[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY]

Spectrophotometric Investigation of the Mixed Complex Formed by Copper Ions with Both Ammonia and Pyrophosphate Ions in Aqueous Solutions[1]

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RECEIVED JUNE 4, 1953

A new mixed complex ion, $[Cu(P_2O_7)(NH_3)_2]^{2-}$ has been identified and its equilibrium with $[Cu(P_2O_7)_2]^{6-}$ has been investigated in solutions containing moderate excesses of pyrophosphate ions and ammonia. The logarithm of its complexity constant is 14.22 ± 0.15 and its maximum molar extinction coefficient at 650 mμ is 27.0 mole^{-1} cm.$^{-1}$. In pyrophosphate and ammonia-deficient solutions, the complex dissociates stepwise to form $[Cu(P_2O_7)(NH_3)]^{2-}$ and $[Cu(P_2O_7)]^{2-}$. The neutral complex $[Cu_2(P_2O_7)(NH_3)_4]^0$ was detected in very dilute solutions having the corresponding ratios of its constituents.

When ammonia was added to solutions containing copper(II) and pyrophosphate ions, the extinctions were observed to be different from either those of the ammine or pyrophosphate complexes or their mixtures. The identity and equilibria of the mixed complex, $[Cu(P_2O_7)(NH_3)_2]^{2-}$, which is responsible for these deviations is discussed in the present paper, one of a series on mixed complex formation.

The extinction curves and complexity constants for pyrophosphato complexes have been obtained by Watters and Aaron[2] while Bjerrum[3,4] calculated the stepwise formation constants and extinction curves for the various copper(II) ammine complexes. Bjerrum and Nielsen[5] correlated these results with those obtained for the ethylenediamine complex. Vosburgh and Cooper[6] included copper ammines in their excellent study of the method of continuous variations.

The slope-intercept method of determining complexity constants spectrophotometrically which was used in the present investigation has been applied by Benesi and Hildebrand[7] to the iodine complexes with aromatic hydrocarbons. A treatment in which the higher (1:2) complex and absorption by the reactants were also considered appears in papers by McConnell and Davidson,[8] Landauer and McConnell[9] and Lawrey and McConnell.[10] In the present paper the method is applied to equilibria among three components. The symbols used by the authors[2] and by McConnell[9,10] are retained when possible.

Experimental

The apparatus, techniques, and most of the reagents are described in the previous paper.[2] In addition, a stock solution of approximately 0.25 *M* NH_4OH was prepared in a paraffin lined bottle using carbonate-free distilled water and a freshly opened bottle of concentrated ammonium hydroxide. It was standardized just before being used. The buret and reagent bottle were connected by a siphon tube and both were protected from atmospheric contamination by absorption tubes filled with soda lime. In preparing the solutions, various volumes of this reagent were transferred to volumetric flasks by buret and other reagents were added as in the previous study. To obtain the data used in the equilibrium calculations all solutions were purged with nitrogen to remove CO_2. A stock solution of 10 *M* ammonium nitrate was standardized by the classical Kjeldahl distillation into saturated boric acid followed by a titration with standard acid. The spectrophotometric measurements were made at 10 to 20 mμ intervals with the Beckman DU spectrophotometer at 25°. The exit slit width was kept as close to 0.02 mm. as the sensitivity permitted.

Ratio Experiments.—Solutions having various $[Cu^{2+}]:[P_2O_7^{4-}]:[NH_3]$ ratios were prepared by transferring the appropriate volumes of 0.1 *M* $CuSO_4$, 0.2 *M* $Na_4P_2O_7$, 0.25 *M* NH_3 and 10 *M* NH_4NO_3 to 100-ml. volumetric flasks. After adding some water, the 0.1 *M* $CuSO_4$ was added by pipet with rapid swirling and the solution was diluted to volume. The extinction curves for solutions containing 0.025 *M* copper ion with $[Cu^{++}]:[P_2O_7^{4-}]$ ratios of 1:2 and various ratios of $[Cu^{2+}]:[NH_3]$ are shown in Figs. 1 and 2. Similar families of curves were obtained with ratios of $[Cu^{2+}]:[P_2O_7^{4-}]$ from 1:1 to 1:4. An isosbestic point was obtained at 763 mμ for all solutions having $[Cu^{2+}]:[P_2O_7^{4-}]:[NH_3]$ ratios of 1:2:0 to 1:4:6. Practically identical curves were obtained when an increase in the pyrophosphate ion

