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A Study of the Stability and Basicity of Copper(II) Triphosphate Complexes Using the Dropping Amalgam Electrode¹

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The stability and extent of association of hydrogen ions with copper triphosphate complexes have 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 acidity, of the complex. In terms of concentrations, the successive formation constants of $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ are $10^{3.70}$ and $10^{1.69}$. Two hydrogen ions associate readily with each complexed triphosphate ion in both $\text{CuP}_3\text{O}_{10}^{3-}$ and $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$. The stepwise formation constants for the successive addition of hydrogen ions to $\text{CuP}_3\text{O}_{10}^{3-}$ are $10^{6.72}$ and $10^{3.31}$. For $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ they are $10^{3.88}$, $10^{3.69}$, $10^{4.38}$, $10^{3.60}$. The association of any hydrogen ions with $\text{CuP}_3\text{O}_{10}^{3-}$ and more than one hydrogen ion with $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ greatly decreases the stability of the complexes.

Introduction

The purpose of the present study was to determine the stability of copper(II) triphosphate complexes and to establish the extent of association with hydrogen ions and the effect of such association on the stability of the complex.

The ability of triphosphate to form stable complexes² even with alkali and alkaline earth metal ions³ is well known. The tendency of polyphosphate complexes to associate with additional 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 Froneus⁴ eliminate the need for approximations of this type. As shown in earlier papers,^{5,6} Leden's function, expressed in terms of electrode potentials, can be readily applied when the complexes as well as the free ligands tend to associate with hydrogen ions.

A further complication is the fact that alkali metal ions form complexes with triphosphate.³ In the present study, alkali metal ions were

replaced by tetramethylammonium ion in both the triphosphate and in the supporting electrolyte through the use of cation exchange resins. The effect of alkali metal ions on the complexes also was studied.

Polarographic studies of this system using the conventional mercury electrode are somewhat limited because the cathodic polarographic waves are poorly shaped near the diffusion current regions in neutral or alkaline solutions. The dropping copper amalgam electrode, described in a previous paper,⁷ was found applicable in the study of copper(II) polyphosphate complexes since the potentials could be measured at zero current under conditions of equilibria with the bulk of the solution.

Theoretical

As described in earlier papers,^{5,6} the various equilibria can be treated in terms of hydrogen ions and the completely dissociated triphosphate ion instead of species containing associated hydrogen ions, such as $\text{HP}_3\text{O}_{10}^{4-}$ and $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$. 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, triphosphate ion to B, and hydroxyl ion to C in the formulas given in the previous papers.^{5,6} In the following expressions, the symbol L indicates a ligand such as triphosphate including its ionic charge. Ionic charge

(1) Abstracted from theses by E. D. Loughran (1955) and by P. E. Sturrock (1960) submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University.

(2) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part II," Inorganic Ligands Special Publication No. 7, The Chemical Society, Burlington House, W. 1, London, 1958.

(3) J. I. Watters, S. M. Lambert, and E. D. Loughran, *J. Am. Chem. Soc.*, **75**, 4819 (1953); **79**, 3651 (1957); **79**, 5606 (1957); **81**, 3201 (1959).

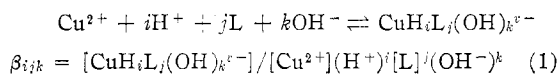
(4) J. C. Sullivan and J. C. Hindman, *ibid.*, **74**, 8091 (1952).

(5) J. I. Watters and J. G. Mason, *ibid.*, **78**, 285 (1956).

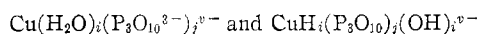
(6) J. I. Watters, J. G. Mason, and O. E. Schupp, III, *ibid.*, **78**, 5782 (1956).

(7) O. E. Schupp, III, T. Youness, and J. I. Watters, *ibid.*, **84**, 505 (1962).

often is omitted for convenience but is indicated by the superscript, v -, in the following equation. Assuming only mononuclear species exist in significant concentrations with a large excess of ligands present one writes the general expressions



Quite generally association with hydrogen and hydroxyl ions may be expected to occur in different pH ranges. The simultaneous association of the complexed ligand with hydrogen ions and the aquometal ion with hydroxyl ions is structurally possible but is not necessarily probable. The formation of this type of complex cannot be detected in studies of the present kind since the activity of water is essentially constant. Thus



are indistinguishable and will be accounted for in terms of the former species.

