

trations are good indications that $\text{Cu}(t\text{-Buaoac})_2$ is not significantly self-associated in cyclohexane in the vicinity of 25° . The change in epr parameters can thus be ascribed to differences in the solvent- $\text{Cu}(t\text{-Buaoac})_2$ interactions and not to partial dimerization. Assuming that the epr parameters measured in cyclohexane best reflect the true molecular values, then the solvents CCl_4 , C_6H_6 , and HCCl_3 cause an increase in $\langle a \rangle$ which can be contrasted with the large decrease in $\langle a \rangle$ caused by basic solvents like pyridine. The opposite directions for changes in $\langle a \rangle$ could result from different sites for the solvent- $\text{Cu}(\beta\text{-dik})_2$ interactions. Chloroform is known to hydrogen bond with chelate ligand,

and the known weak acceptor properties of carbon tetrachloride and the π -complex forming ability of benzene also suggest that these solvents may interact more with the chelate ligand than with the metal. Donor solvents are distinctly different in that they form well-defined complexes through bonding with the metal.

Acknowledgments.—The authors wish to acknowledge the support of this research by the Advanced Research Projects Agency through Contract No. SD-69 and the National Science Foundation through Grant No. GP-3651.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS 02215

Oxidation-Reduction Chemistry of Coordination Complexes with Macrocyclic Ligands. The $\text{Cu}(\text{trans}[14]\text{diene})^+ - \text{Cu}(\text{trans}[14]\text{diene})^{2+}$ System. Electrochemical, Spectral, and Solution Studies^{1a,b}

By JOAN M. PALMER,^{1c} ELIAS PAPACONSTANTINO, AND JOHN F. ENDICOTT^{1d}

Received January 20, 1969

The very careful electrolytic reduction of the macrocyclic Schiff base amine-copper(II) complex $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ yields a highly reactive yellow complex which appears to be $\text{Cu}(\text{trans}[14]\text{diene})^+$. The cathodic reduction of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ has been examined polarographically and by controlled-potential electrolysis and the conditions for the formation of $\text{Cu}(\text{trans}[14]\text{diene})^+$ are described. The $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ couple is strongly reducing, probably indicating that the ligand provides a somewhat unfavorable coordination environment for copper(I). Comparison of the ultraviolet spectra of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$, $\text{Cu}(\text{trans}[14]\text{diene})^+$, and several $\text{M}(\text{trans}[14]\text{diene})^{2+}$ complexes reveals some systematic variations in the energies of absorption maxima; it is suggested that these ultraviolet and near-ultraviolet absorption bands should be assigned to metal-to-ligand charge-transfer transitions.

The chemistry of simpler inorganic systems which can mimic certain of the properties of naturally occurring complexes has been of long and continuing interest.²⁻⁴

Among the simplest of macrocyclic ligands are the cyclic tetramines.⁵⁻⁷ A particularly elegant and fascinating series is the complexes containing 14-, 15-, and 16-membered cyclic amine ligands and their Schiff base precursors which have been prepared and characterized by Curtis and his coworkers.⁷ The most stable and best characterized complexes of this series are those containing the 14-membered macro rings: 5,7,7,12,14,14-

hexamethyl-1,4,8,11-tetraazacyclotetradecane⁸ and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.⁹ (See Figure 1.) Complexes of these particular ligands generally have the nitrogen atoms almost coplanar;⁷ removal of the metal atom from coordination to any of the cyclic complexes is generally a relatively slow process. Thus the $\text{Ni}(\text{trans}[14]\text{diene})^{2+}$, $\text{Ni}(\text{teta})^{2+}$, $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$, and $\text{Cu}(\text{teta})^{2+}$ complexes are all kinetically stable in acidic aqueous solution at room temperature and all four complexes appear to exhibit only weak interaction with the solvent along the axial coordination positions.⁷ Therefore in a sense with these ligands the metal ion is in a coordination "trap." In principle, it should be possible to oxidize or reduce the metal center with little change in coordination geometry. Curtis has reported^{7,10,11} that Ni^{III} -

(1) (a) Research partially supported by the Public Health Service through Research Grant AM 08737 and a grant-in-aid from the Boston University Graduate School. (b) Taken in part from the M.A. Thesis of J. M. Palmer, Boston University, 1968. (c) Graduate Fellow (1966-1967) under the Prospective Teacher Program of the Higher Educational Act of 1965, Title V, C. (d) Author to whom inquiries should be addressed.

(2) D. Busch, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 107 (1964).

(3) E. Bonett, *Chem. Rev.*, **63**, 573 (1963).

(4) See also the papers and discussions in: (a) J. Peisach, P. Aisen, and W. E. Blumberg, Ed., "The Biochemistry of Copper, Proceedings of the Symposium on Copper in Biological Systems (1965)," Academic Press, New York, N. Y., 1966; (b) F. P. Dwyer, and D. P. Mellor, Ed., "Chelating Agents and Metal Chelates," Academic Press, New York, N. Y., 1964.

(5) C. K. Poon and M. L. Tobe, *Coord. Chem. Rev.*, **1**, 81 (1966).

(6) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).

(7) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

(8) Hereafter referred to as *teta*. Only the *meso* (with respect to the asymmetric carbon atoms) isomer⁷ of this ligand has been employed in this study.

(9) Following Curtis' suggestion,⁷ this ligand will hereafter be referred to as the *trans*[14]diene. The two isomeric complexes which can be formed from this ligand (see below) will be distinguished only when necessary for clarity. The studies reported here were performed with isomerically pure complexes. When referring to studies in which $\text{Cu}(\text{dl-trans}[14]\text{diene})^{2+}$ and $\text{Cu}(\text{meso-trans}[14]\text{diene})^{2+}$ exhibit similar chemical behavior, we will simply refer to $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$.

(10) N. F. Curtis, *Chem. Commun.*, 882 (1966).

(11) N. F. Curtis and D. F. Cook, *ibid.*, 967 (1967).

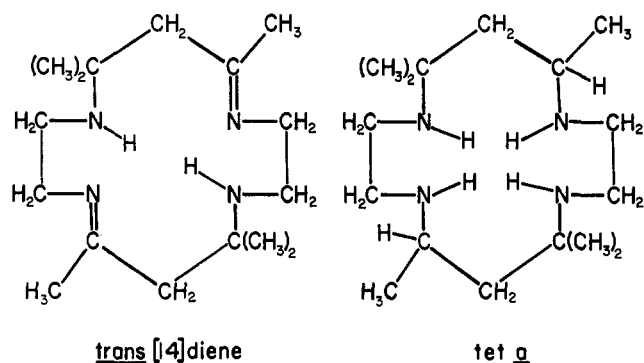


Figure 1.—Macrocyclic ligands: *trans*[14]diene = 5,7,7,12-,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; tetra = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

(*trans*[14]diene), Ni(*trans*[14]triene)²⁺, and Ni(*trans*[14]tetene)²⁺ complexes can be isolated from the nitric acid oxidation of Ni(*trans*[14]diene)²⁺.

