TABLE I

QUANTUM YIELDS FOR OXALATOAMMINECOBALT(III) COMPLEXES IN AQUEOUS SOLUTIONS AT 25°

Compound	Concn × 10^3, M	Excitation wavelength, mμ	Light quanta absorbed, einstein	Moles reacted	Quantum yield
$Co(NH_3)_5C_2O_4H^{2+}$	10.0	500	7.8×10^{-5}	0.21×10^{-6}	$\sim 0.8 \times 10^{-3}$
	10.0	313	2.1×10^{-6}	0.43×10^{-6}	0.21
	10.0	254	1.6×10^{-6}	0.60×10^{-6}	0.38
$Co(NH_3)_4C_2O_4^+$	9.1	508	9.9×10^{-5}	0.45×10^{-6}	$\sim 5 \times 10^{-3}$
	9.1	350	1.6×10^{-6}	0.60×10^{-6}	0.37
	9.1	254	1.8×10^{-6}	1.00×10^{-6}	0.56
$KCo(NH_3)_2(C_2O_4)_2$	3.6	558	1.5×10^{-4}	0.30×10^{-6}	$\sim 2 \times 10^{-3}$
	3.6	355	1.7×10^{-6}	0.88×10^{-6}	0.52
	3.6	254	1.9×10^{-6}	1.22×10^{-6}	0.64
$Co(NH_3)_4C_2O_4^+$	7.1	508	1.01×10^{-4}	0.24×10^{-6}	$\sim 2 \times 10^{-3}$
(in concentrated HCl)	7.1	355	1.44×10^{-6}	0.37×10^{-6}	0.25
	7.1	254	1.65×10^{-6}	0.62×10^{-6}	0.38

original ligands with formation of either cobalt(II) oxide–hydroxide precipitate or $CoCl_4^{2-}$ in concentrated HCl. Apparently, the oxalate group leaves as an anion radical (step 5) which in turn attacks another complex molecule setting the limiting quantum yield to 2 (step 6). An alternate competing possibility is the disproportionation of the $C_2O_4\cdot^-$ particle to CO_2 and $C_2O_4^{2-}$ (step 7).

As the number of sites coordinated by oxalate groups increases from 1 in $Co(NH_3)_5C_2O_4H^{2+}$ to 4 in $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$, the quantum yield obtained on uv excitation increases markedly (see Table I). This is apparently due to the lowering of the electron-transfer energy as well as an increase in the number of sites available for attack to the reactive $C_2O_4\cdot^-$ anion radical. The proposed mechanism takes into account the lower photosensitivity of $Co(NH_3)_5C_2O_4H^{2+}$ which has a monocoordinated acid oxalate group compared to $Co(NH_3)_4C_2O_4^+$ which has a doubly coordinated oxalate dianion. Thus, the easily ionizable proton in $Co(NH_3)_5C_2O_4H^{2+}$ (pH 2.5) undoubtedly acts as a scavenger for the $C_2O_4\cdot^-$ radical ion decreasing the quantum yield to about the same value as for $Co(NH_3)_4C_2O_4^+$ in concentrated HCl (Table I). No photoaquation reaction has been observed with any of the three complexes at any excitation wavelengths studied; the only reaction detected was photoredox decomposition.

In general, we found that all mixed oxalatoamminecobalt(III) complexes behave photochemically more like tris(oxalato)cobalt(III) than like ammine complexes of cobalt(III) in spite of the large number of NH_3 ligands present. However, the photoreactivity varies with the number of oxalate groups and coordination sites in a gradual manner.

CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY,
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Cyclic Amine Complexes of Nickel(I), -(II), and -(III). Electrochemistry, Preparation, and Properties[1]

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The electrochemistry, preparation, and properties of square-planar cyclic amine complexes of Ni(I), Ni(II), and Ni(III) are reported. The unipositive and tripositive oxidation states are unusual for nickel and have been described in only a few isolated cases in the literature. The polarographic behavior of square-planar complexes of two noncyclic amine ligands is included for comparison with the cyclic complexes.

Introduction

The synthesis and properties of square-planar transition metal complexes of some tetradentate macrocyclic amine ligands have been described previously. An extensive review of the subject has been published by Curtis.[2] These complexes are prepared by the condensation of aliphatic amines with ketones in the presence of certain transition metal salts. They are remarkably inert to dissociation which suggested that it might be possible to trap some of the more uncommon oxidation states of the transition metals by reduction or oxidation of the complexes containing the metals in their normal oxidation states. An investigation of the polarographic behavior of some of these complexes indicated that this was the case. This report deals with the electrochemistry, preparation, and properties of complexes containing nickel in the +1, +2, and +3 oxidation

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[1] Presented at the 135th National Meeting of the Electrochemical Society, New York, N. Y., 1969.

[2] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

states. The unipositive and tripositive oxidation states are unusual for nickel and have been reported in only a few isolated cases in the literature.[3,4] (See Figure 1 for the structures of the various ligands.)

Experimental Section

Apparatus.—A controlled-potential polarograph constructed following the circuit published by Durst, Ross, and Hume[5] and a Moseley 2D-2A X-Y recorder were used to obtain polarograms. A platinum wire served as the auxiliary electrode and an Ag–0.10 M $AgNO_3$ in acetonitrile electrode as the reference. The reference electrode was separated from the test solution by a porous Vycor plug and a Corning medium-sintered glass frit. The resistance between the reference and indicator electrodes was 3000 ohms. The dme characteristics of $m^{2/3}t^{1/6}$ were 1.49 at 0 V and 1.48 at −1.60 V. For cyclic voltammetry, a spherical platinum electrode approximately 0.05 cm in diameter was used as the indicating electrode. A scan rate of 90 mV/min was used with the dme and 1.0 V/min was used with the Pt indicating electrode unless otherwise specified. The polarographic cell was set up in a Vacuum Atmospheres Dri-Lab, where oxygen and moisture-sensitive compounds could be handled. The temperature of the cell was maintained at 25.0 ± 0.1°.

A potentiostat constructed in this laboratory was employed for controlled-potential electrolyses. The cell was a 125-ml Erlenmeyer flask with two side arms. One of the side arms contained the reference electrode separated from the cell solution by a Corning medium frit. The other side arm contained an inner and an outer compartment. The inner compartment was 2 cm in length and was separated from the cell solution by a Corning coarse frit and from the outer compartment by a Corning medium frit. The auxiliary electrode was placed in the outer compartment. This arrangement minimized mixing of the products formed at the working and auxiliary electrodes. A platinum foil served as the working electrode. All electrolyses were carried out in the Dri-Lab.

An electronic integrator constructed in this laboratory was employed for the coulometric determination of n values. The visible and ultraviolet spectra were taken with a Cary 14 automatic recording spectrophotometer. A Beckman IR 8 infrared spectrophotometer was used to obtain ir spectra. The magnetic susceptibilities were measured on a Gouy balance. The temperature range covered was liquid nitrogen to room temperature.

Reagents.—The acetonitrile used for the electrochemical work was Mallinckrodt Nanograde purified by a procedure previously described.[6] The solvents used under other circumstances were dried by conventional methods (CaH_2, Na–K, $LiAlH_4$). They were kept oxygen free. Eastman Kodak tetraethylammonium perchlorate recrystallized five times from water and dried under vacuum at 70° was used as supporting electrolyte. All other chemicals were reagent grade.

Polarographic and Spectral Measurements.—For polarographic measurements, 1–5 mM solutions of the complexes were prepared by dissolving a weighed quantity in a measured volume of acetonitrile which was 0.10 M in tetraethylammonium perchlorate. Visible and ultraviolet spectra of the complexes in acetonitrile were obtained using matched quartz cells ranging from 0.1 to 10 mm in length so that the spectra could be obtained without dilution.

Magnetic Measurements.—The magnetic measurements were made by the Gouy method using the solid complexes. The balance was calibrated with diamagnetic and paramagnetic standards. The diamagnetic standard was distilled water and the two paramagnetic standards were ferrous ammonium sulfate and manganese pyrophosphate. μ_{eff} was calculated from the slope of a Curie curve ($1/\chi_M$ *vs.* T). The temperature range covered was from 80 to 300°K. Diamagnetic corrections for the ligands and anions were calculated from Pascal's constants. The field strength was varied between 0 and 9000 G in five steps.

