catalysts at temperatures of 100–150°, at which temperatures reactions such as 4 and 5 are of minor importance. However, reactions like 4 and 5 become increasingly more important as the temperature is increased, indicating that the higher temperatures are necessary to accomplish the rupture of C–C bonds by a step such as 4. In an earlier part of the paper it was remarked that the surface species resulting from the chemisorption of ethylene could conceivably contain propyl and butyl groups as well as the dicarbon species. However, the fact that propane is not formed in the low temperature treatments with hydrogen, but instead requires higher temperatures, tends to cast doubt on the possibility that significant amounts of the propyl group are initially · present, since the hydrogenation of such a group should be relatively easy.

It is of interest that the C_4 product resulting during the hydrogenation experiments is n-butane, with relatively little formation of isobutane. This casts some doubt on the possibility that the adsorbed species leading to the formation of the butane are similar to carbonium ions in their properties, since isobutane would then be expected to be a major product.

Perhaps the most interesting result of the present study was the finding that the presence of a small amount of platinum on Al_2O_3 greatly increased the ease of removal of the adsorbed species by hydrogen treatment. It was shown that the adsorbed species on the Pt–Al_2O_3 catalysts could be completely removed at temperatures 100° below that at which even a part of the adsorbed species could be removed from the Al_2O_3. Since most of the adsorbed ethylene is in all probability

present on the Al_2O_3, this means that the platinum somehow aided the removal of adsorbed species from the Al_2O_3 during hydrogen treatment, and that the greater ease of removal in the case of the Pt–Al_2O_3 catalysts was not simply a matter of removal of adsorbed species originally present on Pt sites. Thus, there appears to be a cooperative effect of Pt and Al_2O_3 sites involved in the process, similar to that mentioned in the Introduction for the reactions of hydrocarbons over bifunctional catalysts. This cooperative effect would seem to arise because the Pt centers activate certain species for further reaction and subsequent desorption from the surface, and indicates some type of migration of reactive intermediates between the Pt and Al_2O_3 centers. This explanation has previously been advanced by two of the present authors[4] to account for the results of ethylene hydrogenation experiments over mixtures of Pt–SiO_2 and Al_2O_3 particles. The results of the present work thus lend additional support to the findings of the previous study.

While the results of this work suggest that migration of reactive species between Pt and Al_2O_3 centers may be important, the nature of the migrating species is still open to question. In the previous work, it was suggested that hydrogen might be the species in question, but there is no direct evidence that this is the case. However, the possibility that hydrocarbon species might migrate from Al_2O_3 centers to Pt to react with hydrogen and desorb from Pt centers has not been ruled out and would not seem too unreasonable in view of current ideas about the action of bifunctional catalysts in promoting certain hydrocarbon reactions.[1-3]

A Study of Nickel(II) and Cobalt(II) Phosphate Complexes[1]

BY GORDON G. HAMMES AND M. LEE MORRELL

The metal binding constants and rate constants have been measured for the formation of the Ni(II) and Co(II) complexes of pyrophosphate and tripolyphosphate. The binding constants were determined with a pH titration method at metal to ligand ratios of 1:1 and 2:1. The binding constants for the Co(II) complexes are slightly greater than the corresponding ones for Ni(II). The rate constants for complex formation and dissociation were measured for some of the complexes with the temperature jump method. The relaxation times measured ranged from 50 μsec. to 3 msec. The results suggest that the rate of dissociation of a water molecule from the inner hydration shell of the metal ion is rate determining for complex formation, but that the highly charged ligands can accelerate this rate somewhat in the case of Co(II).

Introduction

The interaction of metal ions with phosphate compounds is of considerable importance in biological systems.[2] Although the equilibrium properties of metal–phosphate complexes have been studied to some extent,[3] very few kinetic studies have been carried out, primarily because the reactions of interest occur too rapidly to study by conventional methods. How-

ever, the recent application of relaxation techniques to metal complex reactions now permits such studies to be made.[4]

Since pyrophosphate and tripolyphosphate are used as sequestering agents, several equilibrium studies have been made on the Ca(II) and Mg(II) complexes of these two ligands.[3,5] Some data are also available for the Cu(II) complexes of these two polyphosphates.[6] Studies involving other metal ions have been quite incomplete.[3]

Kinetic studies have been made of the reactions of adenosine 5′-triphosphate (ATP) and adenosine 5′-

(1) This work was supported in part by the U. S. Army Signal Corps, Air Force Office of Scientific Research, and Office of Naval Research and in part by the National Institutes of Health (MG-07803).

(2) R. M. Bock, "The Enzymes," Vol. 2, P. D. Boyer, H. Lardy, and K. Myerbäck, Ed., 2nd Ed., Academic Press, Inc., New York, N. Y., 1960, pp. 3–38.

(3) See for example J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1957.

(4) M. Eigen, Z. Elektrochem., 64, 115 (1960).

