In summary, therefore, it appears that shifts in band III with variation of the γ-substituent are in accord with the assignment of the band as a $\pi-\pi^*$ transition, and therefore provide support for this assignment.

It also will be noted that the energy of band II is practically insensitive to variation in the γ-substituent. Such behavior is in accord with the proposed assignment of this band as a charge transfer band as discussed in part III.[2] In particular, the possibility that bands II and III might be the two components of a $\pi_3 \rightarrow \pi_4^*$ transition is rendered very unlikely by the very different degrees of sensitivity of these two bands to γ-substituents.

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CONTRIBUTION FROM McPHERSON CHEMICAL LABORATORY,
OHIO STATE UNIVERSITY, COLUMBUS, OHIO

A Study of the Stability and Basicity of the Copper(II) Pyrophosphate Complexes Using the Dropping Amalgam Electrode[1]

BY ORION E. SCHUPP III, PETER E. STURROCK, AND JAMES I. WATTERS[2]

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The extent of association of hydrogen ions with copper pyrophosphate complexes has been evaluated on the basis of potential measurements using a dropping copper amalgam electrode. Correlations have been made between the number of associated hydrogen ions and the stability as well as the basicity of the complex. In terms of concentrations the stepwise formation constants of $CuP_2O_7^{2-}$ and $Cu(P_2O_7)_2^{6-}$ are $10^{9.07}$ and $10^{4.58}$, respectively, at an ionic strength adjusted to unity with tetramethylammonium nitrate at 25°. One hydrogen ion associates readily with each PO_4 tetrahedron. The stepwise formation constants for the successive addition of hydrogen ions to $CuP_2O_7^{2-}$ are $10^{5.25}$ and $10^{3.31}$. For $Cu(P_2O_7)_2^{6-}$ they are $10^{6.76}$, $10^{5.78}$, $10^{4.40}$, and $10^{3.21}$. The association with hydrogen ions greatly decreases the stability of the complex. Some association of alkali metal ions with $Cu(P_2O_7)_2^{6-}$ is indicated by the slightly increased stability of this complex ion in the presence of up to 0.1 M Na^+ or K^+.

Introduction

The purpose of the present study was to establish the extent of association of hydrogen ions with copper(II) pyrophospate complexes and to determine the effect of this association on the stability of the complex. In addition, various effects which decreased the accuracy of previous studies were eliminated.

It has been known for a long time that pyrophosphate is capable of forming complexes in acidic solutions. Kolthoff and Watters[3] obtained potentiometric evidence that manganese(III) forms a complex with $H_2P_2O_7^{2-}$, while Laitinen and Onstott[4] obtained polarographic evidence for the existence and stability of the copper(II) complexes $CuHP_2O_7^{1-}$ and $Cu(HP_2O_7)_2^{4-}$. Spectrophotometric evidence for the existence and stability of the species $Cu(P_2O_7)^{2-}$ and $Cu(P_2O_7)_2^{6-}$ has been obtained in this Laboratory[5] and confirmed in other laboratories.[6-8]

The tendency of polyphosphate ions even when complexed with a metal ion to associate with hydrogen ions results in fairly complicated equilibria, so that calculations based on the assumption that particular species predominate in particular ranges of pH and ligand concentrations may lead to inaccurate results. Modern functions such as those of Leden, Bjerrum, and Froneus[9] eliminate the need for approximations of this type. As shown in earlier papers,[10,11] Leden's function expressed in terms of electrode potentials can be readily applied when the complexed, as well as the free, ligands tend to associate with hydrogen ions.

A further complication is the fact that alkali metal ions are known to form complexes with pyrophosphate[3,12] and triphosphate.[13] In the present study, alkali metal ions were replaced by tetramethylammonium ion in both the polyphosphate and in the supporting electro-

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[2] Communications should be addressed to J. I. Watters.

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lyte through the use of cation-exchange resins. The effect of alkali metal ions on the complexes also was studied.

It has been observed in this Laboratory that the potentials of stationary copper or copper amalgam electrodes in pyrophosphate solutions drift in a positive direction, presumably due to oxide formation as discussed in a previous paper.[14]

Previous polarographic studies[4,15,16] of this system using the conventional mercury electrode have been limited because poorly shaped cathodic polarograph waves are obtained in neutral or alkaline solutions. As a consequence, conventional polarographic data have never been obtained over a sufficiently broad range of conditions to calculate an internally consistent set of equilibrium constants in which the relative stabilities and acidities of the various complex species are indicated. The dropping copper amalgam electrode, described in a previous paper,[14] was found applicable in the study of copper(II) pyrophosphate complexes since the potentials could be measured at zero current under conditions of equilibrium with the bulk of the solution.