TABLE I

EFFECT OF VARYING THE $[Cu^{2+}]:[P_2O_7^{4-}]:[NH_3]$ RATIO

C_{Cu}[a]	$C_{P_2O_7^{4-}}$[b]	C_{NH_3}	*p*H	*E* per cm., 650 mμ	$\log K_m$
0.025	0.025	0.050	9.90	0.820	
.025	.025	.075	10.32	.918	
.025	.025	.100	10.55	.962	
.025	.025	.125	10.66	1.003	
.025	.025	.150	10.78	1.025	
.025	.025	.250	10.99	1.065	
.025	.050	.025	7.39	0.685	14.29
.025	.050	.050	7.78	.820	14.27
.025	.050	.075	7.97	.926	14.38
.025	.050	.100	8.32	1.01	14.28
.025	.075	.025	7.60	0.650	14.40
.025	.075	.050	7.89	.775	14.39
.025	.075	.075	8.15	.858	14.13
.025	.075	.100	8.31	.935	14.13
.025	.075	.125	8.43	1.00	14.27
.025	.100	.025	7.82	0.630	14.22
.025	.100	.050	8.08	.744	14.13
.025	.100	.075	8.30	.840	14.12
.025	.100	.100	8.46	.940	14.14
.025	.100	.125	8.52	.990	14.44
.002	.020	.0654	8.12	.0820	14.41
.002	.020	.098	8.37	.0860	14.47
					14.27 ± 0.15

[a] C_{Cu}, $C_{P_2O_7^{4-}}$ and C_{NH_3} represent the total concentrations of these species in all forms. [b] The first six solutions contained 1 *M* KNO_3. The remainder contained 1 *M* NH_4NO_3.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the convention of the American Chemical Society at Los Angeles, Calif., March 15, 1953. Part of the data were taken from a thesis submitted by Arnold Aaron in partial fulfillment of the requirements for the M.S. degree, June, 1952.

[2] J. I. Watters and A. Aaron, THIS JOURNAL, **75**, 611 (1953).

[3] J. Bjerrum, *Kgl. Danske Videnskab, Selskab Math. fys. Medd.*, **11**, 5 (1931); **11**, 10 (1932); **12**, 15 (1934).

[4] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941.

[5] J. Bjerrum and E. N. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

[6] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

[7] H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

[8] H. McConnell and N. Davidson, *ibid.*, **72**, 3168 (1950).

[9] J. Landauer and H. McConnell, *ibid.*, **74**, 1221 (1952).

[10] D. M. G. Lawrey and H. McConnell, *ibid.*, **74**, 6175 (1952).

concentration was balanced by an appropriate increase in the ammonia concentrations. This effect is shown in Table I.

Continuous Variation Experiments.—In the first series, solution A contained 0.01 *M* monopyrophosphatocuprate-(II) while solution B contained 0.01 *M* NH_3. The extinction measurements were made at 610, 660 and 720 mμ and the maximum value of *Y* was obtained at $x = 0.67$ for all three wave lengths. In the second series solution A contained 0.0025 *M* diamminecopper(II) ion while solution B contained 0.0025 *M* pyrophosphate ion. The maximum value of *Y* was obtained at $x = 0.50$ for the wave lengths of 610, 660 and 720 mμ.

In a third series to investigate the existence of a complex, $[Cu_2(P_2O_7)(NH_3)_4]^0$, solution A had the composition corresponding to 0.0025 *M* $[Cu(P_2O_7)(NH_3)_2]^{2-}$ while the composition of solution B corresponded to 0.0025 *M* $[Cu(NH_3)_2]^{2+}$. A small maximum in *Y*, close to 0.002 molar^{-1} cm.$^{-1}$ was observed at $x = 0.5$, at the wave length 720 mμ.

That chemical equilibrium was obtained instantaneously in all of the experiments was evident from the fact that the density was independent of the order of addition of the three components, copper ion, pyrophosphate ion and ammonia and from the fact that it did not change in several days. This behavior is typical for most of the complexes of copper-(II) investigated in this Laboratory.

