the complex must be considered less likely than linkage rearrangement.

Solutions of the monotriphenylphosphine derivative in acetonitrile also exhibit infrared spectra distinct from those recorded for the chloroform solutions. However, the reaction that goes to a virtual completion with the arsine complex now appears to be arrested at an intermediate stage. Preliminary spectral measurements indicate attainment of an equilibrium, possibly between the S- and N-bonded linkage isomers of the tetracarbonyl. However, a more complicated behavior, involving also partial replacement of triphenylphosphine by acetonitrile, cannot be ruled out at present.

Finally, it is of interest to compare and contrast our results with those obtained by Burmeister and Basolo[6] for some palladium(II) square-planar thiocyanato complexes.[26] The latter study demonstrated that small differences in ligand structure frequently cause changes in metal–thiocyanate attachment. For example, the complex $Pd(py)_2(NCS)_2$[27] is N-bonded whereas the 4-methylpyridine analog is S-bonded. Furthermore, $Pd[P(C_6H_5)_3]_2(NCS)_2$ and the thermodynamically stable isomer of $Pd[As(C_6H_5)_3]_2(CNS)_2$ are isothiocyanates, but $Pd[Sb(C_6H_5)_3]_2(SCN)_2$ is a thiocyanate. These variations in bonding were attributed to steric and/or electronic factors. By way of contrast, the six-coordinate manganese(I) complexes reported herein do not exhibit such striking differences in metal–thiocyanate bonding with small changes in ligand structure. The derivatives $Mn(CO)_3(py)_2NCS$ and $Mn(CO)_3(\gamma\text{-pic})_2NCS$ contain the same type of Mn–CNS linkage, as do also all carbonyls of the same stereochemistry containing $P(C_6H_5)_3$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$. Therefore, comparison of the results of the two investigations furnishes additional support to our contention that the degree of π bonding, rather than small electronic and steric differences among other coordinated ligands, is the most important single factor determining the type of metal–thiocyanate bonding in carbonyl complexes. Whether this explanation is general or limited only to six-coordinate systems cannot be ascertained at present. However, studies are in progress on thiocyanatocarbonyl complexes of other geometries in order to resolve the issue in question.

Acknowledgment.—The financial support of this investigation by the National Science Foundation is gratefully acknowledged.

[26] Palladium(II) rather than platinum(II) is selected because of the smaller size of the former, which makes comparison with manganese(I) more meaningful.

[27] This and the other thiocyanato complexes of Pd(II) most likely have *trans* structures; see ref. 6.

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Chloro Complexes of Copper(II) and Copper(I) in Acetonitrile

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The stepwise formation constants of the chloro complexes of copper(II) and of copper(I) in acetonitrile have been evaluated by a combination of spectrophotometric and electrochemical methods. Log K values in acetonitrile for the copper(II) complexes are 9.7, 7.9, 7.1, and 3.7, and for the copper(I) complexes 4.9 and 5.9.

The stepwise formation constants of $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$ in water are only 1, 0.2, 0.04, and 0.01, respectively.[1] Because copper(II) and chloride ions are significantly more weakly solvated in acetonitrile than in water,[2] information on the chloro complexes of copper(II) in acetonitrile is, therefore, of considerable fundamental importance. The much higher solvation energy of copper(I) ion in acetonitrile than in water makes the study of the chloro complexes of copper(I) also of special interest.

From spectrophotometric study of acetonitrile solutions of copper(II) and chloride, Baaz, Gutman, Hampel, and Masagner[3] have estimated the stepwise formation constants of the chloro complexes of copper(II) to be $K_{CuCl^+} > K_{CuCl_2} \geq K_{CuCl_3^-} > K_{CuCl_4^{2-}}$. Bromide ion and copper(II) ion have been found to form only two species, $CuBr_3^-$ and $CuBr_4^{2-}$, in acetonitrile.[4] Quantitative study of these complexes in acetonitrile is complicated by the oxidation of bromide by copper(II).

