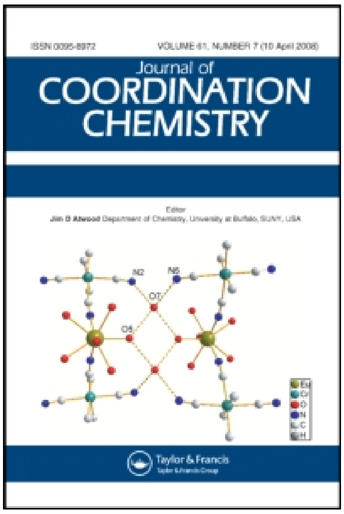

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CADMIUM(II) AND NICKEL(II) COMPLEXES OF PICOLINAMIDE, PICOLINATE AND IMIDAZOLE[1]

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CADMIUM(II) AND NICKEL(II) COMPLEXES OF PICOLINAMIDE, PICOLINATE AND IMIDAZOLE[1]

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The formation constants of the following have been measured with a polarographic method: *binary* cadmium (II) complexes of pyridine-2-carboxamide (picolinamide) and pyridine-2-carboxylate (picolinate), *binary* nickel (II) complexes of picolinamide, and *ternary* cadmium-imidazole-B complexes, where B = picolinamide, picolinate, and 5,5′-diethyl barbiturate. The electrode reaction for the nickel complex is irreversible and the system was studied by using Cd^{2+} as an indicator ion. The highest order nickel (II) picolinamide complex is $Ni(pa)_6^{2+}$.

In the combination of a metal ion with a protein, for instance serum albumin, the metal ion coordinates to the imidazole group of a histidine residue and generally to another group in the protein molecule, and also may coordinate to an added drug, for instance a barbiturate. For this reason, the study of metal-imidazole-ligand complexes is important. It would be desirable to know whether a metal already complexed to the imidazole group of a histidine residue would have the same affinity toward another ligand as the same metal in the absence of imidazole. In this paper we have shown that, at least for the ligands chosen, the presence of imidazole does not affect the metal ion affinity toward the ligand. Moreover, the presence of the ligand does not affect the metal ion affinity to imidazole.

INTRODUCTION

Polarographic studies of copper(II) complexes of pyridine-2-carboxamide (picolinamide) and pyridine-2-carboxylate (picolinate) have been reported by the authors previously.[2] As continuation of our research program, we report in this paper the polarographic results on binary cadmium(II) and nickel(II) complexes of picolinamide and picolinate. Picolinamide was chosen to serve as a derivative of an α-amino acid. In order to compare the relative chelating ability of a carboxylate group with an amide carbonyl group, we have determined the formation constants for picolinate and picolinamide as ligands to cadmium(II) by the same polarographic method. The polarographic reduction of nickel(II) picolinamide is irreversible, and we have investigated the interaction between nickel(II) and picolinamide by an indirect method.

In addition to the above, as part of a research program on ternary metal complexes,[3,4] we include in this paper the result of polarographic studies on ternary cadmium(II) complexes of ligand B and imidazole, where B = picolinamide, picolinate, and 5,5′-diethylbarbiturate. Tanford[5] has shown that in the combination of metal on 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. 5,5′-diethylbarbiturate was chosen as a ligand because the ternary complexes containing metal, imidazole and barbiturate may be illustrative of possible barbiturate binding to metalloenzymes.

The polarographic reduction of the ternary nickel(II) complex of picolinamide and imidazole is irreversible, and we carried out a preliminary study of the complex in the crystalline state.

EXPERIMENTAL

Picolinamide, picolinic acid, and imidazole were obtained from Eastman Kodak Company. Stock solutions of imidazole were prepared and then standardized with standard nitric acid by *p*H titration. The sodium salt of 5,5′-diethylbarbituric

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acid was obtained from Fisher Scientific Company. The bis-(picolinamide)-bisimidazole complex of nickel(II) chloride tetrahydrate was prepared by mixing equal amounts of 0.3 m $NiCl_2$, 0.6 M picolinamide, and 0.6 M imidazole solutions, heating over a steam bath, and left at room temperature to cool and crystallize. Recrystallization was carried out from a water-ethanol mixture.