(5) S. M. Lambert, J. Am. Chem. Soc., 79, 4262 (1957).
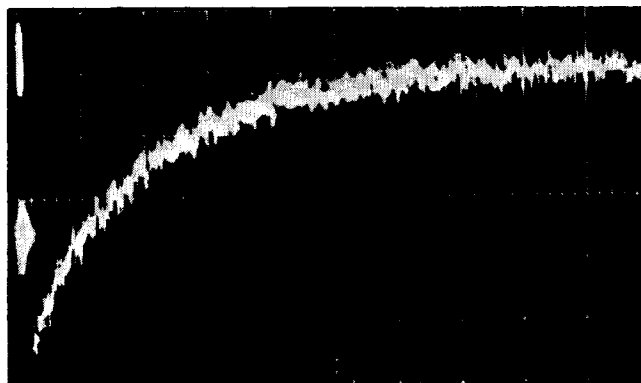
(6) P. E. Sturrock, Dissertation Abstr., 21, 2090 (1960).

Fig. 1.—Relaxation effect in Ni(II)-pyrophosphate system; $\Sigma Ni^{++} = 9.62 \times 10^{-4}\ M$, $\Sigma L = 1.25 \times 10^{-3}\ M$, $\tau = 900\ \mu sec.$, abscissa scale is 500 $\mu sec.$ per major division, ordinate scale is in arbitrary units of decreasing absorbancy.

diphosphate (ADP) with Ca(II) and Mg(II) using the temperature jump method.[7,8]

In this study the binding constants of Ni(II) and Co(II) with pyrophosphate and tripolyphosphate have been determined using a pH titration method. In addition, kinetic studies of these complexes have been carried out using the temperature jump method.

The metal ions Ni(II) and Co(II) were chosen for investigation because the binding constants and rate constants characteristic of complex formation of these metals are conveniently studied with currently available methods. In addition, a comparison with the results obtained from other kinetic studies of complex formation involving Ni(II) and Co(II) can be made.[4,9,10] The polyphosphate ligands, in addition to being excellent models for biological systems, permit information to be obtained concerning the effect of highly charged ligands on complex formation.

A knowledge of the chemical properties of some of these simpler systems can be of value in understanding more complicated biological processes and in understanding the general nature of metal complex formation.

Experimental

Stock solutions of 0.1 M Co(II) and Ni(II) were prepared from reagent grade nitrate salts (Mallinckrodt Chemical Co.) using distilled, deionized water. The metal ion concentration of the solutions was checked by a complexometric titration with ethylenediaminetetraacetic acid using the method developed by Schwarzenbach.[11] All metal solutions used were prepared by dilution of the stock solution with distilled, deionized water.

Pyrophosphate solutions were prepared by passing the reagent grade sodium salt (Mallinckrodt Chemical Co.) through the hydrogen form of Dowex 50 (X2) to eliminate the sodium. The sodium salt of tripolyphosphate (Monsanto Chemical Co.) was recrystallized from ethanol and also passed through Dowex 50. The resulting acid solutions were brought to a pH of about 10.3 with tetramethylammonium hydroxide. Such solutions are quite stable.[12] The solutions were standardized with hydrochloric acid and refrigerated until used. Tetramethylammonium chloride (Eastman Kodak Co.), recrystallized from isopropyl alcohol, was used to adjust the ionic strength of all solutions to 0.1 M.

Titration curves of ligand and metal-ligand solutions were obtained using a Radiometer automatic titrator. The titrating

(7) H. Diebler, M. Eigen, and G. G. Hammes, Z. Naturforsch., 15b, 554 (1960).

(8) M. Eigen and G. G. Hammes, J. Am. Chem. Soc., 82, 5951 (1960); 83, 2786 (1961).

(9) G. G. Hammes and J. I. Steinfeld, ibid., 84, 4639 (1962).

(10) J. I. Steinfeld and G. G. Hammes, J. Phys. Chem., 67, 528 (1963).

(11) G. Schwarzenbach, "Die Komplexometric Titration," F. Enke, Stuttgart, 1956, p. 56.