Experimental

Reagent grade acetonitrile was distilled twice from phosphorus pentoxide and the fraction boiling at 81.0 ± 0.5° collected. Tetraethylammonium perchlorate, $(C_2H_5)_4NClO_4$, was prepared by adding a slight excess of 70% reagent grade perchloric acid to Eastman aqueous 10% tetraethylammonium hydroxide. The product was recrystallized twice from water and dried under vacuum at 80° for 48 hr. Eastman tetraethylammonium chloride, $(C_2H_5)_4NCl$, was purified by recrystallization from acetonitrile. Copper(II) perchlorate hexahydrate (G. F. Smith Chemical Co.) was dried *in vacuo* at 70° for 48 hr.

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[1] J. Bjerrum, *Kem. Maanedsblad*, **26**, 24 (1945).

[2] I. M. Kolthoff and J. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).

[3] M. Baaz, V. Gutman, G. Hampel, and J. Masagner, *Monatsh. Chem.*, **93**, 1416 (1962).

[4] J. Barnes and D. Hume, *Inorg. Chem.*, **2**, 444 (1963).

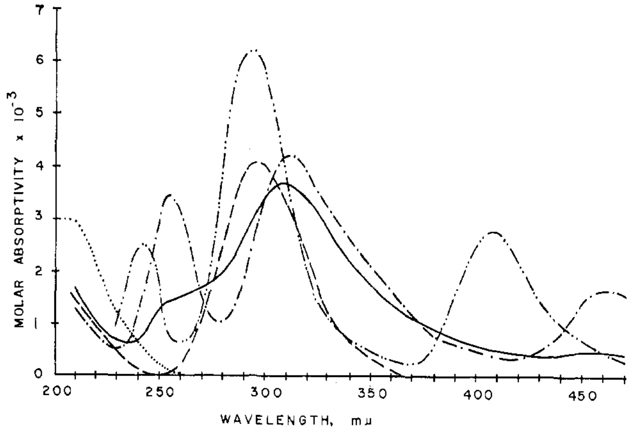

Figure 1.—Effect of chloride ion on the spectrum of copper(II) perchlorate in acetonitrile in the 200–470 mμ region (concentration of $Cu(ClO_4)_2$ 2.2 × 10^{-4} *F*). $Cl^-/Cu(II)$ ratio: ······, 0; – – – –, 1.00; ———, 2.00; –·–·–, 3.00; and –··–··, 500.

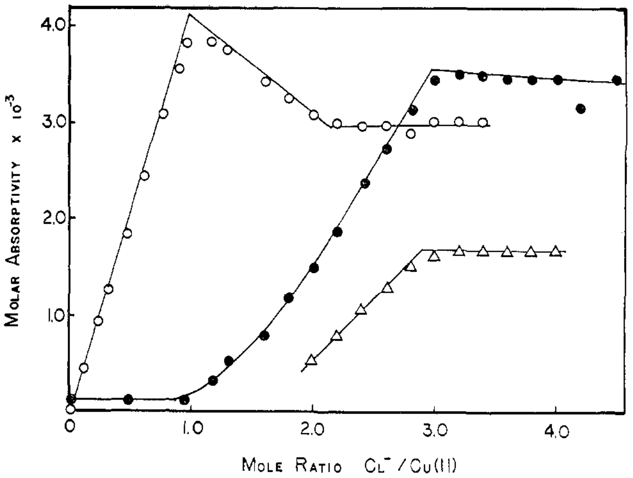

Figure 2.—Molar absorptivity (based on total copper(II) concentration) at 296 mμ, ○; 255 mμ, ●; and 462 mμ, △ *vs.* mole ratio $Cl^-/Cu(II)$ plots. Concentration of copper(II) perchlorate 2.2 × 10^{-4} *F*.

A controlled potential polarograph of the type designed by Kelley, Jones, and Fisher was used to obtain the current–voltage curves. A Leeds and Northrup pH indicator was used in the potentiometric studies. A Beckman DU, a Cary Model 14, and a Perkin-Elmer Model 421 spectrophotometer were utilized in the spectral studies.