Polarography Polargraphic 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 mercury electrode was filled with a 3% agar solution with saturated KCl. The half-wave potentials, after correction for the IR drops, were reproducible to 1 mv, and were determined in the manner previously described.[6] 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) *Cadmium(II) Complexes of Picolinamide and Picolinate*

Polarograms were taken with solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.20 M KNO_3, and varying concentrations of picolinamide in water, *p*H 5.8 to 6.6. The data are used to calculate the number of ligand molecules, *p*, coordinated to each metal ion and the over-all formation constant, K_f of the complex by means of the equations.[6]

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

and

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = -(RT/nF)\ln K_f - p(RT/nF)\ln C_{pa} \quad (2)$$

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 $(E_{\frac{1}{2}})_c$ are half-wave potentials in the presence and absence of ligand, respectively. A plot of $\Delta E_{\frac{1}{2}}$ vs. $-\log C_{pa}$, shown in Figure 1A exhibits two straight lines: in the picolinamide concentration range 0.02 to 0.1 M, the values of *p* and log K_f are calculated to be 1 and 1.8, respectively, while in the range 0.1 to 0.5 M, the values are 2 and 2.8, respectively. According to Conley and Martin,[7] 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.

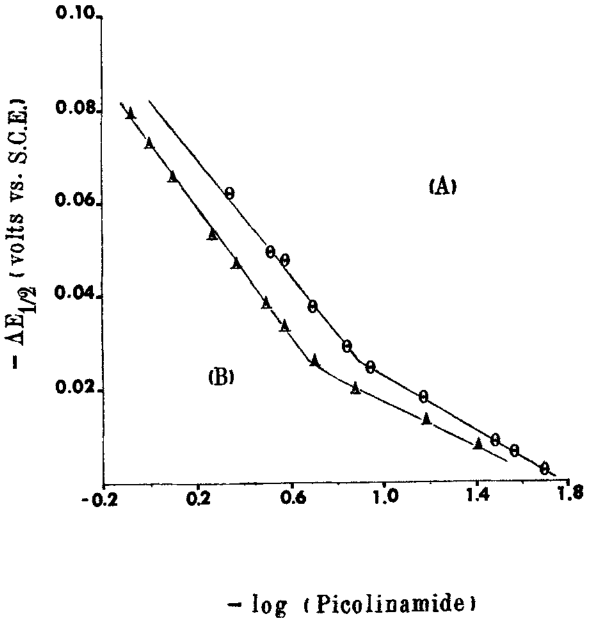

FIGURE 1 Plots of $-\Delta E_{\frac{1}{2}}$ vs. —log (picolinamide)
(A) In the absence of (O) and (B) in the presence of (Δ)0.05 M $Ni(NO_3)_2$

Figure 1A shows that when the picolinamide concentration is below 0.1 M, the complex is $Cd(pa)^{2+}$, whereas when the concentration is above 0.1 M, the complex is $Cd(pa)_2^{2+}$. From the values of log $K_{f,1}$ (=1.8) and log $K_{f,2}$ (=2.8), the value of log K_2 for the reaction

$$Cd(pa)^{2+} + pa = Cd(pa)_2^{2-} \quad (3)$$

is calculated to be 1.0.

For picolinate as ligand, polarograms were taken with solutions containing 5×10^{-4} M $Cd(NO_3)_2$, varying concentrations of picolinic acid each half-neutralized with KOH, *p*H 5.4, and sufficient KNO_3 to maintain the total ionic strength 0.32. The data are shown in Table I. A plot of $\Delta E_{\frac{1}{2}}$ vs. log $C_{pc}-$ in the picolinate concentration range 0.005 to 0.2 M is linear. The slope is 0.09, so that $p = 3$. The calculated log $K_{f,3}$ value for the $Cd(pc)_3^-$ complex is 10.3, which is in good agreement with the sum (=10.1) of log K_1[8] (25°), log K_2[8] (25°), and log K_3 (20°)[9] obtained by other methods.