In previous studies in this Laboratory, methods have been developed for the potentiometric and polarographic investigation of mixed complexes[10,11] and for the application of the dropping amalgam electrode to stepwise complex equilibria.[14] It also has been shown that the various equilibria of polyphosphate complexes can be treated in terms of hydrogen ions and the completely dissociated polyphosphate ion instead of species containing associated hydrogen ions, such as $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$. The corresponding complexity constants are readily converted to forms involving the associated species actually present in the complex. In the present study, copper(II) ion corresponds to M, hydrogen ion to A, pyrophosphate ion to B, and hydroxyl ion to C in the formulas given in the previous papers. In the following expressions, the symbol L indicates the pyrophosphate ligand including its ionic charge, and k_3 and k_4 are the last two acidity constants of pyrophosphoric acid, measured in the absence of complex forming metal ions. The charge on the complex ion is indicated by the superscript, $v-$. Assuming only mononuclear species exist in significant concentrations with an excess of ligands present one writes the general expressions

$$\mathrm{Cu}^{2+} + i\mathrm{H}^+ + j\mathrm{L} + k\mathrm{OH}^- \rightleftharpoons \mathrm{CuH}_i\mathrm{L}_j(\mathrm{OH})_k{}^{v-}$$

$$\beta_{ijk} = [\mathrm{CuH}_i\mathrm{L}_j(\mathrm{OH})_k{}^{v-}]/[\mathrm{Cu}^{2+}](\mathrm{H}^+)^i[\mathrm{L}]^j(\mathrm{OH}^-)^k \quad (1)$$

These are general expressions. Either i or k must be zero in any particular expression. As discussed in the previous study,[17] association of hydrogen and hydroxide ions may be expected to occur in different pH ranges, although this is not structurally necessary. The simultaneous association of the complexed pyrophosphate with hydrogen ions and the complexed copper(II) with hydroxide ion is structurally possible to form the complex $\mathrm{CuH}_i(\mathrm{P}_2\mathrm{O}_7)_j\mathrm{OH}_i{}^{(4j-2)-}$. This species cannot be distinguished from $\mathrm{Cu}(\mathrm{P}_2\mathrm{O}_7)_j{}^{(4j-2)-}$ and both will contribute to the complexity constant of the latter. The concentrations of all species except hydrogen and hydroxyl ions, indicated by brackets, are used in the equilibrium constants. However, when hydrogen or hydroxyl ions are involved in the equilibria, their activities, indicated by parentheses, are used instead of concentrations since their activities were measured by means of a glass electrode standardized in the conventional way.

The form of Leden's function $F(\mathrm{H}^+,\mathrm{L},\mathrm{OH}^-)_0$ used in the present study is

$$F(\mathrm{H}^+,\mathrm{L},\mathrm{OH}^-)_0 = \text{antilog } [(E_{\mathrm{aq}} - E_{\mathrm{c}})(0.4342n\mathfrak{F}/RT)] = \text{antilog } \Delta E(0.4342n\mathfrak{F}/RT) = \sum_{i=0}^{2N}\sum_{j=0}^{N}\sum_{k=0}^{2N} \beta_{ijk}(\mathrm{H}^+)^i[\mathrm{L}]^j(\mathrm{OH}^-)^k \quad (2)$$

Since the term for $i=j=k=0$ is unity

$$F(\mathrm{H}^+,\mathrm{L},\mathrm{OH}^-)_1 = (F(\mathrm{H}^+,\mathrm{L},\mathrm{OH}^-)_0 - 1)/[\mathrm{L}] \quad (3)$$

The latter expression can be expanded for all possible mononuclear complexes

$$F(\mathrm{H}^+,\mathrm{L},\mathrm{OH}^-)_1 = \beta_{010} + \beta_{020}[\mathrm{L}] + \beta_{110}(\mathrm{H}^+) + \beta_{210}(\mathrm{H}^+)^2 + \beta_{120}(\mathrm{H}^+)[\mathrm{L}] + \beta_{220}(\mathrm{H}^+)^2[\mathrm{L}] + \beta_{320}(\mathrm{H}^+)^3[\mathrm{L}] + \beta_{420}(\mathrm{H}^+)^4[\mathrm{L}] + \beta_{011}(\mathrm{OH}^-) + \beta_{012}(\mathrm{OH}^-)^2 + \ldots\ldots \quad (4)$$

The potentials, E_{aq} and E_{c}, are measured in noncomplexing solution and the complexing solution, respectively, which contain the same total concentrations of copper(II), copper amalgam, and supporting electrolyte. These potentials may be spontaneous potentials or half-wave potentials. The original complexity constants were calculated in terms of the equilibrium with H^+, $\mathrm{P}_2\mathrm{O}_7{}^{4-}$, and OH^-. The numerical subscripts after β indicate the number of each of these species. These are converted to equivalent equilibria and complexity constants in terms of the species containing associated hydrogen ion such as $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$ and these constants are indicated by $\beta^{\mathrm{M}}{}_{\mathrm{MHL}}$. The latter have the advantage over those solved by determinants in that their magnitude is an indication of the stability of the complex. Equilibria among the species can be considered in terms of stepwise formation constants for association with hydrogen ion which show the influence of complex formation on the acidity of the ligands. These constants are indicated by symbols such as $K^{\mathrm{ML}}{}_{\mathrm{MHL}}$. Details concerning the calculations, general experimental techniques, and apparatus are described in previous publications.[16,17]

Results and Discussion

In Fig. 1 are shown typical anodic–cathodic polarograms of copper(II) in the ligand-free supporting electrolyte and in pyrophosphate solutions having various pH values. As observed by Laitinen and Onstott[4] for cathodic waves of the complex, it is evident that the