In the present paper we report some studies of the redox chemistry of Cu(*trans*-[14]diene)²⁺ and Cu(*tetra*)²⁺. Copper ions often function as redox catalysts in chemical systems¹² and copper complexes have been implicated in oxidation-reduction reactions in biological systems.⁴ The one-electron reductions of Cu(*trans*[14]diene)²⁺ and Cu(*tetra*)²⁺ seemed particularly interesting as the coordination geometry of copper(I) is generally assumed to be linear (two-coordinate) or tetrahedral (four-coordinate).¹³ Thus standard reduction potentials of copper(II)-copper(I) couples have been observed to become more negative for complexes which make a tetrahedral geometry sterically unlikely¹⁴ and more positive when a tetrahedral geometry is sterically favored.^{15,16} On the other hand, in copper(II)-porphyrin complexes, the ligand is reduced (at very negative potentials) before the copper center.¹⁷ By analogy, the Cu(*trans*[14]diene)²⁺ and Cu(*tetra*)²⁺ complexes might be expected to be reduced at relatively negative potentials uncomplicated by ligand reduction. At the same time, the rates of electron transfer to the copper center might be relatively facile if the reduction is accompanied by only small changes in coordination geometry.¹⁸ The studies reported here confirm the above line of reasoning.

Experimental Section

A. Preparation of the Complexes.—Cu(*trans*[14]diene)²⁺ was prepared as described in the literature either by acetone condensation on [Cu(en)₃](ClO₄)₂¹⁹ or by the reaction of Cu(O₂CCH₃)₂ with (*trans*[14]diene)·2HClO₄ in methanol.^{20,21} The orange crystals of [Cu(*meso-trans*[14]diene)](ClO₄)₂^{19b} were separated from the red crystals of [Cu(*dl-trans*[14]diene)](ClO₄)₂^{19b} by recrystallization from 80% methanol.

(12) For example, see J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

(13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1966.

(14) M. Calvin and R. H. Bailes, *J. Am. Chem. Soc.*, **68**, 949 (1946).

(15) B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961).

(16) C. J. Hawkins and D. D. Perrin, *ibid.*, 1351 (1962).

(17) R. A. Felton and H. Linschitz, *J. Am. Chem. Soc.*, **88**, 1113 (1966).

(18) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

(19) (a) M. M. Flight and N. F. Curtis, *J. Chem. Soc.*, 3016 (1962); (b)

N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *ibid.*, 1015 (1966).

(20) N. F. Curtis and K. W. Hay, *Chem. Commun.*, 524 (1966).

(21) N. Sadasivan and J. F. Endicott, *J. Am. Chem. Soc.*, **88**, 5468 (1966).

[Cu(*tetra*)](ClO₄)₂ was prepared as described in the literature.²² [Co(NH₃)₃Br](ClO₄)₂ was prepared, metathesized, and recrystallized using standard literature techniques.²³ The purity of the preparations was monitored by comparison of visible and ultraviolet spectra with literature values.

Hexaammineruthenium(III) chloride was obtained from Johnson Matthey, Inc., and recrystallized. All other chemicals were reagent or spectral grade.

B. Spectra.—Infrared spectra of samples in Nujol Mulls (or KBr pellets) were determined using a Perkin-Elmer 237 spectrometer. A list of the most important frequencies and their assignments is presented in Table I. The infrared spectra of Cu(*meso-trans*[14]diene)²⁺ and Cu(*dl-trans*[14]diene)²⁺ differ most significantly in the perchlorate region (Figure 2).

TABLE I
DISTINCTIVE INFRARED ABSORPTION FREQUENCIES FOR
[Cu(C₁₆H₃₂N₄)](ClO₄)₂^a

Cu(<i>meso-trans</i> [14]- diene) ²⁺	Cu(<i>dl-trans</i> [14]- diene) ²⁺	Assignment
3220 s, sp	3210 s, sp	N—H str
1675 s, sp	1660 s, sp	C=N str
1415 m	1425 m	
1400 m	1390 m	
1170 m	1170 m	C—N str
1095 vs, b	1095 vs, b	ClO ₄ ⁻

^a Abbreviations: s, strong; sp, sharp; m, medium; b, broad; v, very.

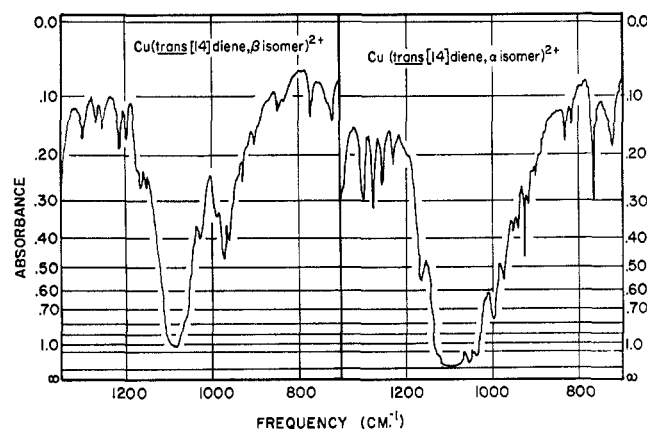


Figure 2.—Infrared spectra of the Cu(*trans*[14]diene)²⁺ complexes in the perchlorate region.

Visible and ultraviolet spectra were determined of aqueous solutions of the complexes using a Cary 14 spectrophotometer. Since previous determinations^{19,21} of the spectra of these complexes either were in error or were not for isomerically pure species, our determinations are reported in Table II.

C. Electrochemistry.—Conventional polarography was performed with a Sargent Model XXI polarograph, equipped with a conventional H cell with a coarse fritted disk augmented with a saturated KCl agar bridge. The polarograph was standardized with Cd(NO₃)₂ solution in 1 M HClO₄.²⁴ Maxima were suppressed with Triton X-100 (Rohm and Haas Co.). A 0.2% solution (0.1 ml) was used, when necessary for every 10 ml of polarographic solution. The capillary employed had a drop time of 4.23 sec and a flow rate of 1.742 mg/sec, at -0.8 V in a buffer solution made up of a mixture of 0.2 M Na₂HPO₄ and 0.1 M citric acid of pH 5.99. The cell was maintained at a temperature of 25.0 ± 1°.

Oscillographic polarography was performed with a Chemtrix Model SSP-2 oscillographic polarograph.

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

(23) H. S. Booth, *Inorg. Syn.*, **1**, 187 (1939).

(24) J. Heyrovsky and J. Kuta, "Principles of Polarography," Academic Press, New York, N. Y., 1966, p 534.

