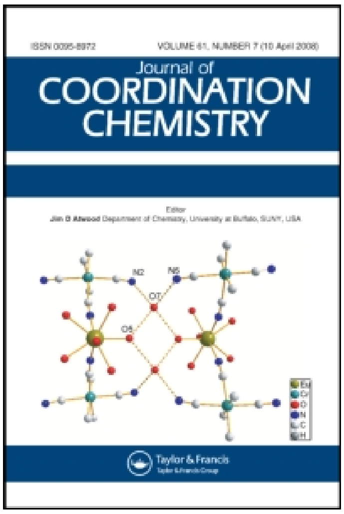
This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COPPER(II) AND COBALT(II) COMPLEXES OF PYRIDINE-2-CARBOXAMIDE AND PYRIDINE-2-CARBOXYLIC ACID

Shih C. Chang[a]; K. H. Joseph[a]; Jin Tsai Wang[a]; Norman C. Li[a]
[a] Duquesne University, Pittsburgh, Pa

To cite this Article Chang, Shih C. , Joseph, K. H. , Wang, Jin Tsai and Li, Norman C.(1972) 'COPPER(II) AND COBALT(II) COMPLEXES OF PYRIDINE-2-CARBOXAMIDE AND PYRIDINE-2-CARBOXYLIC ACID', Journal of Coordination Chemistry, 2: 1, 31 — 38

To link to this Article: DOI: 10.1080/00958977208072943

URL: http://dx.doi.org/10.1080/00958977208072943

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1972, Vol. 2, pp. 31–38

Printed in Woking, England

COPPER(II) AND COBALT(II) COMPLEXES OF PYRIDINE-2-CARBOXAMIDE AND PYRIDINE-2-CARBOXYLIC ACID

SHIH C. CHANG, JOSEPH K. H. MA, JIN TSAI WANG, and NORMAN C. LI†

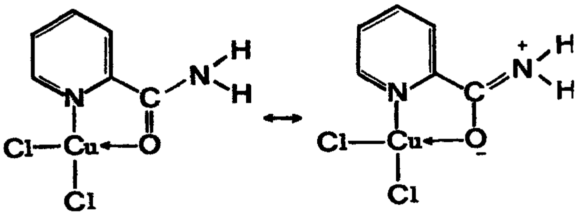
Duquesne University, Pittsburgh, Pa. 15219

(*Received June* 9, 1971; *in final form August* 20, 1971)

The formation constants of the following have been measured with a polarographic method: *binary* copper(II) complexes of pyridine-2-carboxamide (picolinamide) and pyridine-2-carboxylic acid (picolinic acid), a *ternary* copper(II) complex of picolinic acid and imidazole, and a binary copper(I)-imidazole complex. The larger formation constant for picolinic acid over picolinamide is ascribed to the greater chelating ability of a carboxylate group over an amide carbonyl oxygen. The crystal and molecular structure of diaquobis(picolinato)cobalt(II) dihydrate, $[Co(H_2O)_2(pc)_2].2H_2O$, has been determined from three-dimensional MoKα X-ray collected by the multiple-film Weissenberg method. The unit cell dimensions are: $a = 9.89 \pm 0.02$ A, $b = 5.17 \pm 0.01$ A, $c = 17.50 \pm 0.06$ A, $\beta = 123.8 \pm 0.4°$. The space group is $P2_1/c$, and the calculated density is 1.67 g cm^{-3} with two formula weights per cell. The measured density is 1.67 g cm $^{-3}$. The structure was solved by the Patterson method and refined by a least-squares method. With a total of 1659 observed independent reflections, the final R factor is 10.2% without the hydrogens and 9.7% with the hydrogens. The two picolinate groups are planar and related by an inversion center at the cobalt atom. The cobalt atom is coordinated by a distorted octahedron formed by the two nitrogens of the pyridine rings, two oxygens from the carboxyl groups, and two oxygens of coordinated water molecules. The molecules are hydrogen-bonded into layers parallel to the bc plane. Between adjacent layers, only van der Waal's contacts are observed.

INTRODUCTION

Conley and Martin[2] reported that pyridine-2-carboxamide, a derivative of an α-amino acid, forms different complexes with Cu^{2+} in aqueous solution at different *p*H values and found that titration of solutions containing 2 mol of pyridine-2-carboxamide per mol of Cu^{2+} requires the addition of 2 equiv of base per mol of metal ion to reach *p*H 10. The original blue solution at the beginning of the titration changes color to violet during the course of the titration, and the color change is typical of those found in peptides where amide hydrogens undergo cupric[3] ion promoted ionization. They suggested that cupric ion promotes the ionization of two amide hydrogens forming at high *p*H a 2:1 ligand-metal complex with the ligand chelated through nitrogen atoms. From solutions at lower *p*H, Nagano, *et al.*,[4] isolated in the solid state a 1:1 $CuCl_2$ complex of pyridine-2-carboxamide and suggested that the structure of the complex is I.