Preparation of the Complexes.—The Ni(II) cyclic amine complexes exist as a number of different isomers. These have recently been discussed in the literature.[7]

If the preparation of the ethylenediamine–acetone cyclic amine complex is carried out at room temperature, about 70% of structural isomer III and 30% of structural isomer IV is obtained. (See Figure 1 for labeling of the ligands.) These two isomers have been separated by fractional crystallization from acetonitrile. Ni(*cis*-diene)$(ClO_4)_2$ is less soluble than Ni(*trans*-diene)$(ClO_4)_2$.

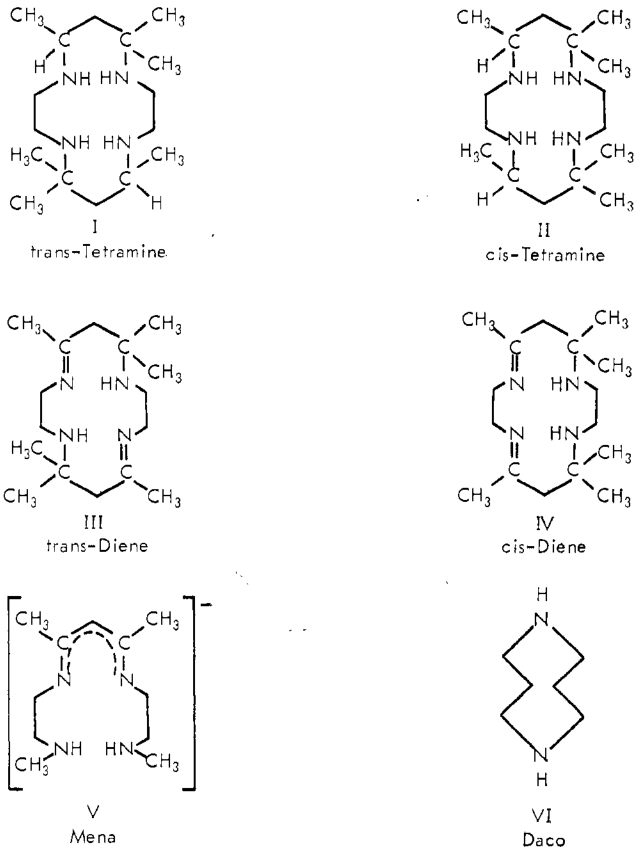

Figure 1.—Structures of the various amine ligands.

A second type of isomerism exists. Thus Ni(*trans*-diene)$(ClO_4)_2$ and Ni(*trans*-tetramine)$(ClO_4)_2$ have several forms which are identical except for the positions of the nitrogen hydrogens with respect to the plane of the complex. These isomers can be obtained by crystallization using a judicious choice of solvent, anion, or some other parameter. All of the discussion except that of ir spectra deals with the isomers that are stable to isomerization in acetonitrile.

Ni(*trans*-tetramine)(ClO_4) can be prepared by two methods. The corresponding Ni(II) complex can be reduced by constant potential electrolysis or by sodium amalgam. For sodium amalgam reduction, 2 mmol of Ni(*trans*-tetramine)$(ClO_4)_2$ was dissolved in 50 ml of dry, oxygen-free acetonitrile. This solution was poured on the top of the sodium amalgam containing 0.25 g of Na/100 g of Hg. Immediately, the yellow solution turned dark. The reaction had to be stirred vigorously for about 6 hr. The solution was filtered and the last traces of acetonitrile were removed under vacuum at room temperature. A non-

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(3) L. Porri, H. C. Gallazzi, and G. Vitulli, *Chem. Commun.*, 228 (1967).

(4) C. C. Addison and B. G. Ward, *ibid.*, 819 (1966).

(5) R. A. Durst, J. W. Ross, and D. M. Hume, *J. Electroanal. Chem.*, **7**, 248 (1964).

(6) E. O. Sherman, Jr., and D. C. Olson, *Anal. Chem.*, **40**, 1174 (1968).

(7) (a) N. F. Curtis, *Chem. Commun.*, 881 (1966); (b) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Am. Chem. Soc.*, **89**, 703 (1967); (c) *ibid.*, **90**, 6938 (1968).

TABLE I

POLAROGRAPHIC DATA OBTAINED WITH DME

Ligand	Electrode reaction	$E_{1/2}$,[a] V	Slope,[b] mV	I_d
trans-tetramine	$NiL^{2+} + e \rightarrow NiL^{+}$	−1.570	60	2.30
trans-tetramine	$NiL^{+} - e \rightarrow NiL^{2+}$	−1.576	65	...
cis-tetramine	$NiL^{2+} + e \rightarrow NiL^{+}$	−1.584	70	2.53
cis-tetramine	$NiL^{+} - e \rightarrow NiL^{2+}$	−1.565	64	2.79
trans-diene	$NiL^{2+} + e \rightarrow NiL^{+}$	−1.567	59	2.54
trans-diene	$NiL^{+} - e \rightarrow NiL^{2+}$	−1.551	63	2.68
cis-diene	$NiL^{2+} + e \rightarrow NiL^{+}$	−1.574	61	2.84
cis-diene	$NiL^{+} - e \rightarrow NiL^{2+}$	−1.564	61	2.93
mena	$NiL^{+} + e \rightarrow NiL$	−2.220	58	3.38
mena	$NiL^{+} - e \rightarrow NiL^{2+}$	+0.06	*c*	...
daco	$NiL_2^{2+} + 2e \rightarrow Ni(am) + 2L$	−1.6	*c*	6.20

[a] *Vs.* Ag–0.10 *M* $AgNO_3$ in acetonitrile. [b] *E vs.* log $(i/(i_d - i))$. [c] Maximum prevented analysis of wave.

crystalline dry residue remained. To this was added about 50 ml of oxygen-free water. Ni(*trans*-tetramine)(ClO_4) precipitated as a black crystalline solid which was filtered immediately and dried quickly under vacuum. Unreduced Ni(II) dissolves in the water. If some acetonitrile is left, Ni(*trans*-tetramine)$^+$ will react quickly with the water. This separation works because the reduced compound is extremely insoluble in water. The electrolytic reduction was carried out in acetonitrile in the absence of supporting electrolyte; the complex acts as the electrolyte. The rest of the procedure was identical with that given above.

Ni(*trans*-tetramine)(ClO_4) is extremely reactive and induces perchlorate decomposition. Any measurements must be carried out soon after isolation. This problem exists also with Ni(*cis*-tetramine)(ClO_4) to a lesser degree, but not with Ni(*trans*-diene)(ClO_4) or Ni(*cis*-diene)(ClO_4), or if one replaces ClO_4^- with BF_4^-.

Ni(*cis*-tetramine)(ClO_4), Ni(*trans*-diene)(ClO_4), and Ni(*cis*-diene)(ClO_4) can be prepared in identical fashion. The last two compounds were stored in the crystalline state for a number of months.

The Ni(I) complexes must be prepared in an inert atmosphere. They can be obtained 96% pure. The remaining 4% consists mostly of the Ni(II) complex, but occasionally also some of the products of the reaction of the Ni(I) complex with O_2. The following results of elemental analyses of the Ni(I) complexes are compared with the expected values for a product containing 96% $NiL(ClO_4)$ and 4% $NiL(ClO_4)_2$. The products were analyzed polarographically for NiL^+ and NiL^{2+} content. *Anal.* Calcd for $NiL(ClO_4)$ where L = I + II: Ni, 13.2; C, 43.0; H, 8.2; N, 12.6; Cl, 7.9; O, 14.4. Found: Ni, 13.4; C, 42.7; H, 8.1; N, 12.6; Cl, 8.0; O, 15.3. Calcd for $NiL(ClO_4)$ where L = III + IV: Ni, 13.3; C, 43.7; H, 7.3; N, 12.7; Cl, 8.0. Found: Ni, 13.4; C, 43.5; H, 7.6; N, 12.6; Cl, 7.9.