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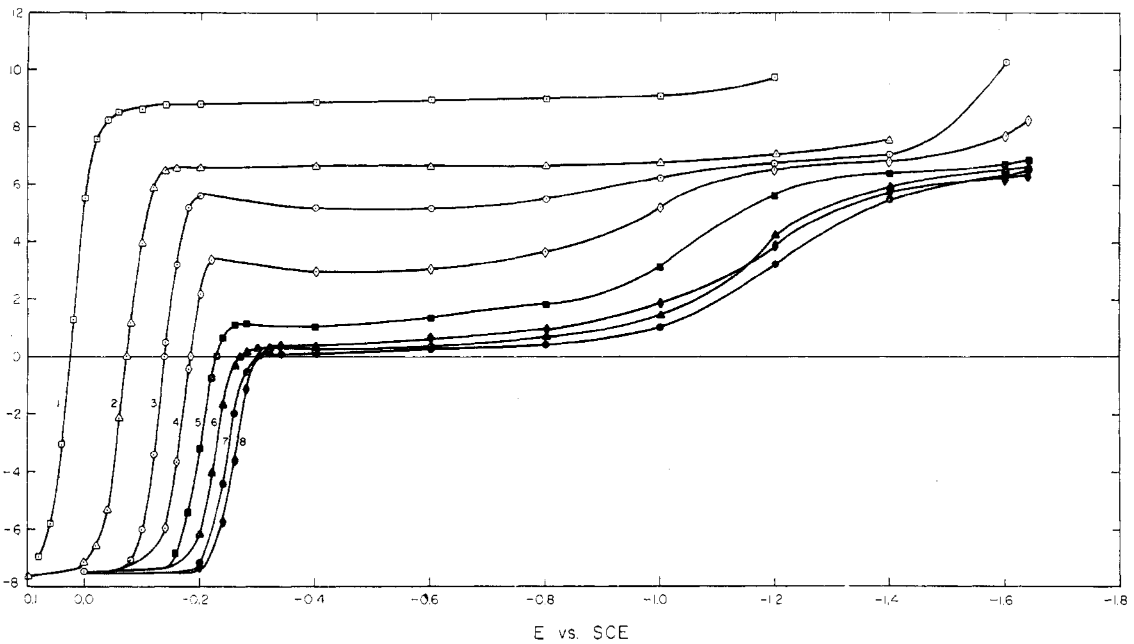

Fig. 1.—Anodic–cathodic polarograms obtained with the dropping copper amalgam electrode and copper(II) in pyrophosphate solution at various pH values: $C_{P_2O_7^{4-}}$ = 0.0500 *M* (except in polarogram 1); C_{Cu} = 1.000 m*M*; μ = 1.00 with $N(CH_3)_4NO_3$; methyl red = 0.0005%; amalgam = 0.0005% Cu. Polarogram 1, pH 3.10 (no $P_2O_7^{4-}$); 2, pH 4.78; 3, pH 6.03; 4, pH 6.89; 5, pH 7.70; 6, pH 8.44; 7, pH 9.60; 8, pH 10.53.

entire waves are essentially reversible in fairly acidic pyrophosphate solutions and in the acidic solution containing no complexing agent since the waves cross the zero current axis without inflection and have the theoretical slope ($\Delta E/\Delta \log (i_{d_c} - i)/(i - i_{d_{an}})$) of 0.030 volt for a two-electron electrode reaction. Furthermore, the diffusion current constant of 3.79 μa./m*M* concentration of copper(II) per unit capillary characteristic is consistent with a two-electron reduction of copper(II) directly to free copper. In moderately alkaline pyrophosphate solutions the waves have an anomalous appearance since the cathodic current does not develop normally. In fact, a cathodic current decrease with increasing voltage has been obtained in several laboratories.[4,5,14] The final irreversible wave which finally yields a comparable total diffusion current is attained at a much higher applied potential.

With copper(II) ions absent in the bulk of the pyrophosphate solution, reversible anodic waves having the theoretical slope of 0.030 volt are obtained at all pH values except in the regions close to 7.5 and 4.0, where the slopes are about 0.36. This increase in slope is due to the poor poise[18] of the electrode at the acidic equivalence points of pyrophosphoric acid discussed in a previous paper[14] and is not due to electrode irreversibility. With increased acidity, the waves shift in a regular manner consistent with the proposed complex equilibria. The shift in anodic half-wave potential due to complex formation in solutions of similar ligand composition agrees well with the shift in spontaneous potential of the composite wave if the pH is below 6. At higher pH values the shifts of the anodic waves due to complex formation at the surface of the drops are less than the corresponding shifts of the cathodic waves due to reduction of the complex already present. Our attempt to resolve this difference led to a logical explanation for the anomalous shape of cathodic waves obtained in alkaline solutions. Evidence obtained in this study indicates that the dipyrophosphate complex containing no associated hydrogen which is produced anodically has a less stable configuration than the form which is present after final equilibrium is attained. The latter form is finally irreversibly reduced at a much higher potential.