Results and Discussion

Spectrophotometric Study.[5]—The chloride complexes of copper(II) have intense ultraviolet charge-transfer absorption bands The spectra observed at various chloride to copper(II) ratios are shown in Figure 1. Acetonitrile solutions of copper(II) perchlorate show an absorption edge in the 200–250 mμ region. As chloride is added, an intense absorption band appears at 296 mμ. The absorbance of this band increases with chloride until the chloride to copper(II) ratio reaches 1:1. As the chloride to copper(II) ratio is increased from 1:1 to 2:1, the band at 296 mμ broadens, decreases in intensity, and shifts to 308 mμ. Solutions in which the total chloride to total copper(II) ratio is between 2:1 and 3:1 show in addition to the band at *ca.* 310 mμ two new bands, one at 255 mμ and the other at 462 mμ. The intensity of these new bands increases with added chloride until the ratio of chloride to copper(II) reaches 3:1. In addition, the band at 308 mμ shifts to 312 mμ. The intensity of this latter band, however, increases much more slowly with increasing chloride concentration than the 255 or the 462 mμ band. These marked spectral changes with increasing chloride concentration cease abruptly at a chloride to copper(II) ratio of 3:1. Beyond this point, the spectra of copper(II) chloride solutions change slowly with added chloride and show isosbestic points at 382 and 442 mμ. Finally, in a large excess of chloride (500:1) a fourth entirely different spectrum is observed with bands at 242, 293, and 406 mμ.

Examination of the spectra and of the absorbance *vs.* mole ratio plots at 255 ($CuCl_3^-$), 296 ($CuCl^+$), and 462 mμ ($CuCl_3^-$) indicates the formation of $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$ (see Figure 2). In solutions containing as much as 0.1 *F* chloride to 2.2 × 10^{-4} *F* copper(II) no evidence for any higher complexes was found. Evaluation of the spectral data of solutions with low chloride to copper(II) ratios indicates that the first three complexes are quite stable (the stepwise formation constants must be at least 10^7) and the fourth is definitely less stable than the first three. Absorbance measurements at 405 mμ ($CuCl_4^{2-}$) and 462 mμ ($CuCl_3^-$) of high chloride solutions indicate the stepwise formation constant of $CuCl_4^{2-}$ to be (5.0 ± 0.5) × 10^3. [The following spectral data ($C_{(C_2H_5)_4NCl}$, absorbancy) were used: For $Cu(ClO_4)_2$ solution 4.0 × 10^{-4} *F* at 405 mμ: (1.20 × 10^{-3}, 0.208 and 0.210), (1.80 × 10^{-3}, 0.498 and 0.502), (2.40 × 10^{-3}, 0.677 and 0.683), (3.00 × 10^{-3}, 0.760 and 0.762), (4.20 × 10^{-3}, 0.845 and 0.856), (6.00 × 10^{-3}, 0.913 and 0.925). For $Cu(ClO_4)_2$ solution 5.0 × 10^{-4} *F* at 462 mμ: (1.50 × 10^{-3}, 0.842 and 0.850), (2.00 × 10^{-3}, 0.630 and 0.621), (3.00 × 10^{-3}, 0.443 and 0.416), (5.00 × 10^{-3}, 0.325 and 0.322), (7.50 × 10^{-3}, 0.274 and 0.262), (1.00 × 10^{-2}, 0.244 and 0.245).] Because of the high stability of the first three complexes, spectrophotometric evaluation of their formation constants is not possible. The ratio of the stepwise formation constants of $CuCl^+$ and $CuCl_2$ and that of $CuCl_2$ and $CuCl_3^-$, however, can be obtained from absorbance measurements at 296 and 462 mμ, respectively. The ratio K_{CuCl^+}/K_{CuCl_2} was found to be between 10 and 100, and $K_{CuCl_2}/K_{CuCl_3^-}$ was 6 ± 2. As will be seen later, these values are in line with the potentiometric and polarographic data.

Electrochemical Study.[5]—Before the formation constants of the chloro complexes of copper(II) can be evaluated by polarography or potentiometry, the formulas and the formation constants of the chloro complexes of copper(I) must first be established.