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

$$F(\text{H}^+, \text{L}, \text{OH}^-)_0 = \text{antilog} [0.4342(E_{\text{aq}} - E_0)n\bar{v}/RT] =$$

$$\text{antilog} (0.4342\Delta E n\bar{v}/RT) =$$

$$\sum_{i=0}^{2N} \sum_{j=0}^N \sum_{k=0}^{2N} \beta_{ijk}(\text{H}^+)^i[\text{L}]^j(\text{OH}^-)^k \quad (2)$$

The potentials, E_{aq} and E_0 , are measured in the non-complexing solution and the complexing solution, respectively, which contained the same total concentrations of copper(II), copper amalgam, and supporting electrolyte. These potentials may be spontaneous potentials or half-wave potentials. In all of these expressions molar concentrations are indicated by brackets while the activities of hydrogen or hydroxyl ions which are measured by means of a glass electrode are indicated by parentheses.

The triphosphate ion concentration in the pH range above 3 is calculated from the following equation in terms of the hybrid acidity constants of $\text{H}_3\text{P}_3\text{O}_{10}$ determined in similar concentrations of the same indifferent electrolyte.³ The total concentrations of triphosphate and Cu in all forms are indicated by $[\text{P}_3\text{O}_{10}^{5-}]_t$ and $[\text{Cu}^{2+}]_t$ while the mean number of complex bound triphosphate ions is indicated by \bar{n} .

$$[\text{P}_3\text{O}_{10}^{5-}] = (K_3K_4K_5[\text{P}_3\text{O}_{10}^{5-}]_t - \bar{n}[\text{Cu}^{2+}]_t) +$$

$$[K_3K_4K_5 + K_3K_4(\text{H}^+) + K_3(\text{H}^+)^2 + (\text{H}^+)^3]$$

The term, \bar{n} , first is assigned a value of 2 which later is corrected on the basis of the data illustrated in Fig. 2.

Since the term for $i = j = k$ is unity, the expression for Leden's function, $F(\text{H}^+, \text{L}, \text{OH}^-)_1$ is

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

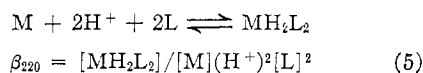
Only mononuclear complexes were obtained in this study since an excess of the ligand always was present. The latter expression may be expanded as follows for all possible mononuclear complexes

$$F(\text{H}^+, \text{L}, \text{OH}^-)_1 = \beta_{010} + \beta_{020}[\text{L}] + \beta_{110}(\text{H}^+) + \beta_{210}(\text{H}^+)^2$$

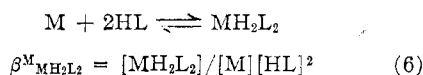
$$+ \beta_{120}(\text{H}^+)[\text{L}] + \beta_{220}(\text{H}^+)^2[\text{L}] + \beta_{320}(\text{H}^+)^3[\text{L}] +$$

$$\beta_{420}(\text{H}^+)^4[\text{L}] + \beta_{011}(\text{OH}^-) + \beta_{012}(\text{OH}^-)^2 \quad (4)$$

The original complexity constants were calculated in terms of the equilibrium with H^+ , L , and OH^- . The subscripts after β indicate the number of each of these species. Thus β_{220} refers to the equilibrium



These can be converted to equivalent equilibria and complexity constants in terms of the species containing associated hydrogen ion, thus

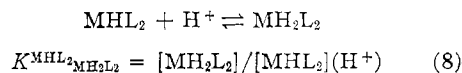


The latter have the advantage over the original constants in that their magnitude is a measure of the stability of the complex.

The relations between these constants and the last acidity constant of the ligand acid, K_N and K_{N-1} , are readily derived. For example

$$\beta_{220}K_N^2 = \beta_{\text{MH}_2\text{L}_2}^{\text{M}} \quad (7)$$

The acidity constants are calculated from data obtained in the same supporting electrolyte with complex forming ions absent. 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 ligand's acidity, thus



Experimental

The current-voltage data were obtained in solutions containing copper(II) and triphosphate, at varied pH, using the dropping copper amalgam electrode (0.0005% copper by weight) described in the previous publication.⁷ Similar data were obtained in solutions containing the same copper(II) ion and supporting electrolyte concentrations. The differences in the spontaneous potentials, obtained with an open circuit, or the half-wave potentials of the complex-free and the complex-containing solutions were used to calculate Leden's functions accord-

ing to eq. 4. Current-voltage data for purely anodic waves also were obtained using the copper amalgam electrode in similar solutions but with copper(II) ion absent. Within experimental error, for solutions of the same triphosphate concentration and pH, the differences in half-wave potentials were essentially identical with the shift in the spontaneous potential. The latter were used in the final calculations since they were measured more easily and with more precision. Typical spontaneous potential data for two triphosphate concentrations are given in Table I. The experimental values obtained for Leden's $F(H^+, L, OH^-)$ as well as those calculated on the basis of the solved equilibrium constants also are included.

