

ence of  $[(\text{CH}_3)_2\text{Pb}(\text{OH})_2\text{Pb}(\text{CH}_3)_2]^{2+}$ ,  $(\text{CH}_3)_2\text{Pb}(\text{OH})_2$ , and  $[(\text{CH}_3)_2\text{Pb}(\text{OH})_3]^-$ , the same is not true about the fourth complex assumed in fitting the data. Since this is a small effect and the other assumptions give rather good fits to the data, it is possible that there are very low concentrations of more than one additional species. The addition of more base to the dimethyllead(IV) solution breaks down the dimer and any other polynuclear species, and  $(\text{CH}_3)_2\text{Pb}(\text{OH})_2$  is essentially the

only complex in solution at  $\text{pH} \sim 10.5$ . Since cleavage of the lead-carbon bond occurs rather rapidly in strongly alkaline solutions, it is difficult to study the anionic species which are formed at high pH.

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CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY,  
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

## A Study of the Complexity and Basicity Constants of the Complexes of Copper(II) with Tetraphosphate Using the Dropping-Amalgam Electrode

By JAMES I. WATTERS AND SABURO MATSUMOTO

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The shapes of anodic and the first portions of the cathodic polarographic waves obtained with the dropping copper amalgam electrode in solutions containing copper(II) and excess tetraphosphates correspond to a reversible electrode reaction. The cathodic diffusion current region is poorly developed in alkaline solutions. The reversible behavior of the electrode in equilibrium with the bulk of the solution permits the determination of formulas, stabilities, and acidities of the complexes formed between copper(II) and tetraphosphate on the basis of the pH measured by a glass electrode and the potential of a dropping copper amalgam electrode. The stepwise formation constants for  $\text{Cu}^{2+}$  with  $\text{P}_4\text{O}_{13}^{6-}$  are  $10^{9.44}$  and  $10^{1.16}$ . The 1:1 complex is the predominant species in a solution containing tetraphosphate in excess above a pH of 7 owing to the quadridentate bonding capacity of the tetraphosphate ion and the corresponding usual coordination number of copper(II). The successive addition of hydrogen ions to the complex containing two tetraphosphate ligands produces a relatively smaller effect on the complexity constant, presumably because the excess dangling  $\text{PO}_3$  tetrahedra can be protonated without greatly affecting the complex bonding. A method of predicting polyphosphate complexity constants is shown from the observation that the mean free energy associated with the complex bond formation in all copper polyphosphate complexes is essentially a linear function of the mean ionic charge of the bonding  $\text{PO}_4$  tetrahedra.

### Introduction

The present investigation is one of a series concerned with the complexes of copper(II) with linear polyphosphates<sup>1,2</sup> and another concerned with the chemistry of tetraphosphates in aqueous solutions. The tetraphosphate papers are concerned with acidity constants<sup>3</sup> and complexes with mercury(I)<sup>4</sup> as well as the guanidinium ion.<sup>5</sup>

The complex-forming properties of linear polyphosphates are influenced by the presence of several positions in the molecule at which protonation or complexation can occur. Consequently, the possibility of forming polynuclear species exists in ligand-deficient solutions, and protonated complexes are formed in acidic solutions. The reversible behavior of the copper amalgam electrode in equilibrium with the copper polyphosphates permits a complete interpretation of the very complex equilibria which would other-

wise be exceedingly difficult, if not impossible. The accuracy of the results is enhanced by the fact that the electrode is also reversible in ligand-free solutions if the pH is of the order of 3.0 or less.

In particular, a series of studies under similar experimental conditions in which only the length of the ligand chain and the number of coordinating positions are changed permits a greater insight concerning the statistical, as well as intrinsic, factors influencing complex bonding. Furthermore, the results can be extrapolated to predict the properties of polyphosphate complexes of other metal ions for which no reversible electrode is available.

Since Thilo and Ratz<sup>6</sup> first prepared tetraphosphate by the alkaline hydrolysis of cyclic tetraphosphate and Quimby<sup>7</sup> crystallized its guanidinium salt, several papers have also been written on its separation by various chromatographic procedures, its crystallization by heavy metal ions, and the irreversible polarography of the Zn, Cd, and Pb salts. Many of these references and the procedure for preparing the tetraphosphate are given in the first paper of this series,

(1) P. E. Sturrock, E. D. Loughran, and J. I. Watters, *Inorg. Chem.*, **1**, 457 (1962).

(2) O. E. Schupp, III, P. E. Sturrock, and J. I. Watters, *ibid.*, **2**, 106 (1963).

(3) J. I. Watters, P. E. Sturrock, and R. E. Simonaitis, *ibid.*, **2**, 765 (1963).

(4) J. I. Watters and R. A. Simonaitis, *Talanta*, **11**, 247 (1964).

(5) J. I. Watters and S. Matsumoto, *J. Am. Chem. Soc.*, **86**, 3961 (1964).