Discussion

The extinction in curves 1 and 9, Fig. 1, are due[2,3] essentially to $[Cu(P_2O_7)_2]^{6-}$ and to $[Cu(NH_3)_4]^{2+}$, respectively. If the addition of increasing concentrations of ammonia to solutions of the former had yielded a mixture of these two complex ions, a family of curves having an isosbestic point at their intersection, 713 mμ, should have been obtained. Instead, all solutions having $[P_2O_7^{4-}]:[Cu^{2+}]$ ratios of 2 or larger had a well-defined isosbestic point at 763 mμ indicating an equilibrium between $[Cu(P_2O_7)_2]^{6-}$ and one new specie. The enhanced extinction in the area bounded by curves 1, 8 and 9 between 663 and 763 mμ must be due to species other than these two simple complexes. Since this effect was independent of *p*H, it was not due to the hydroxomonopyrophosphato complex for which Laitinen and Onstott[11] have determined the complexity constant.

The method of continuous variations was applied to the identification of this complex containing three constituents on the basis of the following considerations. Since monopyrophosphatocuprate(II) undergoes practically no dissociation,[2] equal concentrations of this complex and ammonia can be used as the reacting species. The maximum in the first series at $x = 0.67$ indicates the formation of a complex containing two ammonia molecules for each monopyrophosphatocuprate(II) ion. Since a similar argument can be applied to diamminecopper(II), the maximum in the second series at $x = 0.5$ indicates the complex also contains one pyrophosphate ion. A large variety of similar experiments which did not fulfill the requirement that concentrations of species A and B be equal yielded results which, without exception, were also consistent with the formula $[Cu(P_2O_7)(NH_3)_2]^{2-}$.

The formation of this complex, $[Cu(P_2O_7)(NH_3)_2]^{2-}$, is quite reasonable since the stability of monopyrophosphatocuprate(II) is considerably greater than that of the corresponding diamminecopper(II). However, the bonding of a second pyrophosphate ion by monopyrophosphatocuprate(II) is hindered by the electric repulsion of the two anions,[2] a factor which is no longer effective when the ligands placed in the third and fourth coördination positions are neutral ammonia molecules. This argument is supported by the relatively small differences among the successive formation constants of tetraamminecopper(II). Furthermore, on the basis of statistical considerations alone, the entropy and the probability of forming the mixed complex should be greater than that of a mixture of the two complexes.

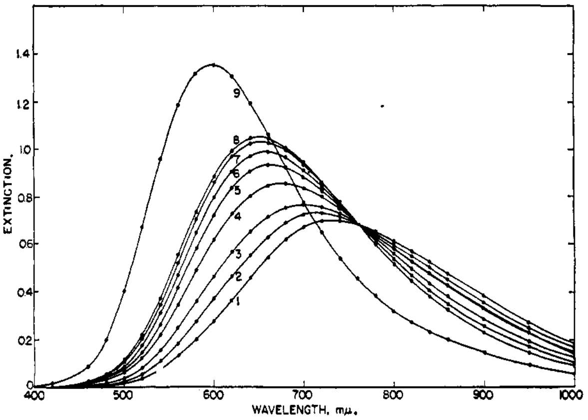

Fig. 1.—The effect of moderate increases in the concentration of ammonia on the extinction curves in solutions containing 0.025 *M* $CuSO_4$, 0.050 *M* $Na_4P_2O_7$ and 1 *M* NH_4NO_3 with the following ratios of $[Cu^{2+}]:[P_2O_7^{4-}]:[NH_3]$: 1, 1:2:0; 2, 1:2:1/2; 3, 1:2:1; 4, 1:2:2; 5, 1:2:3; 6, 1:2:4; 7, 1:2:5; 8, 1:2:6; 9, 1:0:18. Extinction = $\log_{10} I_0/I$. Cell length = 1 cm.