Polarographic Study of the Copper(I) Complexes.—The following points call for special consideration in the polarographic investigation of complex formation between copper(I) and chloride ion in acetonitrile:

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[5] For detailed experimental data the reader is referred to S. E. Manahan, Ph.D. Thesis, University of Kansas, 1965.

reversibility of the electrode reaction, liquid-junction potential change at high chloride concentration, effect of ion-pair formation between tetraethylammonium ion and chloride ion and tetraethylammonium ion and perchlorate ion, and correction of the chloride ion concentration for bound chloride in cases in which the total chloride concentration is less than a hundred times the copper(I) concentration.

The reduction of copper(I) ion at the dropping mercury electrode (d.m.e.) in acetonitrile 0.10 F in $(C_2H_5)_4NClO_4$ proceeds reversibly at −0.32 v. *vs.* s.c.e. In the presence of chloride, however, the polarographic wave assumes an irreversible form as indicated by a slope greater than 0.059 for the plot of $E_{\text{d.m.e.}}$ *vs.* log $(i_d - i)/i$; typical values are 0.075 in 0.010 F chloride and 0.090 in 0.10 F chloride. As the chloride concentration or the copper(I) concentration is increased, the wave becomes more irreversible. Above 5×10^{-4} F for the copper(I) concentration in chloride medium the waves are unsuitable for analysis. When the copper(I) concentration is kept low (10^{-4} F), however, the slope of the $E_{\text{d.m.e.}}$ *vs.* log $(i_d - i)/i$ plot has the reversible value of 0.059 for the foot of the polarographic wave, *i.e*, in the region from zero current to *ca.* $^1/_5\, i_d$, up to a value of 0.10 F for the chloride concentration. With a dropping copper amalgam electrode, the composite anodic–cathodic waves of copper(I) solutions containing chloride pass through zero current without inflection. This characteristic of the composite anodic–cathodic waves suggests that potential values near zero current are quite close to the reversible values. Using the above information, we have obtained half-wave potentials for conventional polarograms of copper(I) solutions containing chloride and dropping copper amalgam electrode polarograms of low chloride solutions by fitting a model of a reversible wave to the foot of each experimental wave. In the latter case, the half-wave potential determined by this technique is that for the ligand concentration in the bulk of the solution (and at the electrode surface at zero current). Half-wave potentials for chloride–copper(I) solutions were also obtained by the use of a dropping copper amalgam electrode (d.a.e.) of the appropriate concentration so that the half-wave potentials of the composite anodic–cathodic waves occurred very near zero current.

Changes in liquid-junction potential at high chloride concentrations were estimated from the changes in half-wave potential for the oxidation of ferrocene.[6] In 0.1 F $(C_2H_5)_4NClO_4$, the half-wave potential for the oxidation of ferrocene in acetonitrile is +0.396 v. *vs.* s.c.e., whereas in 0.1 F $(C_2H_5)_4NCl$ it is +0.445 v. *vs.* s.c.e. A half-wave potential measured in 0.1 F $(C_2H_5)_4NCl$ is corrected to 0.1 F $(C_2H_5)_4NClO_4$ medium by subtracting 0.049 v. A proportional correction is made in mixtures of $(C_2H_5)_4NCl$ and $(C_2H_5)_4NClO_4$.

Ion-pair formation between $(C_2H_5)_4N^+$ and Cl^- and $(C_2H_5)_4N^+$ and ClO_4^- affects the chloride ion concentration. The following ion-pair formation constants have been used to establish the free chloride ion concentration in acetonitrile: $K_{(C_2H_5)_4N^+,ClO_4^-} = 11.2$; $K_{(C_2H_5)_4N^+,Cl^-} = 35$.[7]

The formulas and stepwise formation constants of the complexes of copper(I) ion with chloride ion in acetonitrile may be evaluated from the expression below for the dependency of the half-wave potential of the Cu(I),Cu(Hg) wave on the concentration of chloride: $(E_{1/2})_c - (E_{1/2})_s = -0.059 \log \{1 + K_1 \cdot [Cl^-]_0 + \ldots\ldots + K_1 \ldots K_p[Cl^-]_0^p\}$.[8] The K's are the stepwise formation constants of the copper(I) complexes and subscript zero denotes concentration at the electrode surface. The other terms have their usual significance.[9]

