/2}(3)$, Table I). It appears that with each complex, the end product obtained is the species $Ni^I(CR + 4H)^+$. In conjunction with this, it is suggested that, in methanol, the process associated with $E_{1/2}(2)$ in Table I for each complex involves hydrogenation of the double bonds present in the macrocyclic ring structure. Several observations support this idea. First, the potentials for the last one-electron reduction process ($E_{1/2}(3)$) are relatively constant throughout the entire series of complexes. This wave has been assigned to the reduction Ni(II) → Ni(I) and is presumed to be superimposed on the reduction of all the azomethine linkages of each ligand. Second, the total number of electrons involved in the reduction of each complex corresponds to the amount needed to hydrogenate the ring double bonds as well as yield an end product containing formally univalent nickel.

With $Ni(CR + 2H)^{2+}$, presumably the electron density is sufficiently localized on the azomethine function to favor energetically an initial overall two-electron reduction accompanied by protonation, *i.e.*, hydrogenation of the azomethine linkage. This is not the case with the $Ni(CR)^{2+}$ and $Ni(CR - 2H)^{2+}$ whose initial one-electron reduction products are stable enough to give separate polarographic waves. It is probably significant that the stabilization of the first one-electron reduction product occurs for the systems having the most extensive delocalized π-electron systems.

The absence of such complicated electrode behavior in the more aprotic acetonitrile solvent is consistent with the hydrogenation mechanism proposed. Also noteworthy is the fact that, in acetonitrile, a comparison of the reversible electrode sequences of $Ni(CR)^{2+}$ and $Ni(CR - 2H)^{2+}$ shows that the change in the values of the first reduction potential parallels the corresponding change observed for the last reduction step. This reflects the continuing influence of the ligand unsaturation throughout the series of electrode processes, a result not obtained in methanol, as seen from the constancy of $E_{1/2}(3)$ in Table I.

The influence of the ligand unsaturation on the addition of the first electron to each complex is evident in both solvents, as seen by the similar trends observed for $E_{1/2}(1)$ in Table I. This result is particularly interesting in the case of $Ni(CR - 2H)^{2+}$, where the increased ease of reduction is apparently due to the presence of an imine which is not in conjugation with the other sites of unsaturation in the ring structure. This suggests that the effect of the isolated imine is transmitted through the metal ion and that the added electron density is delocalized throughout the molecular framework.

Experimental Section

Materials.—**2,6-Diacetylpyridine** was obtained from the Aldrich Chemical Co. and was used without further purification. Starting materials, α-*meso*-$Ni(CR + 4H)(ClO_4)_2$ and $Ni(CR)(ClO_4)_2$, were prepared by methods already reported.

2,12-Dimethyl-3,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,6,11,13,15-hexaenenickel(II) Perchlorate, $Ni(CR - 2H)(ClO_4)_2$.—The complex $Ni(CR)(ClO_4)_2$ was dissolved in a minimum amount of concentrated nitric acid to give a dark solution. Gentle warming on a steam bath for 3–5 min caused evolution of a brown gas and produced a red-orange solution. The solution was cooled by evaporation under a stream of air, and when the solution became a thick syrup, the addition of cold acetone caused crystallization of dark red crystals which were recrystallized from methanol–water mixed solvent. Yields were near quantitative. *Anal.* Calcd for $NiC_{15}H_{20}N_4(ClO_4)_2$: C, 35.02; H, 3.89; N, 10.90. Found: C, 35.50; H, 3.87; N, 10.95.

2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-

1(17),2,13,15-tetraenenickel(II) Perchlorate, Ni(CR + 2H)-(ClO_4)$_2$.—This complex was prepared in two ways: (1) by air oxidation of α-*meso*-Ni(CR + 4H)(ClO_4)$_2$ and (2) by partial chemical reduction of Ni(CR)(ClO_4)$_2$.

(1) α-*meso*-Ni(CR + 4H)(ClO_4)$_2$ (5 g) was dissolved in 250 ml of hot water. This solution was maintained at ~80° for 20 hr while bubbling air through it. The solution was then evaporated to dryness on a rotary evaporator and the solid was then fractionally crystallized from methanol. The last crop of material contained ~0.3 g of the desired product. This fraction was twice recrystallized from methanol. *Anal.* Calcd. for $NiC_{15}H_{24}N_4$(ClO_4)$_2$: C, 34.75; H, 4.63; N, 10.81. Found: C, 35.42; H, 4.72; N, 10.92.

(2) Ni(CR)(ClO_4)$_2$ (4 g) was dissolved in 50 ml of water at 65° and this solution was then treated with 80 mg of $NaBH_4$ mixed with 20 mg of borax and heated for 30 min. The reaction mixture was then neutralized with perchloric acid and evaporated to near dryness. The resulting oil was fractionally crystallized from methanol, the more soluble fraction being the desired one. The yield was 25%. The infrared and nmr spectra of this compound are identical with those of the complex obtained by aerial oxidation of Ni(CR + 4H)$^{2+}$.