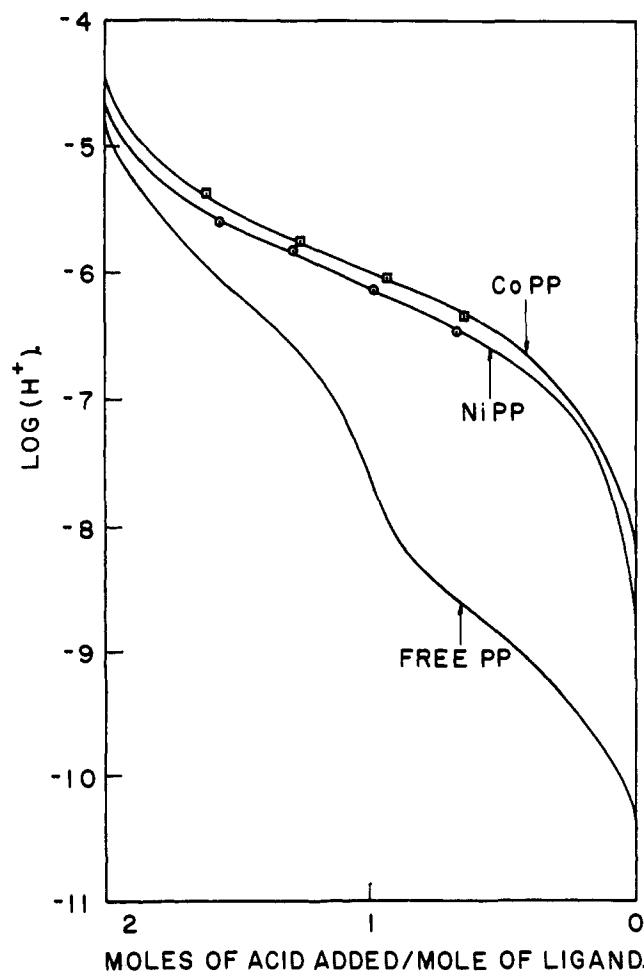(12) J. D. Crowther and A. E. R. Westman, Can. J. Chem., 32, 42 (1954).

Fig. 2.—Experimental titration curves of pyrophosphate and 1:1 metal–ligand solutions. The points are calculated as described in the text. The detailed experimental conditions are also cited there.

agent was 0.0685 M hydrochloric acid. The temperature of the reaction vessel was maintained at 25.0 ± 0.1° by use of a Brownwell constant temperature circulator. Nitrogen gas was passed over the solution to prevent CO_2 absorption and air oxidation.

Metal–ligand titration curves were measured at metal to ligand ratios of 1:1 and 2:1. The 1:1 ratio of metal to ligand solutions were prepared by pipetting together 5 ml. of $10^{-3}\ M$ metal, 5 ml. of $10^{-3}\ M$ ligand, and 5 ml. of 0.1 M tetramethylammonium chloride solution. Both the metal and ligand solutions were 0.1 M in the tetramethylammonium chloride salt. All 2:1 solutions were prepared by pipetting 1 ml. of $10^{-2}\ M$ metal, 5 ml. of 10^{-3} M ligand, and 10 ml. of 0.1 M tetramethylammonium chloride solution. Solutions for the measurement of the acid ionization constants were prepared by adding 5 ml. of $10^{-3}\ M$ ligand to 10 ml. of a 0.1 M salt solution.

The titration curves were corrected for the contribution from water by subtracting a titration curve obtained for water alone under conditions identical with those described above. All of the titration curves used for the calculation of binding constants were run in duplicate and were identical within experimental error. A check was also made on each of the solutions by titrating from the acid end of the curve to the basic end using dilute tetramethylammonium hydroxide as a titrating agent. These curves also all agreed within experimental error with the former titrations.

Kinetic studies were carried out using the temperature jump method. The temperature jump apparatus and the general experimental procedure have been described elsewhere.[9,13,14]

Solutions were prepared by adding the necessary volume of 10^{-3} M or $10^{-2}\ M$ metal and ligand solutions with sufficient 1.0 M tetramethylammonium chloride solution to adjust the ionic strength to 0.1 M. In addition, chlorophenol red ($2 \times 10^{-5}\ M$)

(13) G. Czerlinski and M. Eigen, Z. Elektrochem., 63, 652 (1959).

(14) G. G. Hammes and P. Fasella, J. Am. Chem. Soc., 84, 4644 (1962).

was added to each solution as a pH indicator. The pH of each solution was adjusted by the addition of a dilute solution of hydrochloric acid and measured using a Radiometer pH meter. All water used was freshly boiled to minimize cavitation effects.

The course of the metal complex reaction was studied by following the pH changes coupled with the metal–ligand reaction utilizing a pH indicator. Blank solutions of indicator–metal and indicator–ligand were tested to be certain that the observed relaxation effects were related to the metal complexing reaction. An example of the relaxation effect observed is shown in Fig. 1.

Results and Calculations

Determination of Acid and Metal Equilibrium Quotients.—The acid equilibrium quotients

$$K_{A1} = \frac{(HP_2O_7{}^{3-})}{(H^+)(P_2O_7{}^{4-})}$$

$$K_{A2} = \frac{(H_2P_2O_7{}^{2-})}{(H^+)(HP_2O_7{}^{3-})}, \text{ etc.} \qquad (1)$$

for tripolyphosphate were calculated from the acid titration curves (see Fig. 2 and 3). The hydrogen ion concentration was calculated from the pH measurements assuming an activity coefficient of 0.796 for the hydrogen ion.[15] The results are given in Table I.