TABLE I
POTENTIAL DATA OF THE TRIPOLYPHOSPHATE-COPPER(II)
SYSTEM

$[Cu^{2+}]_t = 0.001 M$, $\mu = 1.0 \pm 0.2$ with $[N(CH_3)_4]NO_3$,
 $E_{aq} = 0.02525 v.$, amalgam = 0.0005% Cu

pH	ΔE	$-\log$	$\log F$	$\log F$
		$[P_3O_{10}^{5-}]$ corr.	(H, L, OH^-) , exptl.	(H, L, OH^-) , calcd.
(A) 0.00979 M triphosphate added				
2.50	0.0314	11.88	12.90	12.88
3.29	.0402	10.17	11.51	11.54
3.81	.0509	9.11	10.82	10.81
4.46	.0674	7.82	10.10	10.09
4.98	.0829	6.81	9.61	9.62
5.65	.1045	5.64	9.17	9.18
6.01	.1161	5.10	9.03	9.02
6.48	.1296	4.49	8.87	8.89
7.48	.1589	3.43	8.80	8.79
8.32	.1809	2.69	8.81	8.81
8.79	.1902	2.38	8.81	8.85
9.19	.1960	2.22	8.85	8.90
9.80	.2045	2.11	9.02	9.02
(B) 0.0587 M triphosphate added				
2.92	0.0682	10.13	12.43	12.44
3.78	.0819	8.35	11.12	11.13
4.45	.1033	7.02	10.41	10.39
5.30	.1287	5.41	9.76	9.76
6.06	.1528	4.21	9.38	9.40
7.10	.1809	2.99	9.11	9.12
7.41	.1896	2.68	9.09	9.10
8.03	.2082	2.10	9.14	9.12
8.65	.2245	1.64	9.23	9.21
9.07	.2326	1.44	9.30	9.29
9.43	.2370	1.34	9.35	9.34
9.73	.2401	1.29	9.41	9.39

The general experimental techniques and apparatus are described in the previous publication.⁷ The first salt bridge contained 1 M tetramethylammonium nitrate instead of 1 M KNO₃. At the potential of the saturated calomel reference electrode (s.c.e.), the amalgam drop time was 3.35 sec. and its flow rate was 2.47 mg. of amalgam per sec., corresponding to a capillary characteristic, k , of 2.235 mg.^{2/3} sec.^{-1/2}.

The preparation of solutions and the replacement of alkali metal ions by tetramethylammonium ions have been described previously.⁸ Tetramethylammonium nitrate

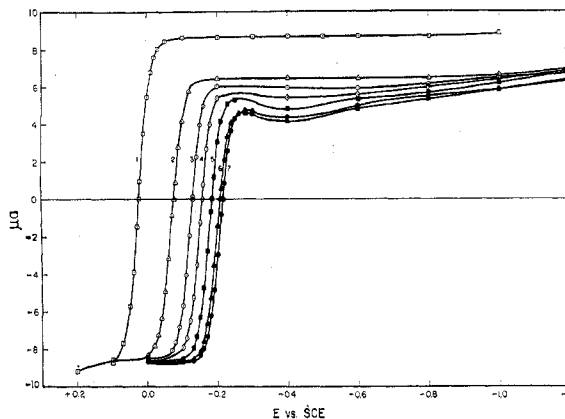


Fig. 1.—Anodic-cathodic polarograms of copper(II) ions in triphosphate solution at various pH values using the dropping copper amalgam electrode: $[P_3O_{10}^{5-}]_t = 0.0587 M$ (except in polarogram 1); $[Cu^{2+}]_t = 1.00 mM$; $\mu = 1.00 \pm 0.20$ with $N(CH_3)_4NO_3$; methyl red = 0.0005%; amalgam = 0.00064% Cu; polarogram 1, pH = 3.00 (no triphosphate); 2, pH = 4.45; 3, pH = 6.06; 4, pH = 7.10; 5, pH = 8.03; 6, pH = 9.03; 7, pH = 9.70.

was prepared by neutralizing tetramethylammonium hydroxide (Eastman reagent grade) with nitric acid, evaporating to dryness with the rotary vacuum drier, and recrystallizing from a solution containing methanol and acetone.⁸

All solutions were kept free of air and carbon dioxide through purging with purified nitrogen and were thermostatically maintained at 25°. The experiments were performed continuously once the triphosphates were dissolved in order to minimize hydrolysis. In order to vary the pH with a minimum of hydrolysis and dilution, freshly boiled concentrated HNO₃ was added to the solutions. These solutions contained the tetramethylammonium triphosphate along with sufficient tetramethylammonium nitrate to produce an ionic strength of unity when the triphosphate was associated with one hydrogen ion. In this way the ionic strength was maintained close to unity and never varied more than ± 0.20 . Small corrections were applied for the dilution which amounted to less than 4%. The lower concentration limit of the triphosphate was determined by the fact that a large excess of triphosphate relative to the concentration of complex formation at the electrode surface was required to keep the electrode well poised without the formation of Cu₂O and to obtain accurate values for the ligand concentrations. The spontaneous potential and current voltage data were very steady and reproducible to $\pm 0.1 mv.$