I, picolinamide-cupric chloride

Since there has been no report of formation constant for pyridine-2-carboxamide (picolinamide) as ligand, we have measured the formation constants of its copper(II) chelate by a polarographic method. In order to compare the relative chelating ability of a carboxylate group with an amide carbonyl oxygen, we have determined the formation constant for pyridine-2-carboxylic acid (picolinic acid) as ligand to copper(II) by the same method. The polarographic reduction of cobalt(II)-picolinate is irreversible, and we have investigated the complex by an X-ray diffraction method.[5, 6]

In addition to the above, as part of our research program on ternary metal complexes,[7, 8] we include in this paper the result of a polarographic study on copper(II)—picolinic acid-imidazole. Tanford[9] has shown that in the combination of copper ion with serum albumin the principal binding sites are the imidazole groups of the histidine residues of the protein molecule, so that imidazole complexes are of prime biological importance.

---

† To whom correspondence should be addressed.

EXPERIMENTAL

Material Picolinamide, picolinic acid, and imidazole were obtained from Eastman Kodak Co. Stock solutions of imidazole were prepared and then standardized with standard nitric acid by *p*H titration. Diaquobis(picolinato)-cobalt(II) dihydrate were prepared by the method of Bailes and Calvin.[10] *Anal.* Calcd. for $CoC_{12}H_{16}N_2O_8$: Co, 15.75; C, 38.40; H, 4.26; N, 7.47. Found: Co, 15.70; C, 38.77; H, 4.34; N, 7.96. The yellow-orange crystals changed to brown and then pink when heated in *vacuo*, and a weight loss of 19.07% was observed, calcd. for $4H_2O$, 19.2%. When allowed to stand open to air the pink crystals slowly absorbed water and changed back to yellow-orange.

X-ray Diffraction The crystals were of the size 0.15 × 0.2 × 0.2 mm. Filtered MoKα radiation was used and no absorption correction was made, $\mu = 3.63\ \text{cm}^{-1}$. Lorentz and polarization corrections were made and the intensity data were reduced to a common scale by a program written by Shiono,[11] using the least-squares method of Hamilton, *et. al.*[12] The unit cell parameters at 22°, as determined from the equatorial Weissenberg photographs taken from two crystals aligned on the *a* and *b* axes, are $a = 9.89 \pm 0.02$ A, $b = 5.17 \pm 0.01$ A, $c = 17.50 \pm 0.06$A, $\beta = 123.8 \pm 0.4°$. The errors are maximum possible errors as estimated from maximum eccentricity of crystal samples, uncertainty in radius of camera, and film shrinkage. The systematic absences observed on Weissenberg photographs are (h0l) with l odd and (0k0) with *k* odd. This determines the space group as $P2_1/c$. For two formula weights in the cell the calculated density is $1.67\ \text{g cm}^{-3}$; the observed density is $1.67\ \text{g cm}^{-3}$ determined by flotation in a mixture of n-butyl bromide and tetrabromoethane. The three-dimensional intensity data were collected from two crystals oriented along the a and b axes. They were recorded on multiple films using the equi-inclination Weissenberg technique and estimated visually against a standard scale. The total number of independent observations was 2264 with 1659 observed reflections.

Polarography Polarographic measurements were made with a Sargent Recording Polarograph, Model XVI. An H cell was used with a saturated calomel electrode and the connecting bridge to the dropping electrode was filled with a 3% agar solution with saturated KCl. The half-wave potentials, after correction for the IR drop, were reproducible to 1 mv, and were determined in the manner previously described.[13] The *p*H was measured with a Corning *p*H meter, Model 10. Solutions were maintained at constant temperature at 25 ± 0.1°.

RESULTS AND DISCUSSION

(A) *Copper(II) Complexes of Picolinamide and Picolinate*

For picolinamide as ligand, polarograms were taken with solutions containing 5×10^{-4} M $Cu(NO_3)_2$, 0.20 M KNO_3 and varying concentrations of picolinamide in water, *p*H 6.4 to 6.6. The data are used to calculate the number of ligand molecules, *p*, coordinated to each copper ion and the over-all formation constant, K_f, of the complex by means of the equations[13]

$$\Delta E_{\frac{1}{2}}/\Delta \log C_{Pa} = -(RT/nF)p(2.303) \qquad (1)$$

and

$$(E_{\frac{1}{2}})_c - (E\tfrac{1}{2})_s = -(RT/nF)\ln K_f - p(RT/nF)\ln C_{Pa} \qquad (2)$$

All potentials are referred to the saturated calomel electrode (S.C.E.) and plots of log $i/(i_d - i)$ vs. E show that in each case the electrode reaction is reversible and $n = 2$. $(E_{\frac{1}{2}})_c$ and $(E_{\frac{1}{2}})_s$ are half-wave potentials in the presence and absence of ligand, respectively, with $(E_{\frac{1}{2}})_s = +0.016$ v. A plot of $E_{\frac{1}{2}}$ vs. C_{Pa} in the picolinamide (*Pa*) concentration range 0.01 to 0.06 M is linear, from which the values of *p* and log K_i are calculated to be 2 and 7.4, respectively. According to Conley and Martin,[2] the pyridinium hydrogen of picolinamide exhibits $pK_a = 1.9$ and ionization of the amide hydrogen is not expected until *p*H is larger than 13, so that under our experimental condition the picolinamide exists as the uncharged neutral species.