Comparison of the results obtained with picolinamide and picolinate as ligands to cadmium(II)

TABLE I

Polarographic results for solutions containing 5×10^{-4} M $Cd(NO_3)_2$, $\mu = 0.32$, pH 5.36–5.40

(picolinate), *M*	$-\Delta E_{\frac{1}{2}}$
0.0054	0.1018
0.0100	0.1257
0.0203	0.1520
0.0308	0.1684
0.0526	0.1886
0.0995	0.2146
0.1989	0.2430

shows that picolinate has a much greater affinity for cadmium(II) than picolinamide, and may be explained by the greater chelating ability of a carboxylate group over an amide carbonyl oxygen. The same conclusion was reached in comparing copper(II) complexes of picolinamide and picolinate.[2] The difference between copper(II) and cadmium(II) is that while tris-(picolinate) complex of cadmium exists, the highest-order copper complex is the bis-(picolinate). No evidence for copper(II) ion-promoted amide hydrogen ionization appeared at the low *p*H used in the picolinamide experiments, so that chelation through the amide nitrogen does not occur. It is interesting to note that the larger formation constant for glycinate over glycine amide, as well as the larger formation constant for histidinate over histidinamide, have been ascribed to the greater chelating ability of a carboxylate group over an amide carbonyl oxygen also.[10, 11]

(B) *Nickel(II) Complexes of Picolinamide*

The nickel(II) complexes of picolinamide have reduction potentials which are too negative and the reduction waves are irreversible. For the measurement of the metal complexes, an indirect polarographic method, suggested by the work of Eriksson[12, 13] and of Li, *et al.*,[14] was developed. In essence the half-wave potentials of solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.2 M KNO_3, and varying concentrations of picolinamide in the absence and presence of 0.05 M $Ni(NO_3)_2$ are determined. In the absence of $Ni(NO_3)_2$ the picolinamide concentration range is from 0.02 to 0.45 M, with *p*H 5.8 to 6.6. In the presence of 0.05 M $Ni(NO_3)_2$, the total picolinamide concentration is in the range of 0.04 to 1.2 M, with *p*H varying from 5.4 to 5.9. The first polarographic waves in all solutions are due to the reduction of the cadmium ion, and therefore the dropping mercury electrode reactions are reversible. Plots of $\Delta E_{\frac{1}{2}}$ vs. total picolinamide concentration, in the absence and presence of 0.05 M $Ni(NO_3)_2$, are shown in Figure 1 (A) and (B) respectively. In the absence of $Ni(NO_3)_2$, curve (A), the total picolinamide concentration is taken to be the free ligand concentration, while in the presence of 0.05 M $Ni(NO_3)_2$ at a given total picolinamide concentration, the free ligand concentration is obtained by reading horizontally from curve (B) to curve (A) at the $\Delta E_{\frac{1}{2}}$ value corresponding to the total picolinamide concentration given in curve (B). This procedure is adopted because in the presence of $Ni(NO_3)_2$, some of the picolinamide is complexed to the nickel(II) resulting in a decrease in free picolinamide concentration, which in turn gives rise to a lowered value of $\Delta E_{\frac{1}{2}}$ in curve (B) relative to curve (A). The values of $\bar{n}$, defined as

$$\bar{n} = \frac{\begin{array}{l}\text{total picolinamide concn.}\\ \qquad - \text{free picolinamide concn.}\end{array}}{\text{total } Ni(NO_3)_2 \text{ concn.}} \tag{4}$$

are listed in Table II, and the data indicates that the highest-order complex is $Ni(pa)_6{}^{2+}$.

TABLE II

Polarographic results for solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.20 M KNO_3 and varying concentrations of picolinamide in the presence of 0.05 M $Ni(NO_3)_2$, *p*H 5.4 to 5.9

Total picolinamide concn.	Free picolinamide concn.	$\bar{n}$
0.0390	0.0309	0.17
0.0654	0.0462	0.39
0.1322	0.0804	1.03
0.1973	0.1245	1.46
0.2635	0.1654	1.98
0.3225	0.1995	2.46
0.4307	0.2691	3.25
0.5449	0.3449	4.00
0.7950	0.5346	5.21
1.0000	0.7111	5.76
1.2000	0.9017	5.96