TABLE I
EQUILIBRIUM BINDING CONSTANTS[a]

Cation (metal:ligand)	Log K_1 (M^{-1})	Log K_2 (M^{-1})
	Pyrophosphate	
H$^+$	9.00 ± 0.02	6.23 ± 0.02
Ni^{++} (1:1)	7.01 ± .04	3.81 ± .04
Ni^{++} (2:1)	6.94 ± .04	3.85 ± .04
Co^{++} (1:1)	7.36 ± .04	4.07 ± .04
Co^{++} (2:1)	7.11 ± .04	4.03 ± .04
	Tripolyphosphate	
H$^+$	8.74 ± 0.02	6.02 ± 0.02
Ni^{++} (1:1)	7.90 ± .04	5.01 ± .04
Ni^{++} (2:1)	7.90 ± .04	5.01 ± .04
Co^{++} (1:1)	8.13 ± .04	5.16 ± .04
Co^{++} (2:1)	8.20 ± .04	5.18 ± .04

[a] 25°, $\mu = 0.10\ M$.

The metal formation constants were derived using the following mass balance equations and equilibrium quotients.

$$(H^+) = (H^+)_{add} + (H^+)_{init} - (HP_2O_7{}^{3-}) - $$
$$2(H_2P_2O_7{}^{2-}) - (MHP_2O_7{}^-) \qquad (2)$$

$$C_M = (MP_2O_7{}^{2-}) + (MHP_2O_7{}^-) + (M^{2+}) \qquad (3)$$

$$C_0 = (P_2O_7{}^{4-}) + (HP_2O_7{}^{3-}) + (H_2P_2O_7{}^{2-}) + $$
$$(MHP_2O_7{}^-) + (MP_2O_7{}^{2-}) \qquad (4)$$

$$K_{A1} = \frac{(HP_2O_7{}^{3-})}{(H^+)(P_2O_7{}^{4-})} \qquad K_{A2} = \frac{(H_2P_2O_7{}^{2-})}{(H^+)(HP_2O_7{}^{3-})} \qquad (5)$$

$$K_1 = \frac{(MP_2O_7{}^{2-})}{(M^{2+})(P_2O_7{}^{4-})} \qquad K_2 = \frac{(MHP_2O_7{}^-)}{(M^{2+})(HP_2O_7{}^{3-})} \qquad (6)$$

where (H^+) = hydrogen ion concentration in the solution, $(H^+)_{add}$ = concentration of hydrogen ion added, $(H^+)_{init}$ = initial hydrogen ion concentration, C_0 = total ligand concentration, C_M = total metal concentration. These equations are valid if polyligand and polynuclear complexes are not formed and if $H_2P_2O_7$ does

(15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 547.
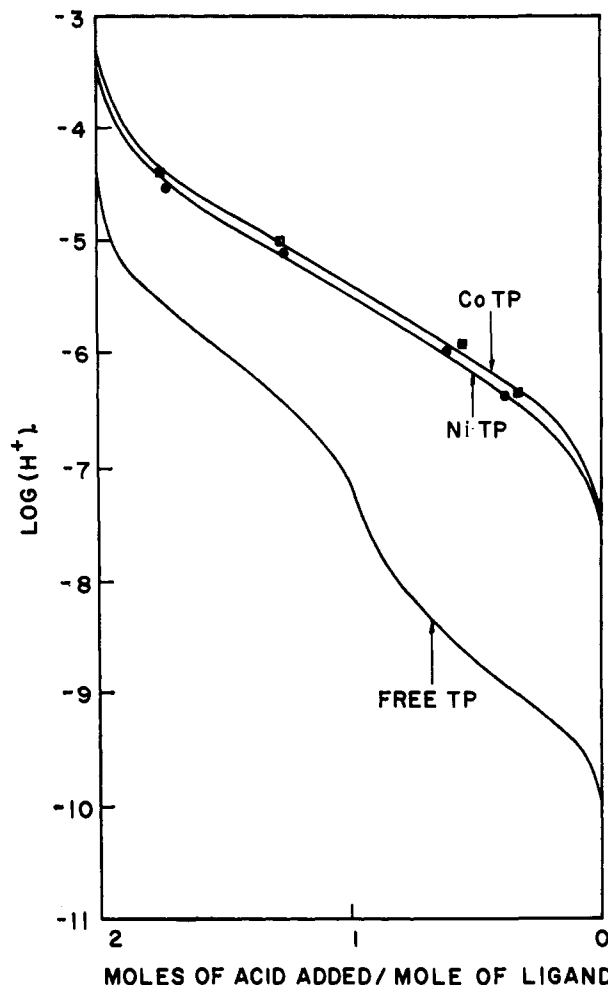

Fig. 3.—Experimental titration curves of tripolyphosphate and 1:1 metal–ligand solutions. The points are calculated as described in the text. The detailed experimental conditions are also cited there.

not complex with the metals. The equations are written in terms of pyrophosphate species, but apply to tripolyphosphate with obvious modifications.