Infrared spectra were obtained on Nujol mulls using a Perkin-Elmer 337 spectrophotometer. Nmr spectra were obtained on 10–15 wt % trifluoroacetic acid solutions using a Varian A-60 spectrometer. Chemical shift data are in ppm *vs.* internal TMS. Visible spectra were obtained on a Cary 14 spectrophotometer using 1-cm quartz cells. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Electrochemistry.—Conventional polarography and cyclic voltammetry were performed with an Indiana Instrument and Chemical Corp. Controlled-Potential and Derivative Voltammeter, Model ORNL-1988A. A Hewlett-Packard/Moseley Division X-Y recorder was used to obtain permanent records of current–potential curves.

Electrochemical measurements in acetonitrile were carried out in a Vacuum Atmospheres Dri-Train with a nitrogen atmosphere. Experimental runs were made using a three-compartment H-type polarographic cell. A silver wire immersed in a 0.1 *M* $AgNO_3$–CH_3CN solution was used as the reference electrode. A glass capillary extending into the working electrode compartment made possible optimum placement of the working electrode with respect to the reference electrode. This minimized the solution resistance observed for the cyclic voltammetric studies. The rotating platinum wire electrode used was driven by a 600-rpm synchronous motor (Welch Scientific Co.). A stationary platinum wire electrode, 20 gauge and approximately 6 mm in length, was used for the cyclic voltammetry studies. Pretreatment involved washing with solvent and preanodizing at a small positive potential. Excellent reproducibility was obtained for a series of polarograms on the same compound. The platinum surface was periodically tested for constancy with standard compounds.

For the studies in methanol, a thermostated cylindrical cell served as the polarographic vessel and was connected through a salt bridge to an aqueous sce reference electrode. Nitrogen used to deaerate the solutions was obtained from Burdett Oxygen Co. (99.96% pure) and further purified by passing through a column packed with activated BASF catalyst to remove trace oxygen and then through a column packed with molecular sieves (5 Å) to remove the last traces of water. The dropping mercury electrode employed had a value of $m^{2/3}t^{1/6} = 1.92$ mg$^{2/3}$ sec$^{-1/2}$ at an applied potential of 0.0 V *vs.* sce and a mercury column height of 50 cm.

Spectroquality acetonitrile was obtained from Matheson Coleman and Bell (Spectroquality AX145) and was further purified for electrochemical use by the method described by Kuwana.[15] Polarographic grade tetraethylammonium perchlorate was purchased from Southwestern Analytical, Inc., and dried over P_4O_{10} *in vacuo* for 1 week before use. Methanol (Baker AC) was used without further purification.

Polarographic measurements were made, using millimolar concentrations of complex dissolved in the appropriate solvent, with 0.05 *M* tetraethylammonium perchlorate as supporting electrolyte.

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Steric Effects in Chelation Kinetics. III. Reactions of Aquonickel(II) Ion with *N*-Alkyl-Substituted Ethylenediamines[1]

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The formation and dissociation rates for the reaction of aquonickel(II) ion with several *N*-alkyl-substituted ethylenediamines have been studied at 25° and 0.1 *M* ionic strength over a pH range of 5.8–7.6 using stopped-flow techniques. The ligands studied (in order of decreasing formation rate constants) were *N,N*-diethyl-, *N,N'*-diethyl-, *N,N,N',N'*-tetramethyl-, *N,N,N'*-triethyl-, and *N,N,N',N'*-tetraethylethylenediamine. Protonation constants of the ligands and stability constants of the 1:1 Ni(II) complexes were also determined under the above conditions. Large differences in the formation rate constants are attributed to three contributing factors: steric hindrance by the substituted alkyl groups, changes in ligand conformation influenced by the alkyl groups, and (in the case of the unprotonated species) internal conjugate base effects. For highly substituted ligands, a shift in the rate-determining step to the point of second bond formation is implied. Differences in dissociation rate constants are assigned to a decreasing rate of second bond re-formation with increasing *N*-alkyl substitution and the possibility of a slight increase in the rates of bond ruptures as a result of steric strain. The pronounced differences in kinetic reactivity exhibited by Ni(II) ion toward primary, secondary, and tertiary nitrogen donor atoms are correlated to the reaction mechanisms of larger multidentate ligands.

Introduction

In contrasting the kinetic behavior of unidentate and multidentate ligands, we have previously investigated the kinetics of Ni(II) ion reacting with ammonia[3] and with higher polyamines[4] in aqueous solution. Whereas the rate constant for the former reaction has

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