For picolinic acid as ligand, polarograms were taken with solutions containing 5×10^{-4} M $Cu(NO_3)_2$, 0.20 M KNO_3 and varying concentrations of picolinic acid (*pc*) in water, *p*H 3.21 to 3.27. Since the hydrogen ion concentration of the solution is much greater than the acid dissociation constant ($pK = 5.37$) of picolinic acid, we have used the equation given by Li and Doody[14]

$$(E_{\frac{1}{2}})_c = p0.0296\,(p\text{K} - p\text{H}) - 0.0296 \log K_f - p(0.0296)\log C_{pc} + (E_{\frac{1}{2}})_s \qquad (3)$$

to calculate p and K_f. A plot of $E_{\frac{1}{2}}$ vs. C_{pc} in the concentration range 0.01 to 0.46 M is linear, from which the values of p and log K_f are calculated to be 2 and 16.1, respectively. Our value of log K_f is in excellent agreement with the value 16.0 obtained by a spectrophotometric method in 0.1 (KNO_3) medium.[15]

The larger formation constant for picolinic acid over picolinamide may be ascribed to the greater chelating ability of a carboxylate group over an amide carbonyl oxygen. No evidence for copper (II) ion promoted amide hydrogen ionization appears at the relatively low *p*H used in our experiments, so that chelation through the amide nitrogen does not occur. It is interesting to note that the larger formation constant for glycine over glycine amide, as well as the larger formation constant for histidine over histidinamide have been ascribed to the greater chelating ability of a carboxyl group over an amide carbonyl oxygen.[16, 17]

(B) *Ternary Copper(II)-Picolinic Acid-Imidazole System*

Polarograms were taken for solutions containing 5×10^{-4} M $Cu(NO_3)_2$, 0.20 M KNO_3, 0.0186 M picolinic acid, and varying concentrations of imidazole in the *p*H range 8.4 to 9.0. Another set of polarograms were taken for solutions containing 5×10^{-4} M $Cu(NO_3)_2$, 0.20 M KNO_3, 0.20 M imidazole, and varying concentrations of picolinic acid, in the *p*H range 7.6 to 8.6. Plots of $E_{\frac{1}{2}}$ vs. − log (imidazole), at constant picolinic acid concentration, and of $E_{\frac{1}{2}}$ vs. log (picolinic acid), at constant imidazole concentration, are given in Figures 1 and 2, respectively. The waves resemble somewhat those obtained for copper-imidazole complexes[13] in that each polarogram consists of two waves of approximately equal height and each wave is due to a one-electron change ($E_{3/4} - E_{1/4} = -0.050$ for each wave, as compared to the theoretical value of −0.056). The same treatment accorded to copper-imidazole complex is therefore adopted here.

If we regard the reaction of the first and second waves to be

$$Cu(pc)_m(\mathrm{Im})_p^{(2-m)+} + e^- = \mathrm{Cu}(pc)_n(\mathrm{Im})_q^{(1-n)+} + (m-n)pc^- + (p-q)\,\mathrm{Im} \quad (4)$$

and

$$Cu(pc)_n(\mathrm{Im})_q^{(1-n)+} + e^- + \mathrm{Hg} = Cu(Hg) + npc^- + q\,\mathrm{Im} \quad (5)$$

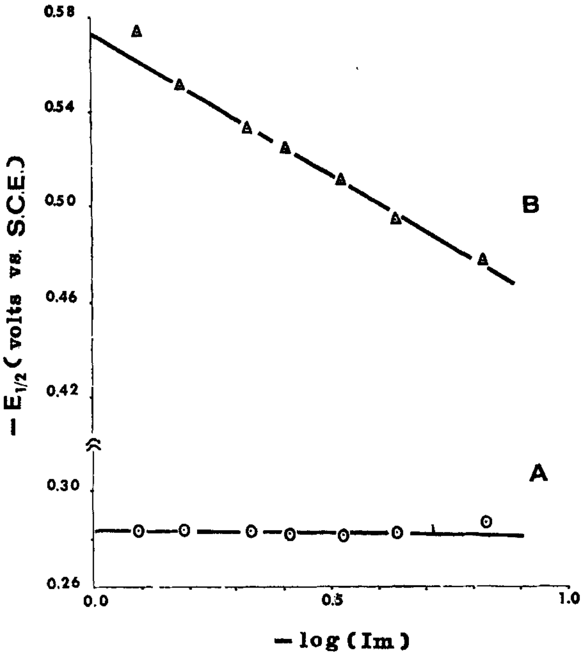


FIGURE 1 Plots of $E_{\frac{1}{2}}$ vs. − log (Im), for solutions containing 5×10^{-4} M $Cu(NO_3)_2$, 0.20 M KNO_3, 0.0186M picolinic acid, and varying concentrations of imidazole. (A) first wave, (B) second wave.