TABLE II
VISIBLE AND ULTRAVIOLET ABSORPTION MAXIMA FOR
(CuL)(ClO₄)₂ COMPLEXES IN AQUEOUS SOLUTIONS

Band assignment	Wavelength of max, Å (molar absorptivity)		
	<i>dl-trans</i> [14]diene	<i>meso-trans</i> [14]diene	teta
Metal ion	5040 (105) ^a	5010 (122)	5150 (133)
Charge transfer ^b	2600 (5460) ^c	2600 (6550) ^c	2720 (8310)
$\pi-\pi^{*}$ ^d	<2000 (>1.1 × 10 ⁴)	<2000 (>1.1 × 10 ⁴)	Absent

^a The wavelength (and molar absorptivity) of this absorption maximum is dependent on solvent and other ionic species present. The range of values is from λ_{\max} 5000 Å (ϵ 100) in 1 M HClO₄ to λ_{\max} 5350 Å (ϵ 155) in pure pyridine. ^b See discussion below concerning this assignment. ^c We have found the ultraviolet absorption band reported at ~260 nm for Cu(*trans*-[14]diene)²⁺ to be extraordinarily broad. The breadth of this band seems to be independent of isomerism, recrystallization, or the preparative method.

An H-type cell especially designed for this purpose was employed in controlled-potential electrolysis. The working electrode in the cathode compartment could be either a mercury pool or a platinum wire gauze. The potential of the cathode was determined by measuring the emf established between the cathode and the reference electrode. The potential was controlled manually by means of a Variac, a dc power supply (ATR Manufacturing Co., Inc., Model GIOC-ELIF), and a pH meter (Beckman Zeromatic II).

The number of coulombs of electricity which were passed through an electrolyzed solution was measured approximately using an ammeter and a stopwatch. The accuracy of this method was estimated by connecting the electrolysis system to a silver-silver nitrate coulometer and titrating the accumulated AgNO₃ with standard Na₂S₂O₃ after a measured time period. The measurement of current was the limiting factor in our method and this precision can be expressed as ± 0.002 A. Electrolyzed solutions were transferred either by means of a syringe or, in a few experiments, through an all-glass airtight system connecting the electrolysis cell with a spectrophotometric cell or a reaction vessel.

D. Calculation of Formation Constants.— $K' = x/(a - x)(b - x)$ and $A - A' = x\Delta\epsilon l$, where x is the concentration of the associated species, a is the concentration of the original complex, b is the anion concentration, A is the absorbance of the solution containing Cu(*trans*[14]diene)²⁺ and a "complexing" anion, $A' = a\epsilon_0 l$, and $\Delta\epsilon = \epsilon_x - \epsilon_0$.²⁶ Assuming a and x to be the concentration of the only absorbing species present, with x much less than $a + b$, then $ab/(A - A') = [(a + b)/l\Delta\epsilon] + (1/l\Delta\epsilon K')$, and a plot of $ab/(A - A')$ vs. $a + b$ will have a slope of $1/l\Delta\epsilon$ and an intercept of $1/l\Delta\epsilon K'$.

Results

A. Spectral Evidence for Solvent and Ionic Association.—The metal ion absorption maximum shifts to longer wavelengths in complexing solvents⁷ (see also Table II). If benzene is added to a saturated solution of [Cu(*meso-trans*[14]diene)](ClO₄)₂ in pyridine, a purple solid precipitates. The infrared spectrum of this solid indicates that both Cu(*meso-trans*[14]diene)²⁺ and pyridine are present. Recrystallization of this material from water yields only [Cu(*meso-trans*[14]diene)](ClO₄)₂. Spectrophotometric measurements on 0.002 M solutions of the Cu(*trans*[14]diene)²⁺ complex with a variety of concentrations of I⁻ and SCN⁻ showed very little change in the visible and ultraviolet spectra of the complex. Similar measurements of S₂O₃²⁻ solutions showed an increase in absorbance and

a significant (but small) shift in the visible band. In order to obtain these small spectral changes, high concentrations (up to 1.0 M) of the anion were needed. High concentrations of inert electrolytes are reputed to alter molar absorbancies of ionic species;²⁵ a similar phenomenon may account for the small spectral changes observed in this case. However, an effort was made to establish a maximum possible value for the equilibrium constant for the association (or complexation) of each anion with the macrocyclic complex. An attempt to carry out the I⁻ studies at constant ionic strength indicated that ClO₄⁻ either suppresses the association with I⁻ or associates with the complex to a similar degree. In fact the absorption maximum shifts to shorter wavelengths in the presence of high concentrations of either ClO₄⁻ or I⁻. Thus the values of K' ²⁶ in Table III are necessarily qualitative, at best representing an upper limit to the true K' value, and also, when high concentrations of anion are used, the thermodynamic equilibrium constant for the complexation will be approximately an order of magnitude larger than K' .

TABLE III
APPROXIMATE MOLAR EQUILIBRIUM CONSTANTS FOR THE
ASSOCIATION OF Cu(*trans*[14]diene)²⁺ WITH
VARIOUS ANIONS AT 25°

Anion	$\lambda, \text{Å}$			$\Delta\nu K', M^{-1}$
	5050	6100	6500	
I ⁻	7	8.6		7.8 ± 0.8
SCN ⁻	8.7	3.4		6.0 ± 2.7
S ₂ O ₃ ²⁻	19	45	30	31 ± 9

The extremely small values calculated for K' with SCN⁻ and I⁻ indicate that there is little Cu(*dl-trans*[14]diene)²⁺ complexation by these anions. This result is to be contrasted to the reactivity of Cu²⁺ with I⁻ and the fact that Cu²⁺ has been shown to form both sulfur-bonded and nitrogen-bonded thiocyanate complexes.²⁷ On the other hand, the K' value for S₂O₃²⁻ indicates a moderate degree of association with the macrocyclic complex. The associated species in this latter case appears to exhibit an absorption maximum at about 5600 Å. As the value of K' is an upper limit, Cu(*dl-trans*[14]diene)²⁺ evidently has a lower affinity for S₂O₃²⁻ than does Cu(en)²⁺.^{28,29}

B. Electrochemical Reduction Studies. Polarography.—Table IV summarizes the results of the conventional polarographic (dme) reduction of the Curtis copper(II) complexes. The first wave for the copper complexes seems to correspond to the addition of two electrons; the second wave observed for the Cu(*trans*[14]diene)²⁺ complexes appears to be twice as large. The number of electrons involved has been

(25) G. Stein and A. Trenin, *Trans. Faraday Soc.*, **56**, 1393 (1960).

(26) K' is the molar equilibrium constant, $K' = [C][D]/[A][B]$, A' is the absorbance of Cu(*trans*[14]diene)²⁺ in water, l is the path length of the spectrophotometric cell, and ϵ_x and ϵ_0 are the molar absorptivities of the Cu(*trans*[14]diene)²⁺·X⁻ complex (or ion pair) and Cu(*trans*[14]diene)²⁺, respectively.

(27) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966).

(28) Matheson²⁹ has calculated K' for the association of S₂O₃²⁻ with Cu(en)²⁺ as 31.2 M⁻¹ at 0.099 M ionic strength at 25°.

(29) R. A. Matheson, *J. Phys. Chem.*, **71**, 1302 (1967).

