Cyclic Amine Complexes of Copper(I), -(II), and -(III). Electrochemistry, Preparation, and Properties

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The synthesis of some new cyclic amine complexes of Cu(I) and Cu(III) using an electrochemical approach is described. The Cu(III) compounds represent an uncommon oxidation state for copper. A comparison of the redox properties and spectra of the copper and the previously reported nickel complexes is made.

Introduction

The remarkable ability of certain tetradentate cyclic amines (see Figure 1) to stabilize unusual oxidation states of the transition metals was recently demonstrated by the preparation and isolation of Ni(I) and Ni(III) complexes.[1] The Ni(I) and Ni(III) compounds were prepared by electrochemical reduction and oxidation of the corresponding Ni(II) componds in acetonitrile. Apparently the inertness of the cyclic amine ligands to dissociation can lead to the formation and trapping of the less common oxidation states.

In a recent electrochemical study of Cu(II) cyclic amines in aqueous solution, Endicott and coworkers[2] produced electrolytically a strongly reducing "bright yellow species" which appeared from considerable evidence to be a Cu(I) complex. However, they were not able to isolate the compound for characterization. In a continuing study of the complexes of the cyclic amines, we have carried out an electrochemical investigation of the copper compounds in acetonitrile. Compared to water, acetonitrile provides a wider potential range and a more stable environment for strongly reducing and oxidizing electrode products. Generally, transition metal complexes exhibit simpler electrode processes in acetonitrile than in aqueous solution. Both the Cu(I) and Cu(III) cyclic amines were prepared and isolated. This report deals with the electrochemistry, preparation, and properties of Cu(I), Cu(II), and Cu(III) cyclic amines in acetonitrile. Some comparisons are made between the copper and nickel complexes since their redox chemistry follows a similar pattern.

Results

Isomers.—The structures of the ligands are shown in Figure 1. The cyclic amine complexes exist as a number of isomers.[3,4] The isomers of the copper complexes used in the present study were identified by comparison of infrared spectra with the corresponding nickel complexes. The conformations of the nickel

complexes have previously been determined by Busch and coworkers.[4] The infrared spectra of the isomers are characteristic and have been used before for isomer identification of the copper complexes.[2]

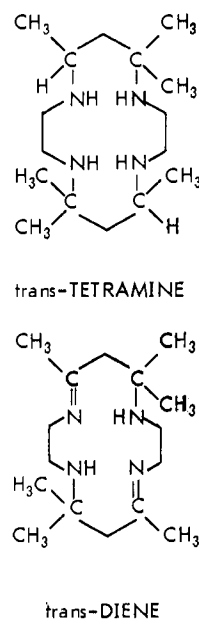
trans-TETRAMINE

trans-DIENE

Figure 1.—Structure of the cyclic amine ligands.

The literature and nomenclature of the various isomers are scattered and sometimes confusing and a short summary may be helpful to the reader. The diene has two noninterconvertible geometric forms which differ in the position of the methyl groups (trans or cis with respect to the center of the molecule). Because of the asymmetry of the complexed nitrogens other isomers can exist. These are interconvertible because the hydrogens on the nitrogens can undergo exchange under the proper conditions. Only one form (*dl*) of the cis complexes has been isolated while two stable trans forms are known (meso or *dl*).

Hydrogenation of the *trans*-diene complex leads to the formation of two asymmetric carbons. As a consequence there are two more noninterconvertible isomers (meso and *dl*). Again the bonded nitrogens can lead to interconvertible forms. Only one meso complex has been found while two *dl* forms are now known (α or β). For a thorough explanation of the differences

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

(2) J. M. Palmer, E. Papaconstantinou, and J. F. Endicott, *ibid.*, **8**, 1516 (1969).

(3) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 3016 (1962); N. F. Curtis, *ibid.*, 2644 (1964); N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *ibid.*, 1015 (1966).

(4) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968); L. G. Warner and D. H. Busch, *ibid.*, **91**, 4092 (1969).
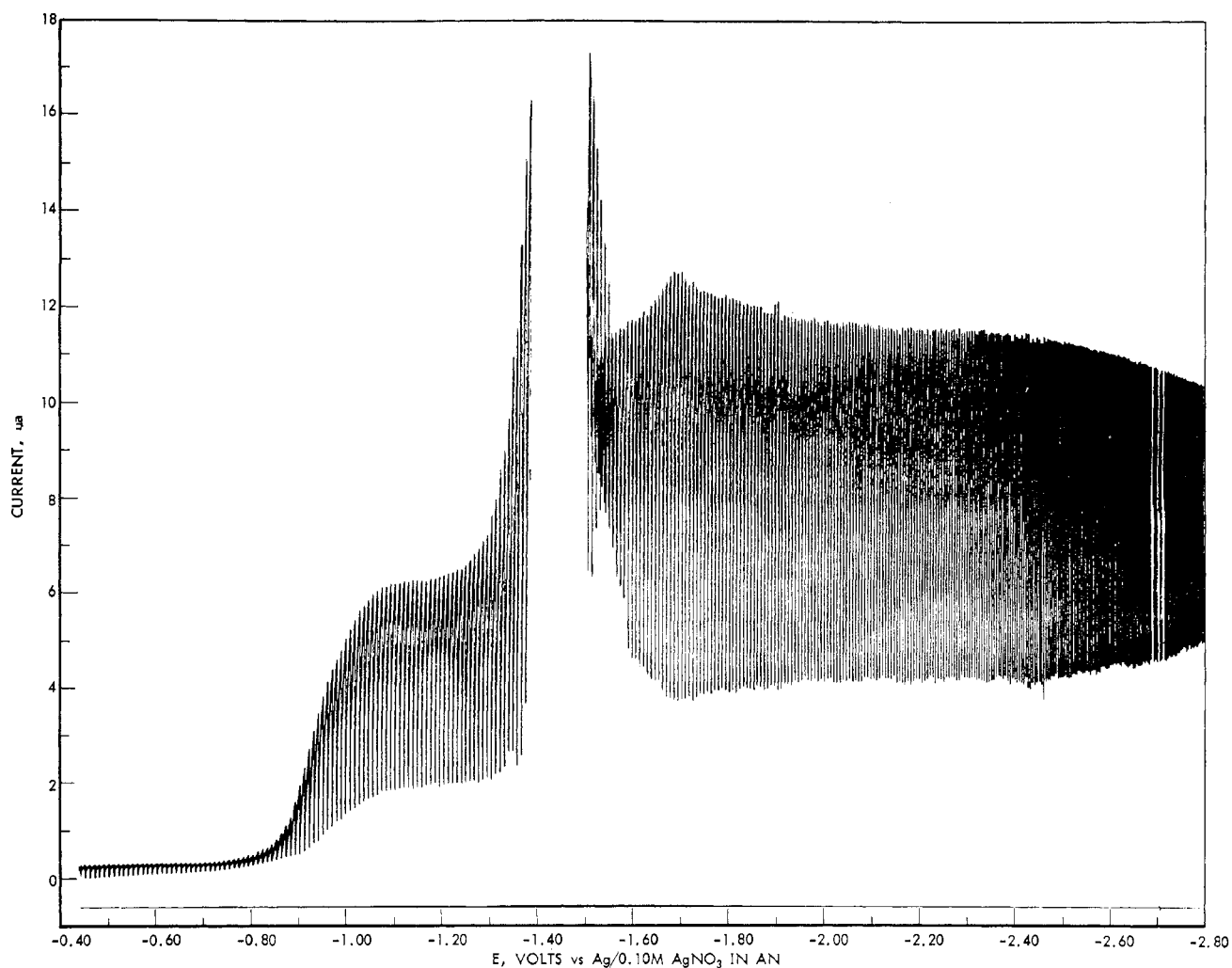
Figure 2.—Polarogram of 10^{-3} M Cu(*trans*-diene)$^{2+}$ in acetonitrile.

