A chain mechanism involving rhodium(II) cannot, however, be disregarded, assuming that rhodium(II) complexes are labile. The reason for preferring rhodium(I) as the catalytic species is, first, that $[Rh(CO)_2Cl]_2$, which must rapidly yield $[Rh(py)_4]^+$, is a powerful catalyst for the reaction. The fact that the other Rh(I) compounds tested did not catalyze the reaction is probably explained not only by their insolubility, but also by the strong stabilizing influence of the phosphine ligands in the complexes. In the presence of pyridine, the reaction to form $[Rh(py)_4]^+$ does not proceed to any significant extent.[9] The second reason is that the +1 oxidation state of rhodium is well established. Few compounds of rhodium(II) have been prepared to date, and none of them is monomeric. The third reason involves the stoichiometry and configuration of the product. Since rhodium(I) forms planar complexes, the *trans* product is a necessary consequence of the proposed mechanism, while rhodium(II) might give either the *cis* or *trans* product. The same reasoning explains why rhodium will not pick up a fifth pyridine ligand even though the reaction is run at a fairly high concentration of pyridine: rhodium(I) is very unlikely to associate with more than four pyridines. It is also of interest to note that this mechanism for the Rh(I) catalysis of Rh(III) reactions is strictly analogous to the mechanism for Pt(II) catalysis of reactions of Pt(IV) complexes.[10] Finally, the magnetic evidence cited above suggests the presence of rhodium(I) in the reduced solutions.

Acknowledgments.—This research was supported by the U. S. Atomic Energy Commission under contract No. AT(11-1)-1087.

---

[9] L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

[10] F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS

Polarographic Evaluation of the Formation Constants of Aquo-Copper(II) Complexes in Acetone

BY IVORY V. NELSON AND REYNOLD T. IWAMOTO

Received October 22, 1963

Formation constants for the four aquo-copper(II) complexes $Cu(H_2O)^{+2}$, $Cu(H_2O)_2^{+2}$, $Cu(H_2O)_3^{+2}$, and $Cu(H_2O)_4^{+2}$ in acetone have been evaluated. Log k values are 1.75, 1.50, 1.00, and 0.75 in 0.1 M $LiClO_4$ solution and 1.75, 1.25, 0.80, and 0.65 in 0.1 M $(C_2H_5)_4NClO_4$ solution.

Because even the most careful purification of an organic solvent leaves a surprisingly large amount of water in the solvent, *e.g.*, a solvent which is 99.98% pure, *i.e.*, 0.02% in water, is 0.01 M in water, one of the most important problems with regard to the interpretation of experimental results on studies dealing with the nature and behavior of inorganic ions in nonaqueous media is the effect of residual water. In a previous communication,[1] we presented information, in the form of formation constants for the aquo-copper(II) complexes, on the preferential solvation of copper(II) ion by residual water molecules in nitromethane and ethanol. Because these two solvents exhibit opposite extremes of behavior with regard to compatibility with water, we have evaluated the formation constants of aquo-copper(II) complexes in acetone, a solvent whose compatibility with water is between those of nitromethane and ethanol. This information should provide a better understanding of the magnitude of the effect of residual water on the behavior of metal ions in nonaqueous solutions than that which is possible from the results of the previous study alone.

Experimental

Reagent grade acetone was treated with potassium permanganate, dried over anhydrous potassium carbonate, and distilled from phosphorus pentoxide. All other pertinent experimental information has been presented elsewhere.[1,2]

Results

The temporary constants in Table I were obtained by graphical evaluation of plots of $E_{1/2\,Cu(II)/Cu(I)}$ *vs.* $-\log [H_2O]$ (Fig. 1). Because the limiting slopes of the curves at high water concentrations (0.1–1 M) were *ca.* 0.24, only four constants were obtainable. These constants were refined by the method of successive approximations. The refined values are presented in Table II. A detailed discussion of the treatment of the experimental data was presented previously.[1]

TABLE I
TEMPORARY FORMATION CONSTANTS FOR THE AQUO-COPPER(II) COMPLEXES IN ACETONE

0.1 M $LiClO_4$	0.1 M $(C_2H_5)_4NClO_4$
$\log k_1 = 1.89$	$\log k_1 = 1.96$
$\log k_2 = 1.52$	$\log k_2 = 1.37$
$\log k_3 = 1.05$	$\log k_3 = 0.84$
$\log k_4 = 0.64$	$\log k_4 = 0.33$

---

[1] R. C. Larson and R. T. Iwamoto, *Inorg. Chem.*, **1**, 316 (1962).