TABLE IV
POLAROGRAPHIC (DME) RESULTS FOR MACROCYCLIC
COPPER COMPLEXES, CuL^{2+}

pH	Ligand, L	$-E_{1/2}(\text{I}),^a$ V	$-E_{1/2}(\text{II}),^a$ V
5.99	<i>trans</i> [14]diene	0.57	1.43
5.99	<i>trans</i> [14]diene ^b	0.54	1.43
5.99	teta	0.62	...

^a $E_{1/2}$ values of all the copper complexes vary with pH. See text. ^b With 0.002% Triton X-100.

found in these cases by comparing the height of the observed polarographic wave with polarographic waves obtained for cadmium(II) and zinc(II) under the same conditions.^{30,31}

The limiting currents for both waves of the copper complexes have been shown to be proportional to the square root of the height of the mercury head. In addition the limiting currents varied by less than 2%/deg. These observations demonstrate that the reduction waves are diffusion controlled.

The first reduction wave seems to be somewhat irreversible. Tomes plots of $\log [i/(i_d - i)]$ vs. E most frequently gave slopes of 0.038 ± 0.001 ³² for all three complexes. These plots were occasionally nonlinear and observed slopes of the apparent linear components varied from 0.0254 to 0.0645. These latter observations suggest either irreversibility with a complicated mechanism³³ or small maxima incorporated into the wave. It seems most reasonable to consider the first wave for the copper complexes as irreversible or, at best, quasireversible.

The second wave in the polarographic reduction of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ has been found to be highly irreversible with Tomes slopes in the vicinity of 0.040. This is to be compared to a slope of 0.0147 for a reversible wave with $n = 4$, at 25°. It is important to observe that this wave is absent in the polarographic reduction of $\text{Cu}(\text{teta})^{2+}$.

The reduction of the copper complexes has been found to be pH dependent. This implies participation of hydrogen ions in an essential step of the electrochemical process. The variation of $E_{1/2}$ with pH is shown in Figures 3-5. Note the difference in the pH-dependent reductions of the $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ complexes and $\text{Cu}(\text{teta})^{2+}$.

For the $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ complexes the pH dependence of the second wave (slope ~ 0.060) implies 1:1 addition of electrons and protons (Figure 5) as would be expected for the reduction (hydrogenation) of the double bonds.³⁴⁻³⁷

Considerable additional insight into the electrode processes is provided by cyclic voltammetry (*i.e.*, cath-

(30) Such comparisons occasionally lead to error in the estimate of the equivalents of electrons.³¹ In the present case, however, the correctness of the comparison has been demonstrated by the stoichiometric consistency (see below) and the observation that similar reductions of macrocyclic complexes of cobalt(III) result in a 1-equiv $\text{Co}(\text{III}) \rightarrow \text{Co}(\text{II})$ wave.

(31) L. Meites, "Polarographic Techniques," Interscience Publishers, New York, N. Y., 1955, p 71.

(32) For a reversible wave the slope RT/nF for $n = 2$ and $T = 25^\circ$ is 0.0295.^{34,31}

(33) P. Zuman in "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilly, Ed., Interscience Publishers, New York, N. Y., 1963.

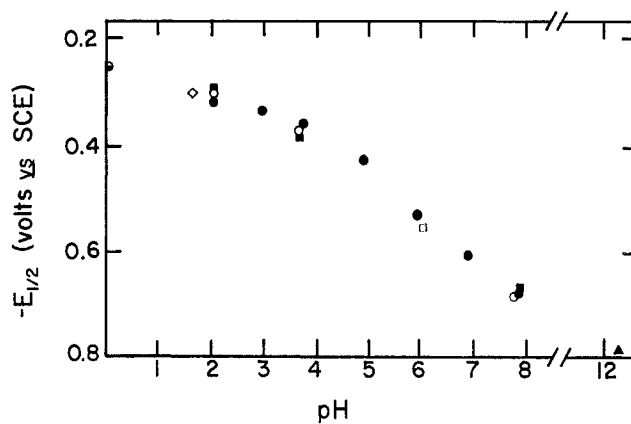


Figure 3.—Variation of $E_{1/2}$ of the Cu wave with pH for the $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ complexes. For $[\text{Cu}(\text{dl-trans}[14]\text{diene})^{2+}] = 5 \times 10^{-4} M$: \bullet , 1 M HClO_4 ; \diamond , 0.1 M NaClO_4 , 0.025 M HClO_4 ; \blacktriangle , buffer mixtures of 0.2 M Na_2HPO_4 and 0.1 M citric acid; \blacklozenge , 0.1 M NaClO_4 , 0.05 M NaOH ; \circ , buffer mixtures (Na_2HPO_4 and citric acid) at ionic strength 0.61 M (NaClO_4). For $[\text{Cu}(\text{meso-trans}[14]\text{diene})^{2+}] = 3 \times 10^{-4} M$: \blacksquare , buffer mixtures (Na_2HPO_4 and citric acid) at ionic strength 0.63 M (NaClO_4); \square , buffer mixtures (Na_2HPO_4 and citric acid).

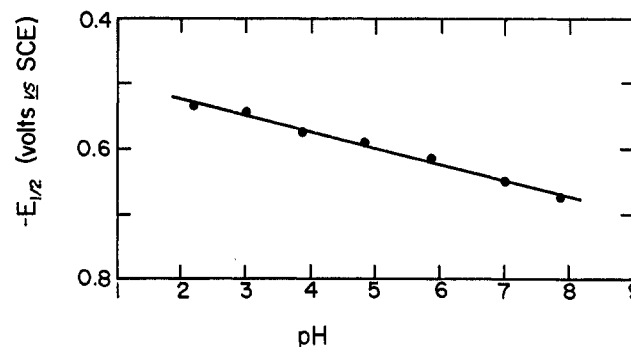


Figure 4.—Variation of $E_{1/2}$ with pH for $\text{Cu}(\text{teta})^{2+}$ in buffered solutions (Na_2HPO_4 and citric acid); $[\text{Cu}(\text{teta})^{2+}] = 5 \times 10^{-4} M$.

odic and anodic sweeps within a fraction of 1 sec).³⁸ The $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ complexes are reduced in two steps, the second wave being twice as large as the first (Figure 6). The pH dependencies of these waves are identical with that described above for conventional polarography. Complete cyclic sweeps within 0.2 sec have failed to show any residue of the corresponding anodic waves (Figure 6) following reduction. Furthermore an anodic wave was formed in the vicinity of the copper wave, which can be identified with the reoxidation of copper amalgam, $\text{Cu}(\text{Hg})$; this anodic wave increased with repetitive polarograms, and eventually a

(34) For a reversible process $A + m\text{H}^+ + ne \rightarrow \text{AH}_m^{m-n}$ it has been shown^{35,36} that E becomes more negative by $0.059m/n$ mV per pH unit at 25°. It should be emphasized that for an irreversible process, such as the reduction of the double bonds, the slope is not $0.058m/n$ but rather $0.059m/\alpha n$ where α is the transfer coefficient, that is, the fraction of the applied potential used in forming the activated complex.³⁷ This number, which varies from 0 to 1 and is unknown in this case, may upset the calculated stoichiometry of hydrogen. However it seems unlikely that other than four protons participate in the reduction.