Plots of $(E_{1/2})_c - (E_{1/2})_s$ *vs.* −log $[Cl^-]$ of the d.m.e. data for 5×10^{-4} F copper(I) solutions 10^{-3} to 5×10^{-2} F in chloride and 0.10 F in $(C_2H_5)_4NClO_4$ and of the combined d.a.e. data for 0.10 F $(C_2H_5)_4NClO_4$ solutions 5×10^{-4} F in copper(I) and 3×10^{-4} to 4×10^{-2} F in chloride and without copper(I) and 3×10^{-5} to 4×10^{-2} F in chloride were straight lines with slopes of 0.116 and 0.112, respectively, indicating $CuCl_2^-$ as the only copper(I) complex present in solution in the concentration range of chloride investigated. The over-all formation constant for $CuCl_2^-$, $\beta_{CuCl_2^-}$, from both sets of data is $10^{11.0}$. If we assume that below 3×10^{-5} M chloride the plot of $(E_{1/2})_c - (E_{1/2})_s$ *vs.* −log $[Cl^-]$ changed from a 0.118 slope to a 0.059 slope, a maximum value for the formation constant of CuCl of $10^{6.5}$ is obtained.

Potentiometric Study of the Copper(I) Complexes.—The stepwise formation constants of CuCl and $CuCl_2^-$ were evaluated from potentiometric data obtained from the titration of 5.00×10^{-4} F copper(I) solution 0.10 F in $(C_2H_5)_4NClO_4$ with a 2.50×10^{-3} F solution of chloride. The concentrations of $(C_2H_5)_4NClO_4$ and of copper(I) were kept constant by making the titrant also 5.00×10^{-4} F in copper(I) and 0.10 F in $(C_2H_5)_4NClO_4$. The titration curve shows only one break at a ratio of 2:1 for added chloride to copper(I), indicating, as suggested in the polarographic work, that the formation constant of CuCl is not much greater than that for $CuCl_2^-$. From potential data beyond the break in the titration curve, average values of 2.1 for ligand number and $10^{10.8}$ for $\beta_{CuCl_2^-}$ were calculated. These values are in good agreement with those obtained by polarography. An expression similar to that described previously for the analysis of the polarographic data was used to evaluate these two quantities.

The formation constant of CuCl was calculated from potential information on solutions of low formal chloride concentration, up to a ratio of chloride to copper(I) of 2:1. Use was made of the following relationships: total chloride = $[Cl^-] + [(C_2H_5)_4NCl] + [CuCl] + 2[CuCl_2^-]$, and total copper(I) = $[Cu^+] + [CuCl] + [CuCl_2^-]$. The over-all formation constant for $CuCl_2^-$, $\beta_{CuCl_2^-}$, was taken to be $10^{10.8}$. The values

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[6] I. V. Nelson and R. T. Iwamoto, *Anal. Chem.*, **35**, 867 (1963).

[7] C. W. Davies, "Ion Association," Butterworths, London, 1962, p. 96.

[8] H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 286.

[9] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, 2nd Ed., Interscience Publishers, New York, N. Y., 1952, Chapters 11, 12.

for $K_{(C_2H_5)_4N^+,ClO_4^-}$ and $K_{(C_2H_5)_4N^+,Cl^-}$ have been given previously. The concentration of copper(I) was calculated from the Nernst relationship. From the examination of a number of points before the break in the titration curve, an average value for K_{CuCl} of $10^{4.9\pm0.2}$ was obtained. The constant $K_{CuCl_2^-}$, therefore, is $10^{5.9\pm0.2}$, and the equilibrium constant for the disproportionation reaction $2CuCl \rightleftharpoons Cu^+ + 2CuCl_2^-$ is 10. A similar disproportionation reaction has been observed in acetonitrile for copper(II) bromide.[4]

Nature of the Copper(I) Complexes.—Copper(I) perchlorate precipitated from acetonitrile has the following composition: $Cu(CH_3CN)_4ClO_4$. This copper(I) acetonitrile solvate can be exposed to the atmosphere for several hours without any evidence of decomposition. To determine whether the dichlorocopper(I) anion has the composition $Cu(CH_3CN)_2Cl_2^-$, we prepared equimolar mixtures of copper(I) chloride and $(C_2H_5)_4NCl$ in acetonitrile and evaporated the solvent under nitrogen. A white solid which was quite stable when kept under nitrogen was obtained. Within a matter of minutes after exposure to the atmosphere, however, the white solid turns dark brown. The white material shows no trace of a nitrile band in the 2300 cm.$^{-1}$ region in the infrared. The sirup formed by adding acetonitrile to the white solid so that CH_3CN:Cu(I) is 2.0 also shows no band for bound nitrile in the infrared.