of the various forms one should consult the two papers by Busch and coworkers.[4]

The present study deals only with the trans isomers. Therefore the following possibilities exist: *trans-meso*-diene, *trans-dl*-diene, *trans-meso*-tetramine, *trans-α-dl*-tetramine, and *trans-β-dl*-tetramine. The crystalline Cu(II) complexes used in our study were trans-meso with both the diene and tetramine compounds. The same holds true for the solution chemistry since the meso forms are the more stable ones under the experimental conditions.

It is assumed that in the case of Cu(I) and Cu(III) no conformational changes take place at the electrode and thus meso isomers are obtained.

The electrochemistry of the complexes[1] is not sensitive to the type of isomer that is present. However, other properties such as ir, uv, and visible spectra can differ appreciably.

Preparation and Electrochemistry

Cu(II) Complexes.—The orange form of the *trans*-diene–copper(II) complex was synthesized by treating Cu(NH$_3$)$_6$(ClO$_4$)$_2$ first with acetone and then with 2 mol of ethylenediamine in acetone. This method gives a better yield than the procedure reported in

the literature.[5] The *trans*-tetramine–copper(II) complex was obtained by treating the anhydrous ligand with Cu(CH$_3$CN)$_4$(BF$_4$)$_2$ in acetonitrile to ensure the absence of coordinated water.

Polarograms of the Cu(II) complexes were obtained at both a dropping mercury electrode (dme) and a platinum sphere electrode. It may be helpful to point out that the potential range available in acetonitrile at a dme is $+0.30$ to -3.2 V $vs.$ the silver reference electrode. The range is $+2.0$ to -2.5 V at a Pt electrode. The relatively limited anodic span of the dme is due to the low dissolution potential of mercury. The Pt electrode is very useful for studying oxidations which occur at potentials more positive than 0.30 V. For example, the oxidation of the Cu(II) complexes can be observed only at the Pt electrode.

At the dme, Cu(*trans*-diene)$^{2+}$ gave two single-electron cathodic waves as shown in Figure 2. The first step is due to the reduction of Cu(II) to Cu(I) while the second corresponds to

$$\text{Cu(I)} \xrightarrow{\text{1e}} \text{Cu(0)}$$
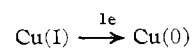
A log plot (E $vs.$ log $[i/(i_d - i)]$ of the first wave was

(5) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 3016 (1962).

nearly linear with a slope of 74 mV. A slope of 60 mV is expected for a reversible one-electron wave.[6] The second wave was distorted by a large maximum which prevented a log analysis. Although with Ni(*trans*-diene)$^{2+}$ a cathodic wave attributable to the reduction of the imine double bonds was observed at -2.7 V,[1] a corresponding wave did not occur with the Cu(II) complex.

At the Pt indicating electrode, Cu(*trans*-diene)$^{2+}$ gave an anodic and two cathodic peaks as seen in the cyclic voltammograms in Figure 3. The two
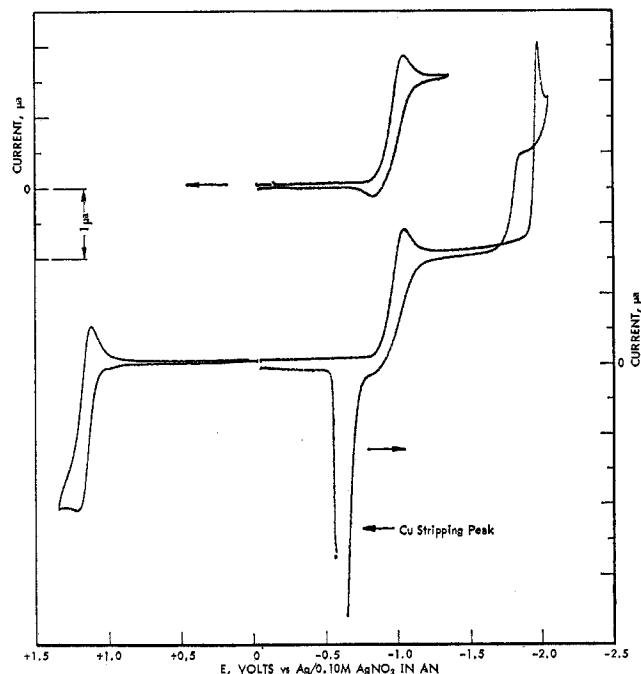