Results and Discussion

In Fig. 1 are shown typical anodic-cathodic polarograms of copper(II) in the ligand-free supporting electrolyte and in triphosphate solutions having various pH values. As observed by

(8) P. L. Pickard and W. E. Neptune, *Anal. Chem.*, **27**, 1358 (1955).

Laitinen and Onstott⁹ for cathodic waves of the copper pyrophosphate complex, it is evident that the entire waves are essentially reversible in fairly acidic triphosphate 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 $(\Delta E/\Delta \log(i_{da} - i)/(i - i_{da}))$ of 0.030 v. for a two-electron electrode reaction. Furthermore, the diffusion current constant of 3.8 $\mu\text{amp./mM}$ concentration of copper(II) per unit capillary characteristic is consistent with a two-electron reduction of copper(I) directly to free copper. In moderately alkaline triphosphate solutions the waves have a somewhat anomalous appearance since the complete cathodic diffusion current does not develop normally.

With copper(II) ions absent in the bulk of the triphosphate solution, reversible anodic waves having the theoretical slope of 0.030 v. obtained at all pH values except in the regions close to 7.3 and 3.9, where the slopes are somewhat larger. This increase in slope is due to the poor poise of the electrode at the acid equivalence points of triphosphoric discussed in the previous paper⁷ and are not due to electrode irreversibility.

The calculation of the equilibrium constants was simplified by including only terms for the most probable species, $\text{CuP}_3\text{O}_{10}^{3-}$, $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$, and $\text{CuHP}_3\text{O}_{10}^{2-}$, with the data from a pH of 7 to about 9.5. Determinates were set up and solved using potential data obtained at three different pH values in this range according to the equation

$$\text{antilog}(\Delta E - 0.4342nF/RT) = \beta_{010} + \beta_{020}[\text{L}] + \beta_{120}(\text{H}^+)[\text{L}] \quad (9)$$

These then were included as knowns to solve preliminary constants for the species, $\text{CuH}_2(\text{P}_3\text{O}_{10})_2^{6-}$, $\text{CuH}_3(\text{P}_3\text{O}_{10})_2^{5-}$, and $\text{CuHP}_3\text{O}_{10}^{2-}$, in the pH range of 4.5 to 7 according to the equation

$$\text{antilog}(\Delta E - 0.4342nF/RT) - \beta_{010} - \beta_{020}[\text{L}] - \beta_{120}(\text{H}^+)[\text{L}] = \beta_{110}(\text{H}^+) + \beta_{220}(\text{H}^+)^2[\text{L}] + \beta_{320}(\text{H}^+)^3[\text{L}] \quad (10)$$

The remaining species, $\text{CuH}_4(\text{P}_3\text{O}_{10})_2^{4-}$ and $\text{CuH}_2\text{P}_3\text{O}_{10}^{1-}$, were solved in a similar way below a pH of 4.5 and $\text{Cu}(\text{P}_3\text{O}_{10})(\text{OH})^{9-}$ above a pH of 9. The fractional abundance of each species was solved at each pH from its term divided by the summation of all of the terms in the right side of Leden's eq. (2). Finally, determinants, including

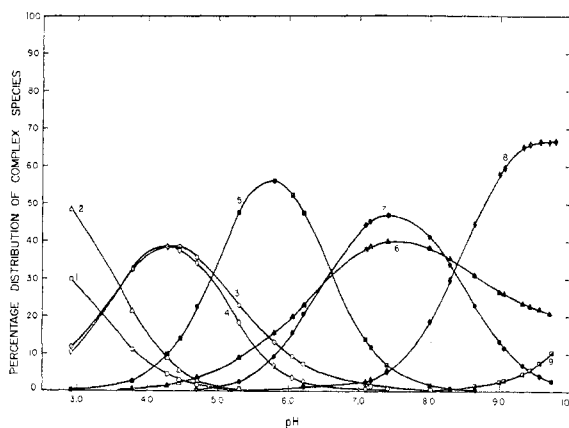


Fig. 2.—Percentage distribution of copper(II) triphosphate complex species as a function of pH: $[\text{Cu}^{2+}]_t = 1.00 \text{ mM}$; $[\text{P}_3\text{O}_{10}^{5-}]_t = 0.0587 \text{ M}$. Complex species: curve 1, CuH_2L ; 2, CuH_4L_2 ; 3, CuHL ; 4, CuH_3L_2 ; 5, CuH_2L_2 ; 6, CuL ; 7, CuHL_2 ; 8, CuL_2 ; 9, CuLOH .

