Stability Order in Metal Chelate Compounds. IV.⁽¹⁾ 2-Pyridylmethanol Complexes*,**

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As a part of our investigation of the stability order of the metal chelates formed by the bivalent metals of the first transition series, 2-pyridylmethanol as a chelating agent has been chosen for this study. One of the interesting aspects of this ligand lies in the behavior of the alcoholic hydroxyl group toward metal ions in the process of complex formation. Much work has been done recently on the coördination ability of an alcoholic hydroxyl group present in alkanol-substituted amines. Martell and his coworkers(2) have postulated that the direct coördination of the alkoxy group in its anionic form to the metal ion occurs in a relatively high pH region in aqueous media.

Hall and his associates(3-6) investigated the

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[*] Contribution No. 79 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

[**] Presented in part at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) Part III: Y. Murakami and M. Tokunaga, This Bulletin, **37**, 1562 (1964).

2) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, *J. Am. Chem. Soc.*, **79**, 3036 (1957).

3) J. L. Hall, F. R. Jones, C. E. Delchamps and C. W. McWilliams, ibid., **79**, 3361 (1957).

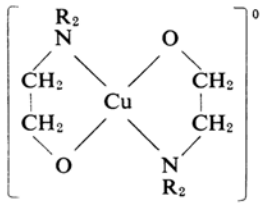
4) J. L. Hall and W. E. Dean, ibid., **80**, 4183 (1958).

5) J. L. Hall and W. E. Dean, ibid., **82**, 3300 (1960).

6) J. L. Hall, W. E. Dean and E. A. Pacofsky, ibid., **82**, 3303 (1960).

reaction between alkanol-substituted ethylenediamines and bivalent metal ions in the presence of a strong base by means of spectrophotometric, conductometric and potentiometric methods. The alcoholic hydroxyl group was found to coördinate to the metal ion on the liberation of its proton, thus forming a new and stable chelate ring which involves an amine-nitrongen and an anionic hydroxyl oxygen as donor atoms. The acid dissociation constants of various metal chelates of such alkanol-substituted ethylenediamines have also been estimated.[6)]

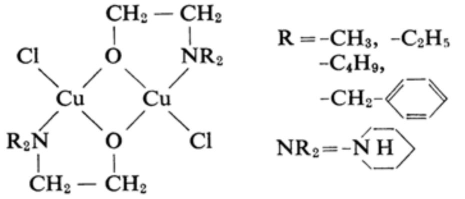
The behavior of *N*-substituted ethanolamine-copper(II) systems upon the addition of a strong base was studied by Ojima and Sone[7)] by the spectrophotometric measurement in the visible region and by the paper electrophoresis method. They detected the formation of electrically-neutral chelate species and assigned structure I to them:



R = -H, -CH$_3$ -C$_2$H$_5$

I

Hall et al.[8,9)] have also studied the interaction between copper(II) and ethanolamines, such as monoethanolamine (MEA), diethanolamine (DMA), and triethanolamine (TEA), in the presence of a strong base. The methods employed in their study were polarography, spectrophotometry and electrical migration. The presence of neutral and anionic species of metal complexes was detected in a relatively high pH region, and the corresponding equilibrium constants were evaluated. The metal complexes reported are as follows: [Cu(MEA)$_2$(OH)$_2$], [Cu(DEA)$_2$(OH)$_2$], [Cu(TEA)(OH)$_2$] and [Cu(TEA)(OH)$_3$]$^-$, where OH represents the coördination of either the hydroxide ion or the alkoxide ion. Further information on the behavior of ethanolamines was added by Hein and Beerstecher.[10)] Upon the reaction of *N*,*N*-disubstituted ethanolamines with cupric chloride in absolute ethanol, a series of crystalline metal chelates was obtained; the dinuclear structure II was proposed for these materials:



II

From the above survey, it is clear that the hydroxyl group of amine-containing ligands is a good donor group and is more likely to undergo coördination in the anionic form under suitable conditions.