The anomalous wave shape has been ascribed to stepwise reduction,[16] to film formation,[15] and to the presence of different complexes in sluggish equilibrium.[4] The first possibility has been eliminated because stepwise waves of equal height usually are not obtained. The possibility of film formation was eliminated in this Laboratory when it was observed that the current decrease with increasing cathodic voltage could be eliminated by the addition of sufficient maximum suppressor. Furthermore, film formation itself is known to suppress maxima.[19] By no conceivable variation of ligand or copper(II) ion concentration was it possible to obtain a single reversible wave. Conditions such as low copper(II) ion concentration and high ligand concentration which should have hindered the formation of a precipitate of, for example, $Cu_2P_2O_7$, always decreased the height of the first wave. No film could be observed visually on the drop or on a large mercury pool even after prolonged electrolysis.

The possibility remained that some complex species

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[19] I. M. Kolthoff and Y. Okinata, *J. Am. Chem. Soc.*, **83**, 47 (1961).

in sluggish equilibrium with other species is not readily reduced so that cathodic currents decrease in magnitude. At zero current, this condition should not influence the electrode potential if, in the process of measuring the potential, there is no appreciable change in the concentration of electrolyzable species which rapidly reach equilibrium with the electrode but reach equilibrium more slowly with other non-electrolyzable species.

The first evidence was obtained by slope analysis. If the final cathodic diffusion currents of the anomalous wave are used in this analysis, curved lines are always obtained in the ΔE *vs.* $\Delta \log (i_{\mathrm{dc}} - i)/(i - i_{\mathrm{dan}})$ plots even in the anodic region. However, if the first cathodic diffusion current is used, linear plots with the reversible slope of 0.030 volt are obtained. This evidence indicates that some complex species, probably $Cu(P_2O_7)_2^{6-}$, behaves as though it is absent insofar as any cathodic reduction is concerned. The possibility that this complex is absent in the anodic equilibrium also was investigated. However, the shift in the anodic waves with variation in the total pyrophosphate concentration at constant pH conforms with a mean number of bound ligands, $\bar{n}$, close to 2, thus

$$\Delta E = \bar{n}2.303n\mathfrak{F}/RT \log (P_2O_7^{4-})_1/(P_2O_7^{4-})_2 \qquad (5)$$

where $(P_2O_7^{4-})_1$ and $(P_2O_7^{4-})_2$ are two different pyrophosphate concentrations at the same pH.[3,4] Furthermore, the presence of this complex is necessary to account for the shift in the spontaneous or half-wave potential in Leden's expression.

In Table I are given the spontaneous potential data along with the experimental and calculated values of F_1 based on the values obtained for the various original complexity constants calculated in terms of Cu^{2+}, H^+, $P_2O_7^{4-}$, and OH^-. After showing that the mean number of bound ligands in the higher pyrophosphate concentrations was two by means of eq. 5, third-order determinants were used to obtain preliminary values for the constants β_{020}, β_{120}, and β_{220} above a pH of about 5.5. Above pH 9 an accurate value could be obtained for β_{020}. Then a third-order determinant with β_{020} as a known yielded an accurate value for β_{120} and preliminary values for β_{220} and β_{010}. The remaining constants finally were calculated in a similar manner from the data in the lower pH range.

TABLE I

POTENTIAL DATA OF THE PYROPHOSPHATE–COPPER(II) SYSTEM $C_{\mathrm{Cu}} = 0.001\ M$, $\mu = 1.0 \pm 0.2$ with $N(CH_3)_4NO_3$, $E_{\mathrm{aq}} = 0.0252$ v. *vs.* s.c.e., amalgam = 0.0005% Cu

pH	ΔE	$-\log$ $[P_2O_7^{4-}]$	$\log F_1$ exptl.	$\log F_1$ calcd.
	(A)	$C_{P_2O_7^{4-}} = 0.01\ M$		
2.27	0.01596	12.77	13.16	13.14
2.94	.02164	11.28	11.92	11.93
3.63	.03170	9.87	10.91	10.91
3.88	.03729	9.38	10.62	10.60
4.70	.06380	7.75	9.90	9.85
5.85	.11496	5.63	9.53	9.50
6.44	.14359	4.75	9.61	9.61
7.00	.17010	4.09	9.84	9.85
7.53	.19812	3.54	10.24	10.21
7.95	.21938	3.13	10.55	10.56
8.44	.24360	2.71	10.95	10.95
9.08	.26560	2.32	11.30	11.34
9.54	.27340	2.19	11.43	11.46
	(B)	$C_{P_2O_7^{4-}} = 0.05\ M$		
2.51	0.04115	11.45	12.82	12.84
3.02	.0479	10.35	11.98	11.98
3.60	.0479	9.20	11.15	11.14
4.49	.0856	7.39	10.31	10.32
5.50	.1347	5.45	10.03	10.03
6.50	.1872	3.91	10.24	10.27
7.53	.24345	2.76	10.99	10.97
8.40	.2890	1.97	11.74	11.69
9.47	.3216	1.43	12.30	12.22
10.05	.32445	1.35	12.32	12.30

After calculating the fraction of each species present from its term in the summation divided by the entire summation term, third-order determinants containing the constants for minor species as knowns were used to solve accurate values for all of the constants. In this way the original constants having the form of eq. 1 were calculated

$$\beta_{010} = [CuP_2O_7^{2-}]/[Cu^{2+}][P_2O_7]^{4-} = 10^{9.07} \qquad (6)$$

$$\beta_{020} = [Cu(P_2O_7)_2^{6-}]/[Cu^{2+}][P_2O_7^{4-}]^2 = 10^{13.65} \qquad (7)$$

$$\beta_{110} = [CuHP_2O_7^{1-}]/[Cu^{2+}](H^+)[P_2O_7^{4-}] = 10^{14.30} \qquad (8)$$