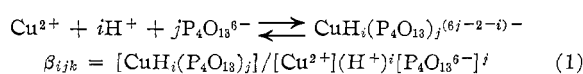
(6) E. Thilo and R. Ratz, *Z. Anorg. Allgem. Chem.*, **260**, 255 (1959).

(7) O. T. Quimby, *J. Phys. Chem.*, **58**, 615 (1954).

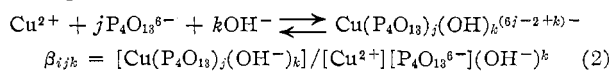
which is concerned with the acidity of tetraphosphate.<sup>3</sup> The properties of tetraphosphate are similar to those of pyro- and triphosphate in that it forms fairly stable complexes with alkali metal ions and it also undergoes hydrolysis to lower phosphates in acidic solutions to an appreciable extent within 1 hr. As in the previous studies of this series the former difficulty was overcome through the replacement of alkali metal or guanidinium ion used in the preparation of the salt by tetramethylammonium ions by means of cation-exchange resins and the use of a relatively large concentration of tetramethylammonium nitrate, 0.5 to 0.9 *M*, as the supporting electrolyte.

Experimental apparatus and procedures and the general mathematical method for treating the data are included in the papers on copper(II) pyrophosphate<sup>2</sup> and triphosphate.<sup>1</sup> These papers contain references to earlier studies in this laboratory in which mathematical procedures related to Leden's method were developed for treatment of data obtained with the copper amalgam and with systems containing mixtures of ligands, including the hydroxide ion and protonated ligands.

In this method the equilibrium constants are expressed in terms of concentrations of the metal ion, the free ligand, and the complex species, indicated by formulas in brackets, and in terms of hydrogen and hydroxide ion activities, indicated by formulas in parentheses. These equilibrium constants are indicated by the symbol  $\beta_{ijk}$ , in which *i*, *j*, and *k* indicate the numbers of H<sup>+</sup>, P<sub>4</sub>O<sub>13</sub><sup>6-</sup>, and OH<sup>-</sup> ions, respectively, in the complex. In general, complex ionic charges are omitted for convenience. In the region where association of hydrogen ions with the complexed ligands takes place the following general expressions can be written



In the regions where hydroxide ions are associated with the complex



Equilibrium constants in the above form can be converted to equivalent constants in terms of concentrations of protonated ligands indicated by symbols having the form  $\beta_{M\text{H}_3\text{L}_2}^M$ . For example

$$\beta_{\text{CuH}_3\text{L}_2}^{\text{Cu}} = [\text{CuH}_3\text{L}_2] / [\text{Cu}^{2+}][\text{HL}][\text{H}_2\text{L}] \quad (3)$$

With the excess ligand used in these experiments, only mononuclear species were obtained. Under these conditions Leden's second function was expressed as follows, in terms of the species required to account for the experimental data

$$F(\text{H}^+, \text{P}_4\text{O}_{13}^{6-}, \text{OH}^-)_1 = \left\{ \text{antilog}[(E_{\text{aq}} - E_0) \times (0.4342)nF/RT] - 1 \right\} / [\text{P}_4\text{O}_{13}^{6-}] = \left\{ \text{antilog}[\Delta E(0.4342)nF/RT] - 1 \right\} / [\text{P}_4\text{O}_{13}^{6-}] = \beta_{011}(\text{OH}^-) + \beta_{010} + \beta_{620}[\text{P}_4\text{O}_{13}^{6-}] + \beta_{110}(\text{H}^+) + \beta_{210}(\text{H}^+)^2 + \beta_{120}(\text{H}^+)[\text{P}_4\text{O}_{13}^{6-}] + \beta_{220}(\text{H}^+)^2[\text{P}_4\text{O}_{13}^{6-}] + \beta_{320}(\text{H}^+)^3[\text{P}_4\text{O}_{13}^{6-}] + \beta_{420}(\text{H}^+)^4[\text{P}_4\text{O}_{13}^{6-}] \quad (4)$$

In all experiments the ionic strength was initially adjusted to be close to unity in the particular pH range being investigated with 0.5 to 0.9 *M* tetramethylammonium nitrate, and the temperature was maintained at 25 ± 0.1°. Because appreciable hydrolysis to lower phosphates was detected in less than 30 min, in acidic solutions by the phosphomolybdate test, the measurements were made immediately after the pH was adjusted through the addition of 2 *M* HNO<sub>3</sub> to the final solutions. The effect of the slight dilution was considered in the calculations but was found to be negligible. The potential of the copper amalgam electrode in the ligand-free solution was measured at a pH of 3.0. In addition to copper(II), tetraphosphate, tetramethylammonium, hydrogen, and nitrate ions, all solutions contained 0.0005% methyl red as a maximum suppressor.