Figure 3.—Cyclic voltammograms of 10^{-3} M Cu(*trans*-diene)$^{2+}$ in acetonitrile.

cathodic peaks correspond to the waves obtained on the dme. The first step was at best quasireversible with an anodic peak due to the Cu(*trans*-diene)$^+$ observable on the reverse sweep. No Cu metal is produced by the first step. The second step deposited copper metal as seen by a stripping peak on the reverse scan. The anodic peak of Cu(II) due to its oxidation to Cu(III) was reversible as judged from the separation of the peak potentials and the relative heights of the peaks obtained on the forward and reverse scans.[7a] A flat base line for measuring the height of the reverse peak was established by holding the potential constant positive to the peak on the forward sweep for about 30 sec and then reversing the sweep.[7b]

Figure 4 shows a polarogram of Cu(*trans*-tetramine)$^{2+}$ on the dme. A single cathodic wave was obtained the height of which corresponded to the uptake of two electrons. The maximum can be eliminated by dilution. A log plot of the wave was then linear
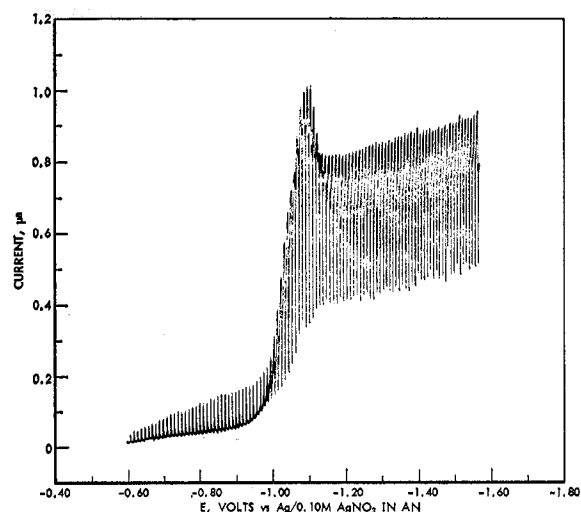
(6) L. Meites, "Polarographic Techniques," Interscience, New York, N. Y., 1955.

(7) (a) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); (b) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969.

Figure 4.—Polarogram of 0.7 × 10^{-3} M Cu(*trans*-tetramine)$^{2+}$ in acetonitrile.

with a slope of 51 mV which indicated an irreversible two-electron reduction. On a Pt electrode a distinctly different behavior was observed. A cyclic voltammogram was nearly identical with that of the unsaturated complex (Figure 3) with the exception of a shift in the peak potentials of the cathodic steps. (The complex must be carefully recrystallized to remove all traces of Cu(CH$_3$CN)$_4$(BF$_4$)$_2$ starting material or a Cu stripping peak will be observed on reversing after the first step.) This allows one to carry out constant potential electrolysis to obtain Cu(*trans*-tetramine)$^+$ with a Pt but not a mercury electrode. A reversible single-electron oxidation peak was also observed for Cu(*trans*-tetramine)$^{2+}$ at Pt.

In selected cases the number of electrons, n, involved in the electrode processes was measured by coulometry (Table III). The n values for the remaining electrode reactions were estimated from observed wave heights.

The electrochemical data are summarized in Tables I–III.

TABLE I

POLAROGRAPHIC DATA OBTAINED WITH DME

Ligand	Electrode reaction	$E_{1/2}$,^{a} V	Slope,^{b} mv	$I_d{}^c$
trans-Diene	CuL^{2+} + e$^-$ → CuL$^+$	-0.930	74	2.76
trans-Diene	CuL$^+$ + e$^-$ → Cu + L	-1.4 to -1.5^d		2.5
trans-Diene	CuL$^+$ − e$^-$ → CuL^{2+}	-0.929	60	2.90
trans-Tetramine	CuL^{2+} + 2e$^-$ → Cu + L	-1.018	51	5.90
trans-Tetramine	2CuL$^+$ + Hg → Cu(Hg) + CuL^{2+}	-1.0		

^{a} *Vs.* Ag–0.10 M AgNO$_3$ in acetonitrile. ^{b} E *vs.* log [$i/(i_d - i)$]. ^{c} $I_d = i_d/Cm^{2/3}t^{1/6}$, where i_d is in microamperes, C is in millimoles per liter, m is in milligrams per second, and t is in seconds. ^{d} Maximum prevented analysis of wave.

Cu(I) Complexes.—Both Cu(*trans*-diene)$^+$ and Cu(*trans*-tetramine)$^+$ were prepared by constant-potential reduction of the corresponding Cu(II) complexes. Cu(*trans*-diene)$^+$ was precipitated as the perchlorate salt but Cu(*trans*-tetramine)$^+$ was not isolated from solution. The unsaturated complex was found to be stable in the absence of oxygen and moisture. The saturated complex, on the other hand, is thermodynamically

Ligand	Electrode reaction	$E_{1/2}$ or E_p, V
trans-Diene	$CuL^{2+} + e^- \rightarrow CuL^+$	-1.023^b
trans-Diene	$CuL^+ - e^- \rightarrow CuL^{2+}$	-0.773^b
trans-Diene	$CuL^{2+} - e^- \rightarrow CuL^{3+}$	$+1.22,^c +1.180^d$
trans-Diene	$CuL^{3+} + e^- \rightarrow CuL^{2+}$	$+1.133^d$
trans-Diene	$CuL^+ + e^- \rightarrow Cu(0) + L$	-2.0^b
trans-Tetramine	$CuL^{2+} + e^- \rightarrow CuL^+$	-1.161^b
trans-Tetramine	$CuL^+ - e^- \rightarrow CuL^{2+}$	-1.0^b
trans-Tetramine	$CuL^{2+} - e^- \rightarrow CuL^{3+}$	$+1.215,^c +1.197^e$
trans-Tetramine	$CuL^{3+} + e^- \rightarrow CuL^{2+}$	$+1.119^e$
trans-Tetramine	$CuL^+ + e^- \rightarrow Cu(0) + L$	-2.20^b

[a] Reference electrode was Ag–0.10 M AgNO$_3$ in acetonitrile. [b] E_p. [c] $E_{1/2}$ = potential at $i = 0.852i_p$. [d] $E_{1/2}$ at $-18°$. [e] $E_{1/2}$ at $-14°$.