Using eq. 2 and 4 along with the four equilibrium quotients 5 and 6, the following equation can be derived.

$$(H^+)_{add} + (H^+)_{init} = (H^+) + $$
$$\frac{C_0[1 + 2K_{A2}(H^+) + K_2(M^{2+})]}{1 + K_{A2}(H^+) + K_2(M^{2+}) + \dfrac{K_1(M^{2+})}{K_{A1}(H^+)} + \dfrac{1}{K_{A1}(H^+)}} \qquad (7)$$

With the use of eq. 3 and 4 and the four equilibrium quotients, an equation for the free metal concentration can be derived.

$$(M^{2+}) = \frac{-B + \sqrt{B^2 + 4AC}}{2A} \qquad (8)$$

where

$$A = [K_2 K_{A1}(H^+) + K_1]$$

$$B = [C_0 K_1 + C_0 K_2 K_{A1}(H^+) - C_M K_1 - $$
$$C_M K_2 K_{A1} (H^+) + K_{A1} K_{A2}(H^+)^2 + K_{A1}(H^+) + 1]$$

$$C = [C_M K_{A1}(H^+) + C_M K_{A1} K_{A2}(H^+)^2 + C_M]$$

Values for $(H^+)_{add}$, $(H^+)_{init}$, and (H^+) can be determined from the titration curves. Using the values obtained from two different points along the curve, two simultaneous equations are obtained (*cf.* eq. 7). They are of the form

$$a_1 K_1(M^{2+}) + b_1 K_2(M^{2+}) = C_1$$

$$a_2 K_1(M^{2+}) + b_2 K_2(M^{2+}) = C_2 \quad (9)$$

If a first approximation to the value of (M^{2+}) is substituted into these two equations, values for K_1 and K_2 can be computed. Using these values for K_1 and K_2 along with eq. 8, a second approximation for the free metal concentration (M^{2+}) can be obtained. By repeating the process until the free metal concentrations used in eq. 9 and 8 are equal, the true values for K_1 and K_2 can be determined. This procedure was carried out with permutations of four points from each titration curve. Using eq. 7, the measured pH, and average values of the metal binding constants obtained by the above procedure, a theoretical value for $(H^+)_{add}$ can be calculated and compared with the experimental value. The difference between theory and experiment can be minimized by modifying the metal binding constants until a best fit is obtained. In the final analysis, an average deviation of about ±4% between theory and experiment was found. Experimental titration curves and theoretical points for the 1:1 metal–ligand solutions are shown in Fig. 2 and 3. Some Ni(II) hydrolysis was detected in the 2:1 titration curves making the constants obtained from these curves somewhat less reliable. The metal–ligand equilibrium quotients obtained are given in Table I. Included in the tables are estimates of the absolute uncertainty in the constants. The standard deviations were considerably smaller than the error limits quoted.

Determination of the Rate Constants.—Since relaxation methods demand comparable concentrations of all reaction components at equilibrium only the metal–complex step represented by

$$M + HL \rightleftarrows MHL$$
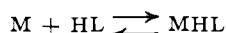
can be studied. Here M is either Co(II) or Ni(II) and LH is either $HP_2O_7^{3-}$ or $HP_3O_{10}^{4-}$. Concentrations can be adjusted so that the following scheme represents the actual situation adequately

$$M + HL \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MHL \underset{H^+}{\rightleftarrows} ML \quad (10)$$

$$\uparrow\downarrow H^+$$

$$H_2L$$
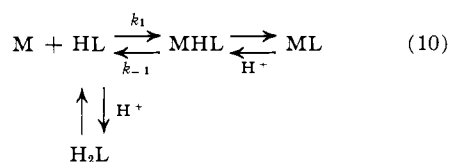
Here a new constant can be defined

$$K_{MA} = (MHL)/(ML)(H^+)$$

(Charges are not balanced for the sake of simplicity.)

Assuming that eq. 10 represents the actual mechanism, the usual rate expression is obtained.

$$-d(M^{2+})/dt = k_1(M^{2+})(HL) - k_{-1}(MHL) \quad (11)$$

Assuming that the protolytic steps occur fast relative to the metal complexing step, a rate equation which is valid in the neighborhood of equilibrium can

be obtained.[4] The following mass balance equations are used

$$(M^{2+}) = \overline{(M^{2+})} + \delta(M^{2+}) \quad (12)$$

$$(HL) = \overline{(HL)} + \delta(LH) \quad (13)$$

$$(MHL) = \overline{(MHL)} + \delta(MHL) \quad (14)$$

$$\delta(M^{2+}) = \delta(HL) + \delta(H_2L) \quad (15)$$

$$\delta(HL) + \delta(H_2L) + \delta(MHL) + \delta(ML) = 0 \quad (16)$$

The result is

$$\frac{d\delta(M^{2+})}{dt} =$$

$$k_1\left[\overline{(HL)} + \frac{\overline{(M^{2+})}}{1 + \dfrac{\delta(H_2L)}{\delta(HL)}} + \frac{k_{-1}/k_1}{1 + \dfrac{\delta(ML)}{\delta(MHL)}}\right]\delta(M^{2+})$$

$$(17)$$

where $(\overline{})$ denotes the equilibrium concentration and δ is the deviation of the concentration from its equilibrium value.