the preliminary constants for minor species as knowns, again were solved for the predominant species. No other species were detected since the inclusion of terms for their complexity constants yielded very small random positive or negative values for their constants. The following original complexity constants were calculated

$$\beta_{010} = [\text{CuP}_3\text{O}_{10}^{3-}]/[\text{Cu}^{2+}][\text{P}_3\text{O}_{10}^{5-}] = 10^{8.70} \quad (11)$$

$$\beta_{020} = [\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}]/[\text{Cu}^{2+}][\text{P}_3\text{O}_{10}^{5-}]^2 = 10^{10.60} \quad (12)$$

$$\beta_{110} = [\text{CuHP}_3\text{O}_{10}^{2-}]/[\text{Cu}^{2+}](\text{H}^+)[\text{P}_3\text{O}_{10}^{5-}] = 10^{14.42} \quad (13)$$

$$\beta_{210} = [\text{CuH}_2\text{P}_3\text{O}_{10}^{1-}]/[\text{Cu}^{2+}](\text{H}^+)^2[\text{P}_3\text{O}_{10}^{5-}] = 10^{17.75} \quad (14)$$

$$\beta_{120} = [\text{CuH}(\text{P}_3\text{O}_{10})_2^{7-}]/[\text{Cu}^{2+}](\text{H}^+)[\text{P}_3\text{O}_{10}^{5-}]^2 = 10^{18.86} \quad (15)$$

$$\beta_{220} = [\text{CuH}_2(\text{P}_3\text{O}_{10})_2^{6-}]/[\text{Cu}^{2+}](\text{H}^+)^2[\text{P}_3\text{O}_{10}^{5-}]^2 = 10^{25.45} \quad (16)$$

$$\beta_{320} = [\text{CuH}_3(\text{P}_3\text{O}_{10})_2^{5-}]/[\text{Cu}^{2+}](\text{H}^+)^3[\text{P}_3\text{O}_{10}^{5-}]^2 = 10^{30.33} \quad (17)$$

$$\beta_{430} = [\text{CuH}_4(\text{P}_3\text{O}_{10})_2^{4-}]/[\text{Cu}^{2+}](\text{H}^+)^4[\text{P}_3\text{O}_{10}^{5-}]^2 = 10^{33.33} \quad (18)$$

$$\beta_{011} = [\text{Cu}(\text{P}_3\text{O}_{10})(\text{OH})^{9-}]/[\text{Cu}^{2+}][\text{P}_3\text{O}_{10}^{5-}](\text{OH}^-) = 10^{12.67} \quad (19)$$

The relative abundance of each of these species as a function of pH in a solution containing 0.001 M copper(II) and 0.0587 M $[\text{P}_3\text{O}_{10}^{5-}]_t$ is shown in Fig. 2. No single species is predominant in any pH region. The value of the second formation constant for $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ was confirmed by a spectrophotometric procedure¹⁰ in which the ratio of $\text{CuP}_3\text{O}_{10}^{3-}$ to $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ was observed as a function of $\text{P}_3\text{O}_{10}^{5-}$ concentration. As one might

(9) H. A. Laitinen and E. I. Onstott, *J. Am. Chem. Soc.*, **72**, 4729 (1950).

(10) J. I. Watters and A. Aaron, *ibid.*, **75**, 611 (1953).

predict the species $\text{Cu}(\text{P}_3\text{O}_{10})\text{OH}^{4-}$ also was detected. However, the accuracy of this constant is limited by the fact that the electrode became unreliable due to the formation of Cu_2O in the pH range where this species might be expected to become predominant.

Upon comparing Fig. 1 and Fig. 2 it is evident that the poor development of the diffusion current occurs in the region where $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ becomes increasingly predominant. It is probable that its reduction at the electrode is somewhat slower than its rate of diffusion or that a part of the $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ has a configuration which does not undergo reduction until a higher potential is reached. Support for either of these explanations is found in the fact that the wave shape improved when the solution was warmed. The effect increased in the presence of alkali metal ions which, as will be shown, tend to increase the stability of the complex. Laitinen and Onstott⁹ explained the much larger effect observed in the copper pyrophosphate system in a similar way. This effect does not influence the results obtained at zero current when Leden's expression is used since there are adequate concentrations of reversibly reduced species to permit the potential measurements without altering equilibrium concentrations. Furthermore, the same results were obtained on the basis of anodic half-wave potentials where the effect was absent.