(35) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, 2nd ed, Interscience Publishers, New York, N. Y., 1955, pp 246-247.

(36) See ref 24, p 162.

(37) P. S. Elving, *Pure Appl. Chem.*, **2**, 423 (1963).

(38) Z. Galus, H. Y. Lee, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 17 (1963).

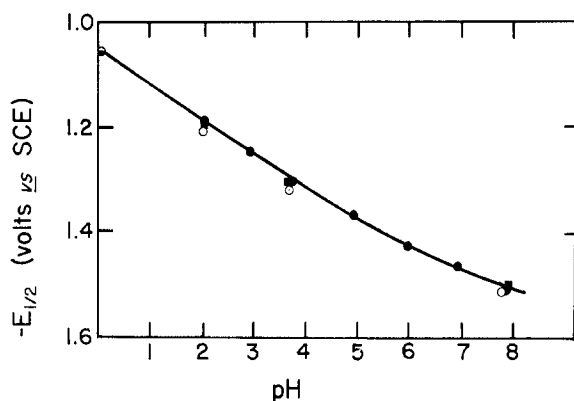


Figure 5.—Variation of $E_{1/2}$ of the ligand wave with pH for the $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ complexes. For $[\text{Cu}(\text{dl-trans}[14]\text{diene})^{2+}] = 5 \times 10^{-4} M$: \ominus , $0.1 M \text{HClO}_4$; \bullet , buffer mixtures (Na_2HPO_4 and citric acid); \circ , buffer mixtures (Na_2HPO_4 and citric acid) at ionic strength $0.61 M (\text{NaClO}_4)$. For $[\text{Cu}(\text{meso-trans}[14]\text{diene})^{2+}] = 3 \times 10^{-4} M$: \blacksquare , buffer mixtures (Na_2HPO_4 and citric acid) at ionic strength $0.63 M (\text{NaClO}_4)$.

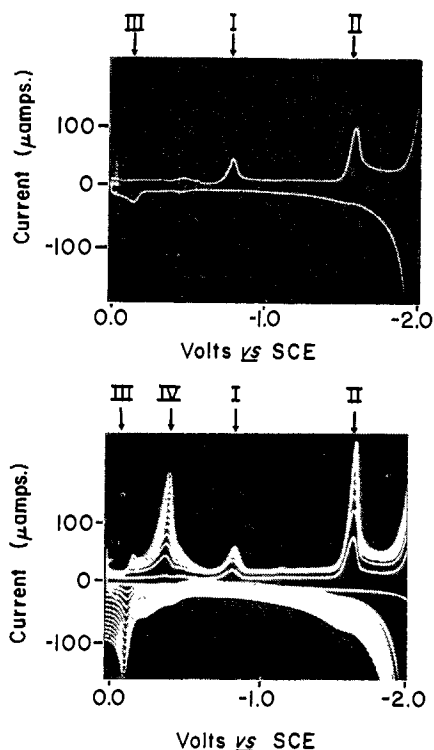


Figure 6.—Top: oscillographic polarogram of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ in buffered solution (Na_2HPO_4 and citric acid; pH 8.01); $[\text{Cu}(\text{trans}[14]\text{diene})^{2+}] = 5 \times 10^{-4} M$; sweep time 0.05 sec/division; normal mode of operation. Bottom: repetitive sweep oscillographic polarograms of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ in buffered solution (Na_2HPO_4 and citric acid; pH 8.01); $[\text{Cu}(\text{trans}[14]\text{diene})^{2+}] = 5 \times 10^{-4} M$; sweep time 0.01 sec/division; derivative mode of operation. Key to waves: I, copper wave; II, ligand wave; III, $\text{Cu}(\text{Hg}) \rightarrow \text{Cu}^{2+}$; IV, $\text{Cu}^{2+} \rightarrow \text{Cu}(\text{Hg})$.

cathodic wave appeared at more positive voltage than the copper wave of the complex (Figure 6, bottom). This latter wave also increased with repetitive sweeps and with faster sweeps. The positions and slopes of these new cathodic and anodic waves were identical with those exhibited by solutions containing $\text{Cu}(\text{ClO}_4)_2$. All three cyclic copper(II) complexes show evidence for formation of $\text{Cu}(\text{Hg})$ during the cathodic sweep.

Electrolytic reductions of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ with a platinum cathode often give qualitatively different results from reductions using a mercury cathode under identical conditions. Polarographic studies of the reduction of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ using a rotating platinum electrode have not been very successful owing partly to the sensitivity of electrolyzed solutions to air oxidation, partly to the low hydrogen overvoltage on platinum, and finally to the sensitivity of the platinum electrode surface to contamination. We did obtain a reasonably well-defined cathodic wave with $E_{1/2} = -0.88 \text{ V}$ at pH 12.

The platinum electrode always showed a strong absorption wave in oscillographic polarography (Figure 7) at -0.4 V regardless of the procedure used to prepare the electrode for the experiment; the size, shape, and position of the absorption wave did depend on the pre-treatment of the electrode. These studies did exhibit one qualitatively noteworthy feature: the cathodic metal ion wave at about -0.9 V (I in Figure 7) seemed to be associated with a weak anodic wave at about -0.75 V (II in Figure 7).

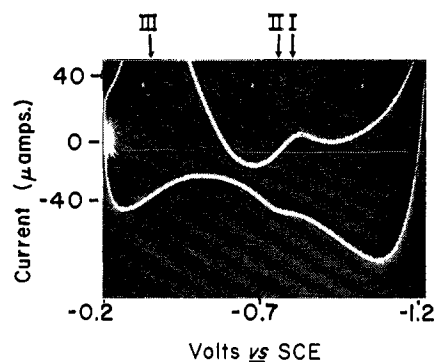


Figure 7.—Oscillographic polarogram with stationary platinum electrode; $[\text{Cu}(\text{trans}[14]\text{diene})^{2+}] = 5.05 \times 10^{-4} M$ in $0.1 M \text{NaClO}_4$ and $0.05 M \text{NaOH}$. Key to waves: I, copper wave; II, apparent anodic copper wave; III, adsorption wave.

C. Direct-Current Electrolysis of CuL^{2+} Complexes.

—The electrolysis of solutions of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ with a platinum working electrode can produce a bright yellow³⁹ species (R) which is a powerful and facile reducing agent. This species has only been successfully generated in solutions of pH greater than 3, with NaCl , KCl , NaClO_4 , or KBr as the supporting electrolyte. In addition, the platinum electrode must be carefully cleaned and oxygen must be rigorously excluded from the cell prior to electrolysis. In our work we have often applied very high potentials across the electrodes of the electrolysis cell; however, we have observed that the generation of the reduced species R is really successful only under conditions that no hydrogen is evolved at the cathode. Thus the working potential of the cathode must be more positive than -1 V (*vs. sce*).