The chemical oxidation of the Ni(II) cyclic amines was not employed because the removal of the products of the oxidizing agent is difficult and time consuming. Oxidation was carried out by constant-potential electrolysis. In a typical preparation, 1 g of $NiL(ClO_4)_2$ was dissolved in 125 ml of acetonitrile, which was 0.10 *M* in tetraethylammonium perchlorate, and oxidized at +1.7 V. The solution turned from yellow to green during the oxidation. When the ligand in the complex was III, the product precipitated from solution. In the case of the other three ligands, the solution was evaporated to about 20 ml before the product precipitated. The product was filtered, washed with acetonitrile, and dried under vacuum at room temperature. Two molecules of acetonitrile per molecule of complex were present in the product which cannot be removed under vacuum (10^{-6} Torr) at room temperature. The following results were obtained from elemental analyses of the products. *Anal.* Calcd for $NiL(ClO_4)_3(CH_3CN)_2$ where L = I + II: Ni, 8.12; C, 33.2; H, 5.9; N, 11.6; Cl, 14.7; O, 26.5. Found: Ni, 8.00; C, 33.4; H, 6.0; N, 11.8; Cl, 14.7; O, 26.7. Calcd for $NiL(ClO_4)_3(CH_3CN)_2$ where L = III + IV: Ni, 8.17; C, 33.4; H, 5.3; N, 11.7; Cl, 14.8; O, 26.7. Found: Ni, 8.07; C, 33.4; H, 5.3; N, 11.3; Cl, 14.6; O, 27.3.

The diamine daco was prepared by a previously reported method.[8] The nickel complex was made by mixing the reactants in absolute ethanol and filtering the bright yellow product.[9]

Ni(mena)ClO_4 was prepared by the following method. $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ was dissolved in water and 2 equiv of N-methylethylenediamine was added. After a few minutes 2 equiv of concentrated acetic acid was poured in followed by 2 equiv of acetylacetone. A dark crystalline material formed immediately. The mixture was refluxed overnight. Enough sodium hydroxide was added to make the solution basic. A red color appeared. The solution was filtered hot and upon cooling red Ni(mena)($C_2H_3O_2$) crystallized. The perchlorate salt was made by adding 1 mol of perchloric acid and boiling out acetic acid. An ion-exchange resin can also be used.

Elemental analyses were carried out on the same type of product obtained by substituting ethylenediamine for N-methylethylenediamine and Cl^- for ClO_4^-. *Anal.* Calcd: Ni, 21.2; C, 39.0; H, 6.9; N, 20.2; Cl, 13.8. Found: Ni, 21.2; C, 38.8; H, 7.0; N, 19.7; Cl, 14.3.

Ni(mena)(ClO_4) was then identified by infrared, visible, and ultraviolet spectra which were essentially identical for the above two products.

Results

Electrochemistry. Ni(II) Complexes.—Polarograms of the Ni(II) complexes of ligands I–V[10] revealed that they undergo both reduction and oxidation in acetonitrile. At the dropping mercury electrode (dme), the complexes of I, II, and V gave a single well-defined cathodic (reduction) wave. Log plots of the waves [*E vs.* log $(i/(i_d - i))$] were linear with slopes close to the theoretical value of 59 mV for a reversible one-electron reduction, except for the complex of II, which gave a slope somewhat larger. The larger slope obtained with the complex of II was not due to irreversibility since cyclic voltammetry showed a reversible electrode reaction for this complex, as well as for the others. Nickel metal was not detected as a product. The complexes of III and IV gave two reduction waves on the dme. Analysis of the first wave indicated that it was due to a reversible one-electron reduction which was confirmed by cyclic voltammetry. The second wave was irreversbile with an $E_{1/2}$ of −2.7 V and appeared to be due to the reduction of the ligand double

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[8] E. L. Buble, A. M. Moore, and F. G. Wiseloge, *J. Am. Chem. Soc.*, **65**, 29 (1943).

[9] W. K. Musker and M. S. Hussain, *Inorg. Chem.*, **5**, 1416 (1966).

[10] See Figure 1.

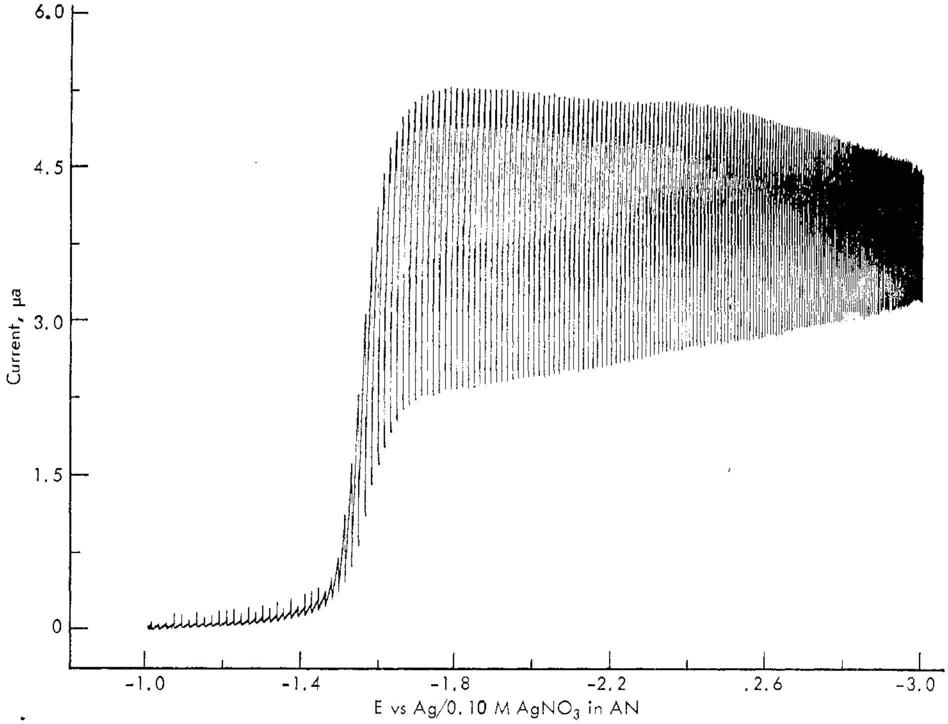

Figure 2.—Polarogram of 10^{-3} M Ni(*trans*-tetramine)$^{2+}$ in acetonitrile.

bonds. The complex of VI gave a cathodic wave with a maximum. The height of the wave indicated a two-electron reduction. Cyclic voltammetry showed that nickel metal was a product of the reduction.

The oxidation of the Ni(II) complexes of I–IV occurred at potentials positive to the dissolution of mercury requiring the use of a platinum indicating electrode. The complexes of I and II gave a single anodic (oxidation) peak which was shown by cyclic voltammetry to be due to a reversible electrode reaction. The complexes of III and IV gave a single irreversible peak; a cathodic peak due to the product was obtained on the reverse sweep. An anodic wave was obtained on the dme for the complex of V. Owing to a maximum which could be diminished but not completely eliminated by dilution, analysis of the wave was impossible so that only an approximate $E_{1/2}$ value was obtained. Cyclic voltammetry with a platinum indicating electrode revealed an irreversible electrode reaction.

Polarograms and cyclic voltammagrams of Ni(*trans*-tetramine)$^{2+}$ and Ni(*trans*-diene)$^{2+}$ are shown in Figures 2–5. The *cis* and *trans* complexes gave essentially identical waves.

The number of electrons involved in the reduction and oxidation of a selected number of cyclic amine–nickel(II) complexes were measured coulometrically and found to be one in all cases. Since all of the complexes are of similar geometry and size, the n values for the remaining complexes could be ascertained by comparison of diffusion current constants. The relevant electrochemical data are summarized in Tables I–III.

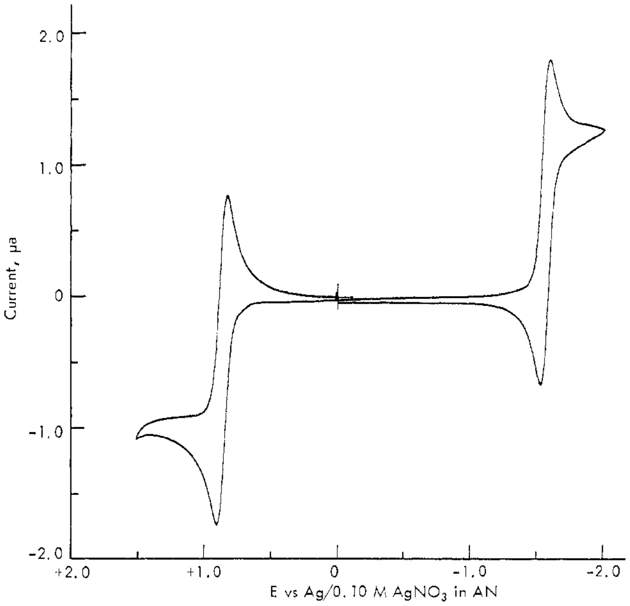

Figure 3.—Cyclic voltammogram of 10^{-3} M Ni(*trans*-tetramine)$^{2+}$ in acetonitrile.