In order to observe the effect of associated hydrogen ions on the strength of the complex bond, the constants for acidic complexes were converted to the following in terms of the concentrations of the triphosphate species actually present in the complex.

$$\beta^{\text{Cu}}_{\text{CuHL}} = \beta_{110}K_5 = \frac{[\text{CuHP}_3\text{O}_{10}^{5-}]/[\text{Cu}^{2+}][\text{HP}_3\text{O}_{10}^{4-}]}{10^{9.69}} \quad (20)$$

$$\beta^{\text{Cu}}_{\text{CuH}_2\text{L}} = \beta_{210}K_4K_5 = \frac{[\text{CuH}_2(\text{P}_3\text{O}_{10})_2^{6-}]/[\text{Cu}^{2+}][\text{H}_2\text{P}_3\text{O}_{10}^{3-}]}{10^{9.19}} \quad (21)$$

$$\beta^{\text{Cu}}_{\text{CuHL}_2} = \beta_{120}K_5^2 = \frac{[\text{CuH}(\text{P}_3\text{O}_{10})_2^{7-}]/[\text{Cu}^{2+}][\text{HP}_3\text{O}_{10}^{4-}][\text{P}_3\text{O}_{10}^{5-}]}{10^{10.13}} \quad (22)$$

$$\beta^{\text{Cu}}_{\text{CuH}_2\text{L}_2} = \beta_{220}K_5^2 = \frac{[\text{CuH}_2(\text{P}_3\text{O}_{10})_2^{6-}]/[\text{Cu}^{2+}][\text{HP}_3\text{O}_{10}^{4-}]^2}{10^{7.99}} \quad (23)$$

$$\beta^{\text{Cu}}_{\text{CuH}_3\text{L}_2} = \beta_{320}K_4K_5^2 = \frac{[\text{CuH}_3(\text{P}_3\text{O}_{10})_2^{5-}]/[\text{Cu}^{2+}][\text{H}_2\text{P}_3\text{O}_{10}^{3-}][\text{HP}_3\text{O}_{10}^{4-}]}{10^{7.04}} \quad (24)$$

$$\beta^{\text{Cu}}_{\text{CuH}_4\text{L}_2} = \beta_{420}K_4^2K_5^2 = \frac{[\text{CuH}_4(\text{P}_3\text{O}_{10})_2^{4-}]/[\text{Cu}^{2+}][\text{H}_2\text{P}_3\text{O}_{10}^{3-}]^2}{10^{4.81}} \quad (25)$$

For complexes in which only one kind of ligand, L, HL, or H_2L , is present, the expression $1/N$

$\log \beta_N$ is, as discussed in a previous paper,¹¹ a measure of the free energy of complex formation with each ligand. The following equation can be used to predict the constants for the complex containing any two of these ligands, for example L and HL.

$$\log \beta^{\text{Cu}}_{\text{CuHL}_2} = 1/2 \log \beta^{\text{Cu}}_{\text{CuL}_2} + 1/2 \log \beta^{\text{Cu}}_{\text{CuHL}} + \log 2 + 0.40 \pm 0.10 \quad (26)$$

The $\log 2$ term is a statistical effect and the last term is an empirical correction for copper complexes presumably resulting from hydrogen bonding. In this way one calculates a theoretical value of $10^{9.95}$ for $\beta^{\text{Cu}}_{\text{CuHL}_2}$ compared to the experimental value of $10^{10.13}$. A similar calculation for $\beta^{\text{Cu}}_{\text{CuH}_2\text{L}_2}$ in terms of $\beta^{\text{Cu}}_{\text{CuH}_2\text{L}}$ and $\beta^{\text{Cu}}_{\text{CuHL}_2}$ yields a value of $10^{7.10}$ compared to the experimental value of $10^{7.04}$. These calculations indicate that the constants are consistent.

In discussing this and other effects it will be assumed that $\text{P}_3\text{O}_{10}^{5-}$ is capable of forming three bonds in a structure involving two six-membered rings compared to pyrophosphate, which is capable of forming only two bonds. Copper(II) ion, on the other hand, is capable of forming only four strong tetrahedral or square bonds and a fifth considerably weaker bond at the apex of a square pyramid in the latter case. A sixth very weak bond producing an octahedral configuration also may be possible. The relatively large value of the first $\text{P}_3\text{O}_{10}^{5-}$ stepwise constant compared to the second is consistent with the postulate that the first $\text{P}_3\text{O}_{10}^{5-}$ ion can be bonded by three strong square or tetrahedral bonds. The second formation constant is relatively small because it involves the formation of only one additional strong bond and a weak fifth bond. It is probable that, in $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$, each $\text{P}_3\text{O}_{10}^{5-}$ is bonded as a bidentate six-membered chelate ring. Thus, one terminal PO_4 tetrahedron may be left unbonded and dangling when the corresponding terminal PO_4 of the second $\text{P}_3\text{O}_{10}^{5-}$ is bonded. The presence of this dangling PO_4 tetrahedron is indicated by the relatively large complexity constant of $\text{CuH}(\text{P}_3\text{O}_{10})_2^{7-}$, which is only $10^{0.37}$ smaller than that of $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$. It also will be shown that this first hydrogen ion is bonded practically as strongly as in the free ligand ion.