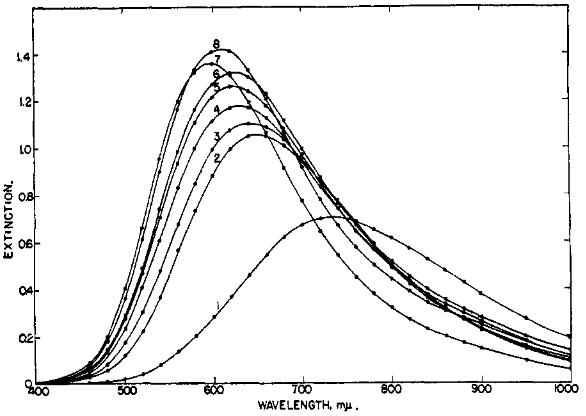

Fig. 2.—The effect of larger concentrations of ammonia on the extinction curves in solutions containing 0.025 *M* $CuSO_4$, 0.050 *M* $Na_4P_2O_7$ and 1 *M* NH_4NO_3 with the following ratios of $[Cu^{2+}]:[P_2O_7^{4-}]:[NH_3]$: 1, 1:2:0; 2, 1:2:6; 3, 1:2:10; 4, 1:2:18; 5, 1:2:30; 6, 1:2:40; 7, 1:0:18; 8, 1:0:40. Extinction = $\log_{10} I_0/I$. Cell length = 1 cm.

The isosbestic point at 763 mμ, where the molar extinction coefficient is 27.2 molar^{-1} cm.$^{-1}$, was common to all extinction curves for solutions of 0.025 *M* dipyrophosphatocuprate(II) and zero to 0.02 *M* ammonia. This evidence supports the deduction that only $[Cu(P_2O_7)_2]^{6-}$ and $[Cu(P_2O_7)(NH_3)_2]^{2-}$ were involved in the equilibrium. The formation of any appreciable concentration of tetraamminecopper(II) ion would, of course, have resulted in a shifting of curve 8, Fig. 1, toward curve

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[11] H. A. Laitinen and E. I. Onstott, THIS JOURNAL, **72**, 4729 (1950).

9. Further evidence for the equilibrium is the increase in the extinction from that of curve 2, Fig. 1, toward a limit close to curve 8 with a linear increase in the ammonia concentration. Finally, the effect on the extinction resulting from increasing the concentration of pyrophosphate ion can be compensated by the proper increase in the ammonia concentration. The following equation is accordingly postulated for the equilibrium.

$$[Cu(P_2O_7)_2]^{6-} + 2NH_3 \rightleftharpoons [Cu(P_2O_7)(NH_3)_2]^{2-} + P_2O_7{}^{4-} \quad (1)$$

This equilibrium was verified and the molar extinction of the mixed complex was also obtained by the previously mentioned slope-intercept method. The treatment is simplified if attention is confined to those solutions having extinction curves which pass through the isosbestic point at 763 mμ. In these solutions, only two complexes are present, namely, $[Cu(P_2O_7)_2]^{6-}$ and some other complex postulated to be $[CuP_2O_7(NH_3)_2]^{2-}$. The following equations may be written for the corresponding complexity constants. Brackets indicate molar concentrations.

$$Cu^{2+} + 2P_2O_7{}^{4-} \rightleftharpoons [Cu(P_2O_7)_2]^{6-} \quad (2)$$

$$K_p = \frac{[[Cu(P_2O_7)_2]^{6-}]}{[Cu^{2+}][P_2O_7{}^{4-}]^2} \quad (3)$$

$$Cu^{2+} + P_2O_7{}^{4-} + 2NH_3 \rightleftharpoons [Cu(P_2O_7)(NH_3)_2]^{2-} \quad (4)$$

$$K_m = \frac{[[Cu(P_2O_7)(NH_3)_2]^{2-}]}{[Cu^{2+}][P_2O_7{}^{4-}][NH_3]^2} \quad (5)$$

It is not necessary to consider intermediate complexes since an excess of ligands is present. The equilibrium constant, K_r, combined with the values for K_p and K_m for the equilibrium in equation 1 may be expressed as

$$K_r = \frac{[[Cu(P_2O_7)(NH_3)_2]^{-2}][P_2O_7{}^{4-}]}{[[Cu(P_2O_7)_2{}^{6-}]][NH_3]^2} = \frac{K_m}{K_p} \quad (6)$$