Ni(I) and Ni(III) Complexes.—The preceding electrochemical results indicate that the Ni(II) complexes of I–IV undergo one-electron reduction and oxidation in acetonitrile to form stable products. The formal valence state of nickel in the reduction products is +1 and in the oxidation products +3. Both the Ni(I) and the Ni(III) complexes were prepared and isolated.

The Ni(I) complexes gave a well-defined anodic wave on the dme. Analyses of the waves indicated a reversible one-electron oxidation in all cases. The $E_{1/2}$ values agreed within several millivolts with those of the reduction of the corresponding Ni(II) complexes which is consistent with reversible behavior. The Ni(III) complexes gave two cathodic peaks at a platinum indi-

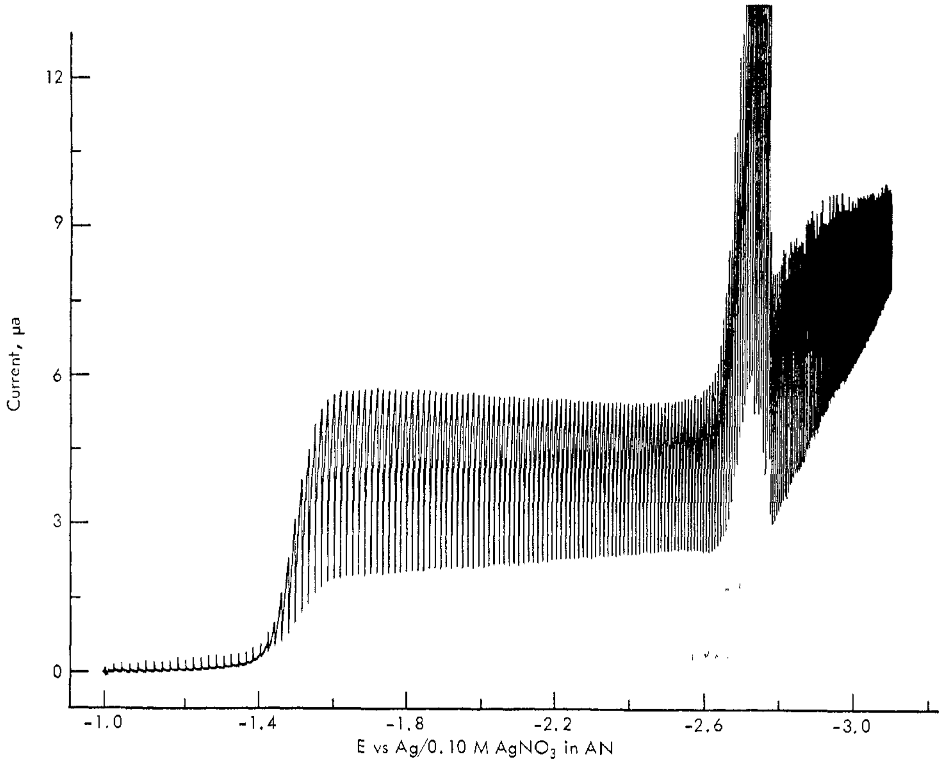

Figure 4.—Polarogram of 10^{-3} M Ni(*trans*-diene)$^{2+}$ in acetonitrile.

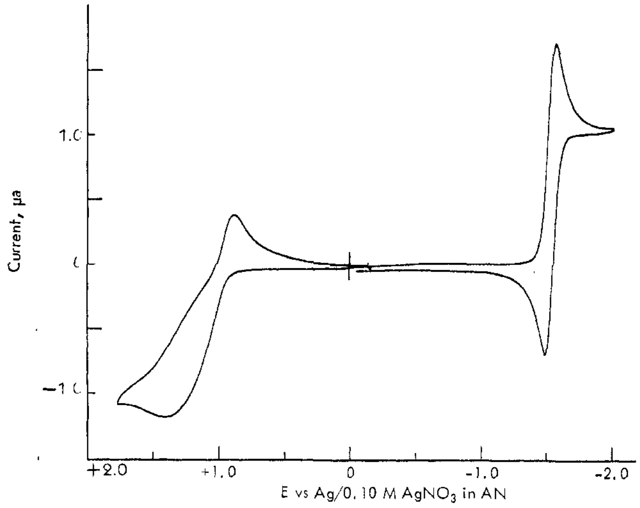

Figure 5.—Cyclic voltammogram of 10^{-3} M Ni(*trans*-diene)$^{2+}$ in acetonitrile.

cator electrode. The $E_{1/2}$ values of the first peak of the complexes of I and II were in close enough agreement with those for the oxidation of the corresponding Ni(II) complexes to be consistent with reversible, or nearly reversible, behavior. The second peak of all four complexes was reversible and $E_{1/2}$ values agreed with those of the first reduction wave of the corresponding Ni(II) complexes.

The pertinent electrochemical data are summarized in Tables I and II.

Spectra.—Ultraviolet and visible absorption spectra of the Ni(I), Ni(II), and Ni(III) complexes in acetonitrile were obtained. The spectra are shown in Figures 6–10. The energies (cm^{-1}) and intensities (l. mol^{-1} cm^{-1}) are listed in Table IV.

Ir spectra were obtained in a KBr matrix. The absorption lines appearing in the regions 3600–2800 and 1900–1200 cm^{-1} are shown in Table V. The rest of the spectra between 625 and 4000 cm^{-1} contain the

TABLE II

ELECTROCHEMICAL DATA OBTAINED WITH Pt ELECTRODE

Ligand	Electrode reaction	$E_{1/2}$,[a] V
trans-tetramine	$NiL^{2+} + e \rightarrow NiL^{+}$	-1.584[b]
trans-tetramine	$NiL^{2+} - e \rightarrow NiL^{3+}$	$+0.876$[b]
trans-tetramine	$NiL^{3+} + e \rightarrow NiL^{2+}$	$+0.850$[b]
cis-tetramine	$NiL^{2+} + e \rightarrow NiL^{+}$	-1.579[b]
cis-tetramine	$NiL^{2+} - e \rightarrow NiL^{3+}$	$+0.856$[b]
cis-tetramine	$NiL^{3+} + e \rightarrow NiL^{2+}$	$+0.840$[b]
trans-diene	$NiL^{2+} + e \rightarrow NiL^{+}$	-1.558[b]
trans-diene	$NiL^{2+} - e \rightarrow NiL^{3+}$	$+1.63$[c]
trans-diene	$NiL^{3+} + e \rightarrow NiL^{2+}$	$+0.79$[d]
cis-diene	$NiL^{2+} + e \rightarrow NiL^{+}$	-1.584[b]
cis-diene	$NiL^{2+} - e \rightarrow NiL^{3+}$	$+1.55$[c]
cis-diene	$NiL^{3+} + e \rightarrow NiL^{2+}$	$+0.86$[d]

[a] *Vs.* Ag–0.10 M AgNO$_3$ in acetonitrile. [b] Potential at which $i = 0.852i_p$. [c] Irreversible peak; E_p given at scan rate of 3.0 V/min. [d] Irreversible peak; E_p given at scan rate of 1.0 V/min.