Electrolysis of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ with a mercury cathode has never produced the yellow reduced species R.

(39) $\lambda_{\text{max}} 4110 \text{ \AA}$ ($\epsilon \sim 2 \times 10^3$).

Electrolysis of $\text{Cu}(\text{teta})^{2+}$ has not produced solutions with detectable reducing properties even under the most carefully chosen conditions. Electrolysis of $\text{Cu}(\text{teta})^{2+}$ does plate copper metal on the cathode; if electrolysis of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ is carried far enough or performed under the wrong conditions, copper metal also plates onto the cathode.

D. Characterization of Solutions Containing the Reduced Species R.—We have attempted to compare the number of reducing equivalents of reduced species formed to the number of equivalents of electrons passed through the solution during electrolysis. We have used $\text{Co}(\text{NH}_3)_6\text{Br}^{2+}$ to determine the reducing titer of electrolyzed solutions. Results of these determinations are summarized in Table V. Despite the possibility of some hydrogen evolution and air oxidation, Table V shows that electrolysis of solutions of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ can approach a 1-equiv reduction.

TABLE V
STOICHIOMETRY OF THE REACTION OF THE
REDUCED SPECIES R WITH $\text{Co}(\text{NH}_3)_6\text{Br}^{2+}$

Time under N_2 before electrolysis ^a	Faradays $\times 10^5$	Actual $\text{Co}(\text{NH}_3)_6\text{Br}^{2+}$ consumed in reaction $\times 10^5$, ^b mol
45 min	0.63 ± 0.06	0.31 ± 0.08
90 min	0.71 ± 0.06	0.54 ± 0.08
3 hr	0.59 ± 0.06	0.50 ± 0.08
3 hr	0.69 ± 0.06	0.58 ± 0.08

^a In these experiments electrolyzed solutions were passed from the electrolysis cell through an all-glass system to a reaction vessel containing a weighed amount of solid $[\text{Co}(\text{NH}_3)_6\text{Br}](\text{ClO}_4)_2$. The whole system had to be flushed with N_2 prior to electrolysis. It was apparently difficult to remove traces of O_2 from all parts of this apparatus. ^b Using $\epsilon = 1.65 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} 2525 \text{ \AA}$.

Changes in electrode potential have been determined in solutions containing varying amounts of the reduced species R and $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$. These potential measurements have been made at 25° in solutions differing in their ratios of [R] to $[\text{Cu}(\text{trans}[14]\text{diene})^{2+}]$ (in the range of 0 to 1:1) and at several ionic strengths (0.01–0.1 M NaCl). These potential measurements have been compared to the identical measurements of potential in solutions containing $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ in the same apparatus under the same conditions. Using a value of +0.10 V for the $\text{Ru}(\text{NH}_3)_6^{2+},^{3+}$ couple⁴⁰ and assuming a 1-equiv reduction of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$, we obtain for the $\text{Cu}(\text{trans}[14]\text{diene})^{1+},^{2+}$ couple a standard potential of $E^\circ = -0.49 \pm 0.03 \text{ V}$.⁴¹ The [R] {or $[\text{Cu}(\text{trans}[14]\text{diene})^+]$ } in these determinations was deduced from the current passed through the solution and so was uncertain (see Table V); however, E° values were calculated for relatively high extents of reduction where a 10% error in $[\text{Cu}(\text{trans}[14]\text{diene})^+]$ results in less than a 2% error in E° .

Attempts to generate the yellow species R by homogeneous chemical reductions have generally failed. A possible exception is the reaction of Cr^{2+} with $\text{Cu}(\text{trans}$

$[14]\text{diene})^{2+}$ in 0.1 M NaSCN which led to an insoluble pink powder. This pink solid contained SCN^- (intense, broad ir band at 2080 cm^{-1}) and the Schiff base ligand ($\nu_{\text{C=N}}$ at 1670 cm^{-1}). A partial chemical analysis fits the formulation $\text{Cu}(\text{C}_{16}\text{H}_{32}\text{N}_4) \cdot \text{Cr}(\text{SCN})_4$ reasonably well. *Anal.* Calcd: C, 38.2; H 5.10; N, 17.8. Found: C, 36.86 ± 0.1 ; H, 5.10 ± 0.06 ; N, 17.4.

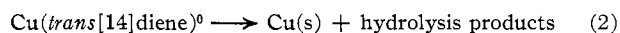
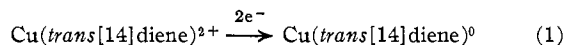
Discussion

A. The $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ Species in Solution.—There is ample evidence that the macrocyclic complexes of copper(II) can associate with a fifth ligand in solution. This has been most clearly demonstrated in the case of CN^- ,⁴² with limited evidence for association with ammonia,⁷ pyridine, and $\text{S}_2\text{O}_3^{2-}$. Other cases seem more ambiguous. In fact the red color of $\text{Cu}(\text{teta})^{2+}$ and the $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ complexes in solution most likely results from the extreme tetragonality of the coordination environment of the copper center.⁴³ The apparent shift to higher energies of the metal ion absorption maximum in solution containing high concentrations of I^- or ClO_4^- suggests that neither these anions nor water is strongly associated with the metal ion and that the observed spectral changes are due to changes in the solvation environment (of the cation) on formation of ion pairs. Certainly the "formation constants" in Table III are to be regarded as maximum values.

B. Oxidation-Reduction Reactions.—The oxidation-reduction chemistry of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ is complex. The polarographic reduction of this complex (dme) is deceptively simple, showing an "almost reversible" two-electron metal ion reduction and a very irreversible reduction of the ligand. The ligand wave must correspond to hydrogenation of the two imine groups of the $\text{trans}[14]\text{diene}$ ligand. This ligand wave is absent in the reduction of $\text{Cu}(\text{teta})^{2+}$ and the polarographic reduction of the C=N bond is sufficiently well defined that it has been proposed as a part of an analytical scheme for carbonyl compounds.³³

In marked contrast, electrolytic reductions using a platinum electrode can result in the formation of a substance which seems best formulated as $\text{Cu}(\text{trans}[14]\text{diene})^+$. Although the identification of this species as a copper(I) complex is not unequivocal, the weight of evidence and precedent is considerable. It is clear that the formation of copper(0) is associated with the decomposition of the complex. It is also clear that the electrode reactions on either mercury or platinum electrodes are complex.

A question of some interest is whether the presence of $\text{Cu-N}(\text{imine})$ groups in the $\text{trans}[14]\text{diene}$ complex stabilizes the $\text{Cu}(\text{trans}[14]\text{diene})^+$ complex in any sense (*i.e.*, kinetic or thermodynamic). Reactions 1–4 below represent a relatively simple mechanism to ac-

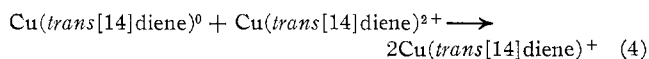
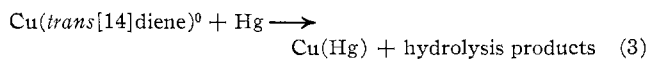


(40) T. J. Myer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(41) Potentials are given as reduction potentials.