All other possible mononuclear species containing one or two pyrophosphate ions and one or two hydrogen ions for each pyrophosphate ion were found to be present. Their formulas and complexity constants having forms similar to that of eq. 8 but with (H^+) and $P_2O_7^{4-}$ raised to the appropriate powers were: $CuH_2P_2O_7$, $\beta_{210} = 10^{17.61}$; $CuH(P_2O_7)_2^{5-}$, $\beta_{120} = 10^{20.41}$; $CuH_2(P_2O_7)_2^{4-}$, $\beta_{220} = 10^{26.93}$; $CuH_3(P_2O_7)_2^{3-}$, $\beta_{320} = 10^{30.59}$; and $CuH_4(P_2O_7)_2^{2-}$, $\beta_{420} = 10^{33.80}$. No hydroxide complex was detected in the pH range below 10. With an excess of $P_2O_7^{4-}$ present it is probable that only the complex $CuP_2O_7(OH)_2^{4-}$ would be formed since observations in this Laboratory always have indicated that, in copper(II) complexes, monodentate ligands replace bidentate ligands in pairs. The electrode became unstable with respect to the formation of Cu_2O above a pH of 10, where hydroxide complexes should be detected.

The distribution of the various species as a function of pH is shown in Fig. 2. Also shown as a dashed curve is the fractional decrease in the first diffusion current as a function of pH. It can be observed that this dashed curve follows the curve for the relative abundance of $Cu(P_2O_7)_2^{6-}$ rather closely. This is strong evidence that the $Cu(P_2O_7)_2^{6-}$ species which is finally present does not undergo reversible electrolytic reduction at all and that at least a part of the $CuH(P_2O_7)_2^{5-}$ species may not be completely reversibly reduced. This is in agreement with a deduction by Laitinen and Onstott[4] based on the fact that the wave height decreased in the region where these species might reasonably be expected to exist. A $Cu(P_2O_7)_2^{6-}$ species having a complexity constant of $10^{12.50}$ was confirmed on the basis of the shift in the anodic half-wave potentials. This evidence indicates that the anodically

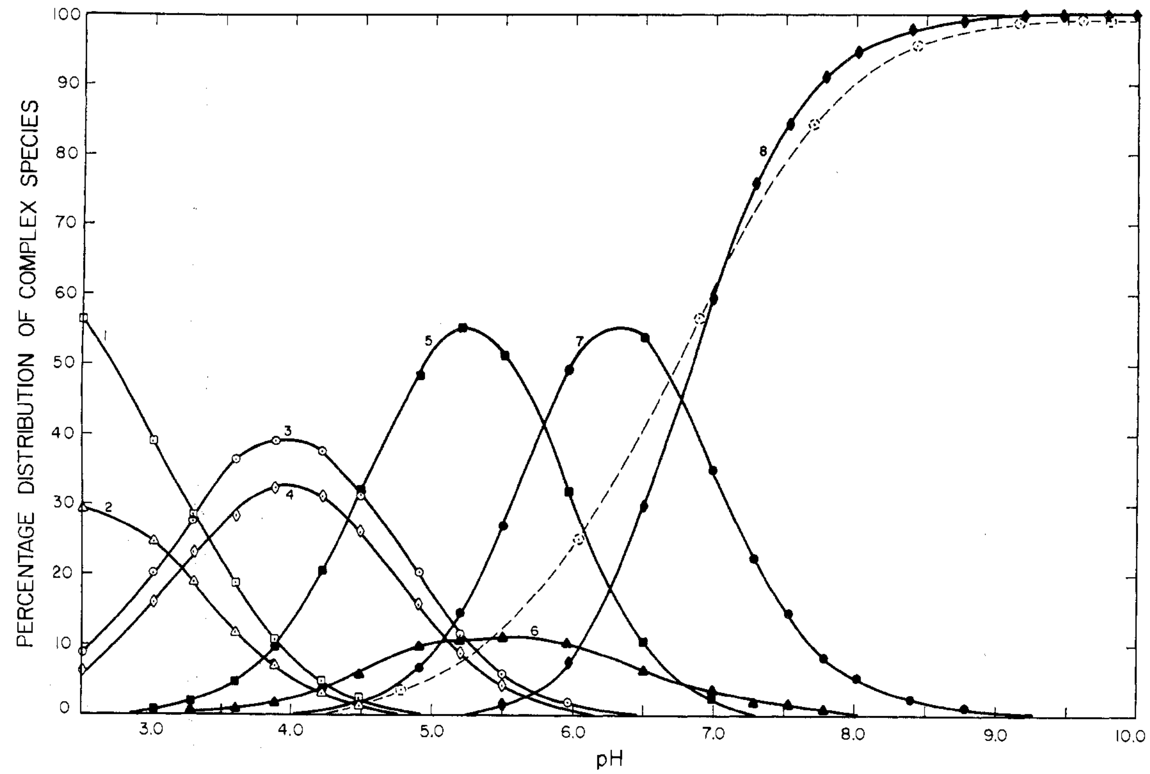

Fig. 2.—Percentage distribution of copper(II) pyrophosphate complex species as a function of pH: C_{Cu} = 1.00 m*M*; $C_{P_2O_7^{4-}}$ = 0.05 *M*. Complex species: curve 1, $CuH_2P_2O_7$; 2, $CuH_4(P_2O_7)_2^{2-}$; 3, $CuHP_2O_7^-$; 4, $CuH_3(P_2O_7)_2^{3-}$; 5, $CuH_2(P_2O_7)_2^{4-}$; 6, $CuP_2O_7^{2-}$; 7, $CuH(P_2O_7)_2^{5-}$; 8, $Cu(P_2O_7)_2^{6-}$; 9 (dashed curve), fractional decrease in the first diffusion current as a function of pH.