[2] I. V. Nelson and R. T. Iwamoto, *ibid.*, **1**, 151 (1962).

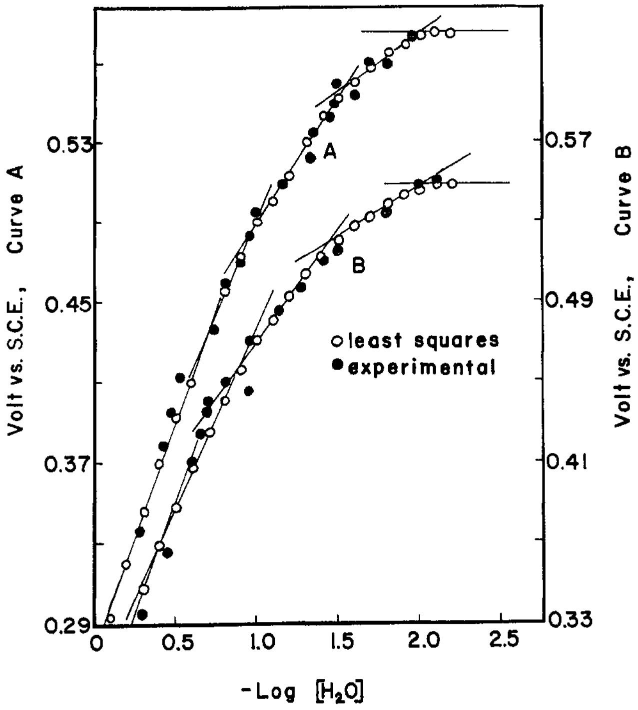


Fig. 1.—Half-wave potential, $E_{1/2}$, for the Cu(II),Cu(I) wave in acetone as a function of $-\log$ [H_2O]: curve A, 0.1 *M* $LiClO_4$, supporting electrolyte; curve B, 0.1 *M* $(C_2H_5)_4NClO_4$, supporting electrolyte.

Table II

Refined Values of the Formation Constants for the Aquo-Copper(II) Complexes in Acetone Obtained by the Method of Successive Approximations[a]

0.1 *M* $LiClO_4$	0.1 *M* $(C_2H_5)_4NClO_4$
$\log k_1 = 1.75$	$\log k_1 = 1.75$
$\log k_2 = 1.50$	$\log k_2 = 1.25$
$\log k_3 = 1.00$	$\log k_3 = 0.80$
$\log k_4 = 0.75$	$\log k_4 = 0.65$

[a] All values of log *k* have been rounded off to the nearest 0.05 log *k* value.

Discussion

Copper(II) ion is reduced in two one-electron steps in acetone,[3] and with increasing concentration of water, the Cu(II),Cu(I) wave shifts to negative values. Because the half-wave potential of the Cu(I),Cu(Hg) wave is affected very little (5 mv.) over the range of 0 to 0.5 *M* water concentration, and because there is no change in the liquid-junction potential over the range of water concentration studied,[4] with either supporting electrolyte, the change in the half-wave potential of the Cu(II),Cu(I) wave with variation in water concentration is due entirely to complexation of copper(II) ion by water.

Approximate values of log k_1 obtained, as described previously, from the temporary values of the other individual constants gave $E^{0\prime}_{Cu(II),Cu(I)}$ of +0.547 v. *vs.* s.c.e. for 0.1 *M* $(C_2H_5)_4NClO_4$ solutions and +0.580 v. for 0.1 *M* $LiClO_4$ solutions.

The refined values of the formation constants for the aquo-copper(II) complexes in acetone are in line with those reported previously for the complexes in nitromethane and ethanol.

The slightly lower values of the individual formation constants in 0.1 *M* $(C_2H_5)_4NClO_4$, in which the concentration of free perchlorate ion is higher, as compared with those of 0.1 *M* $LiClO_4$, suggest that a certain amount of Cu^{+2},ClO_4^- ion-pair formation occurs in this system. The higher perchlorate ion concentration in $(C_2H_5)_4NClO_4$ solutions than in $LiClO_4$ solutions of the same concentration is due to the lower formation constant of the $(C_2H_5)_4N^+,ClO_4^-$ ion pair than of the Li^+,ClO_4^- ion pair.[5] The aquo-copper(II) formation constants in 0.1 *M* $LiClO_4$ solution are undoubtedly affected by some preferential solvation of lithium ion by water in acetone. No quantitative information, unfortunately, is available on this interaction. The magnitude of this interaction between lithium ion and water molecules in acetone, however, must not be very large in view of the good agreement between the expected and observed change from k_4 in 0.1 *M* $LiClO_4$ to k_5 (see next paragraph) in 1 *M* $NaClO_4$.