(42) Y. M. Curtis and N. F. Curtis, *Australian J. Chem.*, **18**, 1933 (1965).

(43) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).



count for the electrochemical behavior and also serve to demonstrate that the present evidence does not necessarily reflect on the relative stabilities of $\text{Cu}(\text{trans}[14]\text{-diene})^+$ and $\text{Cu}(\text{teta})^+$ complexes. Both (2) and (3) are pH dependent. If the first step is more or less reversible and (2), (3), and (4) are all competitive (with (3) being very fast),⁴⁴ then these reactions are consistent with the observations reported above as well as the qualitative observations that electrolysis often results in some loss of complex and that electrolyses of solutions with $[\text{Cu}(\text{trans}[14]\text{diene})^{2+}] < 10^{-4} M$ have not resulted in detectable amounts of $\text{Cu}(\text{trans}[14]\text{diene})^+$. Reactions 2 and 3 are very favorable thermodynamically in acidic aqueous solution. The hydrogen ion dependence of the metal ion reduction wave suggests an irreversible reduction of $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ and an H^+ -catalyzed aqution of $\text{Cu}(\text{trans}[14]\text{diene})^0$ (the inverse of the H^+ inhibition of the formation of the porphyrin complexes⁴⁵ and similar to acid catalysis of the dissociation of porphyrin complexes⁴⁶). The fact that we have been unable to prepare any substance corresponding to $\text{Cu}(\text{teta})^+$ suggests either that the reaction analogous to (4) is slow for this complex or that $\text{Cu}(\text{teta})^+$ is less stable than $\text{Cu}(\text{trans}[14]\text{diene})^+$ and does not necessarily reflect on the relative stability of the former.

C. The Reduced Species, $\text{Cu}(\text{trans}[14]\text{diene})^+$.—It is evidently difficult to reduce copper(II) coordinated to a macrocyclic ligand which has a strong tendency to be planar. The relatively negative values of polarographic half-wave potentials (probably $\text{Cu}(\text{II}) \rightarrow \text{Cu}(0)$) and the standard potential suggest that the planar coordination favored by the *trans*[14]diene and *teta* ligands⁷ is not a favorable coordination geometry for either copper(I) or copper(0). This does seem to be in the direction of the polarographic behavior of the porphyrins²⁷ and is to be contrasted to the changes in potential observed when the ligands sterically prohibit formation of planar complexes.^{15,16} The high reducing potential of $\text{Cu}(\text{trans}[14]\text{diene})^+$ and the rapidity of its reactions make it a very difficult species to handle. Owing to its reactivity toward a variety of substances, we have not yet been able to demonstrate whether $\text{Cu}(\text{trans}[14]\text{diene})^+$ is stable or unstable to disproportionation (*i.e.*, whether reaction 4 is thermodynamically feasible). So far we have found that with very great care solutions of $\text{Cu}(\text{trans}[14]\text{diene})^+$ may be stored for several hours without noticeable decomposition and that decomposition of these solutions rarely involves formation of copper metal. It should be noted, however, that even solutions of $\text{Cu}^+(\text{aq})$ may be stored for periods of time on the order of 1 hr.⁴⁷

D. Concerning the Assignment of Ultraviolet Ab-

(44) Note that (1) and (3) are necessarily reactions which take place at or near the electrode.

(45) S. J. Baum and R. A. Plane, *J. Am. Chem. Soc.*, **88**, 910 (1966).

(46) R. Snellgrove and R. A. Plane, *ibid.*, **90**, 3185 (1968).

sorption Bands in Complexes with the Curtis-Type Macrocyclic Ligands.—Some contradictory assignments of the ultraviolet absorption bands of these complexes appear in the literature.^{7,21} Spectral information is now available about a large number of relevant complexes and band assignments can be assessed systematically.

Most of the $\text{M}(\text{trans}[14]\text{diene})^{n+}$ complexes exhibit relatively low intensity ($\epsilon < 10^4$) ultraviolet absorption bands which are frequently absent in the corresponding $\text{M}(\text{teta})^{n+}$ complexes.⁷ These bands vary a great deal in energy with changes in the kind of central metal or with the oxidation state of the central metal. By way of comparison it is to be observed that $\pi \rightarrow \pi^*$ transitions in bipyridyl and *o*-phenanthroline complexes of nickel(II), cobalt(II), and zinc(II) have molar absorptivities greater than 10^4 and are nearly independent of the central metal in their energy.^{48,49} We have observed that these bands occur at relatively low energy for copper(I) and cobalt(II)⁵⁰ complexes with *trans*[14]diene. In fact the energy of the bands in question approximately parallels changes in ionization potential⁵¹ of the metals (see Table VI) which suggests that

TABLE VI
ULTRAVIOLET ABSORPTION BANDS AND ASSIGNMENTS
FOR $\text{M}(\text{trans}[14]\text{diene})^{n+}$ COMPLEXES

Proposed assignment	M^{n+}	$10^{-3} \bar{\nu}$, cm^{-1}	$\epsilon \times 10^{-3}$	Ionization potential, ^a eV
Metal \rightarrow ligand	Cu^+	24.3	~ 2	20.29
	$\text{Co}^{2+ b}$	30.3	2.0	33.49
	$\text{Ni}^{2+ c}$	35.4	5.0	35.16
	Cu^{2+}	39.2 ^d	5.5	36.83
	Zn^{2+}	40.5 ^e	0.43	39.7
Ligand \rightarrow metal	Cu^{2+}	38.4 ^d	5.5	
	Co^{3+}	38.4	15	
	$\text{Ni}^{2+ c}$	46.5	16	

^a For the gaseous metal ions: $\text{M}^n \rightarrow \text{M}^{(n+1)+} + e^-$. Values taken from ref 13, p 797. ^b Reference 51. ^c Reference 7. ^d It is assumed that the unusual broadness of this band is due to overlap metal \rightarrow ligand and ligand \rightarrow metal bands. $\text{Cu}(\text{teta})^{2+}$ exhibits an absorption maximum near this energy. ^e N. Ellin and J. F. Endicott, unpublished observations.

these bands are actually metal \rightarrow ligand charge-transfer bands. Naturally such bands are present in the Schiff base but not the tetramine complexes.⁵² The $\pi \rightarrow \pi^*$ transitions for the *trans*[14]diene ligands probably occur at high energies (generally $> 50 \times 10^3 \text{ cm}^{-1}$). The bands of intermediate energy probably correspond to ligand \rightarrow metal charge-transfer transitions. These latter absorptions should be present and have similar

(47) (a) J. A. Altermatt and S. E. Manahan, *Anal. Chem.*, **40**, 655 (1968); (b) J. H. Espenson, private communication.

(48) H. L. Schlafer, *Z. Physik. Chem. (Frankfurt)*, **8**, 373 (1956).

(49) K. Sone, P. Krumbholz, and H. Stammreich, *J. Am. Chem. Soc.*, **77**, 777 (1955).