Since 2-pyridylmethanol is likely to form a chelate ring similar to those of ethanolamine and other alkanol-substituted amines, there remains a good chance for its hydroxyl group in its anionic form to coördinate with metal ions when experimental conditions are adjusted suitably. So far, two research groups[11,12)] have investigated potentiometrically the interaction of 2-pyridylmethanol with one or two bivalent metal ions to a limited extent in an attempt to evaluate the formation constants of the corresponding metal chelates. In the present work, cadmium(II), magnesium(II) and several bivalent first transition metals (manganese, cobalt, nickel, copper and zinc) were employed, and a detailed potentiometric investigation was carried out in order to determine the complexing behavior of 2-pyridylmethanol with these metal ions. In addition, in order to clarify the behavior of the hydroxyl group of the ligand toward metal ions, several copper chelates were isolated and their properties investigated.

Experimental

2-Pyridylmethanol. — 2-Pyridylmethanol (III) was prepared from 2-picoline through the intermediate compounds, 2-picoline-*N*-oxide and 2-pyridylmethanol acetate in this order, by a method described by Boekelheide and Linn;[13)] b. p. 88—93°C at 4 mmHg (reported[14)] b. p. 111—112°C at 15 mmHg); the picrate, m. p. 160.2—161.5°C (reported[13)] m. p. 160.5—161°C); a total yield of 40%. The product is a hygroscopic and colorless liquid, but it gradually turnes yellow in the air. III was, therefore, transformed into the corresponding nitrate salt (IV) by adding concentrated nitric acid to the acetone solution, the salt being isolated as colorless crystals; after repeated recrystallizations

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[7)] H. Ojima and K. Sone, *Z. anorg. u. allgem. Chem.*, **309**, 110 (1961).

[8)] J. F. Fisher and J. L. Hall, *Anal. Chem.*, **34**, 1094 (1962).

[9)] J. M. Bolling and J. L. Hall, *J. Am. Chem. Soc.*, **75**, 3953 (1953).

[10)] F. Hein and W. Beerstecher, *Z. anorg. u. allgem. Chem.*, **282**, 93 (1955).

[11)] W. D. Luz, S. Fallab and H. Erlenmeyer, *Helv. Chem. Acta*, **38**, 1114 (1951).

[12)] T. J. Lane, C. S. C., A. J. Kandathil and S. M. Rosalie, O. S. F., *Inorg. Chem.*, **3**, 487 (1964).

[13)] V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).

[14)] O. H. Bullitt, Jr., and J. T. Maynard, ibid., **76**, 1370 (1954).

from ethanol, m. p. 116.2—116.7°C; neutralization equivalence, 172.9 (calcd. 172.2).

Found: C, 42.03; H, 4.83; N, 16.16. Calcd. for $C_6H_8O_4N_2$: C, 41.86; H, 4.68; N, 16.27%.

The nitrate IV was dissolved in carbonate-free water in order to prepare a stock solution for potentiometric measurements.

The nitrate was reconverted to its free form for the preparation of the various copper chelates. An aqueous solution of IV was made alkaline with potassium carbonate and extracted with chloroform. After the chloroform solution had been dried over anhydrous potassium carbonate, chloroform was removed from the solution under reduced pressure in order to isolate III. This III was used either in its isolated state or as the chloroform extract mentioned above for the preparation of metal chelates.

Acetato(2-pyridylmethanolato)copper(II). — Five grams of copper acetate (monohydrate) was dissolved in concentrated aqueous ammonia and evaporated to dryness under reduced pressure on a water bath at 50°C or lower. The violet crystals of tetraammineacetatocopper(II) thus obtained was mixed with 2-pyridylmethanol isolated from 5 g. of the corresponding nitrate. A homogeneous deep blue solution was prepared by adding 50 cc. of methanol, and then it was evaporated to dryness under reduced pressure below 50°C. The residue was extracted with chloroform (50 cc.), and the volume of the extract was reduced to 5—10 cc. after the insoluble material had been filtered off. A fine blue precipitate separated from the solution as acetone was added (crude yield, 4.3 g.). This crude product was purified by re-precipitation from the chloroform solution with acetone. The intermediate crop obtained in the process of re-precipitation was used for further study. The product (V) is a fine, blue, crystalline material, stable in the air, which decomposes at 180°C. It is soluble in water, alcohols (yellow solution) and chloroform, and slightly soluble in trichloroethylene, but insoluble in acetone, dioxane, ether, benzene, carbon tetrachloride and ligroin.