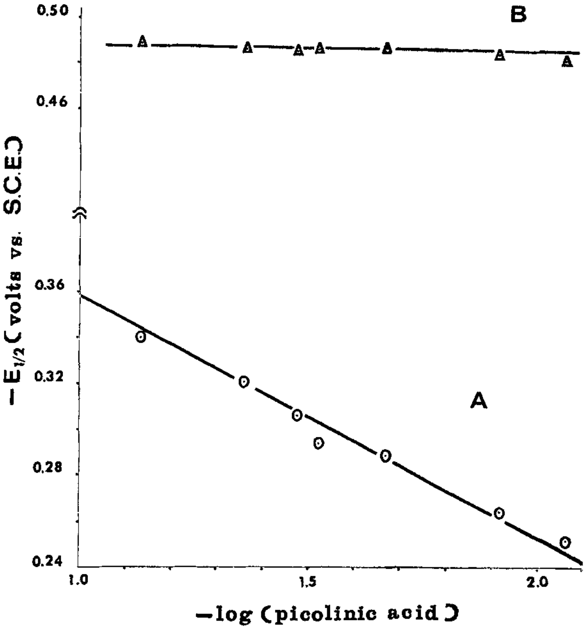


FIGURE 2 Plots of $E_{\frac{1}{2}}$ vs. − log (picolinic acid) for solutions containing 5×10^{-4} M $Cu(NO_3)_2$, 0.20 M KNO_3, 0.20 M imidazole, and varying concentrations of picolinic acid. (A) first wave, (B) second wave.

respectively, then for the first wave we may write

$$
\begin{aligned}
(E_{\frac{1}{2}})_{c,1} - (E_{\frac{1}{2}})_{s,1} = \\
&- 0.0591\,(\log K_{ic} - \log K_{ous}) \\
&- (m\text{–}n)\ 0.0591 \log C_{pc} \\
&- (p\text{–}q)\ 0.0591 \log C_{\mathrm{Im}} \qquad (6)
\end{aligned}
$$

and for the second wave

$$
\begin{aligned}
(E_{\frac{1}{2}})_{c,2} - (E_{\frac{1}{2}})_{s,2} = &- 0.0591 \log K_{ous} \\
&- 0.0591\ \mathrm{n} \log C_{pc} \\
&- 0.0591\ q \log C_{\mathrm{Im}} \qquad (7)
\end{aligned}
$$

Here K_{ic} and K_{ous} are equilibrium constants for the reactions

$$
\begin{aligned}
&Cu^{2+}\ m\,pc^- + p\,\mathrm{Im} \\
&\qquad = Cu(pc)_m(\mathrm{Im})_p^{((2-m)+}\ K_{ic} \qquad (8)
\end{aligned}
$$

$$
\begin{aligned}
&Cu^{+} + n\,pc^- + q\,\mathrm{Im} \\
&\qquad = Cu(pc)_n(\mathrm{Im})q(^{1-n)+}\ K_{ous} \qquad (9)
\end{aligned}
$$

$(E_{\frac{1}{2}})_{s,1}$ is the half-wave potential of the reaction $Cu^{2+} + e^- = Cu^+$, $(E_{\frac{1}{2}})_{s,2}$ is that for the reaction $Cu^+ + e^- + Hg = Cu(Hg)$, and are given the values –0.067 and +0.084, respectively.[13] From Figure 1, $p - q = 0$ and $q = 2$, so that $p = 2$. From Figure 2, $m - n = 2$ and $n = 0$, so that $m = 2$. These results show that the cupric complex is $Cu(\text{picolinate})_2(\text{imidazole})_2$ and that the cuprous complex is $Cu(\text{imidazole})_2{}^+$. Calculation of our polarographic data by means of equations 6 and 7 leads to the following equilibrium constants: $\log K_{ic} = 18.2$, $\log K_{ous} = 11.1$.

Since we have obtained the value $\log K_f = 16.1$ for the reaction

$$Cu^{2+} + 2\,pc^- = Cu(pc)_2 \qquad (10)$$

and since $\log K_f = 18.2$ for the reaction

$$Cu^{2+} + 2\,pc^- + 2\,\mathrm{Im} = Cu(pc)_2(\mathrm{Im})_2, \qquad (11)$$

It is easy to calculate that $\log K_f = 2.1$ for the reaction

$$Cu(pc)_2 + 2\,\mathrm{Im} = Cu(pc)_2(\mathrm{Im})_2 \qquad (12)$$

Walker and Li[18] reported that copper(chelate)$_2$, with chelate = hexafluoroacetylacetonate anion, forms very stable 1:2 adducts with pyridine and 4-methylpyridine. The ternary compounds are: Cu(chelate)$_2$(*py*)$_2$ and Cu(chelate)$_2$(4-*me-py*)$_2$. In this paper we have reported the existence of Cu(chelate)$_2$(Im)$_2$ in solution, where chelate = picolinate. Our treatment of data on the *ternary* copper-picolinic acid-imidazole system leads to a value of $\log K_f = 11.1$ for the cuprous $CuIm_2{}^+$ complex, in fair agreement with the value $\log K_f = 10.8$ found by Li, *et. al.*,[13] from polarographic data on *binary* copper-imidazole system.