Copper(I) chloride reprecipitated from acetonitrile is white and, when dry, is stable for several hours in the atmosphere. Again there is no infrared band for bound nitrile. Likewise, a 1:1 slurry of CuCl and acetonitrile shows no bound nitrile band. It appears that the replacement of an acetonitrile molecule in the coordination sphere with chloride ion alters markedly bonding of the other nitrile molecules in the coordination sphere to copper(I) ion.

Voltammetric Study of the Copper(II) Complexes.—The current–voltage curves obtained with a rotating platinum electrode (r.p.e.) of 0.1 *F* $(C_2H_5)_4NClO_4$ solutions of copper(I), of copper(II), and of mixtures of copper(I) and copper(II) in which (total chloride)/(total copper) is between zero and three are split into two steps, a somewhat drawn-out step at *ca.* +1 v. s.c.e. and a well-defined step at *ca.* +0.5 v. *vs.* s.c.e. The height of the more positive step is related to the total wave height by the ratio [(total copper) − (total chloride)/3]/total copper. When the chloride to copper ratio exceeds 3, the wave, no longer split, shifts to negative potentials with increasing chloride concentration.

The split wave may be understood by considering the following Nernst expression for the potential at any point on the curve (eq. 1) where β represents the over-all formation constants for the respective species and subscript zero denotes concentration at the electrode surface. All other terms have their usual significance.[8] If we assume that all copper(II) and copper(I) species diffuse at the same rate $[(i_d)_c - i]/[i - (i_d)_a]$ may be substituted for $[Cu(II)]_0/[Cu(I)]_0$.

$$E_{r.p.e.} = E^{\circ\prime}{}_{Cu^{2+},Cu^+} + 0.059 \log \left\{ \frac{[Cu(II)]_0}{[Cu(I)]_0} \times \frac{1 + \beta_{CuCl}[Cl^-]_0 + \beta_{CuCl_2^-}[Cl^-]_0{}^2}{1 + \beta_{CuCl^+}[Cl^-]_0 + \beta_{CuCl_2}[Cl^-]_0{}^2 + \beta_{CuCl_3^-}[Cl^-]_0{}^3 + \beta_{CuCl_4^{2-}}[Cl^-]_0{}^4} \right\} \quad (1)$$

In this relationship, $(i_d)_c$ is the cathodic diffusion current and $(i_d)_a$ is the anodic diffusion current. The break in the curve is caused by an abrupt increase in chloride ion concentration when the ratio of total chloride to total copper(II) species at the electrode surface reaches a value of 3. This increase in chloride concentration is due to the small formation constants for $CuCl_4^{2-}$ and $CuCl_2^-$ as compared with the large and relatively close values for $CuCl^+$, $CuCl_2$, and $CuCl_3^-$.

Because $CuCl_3^-$ is the only copper(II) species present at the electrode surface in any appreciable amount at the second (more negative) step of the current–voltage curve, the over-all formation constant for $CuCl_3^-$, $\beta_{CuCl_3^-}$, can be calculated from the $E_{1/2}$ value of the second step, the formation constants of the copper(I) complexes, and the calculated free chloride concentration. An average value of $10^{25.1\pm0.2}$ was obtained from a number of current–voltage curves.

The shape of the first (more positive) step of the split wave is determined by the formation constants of $CuCl^+$, $CuCl_2$, and $CuCl_3^-$. The calculated current–voltage curves for solutions in which the chloride to copper ratio is between 0 and 3 using the stepwise constants $K_{CuCl^+} = 10^{10}$, $K_{CuCl_2} = 10^8$, and $K_{CuCl_3^-} = 10^7$ (see next section) for the copper(II) complexes and $\beta_{CuCl_2^-} = 10^{10.8}$ for $CuCl_2^-$ all fit very closely the experimental curves.