From the equilibrium quotients K_{A1}, K_{A2}, K_{MA}, and

$$K_I = (HIn)/(H^+)(In^-) \quad (= 10^{6.02} \text{ for chlorophenol red})$$

where In designates the pH indicator, the following expressions can be obtained (assuming that the protolytic equilibria are adjusted rapidly compared to the metal complexing step).

$$\delta(H_2L) = \overline{(H^+)}K_{A2}\delta(HL) + \overline{(HL)}K_{A2}\delta(H^+) \quad (18)$$

$$\delta(MLH) = \overline{(H^+)}K_{MA}\delta(ML) + \overline{(ML)}K_{MA}\delta(H^+) \quad (19)$$

$$\delta(HIn) = -\overline{(H^+)}K_I\delta(HIn) + \overline{(In)}K_I\delta(H^+) \quad (20)$$

$$\delta(HIn) + \delta(H^+) + 2\delta(H_2L) + \delta(MHL) + \delta(HL) = 0 \quad (21)$$

With the use of eq. 16, 18, 19, 20, and 21, the following expressions can be derived

$$\frac{\delta(H_2L)}{\delta(HL)} = K_{A2}\overline{(H^+)} \times$$

$$\frac{\left[1 + \dfrac{1}{K_{MA}\overline{(H^+)}} + \dfrac{\overline{(ML)}}{\gamma\overline{(H^+)}} - \dfrac{\overline{(HL)}}{\gamma K_{MA}\overline{(H^+)}^2}\right]}{\left[1 + \dfrac{1}{K_{MA}\overline{(H^+)}} + \dfrac{\overline{(ML)}}{\gamma\overline{(H^+)}} + \dfrac{2K_{A2}\overline{(HL)}}{\gamma K_{MA}\overline{(H^+)}} + \dfrac{K_{A2}\overline{(HL)}}{\gamma}\right]}$$

$$(22)$$

$$\frac{\delta(ML)}{\delta(MHL)} = \frac{1}{K_{MA}\overline{(H^+)}} \times$$

$$\frac{\left[1 + \dfrac{\gamma}{\overline{(HL)}K_{A2}} + \dfrac{\gamma\overline{(H^+)}}{\overline{(HL)}} - \dfrac{K_{MA}\overline{(H^+)}\overline{(ML)}}{\overline{(HL)}}\right]}{\left[1 + \dfrac{\gamma}{\overline{(HL)}K_{A2}} + \dfrac{\gamma\overline{(H^+)}}{\overline{(HL)}} + \dfrac{2\overline{(ML)}}{\overline{(HL)}} + \dfrac{\overline{(ML)}}{K_{A2}\overline{(H^+)}\overline{(HL)}}\right]}$$

$$(23)$$

where

$$\gamma = 1 + \frac{\overline{(In^-)}K_I}{1 + \overline{(H^+)}K_I}$$

Equation 17 can be rewritten as

$$\frac{d\delta(M^{2+})}{dt} = \frac{1}{\tau}\delta(M^{2+}) \qquad (24)$$

with

$$\frac{1}{\tau} = k_1\left[\overline{(HL)} + \frac{\overline{(M^{2+})}}{1 + \frac{\delta(H_2L)}{\delta(HL)}} + \frac{k_{-1}/k_1}{1 + \frac{\delta(ML)}{\delta(MHL)}}\right]$$

(25)

where τ is the relaxation time. Integration of eq. 25 yields

$$(M^{2+}) = (M_0^{2+})e^{-t/\tau} \qquad (26)$$

A plot of the logarithm of the oscilloscope amplitude vs. time permits calculation of the relaxation time τ.

Relaxation times were measured for different metal and ligand concentrations at two different hydrogen ion concentrations. Using the relaxation times and equilibrium quotients, values for k_1 and k_{-1} were calculated. Average values of the metal binding constants obtained for the 1:1 and 2:1 metal–ligand titration curves were used. The results are given in Table II. For each of the solutions, duplicate meas-

TABLE II

RATE CONSTANTS FOR PHOSPHATE COMPLEXES[a]

pH	$\Sigma M \times 10^5$, M	$\Sigma L \times 10^5$, M	τ, msec.	$k_1 \times 10^{-6}$, M^{-1} sec.$^{-1}$
		Ni(II)–pyrophosphate		
5.7	22.6	50.8	1.32	2.27
5.7	71.7	128.6	0.83	2.30
5.7	142.3	231.9	0.68	2.05
6.0	28.9	42.3	1.38	2.05
6.0	96.2	125.0	0.90	1.73