### Results and Discussion

In Figure 1 are shown typical anodic-cathodic polarograms of copper(II) in the solution containing no tetraphosphate and in the tetraphosphate solutions of varied pH. It is evident that, in the acidic solutions having a pH less than 5.9, the entire waves are essentially reversible. The waves cross the zero current axis without inflection and have the theoretical slope  $\Delta E/\Delta \log \{(i_{\text{dc}} - i)/(i - i_{\text{dc}})\}$  of 0.030 v for a two-electron electrode reaction. Furthermore, at a pH of 2.52 the diffusion current constant of 3.7  $\mu\text{a}/\text{mM}$  concentration of copper(II) per unit capillary characteristic is consistent with a two-electron reduction of copper(II) directly to free copper. In the pH region near 5.9, which is close to that of the second equivalence point of tetraphosphoric acid, the plot of  $\Delta E/\Delta \log \{(i_{\text{dc}} - i)/(i - i_{\text{dc}})\}$  is not a straight line. This is due to the poor poise of the electrode near an acidic equivalence point which has been discussed in a previous paper<sup>3</sup> and does not indicate electrode irreversibility.

In alkaline tetraphosphate solutions the waves have an anomalous appearance since the complete cathodic diffusion current does not develop normally. The effect is similar but somewhat greater than that observed in the corresponding triphosphate system and less than that observed in the pyrophosphate system. In the latter study and the present one, as well, the current decrease is approximately proportional to the concentration of the unprotonated polyphosphate complexes. Presumably, the negative charge of the complex prevents a sufficiently close approach to the negatively charged electrode for the electron transfer to occur until an appreciably higher voltage is attained.

In Table I are given the experimental data along with experimental values of  $F_1$  based on the potential shift and  $[\text{P}_4\text{O}_{13}^{6-}]$  and its calculated values obtained in terms of the solved complexity constants, the concentration of P<sub>4</sub>O<sub>13</sub><sup>6-</sup>, and the activities of H<sup>+</sup> or OH<sup>-</sup>. The concentration of P<sub>4</sub>O<sub>13</sub><sup>6-</sup> was calculated

(8) O. E. Schupp, III, T. Youness, and J. I. Watters, *J. Am. Chem. Soc.*, **84**, 505 (1962).