If C_{Cu} indicates the total concentration of copper(II) ions in all forms the following equation is valid for the solutions being considered

$$C_{Cu} = [[Cu(P_2O_7)_2]^{6-}] + [[CuP_2O_7(NH_3)_2]^{2-}] \quad (7)$$

The extinction of these solutions is

$$\log_{10} I_0/I = E = e_m[[Cu(P_2O_7)(NH_3)_2]^{2-}]l + e_p[[Cu(P_2O_7)_2]^{6-}]l = \bar{e}C_{Cu} \quad (8)$$

where $\bar{e}$ indicates the mean molar extinction coefficient of copper(II) ion in all forms, while e_p and e_m indicate the molar extinction coefficients of the pyrophosphato and mixed complexes, respectively, at 650 mμ. The cell length is indicated by l. Combining equations 1 to 8 for all solutions having curves passing through isosbestic at 763 mμ yields

$$\underset{\text{Plot as } Y}{\frac{[NH_3]^2/[P_2O_7{}^{4-}]}{(\bar{e} - e_p)}} = \underset{\text{Intercept } I}{\frac{1}{(e_m - e_r)K_r}} + \underset{\text{Slope } S}{\frac{1}{(e_m - e_p)}} \times \underset{\text{Plot as } X}{\frac{[NH_3]^2}{[P_2O_7{}^{4-}]}} \quad (9)$$

In the range of concentrations for which the postulated equilibrium is correct, a plot of $([NH_3]^2/[P_2O_7{}^{4-}])/(\bar{e} - e_p)$ along the y axis *versus* $[NH_3]^2/[P_2O_7{}^{4-}]$ along the x axis will yield a straight line having a y intercept equal to $1/(e_m - e_p)K_r$ and a slope equal to $1/(e_m - e_p)$. From these values it is possible to calculate K_r and e_m.

To calculate the free pyrophosphate ion concentration, a correction was first applied for the ligand bound in the complex after calculating f_p and f_m, the fractions of the copper ion in the form of the pyrophosphato and the mixed complex, on the basis of spectrophotometric data at 650 mμ from Fig. 1 and Table I as

$$f_m = (\bar{e} - e_p)/(e_m - e_p) \quad (10)$$

$$f_p = 1 - f_m \quad (11)$$

The value of e_m was first estimated from curve 8, Fig. 1 and then its accurate value was obtained by successive solutions of equations 9 to 11.

Then, from the measured pH, the total pyrophosphate concentration, C_p, and the third and fourth successive dissociation constants for pyrophosphoric acid,[2] having the values $10^{-5.61}$ and $10^{-7.68}$, $[P_2O_7{}^{4-}]$ was calculated by the equation

$$[P_2O_7{}^{4-}] = [C_p - (1 + f_p)C_{Cu}]\frac{K_3K_4}{K_3K_4 + K_3a_{H^+} + a^2{}_{H^+}} \quad (12)$$

The following equation was used to calculate the concentration of free ammonia on the basis of the measured pH and the total concentration using $10^{-9.37}$ as the value for K_n, the constant for the dissociation of a hydrogen ion from $NH_4{}^+$. The value of K_n was obtained experimentally and also by interpolating between Bjerrum's data at 22 and 30°. C_n indicates the total concentration of ammonia in all forms.

$$[NH_3] = (C_n - 2f_m\,C_{Cu})\frac{K_n}{K_n + a_{H^+}} \quad (13)$$

In Fig. 3, the linearity of all points satisfying equation 7 confirms the postulated equilibrium. The slope, 4.08×10^{-2} molar cm. divided by intercept, 2.5×10^{-3} molar cm., yielded $10^{1.21}$ as the value for K_r. The sum of the reciprocal slope and e_p having the value 18.6 molar^{-1} cm.$^{-1}$ yielded the value 43.1 molar^{-1} cm.$^{-1}$ for e_m, in close agreement with the limiting value estimated from curve 8, Fig. 1. Substituting this value of K_r and the corrected value,[2] $10^{13.01}$ for K_p defined by equation 3, into equation 6 yields the value $10^{14.22}$ for K_m. It was also calculated from the individual results on the basis of equations 6, 10 and 11. Without exception, the individual results, having a mean value of $10^{14.27}$, are in good agreement with the value $10^{14.22}$ obtained by slope-intercept method.