produced species undergoes some rearrangement to a more stable but not reversibly reducible species at a rate which is slow compared to the rate of thermal diffusion or the establishment of the electrode potential. When the potential corresponding to equilibrium between the electrode and the bulk of the solution is described by Leden's equation it is not necessary that all species be involved directly in the electrode reaction. The only essential condition is that at least one of the species, which can reach equilibrium with the electrode as well as with all other species, must be present in sufficient concentration so that the electrode potential can be measured without appreciably altering this concentration. As is evident from curve 5, Fig. 1, this condition is fulfilled in the present study up to a pH of at least 7.7 and the data below this pH were sufficient to calculate complexity constants for all species.

The original constants containing (H^+) were converted to the following constants in terms of $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$ since the latter indicate the strength of the bond between the ligand and the copper(II)

$$\beta^{Cu}{}_{CuHL} = [CuHP_2O_7^{1-}]/[Cu^{2+}][HP_2O_7^{3-}] = 10^{5.37} \qquad (9)$$

$$\beta^{Cu}{}_{CuH_2L} = [CuH_2P_2O_7]/[Cu^{2+}][H_2P_2O_2^{2-}] = 10^{2.55} \qquad (10)$$

$$\beta^{Cu}{}_{CuHL_2} = [CuH(P_2O_7)_2^{5-}]/[Cu^{2+}][P_2O_7^{4-}][HP_2O_7^{3-}] = 10^{11.48} \qquad (11)$$

$$\beta^{Cu}{}_{CuH_2L_2} = [CuH_2(P_2O_7)_2^{4-}]/[Cu^{2+}][HP_2O_7^{3-}]^2 = 10^{8.33} \qquad (12)$$

$$\beta^{Cu}{}_{CuH_3L_2} = [CuH_3(P_2O_7)_2^{3-}]/[Cu^{2+}][HP_2O_7^{3-}][H_2P_2O_7^{2-}] = 10^{6.60} \qquad (13)$$

$$\beta^{Cu}{}_{CuH_4L_2} = [CuH_4(P_2O_7)_2^{2-}]/[Cu^{2+}][H_2P_2O_7^{2-}]^2 = 10^{3.60} \qquad (14)$$

ion. In Table II the results are summarized as logarithms of stepwise formation constants for the addition of $P_2O_7^{4-}$, $HP_2O_7^{3-}$, and $H_2P_2O_7^{2-}$ to the species indicated in the first column. As one might predict, the successive addition of hydrogen ions to the pyrophosphate greatly decreases the strength of the bond with copper. In $CuP_2O_7^{2-}$ the log of $\beta^{Cu}{}_{CuH_xL}$ decreases from 9.07 to 5.37 and finally to 2.55, which is close to a factor of two for the association with each additional hydrogen ion. In $Cu(P_2O_7)_2^{6-}$ the association with odd-numbered hydrogen ions causes log $\beta^{Cu}{}_{CuH_xL_2}$ to decrease by about 2 units while the association with even-numbered hydrogen ions causes it to decrease by about 3 units. It will be shown that the stepwise constants for the successive addition of hydrogen ions have values which are consistent with the inductive effect if each pyrophosphate ion is assumed to be bonded to the copper ion by a 6-membered chelate ring. No association of more than two hydrogen ions per complexed pyrophosphate ion was detected. This is quite reasonable if one extrapolates to predict the complexity constant for the association of an additional hydrogen ion.

Table II

Summary of Logarithms of Stepwise Formation Constants

Original species	Species added		
	$P_2O_7^{4-}$	$HP_2O_7^{3-}$	$H_2P_2O_7^{2-}$
Cu^{2+}	9.07	5.37	2.55
$CuP_2O_7^{2-}$	4.58	2.41	[a]
$CuHP_2O_7^{1-}$	6.11	2.96	1.29
$CuH_2P_2O_7$	[a]	4.05	1.23

[a] Improbable configuration.

A simple confirmation of the complexity constants containing odd numbers of hydrogen ions can be made on the basis of a calculation of mixed complexity constants described in a previous paper.[20] If the complexes, $CuH(P_2O_7)_2$ and $CuH_3P_2O_7$, are treated as mixed complexes of Cu with $P_2O_7^{4-}$, $HP_2O_7^{3-}$, and $H_2P_2O_7^{2-}$ their constants can be calculated according to eq. 26 of the previous paper.[17] On this basis one calculates $10^{11.68}$ compared to the observed $10^{11.48}$ for ${\beta^{Cu}}_{CuHL_2}$ and $10^{6.66}$ compared to the observed $10^{6.60}$ for ${\beta^{Cu}}_{CuH_3L_2}$.