Found: C, 41.36; H, 4.02; N, 5.98; Cu, 26.68 (as CuO). Calcd. for $C_8H_9O_3NCu$: C, 41.65; H, 3.93; N, 6.07; Cu, 27.54%.

This chelate was also analyzed for 2-pyridylmethanol content by means of spectrophotometry. The absorption intensity was measured in 0.6 N hydrochloric acid at 262 mμ, where free 2-pyridylmethanol has an absorption maximum of $\varepsilon=6830$; N, 6.10% (converted to nitrogen content). The molecular weight of this chelate was measured by means of a vapor pressure osmometer Model 301A (Mechrolab Inc., Mountain View, Calif., U. S. A.) at 37°C in chloroform; 893 (dibenzoyl as standard); 918 (tris(2,4-pentanedionato)chromium(III) as standard); calcd. for the tetramer, 922.8.

An attempt was made to prepare sodium diacetato-(2-pyridylmethanolato)cuprate(II). A concentrated sodium acetate solution and aqueous V were mixed together and allowed to stand for several days. The deep blue crystals which separated from the solution were identified as the hydrated form of V.

Bis(2-pyridylmethanolato)copper(II). — Into a chloroform solution of 2-pyridylmethanol freshly isolated from the corresponding nitrate (0.8 g.), sufficient anhydrous potassium carbonate and V (0.5 g.) were added. The blue mixture, when shaken vigorously in a well-stoppered flask, turned violet in a few minutes. After approximately 30 min. of shaking, the reaction mixture was filtered on a glass filter, and the filtrate was condensed to 2 cc. under reduced pressure on a steam bath below 40°C. Bluish-violet needle-like crystals precipitated out as acetone was added to the concentrated solution; the yield was quantitative. The anhydrous product is hygroscopic enough to absorb one mole of water per mole of copper in the air. It decomposes at 150°C, but more slowly below 150°C in the air. This product was recrystallized from water as its hydrated form,* which was then reconverted to the anhydrous form at 56°C in vacuo. The hydrate is insoluble in ordinary organic solvents except for alcohols.

Found: C, 50.96; H, 4.23; N, 9.91; Cu, 22.29 (as CuO). Calcd. for $C_{12}H_{12}O_2N_2Cu$ (anhydrous form): C, 51.52; H, 4.32; N, 10.01; Cu, 22.71%.

Chloro(2-pyridylmethanolato)copper(II). — An aqueous solution of V and a concentrated potassium chloride solution were mixed, and the resulted precipitate was washed several times with water; green powder; insoluble in organic solvents.

Found: C, 34.33; H, 3.09; N, 6.73. Calcd. for $C_6H_6ONClCu$: C, 34.79; H, 2.92; N, 6.76%.

Iodo(2-pyridylmethanolato)copper(II). — This material was prepared in a manner similar to that used for the corresponding chloro complex; dark yellowish powder; insoluble in water and organic solvents.

Found: C, 24.32; H, 2.21; N, 4.90. Calcd. for C_6H_6ONICu: C, 24.14; H, 2.03; N, 4.69%.

Nitrito(2-pyridylmethanolato)copper(II). — The procedure for the preparation of this complex was similar to that used for the chloro complex; green powder; slightiy soluble in water and insoluble in organic solvents.

Found: C, 33.22; H, 2.94; N, 13.04. Calcd. for $C_6H_6O_3N_2Cu$: C, 33.11; H, 2.78; N, 12.87%.

Thiocyanato(2-pyridylmethanolato)copper(II).— To an aqueous solution of V, a concentrated solution of potassium thiocyanate was added. The bulky precipitate which formed on mixing was repeatedly washed with water by decantation and then allowed to remain in solution for several days. On standing, the precipitate turned to fine deep greenish blue crystals, which were separated by centrifugation; insoluble in water and organic solvents.

Found: C, 36.44; H, 2.81; N, 12.32. Calcd. for $C_7H_6N_2OSCu$: C, 36.59; H, 2.63; N, 12.19%.