This equilibrium evidence alone must be regarded as conclusive proof not only for the existence of the complex but also for the magnitude of

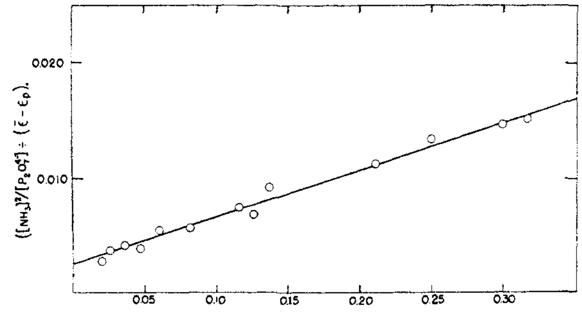

Fig. 3.—Graphic solutions of the equilibrium constant for $[Cu(P_2O_7)(NH_3)_2]^{2-}$ on the basis of equation 9.

its formation constant. The slope intercept results are particularly interesting since they yield the molar coefficient of the mixed complex.

In a similar investigation to be published soon,[12] another mixed pyrophosphoto copper(II) complex was obtained which contained one ethylenediamine molecule instead of two ammonia molecules. In this case the mixed complex formation was even more evident for it was possible to obtain a continuous series of mixtures of the three complexes, namely, the dipyrophosphato, the mixed and the diethylenediamine complex.

In pyrophosphate-deficient solutions such as those containing a $[Cu^{2+}]:[P_2O_7^{4-}]$ ratio of 1:1, a stepwise addition of ammonia to the very stable $[Cu(P_2O_7)]^{2-}$ undoubtedly occurs since no exceptions to this behavior for the addition of ammonia to complexes are known. The following equations for these equilibria and the corresponding formation constants, k_{m1} and k_{m2}, may be written

$$[Cu(P_2O_7)]^{2-} + NH_3 \rightleftarrows [CuP_2O_7(NH_3)]^{2-} \quad (14)$$

$$k_{m1} = \frac{[[Cu(P_2O_7)(NH_3)]^{2-}]}{[CuP_2O_7{}^{2-}][NH_3]} \quad (15)$$

$$[Cu(P_2O_7)(NH_3)]^{2-} + NH_3 \rightleftarrows [CuP_2O_7(NH_3)_2]^{2-} \quad (16)$$

$$k_{m2} = \frac{[[CuP_2O_7(NH_3)_2]^{2-}]}{[[Cu(P_2O_7)(NH_3)]^{2-}][NH_3]} \quad (17)$$

Combining our experimental value of $10^{14.22}$ for K_m, the total complexity constant, with $10^{9.24}$ for k_{p1}, the formation constant for $[Cu(P_2O_7)]^{2-}$, yields a value of $10^{4.98}$ for the product of $k_{m1} \cdot k_{m2}$ which is close to $10^{5.05}$, the product of the corresponding third and fourth formation constants of copper ammine[4] under the same conditions. The latter constants have the values $10^{2.93}$ and $10^{2.12}$, respectively. On this basis k_{m1} and k_{m2} may be expected to have similar values.

When less ammonia than the 1:1:2 ratio for $[Cu^{2+}]:[P_2O_7^{4-}]:[NH_3]$ was present, a precipitate formed and this prevented an investigation of the equilibrium in equation 14 for adding the first ammonia molecule. However, as shown in Table I, the extinctions approached the limit for $[Cu(P_2O_7)(NH_3)_2]^{2-}$ as the ratio was varied from 1:1:2 to 1:1:8. Potassium nitrate was used instead of the more acidic ammonium nitrate to adjust the ionic strength in order to avoid loss of $P_2O_7^{4-}$ ions from the complex by the formation of $HP_2O_7^{3-}$.