TABLE III

COULOMETRICALLY DETERMINED n VALUE OF SOME OF THE NICKEL(II)-CYCLIC AMINE COMPLEXES

Complex	Electrode process	n
Ni(*trans*-tetramine)$^{2+}$	Reduction	1.02
Ni(*trans*-tetramine)$^{2+}$	Oxidation	1.01
Ni(*cis*-tetramine)$^{2+}$	Oxidation	0.93
Ni(*trans*-diene)$^{2+}$	Oxidation	0.96
Ni(*cis*-diene)$^{2+}$	Oxidation	0.97

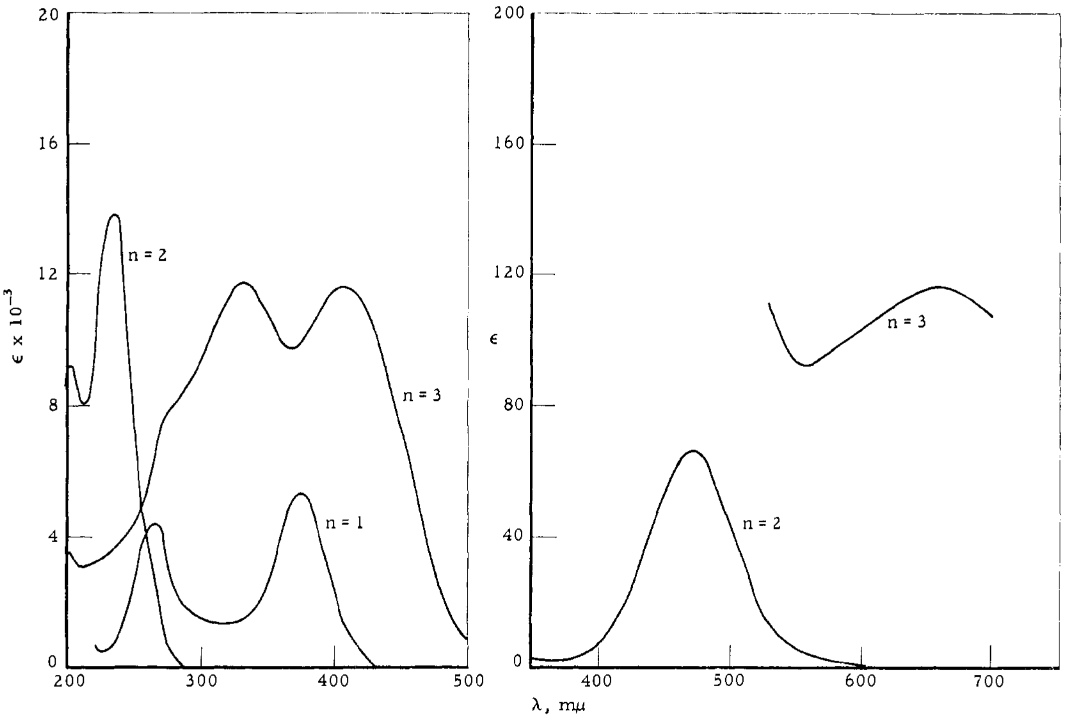

Figure 6.—Absorption spectra of Ni(*trans*-tetramine)$(ClO_4)_n$ in acetonitrile.

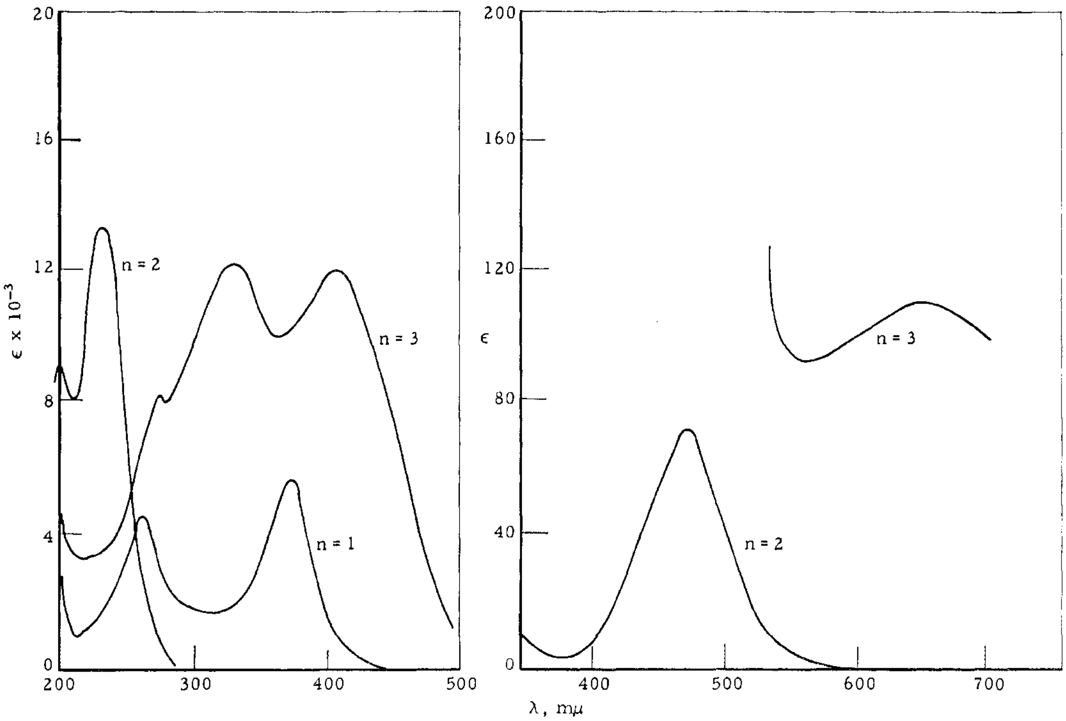

Figure 7.—Absorption spectra of Ni(*cis*-tetramine)$(ClO_4)_n$ in acetonitrile.

intense perchlorate bands and very few others of any interest. Figure 11 shows a sample spectrum of Ni(*trans*-diene)$(ClO_4)_2$.

It should be pointed out that the above spectra represent mixtures of diastereoisomers.

Magnetic Susceptibilities.—The magnetic susceptibilities of the Ni(I) and Ni(III) complexes are given in Table VI. All of the complexes are paramagnetic. The Ni(I) complexes have one unpaired electron as expected for a d^9 metal ion if there were no dimer formation. The Ni(III) complexes also have one unpaired electron which is consistent with a spin-paired d^7 system; again no dimer formation in the solid state is indicated.

Discussion

The redox chemistry of the nickel-cyclic amine complexes has already received some study.[2] With one

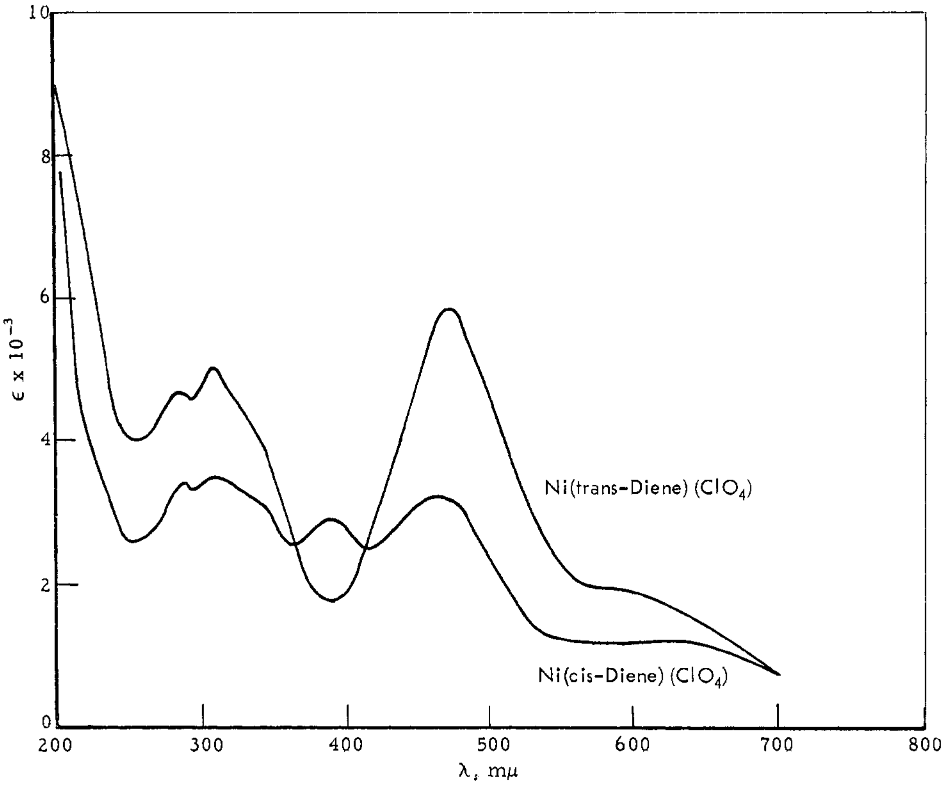

Figure 8.—Absorption spectra of Ni(*trans*-diene)(ClO$_4$) and Ni(*cis*-diene)(ClO$_4$) in acetonitrile.