Av. $k_1 = 2.1 \times 10^6\ M^{-1}$ sec.$^{-1}$, $k_{-1} = 3.1 \times 10^2$ sec.$^{-1}$

		Co(II)–pyrophosphate		
5.7	9.91	2.34	0.069	89.5
5.7	3.71	1.03	.089	101
6.0	12.2	1.86	.074	83.5
6.0	4.35	0.762	.092	100.0

Av. $k_1 = 9.3 \times 10^7\ M^{-1}$ sec.$^{-1}$, $k_{-1} = 8.2 \times 10^3$ sec.$^{-1}$

		Ni(II)–tripolyphosphate		
5.7	9.75	12.88	3.37	6.63
5.7	20.60	25.64	2.30	7.00
5.7	34.65	41.04	1.97	6.70
6.0	13.28	14.80	3.42	6.22
6.0	28.50	30.54	2.12	7.35
6.0	48.60	52.09	1.66	7.35

Av. $k_1 = 6.8 \times 10^6\ M^{-1}$ sec.$^{-1}$, $k_{-1} = 68$ sec.$^{-1}$

		Co(II)-tripolyphosphate		
5.7	4.37	5.84	0.102	417
5.7	1.35	2.13	.200	376
6.0	6.25	6.85	.092	433
6.0	1.79	2.14	.179	405
6.0	22.64	23.87	.055	402

Av. $k_1 = 4.1 \times 10^8\ M^{-1}$ sec.$^{-1}$, $k_{-1} = 2.8 \times 10^3$ sec.$^{-1}$
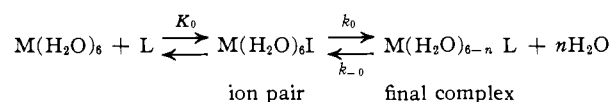
[a] 25°, 0.1 M tetramethylammonium chloride.

urements of the relaxation time were made and the average value for the two measurements was used to calculate the rate constants. The relaxation times are precise to about $\pm 10\%$. The rate constants are estimated to have a maximum error of $\pm 20\%$.

Discussion

The metal binding constants obtained in the 1:1 and 2:1 metal–ligand titrations are identical within experimental error with the exception of K_1 in the case of cobalt pyrophosphate. Since this constant changes in a manner exactly contrary to what would be expected if polynuclear complexes were formed, this change probably is caused by environmental effects due to the variation of the concentration of polyvalent ions. Such phenomena have been noted previously in the case of metal–ATP complexes.[16]

The fact that Co(II) forms stronger complexes with the polyphosphates than Ni(II) is quite unusual.[3] In the case of ATP, Khan and Martell[16] found that Ni(II) formed slightly stronger complexes than Co(II), the actual difference being dependent on the metal to ligand ratio. We have obtained titration curves for Ni– and Co–ATP solutions (ATP = Co = Ni = $10^{-3}\ M$; 0.1 M KNO$_3$) and find that the experimental curves are indistinguishable, indicating identical metal binding constants. In addition, Khan and Martell found a change in the regular Williams–Irving order of complex stability in the case of Co(II) and Mn(II). These data suggest that a somewhat unusual bonding situation may exist in metal–polyphosphate complexes.

A possible explanation arises if we consider the equilibrium quotient in terms of its composite rate constants. For the metal ions, M, under consideration, the mechanism of complex formation with many different ligands has been shown to be[4,9,17]

$$M(H_2O)_6 + L \underset{}{\overset{K_0}{\rightleftharpoons}} M(H_2O)_6I \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} M(H_2O)_{6-n}\ L + nH_2O$$
$$\text{ion pair} \qquad \text{final complex}$$

where n is the number of metal coordination positions filled in the final complex. The rate-controlling step in the transition from ion pair to the final complex is the dissociation of water molecules from the inner hydration shell of the metal ion. Since the concentration of ion pairs is usually quite small compared to that of other species in the mechanism and the process of ion pair formation occurs rapidly compared to the rate of dissociation of water from the inner hydration shell of the metal ion, the rate constant for complex formation k_1 is equal to K_0k_0. Here K_0 is the ion pair association constant and k_0 is the rate constant for water dissociation. The rate constant k_{-1} (= k_{-0}) is then a measure of the ligand–metal bond strength. When n is greater than one, more intermediates actually occur than shown in the simple mechanism above. These intermediates correspond to the successive states of hydration of the metal ion. In this case, k_0 usually reflects the rate of loss of the first water molecule, while k_{-1} is only a rough measure of the bond strength.[9] In cases studied thus far, k_0 for Co(II), Ni(II), and Mn(II) is characteristic of the metal only, i.e., it is

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essentially independent of a variety of ligands.[4,9,10,17,18] However, if the ligand is highly charged, it might loosen the water molecules on the metal ion when an ion pair is formed. The looser the water molecules are bound to begin with, *i.e.*, the weaker the metal–water interaction is, the easier it will be for a ligand to loosen the water molecules. Thus this ligand–water interaction would be most important for Mn, next in importance for Co, and least important for Ni because of the crystal field stabilization energy associated with it. Evidence supporting this hypothesis is found in this study since the ratio of k_0's (and/or k_1's since the ion pair association constants for the two metals can be assumed to be equal) for Co and Ni is about 25 in previously studied cases,[9] 45 in the case of pyrophosphate, and 60 for tripolyphosphate. The net effect then would be a relative increase in the metal binding constant inversely proportional to the strength of the metal–water interactions. Of course, another possible explanation of the data is simply that the mechanism is more complex than depicted here.