TABLE III

COULOMETRICALLY DETERMINED n VALUES

Complex	Electrode process	n
Cu(*trans*-diene)$^{2+}$	Oxidn	1.02
Cu(*trans*-tetramine)$^{2+}$	Oxidn	0.88

unstable with respect to disproportionation at room temperature. The rate of disproportionation is slow except in the presence of certain catalytic surfaces such as mercury. In glass vessels the disproportionation was slow enough to carry out polarographic and spectral measurements.

At the dme Cu(*trans*-diene)$^+$ gave a single-electron anodic wave. A log plot of the wave was linear with a slope of 60 mV. A one-electron cathodic wave due to the reduction of Cu(I) to Cu(0) was also observed. At the Pt electrode two anodic and one cathodic peaks were obtained. The two anodic peaks corresponded to the steps Cu(I) → Cu(II) and Cu(II) → Cu(III) while the cathodic process deposited copper.

Cu(*trans*-tetramine)$^+$ at the dme exhibited a single composite cathodic–anodic wave. The wave crossed zero current at -1.0 V which corresponded to the $E_{1/2}$ of the cathodic wave of Cu(*trans*-tetramine)$^{2+}$. The anodic and cathodic protions of the wave were of equal height. A wave of this type can be explained by disproportionation of Cu(I) at the mercury surface[8]

$$CuL^+ + e^- \xrightarrow{Hg} Cu(Hg)$$

$$CuL^+ - e^- \xrightarrow{Hg} CuL^{2+}$$
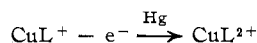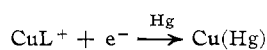
At the Pt electrode Cu(*trans*-tetramine)$^+$ also gave two anodic and one cathodic peaks attributable to the same steps discussed above for the unsaturated complex. Two small anodic peaks at -0.5 and 0 V were not identified but may have been due to impurities which diffused from the anolyte compartment during the electrochemical preparation of the Cu(I) complex.

Cu(III) Complexes.—At room temperature Cu-(*trans*-diene)$^{3+}$ and Cu(*trans*-tetramine)$^{3+}$ were found to be stable on the time scale used in voltammetric measurements. They are unstable on a longer time scale. On constant-potential oxidation of the Cu(II)

(8) J. A. Alternatt and S. E. Manahan, *Inorg. Nucl. Chem. Lett.*, 4, 1 (1968).

complexes at room temperature the current fell to a nearly steady-state level from which it decreased very slowly. Interruption of the electrolysis led to an increase in the height of the anodic peak of the Cu(II) complex as a function of time. These observations indicated a catalytic electrode process involving the regeneration of the starting material by reaction of CuL^{3+} with some component of the solution. However, no reaction of the Cu(III) complexes was observed to occur at -15 to $-20°$. Therefore, (AN$_2$)Cu-(*trans*-diene)(ClO$_4$)$_3$ and (AN)$_2$Cu(*trans*-tetramine)-(BF$_4$)$_3$, where AN is acetonitrile, were prepared by constant-potential electrolysis in the above temperature range. To prevent decomposition, it was found necessary to store the solids below $-15°$.

The voltammetry of the Cu(III) complexes was carried out at low temperatures at the Pt electrode. The $E_{1/2}$ values for the Cu(III) → Cu(II) step are recorded in Table II. Comparison with the $E_{1/2}$ values for the oxidation of the corresponding Cu(II) complexes obtained at the same temperature indicates a quasi-reversible electrode process. It may be recalled that at 25° reversible anodic peaks were observed for the Cu(II) complexes.

Spectra.—Ultraviolet and visible spectra of the Cu(I), Cu(II), and Cu(III) complexes were measured in acetonitrile. The absorption peaks and their intensities are listed together with those of the corresponding nickel complexes in Table IV. Infrared spectra were also obtained and the absorption frequencies are given in Table V.

Spontaneous Reduction of the Cu(III) Complexes in Acetonitrile.—At room temperature the Cu(III) complexes are spontaneously reduced in acetonitrile. The reaction was followed spectrophotometrically with both the saturated and unsaturated complex and with a pH electrode with the latter. The changes in the uv and visible spectra obtained by slowly warming solutions of CuL^{3+} from $-15°$ to room temperature are show in Figures 5 and 6. The presence of isosbestic points indicated a single absorbing product. Time-dependent changes in the C≡N stretch region of the infrared spectra of solid (AN)$_2$CuL(ClO$_4$)$_3$ can be seen
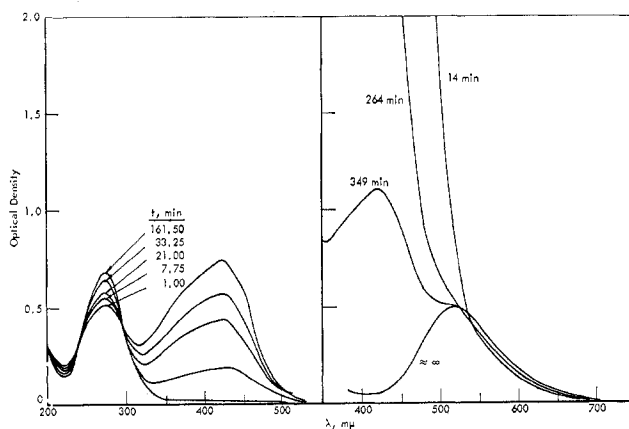

Figure 5.—Spontaneous reduction of Cu(*trans*-tetramine)(BF$_4$)$_3$ in acetonitrile at room temperature as a function of time.