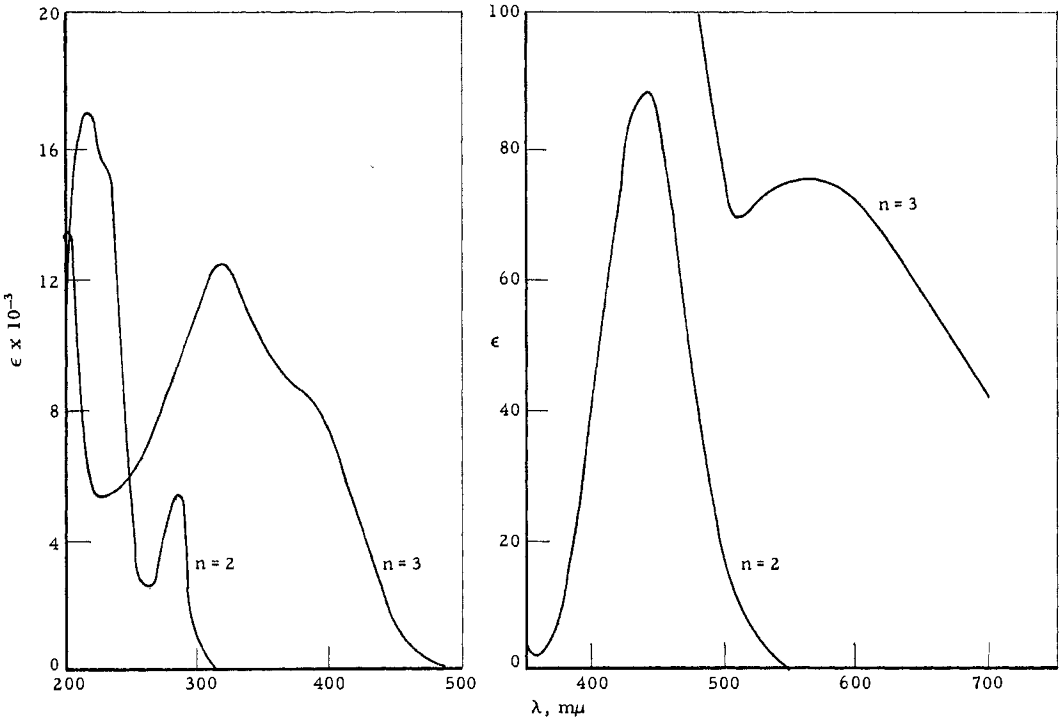

Figure 9.—Absorption spectra of Ni(*trans*-diene)(ClO$_4$)$_n$ in acetonitrile.

exception,[11] reduction or oxidation of the complexed ligand was observed, producing a family of compounds with varying degrees of unsaturation. In the past work, the redox reactions were carried out in aqueous solution using chemical redox reagents.

Our success in detecting and preparing Ni(I) and Ni(III) compounds resulted from the use of electrochemical techniques and an aprotic solvent, acetonitrile, which is relatively resistant to reduction and oxidation. From an analysis of polarographic, cyclic voltammetric, and coulometric data, the nature of the redox reactions of the Ni(II) compounds was ascer-

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[11] A complex Ni(III) compound, Ni(tetramine)(SO$_4$)(ClO$_4$)·$^1/_2$H$_2$SO$_4$, was reported by N. F. Curtis and D. F. Cook, *Chem. Commun.*, 962 (1967).

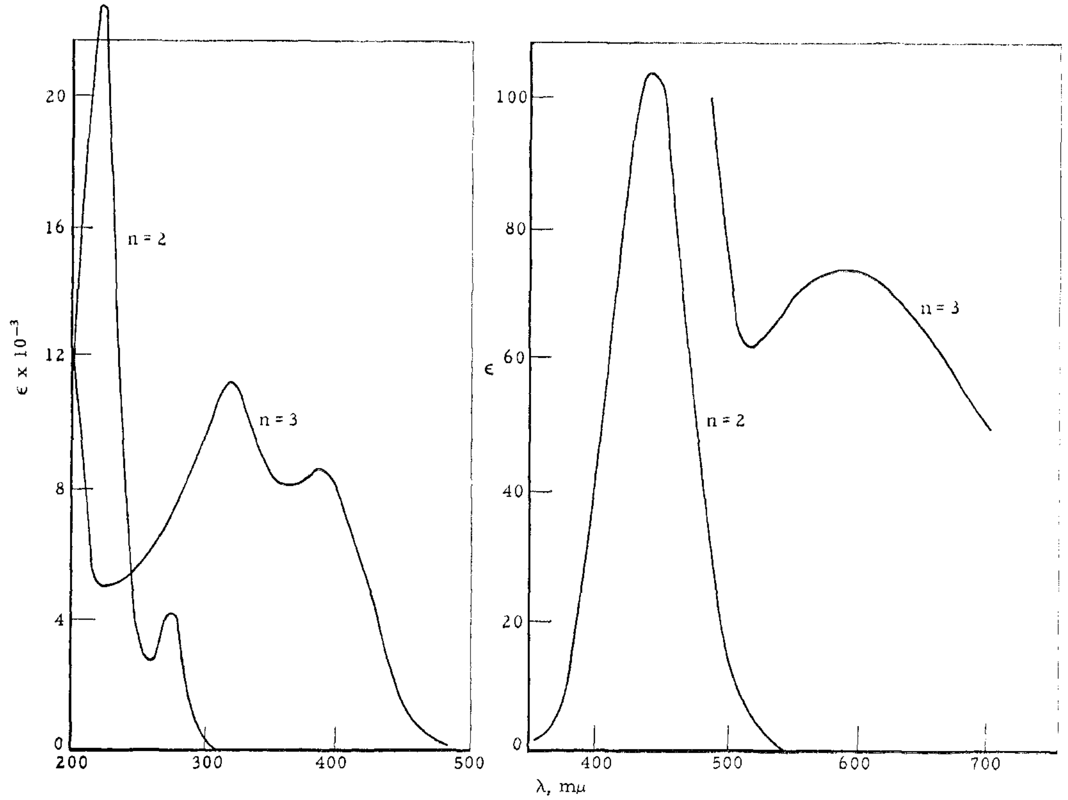

Figure 10.—Absorption spectra of Ni(*cis*-diene)$(ClO_4)_n$ in acetonitrile.

tained. For example, in the reduction process, a one-electron reversible electrode reaction was observed. For inert complexes, such as the nickel–cyclic amines, a reversible electrode reaction is evidence of a simple electron-transfer process with no chemical or structural changes in the depolarizer.[12] The product, therefore, was a cyclic amine complex containing nickel formally in the +1 oxidation state. For direct proof, the products were prepared by constant-potential electrolysis, isolated, and characterized by elemental analyses, polarography, and magnetic susceptibility measurements. The same type of evidence established the oxidation products of the Ni(II) complexes as nickel(III) cyclic amines.

The polarographic behavior of the nickel cyclic amines is of considerable interest since it is rather unusual for nickel compounds. The polarography of a large number of Ni(II) complexes has been studied both in aqueous and in nonaqueous solvents. With regard to the over-all electrochemical reaction, two types of behavior may be noted. The first type is exhibited by compounds which undergo a two-electron reduction yielding the metal as a product. Most nickel compounds fall into this class. The second type is characteristic of a class of compounds having a delocalized ground state, such as those formed by dithiolene[13] and *o*-phenylenediamine[14] ligands. These compounds may be considered complexes of Ni(II) with radical anion ligands. Two or more reversible single-electron polarographic waves are obtained. The electronic change is localized mainly on the ligand so that the valence state of the nickel remains essentially unchanged; *i.e.*, it is primarily the ligand that is reduced or oxidized rather than the metal.[15] One may be tempted to place the nickel cyclic amines in the latter class since they undergo one-electron reversible redox reactions. However, the cyclic amines are not the type of ligands which form complexes with delocalized orbitals; this is particularly true of the saturated ligands I and II where no π orbitals exist. Furthermore, polarographic evidence indicates that with the cyclic amine compounds it is primarily the metal that is involved in the electron change rather than the ligand. First, the cyclic amine ligands themselves are not readily oxidized or reduced, whereas the dithiolate and *o*-phenylenediamine ligands do undergo facile redox reactions. Metal complexes which undergo ligand reduction or oxidation generally exhibit redox reactions similar to those of the free ligand.[16] Second, if the electron change involved primarily the ligand, even a small change in the chemical structure of the ligand would be reflected in a shift of the half-wave potential.[15] However, the half-wave potentials of the cathodic waves of the complexes of the saturated ligands I and II are essentially identical with those of the unsaturated ligands III and IV.