(50) M. P. Liteplo and J. F. Endicott, unpublished observations.

(51) We have used free ion ionization potentials in Table VI. These potentials are used to indicate the order but not the energetics of oxidation of the $\text{M}(\text{trans}[14]\text{diene})^{n+}$ complexes. The ionization potentials run about one order of magnitude higher than the electrode potentials (as reported here, found in ref 50, or implied in Curtis' work) or the energy of the electronic transitions listed in Table VI.

(52) In this connection, it is to be noted that both the "yellow" $\text{Co}(\text{trans}[14]\text{diene})^{2+}$ and the "pink" $\text{Co}(\text{teta})^{2+}$ complexes have been prepared.⁵⁰

energies in both the $M(\text{trans}[14]\text{diene})^{n+}$ and the $M(\text{teta})^{n+}$ complexes. The relatively low molar absorptivity of the ligand \rightarrow metal transitions in Cu-

(*teta*)²⁺^{7,21} and $\text{Cu}(\text{trans}[14]\text{diene})^{2+}$ (where this transition appears to be mixed with a metal \rightarrow ligand transition) complexes is to be noted.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE INSTITUTE FOR ATOMIC RESEARCH,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Reactions Involving Copper(I) in Perchlorate Solution. A Kinetic Study of the Reduction of Iron(III) by Copper(I)¹

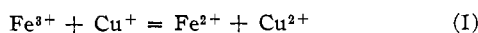
By O. JERRY PARKER AND JAMES H. ESPENSON

Received December 11, 1968

Rate studies were carried out on the oxidation-reduction reaction of iron(III) and copper(I) ions in perchlorate solutions which produces quantitative yields of iron(II) and copper(II). The rate law is first order in each metal ion, with an inverse dependence on hydrogen ion concentration. The values ($\text{sec}^{-1} \times 10^{-4}$, $\mu = 1.00 M$) are 2.48 ± 0.11 (1.6°), 7.67 ± 0.38 (15.8°), and 16.1 ± 0.3 (25.0°), with activation parameters $\Delta H^\ddagger = 12.4 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = 6.7 \pm 0.7$ eu. The reactions of FeN_3^{2+} and FeF^{2+} with Cu^+ are immeasurably rapid by the techniques used, the lower limits at 1.6° and at $\mu = 1.00 M$ being 10^8 and $5 \times 10^6 M^{-1} \text{sec}^{-1}$, respectively. The mechanism is discussed in comparison with related reactions, and it is concluded that an inner sphere process is probably involved.

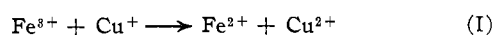
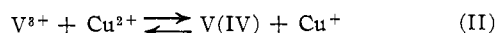
Introduction

The reaction of iron(III) and copper(I) has not been studied previously. The reaction occurring in acidic perchlorate solution is that shown by



Recent studies²⁻⁶ have concerned the preparation and reactions of the metastable Cu^+ ion. Reduction of Cu^{2+} with an insufficient quantity of strong 1-equivalent reducing agents such as V^{2+} and Cr^{2+} affords dilute solutions of Cu^+ which, if protected from oxygen and metal surfaces, survive several hours without disproportionation. Such solutions exhibit strong reducing properties, reacting with VO^{2+} ,⁴ $\text{Co}(\text{III})$ complexes,⁶ and a number of other oxidizing agents,² including Fe^{3+} .

One particular point of interest is the role claimed for the reaction of Fe^{3+} and Cu^+ in the studies of Higginson and Sykes.⁷ The reaction of V^{3+} and Fe^{3+} is catalyzed by Cu^{2+} , and the following scheme was proposed⁷ to account for the observed kinetics



The rate of reaction II is given⁴ by the expression

$$d[\text{Cu}^+]/dt = \{k_1[\text{V}^{3+}][\text{Cu}^{2+}]/[\text{H}^+]\} - k_2[\text{VO}^{2+}][\text{Cu}^+][\text{H}^+] \quad (1)$$

where the hydrogen ion dependence is as shown except for a small medium effect^{4b} on k_1 . Provided the reaction of the Cu^+ intermediate with Fe^{3+} is sufficiently rapid compared to its reaction with VO^{2+} , the forward rate of II will be the measured catalytic rate. This was the claim made,⁷ and one point of interest in these studies is the validity of this approximation.

The reduction of Fe^{3+} to Fe^{2+} by one-electron reducing agents has been the subject of a number of rate studies. The reducing agents studied include V^{2+} ,⁸ Cr^{2+} ,^{9,10} Eu^{2+} ,¹¹ Ti^{3+} ,¹² V^{3+} ,⁷ and Fe^{2+} (electron exchange).¹³ A comparison with these cases is most helpful in settling the question of whether an inner-sphere transition state is involved in the present reaction. This is a particularly relevant point for Fe^{3+} , since established cases of inner-sphere (Cr^{2+}) and outer-sphere (V^{2+}) reactions are known, and those reactions not subject to a direct answer (Eu^{2+} , Fe^{2+}) have several features strongly suggesting they are of the inner-sphere type.

Experimental Section

Materials.—Solutions of Cu^+ were prepared by the reaction⁸ of Cr^{2+} and Cu^{2+} . These solutions were prepared immediately before use in one of the volumetric flasks used as a solution reservoir. The reaction of Cu^{2+} and Cr^{2+} was allowed to proceed to at least 99% completion, the time required (5–35 min) being computed from the known rate constant³ for the conditions of that experiment. At intervals during the course of the experiment, samples of Cu^+ were removed for analysis.⁶

(8) B. R. Baker, M. Orhanović, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).

(9) G. Dulz and N. Sutin, *ibid.*, **86**, 829 (1964).

(10) D. W. Carlyle and J. H. Espenson, *ibid.*, **91**, 599 (1969).

(11) D. W. Carlyle and J. H. Espenson, *ibid.*, **90**, 2272 (1968).

(12) R. Critchley and W. C. E. Higginson, private communication; cited by A. G. Sykes, "Kinetics of Inorganic Reactions," Pergamon Press Ltd., London, 1966, p. 166.

(13) R. J. Campion, T. J. Conoccholi, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964), and references cited therein.

(1) (a) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2465. (b) Based on the Ph.D. thesis of O. J. P., Iowa State University, Sept 1968.

(2) J. H. Espenson, K. Shaw, and O. J. Parker, *J. Am. Chem. Soc.*, **89**, 5770 (1967).

(3) K. Shaw and J. H. Espenson, *Inorg. Chem.*, **7**, 1619 (1968).

(4) (a) K. Shaw and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 6622 (1968);

(b) O. J. Parker and J. H. Espenson, *ibid.*, **91**, 1313 (1969).

(5) O. J. Parker and J. H. Espenson, *Inorg. Chem.*, **8**, 185 (1969).

(6) O. J. Parker and J. H. Espenson, *J. Am. Chem. Soc.*, **91**, 1968 (1969).

(7) W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, **2841** (1962).