TABLE IV
ELECTRONIC SPECTRA IN ACETONITRILE

Copper compounds		Nickel compounds	
Complex	λ_{max}, mμ (ϵ, l. mol^{-1} cm^{-1})	Complex	λ_{max}, mμ (ϵ, l. mol^{-1} cm^{-1})
Cu(*trans*-tetramine)$^+$	560 (7)	Ni(*trans*-tetramine)$^+$	375 (5350)
	241 (7570)		263 (4350)
	219 (9670)		
Cu(*trans*-diene)$^+$	415 (5700)	Ni(*trans*-diene)$^+$	600 sh (1820)
	283 (5600)		472 (5860)
			345 sh (3750)
			308 (4940)
			283 (4620)
Cu(*trans*-tetramine)$^{2+}$	517 (138)	Ni(*trans*-tetramine)$^{2+}$	471 (66)
	273 (9400)		233 (13,830)
			200 (9270)
Cu(*trans*-diene)$^{2+}$	502 (120)	Ni(*trans*-diene)$^{2+}$	441 (89)
	262 (7400)		283 (5400)
	192 (15,800)		230 sh (15,200)
			216 (17,280)
Cu(*trans*-tetramine)$^{3+}$	425 (15,000)	Ni(*trans*-tetramine)$^{3+}$	655 (116)
	375 (12,000)		407 (11,600)
	275 (6700)		330 (11,800)
			275 sh (7800)
Cu(*trans*-diene)$^{3+}$	395 (14,530)	Ni(*trans*-diene)$^{3+}$	565 (76)
	335 (12,690)		380 sh (8660)
			318 (12,500)
			203 (13,500)

TABLE V
INFRARED SPECTRA
(FROM 4000 TO 1100 CM^{-1})^a

Cu(*trans*-tetramine)-(BF$_4$)	Cu(*trans*-diene)-(ClO$_4$)	Cu(*trans*-tetramine)-(BF$_4$)$_2$	Cu(*trans*-diene)-(ClO$_4$)$_2$	Cu(*trans*-tetramine)-(BF$_4$)$_3$· 2CH$_3$CN	Cu(*trans*-diene)-(ClO$_4$)$_3$· 2CH$_3$CN
3225 s	3300 s	3225 s	3265 s	3225 s	3225 m
					3150 m
					3080 m
2980 s	2975 s	2980 s	3000 m	2980 m	2990 m
2975 s	2940 s	2925 m	2985 m	2960 s	2980 s
2920 s	2920 s	2890 m	2965 m	2955 s	2960 s
2895 s	2890 s		2920 m	2900 s	2940 s
	2850 m			2880 s	2905 s
				2855 m	2880 m
					2860 m
				2300 w	2335 w
				2260 m	2300 w
					2260 m
	1630 m		1665 s		1665 s
	1615 m				1660 m
1475 m	1480 m	1475 m	1485 w	1470 w	1475 w
1465 s	1470 s	1460 s	1445 m	1465 m	1460 s
1455 s	1445 s	1435 s	1420 m	1460 s	1445 s
1435 s	1400 s	1400 m	1410 m	1450 s	1430 s
1400 m	1385 m	1375 s	1395 s	1435 s	1420 w
1380 m	1370 s	1360 m	1360 m	1395 w	1400 w
1375 s	1360 m	1280 w	1305 m	1375 w	1370 s
1360 m	1330 s	1235 w	1280 w	1370 s	1350 w
1345 w	1265 s	1195 m	1260 m	1360 w	1295 w
1315 m	1255 w	1165 w	1240 w	1290 m	1270 w
1290 s	1245 w	1145 w	1210 w	1285 m	1255 m
1285 s	1230 s		1180 s	1210 w	1230 w
1230 m	1185 s			1185 w	1220 w
1205 w	1170 w			1150 w	
1185 m	1155 w				
1165 m					

^{a} Abbreviations: s, strong; m, medium; w, weak.

at room temperature. Decomposition is accompanied by a disappearance of the nitrile bands.

In acetonitrile the reduction of Cu(*trans*-diene)$^{3+}$ liberates acid. Figure 7 shows the change in potential of a pH electrode suspended in solution. The appearance of acid causes a positive swing in potential. The total amount of acid liberated was not determined.

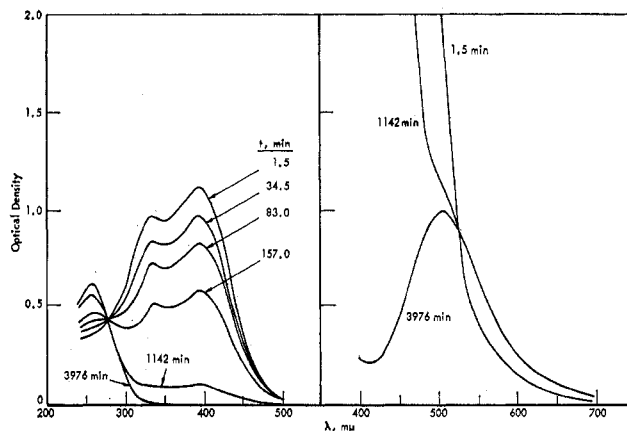In a single experiment a massive oxidative electrolysis

Figure 6.—Spontaneous reduction of Cu(*trans*-diene)(ClO$_4$)$_3$ in acetonitrile at room temperature as a function of time.
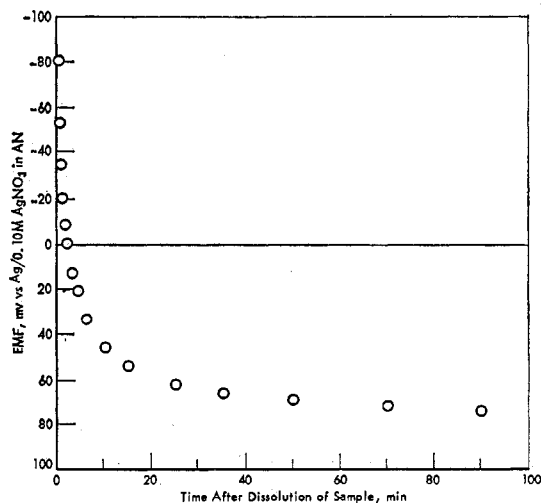

Figure 7.—Liberation of acid by spontaneous reduction of Cu(*trans*-diene)$^{3+}$ in acetonitrile at room temperature followed by a glass pH electrode.