(*C*) *Structure Determination of Diaquobis* (*picolinate*) *cobalt*(*II*) *Dihydrate*

The structure was solved by the Patterson method. The general procedure was as follows: with one heavy atom (cobalt) located at the origin, the relative position of the pyridine ring can be seen from the Patterson function. Then a Fourier synthesis was made with structure factors phased by the cobalt and the pyridine ring atoms. From this Fourier map, other atoms are found. Two-dimensional projection on the *ac* plane was first solved. Without the hydrogen atoms, the R factor, defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, was reduced to 9.8% for the (h0l) data alone. Using the three-dimensional data and knowing the *x*- and *z*-coordinates of each atom, the *y*-coordinates of all the atoms are estimated from the three-dimensional Patterson function. Preliminary refinement was done by using the least-squares method[19] and isotropic temperature factors. The Hughes'[20] weighting scheme was used. This brought the overall *R*-factor to about 12%. Using anisotropic temperature factors, the *R*-factor was reduced to 10.2% without the hydrogens. The location of the hydrogens was found from the difference Fourier synthesis.

A table listing $|F_o|$ and F_c is available for inspection in the files of the Editor. The atomic coordinates and anisotropic thermal parameters are listed in Table I. The coordinates of hydrogens refined well. The thermal parameters of the hydrogen atoms cannot be refined and they are assigned arbitrarily to be the same as the largest thermal parameters found in the structure which belong to the oxygen of one of the waters of hydration. With the hydrogens, the *R*-factor is 9.7%.

The molecular structure of $[Co(H_2O)_2(pc)_2]$ is shown in Figure 3, with the bond lengths and angles indicated. Table II shows the intramolecular and intermolecular bonds in the crystal. After the completion of our structure analysis, we noticed a paper by Takenaka, *et. al.*,[6] on the crystal structures of the corresponding nickel and zinc complexes. The cobalt, nickel and zinc complexes are

TABLE I

(a) Fractional atomic coordinates with their standard deviations

Atom	x	y	z
Co	0.0000[a]	0.0000	0.0000
N	0.2544(8)	−0.0738(14)	0.0651(5)
C(1)	0.3484(10)	−0.2445(14)	0.1302(5)
C(2)	0.5186(9)	−0.2404(16)	0.1773(6)
C(3)	0.5916(10)	−0.0548(19)	0.1567(6)
C(4)	0.4956(9)	0.1200(17)	0.0872(5)
C(5)	0.3260(8)	0.1041(14)	0.0444(5)
C(6)	0.2133(9)	0.2931(14)	−0.0310(5)
O(1)	0.2713(8)	0.4372(14)	−0.0618(4)
O(2)	0.0621(6)	0.2814(10)	−0.0583(4)
O(3)	0.0762(7)	0.2410(11)	0.1166(4)
O(4)	0.0754(11)	−0.0147(13)	0.2588(5)
H(1)	0.288(15)	−0.346(23)	0.145(8)
H(2)	0.575(16)	−0.397(24)	0.227(7)
H(3)	0.710(17)	−0.034(21)	0.200(8)
H(4)	0.540(15)	0.274(24)	0.068(8)
H(5)	0.109(18)	0.002(22)	0.310(9)
H(6)	0.054(16)	0.376(28)	0.122(8)
H(7)	0.088(16)	0.085(25)	0.167(8)
H(8)	0.020(15)	0.260(22)	0.245(8)

(b) Atomic anisotropic thermal parameters[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	$\beta_{23}\times 10^2$
Co	0.39(2)	1.23(4)	0.17(1)	0.03(2)	0.14(1)	0.05(1)
N	0.54(5)	1.78(19)	0.23(2)	−0.01(10)	0.17(4)	−0.10(6)
C(1)	0.91(10)	1.88(22)	0.30(3)	0.02(12)	0.23(5)	−0.20(7)
C(2)	0.56(9)	2.66(27)	0.35(3)	−0.14(13)	0.16(4)	−0.13(8)
C(3)	0.63(10)	3.33(32)	0.32(3)	−0.18(15)	0.13(5)	0.04(8)
C(4)	0.68(9)	3.09(31)	0.31(3)	−0.33(14)	0.24(5)	−0.27(8)
C(5)	0.60(7)	2.14(22)	0.25(2)	0.02(12)	0.27(5)	0.10(7)
C(6)	0.88(10)	1.94(22)	0.28(3)	0.22(12)	0.24(4)	0.10(6)
O(1)	1.08(9)	3.36(23)	0.38(3)	0.06(12)	0.36(4)	−0.43(7)
O(2)	0.73(7)	2.27(17)	0.31(2)	−0.06(9)	0.27(3)	−0.18(5)
O(3)	0.98(8)	2.11(18)	0.29(2)	0.21(10)	0.31(3)	−0.01(5)
O(4)	1.99(14)	3.33(27)	0.29(3)	−0.30(14)	0.35(5)	0.06(7)

---

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

[b] The anisotropic temperature factor is expressed in the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