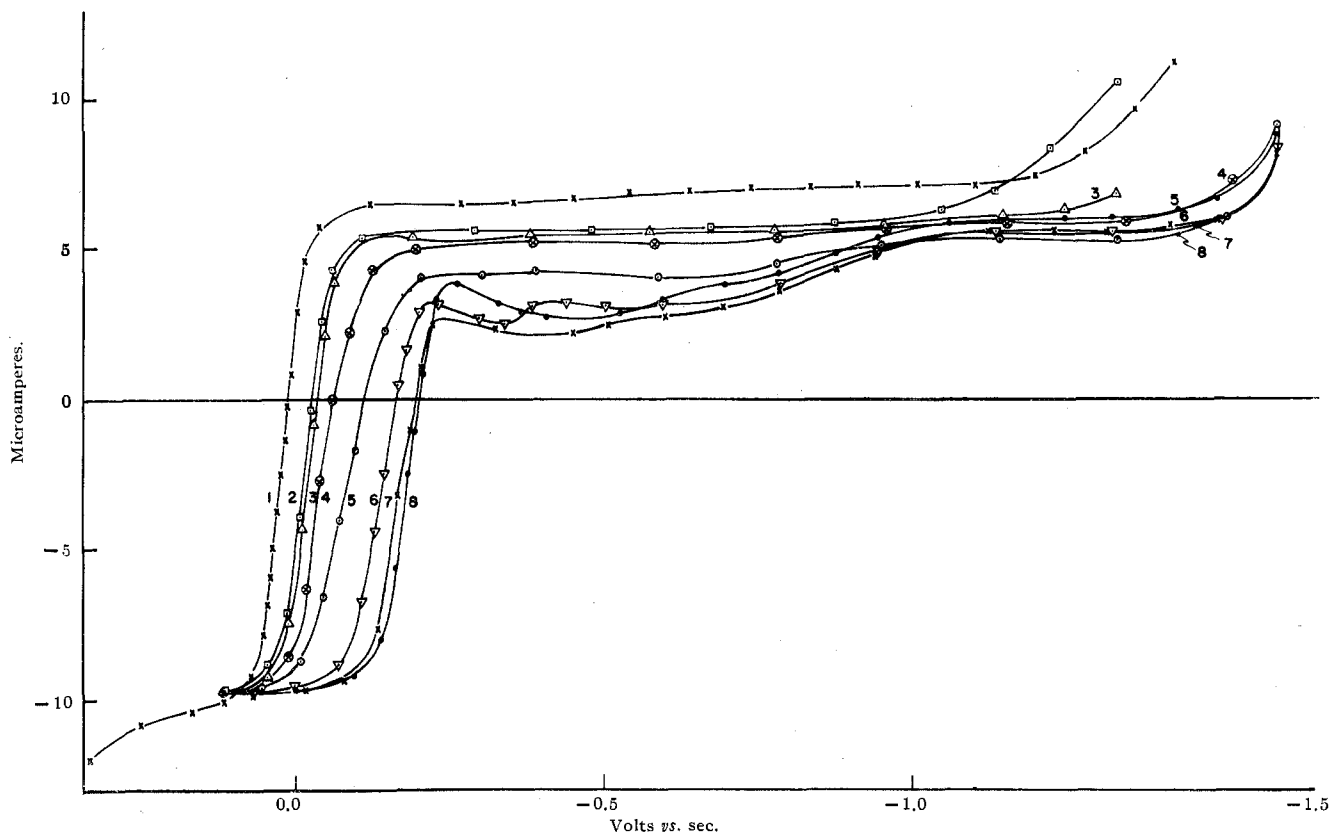


Figure 1.—Anodic-cathodic polarogram of copper(II) ions in tetraphosphate solution at various pH values using the dropping copper amalgam electrode.  $[P_4O_{13}^{6-}]_t = 0.033 M$  (except in polarogram 1);  $[Cu^{2+}]_t = 1.00 mM$ ;  $\mu = 1.00 \pm 0.30$  with  $(CH_3)_4N \cdot NO_3$ ; methyl red = 0.0005%; amalgam = 0.0005%. Polarograms: 1, pH 3.00 (no  $P_4O_{13}^{6-}$ ); 2, pH 2.42; 3, pH 3.34; 4, pH 4.49; 5, pH 5.92; 6, pH 7.06; 7, pH 8.20; 8, pH 9.40.

by the following equation using the values,  $pK_3 = 1.36$ ,  $pK_4 = 2.23$ ,  $pK_5 = 6.63$ , and  $pK_6 = 8.34$ , obtained from a previous paper.<sup>3</sup>

$$[P_4O_{13}^{6-}] = [P_4O_{13}^{6-}]_t K_3 K_4 K_5 K_6 / \{ K_3 K_4 K_5 K_6 + K_3 K_4 K_5 (H^+) + K_3 K_4 (H^+)^2 + K_3 (H^+)^3 + (H^+)^4 \} \quad (5)$$

$[P_4O_{13}^{6-}]_t$  is the total concentration of tetraphosphate which is not complexed. As a first approximation it was assumed that one tetraphosphate ion was associated with each copper ion.

The absence of polynuclear species was first established by the fact that  $F_1$  was found to be independent of the total copper ion concentration in the range of  $10^{-4}$  to  $10^{-2} M$  total copper ion and an excess of tetraphosphate.

In a preliminary survey of the data, the minimum but similar  $\log F_1$  values of 9.49 and 9.58 for the 0.00821 and 0.03285  $M$  tetraphosphate solutions having a pH near 8.5 indicated that the 1:1  $[Cu^{2+}]:[P_4O_{13}^{6-}]$  complex was predominant but that small concentrations of the 1:2 complex might also be present. The increase in the value of  $F_1$  at more alkaline pH values indicated the presence of one or more complex species containing hydroxide ions, and the increase at lower pH values indicated the presence of protonated complexes. Furthermore,  $CuHP_4O_{13}^{3-}$  was considered improbable in the presence of excess  $HP_4O_{13}^{5-}$  since protonation should eliminate or greatly weaken one of the four bonding positions in the ligand. Thus, the

preliminary calculation in the pH range of 6.5 to 8.5 was simplified by including as unknowns only terms for the species  $CuH_2(P_4O_{13})_2^{8-}$ ,  $CuH(P_4O_{13})_2^{9-}$ , and  $CuP_4O_{13}^{4-}$ . Determinants were set up for solving the equilibrium constants of these three species using potential data obtained at various sets of three pH values in this range. Next the terms containing these three constants were included as knowns while solving the equilibrium constants of the anticipated species  $Cu(OH)P_4O_{13}^{5-}$ ,  $Cu(P_4O_{13})_2^{10-}$ , and possibly  $Cu(OH)_2P_4O_{13}^{6-}$  from data above a pH of 8.5. The constants for the remaining species were then solved using data from both ligand concentrations in the pH range below 6.5 with the previous constants included as knowns.

Since the term  $\beta_{ijk}(H^+)^i [P_4O_{13}^{6-}]^j (OH^-)^k$  represents the relative concentration of the corresponding complex, with unity corresponding to the aquo ion,  $[Cu^{2+}]$ , it was possible to solve the percentage of each complex species present as a function of pH. From the distribution found on the basis of the preliminary values for the complexity constants, the pH region was found in which various species attained maximum concentrations. Their complexity constants were then solved from data for a corresponding number of solutions with terms making minor contributions included as knowns. This iterative procedure was repeatedly applied to all data using successively improved values for the constants in regions where their contributions were minor. The relative distribution of the various complex species