of about 3 g of Cu(*trans*-tetramine)(BF$_4$)$_2$ in 110 ml of acetonitrile at 41° was carried out. An attempt was made to find and identify any organic products resulting from the spontaneous reduction of the Cu-(III) compound. About 1150 C was passed which is equivalent to 1.9 cycles of the type

$$CuL^{2+} \xrightarrow{\text{electrode}} CuL^{3+}$$
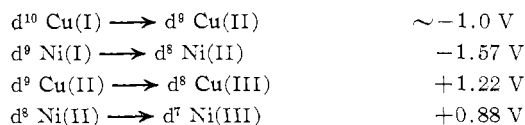$$\uparrow \underline{\quad + R \quad} |$$
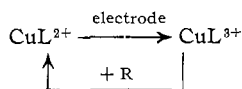
where R is the reducing agent. No organic products were detected by glc of the final solution. Approximately 1 mol of strong acid was formed per coulomb of electricity. About 75% of a Cu(II) complex was recovered indicating that some decomposition had occurred. Part of the Cu(II) compound recovered was unchanged, but part differed by the presence of an ir band at 6 μ where the C=N stretch occurs. A uv spectrum of the latter material was nearly identical with that of Cu(*trans*-diene)$^{2+}$.

Discussion

Electrochemistry.—The electrochemical behavior of the Cu(II) cyclic amines in acetonitrile follows a pattern similar to that of the Ni(II) complexes. Both undergo one-electron reduction and oxidation to form the monovalent and trivalent metal complexes. Some differences do, however, exist between the copper and nickel systems. For the M(II) → M(I) step, the $E_{1/2}$ values for the unsaturated and saturated nickel complexes are essentially identical, whereas the unsaturated copper complex is easier to reduce by about 70 mV then the saturated compound. This could be due to better stabilization of the Cu(I) state by the unsaturated ligand, perhaps due to π back-bonding between the metal and the amine groups. A M(I) → M(0) step is observed for copper but not for nickel. This step occurs at −0.93 V in the case of the unsaturated copper compound. As a consequence the cathodic wave obtained for the nickel complex at −2.7 V corresponding to the reduction of the C=N groups does not occur for copper. Apparently the imine group must be coordinated to a metal to be electroactive. This wave is not observed for copper either because the interaction between the imine group and Cu(0) is too weak to make it electroactive or the Cu(0) complex decomposes before reduction can occur.

A comparison of the half-wave potentials of the reduction and oxidation waves of the copper and nickel complexes reveals some interesting relationships between the redox potentials and electronic structure. Such a comparison is of special interest for these cyclic amine systems because the ligand environments are essentially identical. This provides a better opportunity to separate the effects of oxidation state and the number of d electrons. For this purpose the $E_{1/2}$ values (for reversible electrode reactions, $E_{1/2}$ and the standard redox potential, $E°$, are essentially equal) of the saturated complexes, which tend to give the

most reversible waves, are reproduced below.

d^{10} Cu(I) → d^9 Cu(II)		∼−1.0 V
d^9 Ni(I) → d^8 Ni(II)		−1.57 V
d^9 Cu(II) → d^8 Cu(III)		+1.22 V
d^8 Ni(II) → d^7 Ni(III)		+0.88 V

The $E_{1/2}$ values exhibit a strong dependence on the nature of the central metal ion. A large shift in $E_{1/2}$ is observed as a result of altering either the number of d electrons or the oxidation state. Increasing the number of d electrons, while keeping the oxidation state constant, gives rise to a positive shift in $E_{1/2}$. Thus, Cu(II), a d^9 metal, is more difficult to oxidize than Ni(II), a d^8 metal. If the number of d electrons is held constant and the oxidation state is increased, a more dramatic positive shift in $E_{1/2}$ is observed. For example, Cu(II) is more difficult to oxidize than Ni(I) by 2.8 V.

A dependence is also observed of $E_{1/2}$ on I_p, the ionization potential of the corresponding gaseous central metal ion, as seen for the electrode reactions

	$E_{1/2}$, V	I_p, V
Ni(I) → Ni(II)	−1.57	18.2
Cu(I) → Cu(II)	−1.0	20.3
Ni(II) → Ni(III)	+0.88	35.2
Cu(II) → Cu(III)	+1.22	36.8

The shift in $E_{1/2}$ parallels the change in I_p. Thus, as it becomes more difficult to extract an electron from the gaseous metal ion, the corresponding metal complex becomes more difficult to oxidize (more positive $E_{1/2}$). (A similar relationship between the standard potentials of a series of M(H$_2$O)$_6$$^{3+}$–M(H$_2$O)$_6$$^{2+}$ couples and I_p has been noted previously.[9]) The result of this effect can also be seen with other metal complexes in the fact that the higher oxidation states of the transition metals become more stable as one proceeds to the left of the series. For example, Cu(III) is rare whereas Cr(III) is common.

Spectra.—The wavelengths and intensities of the uv and visible spectra of both the copper and nickel complexes are given in Table IV. Low-intensity (ϵ <150) visible bands due to d–d transitions are observed with some but not all of the complexes. When they are not observed, it is probably due to masking by high-intensity, low-energy charge-transfer bands (*e.g.*, Cu(III) and Ni(I)). A charge-transfer band at 283 mμ present in the unsaturated Ni(II) complex has been assigned to the azomethine group.[10] The 262- and 415-mμ bands in the corresponding Cu(II) and Cu(I) complexes, respectively, have also been assigned to a charge transfer involving the azomethine group.[2] By analogy the 472-mμ band in the Ni(I) complex probably has the same explanation. These bands are believed to be due to a metal→ligand transition because of the direction of their shift on changing the central metal ion. They appear to be absent in the Cu(III) complexes which is consistent with a metal→ligand transition. Other charge-transfer bands

(9) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1960).
(10) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

occur in all of the compounds. Comparison of the saturated d^9 complexes (Cu(II) and Ni(I)) indicates that at least the 375-mμ band in the Ni(I) complex is due to a ligand→metal transition since the only charge-transfer band in the Cu(II) complex occurs at a lower wavelength (273 mμ). Several ligand→metal charge-transfer bands also appear in the Ni(I) unsaturated complex which are not present in the corresponding Cu(II) complex. Comparing the d^8 complexes, the two charge-transfer bands present in the Cu(III) complexes shift to shorter wavelengths on going to Ni(II) and must therefore be due to ligand→metal transitions.