The association of additional hydrogen ions with $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ results in large decreases in the stability of the complex, especially with even

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numbered hydrogen ions. The association with the second hydrogen ion probably removes one terminal PO_4 tetrahedron from the complex. That the intrinsic bond strength of the central PO_4 tetrahedron is less than that of terminal ones is evident from the relative values of the acid dissociation constants. The bonding of a third hydrogen ion with a complexed terminal PO_4 tetrahedron results in a smaller decrease in the complex bond strength, possibly as a consequence of hydrogen bonding to the other complexed terminal tetrahedron.

The smaller bonding capacity of the central PO_4 tetrahedron also is reflected in the relative magnitudes of the first formation constants of $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ and $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$. Even though three bonds are involved with $\text{P}_3\text{O}_{10}^{5-}$, the first formation constants are quite similar.¹⁰ The second formation constant of $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ is only about half that of $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$. The tridentate structure in $\text{CuP}_3\text{O}_{10}^{3-}$ also is indicated by the detection of the species $\text{Cu}(\text{P}_3\text{O}_{10})(\text{OH})^{4-}$.

The basicity of the two complexes, $\text{CuP}_3\text{O}_{10}^{3-}$ and $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$, can be evaluated in terms of the successive formation constants for the stepwise addition of hydrogen ions. For $\text{CuP}_3\text{O}_{10}^{3-}$ these constants are

$$K^{\text{CuL}}_{\text{CuHL}} = \beta_{110}/\beta_{010} = 10^{5.72};$$

$$K^{\text{CuHL}}_{\text{CuH}_2\text{L}} = \beta_{210}/\beta_{110} = 10^{2.75} \quad (27)$$

for $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$, they are

$$K^{\text{CuL}_2}_{\text{CuHL}_2} = \beta_{120}/\beta_{020} = 10^{8.38};$$

$$K^{\text{CuHL}_2}_{\text{CuH}_2\text{L}_2} = \beta_{220}/\beta_{120} = 10^{6.59} \quad (28)$$

$$K^{\text{CuH}_2\text{L}_2}_{\text{CuH}_3\text{L}_2} = \beta_{320}/\beta_{220} = 10^{4.88};$$

$$K^{\text{H}_3\text{L}_2}_{\text{H}_4\text{L}_2} = \beta_{420}/\beta_{320} = 10^{3.60} \quad (29)$$

These values may be compared to the following corresponding values for uncomplexed L in the same supporting electrolyte.³

$$K^{\text{L}}_{\text{HL}} = k_5^{-1} = 10^{8.73}; \quad K^{\text{HL}}_{\text{H}_2\text{L}} = K_4^{-1} = 10^{3.88} \quad (30)$$

$$K^{\text{H}_2\text{L}}_{\text{H}_3\text{L}} = K_3^{-1} = 10^{3.11}; \quad K^{\text{H}_3\text{L}}_{\text{H}_4\text{L}} = K_2^{-1} = 10^{-1.06} \quad (31)$$

There is a statistical factor in these constants which is equal to the number of equivalent sites available to hydrogen ions divided by the number of equivalent hydrogen ions available for ionization after the association with an additional hydrogen ion. Since this effect contributes less than 10^0 ,⁶⁰ it will be neglected in the following discussion. The presence of a complexed copper in $\text{CuP}_3\text{O}_{10}^{3-}$ has a similar effect on basicity to that resulting from the presence of the first hydrogen ion in the uncomplexed $\text{P}_3\text{O}_{10}^{5-}$ ion.