A simple interpretation of the rates of complex dissociation cannot be made. However, in the case of glycine, diglycine, and imidazole the ratio of k_{-1}'s for Co and Ni is about 200, while for pyrophosphate and tripolyphosphate this ratio is 25 and 40, respectively. In the case where sulfate ion is the ligand the corresponding ratio of rate constants is 25.[17] This suggests that the difference in metal–ligand bond strength between Co(II) and Ni(II) complexes is much greater for N ligands than for O ligands, but is roughly independent of the particular ligand for either atom. Note that even though the equilibrium binding constants indicate the Co(II) complexes are more stable than the corresponding Ni(II) complexes, the metal complex dissociation rate constants, which are apparently truer measures of this interaction, indicate that kinetically just the opposite is true.

Previously we have obtained k_0, the rate of water dissociation from the inner hydration shell of the metal ion, by calculating the ion pair constant from Debye–Hückel theory and setting $k_0 = k_1/K_0$. Because of the high ionic strength and the large valencies of the ligands, theoretical calculations of K_0 for the polyphosphates are quite unreliable. A more meaningful procedure is to calculate K_0 from k_1 by estimating k_0 from the other data. In view of the preceding discussion, we will assume k_0 is the same for nickel as found in other complexes, namely about 1.2×10^4 sec.$^{-1}$,[9] while k_0 for Co is 45 times greater for the pyrophosphate complex and 60 times greater for the tripolyphosphate complex. With these assumptions, $K_0 = 175$ M^{-1} for the pyrophosphate complexes and 570 M^{-1} for the tripolyphosphate complexes. These values seem reasonable and are probably reliable to at least a factor of two.

For the sake of comparison, K_0 can be calculated from the equations[19]

$$K_0 = \frac{4\pi N a^3}{3000} e^{-U(a)/kT}$$

$$U(a) = \frac{z_1 z_2 e^2}{aD} - \frac{z_1 z_2 e^2}{D(1 + \kappa a)}$$

$$\kappa^2 = \frac{8\pi N e^2}{1000 DkT} \mu$$

where N is Avogadro's number, a is the distance of closest approach of the ion-pair partners, kT is the Boltzmann energy factor, D is the dielectric constant, z_i is the charge on the ith ion, e is the electron charge, and μ is the ionic strength. Assuming $a = 5$ Å., $K_0 = 88$ and 570 M^{-1} for pyrophosphate and tripolyphosphate complexes, respectively. Considering the inapplicability of the Debye–Hückel theory in this case and the decided lack of spherical symmetry of the ligand, the agreement between the two methods of calculating K_0 is surprising. The first method is by far more reliable.

As a point of interest, the estimated values of k_0 for the first removed water molecule of the aquated metal ions, as determined by several different experimental methods (temperature jump, n.m.r., and ultrasonics) with various incoming ligands, are given in Table III. The n.m.r. value for Co(II) with H_2O as the incoming ligand seems out of line with the other data, but all other values are quite constant for a given metal ion. This relative insensitivity of k_0 to the nature of the ligand, even in the case of polyphosphates where some deviation occurs, indicates that an S_N1 type mechanism describes the situation adequately. It should be mentioned that the rate of dissociation of water molecules from *metal complexes* can be considerably greater than that for the completely aquated ion; this "loosening" effect is very dependent on the nature of the ligand.[9]

TABLE III
RATES OF WATER DISSOCIATION FROM AQUATED METALS

| Incoming ligand | k_0, sec.$^{-1}$ (25°) | | Reference |
	Ni(H$_2$O)$_6^{++}$	Co(H$_2$O)$_6^{++}$	
H$_2$O	2.7×10^4	1.13×10^6	18
Imidazole	1.6×10^4	4.4×10^5	9
Glycine	0.9×10^4	2.6×10^5	9
Diglycine	1.2×10^4	2.6×10^5	9
SO$_4^{-2}$	1.5×10^4	2×10^5	4, 17
HP$_2$O$_7^{-3}$	1.2×10^{4a}	5.3×10^{5b}	This work
HP$_3$O$_{10}^{-4}$	1.2×10^{4a}	7.2×10^{5b}	This work

^{a} Assumed values. ^{b} Calculated from assumed k_0 values for Ni(II) as described in text.

Further studies of this nature are intended with other metals and ligands related to biological processes.

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