After the completion of this work, a paper by Friedman and Plane[6] reporting equilibrium constant values for the equilibria shown below in acetone appeared.

$$K_1 = \frac{[\mathrm{Cu(H_2O)_5(acetone)^{+2}}][\mathrm{H_2O}]}{[\mathrm{Cu(H_2O)_6^{+2}}][\mathrm{acetone}]}$$

$$K_2 = \frac{[\mathrm{Cu(H_2O)_4(acetone)_2^{+2}}][\mathrm{H_2O}]}{[\mathrm{Cu(H_2O)_5(acetone)^{+2}}][\mathrm{acetone}]}$$

The reciprocal of K_2[acetone] is equal to the aquo-copper(II) formation constant k_5. It is interesting to note that the value of 0.56 calculated for log k_5 in 1 *M* $NaClO_4$ solution is in line with the change expected from k_4 to k_5. No value for K_1, from which k_6 could be evaluated, was reported for this solution. Log k_6 in the absence of inert electrolyte is -1.7.

Table III

Per Cent of Unhydrated Cu(II) Species

	Ethanol	Acetone	Nitromethane
0.001 *M* H_2O	. . .	94%	55%
0.01 *M* H_2O	99%	57%	6%
0.1 *M* H_2O	95%	2%	. . .

Using the formation constants obtained, we have calculated the percentages of unhydrated copper(II) species at various levels of water concentration in ethanol, nitromethane, and acetone. These percentages are listed in Table III. They indicate clearly that in solvents such as nitromethane and acetone, with

---

[3] I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. Nucl. Chem.*, **22**, 279 (1961).

[4] This conclusion is based on the fact that the half-wave potentials for the oxidation of tris(4,7-dimethyl-1,10-phenanthroline)iron(II) ion at a rotating platinum electrode in acetone 0.01 *M* in water and 0.5 *M* in water are identical for both 0.1 *M* $LiClO_4$ and 0.1 *M* $(C_2H_5)_4NClO_4$ solutions. $E_{1/2}$ *vs.* s.c.e. in 0.1 *M* $LiClO_4$ solutions 0.01 and 0.5 *M* in water = +0.940 v. $E_{1/2}$ *vs.* s.c.e. in 0.1 *M* $(C_2H_5)_4NClO_4$ solutions 0.01 and 0.5 *M* in water = +0.942 v. See I. V. Nelson and R. T. Iwamoto, *Anal. Chem.*, **35**, 867 (1963).

[5] Because the formation constant of the Li^+,ClO_4^- ion pair in acetone is not available, the formation constants of Li^+,picrate$^-$ ($10^{3.0}$) and $(C_2H_5)_4N^+$, picrate$^-$ ($10^{1.8}$) in acetone and Li^+,picrate$^-$ ($10^{3.6}$) and $(C_2H_5)_4N^+$,picrate$^-$ ($10^{2.4}$) in methyl ethyl ketone have been used to approximate the relative difference between the ion-pair formation constants of Li^+,ClO_4^- and $(C_2H_5)_4N^+,ClO_4^-$ in acetone: C. W. Davies, "Ion Association," Butterworths, Washington, D. C., 1962, pp. 96–98.

[6] N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963).

which water is not very highly compatible, care must be exercised in ascribing the behavior of metal ion species to the completely solvated (unhydrated) metal ion.

Acknowledgment.—The authors wish to acknowledge the support of the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Grants AF-AFOSR-61-8 and AF-AFOSR-220-63).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK 27, NEW YORK

The Electronic Structures of Square-Planar Metal Complexes. II.[1] The Complexes of Maleonitriledithiolate with Copper(II), Nickel(II), Palladium(II), and Platinum(II)

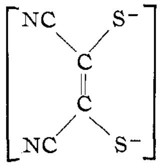
BY E. BILLIG, RAYMOND WILLIAMS, I. BERNAL, JAMES H. WATERS, AND HARRY B. GRAY

Received November 4, 1963

Several square-planar metal complexes containing the dianion of maleonitriledithiol, which we call MNT, are reported. The Ni^{2+}, Pd^{2+}, and Pt^{2+} complexes are diamagnetic, but the presence of very low energy d–d spectral bands indicates that MNT is as weak field as Br^- and I^- in a square-planar situation. The Cu^{2+} complex is a spin doublet, as expected. The electron spin resonance (e.s.r.) spectrum of $Cu(MNT)_2^{2-}$ is reported in several different solvents. The combined electronic spectral and e.s.r. results indicate that axial perturbations due to solvent molecules are very weak or nonexistent in these complexes.