Metal Salts.—The bivalent metal ions employed in the present work were magnesium, manganese, cobalt, nickel, copper, zinc and cadmium in their salt forms of $Mg(NO_3)_2\cdot6H_2O$, $MnSO_4\cdot nH_2O$, $Co(NO_3)_2\cdot6H_2O$, $Ni(NO_3)_2\cdot6H_2O$, $Cu(NO_3)_2\cdot3H_2O$, $Zn(NO_3)_2\cdot6H_2O$ and $Cd(NO_3)_2\cdot4H_2O$ of analytical

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* This hydrate was found to be identical with that isolated from the aqueous mixture of copper salt and 2-pyridinemethanol. The latter procedure was reported by H. Ojima et al. (presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, 1964).

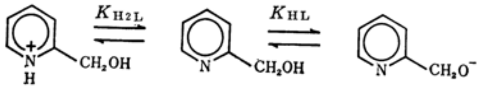
grade obtained from the Wako Pure Chemical Industries, Ltd. These salts were dissolved in carbonate-free water in order to prepare stock solutions which were standardized by the usual methods of chelatometric titration.[15]

Potentiometric Measurements. — The apparatus and procedures for potentiometric measurements have been described in a previous paper.[16] All the titrating solutions in this work were maintained at 25.0±0.1°C and at the ionic strength of 0.10 M (by the addition of potassium nitrate) and were kept under a nitrogen atmosphere throughout the titrations. Titrations of the 2-pyridylmethanol chelate systems of various bivalent metals were performed for 1 : 1, 2 : 1 and 5 : 1 molar ratios of ligand to metal ion.

Spectral Measurements.—The infrared spectra of various copper chelates were measured in Nujol mull with a Koken model DS-301 spectrophotometer equipped with sodium chloride optics. Ultraviolet and visible spectral measurements were performed in aqueous media with a Hitachi EPS-2-type recording spectrophotometer.

Results and Discussion

Acid Dissociation Constant.—The protonated 2-pyridylmethanol may have two processes of proton dissociation; VI → VII, and VII → VIII. The protonated proton undergoes dissociation in a relatively low pH range, as may be seen in Fig. 1. However, the dissociation of an alcoholic proton was hardly detected at all under the present experimental conditions. Thus the cationic species was treated as a monobasic acid, and its dissociation constant was estimated in a usual manner. The estimated pK_{H_2L} of 2-pyridylmethanol at 25°C is 4.89. This is lower than the pK values for pyridine and α-picoline in 0.5 M potassium nitrate which are 5.45 and 6.20 respectively.[17] Although the hydroxymethyl group would change the basicity of a pyridine-nitrogen to a certain limited extent through inductive and resonance interactions,* the lower value of pK_{H_2L} in the present compound seems primarily to be due to strong intramolecular hydrogen bonding between the pyridine-nitrogen and the hydroxyl group.



(H_2L^+) (HL) (L^-)
VI VII VIII

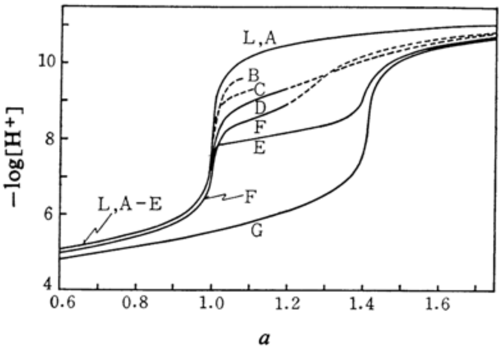
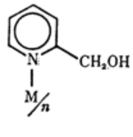
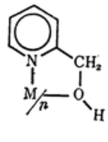


Fig. 1. Potentiometric titration of bivalent metal complexes of 2-pyridylmethanol (nitrate salt) at total ligand concentration of 2.50×10^{-3} M with 5 : 1 molar ratio of ligand to metal ion: A, Mg; B, Mn; C, Cd; D, Co; E, Zn; F, Ni; G, Cu; L, ligand alone; a=moles of base added per mole of ligand; t=25°C; μ=0.10 M (KNO_3).
Dotted curves represent non-equilibrated titrations.

The Interaction of 2-Pyridylmethanol with Bivalent Metal Ions.—A family of titration curves are shown in Fig. 1 for the 2-pyridylmethanol chelate systems of magnesium(II), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) for a 5 : 1 molar ratio of ligand to metal ion. In all the metal chelate systems except the copper system, a distinct inflection region was found at a=1.0. In the lower buffer regions lying below a=1.0, all the potentiometric titrations immediately reached equilibrium and were quite reproducible. Thus, a metal complex either of the ammine type (IX) or of the chelate type, with a hydroxyl group as another donor group (X), is presumably forming in this region.