TABLE I  
POTENTIAL DATA OF THE  
TETRAPOLYPHOSPHATE-COPPER(II) SYSTEM<sup>a</sup>

pH	<i>E</i> vs. sce	$\Delta E$ , v	$-\log [P_4O_{13}^{6-}]$	Log <i>F</i> <sub>1</sub> exptl	Log <i>F</i> <sub>1</sub> calcd
(A) 0.03285 <i>M</i> tetraphosphate added					
9.65	-0.2280	0.2428	1.52	9.73	9.69
9.17	-0.2248	0.2396	1.56	9.66	9.64
8.74	-0.2203	0.2351	1.65	9.60	9.62
8.49	-0.2181	0.2329	1.71	9.58	9.63
8.10	-0.2129	0.2277	1.95	9.65	9.63
7.73	-0.2051	0.2199	2.23	9.66	9.65
7.35	-0.1951	0.2099	2.60	9.70	9.70
6.86	-0.1807	0.1955	3.19	9.78	9.79
6.16	-0.1525	0.1673	4.28	9.94	9.94
5.13	-0.1062	0.1210	6.23	10.30	10.26
4.50	-0.0796	0.0944	7.47	10.66	10.73
4.50	-0.0780	0.0923	7.67	10.81	10.82
3.63	-0.0585	0.0733	9.23	11.71	11.77
3.47	-0.0575	0.0723	9.55	11.99	12.02
2.75	-0.0490	0.0638	11.09	13.25	13.26
(B) 0.00821 <i>M</i> tetraphosphate added					
9.43	-0.2022	0.2170	2.18	9.52	9.55
9.09	-0.2018	0.2166	2.22	9.54	9.52
8.53	-0.1953	0.2101	2.39	9.49	9.49
7.68	-0.1792	0.1940	2.93	9.49	9.50
6.39	-0.1381	0.1529	4.54	9.71	9.62
5.30	-0.0592	0.0740	7.98	10.48	10.54
4.47	-0.0567	0.0715	8.19	10.61	10.65
3.98	-0.0445	0.0593	9.17	11.17	11.19
3.57	-0.0360	0.0508	10.00	11.71	11.74
3.34	-0.0348	0.0496	10.47	12.14	12.10
3.05	-0.0309	0.0457	11.08	12.62	12.59
2.60	-0.0265	0.0413	12.07	13.45	13.40
2.42	-0.0215	0.0363	12.50	13.70	13.70

<sup>a</sup>  $C_{Cu} = 0.001$  *mM*;  $\mu$  adjusted to unity with  $(CH_3)_4N \cdot NO_3$ ;  $E_{aq} = +0.0148$  v vs. sce. No voltage applied. Amalgam contained 0.0005% Cu. At potential of sce drop time was 4.70 sec.  $m^{2/3}t^{1/6}$  was 1.908  $mg^{2/3} sec^{-1/2}$ .

in the more concentrated tetraphosphate solution as a function of pH is shown in Figure 2. No other species were detected since the inclusion of terms for their complexity constants yielded very small random positive and negative values for their constants, and the omission of any terms yielded relatively large deviations. It might be argued that the term for  $CuH_3(P_4O_{13})_2^{7-}$  is relatively small so it might be omitted. However, the term for  $CuH_4(P_4O_{13})_2^{6-}$ , formed by the stepwise addition of  $H^+$ , to this ion is large and important at low pH values. This confirms the presence of  $CuH_3(P_4O_{13})_2^{7-}$ . The species  $CuH(P_4O_{13})_2^{9-}$ ,  $CuH_2(P_4O_{13})_2^{8-}$ , and  $CuHP_4O_{13}^{3-}$  are successively predominant as the pH is decreased. The accuracy of their equilibrium constants is at least  $\pm 10^{0.10}$  since the maximum deviation of the function is  $\pm 10^{0.09}$ .

The following original complexity constants were calculated

$$\beta_{011} = [Cu(P_4O_{13})(OH)^{5-}]/[Cu^{2+}](OH^-)[P_4O_{13}^{6-}] = 10^{13.30} \quad (6)$$

$$\beta_{010} = [CuP_4O_{13}^{4-}]/[Cu^{2+}][P_4O_{13}^{6-}] = 10^{9.44} \quad (7)$$

$$\beta_{020} = [Cu(P_4O_{13})_2^{10-}]/[Cu^{2+}][P_4O_{13}^{6-}]^2 = 10^{10.60} \quad (8)$$

$$\beta_{110} = [CuHP_4O_{13}^{8-}]/[Cu^{2+}](H^+)[P_4O_{13}^{6-}] = 10^{15.00} \quad (9)$$

$$\beta_{210} = [CuH_2P_4O_{13}^{7-}]/[Cu^{2+}](H^+)^2[P_4O_{13}^{6-}] = 10^{18.45} \quad (10)$$

$$\beta_{120} = [CuH(P_4O_{13})_2^{9-}]/[Cu^{2+}](H^+)[P_4O_{13}^{6-}]^2 = 10^{19.00} \quad (11)$$

$$\beta_{220} = [CuH_2(P_4O_{13})_2^{8-}]/[Cu^{2+}](H^+)^2[P_4O_{13}^{6-}]^2 = 10^{26.28} \quad (12)$$

$$\beta_{320} = [CuH_3(P_4O_{13})_2^{7-}]/[Cu^{2+}](H^+)^3[P_4O_{13}^{6-}]^2 = 10^{30.80} \quad (13)$$

$$\beta_{420} = [CuH_4(P_4O_{13})_2^{6-}]/[Cu^{2+}](H^+)^4[P_4O_{13}^{6-}]^2 = 10^{34.85} \quad (14)$$