Reactions of the Cu(I) and Cu(III) Complexes.— One of the interesting reactions of Cu(*trans*-tetramine)$^+$ is its disproportionation, $2CuL^+ \rightarrow CuL^{2+} + Cu$. This reaction is obviously catalyzed by certain surfaces such as mercury and glass. Thus, a one-step, two-electron reduction of Cu(*trans*-tetramine)$^{2+}$ is observed at the dme and Cu(*trans*-tetramine)$^+$ gives a single composite cathodic–anodic wave. At Pt, which does not catalyze the disproportionation, a two-step reduction of the Cu(II) complex is obtained. In a glass vial the rate of disproportionation of the Cu(I) complex drops drastically as soon as the surface is copper plated.

The Cu(III) complexes are unstable in acetonitrile at room temperature undergoing spontaneous reduction to the Cu(II) compounds. As a cold 1 mM solution of the Cu(III) complex is slowly warmed to room temperature, the redox reaction can be followed spectrophotometrically. The presence of isosbestic points in the changing spectra indicates a single absorbing reaction product. When the reaction is carried out at higher concentration and temperature in the presence of the electrode, oxidation of the ligand definitely occurs. Thus, when Cu(*trans*-tetramine)$^{2+}$ is continuously oxidized at an electrode to the Cu(III) complex at 41°, the copper complex recovered from the reaction solution contains material whose uv spectrum matches that of the unsaturated Cu(II) complex. This can be accounted for by an internal redox process of the type
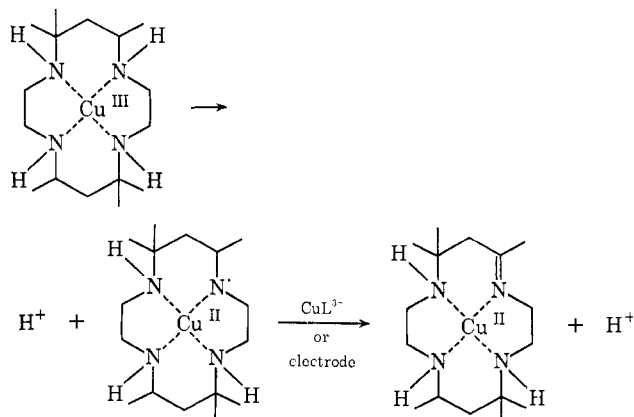
Experimental Section

Apparatus.—The polarograph, recorder, polarographic cell and

electrodes, potentiostat, electronic integrator, and electrochemical procedures are described in a previous report.[1]

A jacketed H cell was used for constant-potential electrolysis. The cell consisted of 25-ml sample and auxiliary compartments separated by a small center compartment. A Corning medium frit was placed between the sample and center compartments and a Corning coarse frit was used between the center and auxiliary compartments. The center section could be filled independently through a standpipe.

Electrochemical measurements were generally carried out at $25.0 \pm 0.1°$. For the low-temperature work, a circulating Dry Ice–IPA bath was used. The temperature, which was monitored with a thermometer in the cell, could be regulated to $\pm 0.5°$ by controlling the rate of circulation of the coolant.

Nearly all the work was carried out in a Vacuum Atmospheres Dri Lab with an N_2 atmosphere. The oxygen and water concentrations were at a few parts per million or less.

Ir spectra in KBr were taken with a Beckman IR-8 provided with an N_2 purge in the sample compartment.

Ultraviolet and visible spectra were obtained with a Cary 14 automatic recording spectrophotometer. The cell compartment was provided with an N_2 atmosphere. The measurements were made using 0.01-, 0.1-, and 1.0-cm cells. The sample concentrations could then be held high enough so that small amounts of impurities would not destroy the very reactive complexes.

The pH meter was an Orion Model 801, used with an A. H. Thomas glass electrode.

Reagents.—The acetonitrile used for the electrochemical work was MCB Pesticide quality purified by a procedure previously described.[11] Ethyl ether was distilled from Na–K alloy and THF from LiAlH$_4$. Acetonitrile used under other circumstances and other solvents were dried over calcium hydride and passed through a column of activated alumina. All solvents were distilled under N_2 and 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 where possible by dissolving a weighed quantity in a measured volume of acetonitrile which was 0.10 M in tetraethylammonium perchlorate. In the case of CuA$^+$ and both of the Cu(III) complexes, the compounds were generated *in situ* by constant-potential electrolysis at low temperatures. The measurements on the Cu(III) complexes were made at the temperature of generation, while the CuA$^+$ solution was first diluted and warmed to 25.0°.

The Pt electrode used for cyclic voltammetry was stored in an inert atmosphere. The only pretreatment used prior to measurements consisted of cycling it between the potential limits in acetonitrile. Reproducibility of voltammograms was usually 10–20 mV.

The ultraviolet and visible spectra were taken of 10–50 mM solutions prepared from the crystalline materials. The amount of decomposition of Cu(III) to Cu(II) was determined spectrally and a correction could be made. Total copper in the case of CuL^{3+} was determined analytically.

Ir spectra were taken in KBr immediately after isolation of the complexes.

The Cu(III) compounds were kept at -15 to $-20°$ until just before their use. At the concentrations used, no more than 20% decomposition occurred before a measurement could be made.

Preparative Chemistry.—It should be pointed out that all copper perchlorate compounds are potentially explosive. The Cu(III) complexes do explode easily, making basic analyses impossible.

NOBF$_4$.—The preparation of NOBF$_4$ was based on published work.[12]

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

(12) B. J. Hathaway, D. G. Holah, and A. E. Underhill, *J. Chem. Soc.*, 2444 (1962).

Concentrated HBF_4 was heated with a stream of N_2 blowing over it until fuming started. A platinum dish should be used. The acid was cooled in an ice bath and N_2O_4 was bubbled in under N_2. A white material formed. The $NOBF_4$ was filtered, yielding a mushy precipitate. The product was dried under vacuum. The material at this point may be somewhat discolored. It was washed three times with acetonitrile and dried. A white powder analyzing very closely as $NOBF_4$ was obtained as the final product. The above procedure can be repeated to obtain a second crop. Twelve grams of $NOBF_4$ can be made from 60 ml of HBF_4.