IX



X

Judging from the extent of the depression of the titration in reference to with that for the free ligand, the stability of the metal chelates with respect to metal ions follows the sequence:

$$\mathrm{Cu(II)} > \mathrm{Ni(II)} > \mathrm{Co(II)} > \mathrm{Zn(II)} > \mathrm{Mn(II)} > \mathrm{Cd(II)}$$

Since titration curves for the free ligand and the magnesium system coincide well with each

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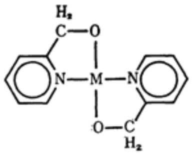
[15] K. Ueno, "Kireto Tekiteiho (Chelatometric Titration)", (in Japanese), Nankodo, Tokyo (1960).

[16] Y. Murakami, *J. Inorg. Nucl. Chem.*, **24**, 679 (1962).

[17] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part I, Organic Ligands," The Chemical Society, London (1957).

* The electron-releasing effect of the hydroxymethyl group described by Lane et al.[12] is not quite convincing to the authors. Further study is needed to clarify this matter.

other over the whole pH range studied, magnesium(II) does not seem to form a chelate with the ligand. Beyond $a=1.0$, where the protonated proton of the conjugate acid is completely neutralized, the downward deviation of the titration curves for manganese and cadmium systems started immediately, followed by the precipitation of the metal hydroxide. For both the cobalt and nickel systems, titration curves demonstrated similar time-dependent behavior. Although no precipitates were observed for these two systems throughout the titrations, equilibrium was not reached in a short period of time beyond $a=1.2$. This sluggish equilibration is considered to be due to the slow formation of the chelates of structure XI and to hydrolytic reactions of the various chelates formed.



XI

In contrast, the titration curve of the zinc chelate system shows another significant inflection around $a=1.4$ in Fig. 1, and it is quite reproducible except in a small region immediately beyond the first inflection ($a>1.0$). Since the hydrolytic tendency of zinc is no greater than those of nickel and cobalt, this second inflection is most probably due to the formation of the 2:1 (ligand to metal) chelate of structure XI.

The titration of a solution containing a 5:1 molar ratio of ligand to copper ion resulted in a large pH depression over the whole pH range studied (especially in $1.0<a<1.4$) and in only one steep inflection at $a=1.4$, as is shown in Fig. 1. Since neither pH drifting nor precipitation was observed throughout the titrations, this inflection may be considered to correspond to the formation of the 2:1 chelate, the structure of which may be represented by XI.

From the behavior of titration curves shown in Fig. 1, the interaction of 2-pyridylmethanolate anions with bivalent metal ions can be seen to increase in the following order:

$$\mathrm{Co(II)},\ \mathrm{Ni(II)} < \mathrm{Zn(II)} \ll \mathrm{Cu(II)}$$

Titration curves for all the bivalent metal chelate systems of the present study were also obtained for the first buffer region (and for the whole pH range with the copper system) at a 2:1 molar ratio of ligand to metal ion; they were found to behave in a manner similar to the 5:1 systems. The copper chelate system was also titrated at a 1:1 molar ratio. pH drifting was observed to start beyond $a=1.5$, followed by the precipitation of copper hydroxide.

TABLE I. STABILITY CONSTANTS OF THE METAL COMPLEXES OF 2-PYRIDYLMETHANOL
$25.0\pm0.1°\mathrm{C}$, $\mu=0.10$ M (KNO_3)

Metal ion	log K_1	log K_2
Mn(II)	~1	—
Co(II)	2.1	—
Ni(II)	2.79	2.60
Cu(II)	3.41	2.81
Zn(II)	1.9	—
Cd(II)	<1	—

$$K_1=\frac{[\mathrm{M(HL)}^{2+}]}{[\mathrm{M}^{2+}][\mathrm{HL}]};\quad K_2=\frac{[\mathrm{M(HL)}_2{}^{2+}]}{[\mathrm{M(HL)}^{2+}][\mathrm{HL}]}$$

HL stands for the neutral species of 2-pyridylmethanol.