The successive formation constants for the bonding of $CuP_2O_7^{2-}$ with hydrogen ions are $10^{5.23}$ and $10^{3.31}$. For bonding with $Cu(P_2O_7)_2^{6-}$ they are $10^{6.76}$, $10^{5.78}$, $10^{4.40}$, and $10^{3.21}$.

The constants for the association of the first hydrogen ion with complexed $P_2O_7^{4-}$ are $10^{5.23}$ for $CuP_2O_7^{2-}$ and $10^{6.76}$ and $10^{5.78}$ for $Cu(P_2O_7)_2^{6-}$, compared to $10^{8.93}$, the corresponding constant for free $P_2O_7^{4-}$. The constants for the association of the second hydrogen ion with each complexed $P_2O_7^{4-}$ are $10^{3.31}$ for $CuP_2O_7^{2-}$ and $10^{4.40}$ and $10^{3.21}$ for $Cu(P_2O_7)_2^{6-}$, compared to $10^{6.13}$, the corresponding second constant for free $P_2O_7^{4-}$.

The magnitudes of these constants are influenced by a purely statistical effect.[21] In discussing this effect it will be assumed that the most stable configuration is predominant. Thus, it is assumed that hydrogen ions associate with the non-bridging oxygen atoms on the PO_4 tetrahedra containing the smaller number of hydrogen ions and that one oxygen atom is primarily involved in the bonding. It is further assumed that ionization occurs predominantly from tetrahedra containing the larger number of hydrogen ions. In $CuP_2O_7^{2-}$ there are four equivalent sites at non-bridging or complexing oxygen atoms for hydrogen ions but the associated form contains only one hydrogen ion. Eliminating this statistical effect of 4/1 reduces the constant from $10^{5.23}$ to $10^{4.63}$. In the next step, two sites are available but, in the associated form, there are two equivalent hydrogen ions to dissociate so that the statistical effect is unity and the second constant retains the value $10^{3.31}$. The statistical effects in the successive basicity constants of $Cu(P_2O_7)_2$ are 8/1, 4/2, 4/3, and 2/4, which change the successive constants to $10^{5.86}$, $10^{5.48}$, $10^{4.28}$, and $10^{3.51}$. Applying the same reasoning to the first two stepwise formation constants of pyrophosphate not complexed with hydrogen ion yields statistical effects of 6/1 and 3/2, which changes the first two successive hydrogen association constants to $10^{8.16}$ and $10^{5.95}$.

The bonding of a copper ion with the pyrophosphate ion in the 1:1 complex reduces the first corrected formation constant for the addition of hydrogen ion from $10^{8.15}$ in $P_2O_7^{4-}$ to $10^{4.62}$ in $CuP_2O_7^{2-}$. In the 1:2 complex the corrected constants for the bonding of single hydrogen ions to the two pyrophosphates are reduced to $10^{5.86}$ and $10^{5.40}$. Thus, the shared copper(II) ion in the 1:2 complex is, as one would predict, less effective than the unshared copper(II) ion in the 1:1 complex in reducing the stepwise formation constant for adding the first hydrogen ion to each pyrophosphate. Furthermore, in both the 1:1 and the 1:2 complexes the copper ion is somewhat more effective in reducing the basicity of $P_2O_7^{4-}$ than is a previously added hydrogen ion. This is reasonable because the copper(II) ion probably is bonded directly to both phosphate tetrahedra while in the simple acid it is reasonable to assume that each hydrogen ion is bonded to only one PO_4 tetrahedron.

The corrected formation constant for the addition of the second hydrogen ion in the 1:1 complex is $10^{3.31}$ and in the 1:2 complex the formation constants for adding the second hydrogens to the two complexed $P_2O_7^{4-}$ ions are $10^{4.10}$ and $10^{4.11}$. In contrast to the above effect these values are much larger than the constant, $10^{1.81}$, for the addition of a third hydrogen ion to $H_2P_2O_7^{2-}$. This indicates that a hydrogen ion combined with the phosphate tetrahedron involved in accepting a second hydrogen ion is much more effective than a copper ion in the same position. This is reasonable because the intrinsic strength of the bond of a copper ion to the pyrophosphate ion is much smaller than that of the hydrogen ion. The free energy change due to complex formation between copper and pyrophosphate is due in a large part to the chelation effect.[17] Therefore, the inductive effect of hydrogen ion on basicity in a particular PO_4 tetrahedron is much greater than that of copper ion when both are bonded to that tetrahedron. As a consequence all complexed PO_4 tetrahedra in pyrophosphate complexes have fairly similar basicities. However, the strength of the bond between the copper ion and the tetrahedron is greatly reduced as a result of association with each successive hydrogen ion. The latter property of the complex offers a method for increasing the concentration of aquocopper ion in a regular manner in a well poised system through variation of pH. It should enhance the usefulness of pyrophosphates in such applications as elution in ion-exchange columns and in certain physiological situations.