After the above constants had been calculated, the consistency of the data was tested by treating the species containing two tetraphosphate ligands and odd numbers of hydrogen ions as mixed complexes of the ligands  $P_4O_{13}^{6-}$ ,  $HP_4O_{13}^{5-}$ , and  $H_2P_4O_{13}^{4-}$  according to eq 26 of a previous paper.<sup>1</sup> These calculations yield  $\beta_{CuHL_2}^{Cu} = 10^{10.60}$  compared to the accepted value,  $10^{10.65}$ , and  $\beta_{CuH_2L_2}^{Cu} = 10^{7.49}$  compared to  $10^{7.41}$ . This agreement is very good particularly when one considers that, as shown in Figure 2, these species are never the predominant ones.

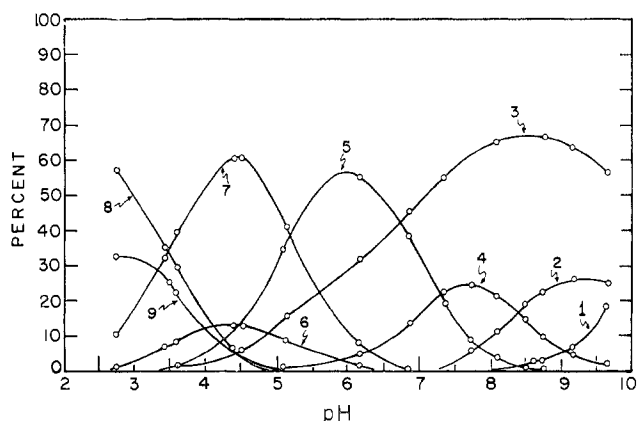


Figure 2.—Percentage distribution of copper(II) tetrapolyphosphate complex species as a function of pH.  $[Cu^{2+}]_t = 1.00$  *mM*;  $[P_4O_{13}^{6-}]_t = 0.0329$  *M*. Complex species: curve 1,  $Cu(P_4O_{13})_2^{10-}$ ; 2,  $Cu(P_4O_{13})_2^{10-}$ ; 3,  $Cu(P_4O_{13})_2^{10-}$ ; 4,  $CuH(P_4O_{13})_2^{9-}$ ; 5,  $CuH_2(P_4O_{13})_2^{8-}$ ; 6,  $CuH_3(P_4O_{13})_2^{7-}$ ; 7,  $CuHP_4O_{13}^{3-}$ ; 8,  $CuH_4(P_4O_{13})_2^{6-}$ ; 9,  $CuH_2P_4O_{13}^{2-}$ .

In order to observe the effect of associated hydrogen ions on the strength of the complex bond, the constants for acidic complexes were calculated in terms of the concentrations of the tetraphosphate species actually present in the complexes. These constants are products of the above constants and the appropriate acidity constants,  $K_5$  and  $K_6$ , of tetraphosphoric acid. The logarithms of these over-all complexity constants are given in Table II along with those for pyro- and triphosphate for comparison. The logarithms of the stepwise formation constants for the association of hydrogen ions with the corresponding complexes  $CuL_2$  are given in Table III. The stability constants for the association of the first and second hydrogen ions with the ligands in  $CuL_2$  in part B of Table III can be compared to those for the first hydrogen ion in the free ligand in part A since statistical as well as inductive effects indicate that the second hydrogen ion should associate mostly with the ligand having no associated hydrogen ions. For similar reasons the stability constants for the association of the third and fourth hydrogen ions in part B can be compared to those for the second hydrogen ion in part A. The first hydrogen ion is as firmly bound to  $Cu(P_4O_{13})_2^{10-}$  as to  $P_4O_{13}^{6-}$ ,  $10^{8.40}$  compared to  $10^{8.34}$ , and it is bound to  $Cu(P_3O_{10})_2^{8-}$  nearly as firmly as to  $P_3O_{10}^{5-}$ ,  $10^{8.36}$  compared

TABLE II  
LOGARITHMS OF OVER-ALL COMPLEXITY CONSTANTS  
OF COPPER(II) WITH PYRO-, TRI-, AND TETRAPHOSPHATE AND  
THEIR PROTONATED IONS<sup>a</sup>

Log $\beta^{\text{CuCuL}}$	Log $\beta^{\text{CuCuHL}}$	Log $\beta^{\text{CuCuHL}_2}$	Log $\beta^{\text{CuCuL}_2}$
9.07	5.37	2.55	14.65
8.70	5.69	3.19	10.50
9.44	6.66	3.53	10.60
Log $\beta^{\text{CuCuHL}_2}$	Log $\beta^{\text{CuCuH}_2\text{L}_2}$	Log $\beta^{\text{CuCuH}_3\text{L}_2}$	Log $\beta^{\text{CuCuH}_4\text{L}_2}$
11.48	8.33	6.60	3.60
10.13	7.99	7.04	4.81
10.66	9.60	7.49	4.91

<sup>a</sup> Under each symbol for the equilibrium constant are given in order the values for the logarithms of the pyro-, tri-, and tetraphosphate. Constants have the form of eq 3.