In order to evaluate the individual formation constants from the data of Table II, we have used the modified Scatchard method.[15, 6] In this case we have defined $Q = \bar{n}/(6 - \bar{n})$ (A), where $\bar{n}$ is the average number of ligand molecules bound per metallic ion present, defined by equation (4), and (A) is the concentration of free ligand molecules, and have plotted log Q vs. $\bar{n}$, obtaining a straight line. Because of the greater error in the extreme high and low $\bar{n}$ regions, some of the points in the extreme ends of the curve are discorded in drawing the graph. The values of log Q at $\bar{n} = 0$ and $\bar{n} = 6$, obtained from extrapolations of the line, are the values of log λ_1 and log λ_6 respectively, where λ_1, and λ_6 are the first and sixth "intrinsic constants". The formation constants are then derived from the equations

$$K_1 = 6\lambda_1;\ K_6 = \lambda_{6/6} \tag{5}$$

The extrapolations of log Q give 0.23 and 0.99 at $\bar{n} = 0$ and $\bar{n} = 6$, respectively, from which the following values are obtained: log $K_1 = 1.0$; log $K_6 = 0.2$, where K_i is defined by the equation

$$K_i = \frac{(NiA_i)}{(NiA_{i-1})\,(\mathrm{A})} \tag{6}$$

The extrapolations of log Q are attended by some uncertainty, but the values of log K_1 and K_6 are probably accurate to ±0.1. The intermediate formation constants are obtained in the way suggested by ref. 6. From the straight line obtained in plotting log Q vs. $\bar{n}$, the values of log Q at $\bar{n} = 1.5$, 2.5, 3.5, and 4.5 are easily obtained. From these, and from the definition of Q, we have calculated the values of —log (A) at $\bar{n} = 1.5$, 2.5, 3.5 and 4.5, which are taken to be the values of log K_2, log K_3, log K_4, and log K_5, respectively.

The successive logarithmic formation constants at 25°, $\mu = 0.35$, for nickel(II) complexes of picolinamide are given in Table III. The values of nickel(II) complexes of ammonia at 30° (2N NH_4 NO_3)[16] and of imidazole at 25°, $\mu = 0.15$,[17] are also given for comparison. The picolinamide complexes are much less stable than the corresponding imidazole and ammonia complexes.

TABLE III

Successive Logarithmic Formation Constants of Picolinamide, Imidazole and Ammonia with Nickel (II) Ion

	Picolinamide	Imidazole	Ammonia
log K_1	1.0	3.27	2.80
log K_2	0.9	2.68	2.24
log K_3	0.7	2.15	1.73
log K_4	0.5	1.65	1.19
log K_5	0.3	1.12	0.75
log K_6	0.2	0.52	0.03

(C) *Some Ternary Cadmium (II) Complexes of Imidazole and Base*

In the simultaneous presence of two ligands imidazole (Im) and base B (B = picolinate, picolinamide, and 5,5′-diethylbarbiturate), forming a ternary complex Cd Im_i B_p, the expression for the half-wave potential (equation 2) becomes

$$(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = -0.030 \log K - i\,0.030 \log (\mathrm{Im}) - p\,0.030 \log (B) \tag{7}$$

Where K is the equilibrium constant of the reaction

$$\mathrm{Cd}^{+2} + \mathrm{i\,Im} + \mathrm{pB} = \mathrm{Cd\,Im}_i\,\mathrm{Bp}$$

For solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.001% gelatin as maximum suppressor,