Potentiometric Study of Copper(II) Complexes.—The current–voltage curves obtained with a rotating platinum electrode of acetonitrile solutions *ca.* 10^{-4} *F* in copper and *ca.* 10^{-3} *F* in chloride ions are close to, but not completely, reversible. The value for the over-all formation constant $\beta_{CuCl_3^-}$ reported in the previous section, therefore, should be considered as only approximately correct. When the total chloride concentration exceeds *ca.* 0.01 *F*, the current–voltage curves become quite irreversible and the anodic scans do not coincide with the cathodic scans. For solutions containing copper(II) and copper(I), the anodic scan is a single badly drawn-out anodic–cathodic composite wave, whereas the cathodic scan, starting from +1.2 v. *vs.* s.c.e., is a split anodic–cathodic composite wave. In all cases, the anodic and cathodic scans of solutions containing copper(II) and copper(I), however, coincide at zero current. It appears that when no current is drawn, the electrode potential is the reversible value and, therefore, that a potentiometric titration of a copper(II)–copper(I) mixture with chloride would involve reversible potential values and should yield reliable formation constants.

Equimolar mixtures of copper(II) and copper(I) ranging from 10^{-4} to 10^{-3} *F* in each ion were titrated

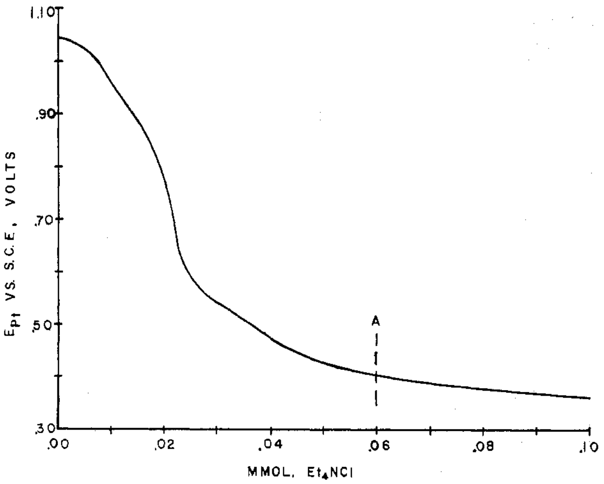

Figure 3.—Potentiometric titration curve of 15 ml. of an acetonitrile solution 0.1 F in $(C_2H_5)_4NClO_4$ containing 0.0075 mmole of $Cu(ClO_4)_2$ and 0.0075 mmole of $CuClO_4$ with 0.010 F $(C_2H_5)_4NCl$ also 0.1 F in $(C_2H_5)_4NClO_4$. Potential values beyond point A were used to evaluate $\beta_{CuCl_3^-}$ and $\beta_{CuCl_4^{2-}}$.

with tetraethylammonium chloride solutions.[10] The solutions of copper(II) and copper(I) and of $(C_2H_5)_4NCl$ were both 0.1 F in $(C_2H_5)_4NClO_4$. A typical titration curve is shown in Figure 3.

Beyond point A in the titration curve, $CuCl_2^-$ is the only copper(I) species and $CuCl_3^-$ and $CuCl_4^{2-}$ are the only copper(II) species present. Using the expression

$$E = E^{\circ\prime}_{Cu^{2+},Cu^{+}} + 0.059 \log \beta_{CuCl_2^-} - 0.059 \log \beta_{CuCl_4^{2-}} - 0.059\{\log (1/K_{CuCl_4^{2-}} + [Cl^-]) + \log [Cl^-]\}$$

we have calculated from potential values beyond point A $\beta_{CuCl_3^-}$ and $\beta_{CuCl_4^{2-}}$. $E^{\circ\prime}_{Cu^{2+},Cu^{+}}$ is the formal potential of the Cu^{2+},Cu^+ couple, +1.05 v. *vs* s.c.e., in acetonitrile (0.1 F $(C_2H_5)_4NClO_4$). The value for the stepwise formation constant of $CuCl_4^{2-}$, 5.0×10^3, evaluated by spectrophotometry (see Spectrophotometric Study) was used. This value for $K_{CuCl_4^{2-}}$ gave a linear plot with a slope of −0.059 for E *vs.* $\{\log (1/K_{CuCl_4^{2-}} + [Cl^-]) + \log [Cl^-]\}$. Four determinations gave an average value for $\beta_{CuCl_4^{2-}}$ of $10^{28.4\pm0.3}$. The formation constant $\beta_{CuCl_3^-}$, therefore, is $10^{24.7\pm0.3}$.