TABLE III  
COMPARISON OF LOGARITHMS OF STEPWISE  
CONSTANTS FOR THE SUCCESSIVE ADDITION OF H<sup>+</sup> IONS TO  
(A) PYRO-, TRI-, AND TETRAPHOSPHATE IONS AND (B) TO THE  
CORRESPONDING COPPER COMPLEX, CuCl<sub>2</sub>

Anion	1st H <sup>+</sup>	2nd H <sup>+</sup>	3rd H <sup>+</sup>	4th H <sup>+</sup>
(A) $\text{P}_2\text{O}_7^{4-}$	8.93	6.13	1.81	0.83
$\text{P}_3\text{O}_{10}^{5-}$	8.81	5.83	2.11	1.06
$\text{P}_4\text{O}_{13}^{6-}$	8.34	6.63	2.23	1.36
(B) $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$	6.76	5.78	4.40	3.21
$\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$	8.36	6.59	4.88	3.60
$\text{Cu}(\text{P}_4\text{O}_{13})_2^{10-}$	8.40	7.28	4.52	3.55

to 10<sup>8.81</sup>. The magnitude of these constants indicates that the hydrogen ions are bonded to dangling terminal tetrahedra and comprises evidence for the presence of the latter. A factor contributing to the strong proton bonding is the relatively small inductive effect of the 2<sup>+</sup> charge of the copper complexed to adjacent<sup>2</sup> or further removed tetrahedra. A second factor enhancing the protonation of the complex is the reduction of the over-all negative ionic charge of the complex. It has previously been shown that association with alkali metal ions also enhances the stability<sup>2</sup> of the complex.

It is evident from Figure 2 that, in alkaline solutions, containing an excess of tetraphosphate, the predominant complex species is  $\text{CuP}_4\text{O}_{13}^{4-}$ . This indicates that the usual copper(II) coordination number of 4 is satisfied by one tetraphosphate ion. The most feasible configuration is the square structure in which one oxygen from each PO<sub>4</sub> tetrahedron is bonded to the copper through a single oxygen atom. By constructing models it was established that bonding between every PO<sub>4</sub> tetrahedron and copper(II) in the form of a square complex is possible with all three linear polyphosphates. These models indicate that the coordination of one oxygen atom on each PO<sub>4</sub> tetrahedron by copper(II) is feasible. The copper ion and the coordinated oxygens can be arranged in a plane just above or below a plane containing the phosphorus atoms and bridging oxygen atoms. In  $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ , the two  $\text{P}_2\text{O}_7^{4-}$  ions can lie on opposite sides of the plane containing the copper ion and the coordinated oxygen atoms so their negative repulsive forces are minimized. In the  $\text{CuP}_3\text{O}_{10}^{3-}$  and  $\text{CuP}_4\text{O}_{13}^{4-}$  the P and bridging oxygen atoms can be arranged essentially in a plane below the

plane containing the Cu<sup>2+</sup> and the 3- and 4-coordinated oxygen atoms, respectively. In all models the P–O–Cu bonds can form angles close to 90°.

The effect of the PO<sub>4</sub> chain length on the bonding is indicated by the relative values of the logarithms of the successive formation constants which are: 9.07 and 5.58 for  $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ , 8.70 and 1.80 for  $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ , and 9.44 and 1.16 for  $\text{Cu}(\text{P}_4\text{O}_{13})_2^{10-}$ . The first rather surprising observation is that an increase in the number of PO<sub>4</sub> tetrahedra available for bonds does not appreciably increase the stability of the 1:1 complex. There is, in fact, a slight decrease in the stability of the 1:1 triphosphate complex. This evidence alone might indicate that only the terminal PO<sub>4</sub> tetrahedra are involved in the bonding. If this were the case the constants for the bonding of the second ligand should be similar. Instead, the second  $\text{P}_2\text{O}_7^{4-}$  is strongly bonded while the tendency to add a second  $\text{P}_3\text{O}_7^{5-}$  or  $\text{P}_4\text{O}_{10}^{6-}$  is relatively small. This suggests that the formation of additional bonds by internal PO<sub>4</sub> tetrahedra does occur but that the average bond free energy is smaller in tri- and tetraphosphates.

It was postulated that this decrease in the average bond free energy might be correlated with 1– ionic charge introduced by internal phosphate tetrahedra compared to 2– introduced by terminal ones. In pyrophosphate the charge on both tetrahedra is 2–, and the strong bonding to two pyrophosphates is feasible. In cyclic polyphosphates in which terminal tetrahedra are absent the ionic charge on each tetrahedron is only 1–, and the bonding of metal ions, and hydrogen ions as well, is much weaker. Thus, Gross and Gryder<sup>9</sup> obtained values of 3.18 and 1.49 for the logarithms of the stepwise formation constants of copper(II) with one and two cyclic tetrametaphosphate ions, respectively. Steric considerations and the relative magnitudes of these two constants indicate that each tetrametaphosphate ion forms two bonds with copper(II). This greater stability of the pyrophosphate complex compared to the tetrametaphosphate complex indicated that the correlation of bond strength with ionic charge of the phosphate might be quite general.