An amine resembling the cyclic amines but probably forming a complex with delocalization of the valence orbitals is ligand V. The nickel complex of V exhibits

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(12) A. A. Vlček, *Progr. Inorg. Chem.*, **5**, 358 (1963).

(13) For an extensive review of the preparation and chemistry of the dithiolene complexes see J. A. Mc Cleverty, *ibid.*, **10**, 49 (1968).

(14) A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 5201 (1966).

(15) D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *ibid.*, **88**, 4876 (1966).

(16) A. A. Vlček, *Progr. Inorg. Chem.*, **5**, 376 (1963).

TABLE IV
ABSORPTION SPECTRA

Complex	Energy × 10^{-4}, cm^{-1}	ϵ, l. mol cm^{-1}
Ni(*trans*-tetramine)$^+$	2.670	5,350
	3.80	4,350
Ni(*cis*-tetramine)$^+$	2.675	5,550
	3.82	4,450
Ni(*trans*-diene)$^+$	1.668	1,820
	2.120	5,860
	2.905	3,750
	3.25	4,940
	3.540	4,620
Ni(*cis*-diene)$^+$	1.639	1,130
	2.160	3,260
	2.580	2,930
	2.927	3,150
	3.25	3,480
	3.475	3,340
Ni(*trans*-tetramine)$^{2+}$	2.123	66
	4.295	13,830
	5.00	9,270
Ni(*cis*-tetramine)$^{2+}$	2.123	73
	4.295	13,280
	5.00	9,460
Ni(*trans*-diene)$^{2+}$	2.269	89
	3.54	5,400
	4.355	15,200
	4.63	17,280
Ni(*cis*-diene)$^{2+}$	2.282	106
	3.63	4,080
	4.51	22,700
Ni(*trans*-tetramine)$^{3+}$	1.526	116
	2.460	11,600
	3.037	11,800
	3.64	7,800
Ni(*cis*-tetramine)$^{3+}$	1.539	112
	2.451	12,030
	3.060	12,170
	3.64	8,165
Ni(*trans*-diene)$^{3+}$	1.772	76
	2.631	8,660
	3.148	12,500
	4.93	13,500
Ni(*cis*-diene)$^{3+}$	1.695	75
	2.580	8,640
	3.148	11,300
	5.13	12,600

polarographic half-wave potentials quite different from the cyclic amine compounds, being much more easy to oxidize and more difficult to reduce.

Another unusual feature of the polarographic behavior of the nickel cyclic amines is the stability of the Ni(I) complexes to further reduction. No polarographic wave corresponding to the reduction of Ni(I) to Ni(0) was observed in the potential range available in acetonitrile. Several reasons for this may be considered. Owing to structural or steric factors, an orbital capable of accepting an electron (probably the d_{z^2} orbital) may be inaccessible to the electrode. Another possibility is that the energy of the orbital is too high to accept an electron from the dme. The inertness of the cyclic amine complexes prevents dissociation to provide an orbital of lower energy. The formation of dimers involving an Ni–Ni bond could also inhibit further reduction. The nonreducibility of $Ni_2(CN)_6^{2-}$ has been attributed to the presence of an Ni–Ni bond.[17] However, the shape and height of the anodic wave of the NiL^+ complexes do not support a dimer as a depolarizer.

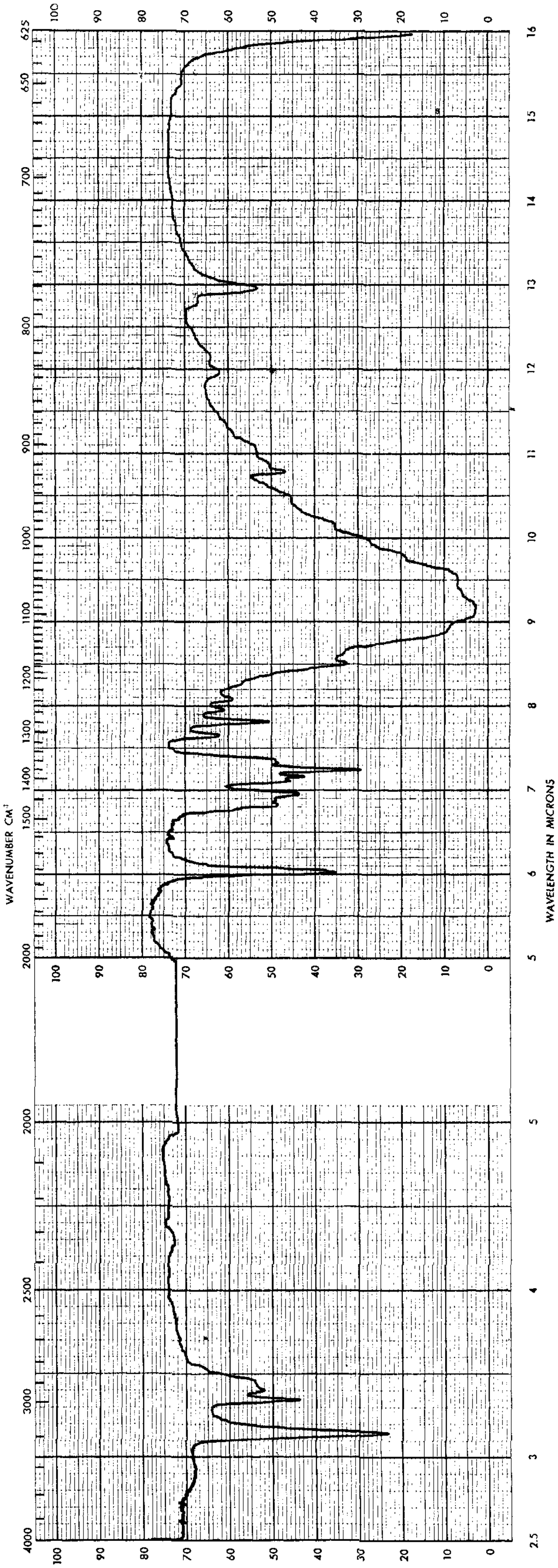

Figure 11.—Infrared spectrum of Ni(*trans*-diene)(ClO$_4$)$_2$.

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[17] A. A. Vlček, *Coll. Czech. Chem. Commun.*, **22**, 948 (1957).

TABLE V[a]

INFRARED SPECTRA (CM^{-1})