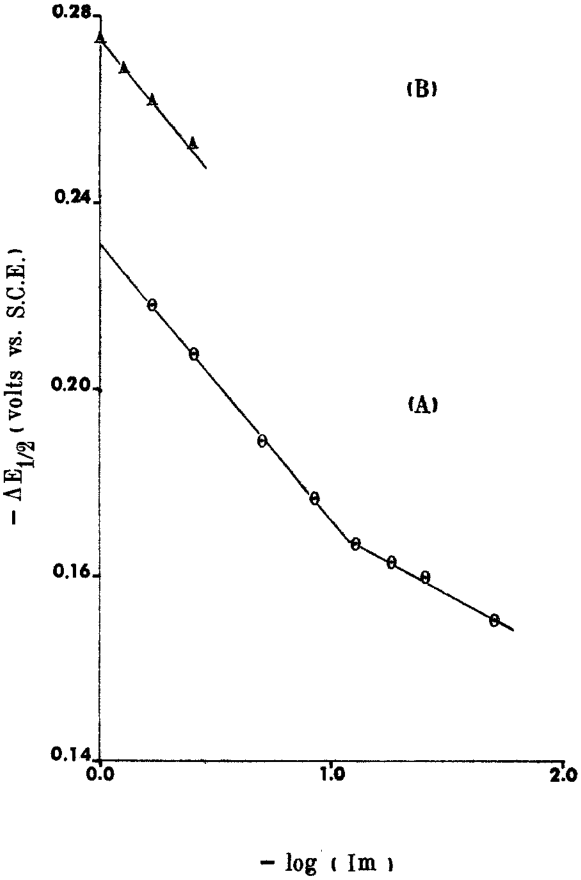

FIGURE 2 Plots of $-\Delta E_{\frac{1}{2}}$ vs. —log (imidazole) at
(A) (picolinate) = 0.0234 M
(B) (picolinate) = 0.2453 M

0.2 M KNO_3, varying concentrations of imidazole, in the presence of 0.0234 M and 0.2453 M picolinate, plots of $\Delta E_{\frac{1}{2}}$ vs. log (Im) are shown in Figure 2 (A) and (B), respectively. From Figure 2 (A) in the imidazole concentration range 0.02 to 0.08 M, the slope is 0.03, while at imidazole concentration above 0.1 M, the slope is 0.06. From equation (7) it is seen that $i = 1$ and 2 at the low and high imidazole concentrations, respectively. Figure 2 (B) shows that with picolinate constant at 0.2453 M in the imidazole concentration range 0.4 to 1.0 M, *p*H 7.1 to 7.7, the slope is again 0.06 so that $i = 2$. Data for lower imidazole concentrations are not included because of decreased *p*H.

Plots of $\Delta E_{\frac{1}{2}}$ vs. log (picolinate) for solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.2 M KNO_3, in the presence of 0.056 M and 0.4 M imidazole, are given in Figure 3 (A) and (B), respectively. The slope in Figure 3 (A) is 0.06 so that $p = 2$. In the presence of 0.4 M imidazole, Figure 3 (B) shows that when picolinate concentration is below 0.05 M and above 0.18 M, the slopes are 0.03 and 0.06, indicating that $p = 1$ and 2, respectively. At intermediate picolinate concentration (0.05 to 0.18 M), the slope is 4.5, so that $p = 1.5$ and a mixture of complexes with $p = 1$ and $p = 2$ is present.

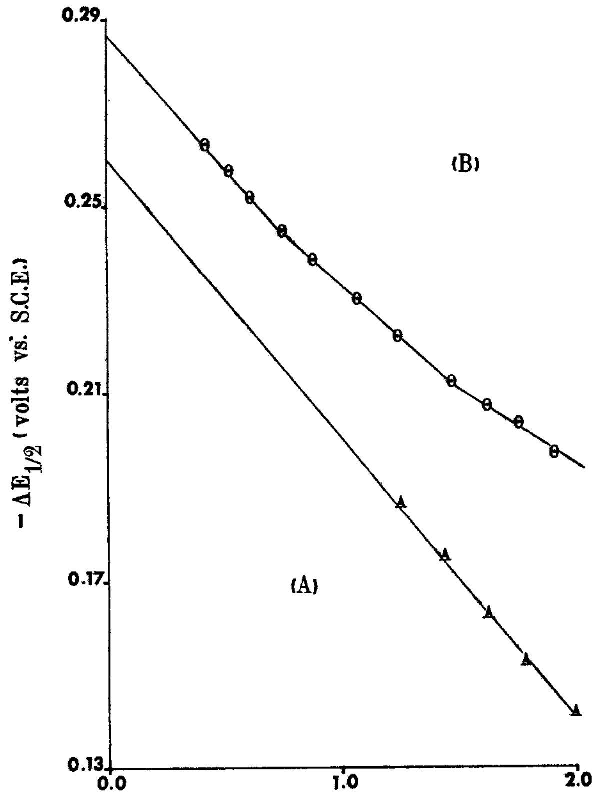

FIGURE 3 Plots of $-\Delta E_{\frac{1}{2}}$ vs. −log (picolinate) at
(A) (imidazole) = 0.056 M
(B) (imidazole) = 0.4 M