In order to determine the extent to which copper polyphosphate complex bonding is ionic and in order to observe possible general relations among the various complexes of a particular metal ion, the logarithms of various complexity constants were plotted vs. the mean ionic charge of the bonding phosphate tetrahedra. The mean ionic charge,  $V^-$ , was evaluated by assuming that terminal and adjacent tetrahedra with their respective 2– and 1– ionic charges were involved in the bond formation insofar as possible. It was further assumed that protonation reduced the ionic charge of the terminal tetrahedra to 1– and that protonated terminal tetrahedra were not involved in complex bond formation if others were available to satisfy the copper(II) coordination number of 4.

The plot of a mean ionic charge is justified by the reasonable assumption that the ionic charge of bonding tetrahedra is distributed over all of the oxygen atoms so the ionic charge of the terminal phosphate tetrahedra is decreased in the presence of internal ones. The exceptionally small value of  $pK_4$  for triphosphoric acid<sup>5</sup> and the anomalous nuclear magnetic resonance properties<sup>10</sup> of  $HP_3O_{10}^{4-}$  may be due to the transfer of charge to the internal phosphate tetrahedron from two adjacent terminal ones. The postulated bonding of a single hydrogen ion by the internal  $PO_4$  tetrahedron<sup>10</sup> and its inclusion in a coiled structure<sup>5</sup> are both consistent with this effect. It is also reasonable that the effective ligand field is equivalent to the mean of that of the various ligands.

In a plot (not shown) of  $\log \beta_n$  along the  $y$  axis *vs.*  $V^-$  along the  $x$  axis, all points fall close to a straight line having a slope of  $-9.47$  and a  $y$  intercept of  $-4.60$ . The empirical equation relating  $\log \beta_n$  to the defined ionic charge,  $V^-$ , is then

$$\log \beta_n + 4.60 = -9.47V^- \quad (15)$$

To test the reliability of this equation, the data given in Table IV for all known saturated copper complexes with ring or linear phosphates containing up to four phosphate tetrahedra were substituted into this equation, and the slopes were calculated. The average relative deviation is only 3.1%. With one exception the maximum relative deviation is 7%. Furthermore, agreement was as good for unstable protonated or metaphosphate complexes as for stable ones.

Equation 15 indicates that a saturated complex in

(10) M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *Inorg. Chem.*, **1**, 813 (1962).

TABLE IV  
THE RELATION OF COMPLEX STABILITY TO THE MEAN  
PHOSPHATE IONIC CHARGE

Complex	Log $\beta_n$	Mean ionic charge, $V^-$	Negative slope
$Cu(P_4O_{12})_{26}^-$	4.67	-1.00	9.27
$Cu(H_2P_2O_7)_2^{2-}$	3.60	-1.00	8.20
$Cu(H_2P_3O_{10})_2^{4-}$	4.81	-1.00	9.41
$Cu(H_2P_4O_{13})_2^{6-}$	4.91	-1.00	9.51
$CuH_3(P_2O_7)_2^{3-}$	6.60	-1.25	8.95
$CuH_3(P_3O_{10})_2^{5-}$	7.04	-1.25	9.31
$CuH_3(P_4O_{13})_2^{7-}$	7.49	-1.25	9.67
$Cu(HP_2O_7)_2^{4-}$	8.33	-1.50	9.29
$Cu(HP_3O_{10})_2^{6-}$	7.99	-1.50	9.60
$Cu(HP_4O_{13})_2^{8-}$	9.70	-1.50	9.47
$CuH(P_3O_{10})_2^{7-}$	10.13	-1.50	9.82
$CuH(P_4O_{13})_2^{9-}$	10.66	-1.50	10.17
$Cu(P_4O_{13})_2^{10-}$	10.60	-1.50	10.13
$Cu(P_3O_{10})_2^{8-}$	10.50	-1.50	10.07
$CuH(P_3O_7)_2^{5-}$	11.48	-1.75	9.19
$Cu(P_2O_7)_2^{6-}$	14.65	-2.00	9.62

Mean  $9.47 \pm 0.31$

which the phosphate ionic charge is zero should have the exceedingly small complexity constant of  $10^{-4.60}$ . It can be concluded that the bonding in the complexes is essentially ionic as indicated by Smith and Alberty<sup>11</sup> in their paper on adenosine phosphate complexes. The relation of the stability constants of copper polyphosphate complexes to the mean ionic charge of complex bonded  $PO_4$  tetrahedra brings order to the large range of stability constants obtained for various copper complexes and furnishes a means of predicting the stabilities of polyphosphate complexes of ions other than copper.

(11) R. M. Smith and R. A. Alberty, *J. Phys. Chem.*, **60**, 180 (1956).