The results obtained in the present study are believed to be more accurate than those of former studies since various complicating factors already discussed have been eliminated. The results are consistent with both the polarographic experimental data obtained in this Laboratory[5] and by Laitinen and Onstott[4] in the presence of alkali metal ions. The difference in the magnitudes of the over-all complexity constant for $Cu(P_2O_7)_2^{6-}$ was due largely to the use of an indirectly determined $E_{1/2}$ for aquocopper ion of +0.0002 v. *vs.* the saturated calomel electrode in the former study[5] instead of +0.024 v., which was measured directly.[14] The difference in the constants for $CuH_2(P_2O_7)_2^{4-}$ was due to the use by Laitinen and Onstott[4] of the acid constants at infinite dilution instead of constants measured in solutions of similar composition. The latter, which are always used in Leden's or Bjerrum's functions, yield complexity constants in terms of concentrations.

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(20) J. I. Watters and R. DeWitt, *J. Am. Chem. Soc.*, **82**, 1333 (1960).

(21) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

In the early phases of this study it was anticipated that the complexity constants of the copper complexes could be calculated by correcting the pyrophosphate concentration for that lost through simple complex formation with the alkali metal ions. Such a procedure would be valid only if no complexes of the type $Na_xCu(P_2O_7)_2^{(6-x)-}$ were formed. On the basis of this assumption the presence of increasing concentrations of alkali metal ions should have decreased the potential shift. Instead, the presence of up to 0.1 *M* Cs^+, K^+, and Na^+ enhanced the potential shift as much as 10 mv. in the more alkaline solutions. In the presence of lithium ions, the voltage shift due to complex formation was enhanced only slightly from a pH of 5 to 8 and was greatly reduced above pH 8. These results constitute good evidence that the copper pyrophosphate complexes also associate with alkali metal ions, which enhances the stability of the complex $Cu(P_2O_7)_2^{6-}$ which is predominant in the more alkaline solutions. The effect is too large to be due to activity effects but is too small to permit a calculation of the extent of association. It is possible that the alkali metal ions are held by loose ion-pair bonds at the outer surface of the complex. Their presence could enhance the stability of the complex by a reduction of the repulsive forces of the two negatively charged pyrophosphate ions which surround the copper(II) ion. Since the strength of the bond with alkali metal ions increases with decreasing ionic radii it is possible that lithium ions not only decrease the repulsive forces but weaken the copper(II) pyrophosphate bond in the same manner as do hydrogen ions. If the apparent acidity constants, measured in the same supporting electrolyte and the same concentrations, are used to calculate the concentrations of $P_2O_7^{4-}$, $HP_2O_7^{3-}$, and $H_2P_2O_7^{2-}$ ions and any association with alkali metals is disregarded, the values obtained for the stability constants of the copper complexes agree reasonably well with those obtained in the absence of alkali metal ions. Their use in practical situations under similar experimental conditions thus is justified.

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CONTRIBUTION NO. 1134 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA[1a]

Stability Constants and Intrinsic Solubility of Several Nickel(II)–*vic*-Dioxime Complexes[1b]

BY CHARLES V. BANKS AND SAMUEL ANDERSON

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The acid dissociation constants for a series of *vic*-dioximes and the stability constants of their nickel(II) complexes were measured in dioxane–water mixtures. Estimates are given for the values of the acid dissociation constants and stability constants in water solution. The solubility product constants for the nickel(II)–*vic*-dioxime complexes were measured in water solution. The stability constants and the solubility product constant were used to calculate the intrinsic solubility. It was found that, in general, an increase in the distance between nickel atoms in the crystal of the complexes results in an increase in the solubility of the complexes. It is believed that the phenomena above may be accounted for in part by metal–metal bonding in some of the nickel(II)–*vic*-dioxime complexes.

Introduction

Several quite insoluble nickel(II)–,[2] palladium(II)–,[2,3] and platinum(II)–*vic*-dioxime[4] complexes have been shown to have, in general, the same crystal structure as does nickel dimethylglyoxime,[5] $[Ni(DMG)_2]$. This rather unique crystal structure in which the metal atoms lie in a straight row extending throughout the length of the crystal led Godycki and Rundle[5] to postulate the presence of metal–metal bonding which could contribute significantly to the crystal energy and thus perhaps explain the limited solubility of these complexes. The fact that nickel(II)-ethylmethylglyoxime,[6] $[Ni(EMG)_2]$, and copper(II)-dimethylglyoxime,[7] $[Cu(DMG)_2]$, are much more soluble in water than is $Ni(DMG)_2$ and that both have crystal structures which are not compatible with metal–metal bonding lends support to this postulate. Banks and Anderson[8] measured the heats of solution of $Ni(DMG)_2$ and $Ni(EMG)_2$ in both *n*-heptane and carbon tetrachloride and found ΔH^0 was about 10 kcal. greater for $Ni(DMG)_2$ than

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) Paper No. XXXI in a series on "Chemistry of the *vic*-Dioximes." Previous papers in this series were No. XXVIII, "Proceedings of the Symposium," Feigl Anniversary Symposium, Birmingham Univ., Birmingham, England, April 9-13, 1962; No. XXIX, *J. Am. Chem. Soc.*, **84**, 1486 (1962); and No. XXX, *J. Phys. Chem.* (Feb., 1963). Abstracted from dissertation submitted by Samuel Anderson to graduate faculty of Iowa State University in partial fulfillment of requirements for the degree of Doctor of Philosophy, 1962.

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