From equation (7) and the data of Figures 2 and 3, we conclude the following:

(*a*) When both picolinate and imidazole concentrations are below 0.08 M, the ternary complex Cd $(pc)_2$ (Im) exists predominantly, with log $K = 10.0$.

(*b*) In the range of $C_{pc} = 0.01$ to 0.03 M and imidazole concentration above 0.1 M, Cd(*pc*) $(Im)_2$ is the predominant ternary complex, with log $K = 9.5$.

(*c*) At high imidazole concentration (>0.1 M), and high picolinate (>0.18 M), a ternary complex is $Cd(pc)_2$ $(Im)_2$.

The equilibrium constant for the formation of the ternary complex, Cd(*pc*) $(Im)_2$, log $K = 9.5$, is in excellent agreement with the sum of log $K_1 = 4.36$ for $Cd(pc)^8$ and log $K_{f,2} = 5.07$ for $Cd(Im)_2{}^6$. The equilibrium constant for the formation of the ternary complex, $Cd(Im)(pc)_2$, log $K = 10.0$, is in fair agreement with the sum (=10.3) of log $K_{f,2} = 7.54$ for $Cd(pc)_2{}^8$ and log $K_1 = 2.80$ for CdIm.[17]

Table IV gives polarographic data for solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.20 M KNO_3, and (A) varying concentrations of picolinamide, *pa*, at constant 0.04 M imidazole, and (B) varying concentrations of imidazole, *p*H 9.0 to 10.0, at constant 0.0432 M picolinamide. A plot of $\Delta E_{\frac{1}{2}}$ vs. −log (*pa*) at constant 0.04 M imidazole is linear with slope of 0.03. A plot of $\Delta E_{\frac{1}{2}}$ vs. −log (Im) at constant 0.0432 M picolinamide reveals that when (Im) = 0.01 to 0.06 M, the slope is 0.06, whereas when (Im) = 0.08 to 0.32 M, the slope is 0.09. The data lead to the conclusion that in the ternary complex $Cd(Im)_i(pa)_p$, $i = 2$ or 3 depending on the concentration range of imidazole used and $p = 1$. From the data of Table IV, log K for $Cd(Im)_2(pa)$ and $Cd(Im)_3(pa)$ are calculated to be 6.7 and 8.2, respectively. The value for $Cd(Im)_2(pa)$ is in excellent agreement with the sum (=6.8) of log $K_{f,2} = 5.07$ of $Cd(Im)_2{}^6$ and log $K_1 = 1.8$ of Cd(*pa*). The value for $Cd(Im)_3(pa)$ is also in excellent agreement with the sum (=8.3) of log $K_{f,3} = 6.45$ for $CdIm_3{}^6$ and log $K_1 = 1.8$ for Cd(*pa*).

A plot of $\Delta E_{\frac{1}{2}}$ vs. −log (5,5′-diethylbarbiturate) for solutions containing 1×10^{-4} M $Cd(NO_3)_2$,

TABLE IV

Polarographic results for solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0.20 M KNO_3, and varying

(a) concentrations of picolinamide at (Im) = 0.04 M, and
(b) concentrations of imidazole at (pa) = 0.0432 M

(a)	(pa), *M*	$-\Delta E_{\frac{1}{2}}$
	0.0432	0.0770
	0.0580	0.0792
	0.0944	0.0876
	0.1436	0.0916
	0.2472	0.0977
	0.2675	0.0994
	0.4036	0.1058
	0.5042	0.1084

(b)	(Im), *M*	$-\Delta E_{\frac{1}{2}}$
	0.0104	0.0436
	0.0160	0.0538
	0.0219	0.0613
	0.0400	0.0770
	0.0800	0.0980
	0.1296	0.1186
	0.2000	0.1368
	0.3200	0.1572