$Cu(CH_3CN)_4(BF_4)_2$.—The preparation of $Cu(CH_3CN)_4(BF_4)_2$ is reported in the literature.[12]

One hundred milliliters of dry ethyl acetate was added to a mixture of 0.6 g of pure copper metal and 2.5 g of $NOBF_4$. The reaction flask was stirred and maintained under vacuum in order to remove the NO that forms. Failure to remove the gas can lead to side reactions. If copper foil is used, the reaction may take 24 hr; with fine copper powder, only 2–3 hr is required. After gas evolution had ceased, the solution was filtered (to remove slight excess of metal) and $Cu(CH_3CN)_4$-$(BF_4)_2$ precipitated by adding acetonitrile.

Anhydrous *trans*-Tetramine.—The preparation of (*trans*-tetramine)$\cdot 2H_2O$ has been described.[10] To a few grams of the dihydrate were added 50 ml of THF and sodium amalgam. All of the amine may not be soluble. The mixture was refluxed for several hours and then cooled. The light precipitate was filtered and recrystallized from THF or CH_3CN to remove the finely divided Hg.

Cu(*trans*-tetramine)$(BF_4)_2$.—Two to three grams of Cu-$(CH_3CN)_4(BF_4)_2$ and an equivalent amount of the anhydrous amine were added to 50 ml of CH_3CN. The solution was refluxed for 1 hr. Addition of ether yielded $CuL(BF_4)_2$. Fast crystallization gave a powder. Slow crystallization gave CuL-$(BF_4)_2 \cdot 2CH_3CN$ with the nitriles held very loosely.

Cu(*trans*-tetramine)$^+$.—Constant-potential electrolysis was used to prepare Cu(*trans*-tetramine)$^+$. A solution of 0.9 g of the Cu(II) complex in 25 ml of acetonitrile was placed in the sample and center compartments of the electrolysis cell. An acetonitrile–tetraethylammonium tetrafluoroborate (TEABF$_4$) solution was used in the auxiliary compartment. Reduction was carried out at -1.2 V at $-20°$ at a platinum foil electrode until the current had dropped to 3% of its original value. The resulting solution was nearly colorless, with a slight tinge of violet. The Cu(*trans*-tetramine)(BF_4) was not isolated from solution.

Cu(*trans*-diene)$(ClO_4)_2$.—Twenty grams of $Cu(ClO_4)_2 \cdot 6H_2O$ was dissolved in 200 ml of 2B alcohol. Then 20 ml of concentrated NH_4OH was added slowly with cooling. The light blue precipitate that formed was filtered and air dried $[Cu(NH_3)_6$-$(ClO_4)_2 \cdot xH_2O]$.

The copper–ammonia complex was added to $\sim$150–200 ml of acetone, yielding a dark blue precipitate. The mixture was allowed to reflux for 1 hr. Next 15.4 ml of ethylenediamine was added with cooling. All precipitate dissolved. The solution was refluxed for $\sim$24 hr. Ammonia was given off and the solution turned dark red.

The solution was cooled to room temperature and the excess acetone was removed under vacuum. Enough absolute ethanol was added to induce crystallization (250–350 ml). The orange product was recrystallized several times. *Anal.* Calcd for Cu(*trans*-diene)$(ClO_4)_2$: Cu, 11.7; C, 35.4; H, 5.9; N, 10.3; Cl, 13.1; O, 23.6. Found: Cu, 11.7, C, 35.5; H, 6.0; N, 10.4; Cl, 13.2; O, 24.0.

Cu(*trans*-diene)(ClO_4).—This was prepared by constant-potential electrolysis. One and a half grams of the Cu(II) complex was dissolved in 25 ml of acetonitrile. The solution was used to fill the sample, reference, and center compartments of the cell. Tetraethylammonium perchlorate (TEAP) was used in the auxiliary compartment. Electrolysis was carried out at -1.5 V at a platinum foil electrode until the reduction was 97% complete. During the reduction the solution turned yellow.

On evaporating the solution under vacuum, the first precipitate to appear was yellowish green and was discarded. The next 500 mg was bright yellow and was dried under vacuum at room temperature. The sample was shown to be pure by polarography ($<3\%$ CuL^{2+}). *Anal.* Calcd for Cu(*trans*-diene)(ClO_4): Cu, 14.0; C, 43.2; H, 7.2; N, 12.6; Cl, 7.9; O, 14.5. Found: Cu, 13.8; C, 43.8, H, 7.5; N, 12.7; Cl, 8.5; O, 14.5.

Cu(*trans*-tetramine)$(BF_4)_3 \cdot 2CH_3CN$ and Cu(*trans*-diene)-$(ClO_4)_3 \cdot 2CH_3CN$.—The Cu(III) complexes were also prepared by constant-potential electrolysis. The temperature of the cell was maintained below $-14°$. About 1 g of the starting material [Cu(*trans*-tetramine)$(BF_4)_2$ or Cu(*trans*-diene)$(ClO_4)_2$] was dissolved in 25 ml of acetonitrile. TEABF$_4$ or TEAP was used in the auxiliary compartment of the electrolysis cell. The oxidation was carried out at $+1.4$ V at a platinum foil electrode to about 97% completion. The solutions were handled at $-18°$ using an ethylene glycol–Dry Ice bath. The solvent was removed under vacuum and the product was dried under vacuum for 2 days.

Voltammograms of the products at $-15°$ showed Cu(*trans*-diene)$(ClO_4)_3$ complex to be 98% pure. The Cu(*trans*-tetramine)$(BF_4)_3$ was 81% pure (19% CuL^{2+}). Both of the Cu(III) complexes were orange-red.

Perchlorate and copper analyses were carried out on a solution of Cu(*trans*-diene)$(ClO_4)_3$. The ClO_4:Cu ratio was found to be 3.0. Other elemental analyses were not carried out because of the instability of the $+3$ complexes at room temperature. From the presence of nitrile bands in the ir and by analogy with the Ni(III) complexes, it is proposed that the complexes are $(AN)_2$-Cu(*trans*-tetramine)$(BF_4)_3$ and $(AN)_2Cu$(*trans*-diene)$(ClO_4)_3$.