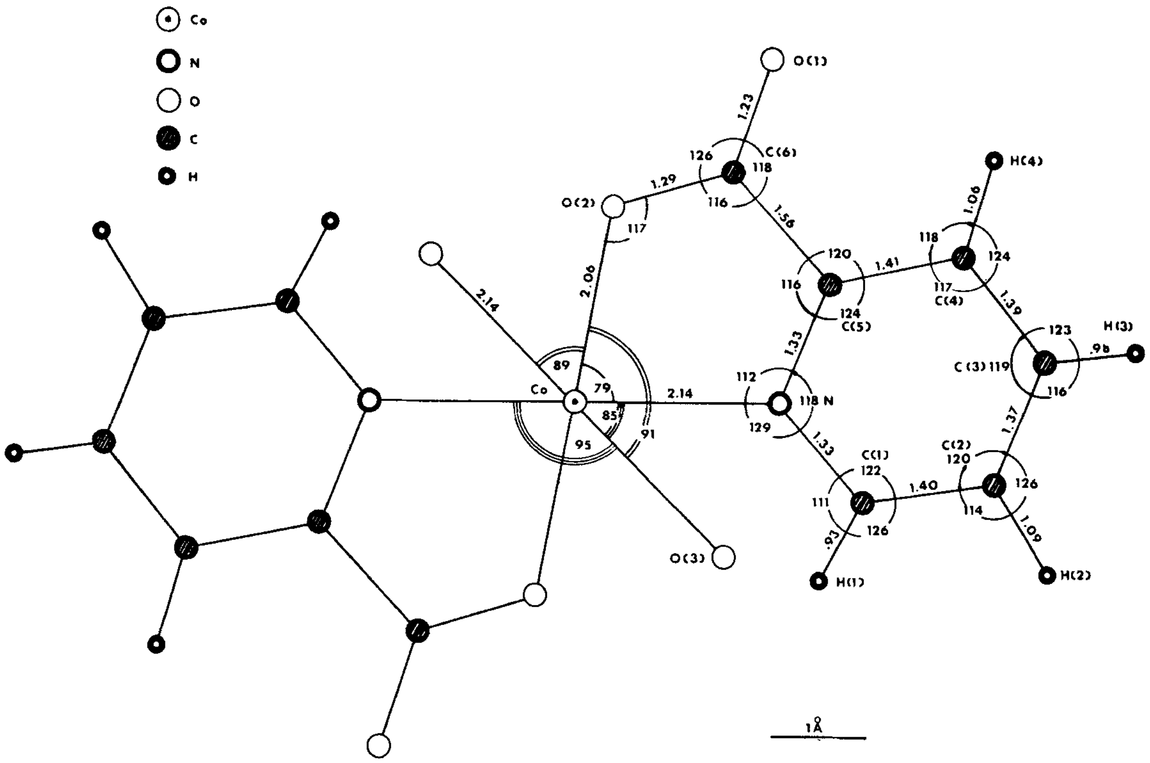


FIGURE 3 Intramolecular bond lengths and angles in dia-quobis(picolinato)cobalt(II) dihydrate.

TABLE II

(a) Bond distances in $[\mathrm{Co(H_2O)_2(pc)_2}]$

Bonds	Distances (A°)	Bonds	Distances (A°)
Co–N	2.14(1)	C(4)–C(5)	1.41(2)
Co–O(2)	2.06(1)	C(5)–C(6)	1.52(2)
Co–O(3)	2.14(1)	C(6)–O(1)	1.23(2)
N–C(1)	1.33(2)	C(6)–O(2)	1.29(2)
N–C(5)	1.33(2)	C(1)–H(1)	0.93(5)
C(1)–C(2)	1.40(2)	C(2)–H(2)	1.09(5)
C(2)–C(3)	1.37(2)	C(3)–H(3)	0.98(5)
C(3)–C(4)	1.39(2)	C(4)–H(4)	1.06(5)

(b) Bond angles in $[\mathrm{Co(H_2O)_2(pc)_2}]$

O(2)–Co–N	78.7(5)	N–C(1)–H(1)	111(3)
O(2)–Co–O(3)	91.0(5)	C(2)–C(1)–H(1)	126(3)
N–Co–O(3)	84.9(5)	C(1)–C(2)–H(2)	114(3)
C(1)–N–Co	129.0(7)	C(3)–C(2)–H(2)	126(3)
C(5)–N–Co	112.2(7)	C(2)–C(3)–H(3)	116(3)
C(1)–N–C(5)	118.0(9)	C(4)–C(3)–H(3)	123(3)
N–C(1)–C(2)	122.2(9)	C(3)–C(4)–H(4)	124(3)
C(1)–C(2)–C(3)	119.6(9)	C(5)–C(4)–H(4)	118(3)
C(2)–C(3)–C(4)	119.1(9)	C(5)–C(6)–O(1)	118.3(9)
C(3)–C(4)–C(5)	117.4(9)	C(5)–C(6)–O(2)	115.5(9)
C(4)–C(5)–N	123.7(9)	O(1)–C(6)–O(2)	126.2(9)
N–C(5)–C(6)	116.0(9)	C(6)–O(2)–Co	116.9(7)
C(4)–C(5)–C(6)	120.4(9)		