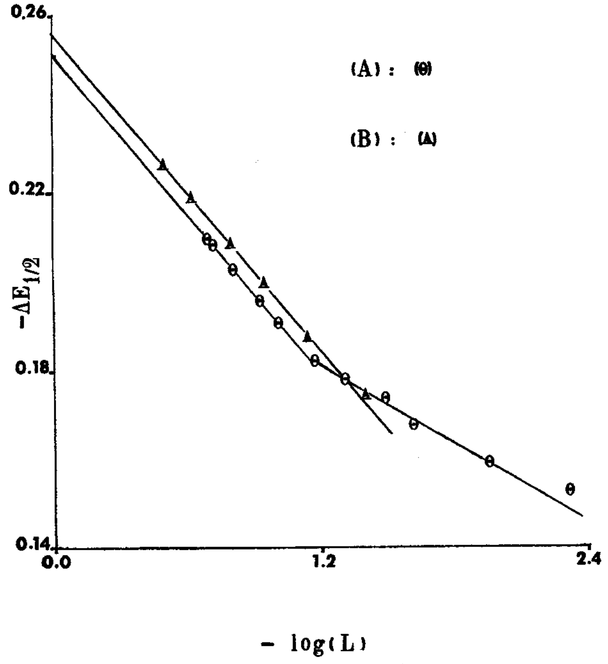

FIGURE 4 Plots of $-\Delta E_{\frac{1}{2}}$ vs. $-\log$ C ligand for solutions containing 1×10^{-4} M $Cd(NO_3)_2$, $\mu = 0.2$, and

(A) varying concentration of ligand 5,5′-diethylbarbiturate, at constant 0.16 M imidazole
(B) varying concentration of ligand imidazole at constant 0.1899 M 5,5′-diethylbarbiturate.

0.16 M imidazole, $\mu = 0.2$, is given in Figure 4 (A). At low barbiturate concentration the slope is 0.03, while at higher barbiturate concentration, the slope is 0.06. This indicates $p = 1$ and 2, respectively, in equation (7). Figure 4 (B) shows plot of $\Delta E_{\frac{1}{2}}$ vs. $-\log$ (imidazole) for solutions containing 1×10^{-4} M $Cd(NO_3)_2$, 0.190 M 5,5′-diethylbarbiturate, $\mu = 0.2$. The slope is 0.06, indicating that $i = 2$ in equation (7). The data of Figure 4 shows that two complexes, $Cd(Im)_2$ (barbiturate) and $Cd(Im)_2$ $(barbiturate)_2$, exist in low and high barbiturate concentrations, respectively. Several metal complexes of the general formula $M(Im)_2(B)_2$, where $M = Ni^{2+}$, Co^{2+}, Cu^{2+} and Zn^{2+}, and B = 5,5′-diethylbarbiturate and phenobarbiturate, have been isolated and their crystal structures determined.[18, 19]

(D) *A Ternary Nickel(II) Complex*

In solutions containing $Ni(NO_3)_2$, picolinamide and imidazole, irreversible polarograms are obtained. Therefore, instead of obtaining the formula of a ternary complex from polarographic studies, we prepared one in the crystalline state: bis-(picolinamide)-bisimidazole-nickel(II) chloride tetrahydrate. *Anal.* Calcd. for $NiC_{18}H_{28}N_8O_6Cl_2$: Ni, 10.0; C, 37.2; H, 4.8; N, 19.3; Cl, 12.1. Found: Ni, 9.9; C, 37.8; H, 4.6; N, 19.4; Cl, 11.7. The crystals are trigonal and the unit cell parameters, as determined from Weissenberg photographes, are $a = b = 22.49 \pm 0.01$ A, $c = 13.77 \pm 0.05$ A, $\alpha = \beta = 90°$, $\gamma = 120°$. For nine formula weights in the cell the calculated density is 1.34 g cm^{-3}; the observed density is 1.33 g cm^{-3} determined by flotation in a mixture of *n*-butyl bromide and tetrabromoethane.

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