The shape of the titration curve before the large break is a function of the relative magnitudes of the stepwise formation constants of $CuCl^+$, $CuCl_2$, and $CuCl_3^-$. Using the information that $K_{CuCl^+}K_{CuCl_2}\cdot K_{CuCl_3^-}$ is $10^{24.7}$, K_{CuCl^+}/K_{CuCl_2} is 10–100, $K_{CuCl}/K_{CuCl_3^-}$ is 6 (see Spectrophotometric Study), and $K_{CuCl_3^-}$ is $10^{7.1}$ (see last section in Discussion), we have found by the process of curve fitting that the values for the formation constants which best describe the titration curve in this section are $K_{CuCl^+} = 10^{9.7\pm0.1}$, $K_{CuCl_2} = 10^{7.9\pm0.1}$, and $K_{CuCl_3^-} = 10^{7.1\pm0.1}$.

The formation of mixed copper(I)–chloride–copper(II) complexes such as those which have been reported in water[11] would greatly complicate polarographic or potentiometric studies of the chloro complexes of copper(II). Such complexes, if they exist, should be readily detectable by spectrophotometric observation of solutions containing copper(I), copper(II), and chloride at various concentrations. Ultraviolet spectra were taken of a series of solutions containing 2.2×10^{-4} F Cu(II) and 2.2×10^{-2} F Cu(I) with total chloride concentration ranging from 6.6×10^{-4} to 5.5×10^{-2} F. Because the copper(II) concentration had to be kept low owing to the large absorptivity of the copper(II) complexes, the copper(I) concentration was made comparatively high to favor the formation of the binuclear complexes. The spectra obtained are all explainable on the basis of separate copper(I) and copper(II) complexes. Mixed complexes, therefore, are not considered to be a complicating factor at the low concentrations of copper(II) and copper(I) employed in the electrochemical studies.

In the presence of excess Cu^+ the equilibrium $CuCl_3^- + Cu^+ = CuCl_2 + CuCl$ lies appreciably to the right when chloride is present in a 3-fold excess over copper(II). The effect of copper(I) concentration on this equilibrium was studied by following the change in the 462 mμ band for $CuCl_3^-$. A value of $10^{-2.2}$ was obtained for the equilibrium constant. The stepwise formation constant for $CuCl_3^-$, therefore, is $10^{7.1\pm0.3}$.

In summary, the combination of spectrophotometric and electrochemical studies has provided the following stepwise formation constants for the chloro complexes of copper(II) and copper(I) in 0.1 F $(C_2H_5)_4NClO_4$ solution. Copper(II): $K_{CuCl^+} = 10^{9.7}$, $K_{CuCl_2} = 10^{7.9}$, $K_{CuCl_3^-} = 10^{7.1}$, $K_{CuCl_4^{2-}} = 10^{3.7}$. Copper(I): $K_{CuCl} = 10^{4.9}$, $K_{CuCl_2^-} = 10^{5.9}$.

No information is available on the ion-pair formation constants of Cu^{2+}, ClO_4^-; $CuCl^+$, ClO_4^-; $(C_2H_5)_4N^+$, $CuCl_3^-$; etc. The above constants, therefore, are formal formation constants in which no differentiation has been made with regard to free and ion-paired copper and chloro complex species.

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(10) The platinum electrode was pretreated by immersion in concentrated nitric acid for 15 min., then in acidic 0.01 F ferrous sulfate for 15 min., followed by polarization in the solution to be titrated at *ca.* −1.0 v. *vs.* s.c.e. for 1 min., then at 0.0 v. for 5 min.

(11) H. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3164 (1950).