This results from the fact that the copper ion is bonded directly to the particular PO_4 tetrahedron accepting the hydrogen ion while the previously bonded hydrogen ion is not. This proximity effect more than compensates for the fact that the intrinsic complex copper(II) bond strength is much less than that of hydrogen ion. That the magnitudes of the complexity constants of $\text{CuP}_3\text{O}_{10}$ and $\text{Cu}(\text{P}_3\text{O}_{10})_2$ are due to an appreciable contribution by chelation is evident when one compares β_4 of $\text{Cu}(\text{NH}_3)_4^{2+}$, which is $10^{13.84}$, to β_2 of $\text{Cu}(\text{en})_2^{2+}$, which is $10^{20.03}$.²

The first hydrogen ion formation constant of $\text{Cu}(\text{P}_3\text{O}_{10})_2^{8-}$ is practically as large as the corresponding first constant of the uncomplexed ion since, as already has been postulated, this hydrogen ion forms a bond with the dangling terminal PO_4 tetrahedron. The second also is large as this hydrogen bond involves only the rupture of the weak fifth bond of the second $\text{P}_3\text{O}_{10}^{5-}$. The next two hydrogen ions which associate with the primarily bonded tetrahedra have the smaller values, $10^{4.88}$ and $10^{3.60}$, which are comparable in magnitude to the second corresponding constant of the uncomplexed $\text{P}_3\text{O}_{10}^{5-}$, namely $10^{5.88}$. As one would expect they are larger than the corresponding constant in the monocomplex.

Before the tetramethylammonium nitrate supporting electrolyte was used in this study, the complexity constant of $\text{Cu}(\text{P}_2\text{O}_7)_2^{8-}$ was calculated by correcting the triphosphate equilibrium concentration for that lost through alkali metal complex formation. This calculation yielded a complexity constant which obviously was too large. This result indicated that, in the presence of an excess of alkali metal ions, a significant proportion of the complex ions also contain alkali metal ions. This postulate was confirmed by the observation that upon including up to 0.1 M sodium ion in the supporting electrolyte the potential shift due to complex formation increased slightly in the alkaline region reaching a maximum of about 10 mv. at a pH close to 8.5. Simple complex formation between $\text{P}_3\text{O}_{10}^{5-}$ and sodium ion without any mixed metal complex formation should have produced the opposite effect. The effect was not large enough to permit the calculation of mixed complexity constants for species such as $\text{Na}_2\text{Cu}(\text{P}_3\text{O}_{10})_2^{(8-x)-}$. It is probable that there is some absorption of alkali metal ions by the complex which enhances its stability slightly. This could result in a slight reduction of the negative charge of the two complexed triphosphate

ions which could decrease their mutual repulsion. If the apparent acidity constants of the triphosphoric acid, obtained in the same concentrations of alkali metal and other ions, are used in the calculation of the concentrations of the various triphosphate species, and the presence of alkali metal ions in the complex is otherwise neglected, the values calculated for the complexity constants agree closely with those obtained in the tetramethylammonium nitrate supporting electrolyte. The significance and values of these apparent acidity constants are discussed in an earlier series of papers.³ This result supports the use of con-

stants of this type by Yamane and Davidson¹² in their calculations of the complexity constants of mercury(I) and mercury(II) with pyro- and triphosphate. Although the values obtained may vary slightly with alkali concentration, there is a practical advantage in that the sodium salt is the usual source of polyphosphates. Furthermore, the replacement by the tetramethylammonium ion is time-consuming and expensive.

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Complexes of the Ethylamines with the Halides of Calcium, Cobalt(II), and Zinc

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Ethylamine forms stable coordination compounds containing two moles of amine per mole of salt with the chlorides, bromides, and iodides of calcium, cobalt(II), and zinc. Pressure-composition isotherms also indicate the existence of higher complexes with appreciable dissociation pressures at 0°. Such higher complexes of the cobalt(II) halides have been reported previously by Ephraim and Linn.² Diethylamine does not interact with calcium chloride at 25°, and gives only the stable 2:1 complexes with cobalt(II) and zinc. Triethylamine does not react with either calcium or zinc halides at 25°, but gives stable 1:1 complexes with the cobalt(II) halides. Magnetic and spectral data for the cobalt(II) complexes are interpreted as indicating tetrahedral coordination.

Introduction

The Ca, Zn, and Co(II) ions have been chosen as examples of the 8, 18, and incomplete shell electronic configurations in a study of the coordinating tendencies of the primary, secondary, and tertiary ethylamines. The halides of all these metals give a series of complexes with ammonia, with a maximum of six, eight, or ten molecules of ammonia bound per metal ion.³ It is well known⁴ that in general the coordinating abilities of the alkyl amines decrease in the series $\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$.

Ethylamine complexes have not been reported for alkaline earth or subgroup II ions other than Hg(II). Some ethylamine complexes of the fatty acid salts of the divalent first transition series metals have been reported.⁵ Nickel cyanide complexes containing one and two molecules of ethylamine are known.⁶ Ephraim and Linn² have studied Mn(II), Co(II), and Ni(II) halide complexes containing four or six molecules of ethylamine per metal ion. Such compounds have appreciable dissociation pressures at 0°.

Diethylamine complexes have not been reported for halides of Group II elements other than Be and Hg(II). For compounds of the divalent metal ions of the first transition series, only the

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