(c) Hydrogen-bonding distances in $[\mathrm{Co(H_2O)_2(pc)_2}]\cdot 2\mathrm{H_2O}$

Bonds	Distances (A)
O(3)H(6)····O(2′)[a]	2.73(2)
O(3)H(7)····O(4)	2.78(2)
O(4)H(5)····O(1′)	2.69(2)
O(4)H(8′)····O(4″)	2.94(2)

(d) Hydrogen-bonding angles in $[\mathrm{Co(H_2O)_2(pc)_2}]\cdot 2\mathrm{H_2O}$

Co——O(3)H(6)····O(2′)	109.5(9)
Co——O(3)H(7)····O(4)	112.8(9)
O(2′)····H(6)O(3)H(7)····O(4)	120.9(9)
O(3)H(7)····O(4)H(8)····O(4′)	76.6(9)
O(3)H(7)····O(4)H(8′)····O(4″)	127.5(9)
O(3)H(7)····O(4)H(5)····O(1′)	128.3(9)
O(4′)H(8)····O(4)H(8′)····O(4″)	123.5(9)
O(4′)H(8)····O(4)H(5)····O(1′)	87.3(9)
O(4″)····H(8′)O(4)H(5)····O(1′)	102.5(9)
C(6)——O(1)····H(5′)O(4‴)	114.0(9)
C(6)——O(2)····H(6′)O(3′)	109.4(9)
Co——O(2)····H(6)O(3)	126.8(9)

---

[a] The primed atoms are symmetry related to their respective unprimed atoms.

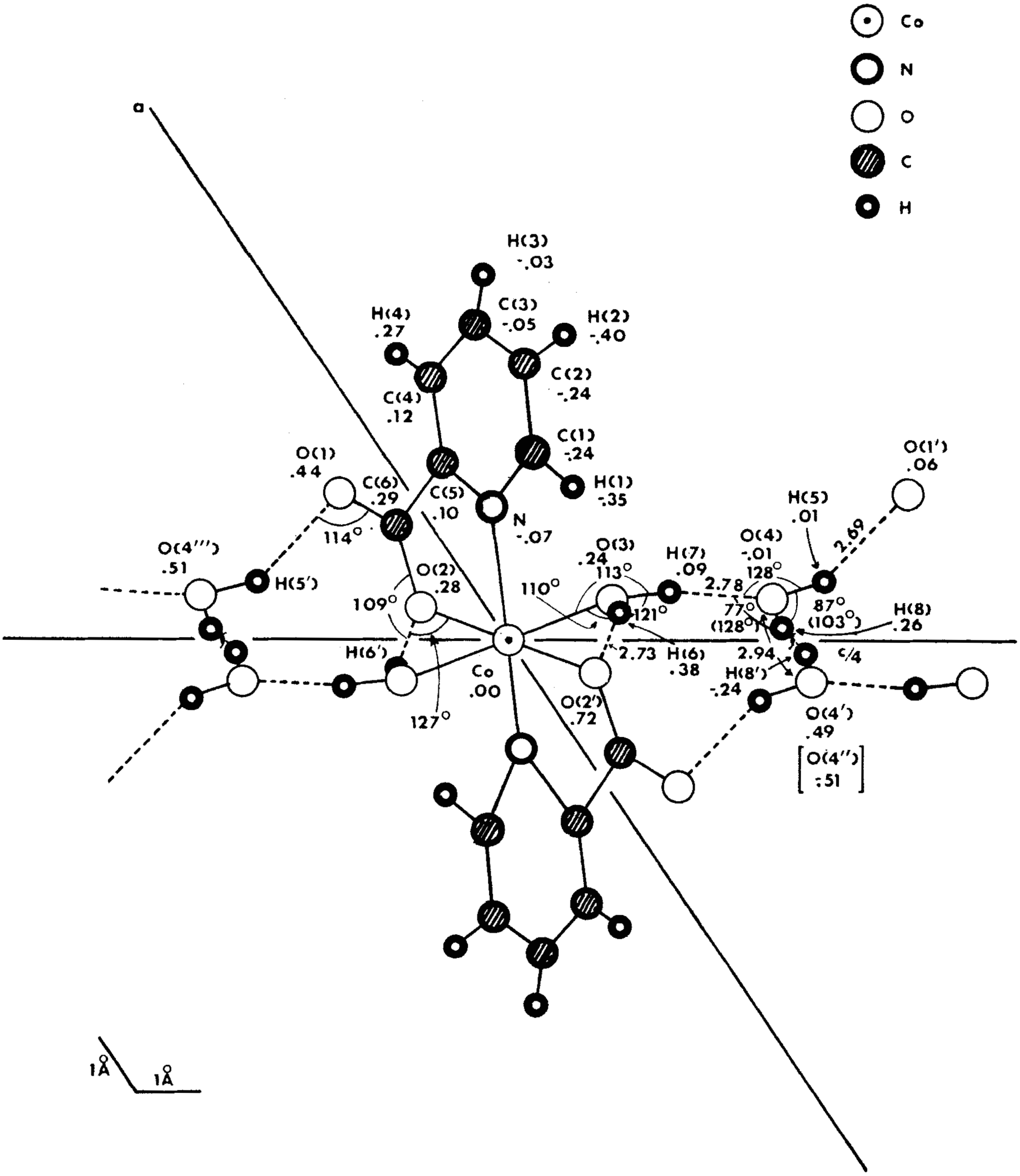


FIGURE 4 The hydrogen bonding scheme and the packing of the molecules in the crystal of $[Co(H_2O)_2(pc)_2]\cdot 2H_2O$