TABLE II. STABILITY CONSTANTS OF THE METAL COMPLEXES OF PYRIDINE[17]
25°C, $\mu=0.5$ M (C_5H_5N, HNO_3)

Metal ion	log K_1	log K_2
Co(II)	1.14	0.4
Ni(II)	1.78	1.05
Cu(II)	2.41	1.88
Zn(II)	0.95	0.5
Cd(II)	1.27	0.8

$$K_1=\frac{[\mathrm{ML}^{2+}]}{[\mathrm{M}^{2+}][\mathrm{L}]};\quad K_2=\frac{[\mathrm{ML}_2{}^{2+}]}{[\mathrm{ML}^{2+}][\mathrm{L}]}$$

L stands for the neutral species of pyridine.

Equilibrium Constants.—In the first buffer region ($a<1.0$) of the chelate systems of manganese, cobalt, nickel, zinc, cadmium and in the early part of the titration curve of the copper chelate system, two types of reactions are considered to compete with each other. One is the acid dissociation of the ligand (VI→VII), and the other is the formation of metal complexes of either structure IX or X. Thus the stability constants were calculated by the usual algebraic method, assuming 2:1 and 1:1 complex formations. The evaluated data are summarized in Table I. The stability constants of these metal complexes are greater than the corresponding pyridine complexes (Table II)[17] by one unit in log K, with the exception of the cadmium complexes. Since the hydroxymethyl group does not seem to increase the basicity of a pyridine-nitrogen to a significant extent, the increased stability of the present complexes may be ascribed to chelate ring formation involving the hydroxyl group. Thus, structure X is prefered to the ammine-type complex, IX.

For the equilibrated region of the copper chelate system at a 1:1 molar ratio, the following two successive reactions were considered:

$$\mathrm{Cu^{2+}+HL \rightleftharpoons Cu(HL)^{2+}} \qquad K_1=\frac{[\mathrm{Cu(HL)^{2+}}]}{[\mathrm{Cu^{2+}}][\mathrm{HL}]}$$

$$\mathrm{Cu(HL)^{2+} \rightleftharpoons CuL^{+}+H^{+}} \qquad K^{\mathrm{H}}_{\mathrm{MHL}}=\frac{[\mathrm{CuL^{+}}][\mathrm{H^{+}}]}{[\mathrm{Cu(HL)^{2+}}]}$$

Treating the titration data in the region, a=0.4—1.1, it was estimated that $\mathrm{p}K^{\mathrm{H}}_{\mathrm{MHL}}=5.5$.

Since the copper ion is known to form rather stable chelates of structure X, the two acid dissociation reactions of the 2:1 chelate were considered to occur in addition to the neutralization of the protonated free ligand in the buffer region lying near the inflection of the 5:1 titration (Fig. 1). These two reactions are:

$$\mathrm{Cu(HL)_2{}^{2+} \rightleftharpoons CuL(HL)^{+} + H^{+}}$$

$$K^{\mathrm{H}}_{\mathrm{M(HL)_2}}=\frac{[\mathrm{CuL(HL)^{+}}][\mathrm{H^{+}}]}{[\mathrm{Cu(HL)_2{}^{2+}}]}$$

$$\mathrm{CuL(HL)^{+} \rightleftharpoons CuL_2 + H^{+}}$$

$$K^{\mathrm{H}}_{\mathrm{ML(HL)}}=\frac{[\mathrm{CuL_2}][\mathrm{H^{+}}]}{[\mathrm{CuL(HL)^{+}}]}$$

The estimated dissociation constants are $\mathrm{p}K^{\mathrm{H}}_{\mathrm{M(HL)_2}}=5.55\pm0.01$, and $\mathrm{p}K^{\mathrm{H}}_{\mathrm{ML(HL)}}=6.36\pm0.01$.*

These pK values are slightly lower than those of the alkanol-substituted copper chelates of a 1:1 composition: *N*-hydroxyethylethylenediamine, 7.21,[6] 7.30[18]; *N, N'*-dihydroxyethylethylenediamine, 7.18,[6] 7.15[18]; *N,N'*-dihydroxypropylethylenediamine, 7.34[6]; *N, N, N', N'*-tetrahydroxypropylethylenediamine, 6.77.[6] The resonance interaction of the pyridine ring with the chelate ring would produce an additional stabilization of the chelate ring. This stabilization presumably results in an increased labilization of the hydroxyl proton of the chelate.