Introduction

In a recent communication[1] we briefly described the characterization of Co^{2+} and Ni^{2+} complexes containing as ligand the dianion of maleonitriledithiol (MNT), which is shown below.



MNT^{2-}

The complexes we reported first have the general formula $R_2[M(MNT)_2]$, where R is some unipositive ion. More recently, stable complexes of the type $R[M(MNT)_2]$ have been reported.[2,3]

The structure of the $[(CH_3)_4N]_2[Ni(MNT)_2]$ complex has been solved by a combination of three-dimensional Patterson, Fourier, and least-squares techniques.[4] The $Ni(MNT)_2^{2-}$ group is planar, and the Ni^{2+} is truly four-coordinate in the crystal. The $[n\text{-}C_4H_9)_4N]_2[Co(MNT)_2]$ complex was claimed to be the first well-authenticated example of a rigorously planar, high-spin metal complex.[1] This claim has recently been challenged by Davison, *et al.*, who believe the $Co(MNT)_2^{2-}$ complex is, in fact, low spin.[5] In view of this situation, we shall describe our experiments on the $Co(MNT)_2^{2-}$ complex in considerable detail in a separate paper. The preparation, characterization, and certain physical properties of the $R_2[M(MNT)_2]$ (with M = Cu^{2+}, Ni^{2+}, Pd^{2+}, and Pt^{2+}) complexes are described in this paper.

Experimental

Preparation of Compounds. Na_2MNT.—Sodium maleonitriledithiolate was prepared according to the published method.[6,7] This yellow hygroscopic salt was dried and stored over calcium chloride in a vacuum desiccator until prior to use.

$[(C_2H_5)_4N]_2[Ni(MNT)_2]$.—A solution of 3.8 g. of Na_2MNT in 17 ml. of 1:1 aqueous methanol was warmed on a steam bath. A solution of 2.4 g. of $NiCl_2$ in 5 ml. of aqueous methanol was added dropwise to the warm Na_2MNT solution, with stirring. The intensely red solution was filtered. To the filtrate was added a solution of 2.6 g. of $(C_2H_5)_4NBr$ in 5 ml. of aqueous methanol. After cooling, the red precipitate which formed was filtered off. Addition to the filtrate of 1.2 g. of $(C_2H_5)_4NBr$ in water produced more of the precipitate. The precipitates were combined, washed with water, and then dried at 60° *in vacuo* The 6 g. of red material was recrystallized from ethanol–acetone, yielding 4.5 g. of large red crystals of $[(C_2H_5)_4N]_2[Ni(MNT)_2]$.

The other $R_2[M(MNT)_2]$ complexes were prepared using essentially this same procedure.

Reaction of $Pd(NH_3)_4Cl_2$ with Na_2MNT.—An olive-green precipitate was obtained from the reaction in aqueous solution of one equivalent of Na_2MNT and $Pd(NH_3)_4Cl_2$, as previously reported.[6] This compound is a 1:1 electrolyte in DMF solution, with Λ = 95 cm.^{2} equiv.$^{-1}$ ohm^{-1}. The electronic spectrum of this compound shows a band at 15,700 cm.$^{-1}$ (ϵ 80) characteristic of $(R_4N)_2[Pd(MNT)_2]$.

Physical Measurements.—Electronic spectra were taken using a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used as received. Static susceptibility measurements were made at room temperature by the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. Conductivities were deter-

---

(1) First paper in the series: H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(2) H. B. Gray and E. Billig, *ibid.*, **85**, 2019 (1963).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 2029 (1963); *Inorg. Chem.*, **2**, 1227 (1963).

(4) R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964).

(5) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 3049 (1963).

(6) G. Bähr and G. Schleitzer, *Ber.*, **88**, 1771 (1955); **90**, 438 (1957).

(7) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962).