There was an isosbestic point at about 770 mμ when 1 *M* KNO_3 was used as the supporting electrolyte. Postulating the specie, $[Cu(P_2O_7)NH_3]^{2-}$, in addition to $[Cu(P_2O_7)(NH_3)_2]^{2-}$ yields the following equations for solutions having curves passing through the 770 mμ isosbestic.

$$C_{Cu} = [[Cu(P_2O_7)(NH_3)]^{2-}] + [[Cu(P_2O_7)(NH_3)_2]^{2-}] \quad (18)$$

$$1/l \log_{10} I_0/I = [[Cu(P_2O_7)(NH_3)]^{2-}]e_{m1} + [[CuP_2O_7(NH_3)_2]^{2-}]e_m \quad (19)$$

where e_{m1} and e_m are the molar extinction coefficients of the respective complexes and l is the cell length. Combining equations 13 to 19 yields the equation

$$\frac{1}{(e_m - \bar{e})} = \frac{1}{(e_m - e_{m1})} + \frac{k_{m2} \times [NH_3]}{(e_m - e_{m1})} \quad (20)$$

The slope intercept method was applied to this equation by plotting $1/(e_m - \bar{e})$ along the *y* axis *versus* $[NH_3]$ on the *x* axis. The amount of ammonia in solution was obtained by subtracting the amount which was found in the complexes from the total added by equations analogous to equations 10 to 13. For this correction, a preliminary value of e_{m1} was first obtained by assuming e_{m1} to be 26.4 molar^{-1} $e_m{}^{-1}$, which is the mean of e_m and e_{p1}. The calculations were repeated using the accurate value, 27.2 molar^{-1} cm.$^{-1}$, obtained later from the slope-intercept data. The extinction measurements were made at 650 mμ where the maximum in the extinction occurs. The value 43.2 molar^{-1} cm.$^{-1}$ for e_m was obtained from the previous slope-intercept calculations. The postulated stepwise equilibrium of equations 14 and 16 was established since the resulting graph was perfectly linear having a slope of 2.89 cm. and a *y* intercept of 0.0575 molar cm. Combining these values yields $10^{1.70}$ for k_{m2}, the second formation constant expressed in equation 17 which is of the order of magnitude predicted by comparing with the ammine.

The reciprocal of the intercept, 17.4 molar^{-1} cm.$^{-1}$, was subtracted from the value 43.2 molar^{-1} cm.$^{-1}$ already calculated for e_m to yield the value 25.8 molar^{-1} cm.$^{-1}$, for e_{m1} at 650 mμ.

It was anticipated that ammonia should replace water in the polynuclear complexes such as $[Cu_2(P_2O_7)(H_2O)_4]$ discussed in the previous paper.[2] The experiment in which 0.0025 *M* $[Cu(P_2O_7)(NH_3)_2]^{2-}$ and 0.0025 *M* $[Cu(NH_3)_2]^{2+}$ were varied continuously had a maximum at $x = 0.5$ corresponding to the complex ion $[Cu_2(P_2O_7)(NH_3)_4]^0$. It is probable that both copper ions are combined with a single pyrophosphate ion by two six-membered rings.[2] Ammonia molecules can then occupy the remaining two coördination positions of each copper ion. This ion was detected only in this pyrophosphate-deficient solution containing the $[Cu^{2+}]:[P_2O_7^{4-}]:[NH_3]$ ratio of 1:1/2:2.

Regarding the extinction curves in more concentrated ammonia, Bjerrum[5] has shown that increasing the concentration of ammonia above about 0.2 *M* without other ligands present causes the extinction maximum of copper(II) to increase and to shift toward longer wave lengths due to the tendency of $[Cu(NH_3)_4]^{2+}$ to accept a fifth ammonia. He observed the same effect when ammonia was added to solutions of the diethylenediamine and the tetrapyridine complexes. That this also occurs in the mixed complex becomes evident on comparing curves 7 and 8, Fig. 2, for solutions containing 0.025 *M* Cu^{2+} with 0.45 and 1.0 *M* NH_3, respectively, but no pyrophosphate with curves 4 and 6 containing the same concentrations of ammonia and also 0.050 *M* pyrophosphate. Curves 7 and 8 illustrate the increase in extinction and its shift toward longer wave lengths as the equilibrium shifts toward the pentammine with increasing ammonia concentrations. Curves 4 to 6 show an even greater shift presumably due to the formation of $[Cu(P_2O_7)(NH_3)_3]^{2-}$. Equilibrium calculations were not made since the effect is small and at least four complex species are involved in the equilibrium.

COLUMBUS, OHIO

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[12] James I. Watters and E. Dan Loughran, THIS JOURNAL, **75**, 4819 (1953).