Although several attempts have been made to analyze the zinc chelate system in its second buffer region (Fig. 1), they have not provided any reasonable results.

The Coördination Ability of the Alcoholic Hydroxyl Group.—There have been several discussions of the coördinating behavior of an alcoholic hydroxyl group. As has already been mentioned, several alkanol-substituted amines are likely to chelate with metal ions, involving an alcoholate anion as a donor group. It has been shown in the present work that 2-pyridylmethanol also acts as a bidentate ligand in its anionic form under appropriate conditions. The evidence for this will now be described.

(1) The copper chelate system demonstrated a sharp inflection in its titration curves at the 2:1 and 5:1 molar ratios. This corresponds to the liberation of one proton from each ligand molecule which is already coördinated to the metal ion.

(2) The color of the solutions of the copper chelate system was light blue at the start of titration in the presence of 5 mol. of the ligand per mole of copper ion. As a base was added to the titrating system, the blue color deepened, while a violet coloration was noticed beyond $a=1.2$. The solution finally turned violet at the inflection point, $a=1.4$; the addition of more base did not bring about any further color change. These color changes were followed spectrophotometrically; the λ_{max} was nearly 800 mμ at the beginning and reached 575 mμ at the end.* The absorption band at 575 mμ may well correspond to the formation of the 2:1 chelate, which involves the alcoholate anion as a donor group.

(3) The 2-pyridylmethanol-copper(II) chelate of a molar ratio of 2:1 was isolated. This neutral chelate contains only 2-pyridylmethanol and copper(II); other constituents, such as hydroxide ions, do not seem to be involved in this chelate.

(4) Several 1:1 (2-pyridylmethanol: copper) chelates, which also contain inorganic anions, have been prepared. Infrared spectral measurements of these chelates did not provide any supporting evidence for the presence of the OH group.

An abnormally high molecular weight was obtained for acetato(2-pyridylmethanolato)-copper(II) in chloroform. Although this molecular weight corresponds to the tetrameric form of the chelate, a stereochemical structure has not been assigned to this species at the present time.

Summary

The complexing behavior of 2-pyridylmethanol with magnesium(II), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) has been studied in aqueous media at 25.0±0.1°C and an ionic strength of 0.10 M ($\mathrm{KNO_3}$). The stability constants for the 1:1 (ligand to metal) complexes of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) with the

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* There may be some uncertainty involved in these values, although good constants were obtained from the data of the 5:1 titration. The above two reactions are simplified versions of the system; some other reactions such as chelate formation would actually be involved in the system. Some further study would clarify this problem.

18) R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 519 (1959).

* Spectroscopic work, and conductometric and electrophoresis studies of this copper chelate system have also been made by Ojima et al. (presented at the 17th Annual Metting of the Chemical Society of Japan, Tokyo, 1964).

neutral 2-pyridylmethanol and also for the 2:1 complexes of nickel(II) and copper(II) have been evaluated. The resulting stability order with respect to the bivalent metals has been found to follow the sequence:

$$\mathrm{Cd(II)} < \mathrm{Mn(II)} < \mathrm{Zn(II)} < \mathrm{Co(II)} < \mathrm{Ni(II)} < \mathrm{Cu(II)}$$

The higher stability of the present complexes relative to the corresponding pyridine complexes may be ascribed to the formation of a chelate ring which involves the hydroxyl group of the ligand.

After the complex formation between metal ions and the neutral ligand has proceeded to a certain extent, the liberation of a hydroxyl proton from the complex was observed to occur in several metal complex systems. This tendency was greatest for the copper complex, followed by the zinc, nickel and cobalt complexes in this order. Acid dissociation constants for the 1:1 and 2:1 copper complexes have also been evaluated.

Several pieces of evidence have been obtained in support of the coördination ability of the hydroxyl group of the present ligand in its anionic form.

The neutral copper chelate, bis(2-pyridylmethanolato)copper(II), as well as other various copper 2-hyridylmethanolate chelates which involve acetate, chloride, iodide, nitrite and thiocyanate ions as the third component, has been isolated. Acetato(2-pyridylmethanolato)-copper(II) has been found to exist as the tetrameric form in chloroform.

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