iso-structural. The cobalt atom is situated at the inversion centre of the molecule. It is octahedrally coordinated by the two nitrogens of the pyridine rings with a distance of 2.14 A, two oxygens from the carboxyl groups with a distance of 2.06 A, and two oxygens of the two water molecules with a distance of 2.14 A. The octahedron is distorted more in the plane of the molecule. The two water molecules are almost perpendicular to the plane. The pyridine rings and the carboxyl groups are essentially planar. The maximum deviation from the plane is about 0.12 A for the major atoms. For the hydrogens the maximum deviation is only about 0.2 A. The bond lengths and angles as shown in Figure 3 are quite reasonable. Although the hydrogen temperature parameters failed to refine by the least-squares method, the hydrogen positions, which are not indicated in Takenaka's paper, are located in this paper. As shown in Figure 3, the hydrogen positions are quite good.

The molecules form layers parallel to the bc plane by two hydrogen-bond chains. As shown in Fig. 4, a stronger hydrogen-bond chain

$$0(2')^{2.73\,\text{Å}}\,\mathrm{HO(3)H}^{2.78\,\text{Å}}\,\mathrm{O(4)H}^{2.69\,\text{Å}}\,\mathrm{O(1')}$$

connects three molecules. With the aid of a weaker hydrogen-bond chain, $\mathrm{O(4'')}^{2.94\,\text{Å}}\,\mathrm{HO(4)}^{2.94\,\text{Å}}$ HO(4′), the layer is formed. It is also observed that, between the layers, only van der Waal's contacts exist.

Comparing with the crystal structure of bis(pyridine-2-carboxamido)nickel(II) dihydrate[21], $\mathrm{Ni(C_6H_5N_2O)_2 \cdot 2H_2O}$, there is a major difference, namely the metal atom in the latter complex is not bonded to the water molecules, whereas in the complex of diaquobis(picolinato)cobalt(II) dihydrate, the cobalt atom is bonded to two water molecules.

ACKNOWLEDGEMENTS

The authors acknowledge valuable discussion with Dr. W. R. Walker on the preparation of the compound, diaquobis(picolinato)cobalt(II) dihydrate.

REFERENCES

1. Research sponsored by a National Science Foundation Grant No. GB-25117 and a NSF Institutional grant.
2. H. L. Conley, Jr. and R. B. Martin, *J. Phys. Chem.* **69,** 2914 (1965).
3. W. L. Koltun, M. Fried, and F. R. N. Gurd, *J. Amer. Chem. Soc.* **82,** 233 (1960).
4. K. Nagano, H. Kinoshita, and A. Hirakawa, *Chem. Pharm. Bull.* (*Tokyo*) **12,** 1198 (1964).
5. At the time this research was undertaken, the crystal and molecular structure of metal complexes of picolinate had not yet received previous investigation. After completion of the structural analysis, we noticed a paper by Takenaka, *et al.*[6] on the crystal structures of the zinc and nickel complexes of picolinate.
6. A. Takenaka, H. Utsumi, N. Ishihara, A. Furusaki, and I. Nitta, *Nippon Kagaku Zasshi* **91,** 921 (1970).
7. S. M. Wang and N. C. Li, *J. Amer. Chem. Soc.* **90,** 5069 (1968).
8. L. S. Kan and N. C. Li, *ibid.* **92,** 281 (1970).
9. C. Tanford, *ibid.* **74,** 211 (1952).
10. R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.* **69,** 1886 (1947).
11. R. Shiono, unpublished work, 1965. This and other programs were taken from the Crystallographic Department of the University of Pittsburgh and modified for the CDC 3200 computer at Duquesne.
12. W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.* **18,** 129 (1965).
13. N. C. Li, J. M. White, and E. Doody, *J. Amer. Chem. Soc.* **76,** 6219 (1954).
14. N. C. Li and E. Doody, *J. Amer. Chem. Soc.* **74,** 4184 (1952).
15. K. Suzuki, M. Yasuda, and K. Yamasaki, *J. Phys. Chem.* **61,** 229 (1957).
16. N. C. Li, E. Doody, and J. M. White, *J. Amer. Chem. Soc.* **79,** 5859 (1957).
17. M. S. Michailidis and R. B. Martin, *ibid.*, **91,** 4683 (1969).
18. W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.* **27,** 2255 (1965).
19. W. R. Busing, K. O. Martin, and H. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program", ORNL-TM-305, Oak Ridge National Laboratory, 1962.
20. E. W. Hughes, *J. Amer. Chem. Soc.* **63,** 1737 (1941).
21. S. C. Chang, D. Y. Park, N. C. Li, *Inorg. Chem.* **7,** 2144 (1968).