Ni(*trans*-tetramine)(BF$_4$)	Ni(*trans* + *cis*-tetramine)(ClO$_4$)	Ni(*trans* + *cis*-diene)(ClO$_4$)	Ni(*trans*-tetramine)(ClO$_4$)$_2$	Ni(*trans*-tetramine)(ClO$_4$)$_2$ interaction with KBr matrix	Ni(*cis*-tetramine)(ClO$_4$)$_2$	Ni(*trans*-diene)(ClO$_4$)$_2$	Ni(*trans*-diene)(ClO$_4$)$_2$ an N-H isomer	Ni(*trans*-diene)(ClO$_4$)$_2$ another N-H isomer	Ni(*cis*-diene)(ClO$_4$)$_2$	Ni(*trans* + *cis*-tetramine)(ClO$_4$)$_3$ ·2 CH$_3$CN	Ni(*trans* + *cis*-diene)(ClO$_4$)$_3$ ·2 CH$_3$CN	Ni(mena)(ClO$_4$)	Ni(daco)$_2$(ClO$_4$)$_2$
			3420	3570 (s) 3420			(s) 3500 (s) 3440	(s) 3460 (s) 3400	(s) 3450		(s) 3400	(w) 3580 (w) 3460 (w) 3400	(s) 3480
(s) 3270 (s) 2970 (s) 2930 (s) 2880	(s) 3260 3220 (s) 2980 (s) 2930 (s) 2870	(s) 3260 3200 (s) 2970 (s) 2930 (s) 2870	(s) 3200 (s) 2990 (s) 2960 2890	(s) 3070 2990 (s) 2960 (s) 2880	(s) 3190 (s) 2980 (s) 2910 2890	(s) 3180 (s) 2990 2940 2890	(s) 3180 (s) 3060 (s) 2995 2940 2910 2880	(s) 3020 (s) 2960 (s) 2860 (w) 2700	(s) 3205 2995 2950 2910 2880	(s) 3200 (s) 3160 (s) 3125 (s) 2975 2890	(s) 3160 (s) 3030 (s) 2980 (s) 2900 (s) 2860	(s) 3300 3120 2990 (s) 2950 (s) 2940 (s) 2870 (s) 2860	(s) 3100 (s) 3080 2970 (s) 2940 (s) 2930 2890 2800
										(w) 2250	(w) 2250		
		1640 (s) 1610	(s) 1625	1625 1600		(s) 1665	(s) 1650	(s) 1650 (w) 1625	(s) 1650		(s) 1650	(w) 1620	(w) 1630
1580 (s) 1460 (s) 1420 (s) 1375 (s) 1360	1580 (s) 1455 (s) 1420 (s) 1375 (s) 1360	1570 (s) 1460 (s) 1430 (s) 1380 (s) 1365 (s) 1340	(s) 1465 (s) 1425 (s) 1400 (s) 1370 1360	1475 (s) 1450 1430 (w) 1390 (s) 1370 1360 (w) 1340	(s) 1460 (s) 1425 1395 (s) 1370 (w) 1340	(s) 1460 (s) 1450 (s) 1430 (s) 1405 (s) 1390 (s) 1380 (s) 1360 (s) 1355	(s) 1470 (s) 1455 (s) 1435 (s) 1415 (s) 1390 (s) 1370 (s) 1355	(s) 1460 (s) 1455 (s) 1450 (s) 1425 (s) 1400 (s) 1395 (s) 1370 (s) 1350	(s) 1455 (s) 1450 (s) 1430 (s) 1415 1390 (s) 1380 (s) 1370 (s) 1350 1340	1475 (s) 1455 (s) 1450 (s) 1425 (s) 1375	(s) 1450 (s) 1440 (s) 1430 (s) 1400 (s) 1390 (s) 1370 (s) 1360	(s) 1555 (s) 1535 (s) 1465 (s) 1435 (s) 1400 1355	(w) 1480 (s) 1460 1455 (s) 1445 (w) 1425 (w) 1385 (w) 1380 (w) 1365 (w) 1360
(w) 1330 1300 1280 1270 (w) 1220	(w) 1330 1300 1280 1265 (w) 1220	1285 1255 1235 1220 (w) 1200 (s) 1165	(w) 1335 (w) 1310 1285 (w) 1235 (w) 1195	(w) 1315 1290 1280 1240	(w) 1305 1280 (w) 1230	1305 1275 (w) 1255 (w) 1235	1295 (w) 1280 (s) 1255 (w) 1240 (w) 1200	1305 1270 1255 (w) 1230 (w) 1205	1300 (w) 1265 1255 (w) 1225 (w) 1215 (w) 1200	(w) 1310 1285 (w) 1270 (w) 1260	1305 (w) 1275 (w) 1250 (w) 1235	(s) 1325 1270 1235	1340 (w) 1335 1300 1280 1260

[a] Abbreviations: s, strong; w, weak.

Furthermore, the Ni(I) complexes are paramagnetic indicating the absence of an Ni–Ni bond.

Probably the major factor responsible for the unusual redox behavior of the nickel cyclic amines is the cyclic nature of the ligands. An example of a noncyclic square-planar complex of Ni(II) is formed by the amine VI. This complex does not undergo one-electron redox reactions. Instead, like most Ni(II) compounds, it gives a two-electron polarographic reduction wave yielding the metal as a product.

Some general features of the electronic spectra of the nickel compounds will be discussed here. In the Ni(II) complexes, a low-intensity peak occurs in the visible region which has previously been reported as due to a d–d transition.[18] This peak shifts toward the blue

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(18) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

TABLE VI

MAGNETIC MOMENTS (LIQUID NITROGEN TO ROOM TEMPERATURE)

Complex	μ, BM
Ni(*trans*- + *cis*-tetramine)(ClO_4)	1.77
Ni(*trans*- + *cis*-diene)(ClO_4)	1.70
Ni(*trans*-diene)(ClO_4)	1.89
Ni(*trans*- + *cis*-tetramine)$(ClO_4)_3$	1.79
Ni(*trans*- + *cis*-diene)$(ClO_4)_3$	1.77
Ni(*trans*-diene)$(ClO_4)_3$	2.03

region in going from the saturated to the unsaturated complexes. A shift in this direction is expected if bonding occurs between filled metal d orbitals and unfilled ligand π orbitals.[19] The Ni(III) complexes also have a low-intensity band in the visible region which can be assigned to a d–d transition. A d–d transition is not observed in the Ni(I) complexes but is probably obscured by one of the charge-transfer bands which extend into the visible region.

In the Ni(II) complexes, a charge-transfer band occurs at 283 mμ in the unsaturated complexes and is absent in the saturated complexes. This peak has previously been assigned to a transition of the π electrons on the C=N groups.[18] It is difficult to decide how this peak shifts on changing the oxidation state of the nickel because of the broad charge-transfer bands of the Ni(I) and Ni(III) complexes. Two new charge-transfer bands show up in the visible region of the spectra of the Ni(I) unsaturated complexes which must be due to metal to ligand transitions since they are not observed in the spectra of the Ni(II) complexes.

Only the most characteristic features of the ir spectra will be mentioned here. For more detail, Table V should be consulted.

In general, the Ni(II) cyclic complexes have a single N–H stretching band in the 3200-cm^{-1} region. This is normal for a secondary amine. In some of the N–H positional isomers (see the section on the preparation of the complexes for further explanation of these isomers) the nitrogen hydrogens interact strongly with the anion or some other part of the molecule so that N–H stretching bands appear in the 3450- and 3050-cm^{-1} regions. For example, thorough grinding of the complexes in KBr will almost always give interaction with Br^- resulting in the 3450- and 3050-cm^{-1} bands. If any of the bands in the 3450- and 3050-cm^{-1} regions are due to water, then the latter was picked up from the potassium bromide or in the grinding process and was not present there initially.

The N–H stretching frequencies of the Ni(I) *cis* and *trans* isomers appear at slightly different wavelengths. Thus in the mixtures I + II and III + IV two bands are observed while in the pure *trans* isomer Ni(*trans*-tetramine)(BF_4) only one of the transitions appears.

The Ni(III) N–H stretching frequencies have been measured only for the isomer mixtures. Wide bands, difficult to resolve, are present.

The C=N stretching vibration occurs at 1650 cm^{-1} in the unsaturated Ni(II) complexes. In the Ni(I) mixture of isomers, three bands are observed. A C=N band for each of the two isomers and a secondary amine deformation band would account for the spectrum. The spectra indicate that there are larger conformational differences between the Ni(I) isomers and between the Ni(III) isomers than between the corresponding Ni(II) complexes.

The C–H deformation region (1470–1300 cm^{-1}) and especially the skeletal vibration region (1300–1160 cm^{-1}) are very characteristic of the type of isomer present. The latter region is useful in identifying pure isomers and their mixtures.

Summary and Conclusions

Polarographic, cyclic voltammetric, and coulometric studies of square-planar nickel(II) cyclic amines in acetonitrile showed that the Ni(II) compounds undergo one-electron reduction and oxidation to form the corresponding Ni(I) and Ni(III) compounds. Polarographic evidence indicates that the redox reactions involve primarily the metal and not the ligand. The nickel(I) and nickel(III) cyclic amines were prepared and isolated as the perchlorate or tetrafluoroborate salts. They are stable in the absence of oxygen and moisture. These oxidation states are rare, and this is the first reported case where the same ligand is capable of stabilizing both. The unusual redox behavior of the nickel cyclic amines is a unique property of their cyclic nature since a noncyclic square-planar nickel(II)–saturated amine complex does not undergo one-electron redox reactions.

The Ni(I) and Ni(III) compounds may find use as one-electron redox reagents since the former is a strong reducing agent and the latter is a strong oxidizing agent.

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[19] L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1960, p 36.